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QUINOXALINE POLYMERS AND COPOLYMERS DERIVED FROM 1,4-BIS(1'-NAPHTHALENYLOXALYL)BENZENE AND THEIR GRAPHITE COMPOSITES

William S. Port

AVCO SYSTEMS DIVISION

Prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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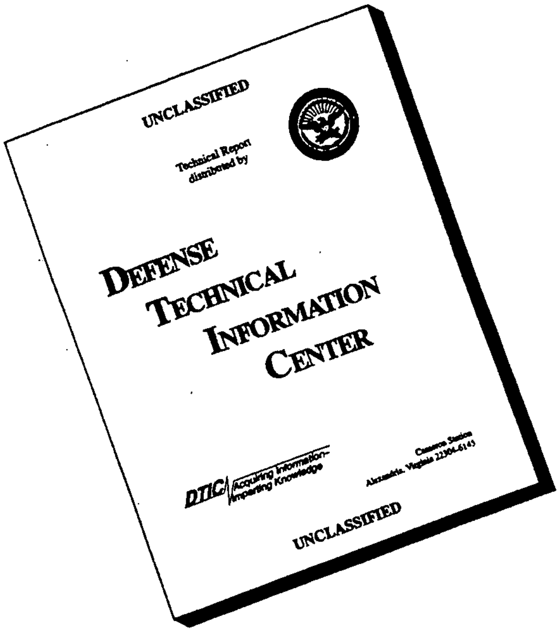
P. Delvigs, Project Manager



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16. Abstract

Experimental studies were performed with new polyquinoxalines and their graphite composites. A new monomer, 1,3-bis[(1'-naphthalenyl)oxalyl]benzene and its precursor, 1,3-bis[(1'-naphthalenyl)acetyl]benzene were synthesized and were characterized. Poly{2,2'-(1,3-phenylene)-6,6'-bis[3-(1-naphthalenyl)]quinoxalinyl} (Polymer II) which was prepared from this monomer and 3,3'-diaminobenzidine was found to be brittle. An isomeric polymer, poly{2,2'-(1,4-phenylene)-6,6'-bis[3-(naphthalenyl)]quinoxalinyl} (Polymer I) was also prepared and found to have excellent film-forming characteristics. A copolymer, poly{2,2'-(1,4-phenylene)-6,6'-bis[3-(1-naphthalenyl) co-(phenyl)(25/75)quinoxalinyl]} (Polymer III) was prepared from 1,4-bis[(1'-naphthalenyl)oxalyl]-benzene, 1,4-bis(phenyloxalyl)benzene and 3,3'-diaminobenzidine. Poly[2,3-(1,4-phenylene)quinoxalinyl], (Polymer IV) prepared from poly(p-benzil) and o-phenylenediamine had a low molecular weight and was brittle. The four polymers prepared were characterized with respect to their inherent viscosity and their elemental analysis. Polymers I and II were characterized further with respect to their transition temperature and were subjected to isothermal gravimetric analysis at 315.6° and 371.1°C. The ultimate tensile strength of Polymer I was measured at 204.4° and 315.6°C and specimens of Polymer I subjected to sustained tensile loading tests at these elevated temperatures did not rupture after 114 hours.

Composites of Hercules HMS graphite fiber and respectively Polymers I and III were fabricated as panels for preliminary evaluation of their mechanical properties. A more detailed evaluation was made of a composite of Polymer I containing 48.8 volume percent of graphite with respect to its flexural strength and modulus, interlaminar shear strength and aging characteristics. At 25°C, the flexural strength, the flexural modulus and the interlaminar shear strength were respectively, 6.68×10^{7}, 1.16×10^{10} and 3.23×10^{6} newtons/m^2; at 315.6°C, they were, respectively, 4.38×10^{7}, 1.05×10^{10} and 2.58×10^{6} newtons/m^2.

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FOREWORD

This report presents the work accomplished by AVCO Corporation during the period of February 7, 1975 to April 30, 1976 on NASA Contract NAS 3-18936, "Development of Improved Polyphenylquinoxaline/Graphite Composites." The work was administered by the National Aeronautics and Space Administration, Lewis Research Center, Cleveland, Ohio, with Mr. Peter Delvigs as Project Manager.

Performance of this contract was under the direction of the AVCO Systems Division, AVCO Corporation. The principal investigator was Mr. William S. Port. The technical assistance in chemical analysis of Mr. B. W. Burrell, in composite fabrication of Dr. C. T. Hughes, and in mechanical test and evaluation of Messrs. M. M. Consoli and C. Theberge is gratefully acknowledged.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF FIGURES (Continued)

LIST OF FIGURES (Concluded)

LIST OF TABLES

I. INTRODUCTION

A. Background

Much work [1-19] has been performed on the synthesis of polyquinoxalines, particularly on arylated quinoxaline polymers, for use as matrix materials for boron and graphite composites. Certain polyquinoxalines are valuable in such applications because, having attractive high temperature properties, they make possible extension of the temperature range of utilization of the composites further toward the ultimate capability of the reinforcement.

Work on the polyphenylquinoxalines [7-19] showed that polymers with high glass transition temperatures (in the order of 250-435°C) and high decomposition temperatures (in the order of 510-560°C) were obtainable. The oxidative resistance in air, as measured by weight loss in thermogravimetric analysis experiments or by isothermal aging at 371°C, was notable; introduction of oxygen linkages into the molecule, however, gave greater oxidative susceptibility in some polymers. On the other hand, the thermoplasticity of the polyphenylquinoxalines above their glass transition temperatures limits the range of their use for structural applications. Furthermore, some polyphenylquinoxalines form highly viscous solutions which wet reinforcing filaments with difficulty. These deficiencies affect adversely the use of these polymers in the preparation of laminates.

Further research on polyquinoxalines was, therefore, directed toward decreasing their high temperature plasticity and toward improving their solubility characteristics. Polymers with decreased plasticity have been sought through ladder polymers and through incorporation of substituents which permit cross-linking of polymer chains after the initial fabrication with the polyquinoxaline has been accomplished. Novel methods for polyquinoxalines were also explored as an answer to the fabrication problem. Among the investigations on ladder polymers may be mentioned the work of Stille and co-workers [20-25], Marvel and co-workers [26-30], Jackson and Schroeder [31], Russo [32], Arnold and Van Deusen [33], and Naarmann [34]. Among the approaches for introducing cross-linking sites may be noted the work of Wentworth and Mulligan [35] and Augl, Duffy and Wentworth [36] who demonstrated that poly-p-tolylquinoxalines could be cross-linked by heating in an argon atmosphere. Hergenrother [37] accomplished cross-linking by introducing p-cyanophenoxyphenyl substituents on the quinoxaline ring in modified polyphenylquinoxalines and heating in an inert atmosphere after fabrication with the linear polymer had been accomplished. Presumably, the cyano-group trimerized to form sym-triazine rings. Cross-linking in this manner raised the glass transition temperature by 50°C. Among the novel approaches used to aid processibility is the method of Serafini, Delvigs and Vannucci [38] who accomplished polymerization in situ from 35% solutions of each of the two monomers and thus avoided the impregnation problems otherwise encountered from high-viscosity, high molecular weight polyphenylquinoxaline solutions.

An approach to a simultaneous solution of the processing problems due to high viscosity polymer solutions and to thermoplasticity at high temperature has been investigated in condensation polymers other than the polyquinoxalines. The method entails the incorporation into the polymer of bulky, planar groups standing crosswise to the polymer chain. Thus, Morgan[39,40] prepared aromatic polyesters from bisphenols in which the phenylene rings were joined by bulky, planar groups derived from phenolphthalein and related compounds or were structures such as diphenylmethylene, 1-indanylidene, 9-fluorenylidene, 9-xanthenylidene and the like. Such structures imparted marked increases in the glass transition temperature and enhanced the solubility in low boiling solvents. Similar approaches were taken by Vinogradova and Korshak[41].

Previous research[42] at AVCO laboratories, sponsored by the NASA Lewis Research Center investigated the potential for decreasing the chemical plasticity of a polyquinoxaline by the introduction of the 1-naphthalenyl ring as a substituent at the 3-position of the quinoxaline ring were comparable to those of a polyquinoxaline containing a phenyl ring in the 3-position. A model reaction study between 2-methyl-3-phenylquinoxaline and N-phenylmaleimide indicated that the Michael condensation would probably occur in the polymer reaction. However, the overall yield in the method used for the preparation of the monomer p-(methyloxalyl)benzil was too low to permit preparation of polymers.

B. Purpose and Scope of Present Work

The present work is concerned with the preparation and preliminary evaluation of quinoxaline polymers and the fabrication and evaluation of composites of graphite fibers and quinoxaline resins. The studies on quinoxaline resins comprised the preparation of polymers from 3,3'-diaminobenzidine and from 1,4- and 1,3-bis[(1'-naphthalenyl)oxalyl]-benzene respectively, the investigation of new methods for preparing p-(methyloxalyl)benzil and the preparation of polyquinoxalines from poly-(p-benzil) and 1,2-aryldiamines. The methods for evaluation of the polymers prepared included determination of inherent viscosity, elemental chemical analysis, measurement of glass transition temperatures, isothermal gravimetric analysis, and determination of tensile strength and of time to rupture and weight loss under sustained tensile loading at elevated temperatures. The requisite monomers and intermediates were characterized by melting point, infrared spectrophotometric analysis, elemental chemical analysis, gas chromatographic analysis and nuclear magnetic resonance spectrophotometry.

Investigations were conducted on polyquinoxaline cross-linking by model reaction studies, infrared analysis and transition temperature determinations.

Two graphite composites were prepared by the polymer solution technique (from two different polymers) and press molding the laminates.

The composites were analyzed for resin content, specific gravity and void content and were evaluated with respect to interlaminar shear strength at room temperature and after short-time exposure at 316°C (600°F). One composite was also evaluated with respect to flexural strength and modulus, interlaminar shear strength and weight loss at 260°C (500°F) and 316°C (600°F) for various exposure times.

II. SUMMARY

Experimental studies were performed with new polyquinoxalines and their graphite composites. A new monomer, 1,3-bis-[(1'-naphthalenyl)oxalyl]benzene, and its precursor, 1,3-bis[(1'-naphthalenyl)acetyl]benzene were synthesized and were characterized by melting point, elemental analysis, infrared and proton nuclear magnetic resonance spectrophotometry. Poly{2,2'-(1,3-phenylene)-6,6'-bis[3-(1-naphthalenyl)]quinoxalinyl} (Polymer II) which was prepared from this monomer and 3,3'-diaminobenzidine was found to be brittle. An isomeric polymer, poly{2,2'-(1,4-phenylene)-6,6'-bis[3-(1-naphthalenyl)]quinoxalinyl} (Polymer I) was also prepared and found to have excellent film-forming characteristics. A copolymer, poly{2,2'-(1,4-phenylene-6,6'-bis[3-(1-naphthalenyl)-co-(phenyl)(25/75)-quinoxalinyl} (Polymer III) was prepared from 1,4-bis[(1'-naphthalenyl)-oxalyl]benzene, 1,4-bis(phenyloxalyl)benzene and 3,3'-diaminobenzidine. Poly[2,3-(1,4-phenylene)quinoxalinyl], (Polymer IV) prepared from poly-(p-benzil) and o-phenylenediamine had a low molecular weight and was brittle.

The four polymers prepared were characterized with respect to their inherent viscosity and their elemental analysis. Polymers I and II were characterized further with respect to their transition temperatures and were subjected to isothermal gravimetric analysis at 315.6° and 371.1°C. The ultimate tensile strength of Polymer I was measured at 204.4° and 315.6°C and specimens of Polymer I subjected to sustained tensile loading tests at these elevated temperatures did not rupture after 114 hours.

Conditions for crosslinking polyquinoxalines by quaternization were determined with model compounds. However, attempts to increase the transition temperature of Polymer I by reaction with p-bis(chloromethyl)-benzene were not successful.

Composites of Hercules HMS graphite fiber and respectively Polymers I and III were fabricated as panels for preliminary evaluation of their mechanical properties. A more detailed evaluation was made of a composite of Polymer I containing 48.8 volume percent of graphite with respect to its flexural strength and modulus, interlaminar shear strength and aging characteristics. At 25°C, the flexural strength, the flexural modulus and the interlaminar shear strength were respectively, 6.68×10^{7}, 1.16×10^{10} and 3.23×10^{6} newtons/m^{2}; at 315.6°C, they were, respectively, 4.38×10^{7}, 1.05×10^{10} and 2.58×10^{6} newtons/m^{2}.

III. EXPERIMENTAL RESULTS

The Experimental Results are reported in two tasks with subtasks as indicated:

Task I: Polymer Synthesis and Characterization

- Subtask A: Monomer Synthesis and Characterization
- Subtask B: Polyquinoxaline Synthesis and Characterization
- Subtask C: Polymer Cross-Linking Studies

Task II: Graphite/Polyquinoxaline Fabrication and Evaluation

- Subtask A: Preliminary Composite Fabrication and Evaluation
- Subtask B: Final Composite Evaluation

TASK I: POLYMER SYNTHESIS AND CHARACTERIZATION

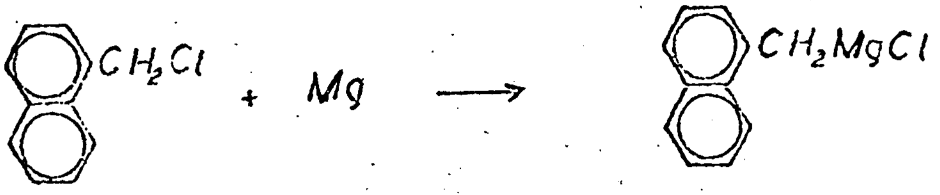
Subtask A: Monomer Synthesis and Characterization

1.1 1,4-Bis[(1'-naphthalenyl)oxalyl]benzene (I)

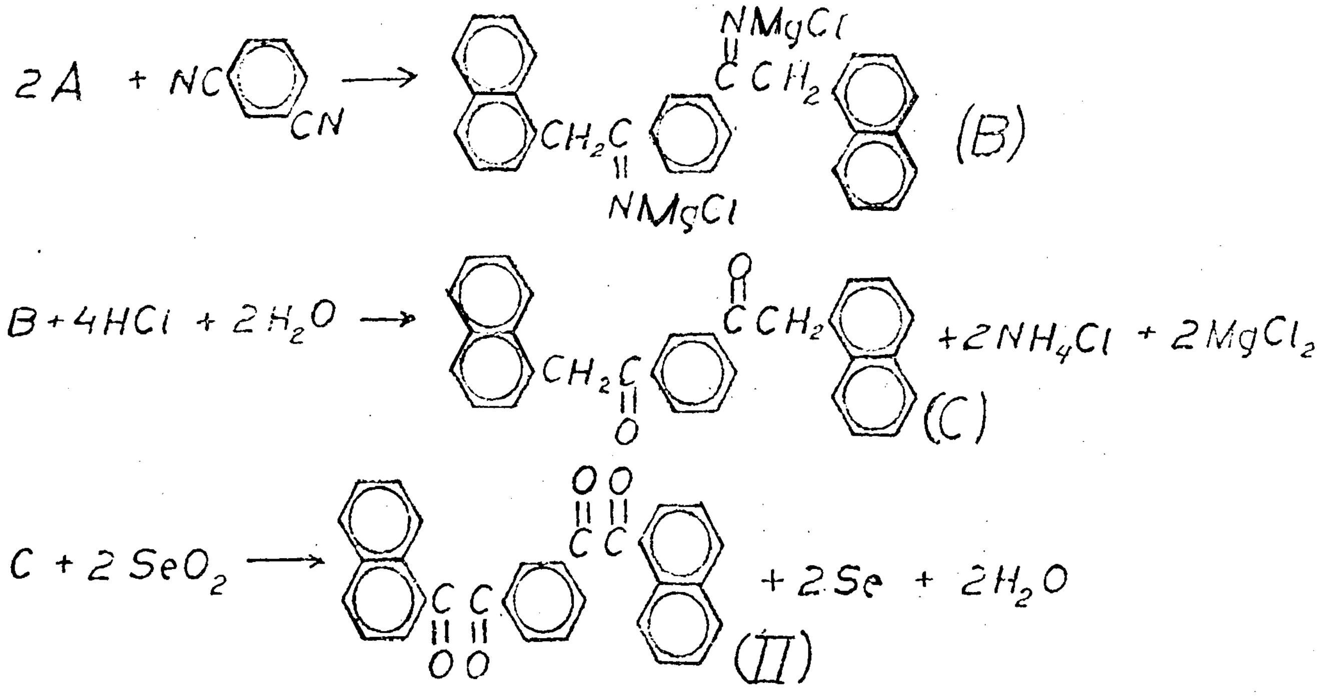
This monomer was prepared by the method of Port and Loszewski[42a].

