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Part II

DETERMINATION OF PHYSICAL AND CHEMICAL STRUCTURE OF NEW HIGH-TEMPERATURE POLYMERS

K. A. Boni

Battelle Memorial Institute

TECHNICAL REPORT AFML-TR-69-292, Part II

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Air Force Materials Laboratory
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio

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DETERMINATION OF PHYSICAL AND CHEMICAL STRUCTURE OF NEW HIGH-TEMPERATURE POLYMERS

by

K. A. Boni

Battelle Memorial Institute
Columbus Laboratories

FOREWORD

This report was prepared by the Columbus Laboratories of Battelle Memorial Institute under USAF Contract F33615-69-C-1095. The contract was initiated under Project No. 7340, "Nonmetallic and Composite Materials", Task No. 734004, "New Organic and Inorganic Polymers". It is administered under the direction of the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, with Dr. T. E. Helminiak as project scientist.

This report covers work conducted from August 31, 1969 to October 31, 1970. The manuscript was released by the author in November 1970 for publication.

This report was prepared by Dr. Kenneth A. Boni, Principal Investigator. Structural analyses were performed by Mr. R. J. Jakobsen and Mrs. E. J. Brewer (IR), Dr. R. L. Foltz (Mass Spectrometry), and Dr. T. M. Sutliff (NMR). Thermal analyses were performed by Mr. R. W. Pfeil. Other characterizations were performed by Mr. G. P. Nance, Mr. K. C. Price. Mr. T. Lyons and Mrs. S. Gunn. The contract was administered by Mr. E. R. Mueller until his untimely death in January 1970. Subsequent to that event, Mr. H. N. Johnston of the Polymer and Paper Technology Division assumed the administrative responsibilities for the contract.

This technical report has been reviewed and is approved.

RICHARD L. VAN DEUSEN
Acting Chief, Polymer Branch
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ABSTRACT

Two polypyrrolone samples containing an anthraquinone moiety were characterized. Procedures for isolation of one of these from solution in strong acid were examined in detail. In addition, the structure (IR and elemental analysis), thermal properties (TGA and DTA), and solubility of both materials were obtained.

A sample of a spiropolyimide was characterized as to its structure (IR and elemental analysis), thermal properties (TGA and DTA), and dilute solution viscosity. The results obtained indicated that the sample contained significant amounts of material with structure different from that proposed for the sample.

Effort to identify the predominant structure of the thermally induced reaction of 1-carboxy-2-chloroferrocene with itself was continued. However, a definitive answer was not obtained. Two chlorinated ferrocene samples were classified as liquid crystals based on their thermal transitions and observed behavior.

Additional effort included a review of molecular weight data on silicon-nitrogen polymers, as well as determination of tensile properties and crystallite size and spacing of films obtained from BBB and BBL. The molecular weight and subambient transitions of a perfluoroalkyl bibenzoxazole sample were also obtained. In addition, the effect of variation of temperature on the extent of solvent property coverage attained during solvent search was studied. The structure, thermal properties, and solubility of a spiropolyester sample were also investigated.

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INTRODUCTION

In recent years, the Air Force has been faced with a growing need for new materials for use in extreme environments. As a result, a sizable polymer synthesis program has been supported. In general, an initial screening for probable structure, possible applications, and upper service temperature is performed as part of these synthesis programs. However, much greater benefit from the synthesis programs is possible if all polymeric products are throughly characterized by a single laboratory whose primary interest is polymer characterization. Accumulation of characterization data by one laboratory eventually leads to development of structure-property correlations which can be used to direct synthesis programs to more fruitful approaches to useful polymers. Additional incentive for characterization of synthesis products by characterization specialists is to provide impartial and rapid recognition of the potential of candidate materials. This report is a description of work performed at Battelle on such a characterization program.

In general, characterization includes structure identification, solvent search, thermal properties, solution viscosity, and molecular weight. Infrared (IR) and nuclear magnetic resonance (NMR) spectra and elemental analysis were used for structure identification. Since determination of the probable structure of samples was part of the synthesis programs, only the general features of the structure were examined. Solubility and swelling behavior of candidate materials was predicted from examination of mixtures of the materials with solvents which provided systematic variation of the electrostatic and covalent solubility parameters.

Differential thermal analysis (DTA) was used to measure the magnitude and temperature range of any thermal transitions produced during programmed temperature rise. An indication of the thermal stability of the material was obtained by thermogravimetric analysis (TGA). In a few cases, the TGA data were supplemented by mass spectral identification of thermal-fragmentation products to provide insight into the fragmentation mechanism.

Solution-viscosity measurements provided an estimate of sample molecular weight. Generally, the specific viscosity was determined at several concentrations to avoid the possibility of not observing polyelectrolyte effects. When more precise molecular weights were desired, osmometric techniques were used to provide number-average molecular weight (M_n). Also, the molecular weight distribution was determined by gel-permeation chromatography (GPC) when suitable solvents were available. Detailed descriptions of the equipment and techniques used in this program have been provided in previous reports of the project activity.[1-3]

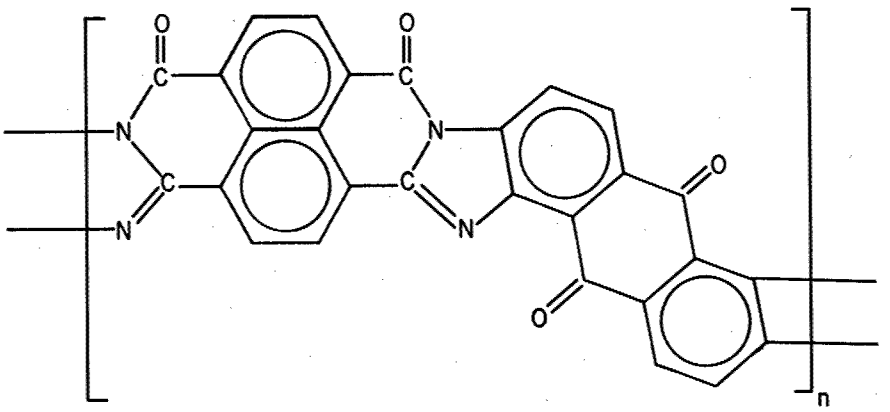
II

RESULTS AND DISCUSSION

Polypyrrolone Polymers

Sample 18E

A polypyrrolone ladder polymer synthesized in C. S. Marvel's laboratory[4] was received for characterization. The sample, labelled 18E, was prepared by a two-stage condensation of 1,2,5,6-tetraaminoanthraquinone with 1,4,5,8-naphthalenetetracarboxylic acid. In the first stage, a prepolymer which is believed to be a tetramer was prepared by heating a solution of the monomers in N,N-dimethylacetamide containing 10 percent glacial acetic acid. The prepolymer was precipitated from the solution and purified before proceeding. The second stage involved further condensation of the prepolymer by heating it in polyphosphoric acid. Based on the IR spectrum and elemental analysis which he obtained, Marvel believes that the structure of the polymeric product is predominantly



although incomplete cyclodehydration with consequent ladder defects is likely. While the cis isomer with respect to the location of the carbonyl groups of the pyrrolone structure is illustrated, condensation as the trans isomer appears equally possible. Also, cis and trans isomers with respect to the orientation of the anthraquinone units relative to the carbonyls appear to be equally favored. Hence, it is expected that the structure of this polymer is a random combination of all the possible isomers in addition to some units having structural defects. A polymer with the proposed structure is of particular interest since dyes containing anthraquinone groups can be reduced with reagents such as sodium hydrosulfite to make them water soluble. Regeneration of insoluble dye is achieved by exposure to air. Obviously, a polymer that could be processed in aqueous solution and converted to an insoluble material on exposure to air would have numerous applications.

A solvent search with the sample as received, using the microscopic technique[1] and the standard solvent list previously given[3], indicated no reactions. However, solutions were formed in concentrated sulfuric acid and methanesulfonic acid as would be predicted by analogy with other heterocyclic polymers. While complete dissolution in methanesulfonic acid was achieved in 24 hours, approximately 5 percent of the sample remained undissolved in 96 percent sulfuric acid after 3 days of stirring at 50 C. This result is consistent with the contention of Marvel[5] that methanesulfonic acid is a better solvent than sulfuric acid for heterocyclic polymers.

In an effort to determine the effect on properties of the portion of the sample that is insoluble in sulfuric acid, effort was devoted to separation of this fraction. Approximately 1 gram of the sample was placed in 50 ml of concentrated H_2SO_4 and stirred for 2 days at room temperature. The insolubles were separated from the solution by filtration through a glass frit. The solution was added slowly and with stirring to approximately ten times its volume of cold water. The voluminous precipitate obtained was separated from the supernatant liquid with a medium-porosity glass frit and washed with approximately 1 liter of distilled water. The washed precipitate was freeze dried, followed by drying for 48 hours in a vacuum oven at 100 C. A slight N_2 bleed was maintained during evacuation to facilitate drying. The elemental analysis of this dried material is given in Table I. The high oxygen content and the discrepancy between 100 percent and the combined percentage of the elements analyzed suggests sulfonation of the sample or formation of a quaternary salt with sulfuric acid. The better agreement of the reported elemental analysis with that calculated for 1 mole of sulfuric acid per repeat unit than that calculated for the expected structure supports this postulate. However, the discrepancy between the calculated and the observed analyses, particularly in the hydrogen and oxygen content, could also reflect contamination of the sample with water in spite of the drying procedure used.

TABLE I. EFFECT OF THE ISOLATION SCHEME ON THE ELEMENTAL CONTENT OF THE POLYPYRROLONE SAMPLE 18E

	Analysis, percent		
Element	Calculated for $C_{28}H_8N_4O_4$	Calculated for $C_{28}H_8N_4O_4 \cdot H_2SO_4$	Found[a]
C	72.41	59.79	55.95
H	1.73	1.79	2.19
N	12.07	9.96	8.67
O	13.79	22.75	26.18
Ash	--	--	0.74

(a) Average of duplicate analysis by Clark on purified sample.

These results suggested that several modifications to the separation procedure should be made. To insure complete removal of any free sulfuric acid and decomposition of quaternary salts, the precipitate was washed with 1.0 N NH_4OH. After washing with approximately 2 liters of the NH_4OH, the wash gave a negative test for sulfate on addition of a few drops of a 5 percent $BaCl_2$ solution. The sample was then washed with distilled water until the wash was neutral. To expedite the washing procedure, the bulky precipitate was separated from the wash solutions by centrifugation rather than with a glass frit. Drying was improved by use of a sublimator in place of the vacuum. The

improvement in drying produced by this change was determined by comparison of the residual water indicated by TGA. After drying for 72 hours at 0.1 torr and 100 C, the oven-dried sample still contained approximately 10 percent residual water while the sublimator-dried sample contained 2 percent water. The cold finger of the sublimator used for this drying is within 2 cm of the surface of the precipitate.

The product from the first attempt at separation of the sulfuric acid solubles was used as the starting material for the modified procedure. The elemental analysis of the product obtained by the modified procedure did not differ appreciably from that given in Table I for the first product. This result suggests that the as-received sample reacted irreversibly with sulfuric acid – probably during exposure to the elevated temperature used in an effort to dissolve the sample completely in sulfuric acid.

Since preparation of a fiber or a film from this polymer could require recovery from solutions in strong acids, development of techniques for separation of the polymer from them in the pure state was pursued. While such separations have been achieved in other laboratories, the details of the procedures have not appeared in the literature. Hence, an added motivation for this work was to put into the literature a description of the "art" of obtaining pure heterocyclic polymers from strong acid solutions. Although methanesulfonic acid is more expensive than sulfuric acid, it was used in this phase of the work because it completely dissolved the sample. In order to eliminate any ambiguity from the effort, a fresh portion of the as-received sample was used as the starting material. In view of the severe difficulty encountered during the filtration and washing steps in the previous procedure, alternate media for precipitation were investigated. It was found that addition of the acid solution to methanol rather than water resulted in a much more tractable precipitate. That is, it coagulated rapidly but was not gelatinous and could be washed readily on a glass frit. Filtration rate was much greater if the precipitate was maintained in suspension rather than allowed to settle on the glass frit during the filtration. This modification reduced the time required for the separation and washing steps from several days to a few hours. As in the previous separation attempt, the water-swollen precipitate was initially freeze dried in order to maintain a somewhat open structure. During the freeze-dry step, carry-over of the precipitate with the water from the flask to the Dry-Ice trap was prevented by insertion of a coarse frit between them. The fluffy material obtained from this step was transferred to the sublimator for a more complete drying at 0.1 torr and 100 C for at least 2 days. An indication of completion of the drying was given by observation of electrostatic attraction of the precipitate to the walls of the container. The charge was dissipated by exposing it to an α-particle source (Po^{210}) before removing it from the sublimator.