1.2 1,3-Bis[(1'-naphthalenyl)oxalyl]benzene (II)

This compound was prepared by a modification of the procedure used for preparing I (except that 1,3-dicyanobenzene was substituted for 1,4-dicyanobenzene) in accordance to the scheme outlined below.



(A)



Unexpectedly, the exact procedure [42a] used for preparing 1,4-bis[(1'-naphthalenyl)acetyl]benzene could not be used for preparing 1,3-bis-[(1'-naphthalenyl)acetyl]benzene (Compound C) by a straightforward substitution of 1,3-dicyanobenzene for the 1,4-isomer since it was found that the solvents used played an important role in the extent of the side reactions occuring and because the solubility of Compound C differed significantly from its 1,4-isomer. A typical example of the successful procedure for preparing Compound C is given and is followed by a brief discussion of the effects of procedural variations.

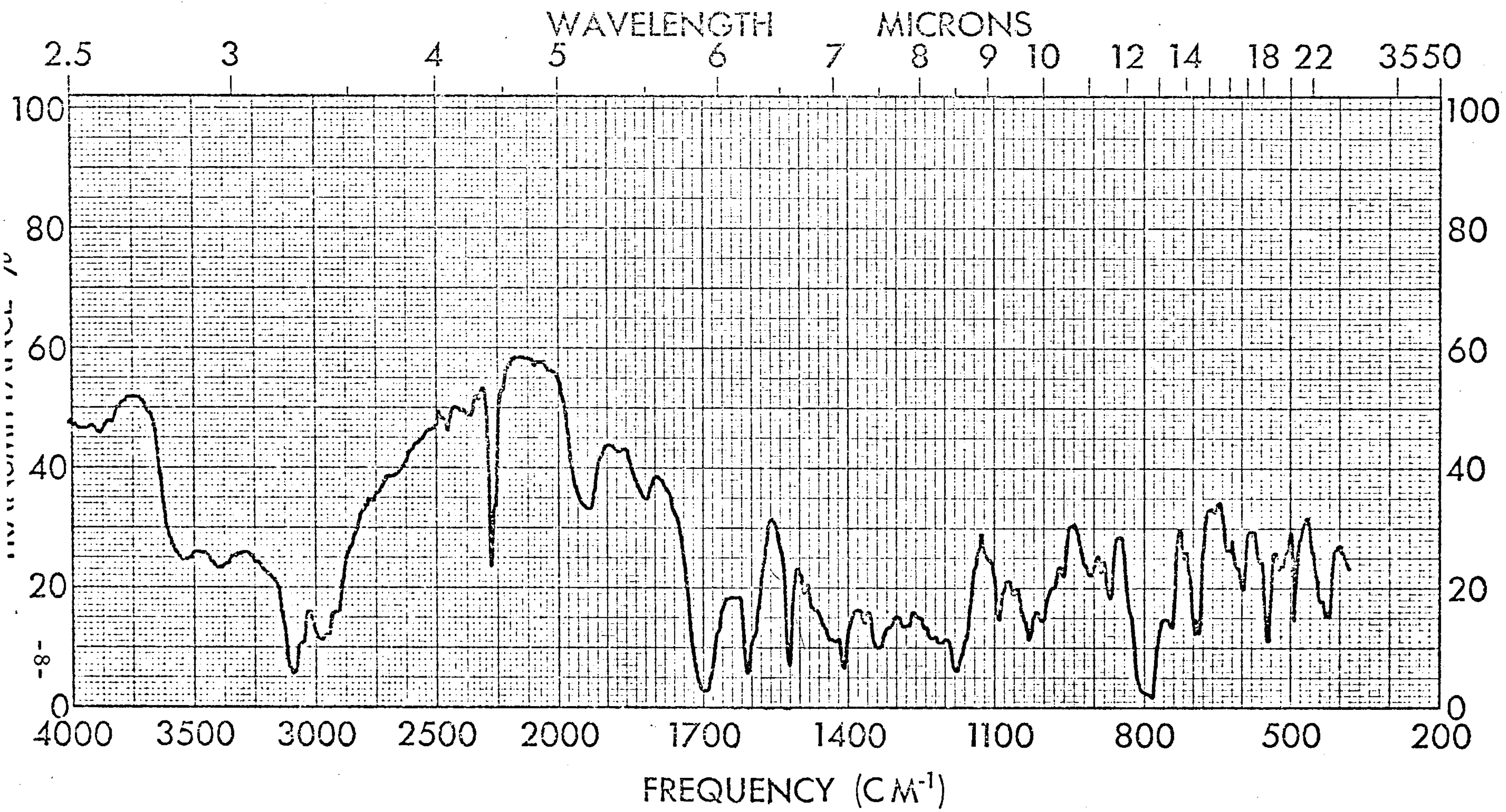
1.2.1 Preparation of 1,3-Bis[(1'-naphthalenyl)acetyl]benzene

1-Naphthalenylmethylmagnesium chloride [43] was prepared in an apparatus comprising a one-liter, 3-necked flask equipped with a large drain stopcock plugged loosely with glass wool, a pressure equalized 500ml dropping funnel, a reflux condenser (capped with a $CaSO_4$ drying tube), a gas inlet tube (for continuous purge with dried nitrogen) and a gas-tight mechanical stirrer. Into the flask were placed 55.5g (2.3 moles) magnesium turnings, and the entire system was evacuated and was flamed out to remove moisture absorbed on the glass walls. After the glass had cooled under the nitrogen purge, 175cc dry ethyl ether (distilled from sodium) and a crystal of iodine were added to the flask. Into the dropping funnel were placed 132.5g distilled 1-chloromethylnaphthalene, a few cc were added to the flask and the mixture was heated with a heat lamp to the reflux point.

After a few minutes, a self-sustaining reaction set in. The remaining 1-chloromethylnaphthalene was diluted with 125 cc ether, the reaction mixture in the flask was diluted with 400 cc ether and drop-wise addition of the diluted 1-chloromethylnaphthalene to the vigorously stirred reaction mixture was begun. The rate of addition was controlled to maintain a gentle reflux without external heating; the addition required 1.75 hours. The mixture was refluxed by external heating for an additional hour and then cooled to room temperature. The green-colored mixture, containing a small amount of a white precipitate was drained into a graduated dropping funnel to determine the volume of solution and then into a one-liter, 3-necked flask. (All equipment had been dried by heating for 24 hours at 120°C). Analysis [44] of aliquots of the ether solution showed an 84.4% yield of the Grignard reagent.

Approximately 2/3 of the ethyl ether was distilled off with the use of an oil bath set at 60 ± 5°C. The mechanically stirred mixture was diluted with 100 cc dry tetrahydrofuran and then treated with 25.7g of 1,3-dicyanobenzene (corresponding to 93% equivalency of the Grignard reagent) dissolved in 300 cc dry tetrahydrofuran. A dark red color developed immediately and vigorous distillation of the solvent occurred. The solution was stirred mechanically and was heated at 65°C for approximately 18 hours. It was cooled and poured into 1200 cc ice and water containing 150 cc concentrated hydrochloric acid. An oil (411-104) formed which gradually turned to a light brown solid. This was filtered off, washed with water and dried yielding 66.2 g of a solid (79.6% crude yield based on 1,3-dicyanobenzene). From the filtrate, 28.4 g of a dark brown oil (411-104-1) was obtained by extraction with 400 cc benzene, extracting the benzene layer with water to remove traces of acid and distilling off the benzene. Figure 1 is the infrared absorption spectrum of 411-104-1 which shows the presence of absorption due to the nitrile group at 2250 cm^{-1}. It is conjectured that 411-104-1 contains some 3-[(1'-naphthalenyl)acetyl] - benzonitrile.

The crude 411-104 was heated in vacuo at 50-60°C (to remove small amounts of 1-methylnaphthalene, identified by a comparison of its infrared absorption spectrum with the spectrum of the authentic compound) and the residual 61 g was recrystallized from 215 cc n-butyl acetate (after treatment with 3 g decolorizing charcoal and hot filtration). The yield of crystals (411-104-2) was 28.4 g, m.p. 141-5°C. When 411-104-2 was recrystallized from 100 cc n-butyl acetate, 17.7 g 411-104-4, m.p. 148-150°C, was obtained (21.4% yield). The infrared spectrum of 411-104-4, shown in Figure 2, bears a strong similarity to the spectrum for the homologous 1,4-bis[(1'-naphthalenyl)acetyl]benzene shown in Figure 3. Both compounds absorb at 2900 cm^{-1} and also at 1690 and 1230 cm^{-1}. According to Colthup assignments [45], the first absorption is related to the presence of $-CH_2-$



SPECTRUM NO. 1575	ORIGIN	LEGEND	REMARKS
SAMPLE 411-104-1		1.	
	PURITY	2.	
	PHASE		
	THICKNESS	OPERATOR WJr	

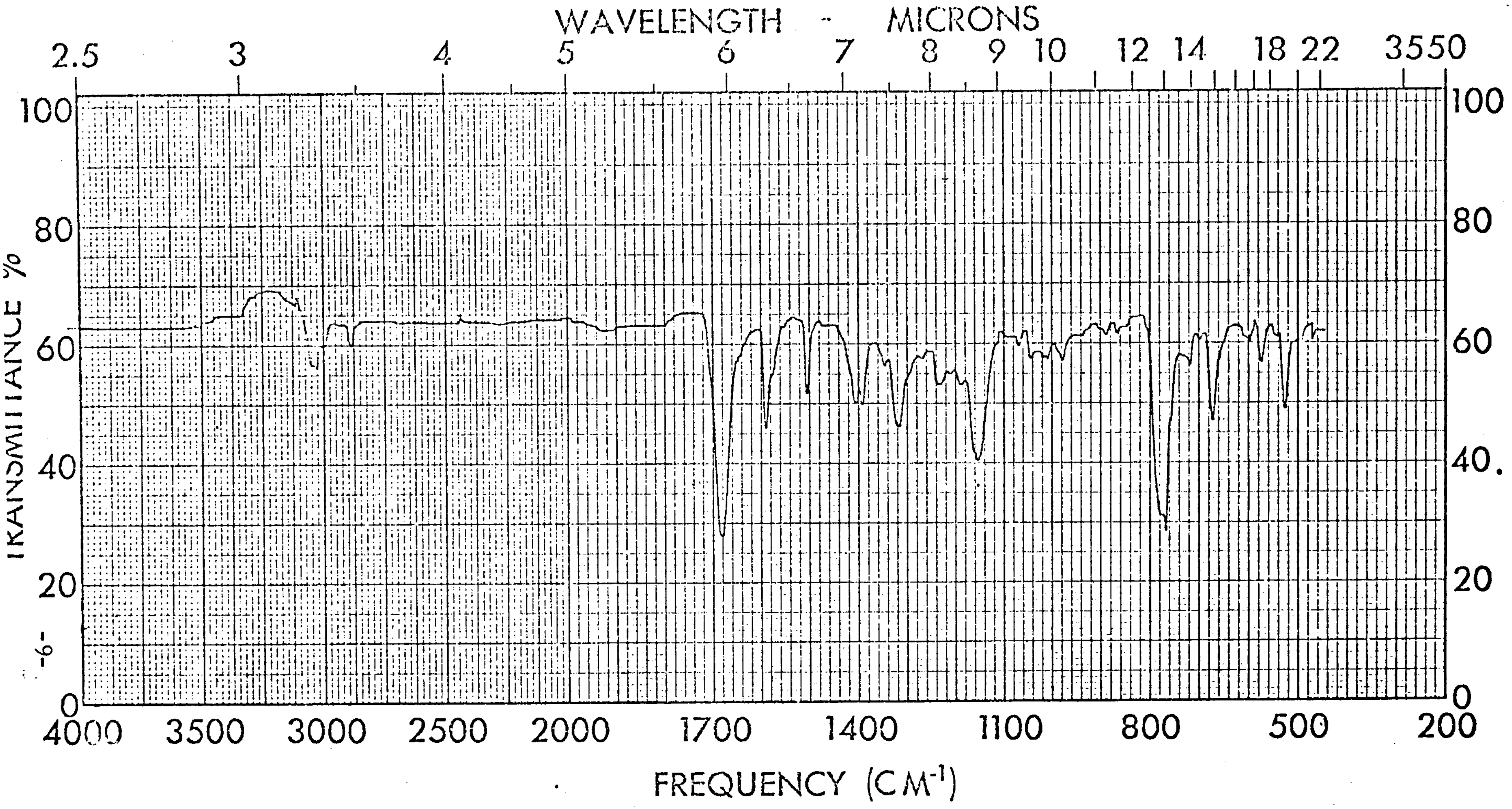
Figure 1. Infrared Spectrum of Liquid Fraction Obtained in the Synthesis of 1,3-Bis[(1'-naphthalenyl)acetyl]benzene.

SPECTRUM NO.

SAMPLE

PART NO. 221-1417

THE PERKIN-ELMER CORPORATION NORWALK, CONN.



SPECTRUM NO. 7877

SAMPLE 411-104-4

1,3-Bis[(1'-naphthalenyl)-acetyl] benzene

ORIGIN

PURITY

THICKNESS

LEGEND

1.

2.

OPERATOR WSP

REMARKS

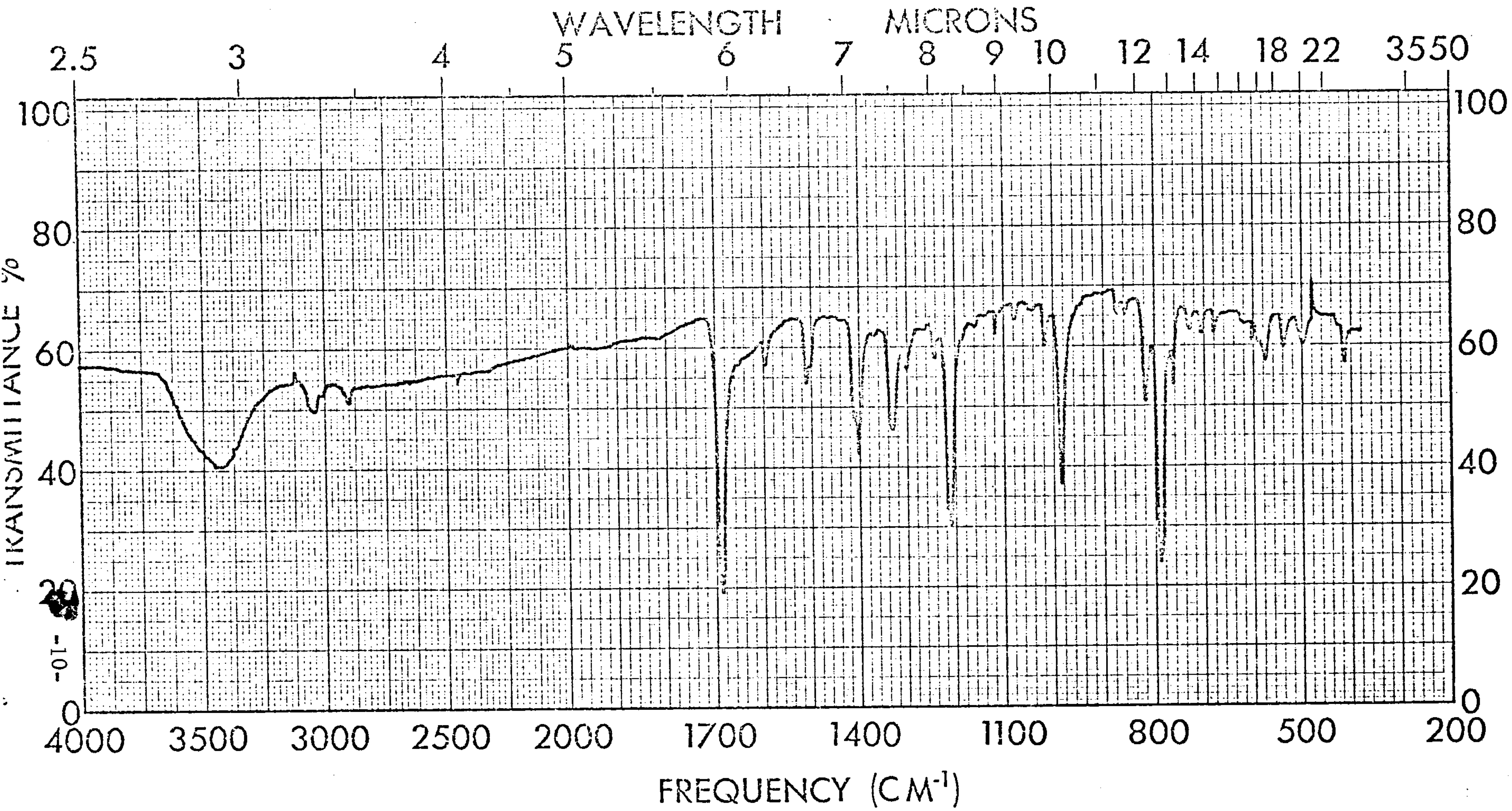
Figure 2. Infrared Spectrum of 1,3-Bis[(1'-naphthalenyl)acetyl]benzene.

SPECTRUM NO.

SAMPLE

PART NO. 221-1617

THE PERKIN-ELMER CORPORATION NORWALK. CONN.



SPECTRUM NO. 7481
SAMPLE
1081-107-1-1H-1

ORIGIN WSP
PURITY
THICKNESS

LEGEND
1.
2.
OPERATOR BWB

REMARKS

Figure 3. Infrared Spectrum of 1, 4-Bis[(1'-naphthalenyl)acetyl]benzene.

SPECTRUM NO.
SAMPLE

PART NO. 221-1617

THE PERKIN-ELMER CORPORATION NORWALK CONN or of $-CH_2\overset{O}{\overset{\|}{C}}$ groups and the second and third absorptions are due to aromatic carbonyl. Absorption due to 1-naphthalenyl substitutions is shown in both spectra at 3040, 1600, 1510, 1400, 790 and 760 cm^{-1} consistent with Colthup [45] assignments. As expected, Figure 2 shows absorption consistent with meta substitution at 1160 cm^{-1}; Bellamy [46a] attributes absorption at 1170 to 1140 cm^{-1} to meta substitution. Figure 3 lacks this absorption, but shows weak absorption peaks in the 1120 to 1090 cm^{-1} region which is attributable, according to Bellamy [46a], to para substitution.

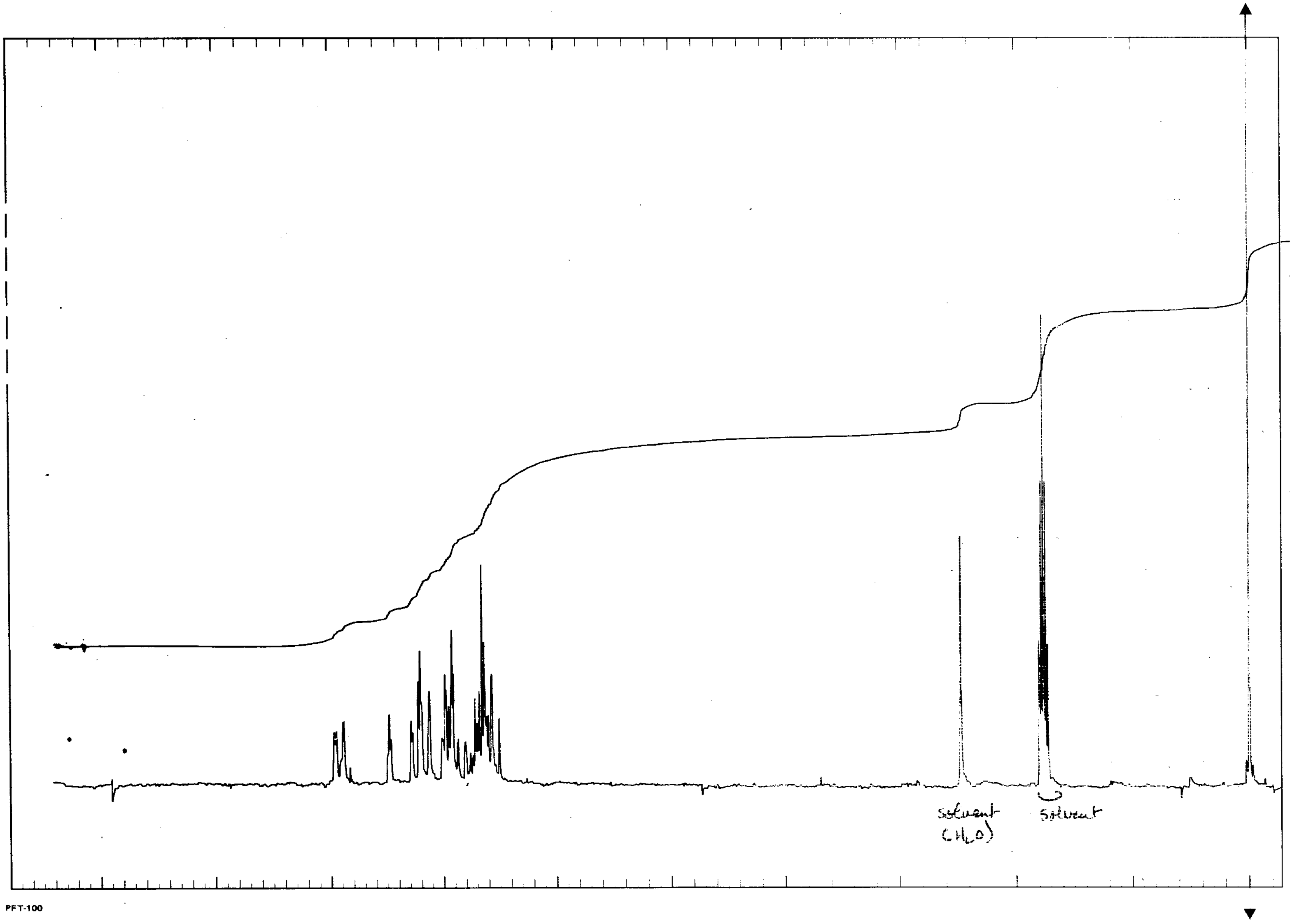
In other attempted preparations of Compound C, toluene was used instead of tetrahydrofuran as the medium for the reaction of the Grignard reagent A with 1,3-dicyanobenzene. Work-up of the reaction product gave crude Compound C for which an infrared spectrum showed strong nitrile absorption. Attempts at purification by crystallization of this material unsuccessful. In other experiments, an attempt was made to substitute tetrahydrofuran for ethyl ether as the reaction medium for the preparation of the Grignard reagent A. Titration [44] showed that none had formed; instead, a compound melting at 157-60°C was isolated which is probably crude 1,2-bis(1'-naphthalenyl)ethane for which Schorigin [47] reported a melting point of 162-3°C.

1.2.2 Preparation of 1,3-Bis[(1'-naphthalenyl)oxalyl]benzene (II)

A solution of 20.7 g (0.05 mole) 1,3-bis[(1'-naphthalenyl)acetyl]-benzene in 150 cc dioxane was treated with 11.3 g (0.102 mole) selenium dioxide. The mixture was stirred and refluxed for 14 hours during which time the mixture turned brown and a black precipitate of selenium formed. The selenium was filtered off and was extracted with dioxane in a Soxhlet extractor until the extract turned colorless. The dioxane filtrate and the dioxane extract were combined and evaporated *in vacuo* to near dryness. The yellow residue (weighing 29g) was dissolved in 62.5 cc boiling n-butyl acetate, treated with 1 g decolorizing charcoal and filtered hot. When the filtrate was cooled, bright yellow crystals (411-98-1) formed. These were filtered off, washed with n-butyl acetate and dried. The yield of 411-98-1 was 13.0g, m.p. 130-1°C.

Figures 4 and 5 are proton nuclear magnetic resonance spectra for 411-98-1, Figure 5 being an expansion of the aromatic region. Since resonance is observed only for protons associated with meta substitution and with 1-naphthalenyl derivatives, no other types of protons are present. These findings are consistent with the assignment of 1,3-bis[(1'-naphthalenyl)oxalyl]benzene as the structure of compound 411-98-1.

Figure 6 is the infrared spectrum of a sample of II. A comparison of Figure 2 and Figure 6 shows in Figure 6 the absence of absorption at 2900 cm^{-1} (due to methylene) which is consistent with its oxidation to carbonyl. Moreover, a close examination of the full-scale spectra shows that the absorption at 1685 cm^{-1} in Figure 2 (due to carbonyl) is twinned in Figure 6. Such twinning is consistent with the presence of the two different aryl ketone types in 1,3-bis[(1'-naphthalenyl)oxalyl]benzene:



SPECTRUM NO. 2
SAMPLE 411-98·1

SOLVENT Acetone-d6
CONC. ~.5%
REFERENCE TMS
TEMP. 20 C°

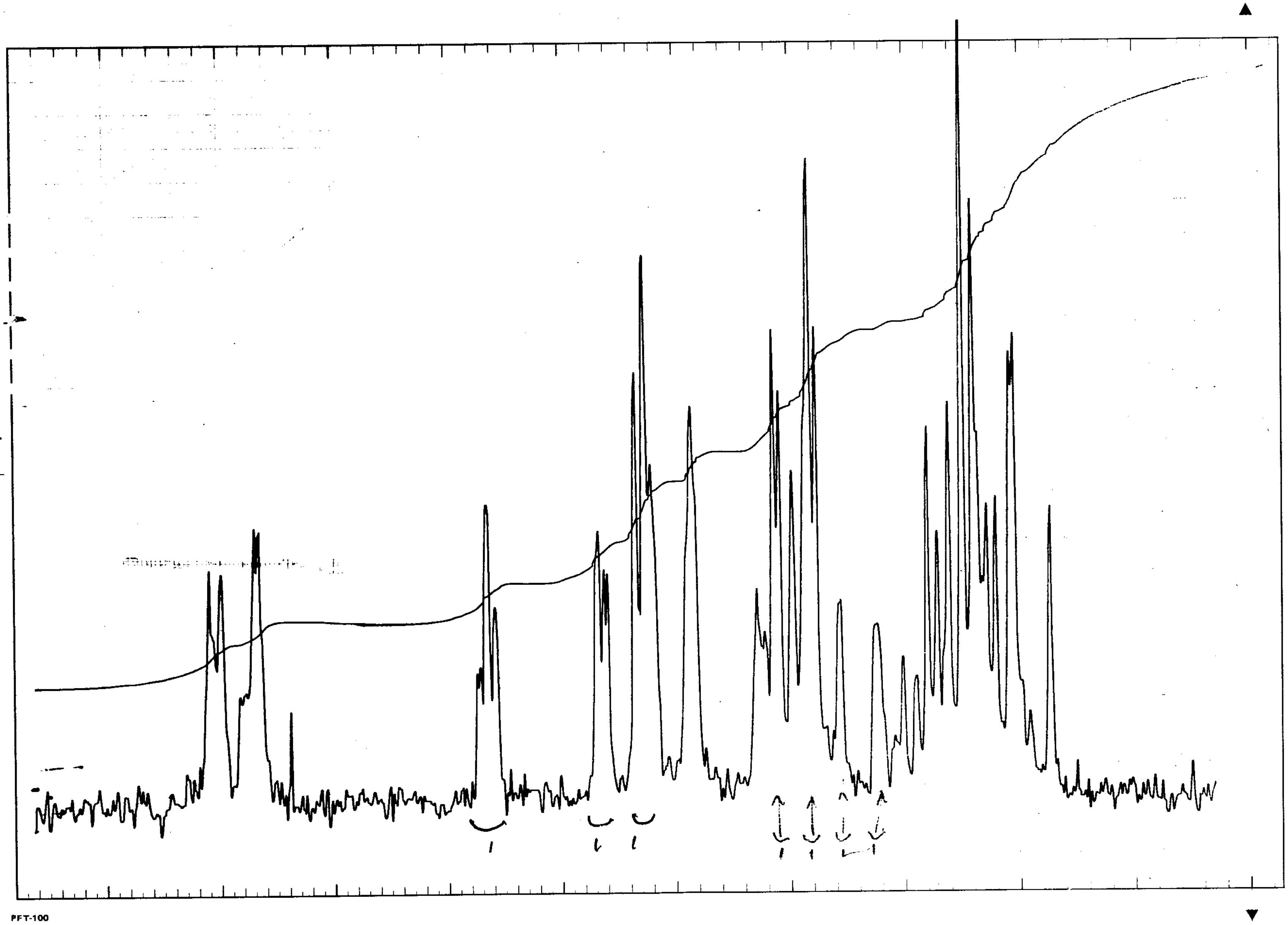
OBSERVE
NUCLEUS ¹H
FREQ. ____ MHz
PULSE: ☒Sing. ☐Mult. ____
WIDTH 26 u sec.
INTERVAL — SEC
REPETITION 4.3 SEC
DATA POINTS 8191
WINDOW EXPONENTIAL T.C.=0
MODE FT
SPECTRUM WIDTH 1250 KHz
FILTER 1250 KHz
AMPL. ____
NO. of SCANS 1

LOCK ☒INT. ☐EXT. ____
FREQ. ____ MHz. (____)
SIGNAL ²D
LEVEL RF 20dB AF ____

SPIN DECOUPLER
FREQ. ____ HZ (____)
POWER ____ B.W. ____ KHz
MODULATION ____
☐CW ☐Noise ☐EXT. ____

DATE Sept 19 1975
OPERATOR RES
REMARKS:

Figure 4 Proton Nuclear Magnetic Resonance Spectrum of 1, 3 - Bis[(1′-naphthalenyl)oxalyl] benzene



SPECTRUM NO. 1
SAMPLE 411-98-1

SOLVENT Acetone-d6
CONC. ~.5%
REFERENCE TMS
TEMP. 20 C°

OBSERVE
NUCLEUS ¹H
FREQ. ______ MHz
PULSE: ☒ Sing. ☐ Mult. ______
WIDTH 26 u sec.
INTERVAL — SEC
REPETITION 4.3 SEC
DATA POINTS 8191
WINDOW EXPONENTIAL T.C.-0
MODE FT
SPECTRUM WIDTH 1250 KHz
FILTER 1250 KHz
AMPL. RF MAX AF 5x10
NO. of SCANS 1

LOCK ☒ INT. ☐ EXT. ______
FREQ. ______ MHz. (____)
SIGNAL ²D
LEVEL RF 20dB AF ______

SPIN DECOUPLER
FREQ. ______ HZ (______)
POWER ______ B.W. ______ KHz
MODULATION ______
☐ CW ☐ Noise ☐ EXT. ______

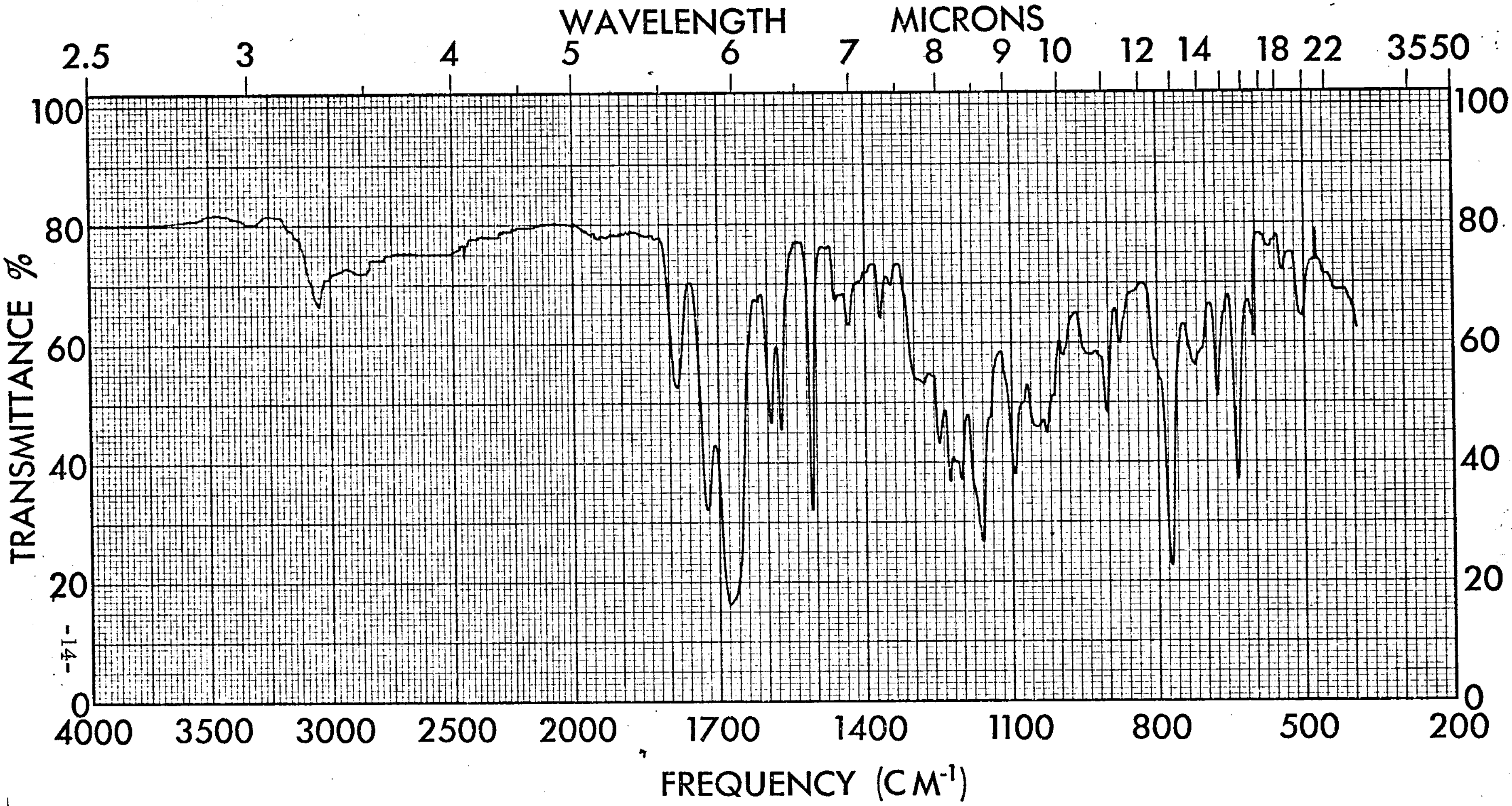
DATE SEPT 19, 1975
OPERATOR RES
REMARKS: MAG: 4↕ × 5↔

1 - peaks for meta-substituted benzene.