The elemental analysis of this sample as well as that calculated for the proposed structure, that obtained for the as-received sample, and that obtained by Loughran[6] are given in Table II. The low-carbon and high-hydrogen contents of these samples as compared with that reported by Loughran suggest that the samples were not dry when they were analyzed. However, comparison of the observed carbon-hydrogen content with values predicted from simple water pickup suggests that the elemental content is not consistent with the proposed structure. This is the case for the samples analyzed by Clark Microanalytical Laboratory and that reported by Loughran. For example, pickup of 1 water molecule per repeat unit would reduce the carbon content to 69.6 percent and raise the hydrogen content to 2.10 percent. Similarly, sorption of 4 molecules of water per repeat unit yields 62.7 percent carbon and 3.01 percent hydrogen. Clearly, no hypothetical water content can be invoked to reconcile the observed carbon-hydrogen content with the proposed structure. It is recognized, of course, that the deviation of

the elemental content from that predicted from proposed structure does not necessarily prove that the proposed structure is inconsistent with the sample. This is a consequence of the difficulties associated with elemental analysis of samples such as this one that are very difficult to convert completely to CO_2 and H_2O. The discrepancy does, however, suggest that interpretation of other characterization data as typical of the proposed structure should be made with caution. The small differences in elemental content between the as-received and the isolated sample suggest that the final separation procedure removed most of the methanesulfonic acid.

TABLE II. ELEMENTAL ANALYSIS OF THE POLYPYRROLONE SAMPLE 18E

	Analysis, percent			
Element	Calculated for $C_{28}H_8N_4O_4$	Found[a]	Found[b]	Found[c]
C	72.41	71.35	65.01	63.98
H	1.73	2.26	3.25	3.08
N	12.07	12.32	--	--
O	13.79	14.07	--	--
Ash	0	0.50	0.89	1.02

(a) Average of duplicate analysis on the "as-received" sample reported by Loughran[6].
(b) Average of duplicate analysis on the "as-received" sample reported by Clark Microanalytical Laboratory.
(c) Average of duplicate analysis on the "isolated" sample reported by Clark Microanalytical Laboratory.

The infrared spectrum of the "as-received" sample (Figure 1) was obtained from a film cast on an Irtran plate. The film was cast from a 2 percent solution in methanesulfonic acid. The acid was removed by use of the sublimator. A film was used for the analysis rather than a KBr pellet following the suggestion of F. E. Arnold and R. L. Van Deusen.[8] They found that they could obtain a superior spectrum by use of a film, particularly in the carbonyl region, which is critical to observation of residual imide groups in the polymer. They attributed the improved spectra obtained with a film to problems with grinding the polymer and drying the KBr when preparing a KBr pellet.

The spectrum contains evidence for anthraquinone (1735 cm^{-1} band), the imidazole ring with adjacent carbonyl (1680 and 1635 cm^{-1} bands), and substituted napthalene (1600, 1520, and 1420 cm^{-1}). In addition, the shoulder at 1760 cm^{-1} and the band at 1800 cm^{-1} are probably produced by anhydride end groups. The spectrum does not contain an appreciable band at 1650-1660 cm^{-1}, which Arnold and Van Deusen[8] have shown arises from residual imide in these systems. The strong, broad band between 1150 and 1250 cm^{-1} is attributable to residual sulfonate.

The TGA thermogram of the pyrrolone Sample 18E which was recovered from methanesulfonic acid (see Figure 2) provides a clue to the reason that difficulties were encountered in obtaining an elemental analysis consistent with the structure. In view of the high apparent water content indicated by the elemental analysis, it appears likely that the gradual loss in weight of the sample up to 300 C may be from loss of this water. Since the rate of loss is a smooth function, loss of water by two mechanisms with different activation energies appears unlikely in this temperature range. The temperature

at which rapid volatilization commences is somewhat lower than that observed with the best BBB and BBL polymer samples. However, if this polymer can be made water soluble, it appears that the penalty in thermal stability for this property is not large – i.e., approximately 25 C.

Sample PE-82B

A previously characterized sample of the polymeric product of the condensation of 1,2,5,6-tetraaminoanthraquinone with pyromellitic acid dianhydride (labelled PE-82) was found to be incompletely condensed.[3] A similar sample labelled PE-82B, which had been prepared by heating a prepolymer longer and at higher temperatures than the conditions used to prepare PE-82[7], was submitted to Battelle for analysis. The TGA of this sample suggested it was much more thermally stable than Sample PE-82.[4]

Of particular interest for this sample is its structure, since previously reported results[3] suggested that thermally induced condensation would also lead to chain defects. An infrared spectrum of this sample obtained with a KBr pellet was weak and hard to interpret. By use of the film casting technique suggested by Arnold and Van Deusen[8] which was successful with Sample 18E, a uniform film was obtained that permitted acquisition of a reasonable infrared spectrum (see Figure 3). Many features of the spectrum were similar to that from Sample 18E as would be predicted from their structures. In particular, there is evidence for anthraquinone (1740 cm^{-1} band) and the imidazole ring with adjacent carbonyl (1680 and 1630 cm^{-1}). This spectrum differs from the one previously reported for Sample PE-82 in the bands at 1660 cm^{-1} and 1290 cm^{-1}. The former is attributable to residual imide and the latter to residual aromatic amine.

A search for solvents for this sample among the list of solvents[3] expected to completely cover the electrostatic and dispersion properties of molecules suggested that strong acids would dissolve the sample. Some interaction occurred with formic acid, while a 2 percent solution could be prepared in methanesulfonic acid after 24 hours of stirring.

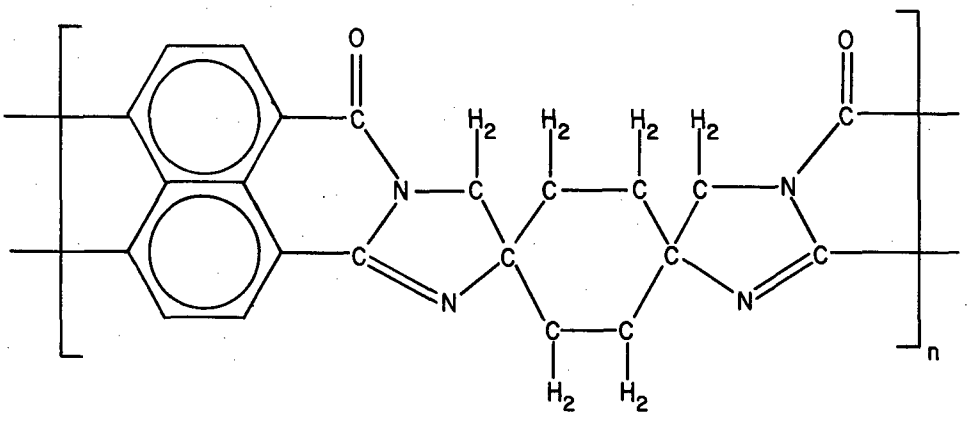
The DTA thermogram of Sample PE-82B (see Figure 4) was very similar to the one previously reported for Sample PE-82 – that is, an initial endotherm consistent with loss of surface volatiles followed by a gradual exothermal process. The exothermal process is not as vigorous as was observed on heating Sample PE-82.

The TGA thermogram of Sample PE-82B, on the other hand, differs appreciably from the one obtained for PE-82. As can be seen in Figure 5, Sample PE-82 lost weight below 500 C at a considerably faster rate than Sample PE-82B, which would explain the difference observed by DTA. However, by 900 C, Sample PE-82B had lost more weight.

Spiropolyimide

While there has been considerable effort directed toward synthesis of double-stranded "ladder polymers", very little work has been reported on synthesis of polymers that are double stranded but joined at regular intervals with a backbone spirocarbon.

Recently, efforts have been initiated by C. M. Sharts[9] and J. Heller, et al[10, 11], to prepare such polymers. A product of the effort at Stanford Research Institute (Heller, et al) that was prepared by condensation of 1,4-bis(aminomethyl)-1,4-diaminocyclohexane and 1,4,5,8-naphthalenetetracarboxylic dianhydride in polyphosphoric acid was examined earlier in this program.[2] A more recent product of the SRI effort, expected to have an appreciably higher molecular weight than the previous sample, was submitted to Battelle for characterization. The polymer is expected to have the structure



The elemental analysis of the recently prepared sample (labelled SRI-470) is not in good agreement with the analysis expected for the proposed structure (Table III). It is consistent with a partially cyclized material or an incompletely dried sample. Part of the discrepancy between the observed analysis and that expected for the proposed structure may reflect the difficulties in analysis of the sample which arise from its "decrepitation" during combustion. The sample submitted to Spang had been ground and carefully dried in the sublimator, which was not the case with the sample submitted to Clark. The differences between the duplicate runs obtained by Spang were much less than those between the analyses reported by Clark.

TABLE III. ELEMENTAL ANALYSIS OF SPIROPOLYIMIDE SAMPLE SRI-470

Element	Analysis, percent			
	Calculated[a]	Calculated[b]	Found[c]	Found[d]
C	71.71	65.33	67.57	67.88
H	4.38	4.99	5.06	4.17
N	15.21	13.85	7.89	14.19
O	8.68	15.83	19.48[e]	13.76[e]

(a) Calculated for completely cyclized polymer ($C_{22}H_{16}N_4O_2$).
(b) Calculated for uncyclized polymer ($C_{22}H_{20}N_4O_4$).
(c) Clark Microanalytical Laboratory.
(d) Spang Microanalytical Laboratory.
(e) By difference.

Thermogravimetric analysis of the sample in a helium atmosphere (see Figure 6) indicates presence of a volatile impurity and a rapid loss of about 8 percent volatiles beginning at about 450 C. The analysis was performed in a helium atmosphere rather than under vacuum as is done usually, because the sample jumped off the TGA pan at about 450 C when in vacuum. It is believed that this was a result of violent liberation of the volatiles. The absence of such an effect when the sample was heated in helium supports this postulate. It is interesting to note that approximately 66 percent of the sample still remained at 800 C.

Several of the volatile products liberated by the sample when heated above 400 C were identified by mass spectral analysis. The sample was heated on the TGA pan and the volatiles were monitored with Battelle's AEI MS-10 low-resolution mass spectrometer. The major component of the spectrum was water. In addition, appreciable quantities of nitrogen and/or carbon monoxide, methane, and ammonia were observed. A minor component of the volatiles was ethane. A likely source of methane and ethane in the volatiles is the saturated ring.

The infrared spectrum of Sample SRI-470 was obtained from a film that had been cast on an Irtran plate from a 2 percent solution of the polymer in formic acid. This technique was chosen in preference to a KBr pellet because work of Arnold and Van Deusen[8] has shown that superior spectra could be attained. Primarily, this is the case because water can be meticulously excluded from the film. The spectrum (see Figure 7) contains evidence for the imidazole ring with adjacent carbonyl (1690 and 1630 cm^{-1} bands), aliphatic C-H which could arise from the cyclohexane ring (2960 cm^{-1} band), skeletal aromatic carbons (810 and 760 cm^{-1}), and residual anhydride (1800 and 1760 cm^{-1}). An unresolved shoulder at about 1650 cm^{-1} is evident which could reflect residual imide. In addition, the distinctive band at 1300 cm^{-1} which is not present in the polypyrrolone sample spectra (PE-82B and 18E) may reflect residual aromatic amine in appreciable quantities. This interpretation differs from that of Heller, et al[14], in assignment of the bands for residual imide. Support for the assignments given herein was obtained from an extensive study by Van Deusen, et al[12], with model compounds as well as from data reported by Berry, et al[13].

The effect of dilution on the viscosity of solutions of the sample in formic acid was consistent with the behavior of a polyelectrolyte. A linear relation was observed between the reciprocal of the reduced viscosity and the square root of concentration rather than between the reduced viscosity and concentration. In addition, the reduced viscosity of a 1×10^{-3} g/ml solution of the sample was decreased from 163.5 ml/g to 141.9 ml/g by addition of 7×10^{-4} g of sodium formate.

In view of the implications of this sample being a polyelectrolyte, additional verification of the initial observations was sought. If the polymer is acting as a polyelectrolyte in solution, maintaining the ionic strength in solution constant will result in a linear relation between η_{sp}/c and c. In order to maintain a constant ionic strength, the concentration of charges produced by the polyelectrolyte must be determined. As a first approximation to this, it was assumed that there were two charges per repeat unit of the polymer. The polymer solution was diluted with a sodium formate solution of sufficient concentration to maintain the ionic strength estimated from the number of charges per repeat unit. The approach did not lead to a linear relationship. While part of the deviation from a linear relation may reflect an error in the assumption of two charges per repeat unit or incomplete ionization of the polyelectrolyte (ion-pair formation), a considerable effect on the efflux time of solvent by itself was observed on

addition of the sodium formate solution. Although formic acid is very hygroscopic and water will reduce the efflux time, the magnitude of the reduction on addition of the sodium formate solution is too large to be explained on this basis. A possible explanation for the reduction in viscosity produced by addition of sodium formate to formic acid is that the accompanying suppression of ionization reduces the concentration of hydrogen-bonded aggregates. This apparent complication made further activity in this direction difficult to justify.

Observation of a polyelectrolyte effect with this polymer sample is inconsistent with the proposed structure. That is, the available modes of rotation of the idealized structure could not appreciably alter the hydrodynamic volume of the polymer upon an increase in interaction of its charges. If there are appreciable defects in the proposed structure, however, a significant amount of rotational freedom would be introduced. Some indication of the concentration of defects which can be present in a rigid molecule without observation of appreciable polyelectrolyte effects is provided by the results of Berry, et al.[13] Their results indicate that a sample of BBB with at least 1 percent of its groups incompletely cyclized did not show appreciable polyelectrolyte effects. The absence of a polyelectrolyte effect with dilute solutions of BBB in concentrated sulfuric acid also has been reported by Boni.[1] However, the ion concentration in 96 percent sulfuric acid may be sufficient to suppress the ionization of BBB. Hence, these data do not demonstrate conclusively that 1 percent defects in a ladder problem are insufficient to be detected as polyelectrolyte effects in an unionized solvent.