Remainder are for 1-naphthalene substitution

JEOL

Figure 5 Expansion of Aromatic Region of Proton Nuclear Magnetic Resonance Spectrum of 1,3-Bis-[(1'-naphthalenyl)oxalyl] benzene



SPECTRUM NO. 7749

SAMPLE 94-47-4

ORIGIN

PURITY

LEGEND

1.

2.

REMARKS

Figure 6. Infrared Spectrum of Sample 94-47-4, 1,3-Bis[(1'-naphthalenyl)oxalyl]benzene.

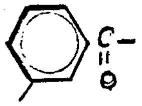
THICKNESS

OPERATOR

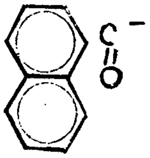
SPECTRUM NO. 7749
SAMPLE

PART NO. 221-1617

THE PERKIN-ELMER CORPORATION NORWALK, CONN.



and

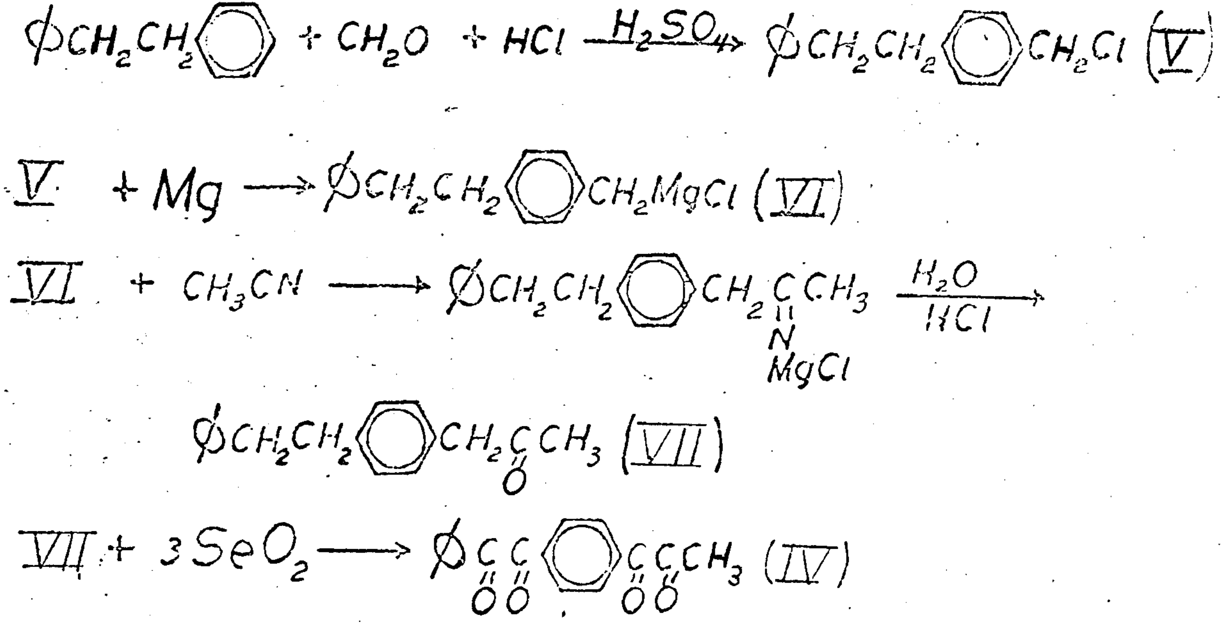


1.3 3,3'-Diaminobenzidine

This monomer was purchased from Research Organic/Inorganic Chemicals Corporation and was purified by the method of Port and Loszewski [42b] or by the method of Hoggatt, Hill and Shdo[48]. The compound melted at 176.5 - 177.5°C.

1.4 p-(Methyloxalyl)benzil (IV)

An unsuccessful attempt was made to prepare this monomer by the method outlined schematically below. A second approach (also unsuccessful) is given in Appendix I.



1.4.1 Preparation of p-Chloromethylbibenzyl (V)

Several attempts at the preparation of V by the method of Massarani [49](in which sulfuric acid was the reaction medium) all gave yields of less than 5%.

Several modifications of the basic method of Blanc [50] for chloromethylation of aromatic hydrocarbons were investigated in the course of which it was found that the following procedure gave the best yield. A solution of 5.5 g zinc chloride and 60.6 g (0.333 mole) bibenzyl in 100 cc acetic acid was held at 55 - 59°C while being mechanically stirred. Hydrogen chloride, generated during the course of 3-1/2 hours by the dropwise addition of 100 cc concentrated hydrochloric acid to 250 cc concentrated sulfuric acid stirred mechanically, was bubbled through the acetic acid solution. A solution of 11 g (0.37 equivalents of HCHO) of paraformaldehyde in 60 cc methanesulfonic acid was prepared by gently heating and was added dropwise to the acetic acid solution during the course of 2 hours. The resulting mixture was cooled to room temperature and was poured into 250 cc ice and water, and the mixture was extracted with 150 cc methylene chloride. The aqueous layer was extracted twice with 125 cc portions of CH_2Cl_2, the $CH_2 Cl_2$ extracts were combined and were freed of acid by extraction successively with 150 cc water, 150 cc dilute $NaHCO_3$, and 150 cc water. The $CH_2 Cl_2$ extract was then dried over anhydrous $CaCl_2$, the solution filtered and the solvent removed by distillation. The residue was distilled at low pressure. Four fractions were collected: 94-53-1 boiling at 111-116° at 1.5 mm was obtained in 24.5 g yield. Its infrared spectrum is shown in Figure 7 and is almost identical with the infrared spectrum for bibenzyl (Figure 8). Fraction 2 boiled at 117°C at 0.3 mm was obtained in 4.5 g yield and its infrared spectrum showed that it was principally bibenzyl. Fraction 3 boiled at 140-146°C at 0.30-0.33 mm in 16.5 g yield and fraction 4 boiled at 148°C at 0.30-0.33 mm in 16.5 g yield. The residue weighed 12.4 g. The infrared spectrum for fraction 3 is shown in Figure 9. A chlorine analysis of fraction 3 showed 14.9% Cl (theory for p-chloromethylbibenzyl is 15.4%) by the Schoniger method [51]. The infrared spectrum for fraction 4 was identical with that for fraction 3.

1.4.2 Synthesis of p-Acetonylbibenzyl

Magnesium turnings, 3.4 g (0.1 mole) were covered with 25 cc dry ethyl ether and a crystal of iodine was added. Five cc of a solution of 15.5 g (0.067 mole) p-chloromethylbibenzyl in 25 cc dry ether was added to the mechanically stirred magnesium/ether suspension. The mixture was refluxed for about 10 minutes by which time the suspension became noticeably cloudy. The mixture was diluted with 50 cc ether and the remainder of the p-chloromethylbibenzyl solution was added dropwise while the mixture was stirred mechanically and was heated.

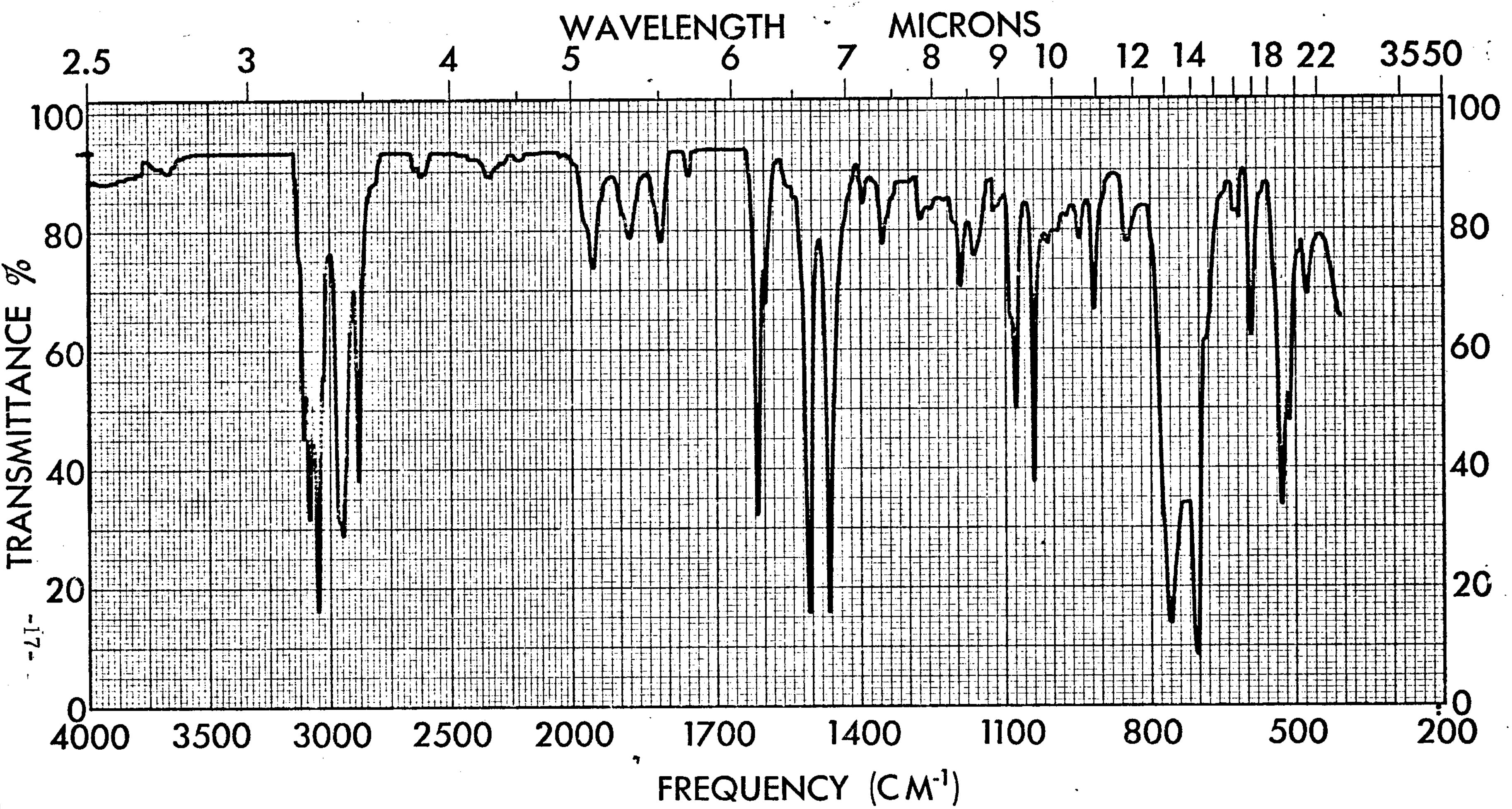


Figure 7. Infrared Spectrum of Fraction 94-53-1.

SPECTRUM NO. 7800

SAMPLE 94-53-1

ORIGIN

PURITY

THICKNESS

LEGEND

1.

2.

OPERATOR wsf

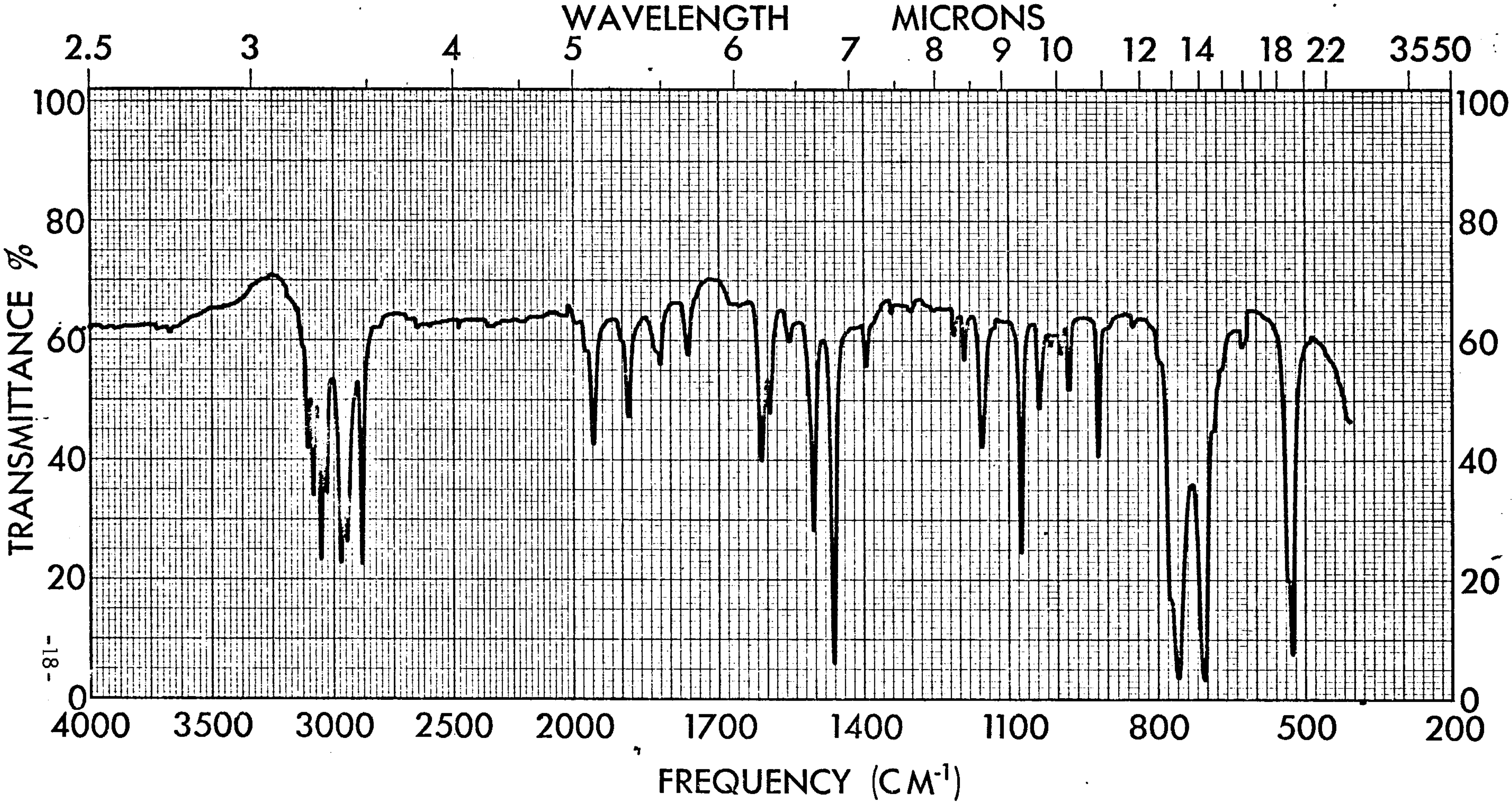
REMARKS

SPECTRUM NO.

SAMPLE

PART NO. 221-1617

THE PERKIN-ELMER CORPORATION NORWALK, CONN.



SPECTRUM NO. 7805

SAMPLE Bibenzyl

ORIGIN Aldrich

PURITY

PHASE

THICKNESS

LEGEND

1.

2.