Ferrocene Derivative

Previous attempts to identify the predominant structure of the thermally induced reaction of 1-carboxy-2-chloroferrocene with itself were inconclusive.[3] These attempts were based on examination of the volatile and nonvolatile products of the reaction. While the nonvolatile product had interesting thermal properties, it was intractable and appeared to be a mixture of several structures.

In an effort to produce a tractable product with thermal properties similar to the product obtained from the melt, the reaction was carried out with a solution of the ferrocene derivative in biphenyl. A 5 percent mixture of the substituted ferrocene (0.10 g) in biphenyl was reacted in a three-necked Bantam-ware flask. A nitrogen bleed was used for agitation and exclusion of air. Heat was applied to the flask by an oil bath at 150 C. The time required for the solution to reach 150 C was minimized by preheating the bath. Within 10 seconds after submersion in the bath, the light-orange powder mixture turned dark brown. After 3 minutes, the mixture was black. The reaction was allowed to continue for 1 hour. After cooling, ethanol was added to the tar-like product. After stirring, the mixture was transferred to a glass frit. A black, powdery residue was separated from a reddish-black solution. The black residue, which was about 36 percent of the original sample (average of duplicate runs), was completely insoluble. A solvent search using the standard list of solvents[3] and the microscopic technique[1] did not identify any solvents for the residue. The infrared spectrum of this residue (see Figure 8) contains a very strong OH/NH stretching band near 3460 cm^{-1}, a carbonyl band at 1715 cm^{-1}, and a broad, strong absorption near 1580 cm^{-1} suggesting a metal salt. The elemental analysis of the insoluble residue given in Table IV suggests that its structure differs considerably from that of the product produced from the melt by F. L. Hedberg.

TABLE IV. ELEMENTAL ANALYSIS OF PRODUCTS OBTAINED BY HEATING 1-CARBOXY-2-CHLOROFERROCENE

Element	Analysis, percent		
	Found[a]	Found[b]	Found[c]
C	46.79	50.10	28.46
H	3.26	3.30	3.11
Cl	15.82	8.73	6.61
Fe	26.10	17.52	18.89
O	8.03	20.35	--

(a) Sample prepared by F. L. Hedberg (LNP) by heating the melt at 230 C for 1 hour.

(b) Insoluble portion of product obtained by heating a 5 percent solution in biphenyl at 150 C for 1 hour.

(c) Ethanol soluble – ether insoluble product.

(d) By difference.

The appreciable color of the ethanol solution coupled with the small percent of starting material which is included in the insoluble residue (36 percent) suggests that the ethanol solution includes products derived from the substituted ferrocene starting material. On evaporation of the ethanol solution (in a rotary evaporator) a crystalline product was obtained which appeared to be a physical mixture of biphenyl and a brown material. Hence, identification of the ethanol-soluble product required development of a scheme to separate it from the biphenyl.

Initially, a solvent-solvent extraction procedure was investigated. It was found that the whole sample dissolved in formamide and, when the formamide solution was shaken with diethyl ether, the color remained in the formamide. Moreover, evaporation of the diethyl ether phase left a white residue. However, removal of the formamide (bp 195 C) from the solution at 50 C with a flash evaporator was extremely slow. Hence, alternative separation procedures were sought.

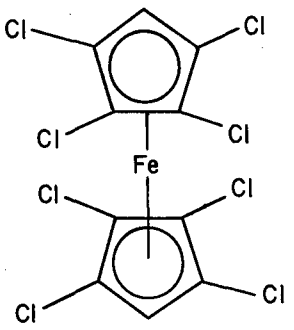
It was found that shaking the solid mixture of biphenyl and unknown with diethyl ether resulted in a partial separation. The ether became slightly yellow and the volume of the solid phase was greatly reduced. Since the ether phase appeared to contain only a minor fraction of the whole sample and only the major products of the pyrolysis are of interest, ether extraction of the solid was chosen as the separation technique. The solids were separated from the ether by centrifugation. The dark red-brown solid was transferred from the centrifuge tube to a 150-ml beaker by washing with ether. The ether was removed from the sample by evacuation at room temperature.

A solvent search on the residue indicated that only formic acid, ethanol, and methanol were solvents. Several hours' contact of the solvent with the dried sample was required before dissolution occurred.

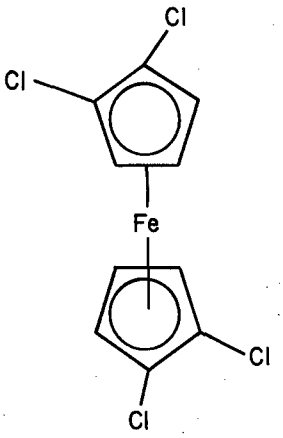
The elemental analysis of this compound, reported by Clark Microanalytical Laboratory, is given in Table IV. The large discrepancy between the total of the reported analysis (57.07) and 100 percent is difficult to rationalize. The only additional element which could be present in the sample is oxygen. However, such a large oxygen content is unlikely.

Chlorinated Ferrocenes

Two samples of chlorinated ferrocenes with unusual thermal properties were submitted to Battelle by F. L. Hedberg and H. L. Rosenberg for examination. Differential scanning calorimetry coupled with microscopic observation of the sample during heating at WPAFB[16] indicated that the sample underwent several transitions between the solid and liquid states. The samples are expected to have the structures



Sample FLH-$FCCl_8$



Sample FLH-$FCCl_4$

The results obtained at WPAFB were confirmed at Battelle. DTA thermograms of the samples (see Figures 9 and 10) indicate that three transitions occur on heating each sample. The small transition at 152 C and the large transition at 169 C that are present in the DTA thermogram of Sample FLH-$FCCl_8$ suggest that the first mesophase reached on heating this sample is of the plastic crystal type; i. e., rotational freedom is greatly increased but the material is still effectively a solid. The absence of any visible change at this point when observed on the hot stage of a polarizing microscope supports this classification. In addition, the structure of Sample FLH-$FCCl_8$ is compact and symmetrical as required for plastic crystals. Classification of the mesophase existing between 169 C and 209 C is not clear-cut. It is likely to be a liquid crystalline phase. Both the initial large transition and the likelihood that the chlorines will line up opposite each other resulting in a long, thin molecule strongly indicate that Sample FLH-$FCCl_4$ should be classified as a liquid crystal. Moreover, the review article of Brown and Shaw[17] indicates that the initial state must be smectic and the mesophase at the higher temperatures must be nematic.

The general classification of materials provides a starting point for identifying potential applications of these materials. The report prepared by E. Drauglis of Battelle in conjunction with Kent State workers under Air Force contract should be of considerable assistance for this purpose.[18]

Silicon-Nitrogen Polymers

It was previously reported[3] that the number-average molecular weights (M_n) of Samples HR-122 and HR-109 determined by vapor-pressure osmometry (VPO) were

inconsistent with those predicted by gel-permeation chromatographic (GPC) analysis. A recheck of the VPO results substantiated the earlier results – i.e., 7,000 for HR-122 and 11,000 for HR-109. This, then, made the GPC results suspect. The M_n is determined from a GPC trace by use of the expression

$$M_n = \frac{\sum_i H_i}{\sum_i H_i/M_i}$$

where H_i is the trace height at retention volume i and M_i is the molecular weight expected to appear at retention volume i. Therefore, if the intervals between retention volumes are sufficiently small[19], the M_n is simply the area of the GPC trace divided by the area under the curve defined by H_i/M_i as a function of retention volume. Plotting the H_i/M_i function permits identification of the relative contribution to M_n of various regions of the GPC trace. As can be seen in Figure 11, the H_i/M_i functions for Samples HR-109 and HR-112 indicate that the primary contribution to the M_n was made by species eluting between 165 and 178 mls. This is in contrast with the H_i function (the GPC trace) where this region makes a minor contribution to the total area. Based on polystyrene calibration, these molecules have molecular weights of less than 1,000 and could be quite different in structure from the bulk polymer. If the response factor of the GPC to these species differs appreciably from the bulk polymer, as is likely[20], then any M_n calculated from the GPC trace could not be used to evaluate the success of the polymerization. The possibility that part of the trace height between 150 and 165 ml is a result of overlap of the species which peaks at approximately 170 ml prevents calculation of an accurate M_n for the polymer sample in the absence of the species peaking at 170 ml. The GPC results indicate that the VPO results for these samples are of limited value.

BBB and BBL Films

F. E. Arnold (LNP) has submitted to Battelle films of BBB and BBL sample polymers prepared in two ways for determination of tensile strength, rupture elongation, and low-angle X-ray diffraction pattern.

The tensile strength and elongation at break of the films (see Table V) were determined on 1.0-cm-wide strips using one of Battelle's Instron Universal Testers. The gage length was 1.758 in. and the cross-head speed was 0.5 in./min. Hence, the rate of elongation was 28.5 percent/min. All measurements were made in a room whose temperature is controlled at 73 F and 50 percent relative humidity. The average thickness of the films was measured with a micrometer. The repeatability of the measurement was about 1×10^{-4} inch. The variation of the film thickness with position appeared to be the same order of magnitude as the repeatability. The density of the films was estimated by dividing their weight by the product of their length, width, and average thickness. In view of the uncertainty of the average thickness, the reported density could differ from the actual density by as much as 25 percent. Since the calculated tensile strength depends on the cross-sectional area of the strip, the uncertainty of the reported values is also quite large.

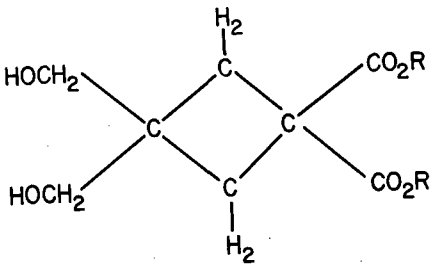
The BBB and BBL films were examined by X-ray diffraction methods to determine the effect of preparation technique and structure on the degree of crystallinity or orientation in them. As crystallite size effects are revealed by the breadth of the diffraction lines produced by them, a diffractometer method (Phillips) was used for the examination. The films were supported on a Si standard block which was then mounted on the axis of the goniometer. Filtered chromium radiation was used for the analysis. The difference between the scattering of the Si block by itself and the intensity observed with the combination was used to determine the peak position and width-at-half-height (W 1/2). The results of this examination are given in Table VI.

An interplanar spacing of 3.5 A is a typical carbon-carbon spacing in graphitic structures. In the case of the BBL films, it appears likely that the planar segments of the molecules often are separated by 3.5 A. Since BBB has much greater rotational freedom than BBL, the absence of a 3.5 A scattering from the BBB film in the plane of the film suggests that a planar configuration does not occur as often with this polymer as with BBL. Observation of a more intense 3.5 A scattering perpendicular to the plane of the film than that observed parallel with the plane suggests that the predominant orientation of the planes of the BBL molecules are parallel with the surface of the film. The interplanar spacing of between 8 and 8.5 A most likely reflects the separation between the regions of high electron density associated with the naphthalenic and benzoic nuclei. Absence of appreciable scattering from spacings of this type perpendicular to the plane of the film suggests that the long axis of the polymer molecules is predominately parallel with the plane of the film. While the X-ray data reported herein is similar to that reported by Berry, et al[13], the interpretation differs somewhat.

The W 1/2 of a peak provides an indication of the size of the crystallites in the material and/or the variation in interplanar spacings. A typical W 1/2 for a crystalline material is less than 1 degree. Clearly, none of the films that were examined have appreciable crystallinity. Comparison of the $W_{1/2}$ values given in Table VI suggests that the 0.133-g film of BBL may have the most regular structure. The differences between the other films are of the same order as experimental error. Hence, it appears that the differences in preparative technique did not appreciably affect the crystallite size in these films.

Spiropolyester

Initial efforts of Sharts and coworkers[21] aimed at scale-up of the polymerization of



IV

TABLE V. TENSILE DATA ON BBB AND BBL FILMS PREPARED BY ARNOLD (WPAFB)

Sample	Average Thickness[a], in. $(10)^4$	Tensile Strength[b], lb/in.^{2}	Ultimate Elongation[c], percent	Density, g/cm^3
BBB 0.266 g (cast)	20	5600[d]	45.5	1.3
BBB 0.133 g (cast)	4	3800[d]	54.0	0.8
BBL 0.266 g	9	4000	2.70	1.4
BBL 0.133 g	5	2500	1.07	1.2
BBL-M-F-M	6	3400	2.49	0.6
BBL-M-F-F	9	1700	1.99	0.9
BBL-M-E	5	1250	1.57	0.55

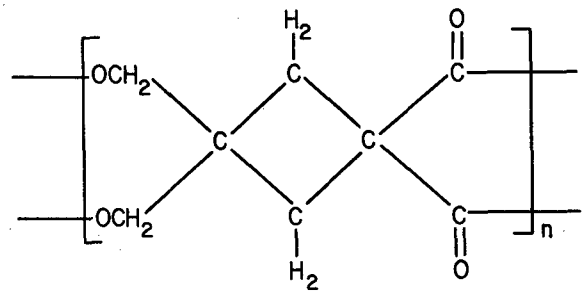
(a) Average of three or four measurements. Measurement uncertainty and thickness variability were about ±0.0001 inch.
(b) Calculated from initial cross-sectional area.
(c) In some cases the sample was not completely severed at this elongation but supported a much smaller load before complete separation.
(d) Cross section of sample at break was half of the initial value.