OPERATOR

REMARKS

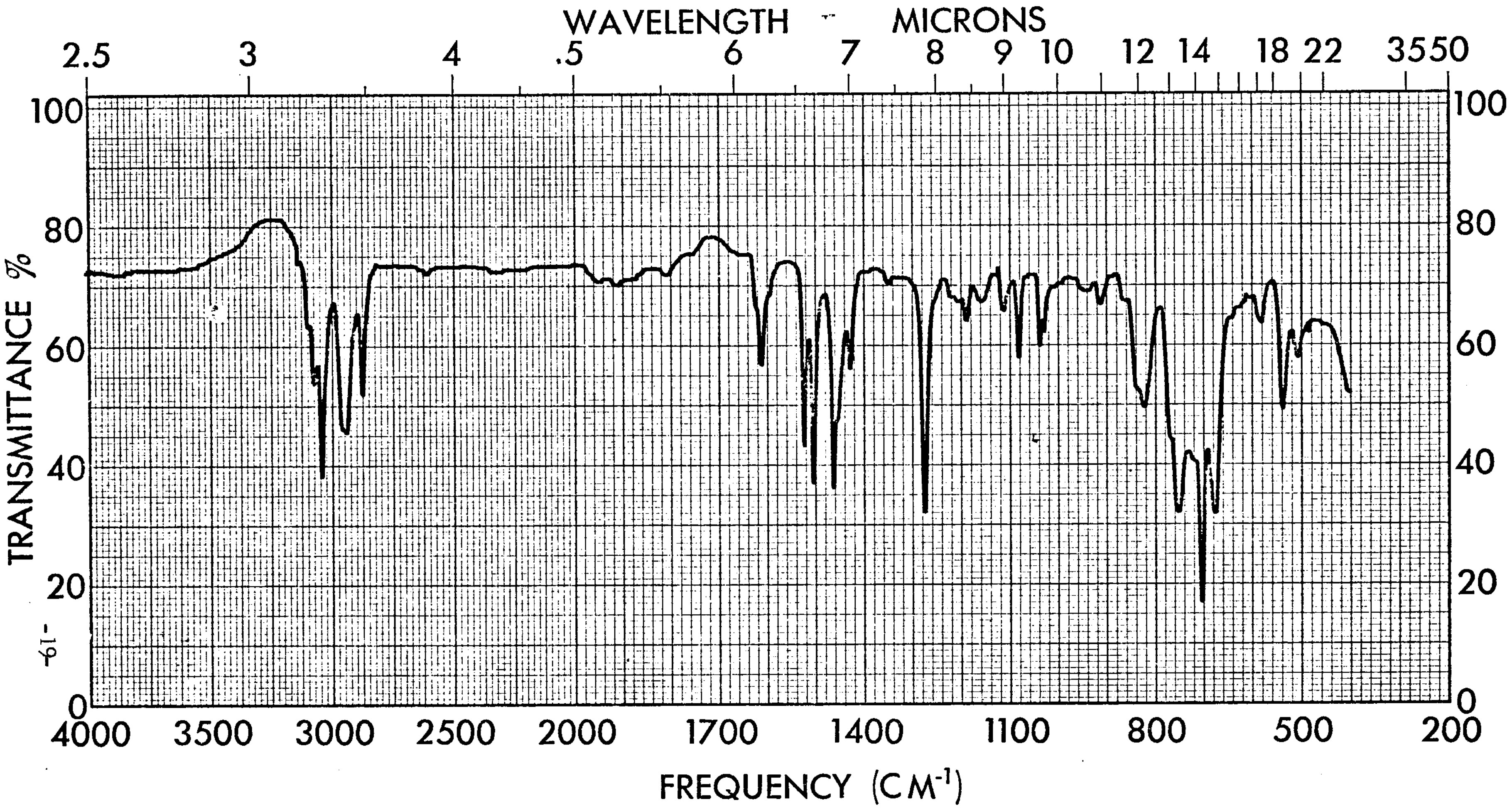
Figure 8. Infrared Spectrum of Bibenzyl.

SPECTRUM NO.

SAMPLE

PART NO. 221-1617

THE PERKIN-ELMER CORPORATION NORWALK, CONN.



SPECTRUM NO. 7804

SAMPLE 94-53-3

ORIGIN

PURITY

THICKNESS

LEGEND

1.

2.

OPERATOR W.S.

REMARKS

Figure 9. Infrared Spectrum of Fraction 94-53-3 (Chloromethylbibenzyl).

SPECTRUM NO.

SAMPLE

PART NO. 221-1617

THE PERKIN-ELMER CORPORATION NORWALK, CONN.

The reaction failed to become self-sustaining until another crystal of iodine had been added. Shortly thereafter an exotherm occurred and a precipitate formed. The mixture was heated and stirred for 30 minutes after the exothermic reaction had ceased. Dry acetonitrile, 12 cc, was added producing a mild exotherm. The mixture was stirred for one hour and then poured into a mixture of 150 cc of ice and 50 cc concentrated hydrochloric acid. The ether layer was separated, the aqueous layer was extracted with 100 cc and 50 cc portions of ether and once with 50 cc toluene. The organic layers were combined, washed free of acid with water and were dried over anhydrous $CaCl_2$. Figure 10 is the infrared spectrum of the residue remaining after the solvent had been flashed off. The absorption at 1720 cm^{-1} is probably due to carbonyl. The weak absorption may be indicative of a low yield, and the presence of such by products as 4-methylbibenzyl (the product of the hydrolysis of 4-bibenzylylmethylmagnesium chloride) and 1,2-bis(bibenzylyl)ethane (the product of the reaction of the Grignard reagent and p-chloromethylbibenzyl) are likely.

The reaction mixture was analyzed by gas chromatography. An F & M Model 720 dual column, temperature programmed chromatograph equipped with dual thermal conductivity detectors was used. The detectors were held at 300°C and the injection ports at 200°C. The separations shown here were carried out on a 12' long by 1/4" diameter stainless steel column packed with 10% SE-30 silicone gum rubber on acid-washed Chromosorb W. The carrier gas was helium at a flow rate of 60 ml/minute. The column was temperature programmed at 5°C per minute from 30°C to 260°C and held at 260°C for five minutes. Chart speed was 0.5 inches per mintue. Figure 11 shows the gas chromatogram obtained. The principal component eluted at 238°C, and its infrared spectrum is shown in Figure 12. The absence of carbonyl absorption (at 1700 cm^{-1}) eliminates the possibility that the material is p-acetonylbibenzyl. A second fraction comprising the remaining components eluted, was collected and its infrared spectrum is shown in Figure 13. Since this fraction does show carbonyl absorption, it is possible that it contains p-acetonylbibenzyl. If the ratio (16:1) of the attenuation factors (Figure 11) for the components is taken as a rough esitmate, the yield of p-acetonylbibenzyl does not exceed 6%. Because additional attempts to improve the yield of p-acetonylbibenzyl were unsuccessful, further work on this approach toward the synthesis of p-(methyloxalyl)benzil was discontinued.

1.5 1,4-Phenylenebismaleimide (VIII)

This compound was prepared by the procedure of Port and Loszewski [42b].

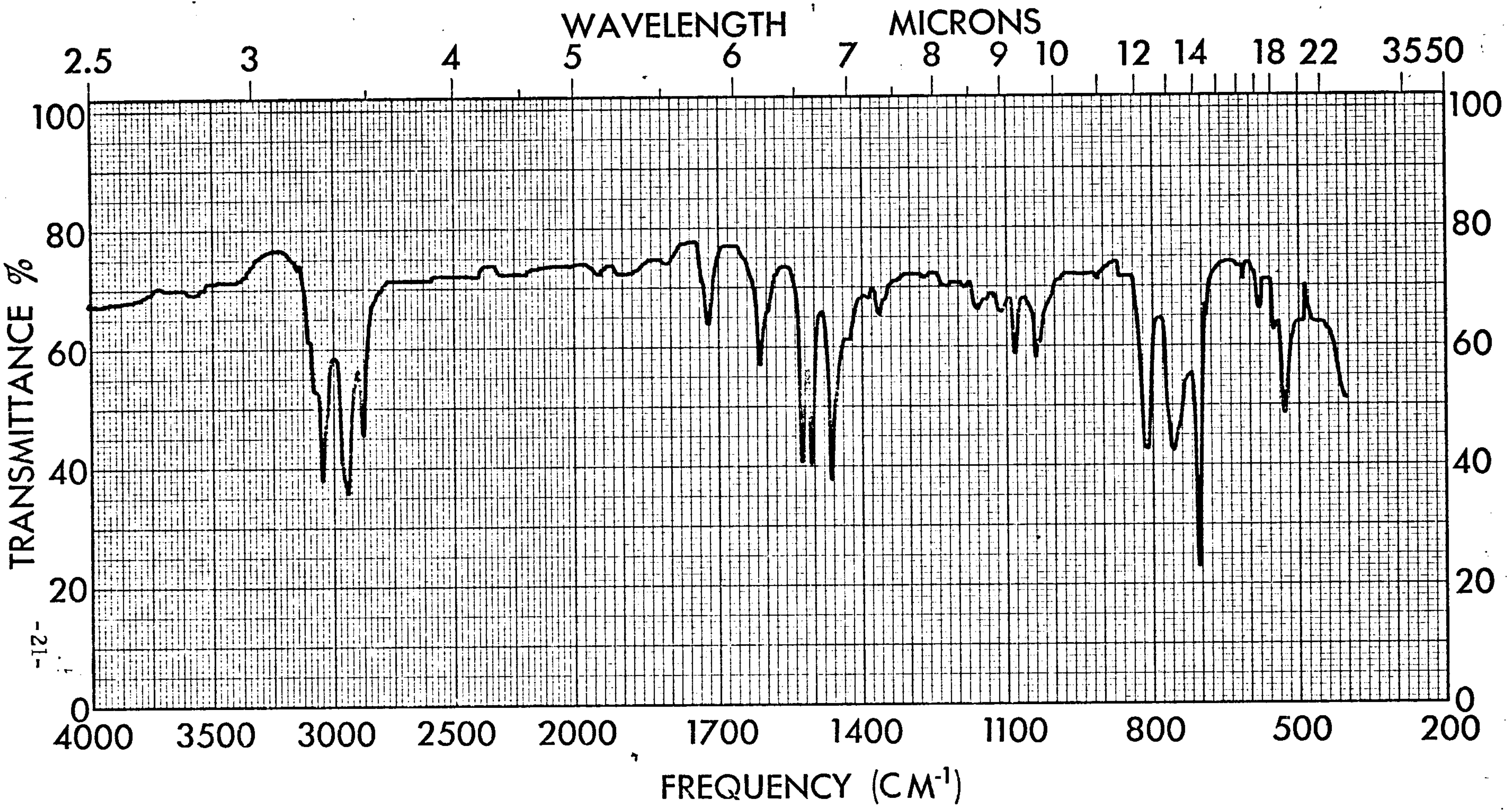


Figure 10. Infrared Spectrum of Crude p-Acetonylbibenzyl.

SPECTRUM NO. 7809
SAMPLE 94-55
Crude 4-Acetonylbibenzyl

ORIGIN
PURITY
THICKNESS

LEGEND
1.
2.
OPERATOR lv SP

REMARKS

SPECTRUM NO.
SAMPLE

PART NO. 221-1617

THE PERKIN-ELMER CORPORATION NORWALK, CONN.

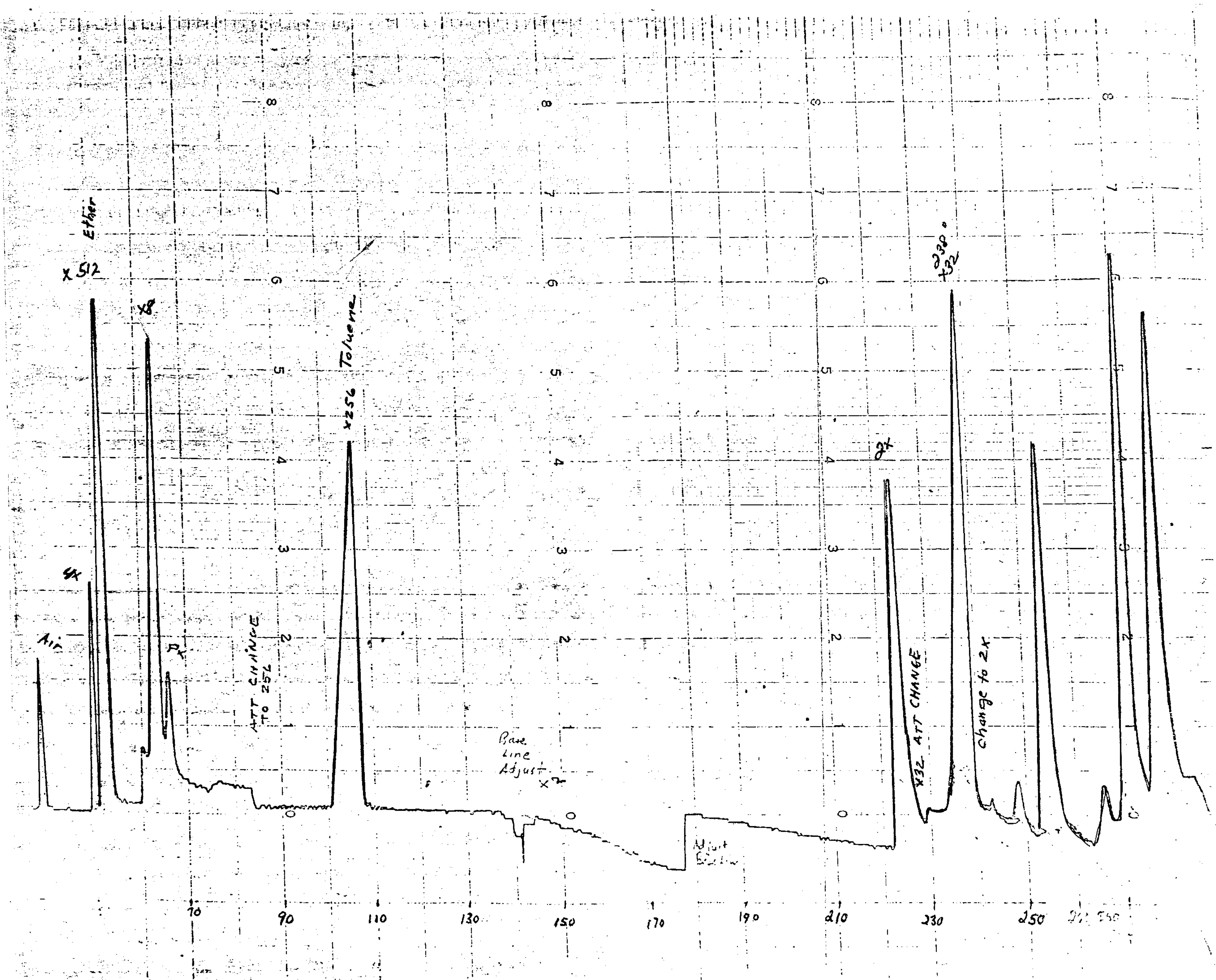
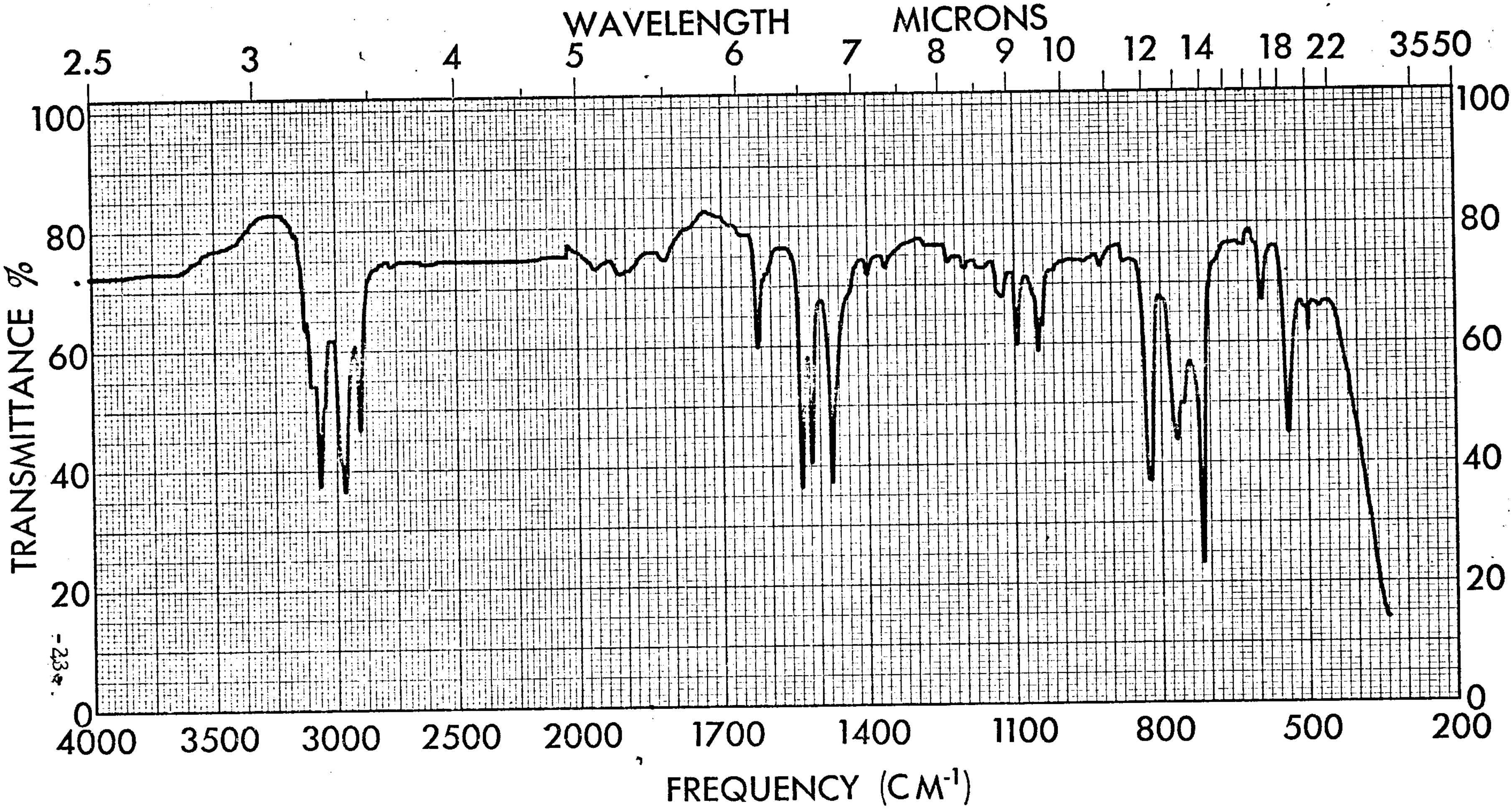


Figure 11 Gas Chromatogram of Product 94-55



SPECTRUM NO. 7840

SAMPLE Peak eluting at

235 °C on 12 ft SE-30
column programmed
from 30°C @ 5°C/min

ORIGIN 30 μl of 94-55

PURITY

THICKNESS

LEGEND

1.