TABLE VI. X-RAY DATA PARALLEL WITH THE PLANE OF BBB AND BBL FILMS

Sample	Major Peak		Minor Peak
	Interplanar Spacings, A	Approximate $W_{1/2}$, °θ	Interplanar Spacing
BBB 0.266 g (cast)	--	--	6.5[a]
BBB 0.133 g (cast)	--	--	6.5[a]
BBL 0.266 g	8.1	2.8	3.5
BBL 0.133 g	8.3	2.4	3.5
BBL M-F-M	8.5	3.2	3.9
BBL M-F-F	8.5	3.3	3.7
BBL-M-E-	8.4	2.8	3.7
BBL 0.266 g	3.4[b]	--	--

(a) Difficult to distinguish from background.
(b) Perpendicular to plane of film.

were disappointing. Recently, Sharts has reported that the properties of the polymer depend on the amount of residual acid in the monomer before polymerization.[22] A sample of a polymerization product obtained under "acid free" conditions from IV where R is a methyl group was submitted to Battelle for characterization. The sample, labelled 34-B-7, had been heated for 12 days at 80 C and 5 days at 120 C in order to aid the condensation. Based on his IR spectrum, Sharts believes the structure of the sample is predominantly



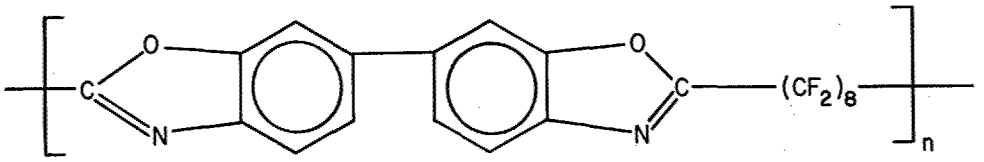
The infrared spectrum of this compound obtained at Battelle (see Figure 12) was in agreement with that expected for an ester. While an appreciable OH absorption was observed, a weak band at 1630-1640 cm^{-1} suggests that water is present. However, indication of CH_3 absorptions in the stretching and bending regions suggests that there is residual $-CO_2CH_3$ in the molecule.

A solvent search on this sample using the microscopic technique[1] and the previously given list of solvents[3] gave no indications of solubility. Since the synthesis route does not preclude cross-linking, the insolubility could reflect occurrence of cross-linking. However, no appreciable swelling was observed.

The DTA thermogram of this sample (Figure 13) indicates several transitions between room temperature and 800 C. The severe noise in the thermograms reflects sample shrinkage during heating. As the sample shrinks, its contacts with the sample pan and the measuring thermocouple change. Also, the sample adheres to the pan after initial heating so that the dimensional shifts also alter the shape of the pan (the sample pan is thin aluminum foil). The two first-order endothermic transitions between room temperature and 300 C suggest that two crystalline phases are present in the ratio 10:90. The two exothermic peaks suggest two separate decompositions. If the sample were a physical mixture of two different structures, its DTA thermogram would be similar to the one observed. However, several alternate structures, such as a block copolymer, could produce the observed thermogram.

Perfluoroalkyl Bibenzoxazoles

Two products of the synthesis program at Dow Chemical Company aimed at preparation of perfluoroalkyl heterocyclic polymers were submitted to Battelle for molecular weight and subambient DTA measurements. These samples were prepared by reaction of dihydroxybenzidine and methyl perfluorosebacimidate, which would be expected to yield a polymer of the structure



The structure and thermal properties of other samples obtained by this reaction were examined at Battelle previously. [2]

Determination of the weight-average molecular weight (M_w) of these samples was made difficult by problems with clarification of the only feasible solvent, which is hexafluoroisopropanol (HFIP), and sensitivity of the scattering envelope to the position of the light-scattering cell relative to the incident beam. Initial clarification attempts were made with the filtration system described previously[3] using a 0.45-μ Solvinert filter (Millipore). Before introduction of filtered HFIP into a light-scattering cell, the cleanliness of the cell was checked by observation of the scattering envelope of benzene in it. It was deemed acceptable if a z-value of less than 1.05 was obtained. Visual observation of foreign matter in the cell containing HFIP which had passed through the filter 20 times was confirmed by observation of a z-value in excess of 1.5 with it. A Gelman α-6 0.45-μ filter and a Selas Flotronics metal membrane filter with a pore size <0.45 μ were tried as alternative filters with no observed improvement in the z-value of filtered HFIP. In addition, a Buchner funnel with a 0.9 to 1.3-μ-pore glass frit modified to permit operation with the syringe recycle system was tried. To minimize water pickup during filtration, molecular sieves were placed on the frit. No improvement in z-value was noted. As a check of the filtering systems, the z-value of benzene was determined after two passes through the system. In all cases, z-values of 1.1 or better were obtained in contrast with values of greater than 1.5 even after ten passes of HFIP. The possibility that suspended air bubbles were the source of the high z-values was minimized by allowing the filtered solvent to sit for 16 hours before determining its z-value. No difference was observed between these z-values and the ones obtained immediately after filtration.

A z-value of 1.04 was obtained with HFIP by filtration through recently purchased Solvinert filters and use of carefully closed light-scattering cells. Use of new Solvinert filters was suggested to the author by Helminiak[24], who had noted that Solvinert filters sold by the Millipore Corporation after January of 1970 appeared to be more inert than those sold previously. Although Teflon caps especially prepared for the light-scattering cells had been used in the previous work, it was observed that in some cases a second phase appeared in the light-scattering cell containing HFIP when suspended in the benzene vat of the instrument for about 15 minutes. Since this never occurred with polymer solutions in HFIP, it is suspected that the formation of the second phase is related to the surface tension of HFIP. Careful fitting of the Teflon caps to the cells eliminated formation of the second phase.

A small amount of insolubles was present in Sample CD 569-1-31 necessitating determination of the solution concentration by evaporation of the solvent. While solution concentrations greater than 0.001 g/ml give scattering intensities more than four times that of the solvent, the Zimm plot obtained from these solutions was difficult to

construct. Use of solutions with concentrations ranging between 1×10^{-4} and 4×10^{-4} g/ml led to a Zimm plot which was approximately linear at the low angles. While these concentrations were appropriate for obtaining the low-angle scattering, they resulted in appreciable sacrifice in accuracy of scattering intensity at 75, 90, and 105 degrees. The value of M_W of 120,000 obtained from the Zimm plot is consistent with the intrinsic viscosity of this sample, which is 61 ml/g. That is, the greater rigidity of the bibenzoxazole unit as compared with a polystyrene molecule leads to the expectation that its M_W should be lower than that of a polystyrene with the same viscosity. The M_W of a polystyrene with intrinsic viscosity of about 60 is 2×10^5.

Attempts to determine the glass transition of these materials by subambient DTA gave inconclusive results. Primarily, the analysis was complicated by the low bulk density of the polymers, which limited the amount of polymer that was in contact with the thermocouple. In an effort to increase the amount of sample in contact with the thermocouple, a special encapsulation procedure was used. This involves compacting of the sample between two of the aluminum DTA pans and then crimping the edges. This procedure permitted use of about 3 mg for the analysis.

The DTA thermogram obtained with Sample CD 569-1-31 is shown in Figure 15. A heating rate of 10 C/min was used instead of the usual 5 C/min heating rate in an effort to magnify the changes associated with the glass transition. The change in trace slope between -60 and -70 C is probably an artifact of the analysis. The transition at 0 C, on the other hand, was observed in thermograms obtained at lower heating rates and could reflect a transition in this sample. A similar peak was observed in the subambient thermogram of Sample 9659-94H, although it was not as strong.

Solvent Search

Recently, Patterson has shown[23] that the lower critical solution temperature (LCST) is a generally occurring phenomenon in polymer solutions. Although the LCST is often above the normal boiling point of the solvent, the "goodness" of the solvent is generally not at its maximum at the solvent boiling point. Patterson has indicated that the solubility-parameter concept is consistent with the LCST phenomenon. This is the case because the molar volume of the solvent, ($\overline{V}$), changes much faster with temperature than that of the polymer. If the solubility parameters of the polymer and solvent are equal at a given temperature, then raising the temperature will make them unequal. As this difference increases, solubility decreases. Since the solvent search technique employed in this program has involved observation of interactions at a number of temperatures, the question arises as to what has been the effect of this variation in temperature on solubility-parameter coverage. Elevated temperatures have been used in order to increase the rate of solution formation. If crystallinity is present in a polymer, it is well known that dissolution rate will be markedly increased above its crystalline melting point. However, increasing temperature will decrease Evap and increase $\overline{V}$. Hence, the solubility parameter of the solvent will decrease. If the decrease in solubility parameter with increasing temperature depends on solvent structure, then the solubility-parameter coverage at 25 C expected from the solvent properties at 25 C will not be obtained at elevated temperatures. However, the temperature dependence of the molar volumes of a number of solvents – i.e., $1/\overline{V}(d\overline{V}/dT)$ – differing in polarity and boiling point was reasonably constant as shown in Table VII. Therefore, while the solubility parameters of all solvents will be reduced by increasing the temperature, it can be

expected that the variation in solubility parameter achieved with the current solvent list will be retained at elevated temperatures. Hence, the benefits of the increased rate of solution at elevated temperatures have not detracted from the solubility-parameter coverage.

TABLE VII. DEPENDENCE OF MOLAR VOLUME ON TEMPERATURE

Solvent	Molecular Weight	Temperature, C	$\overline{V}$	$\frac{1}{\overline{V}}\frac{d\overline{V}^{(a)}}{dT}$
Ethanol	46.07	0	57.14	0.10
		40	59.67	
Benzene	78.11	20	88.86	0.13
		80	96.01	
Nitrobenzene	123.11	25	102.70	0.091
		200	120.48	
Aniline	93.12	20	91.12	0.092
		150	102.92	
Cyclohexane	84.16	0	105.52	0.12
		70	115.19	
Methylethylketone	72.10	0	87.34	0.13
		75	96.49	

(a) Data from International Critical Tables.

III

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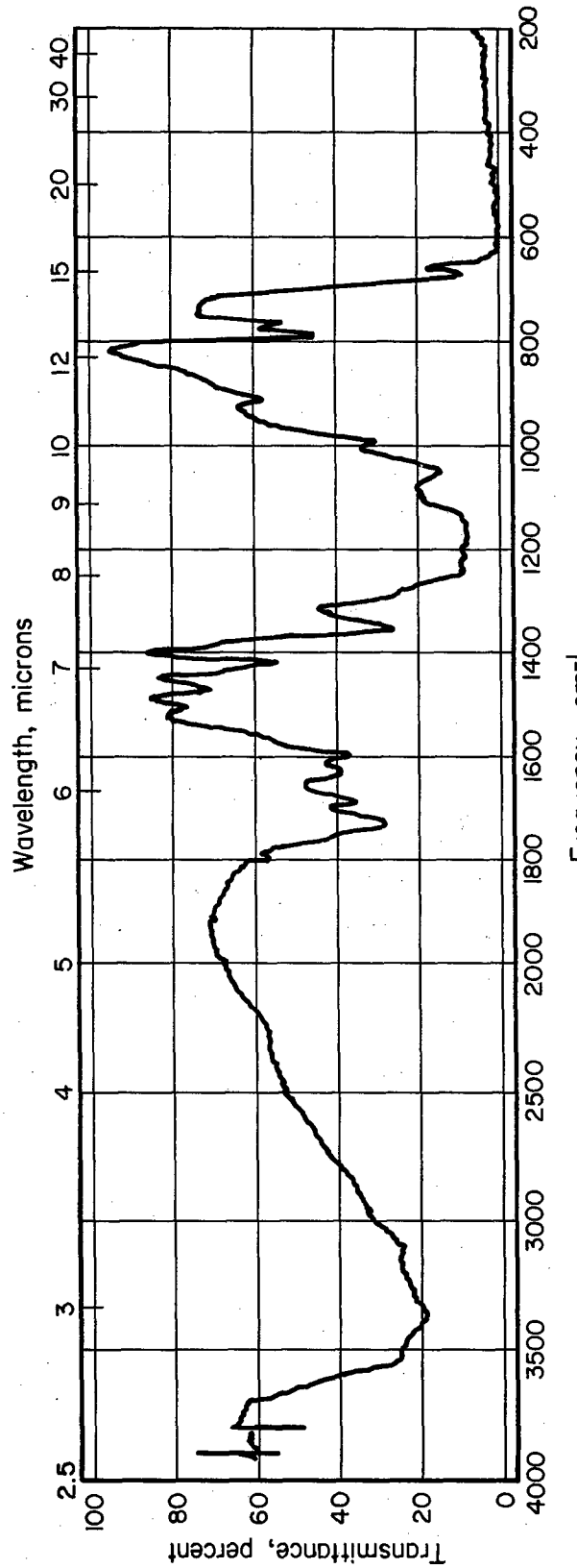