2.

OPERATOR BWB-VSA

REMARKS

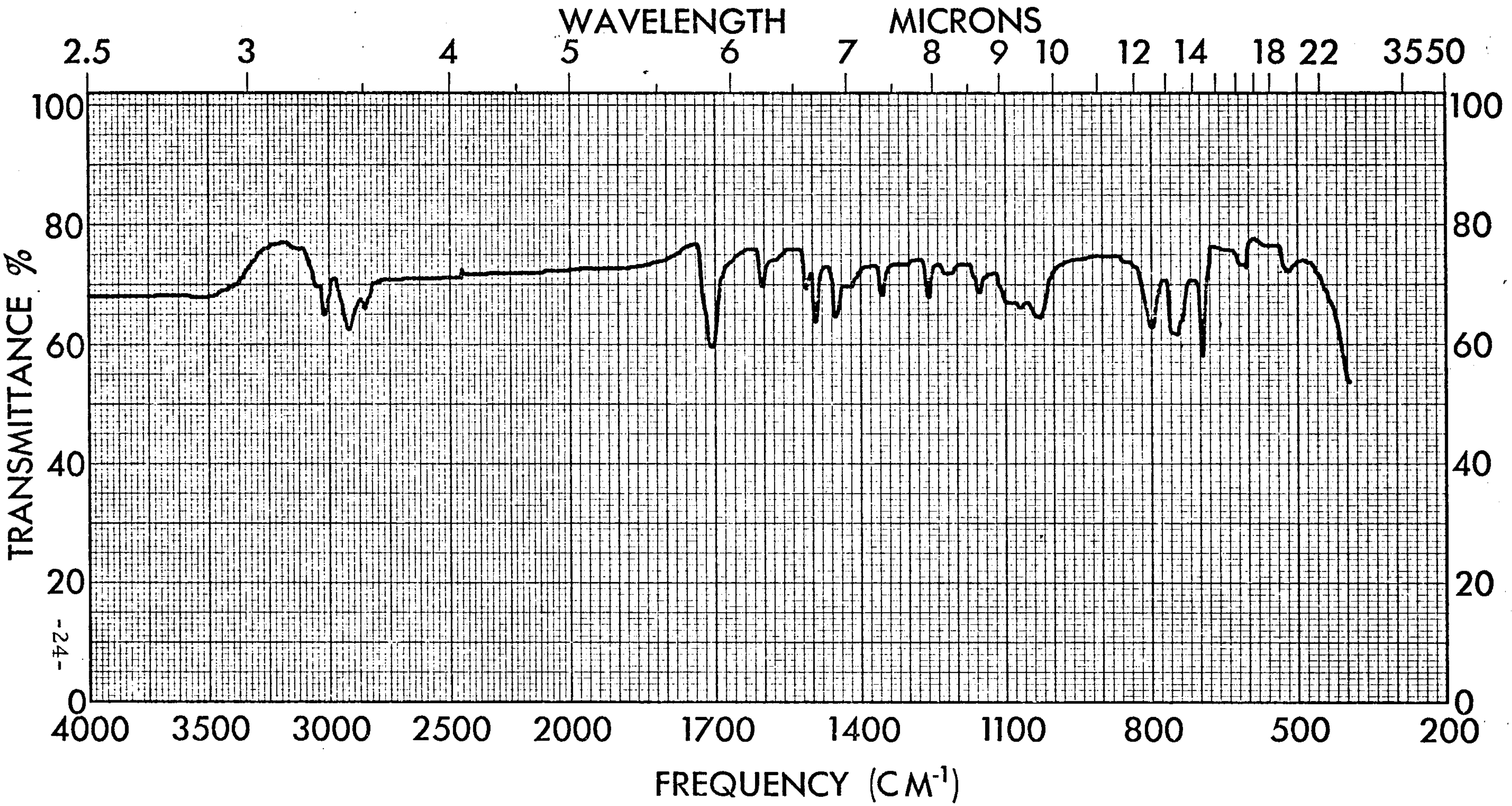
SPECTRUM NO

SAMPLE

Figure 12. Infrared Spectrum of Component from Gas Chromatographic Analysis of 94-55 Eluting at 238°C.

PART NO. 221-1617

THE PERKIN-ELMER CORPORATION NORWALK, CONN.



SPECTRUM NO. 7841
SAMPLE Eluate comprising 5 peaks eluting between 240-260 °C from 94-55 on 12 ft SE-30 column from 30 °C at 5 °C/min.

ORIGIN 30 μl of 94-55

PURITY

THICKNESS

LEGEND

1.

2.

OPERATOR BWB: WSP

REMARKS

SPECTRUM NO

SAMPLE

Figure 13. Infrared Spectrum of Components from Gas Chromatographic Analysis of 94-55 Eluting between 240 - 260°C.

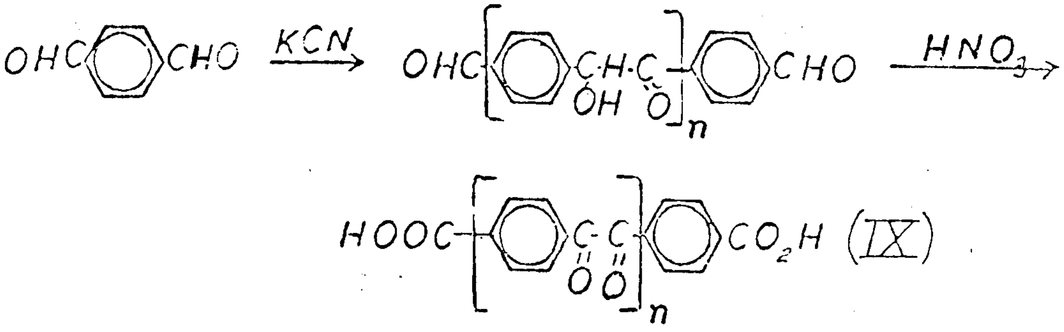
PART NO. 221-1617

THE PERKIN-ELMER CORPORATION NORWALK, CONN.

1.6 p-Polybenzil (IX)

This polymer was desired as an intermediate for the preparation of polyquinoxalines by reaction with o-phenylenediamine and with substituted o-phenylenediamines in which the substituent had latent capability for cross-linking.

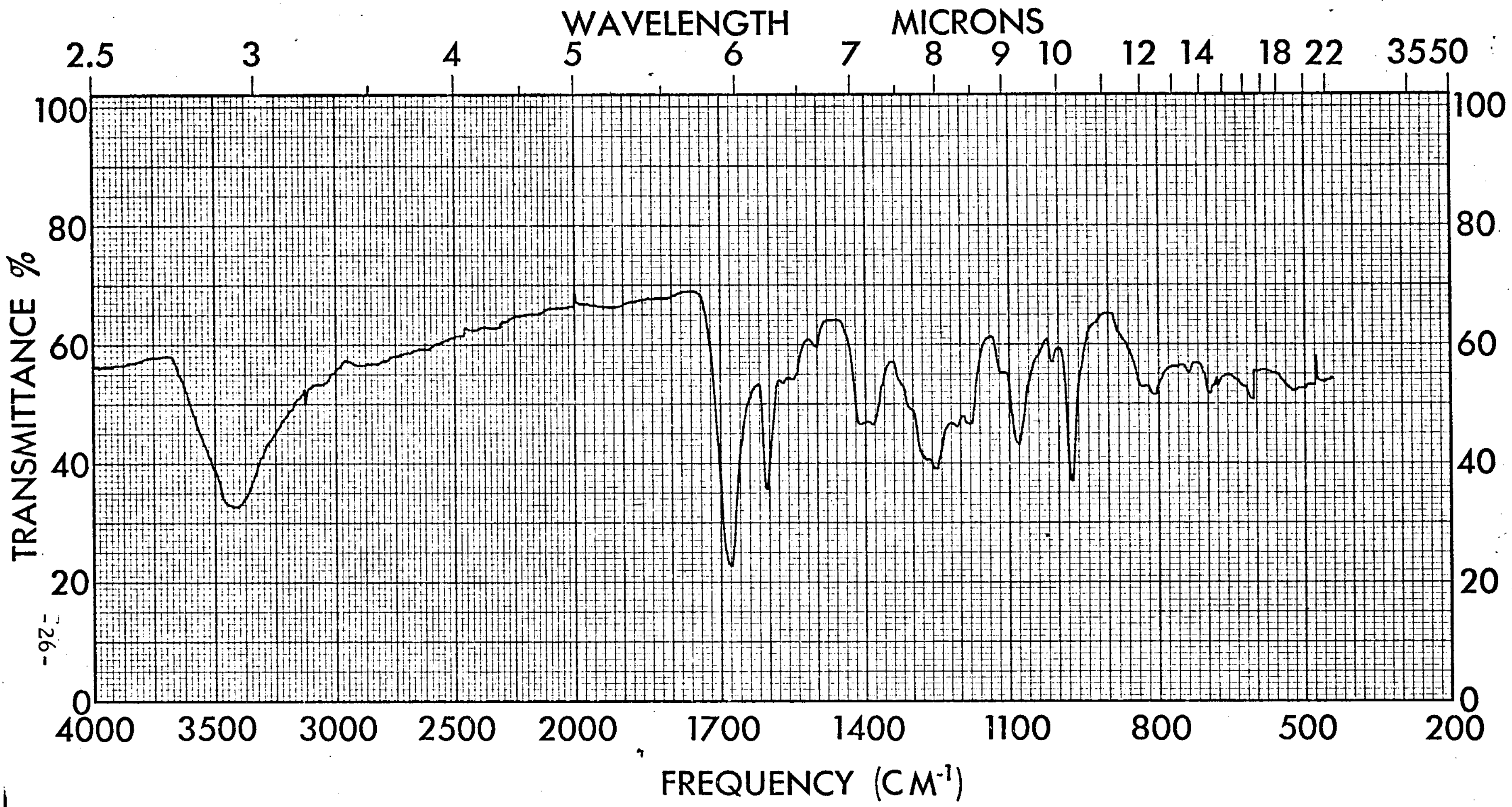
The overall procedure for preparing this p-polybenzil is outlined below:



1.6.1 Poly-p-benzoin

This material was prepared by the method of Jones and Tinker[52]. A solution of 13.4 g (0.1 mole) terephthalaldehyde in 13.3 cc 95% ethanol and 10.6 cc water was treated with 1.06 g sodium cyanide and was refluxed for one hour The solution turned red and an orange precipitate formed. The mixture was treated with 40 cc 50% ethanol and was filtered. The residue was washed with 20 cc 50% ethanol and was dried. The yield was 8.2 g (61.6%). The product was soluble in m-cresol, dimethylformamide and ethylene carbonate, but was insoluble in water, methanol, ethanol, acetic acid, pyridine and nitromethane. It darkened at about 197°, but did not melt below 300°C. The inherent viscosity of a 0.5% solution in dimethylformamide was 0.097 dl/g at 23.0°C. The infrared absorption spectrum of this material is shown in Figure 14. A comparison is made in Table I between the frequencies of the principal absorption bands of this spectrum and that for benzoin. The concurrence of frequencies is suggestive of an assignment of poly-p-benzoin to sample 411-24-1.

A second procedure, based on the method of Wehr [53], did not give a polymer with a higher molecular weight. A solution of hydrogen cyanide in dimethylformamide was prepared by stirring 0.49 g (0.01 mole) sodium cyanide and 1.36 g (0.01 mole) potassium bisulfate in 10 cc dimethylformamide containing 5 drops of water. After 15 minutes of stirring, the mixture was filtered, and the filtrate was treated with 0.35 g of triethylamine.



SPECTRUM NO. 7738

SAMPLE Polybenzoin

ORIGIN 411-24-1

PURITY

THICKNESS

LEGEND

1.

2.

OPERATOR BJV

REMARKS

SPECTRUM NO.

SAMPLE

Figure 14. Infrared Spectrum of Compound 411-24-1 (Poly-p-benzoin).

PART NO. 221-1617

THE PERKIN-ELMER CORPORATION NORWALK, CONN.

TABLE I

COMPARISON OF FREQUENCIES[a] OF PRINCIPAL ABSORPTION BANDS OF BENZOIN AND POLY-p-BENZOIN

BENZOIN	POLY-p-BENZOIN
1680	1680
1610	1610
1575	1575 (weak)
	1510 (weak)
1490	
	1410 (shoulder)
1390	
	1380
1350	
1310	1310 (weak shoulder)
1280	1275 (weak shoulder)
1255	1255
1205	1210 (weak)
1180	1180 - 1170 (broad)
1025	1020
1000	
980	980
925	
860	865
833	835
	810
755	
	745
700	700
680	680

---

[a] cm^{-1}.

3.5 cc of this solution was added to 5 g terephthalaldehyde dissolved in 10 ml dimethylformamide. The resulting solution was stored under nitrogen for 18 hours at room temperature and was then heated for 100 hours at 45°C. The inherent viscosity of the polybenzoin so obtained (0.5% solution in dimethylformamide) was 0.080 dl/g at 23.0°C.

1.6.2 Poly-p-benzil

A mixture of 4 g of poly-p-benzoin, 2 ml of water and 10 ml concentrated nitric acid was heated in a boiling water bath for 2 hours. Nitric oxide was evolved and a fine, yellow, granular solid was produced. The mixture was cooled to room temperature, diluted with 80 ml of cold water and was filtered, washed on the filter, with cold water and dried. The yield was 3.9 g (98.5%). The infrared spectrum of the reaction product is shown in Figure 15 and may be compared with the spectrum for benzil (Figure 16). Table II lists the principal frequencies of the two compounds. Since both materials show a general concurrence of the frequencies of the bands and since both absorb in the 1600 - 1700 and in the 1200 - 1350 cm^{-1} regions (attributed by Colthup to aromatic ketones), an assignment of p-polybenzil to compound 94-39 is suggestive.

1.7 o-Phenylenediamine (X)

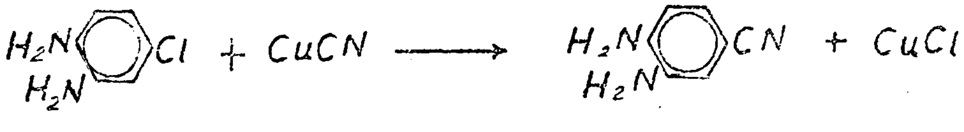
This compound was obtained from commercial sources and was recrystallized from water (m.p. 102-3°C).

1.8 1,4-Bis(chloromethyl)benzene (XII)

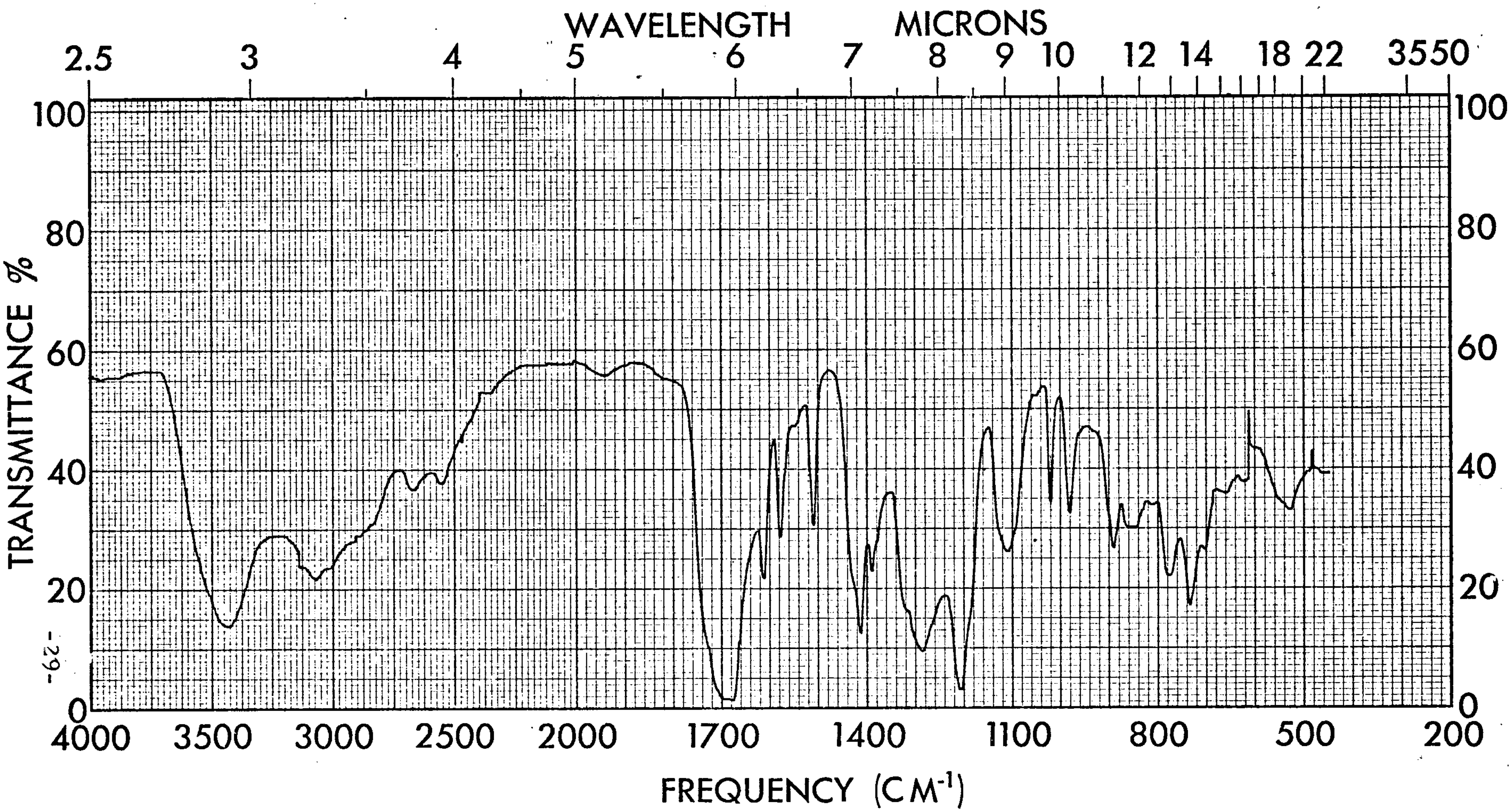
This cross-linking compound was purchased and used without further purification.

1.9 3,4-Diaminobenzonitrile (XIII)

An attempt to prepare this compound by the following procedure did not give the desired material.



A mixture of 20 g (0.14 mole) 4-chloro-2-aminoaniline and 15 g (0.17 mole) cuprous cyanide was heated at 220-250°C for 4 hours under a stream of nitrogen. The melt was cooled, crushed and extracted



SPECTRUM NO. 7737

SAMPLE Poly benzil

ORIGIN 94-39

PURITY

THICKNESS

LEGEND

1.

2.

OPERATOR B.S.

REMARKS

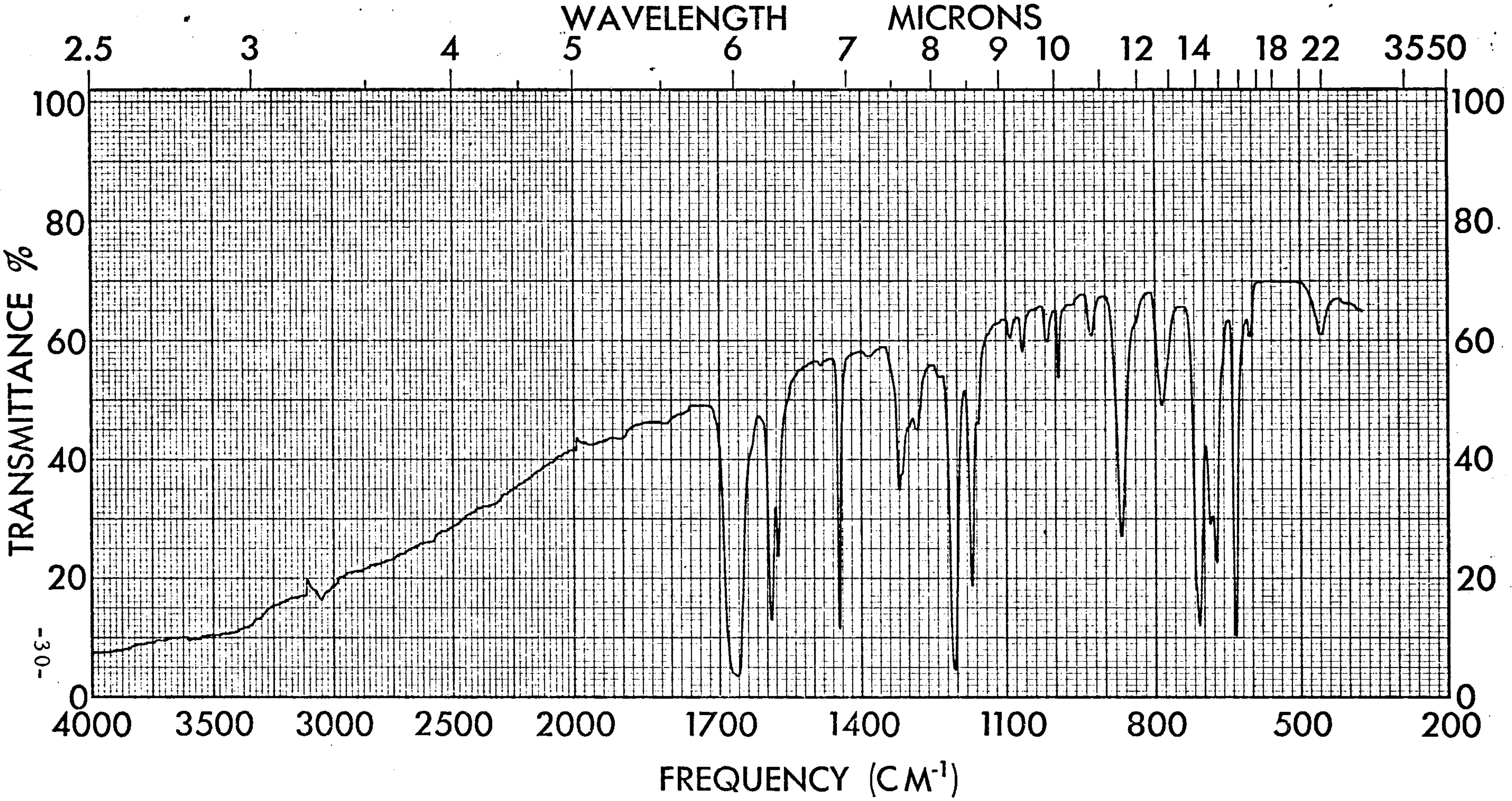
Figure 15. Infrared Spectrum of Compound 94-39 (Poly-p-benzil).

SPECTRUM NO.

SAMPLE

PART NO. 221-1617

THE PERKIN-ELMER CORPORATION NORWALK, CONN.



SPECTRUM NO. 7751

SAMPLE Benzil

ORIGIN Eastman

Lot # 32 #

PURITY

LEGEND

1.

2.

REMARKS

Figure 16. Infrared Spectrum of Benzil.

THICKNESS

OPERATOR B.S.

SPECTRUM NO.

SAMPLE

PART NO. 221-1617

THE PERKIN-ELMER CORPORATION NORWALK, CONN.

TABLE II

COMPARISON OF FREQUENCIES[a] OF PRINCIPAL ABSORPTION BANDS OF BENZIL AND POLY-p-BENZIL

BENZIL	POLY-p-BENZIL
3060	3060
	2660 (weak)
	2540 (weak)
1690, 1670[b]	1720, 1700, 1690, 1670[b]
1600	1610
1580	1575
	1500
1450	
	1425 (shoulder)
	1410
	1385
1320	1320 (shoulder)
1285	1280
1210	1200
1175	1180 (shoulder)
1110, 1095 (weak)	1110 (broad)
1070	
1020	1020
1000	
970 (weak)	975
930	
	885
870	860 - 840 (broad)
790	
	775
	730
715	
690	700 (weak)
680	680
640	
620	610
	525 (broad)

---

[a] cm^{-1} [b] broad absorption band

with aqueous ammonia. The residue was extracted with butyl acetate. The material obtained when the butyl acetate was evaporated did not show the presence of nitrile absorption in infrared analysis.

Subtask B: Polyquinoxaline Synthesis and Characterization

1.10 Poly {2,2'-(1,4-phenylene)-6,6'-bis[3-(1-naphthalenyl)]quinoxalinyl} (Polymer I)

This polymer was prepared in m-cresol solution by the method of Port and Loszewski [42c].

The inherent viscosity of Polymer I, measured in m-cresol solution at 30°C is given in Table III; its elemental chemical composition is given in Table IV.

The glass transition temperature of Polymer I was determined from stress-relaxation measurements by plotting the shift factor, log (1/K), as a function of the reciprocal of the absolute temperature and noting the temperature at which the slope of the shift function, d[log (1/K)/d(1/T)], changes (a detailed description of the experimental procedure is given by Port and Loszewski [42d]). Figure 17 is the master curve for Polymer I from which values for log (1/K) were obtained and plotted as a function of the reciprocal of the absolute temperature in Figure 18. The break in the curve in Figure 18, which occurs at 263°C, is the transition temperature.

Isothermal gravimetric analysis of Polymer I were performed at 315.6°C (600 ± 5°F) and at 371.1°C (700 ± 5°F). The weight losses observed are shown as a function of exposure time in Tables V and VI.

The ultimate tensile strength of Polymer I was found to be 63.79 x 10^6 newtons/m^2 (9250 lbs/in^2) at 204.4°C (400°F) and 29.72 newtons/m^2 (4310 lbs/in^2) at 315.6°C (600°F). Specimens of Polymer I subjected to sustained tensile loading at 75% of ultimate strength at 204.4°C and 50% of ultimate strength at 315.6°C, respectively did not rupture after 114 hours. The specimens showed no weight loss at 204.4°C and a 3.1% weight loss at 315.6°C.

1.11 Poly {2,2'-(1,3-phenylene)-6,6'-bis[3-(1-naphthalenyl)]quinoxalinyl} (Polymer II)

A mixture of 11.928 g (0.027 mole) 1,3-bis[3'-(1-naphthalenyl)-oxalyl]benzene and 5.7865 g (0.027 mole) 3,3'-diaminobenzidi was

TABLE III

INHERENT VISCOSITIES OF SOME QUINOXALINE POLYMERS IN m-CRESOL

Polymer	η_{inh} dl/g at 30.0°C
I	1.80
II	1.44, 1.87
III	2.40
IV	0.14

TABLE IV

ELEMENTAL CHEMICAL ANALYSIS OF SOME QUINOXALINE POLYMERS

Polymer	Polymer Composition, Weight %							
	Theory				Found			
	C	H	N	O	C	H	N	O
I	86.28	4.14	9.58	--	88.02	3.78	9.40	--
II	86.28	4.14	9.58	--	85.88	3.48	8.30	--
III	84.85	4.15	11.00	--	85.25	3.98	10.79	--
IV	81.30	3.94	13.37	1.39	80.1	4.2	13.0	2.8[a]

[a] By difference. Polymer assumed to contain amide groups.

411-95-2

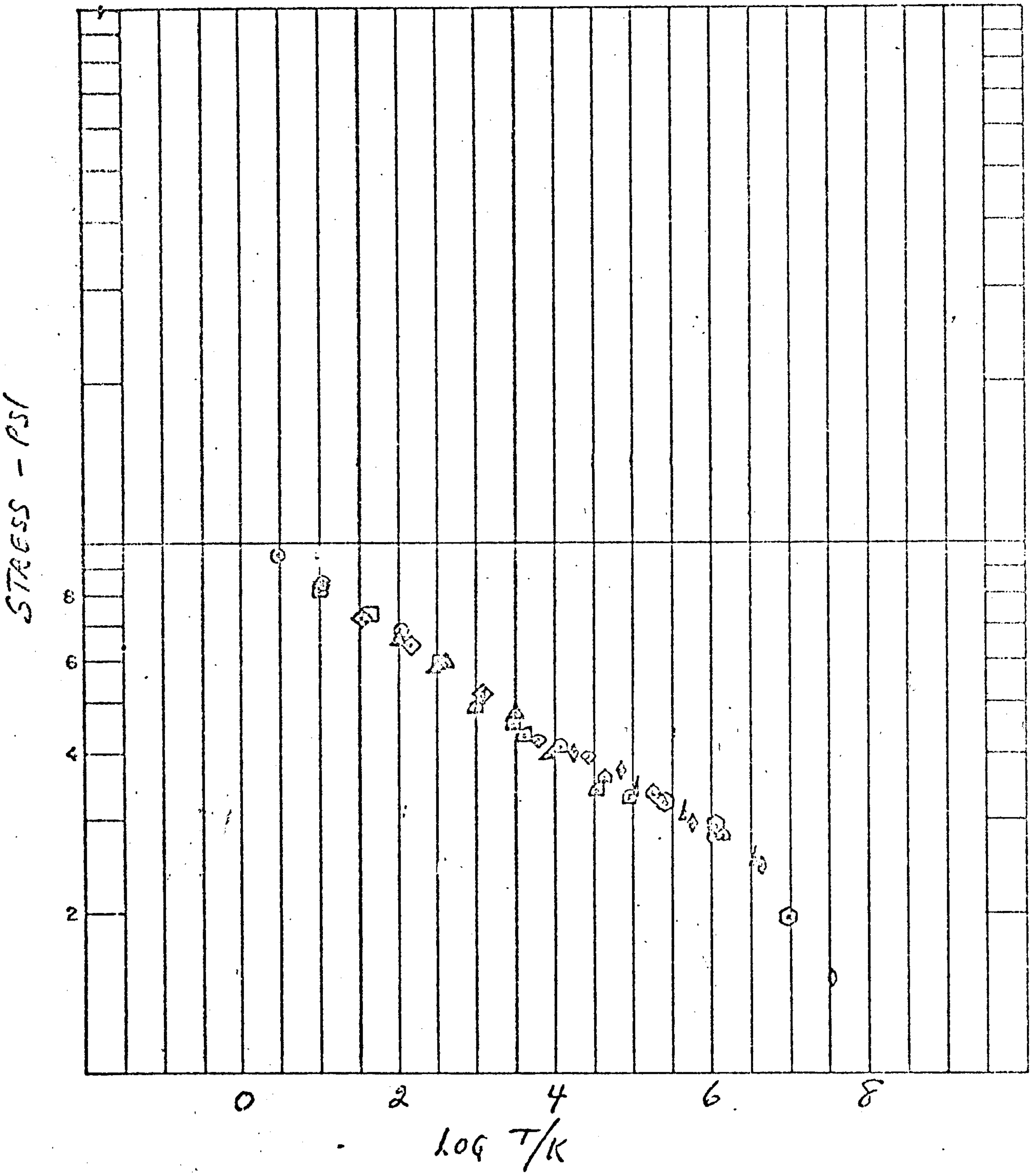


Figure 17. Master Curve for Polymer I.