FIGURE 1. INFRARED SPECTRUM OF POLYPYRROLONE SAMPLE 18E

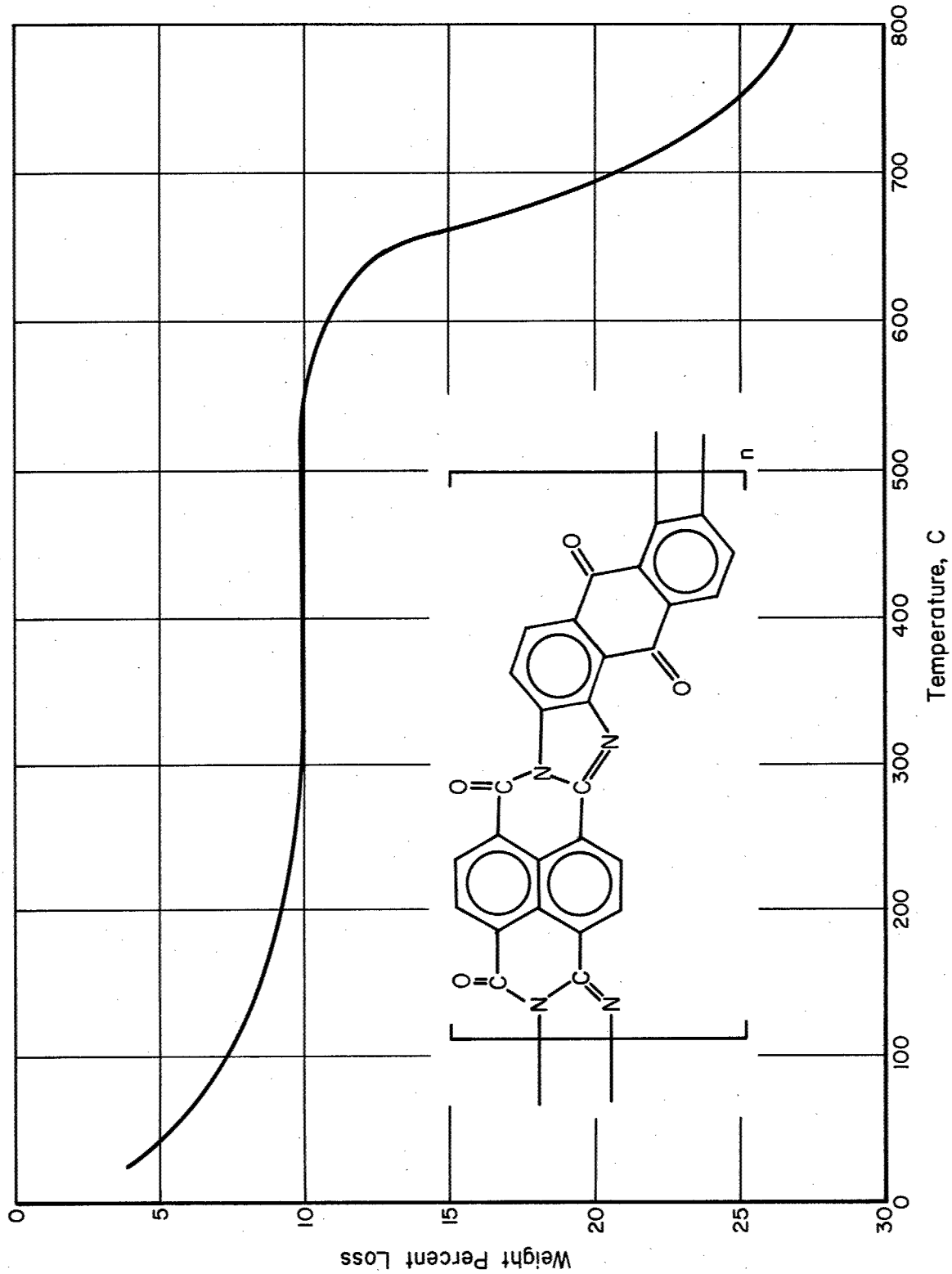

FIGURE 2. TGA THERMOGRAM OF POLYPYRROLONE SAMPLE 18E AT 4 C/MIN HEATING RATE AND 0.1 TORR USING A 12.40-MG SAMPLE

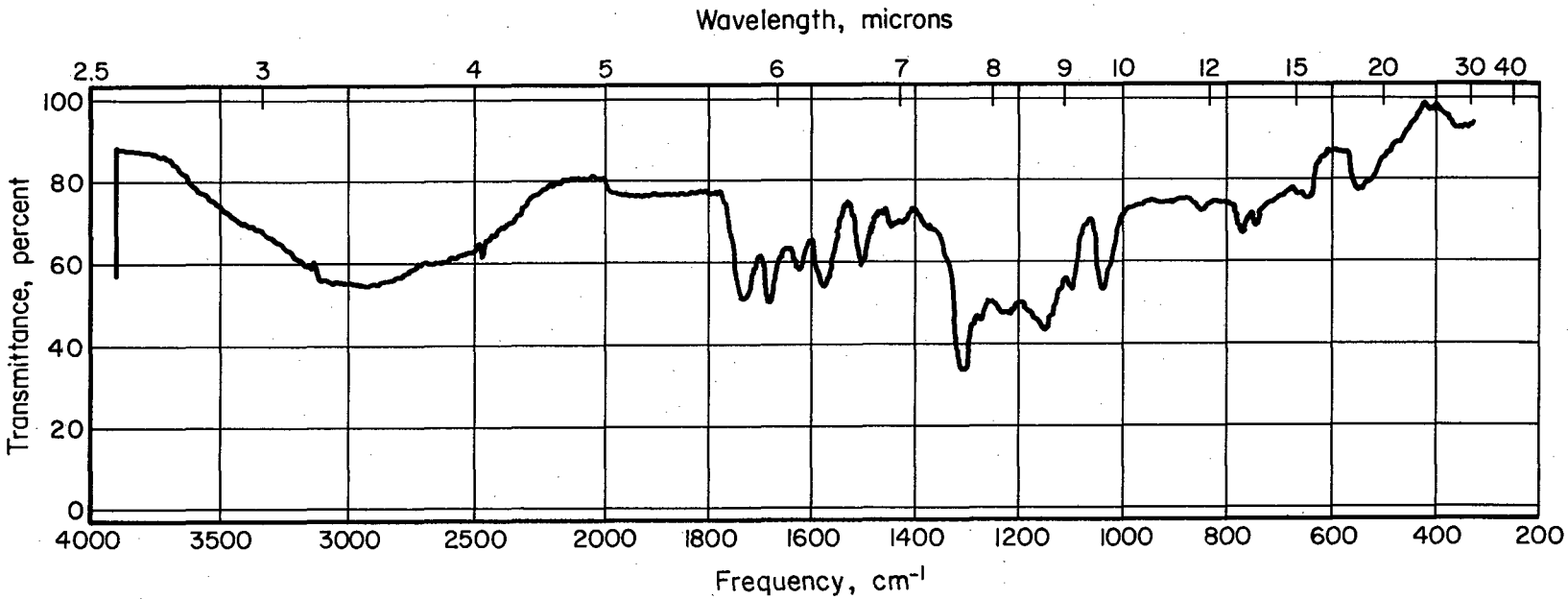

FIGURE 3. INFRARED SPECTRUM OF POLYPYRROLONE SAMPLE PE-82B

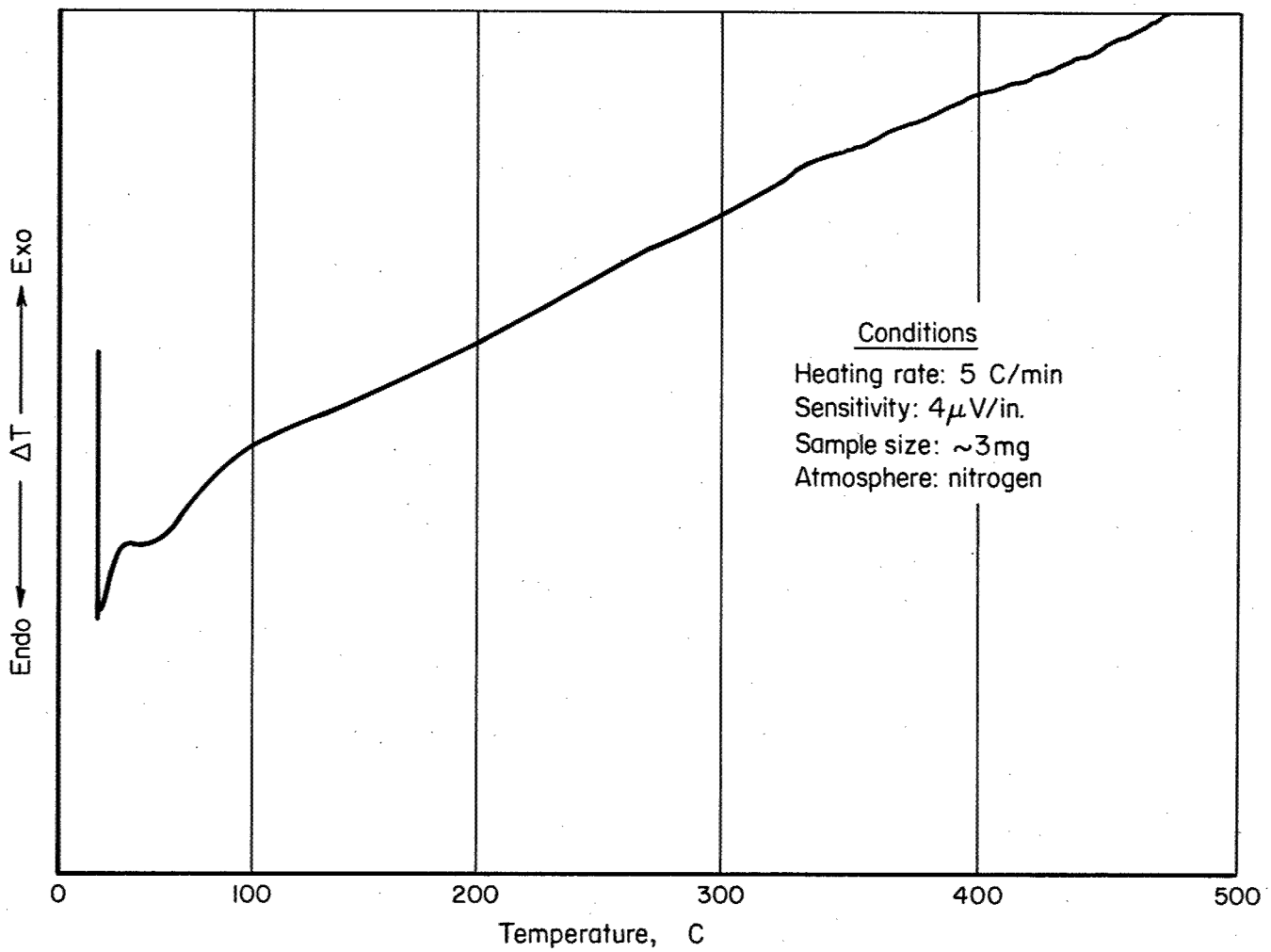

FIGURE 4. DTA THERMOGRAM OF POLYPYRROLONE SAMPLE PE-82B

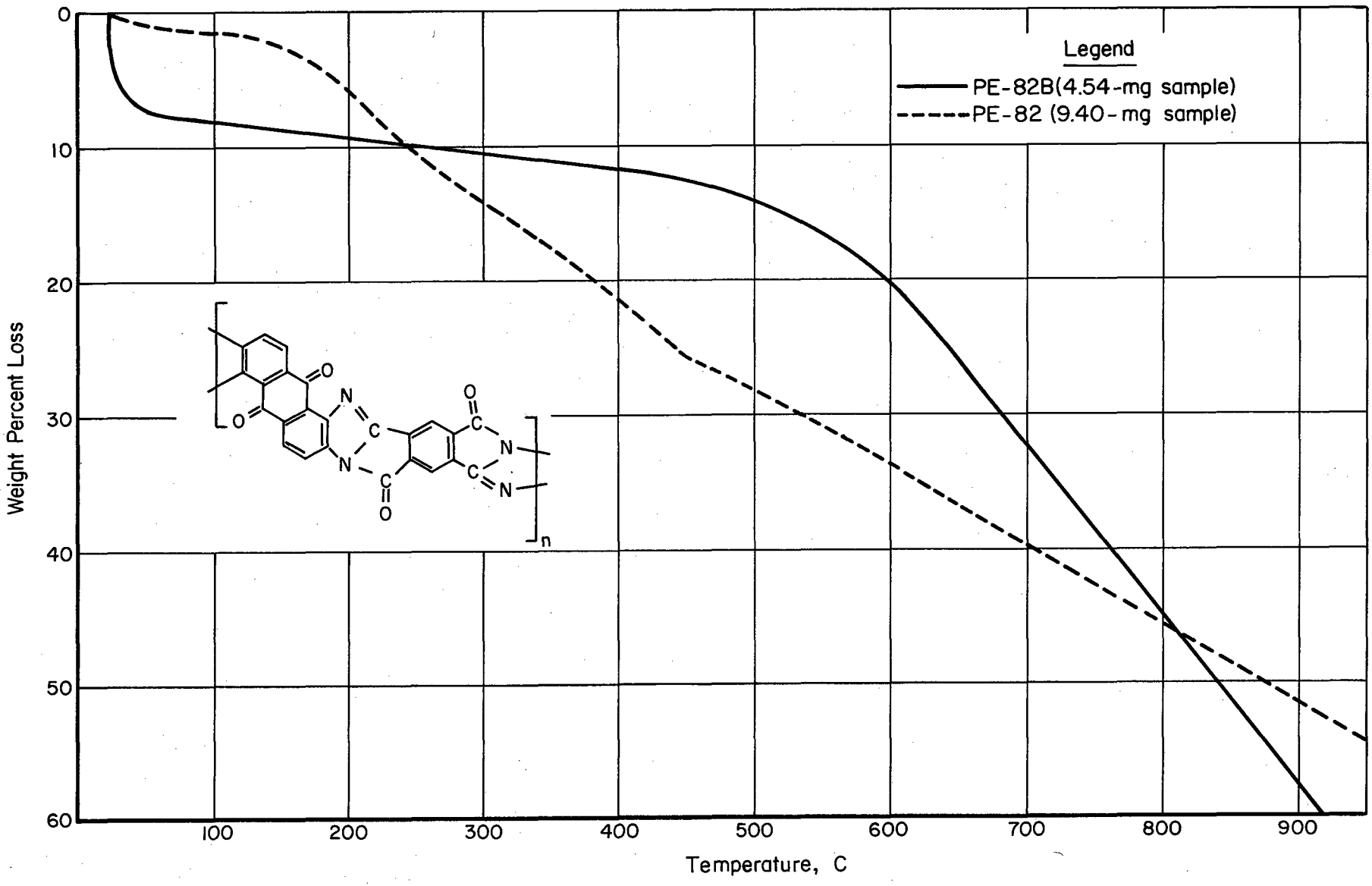

FIGURE 5. TGA THERMOGRAMS OF POLYPYRROLONE SAMPLES PE-82B AND PE-82 AT 4 C/MIN HEATING RATE AND 0.1 TORR

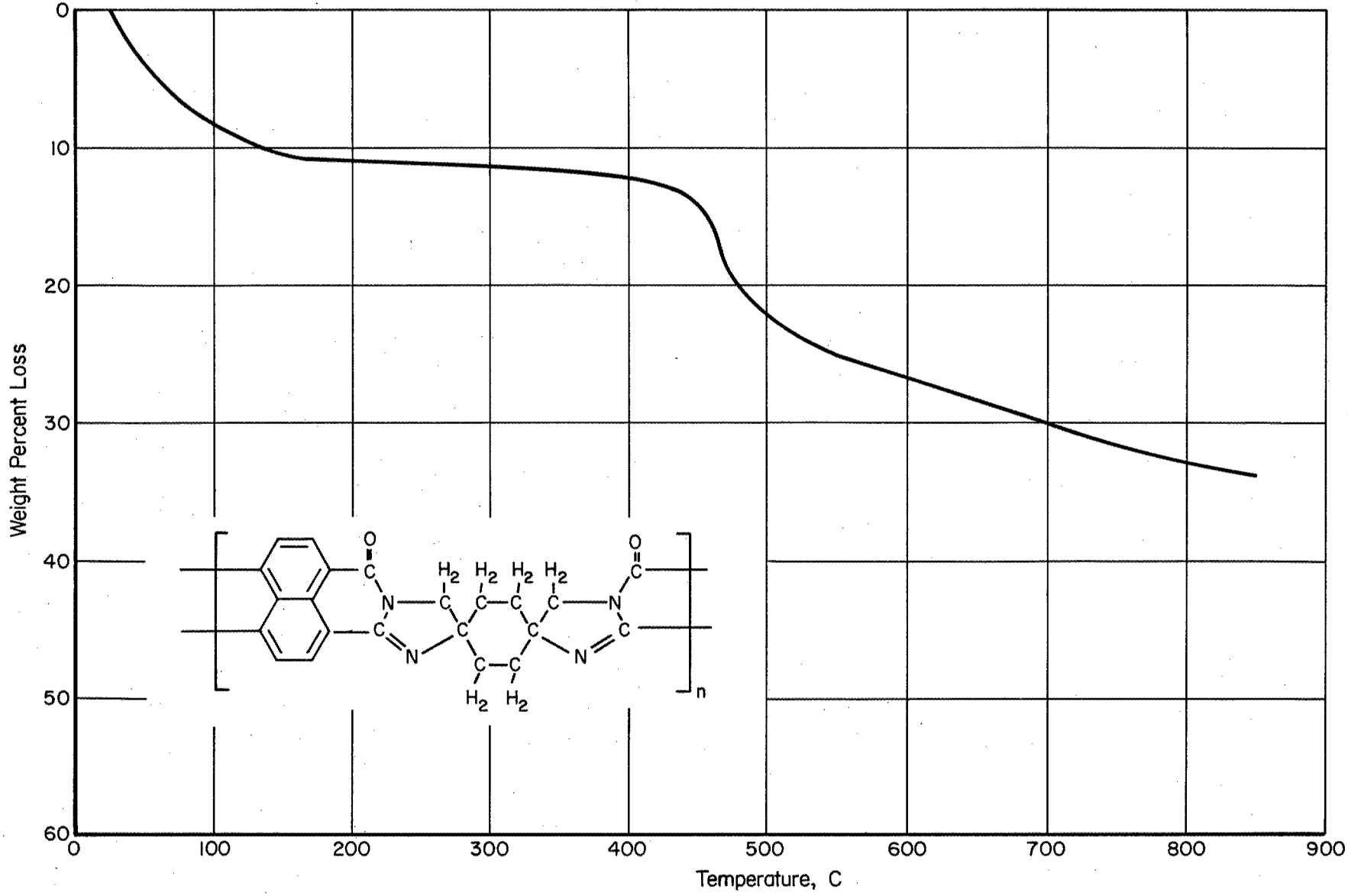

FIGURE 6. TGA THERMOGRAM OF SPIROPOLYIMIDE SAMPLE SRI-470 AT 4 C/MIN HEATING RATE AND 0.1 TORR USING A 4.74-MG SAMPLE

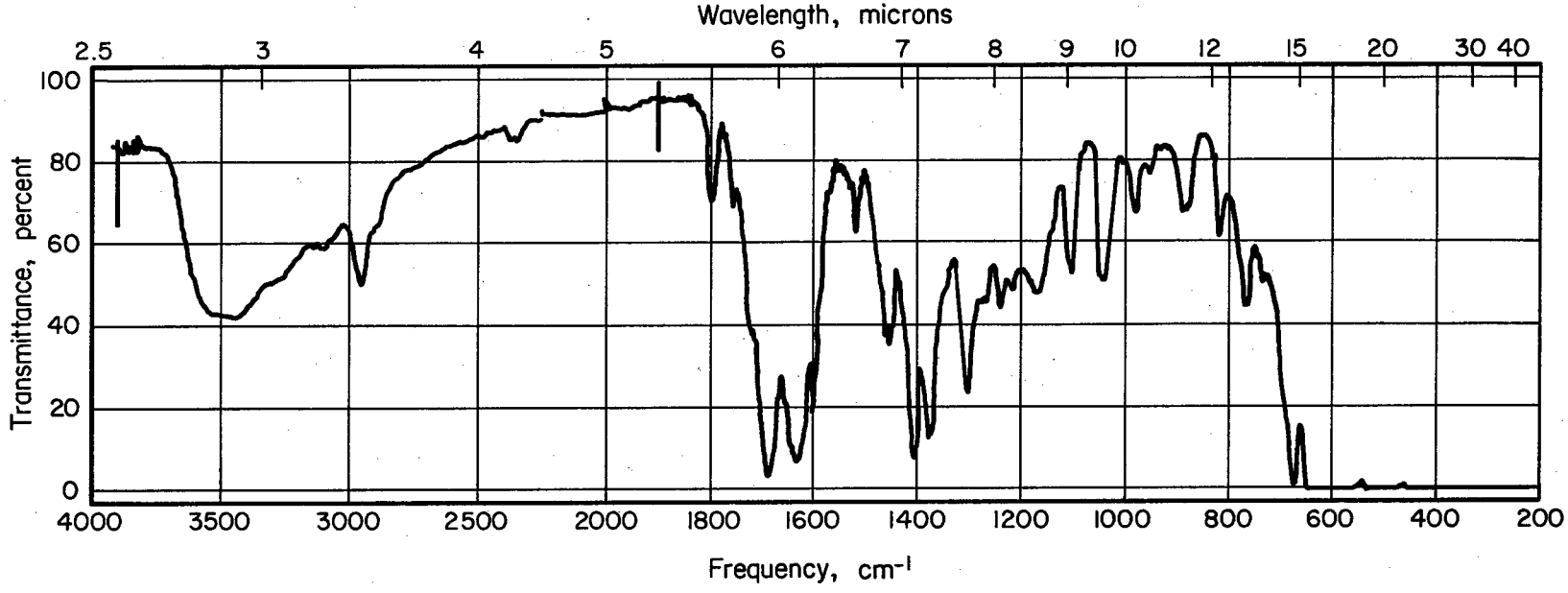

FIGURE 7. INFRARED SPECTRUM OF SPIROPOLYIMIDE SAMPLE SRI-470

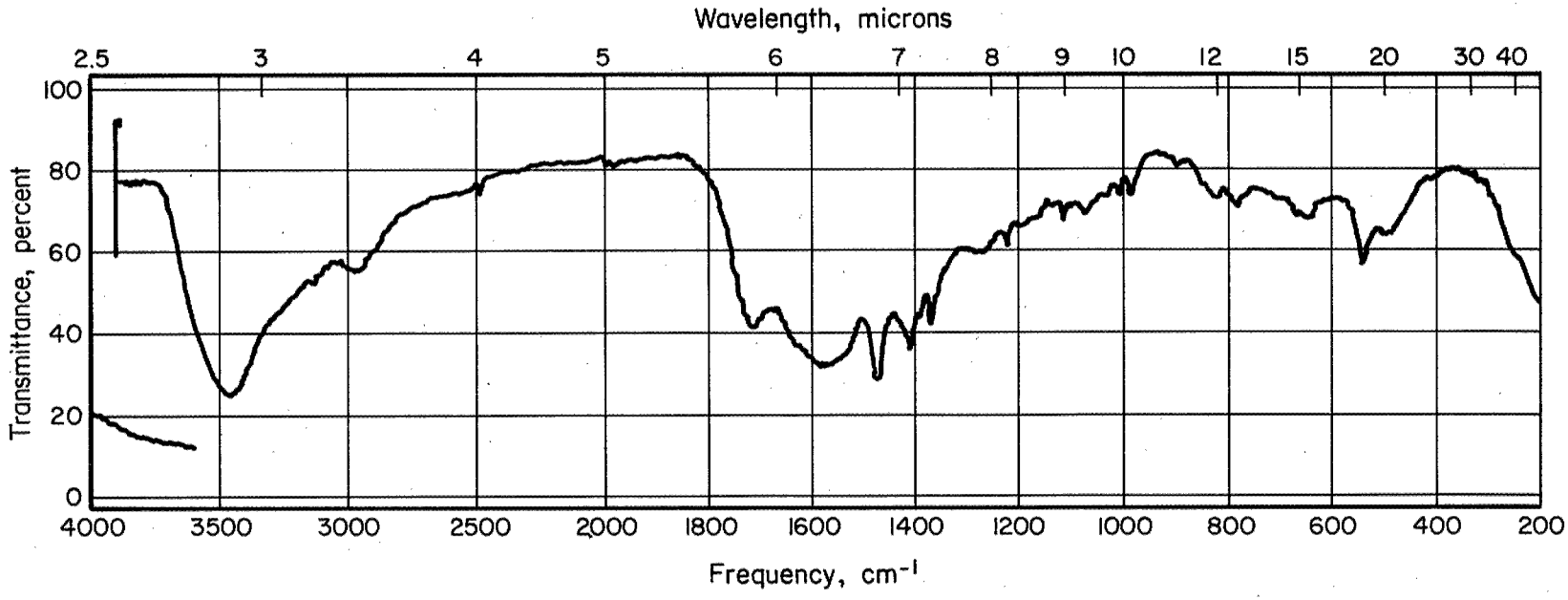

FIGURE 8. INFRARED SPECTRUM OF THERMAL PRODUCT FROM 1-CARBOXY-2-CHLOROFERROCENE

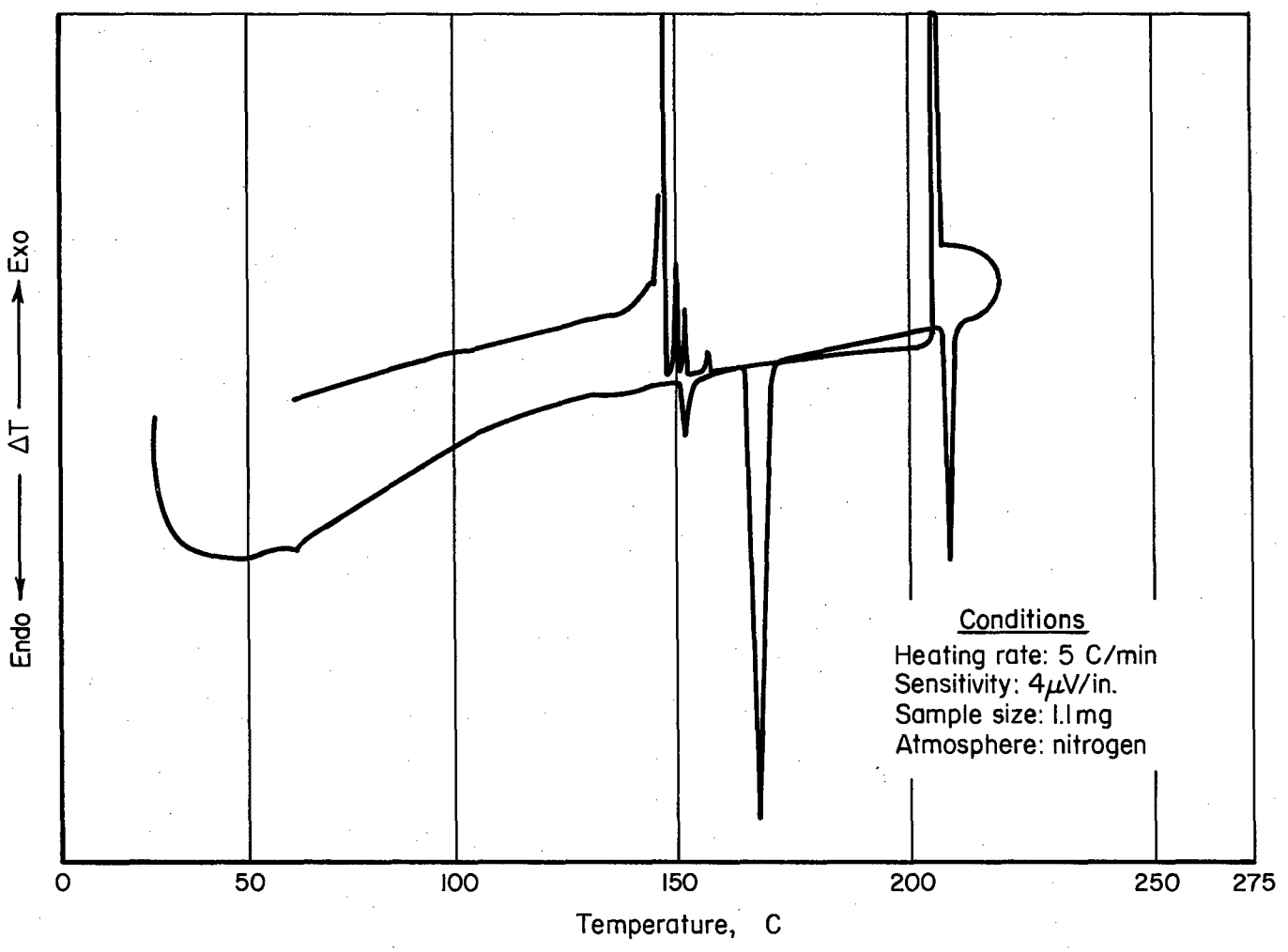

FIGURE 9. DTA THERMOGRAM OF 1,2,3,4,1',2',3',4'-OCTACHLOROFERROCENE SAMPLE FLH-$FCCl_8$

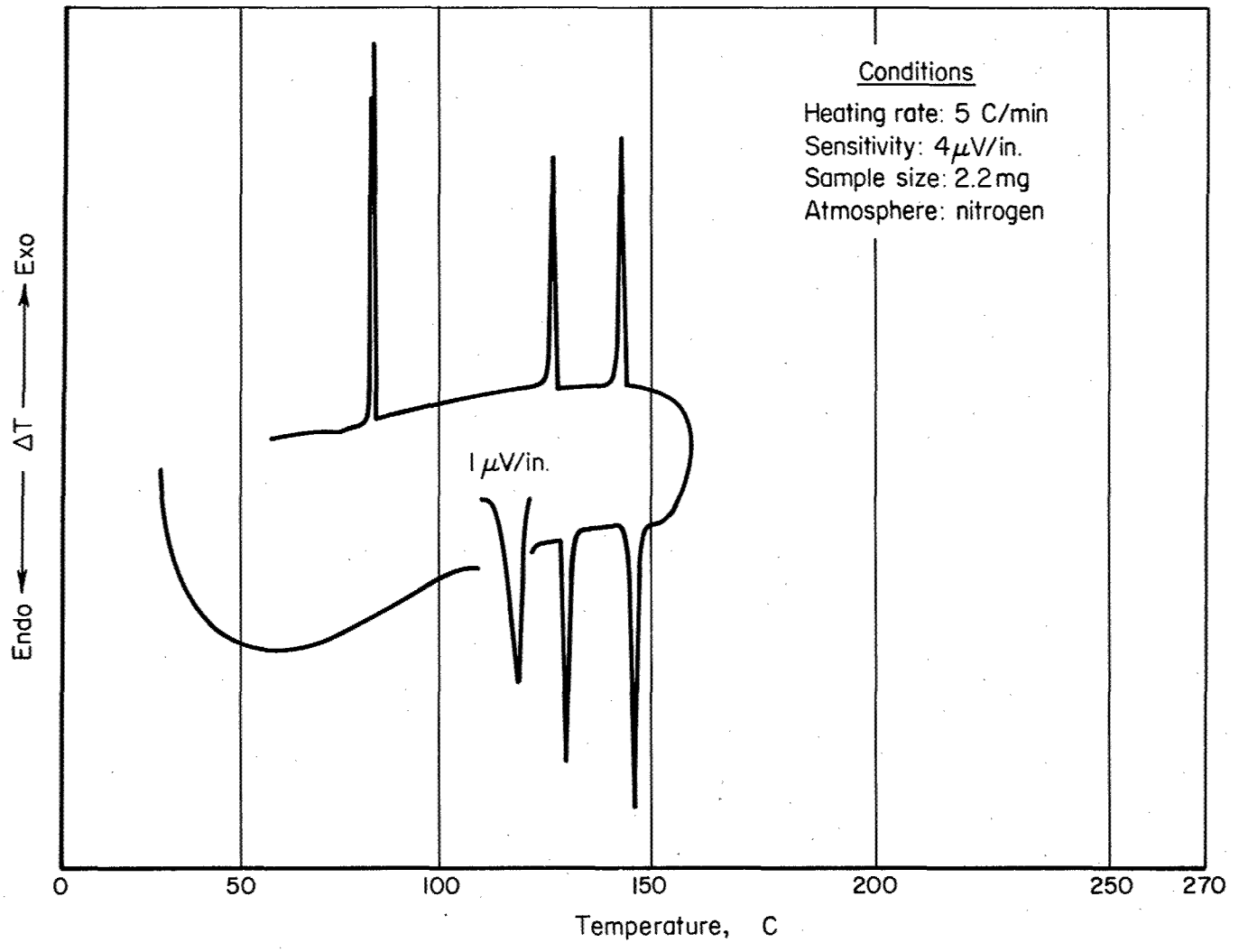

FIGURE 10. DTA THERMOGRAM OF 1,2,1',2'-TETRACHLOROFERROCENE SAMPLE FLH-$FCCl_4$

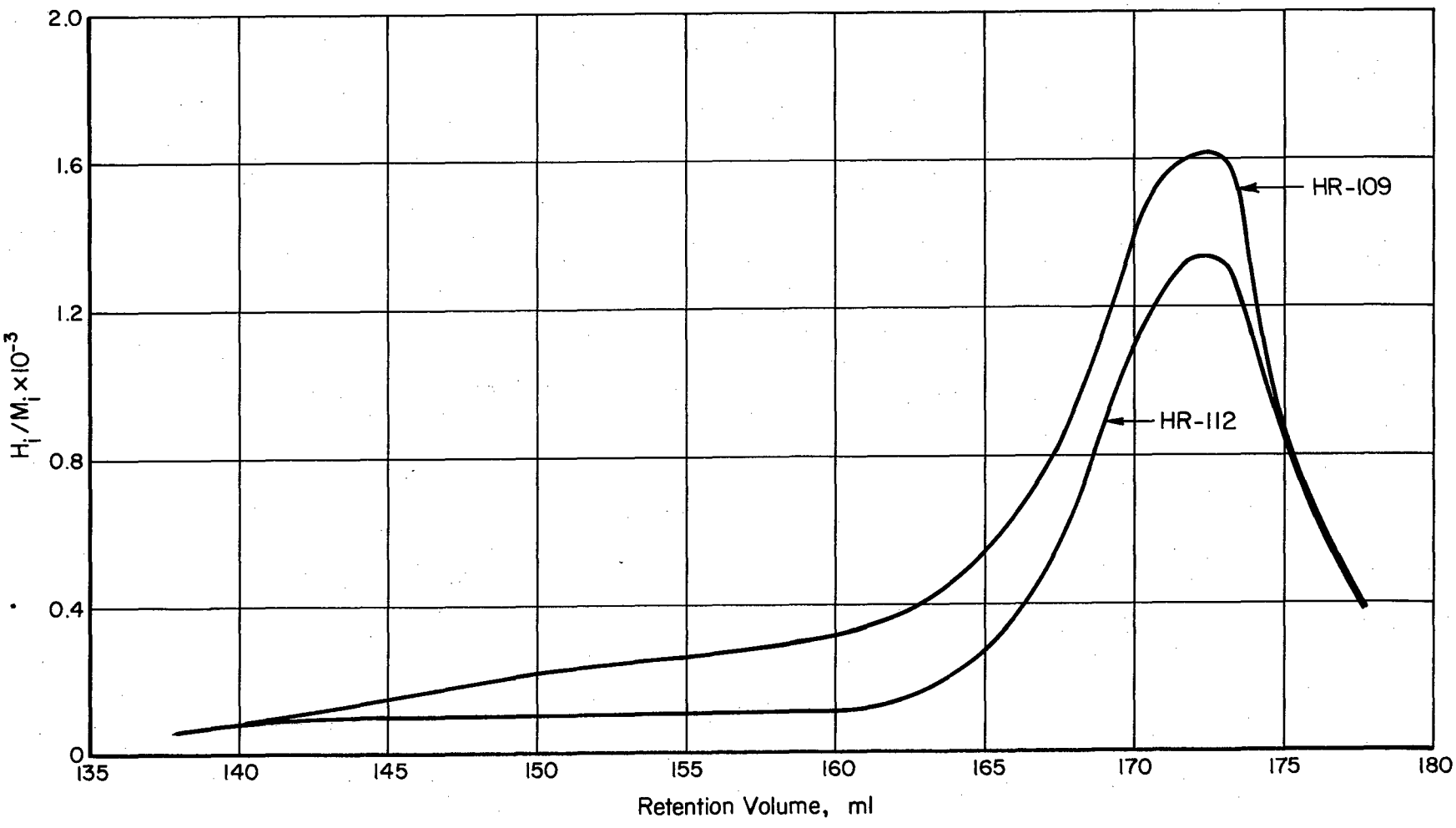

FIGURE 11. DEPENDENCE ON RETENTION VOLUME OF THE Hi/Mi FUNCTION FOR THE GPC TRACES OF SAMPLES OF TWO SILICON-NITROGEN POLYMERS

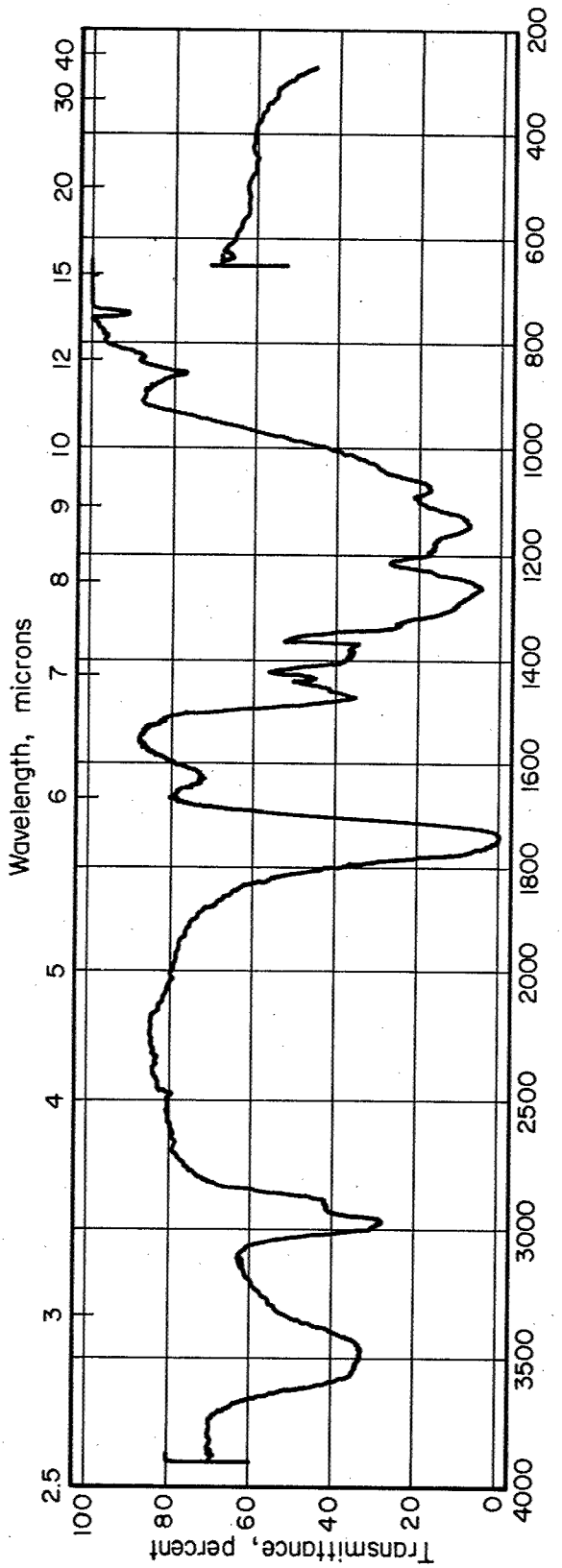

FIGURE 12. INFRARED SPECTRUM OF SPIROPOLYESTER SAMPLE 34-B-7

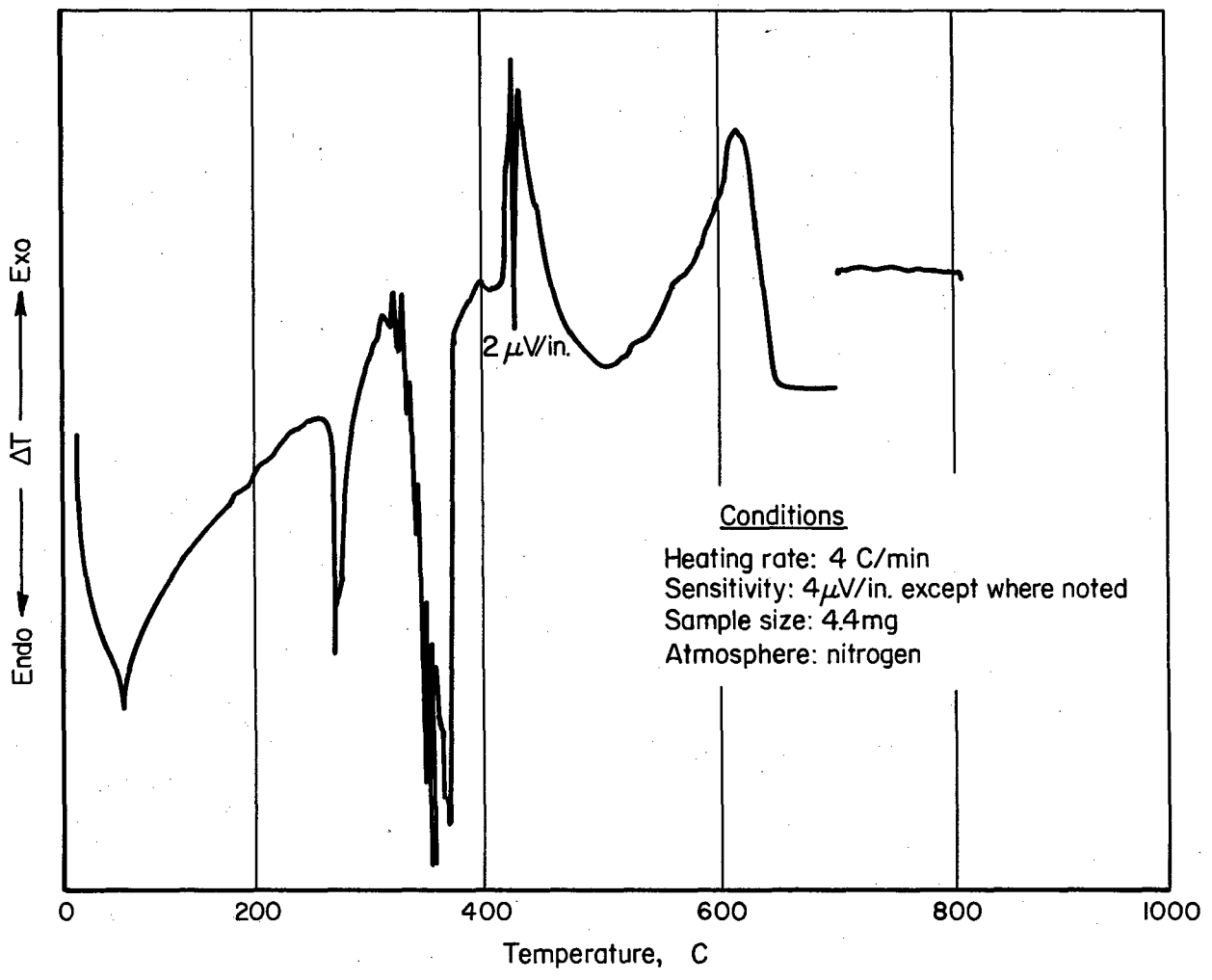

FIGURE 13. DTA THERMOGRAM OF SPIROPOLYESTER SAMPLE 34-B-7

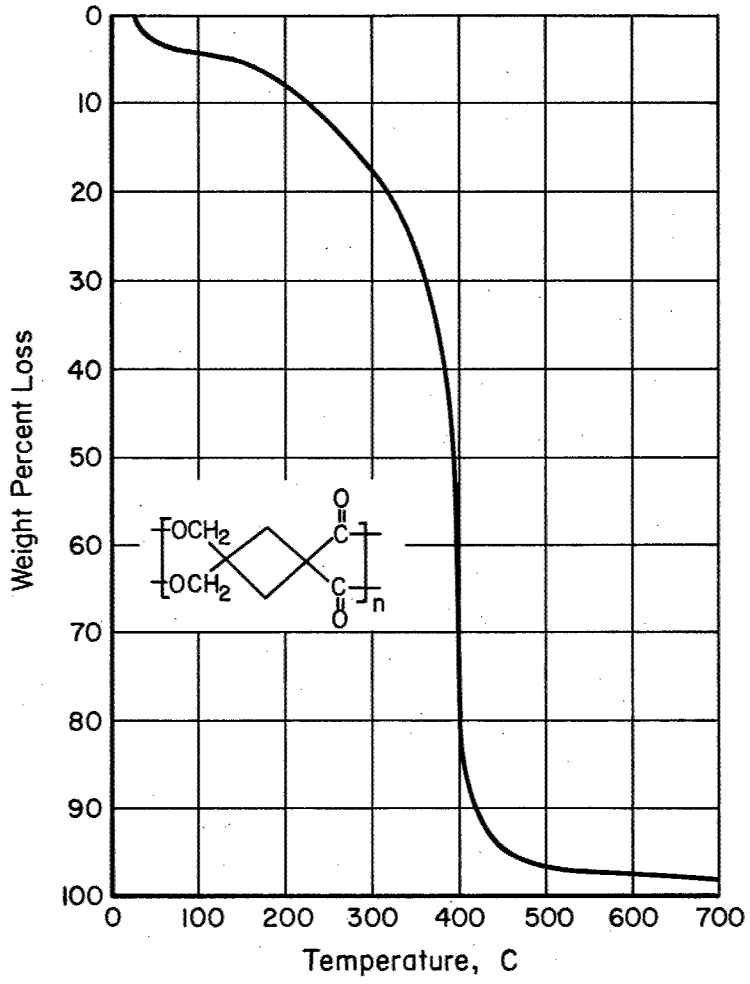

FIGURE 14. TGA THERMOGRAM OF SPIROPOLYESTER SAMPLE 34-B-7 AT 4 C/MIN HEATING RATE AND 0.1 TORR USING A 3.28-MG SAMPLE

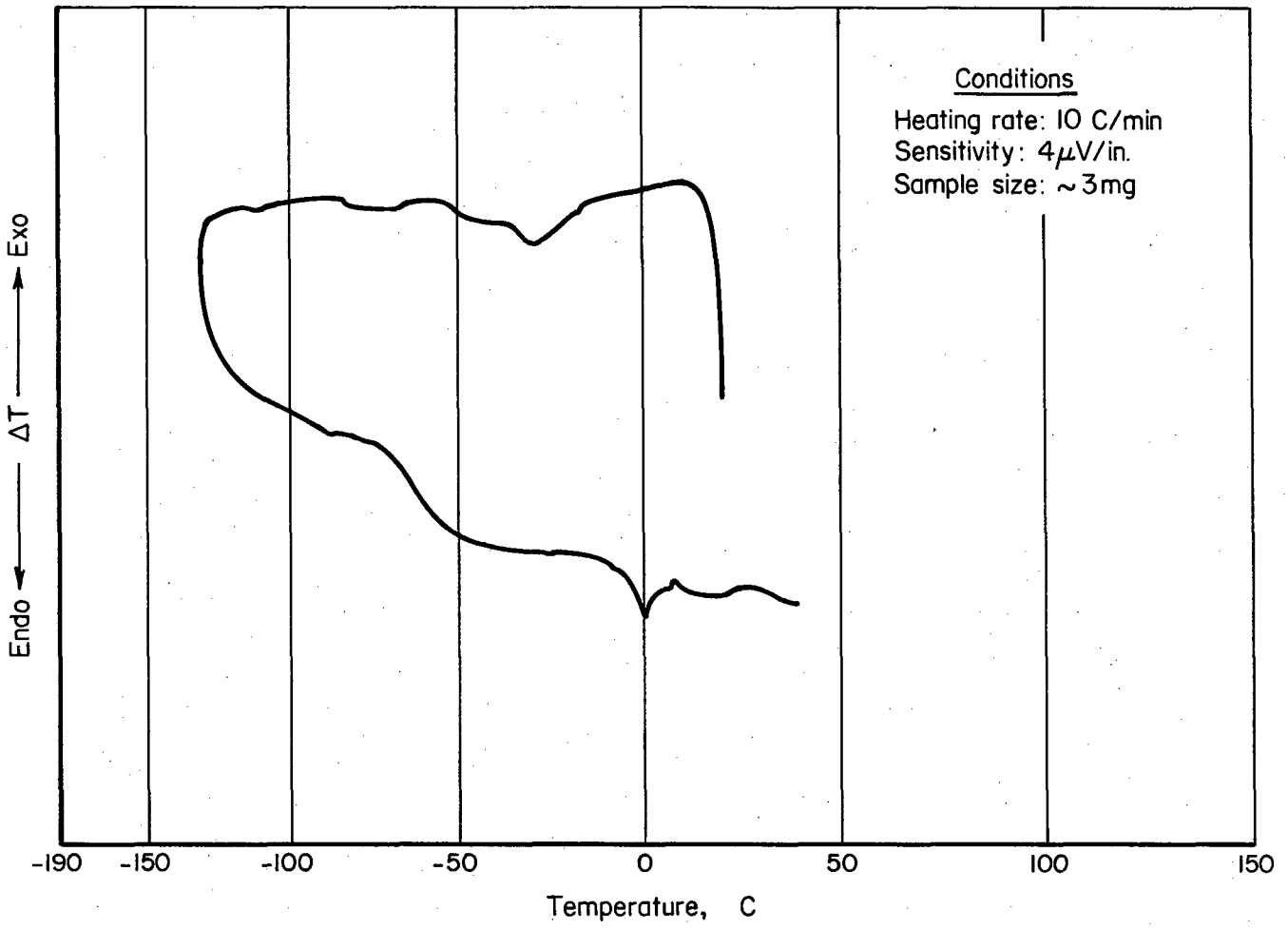

FIGURE 15. SUBAMBIENT DTA THERMOGRAM OF PERFLUOROALKYL BIBENZOXAZOLE SAMPLE CD 569-1-31

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13. ABSTRACT

Two polypyrrolone samples containing an anthraquinone moiety were characterized. Procedures for isolation of one of these from solution in strong acid were examined in detail. In addition, the structure (IR and elemental analysis), thermal properties (TGA and DTA), and solubility of both materials were obtained.

A sample of a spiropolyimide was characterized as to its structure (IR and elemental analysis), thermal properties (TGA and DTA), and dilute solution viscosity. The results obtained indicated that the sample contained significant amounts of material with structure different from that proposed for the sample.

Effort to identify the predominant structure of the thermally induced reaction of 1-carboxy-2-chloroferrocene with itself was continued. However, a definitive answer was not obtained. Two chlorinated ferrocene samples were classified as liquid crystals based on their thermal transitions and observed behavior.

Additional effort included a review of molecular weight data on silicon-nitrogen polymers, as well as determination of tensile properties and crystallite size and spacing of films obtained from BBB and BBL. The molecular weight and subambient transitions of a perfluoroalkyl bibenzoxazole sample was also obtained. In addition, the effect of variation of temperature on the extent of solvent property coverage attained during solvent search was studied. The structure, thermal properties, and solubility of a spiropolyester sample were also investigated.

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