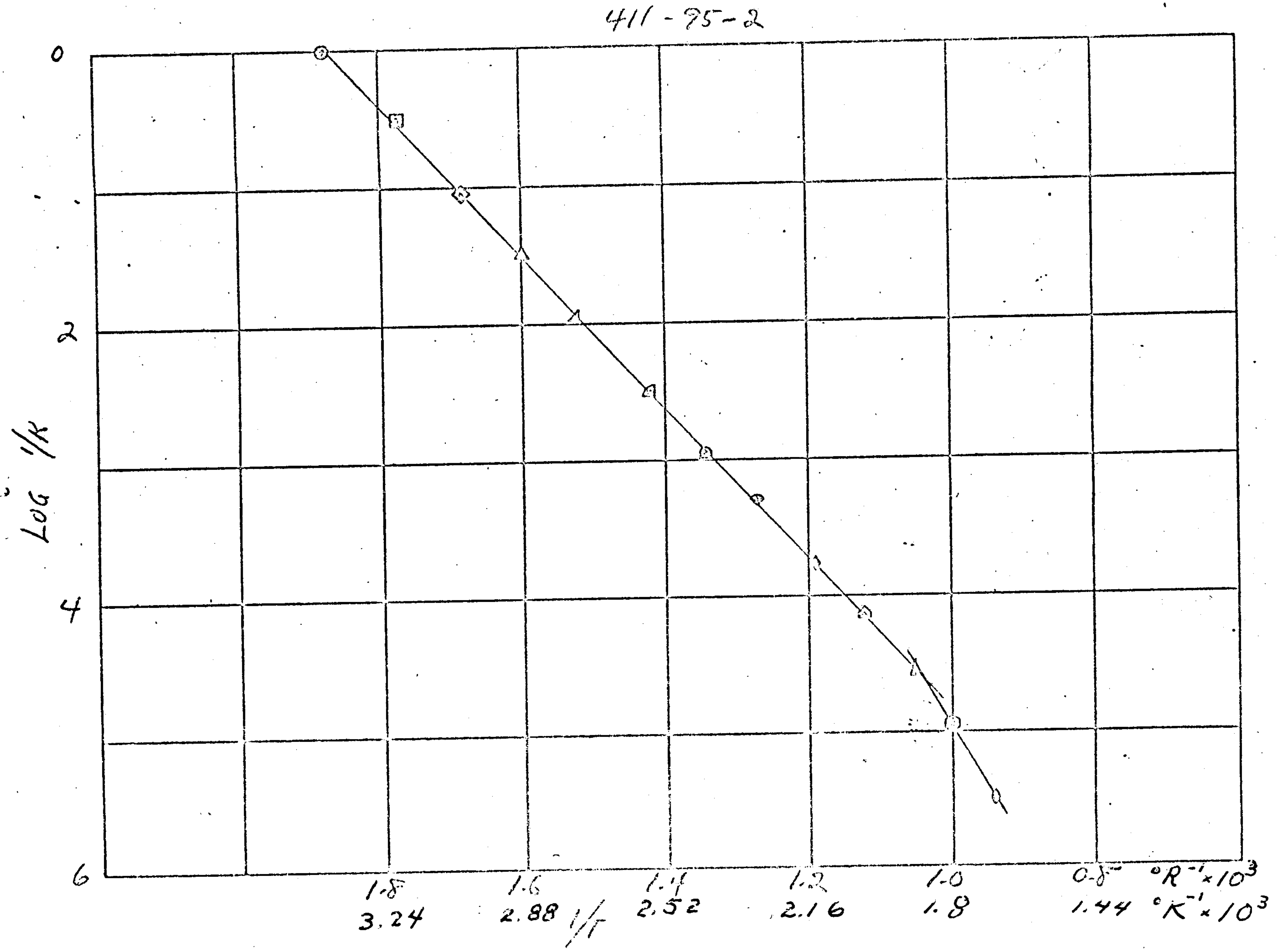


Figure 18. Determination of Second-Order Transition Temperature from Log 1/K vs. 1/T Plot for Polymer I.

TABLE V

ISOTHERMAL GRAVIMETRIC ANALYSIS[a] OF QUINOXALINE POLYMERS AT 315.6°C (600 ± 5°F)

Time, hours	Polymer I		Polymer II	
	Specimen 1	Specimen 2	Specimen I	Specimen II
0	0	0	0	0
24	3.9	4.1	3.8	8.8
144	17.4	15.3	18.8	25.9
192	27.3	27.4	27.2	35.1
217	37.1	37.8	34.3	43.2
288	53.1	51.0	44.9	55.0
336	60.7	57.4	50.4	61.1
384	65.8	62.3	54.6	65.8
456	71.2	68.5	60.5	72.1

[a] Percent weight loss

TABLE VI

ISOTHERMAL GRAVIMETRIC ANALYSIS[a] OF QUINOXALINE POLYMERS AT 371.1°C (700 ± 5°F)

Time, hours	Polymer I		Polymer II	
	Specimen 1	Specimen 2	Specimen 1	Specimen 2
0	0	0	0	0
24	6.6	8.0	18.6	22.8
48	36.4	36.9	49.0	56.6
120	93.2	92.2	88.4	87.7
168	97.7	97.6	91.3	89.7
312	99.7	99.7	94.8	95.2
432	99.9	99.9	99.8	99.6

[a] Percent weight loss

dissolved in 70 cc m-cresol under a current of nitrogen and refluxed for 18 hours. A viscous, dark colored solution resulted. The inherent viscosities of Polymer II of two preparations are given in Table III. Portions of the polymer solution were cast onto glass plates to prepare polymer specimens for test purposes. Figure 19 is the infrared spectrum of this polymer and may be compared with the infrared spectrum (Figure 20) of Polymer I. Figure 20 shows absorption at 1410, 1200, 1140, 1040, 1010, 860, 570 and 540 cm^{-1} not present in Figure 19. Figure 19 shows absorption at 520 and 500cm^{-1} not present in Figure 19. The elemental chemical analysis of Polymer II is given in Table III.

The film specimens of Polymer II were too brittle for stress-relaxation and tensile tests. The glass transition temperature of Polymer II was therefore determined from the change in its linear thermal expansion rate (Figure 21) and was found to be 248.9°C (480°F).

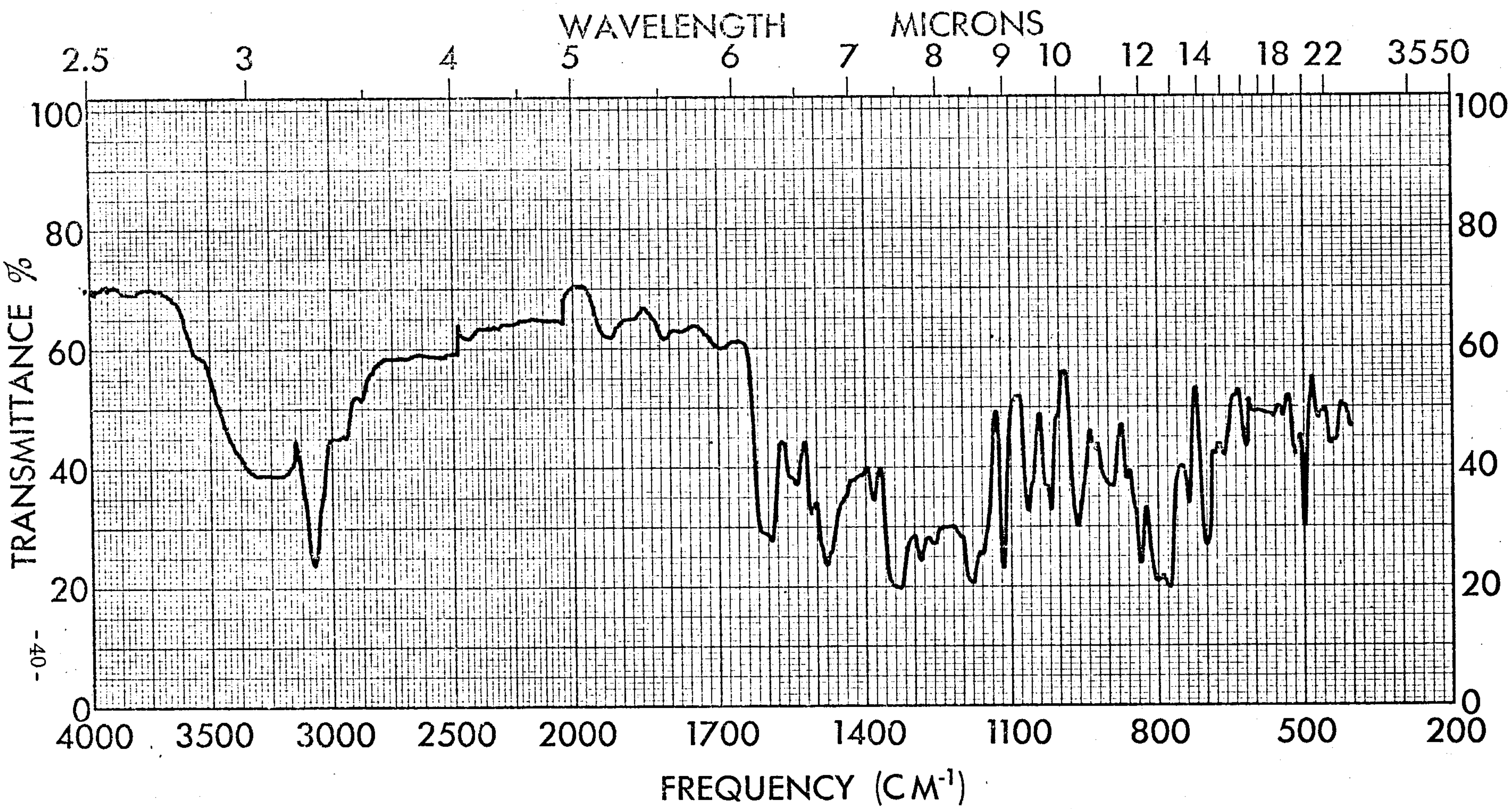
Isothermal gravimetric analyses of Polymer II were performed at 315.6°C (600 ± 5°F) and at 371.1°C (700 ± 5°F). The weight losses observed are shown as a function of exposure time in Tables V and VI.

1.12 Poly{2,2'-(1,4-phenylene)-6,6'-bis[3-(1-naphthalenyl)-co-(phenyl)-(25/75)]quinoxalinyl} (Polymer III)

A mixture of 11.765 g (0.02659 mole) 1,4-bis[(1'-naphthalenyl)-oxalyl]benzene, 27.3993 g (0.08003 mole) 1,4-bis(phenyloxalyl)benzene, 22.8466 g (0.1066 mole) 3,3'-diaminobenzidine and 300 cc m-cresol was slowly heated with mechanical stirring under a stream of nitrogen. The mixture rapidly turned dark red and the components slowly dissolved. As the solution became more viscous, the bath temperature was gradually increased until refluxing occurred. The solution was refluxed for 18 hours and cooled. The inherent viscosity of the resulting Polymer III is given in Table III and the elemental composition of the dried film is shown in Table IV.

1.13 Poly[2,3-(1,4-phenylene)quinoxalinyl] (Polymer IV)

Polymer IV was prepared by refluxing for 18 hours a solution of 10.6513 g polybenzil (0.07872 equivalents on the basis of an assumed degree of polymerization of 10) and 8.5128 g (0.07872 equivalent) of o-phenylenediamine in 60.9 g m-cresol. Traces of water were removed by distilling the mixture until the boiling point reached 203°C. A dark green viscous solution resulted. The inherent viscosity of this polymer is given in Table III. A film cast from this solution was brittle. The film was dried in vacuo at 150°C, and an elemental chemical analysis (Table IV) was performed.



SPECTRUM NO. [illegible]

SAMPLE 411-155

ORIGIN

PURITY

THICKNESS

LEGEND

1.

2.

OPERATOR

REMARKS

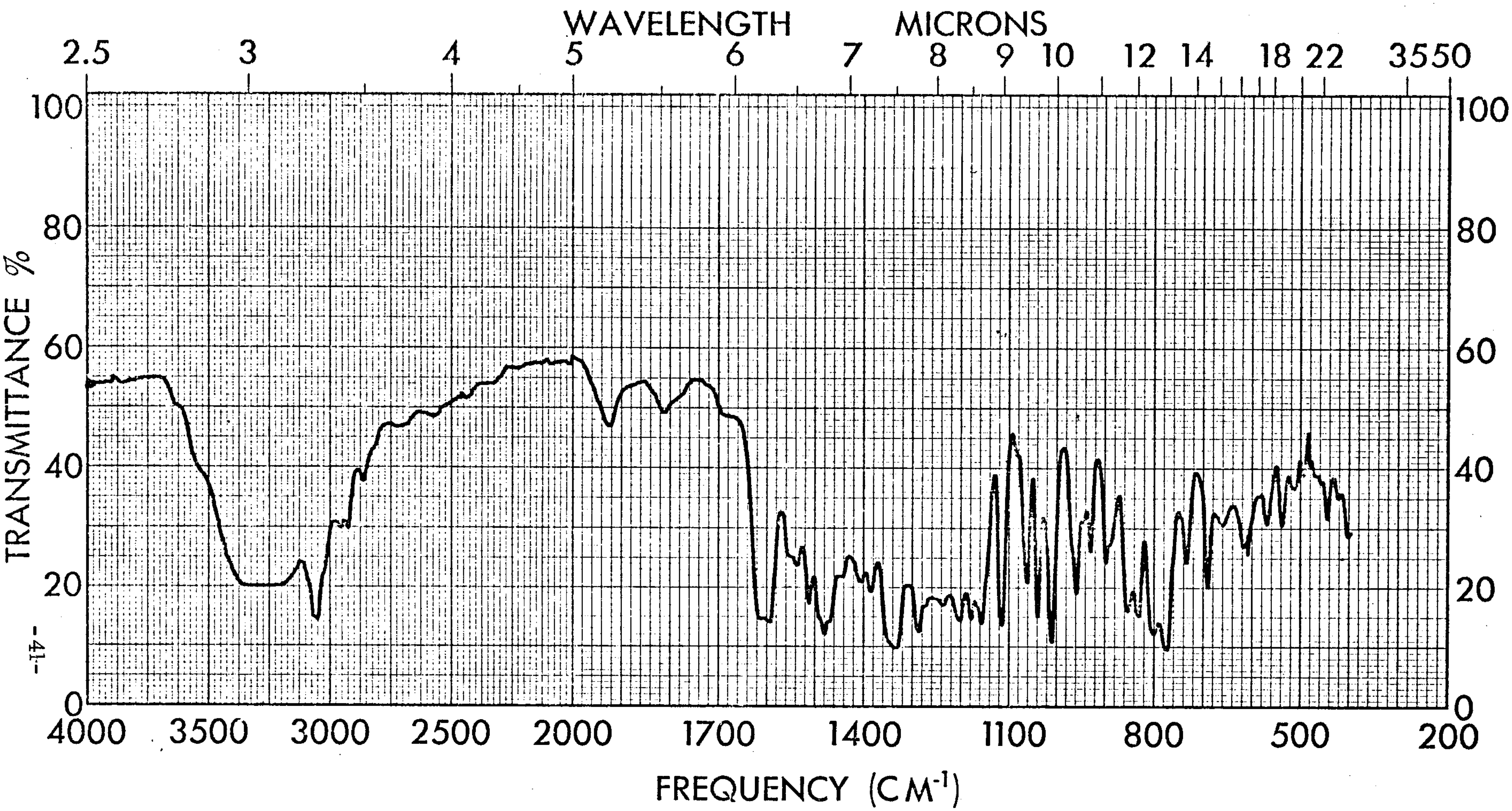
Figure 19. Infrared Spectrum of Poly{2, 2'-(1, 3-phenylene)-6, 6'-bis[3'-(1-naphthalenyl)quinoxalinyl}
(Polymer II).

SPECTRUM NO.

SAMPLE

PART NO. 221-1617

THE PERKIN-ELMER CORPORATION NORWALK, CONN.



SPECTRUM NO. 7852

SAMPLE 411-95-2

ORIGIN

PURITY

THICKNESS

LEGEND

1.

2.

OPERATOR wcr

REMARKS

Figure 20. Infrared Spectrum of Poly{2, 2'-(1, 4-phenylene)-6, 6'-bis[3'-(1-naphthalenyl)quinoxalinyl}
(Polymer I).

SPECTRUM NO.

SAMPLE

PART NO. 221-1617

THE PERKIN-ELMER CORPORATION NORWALK, CONN.

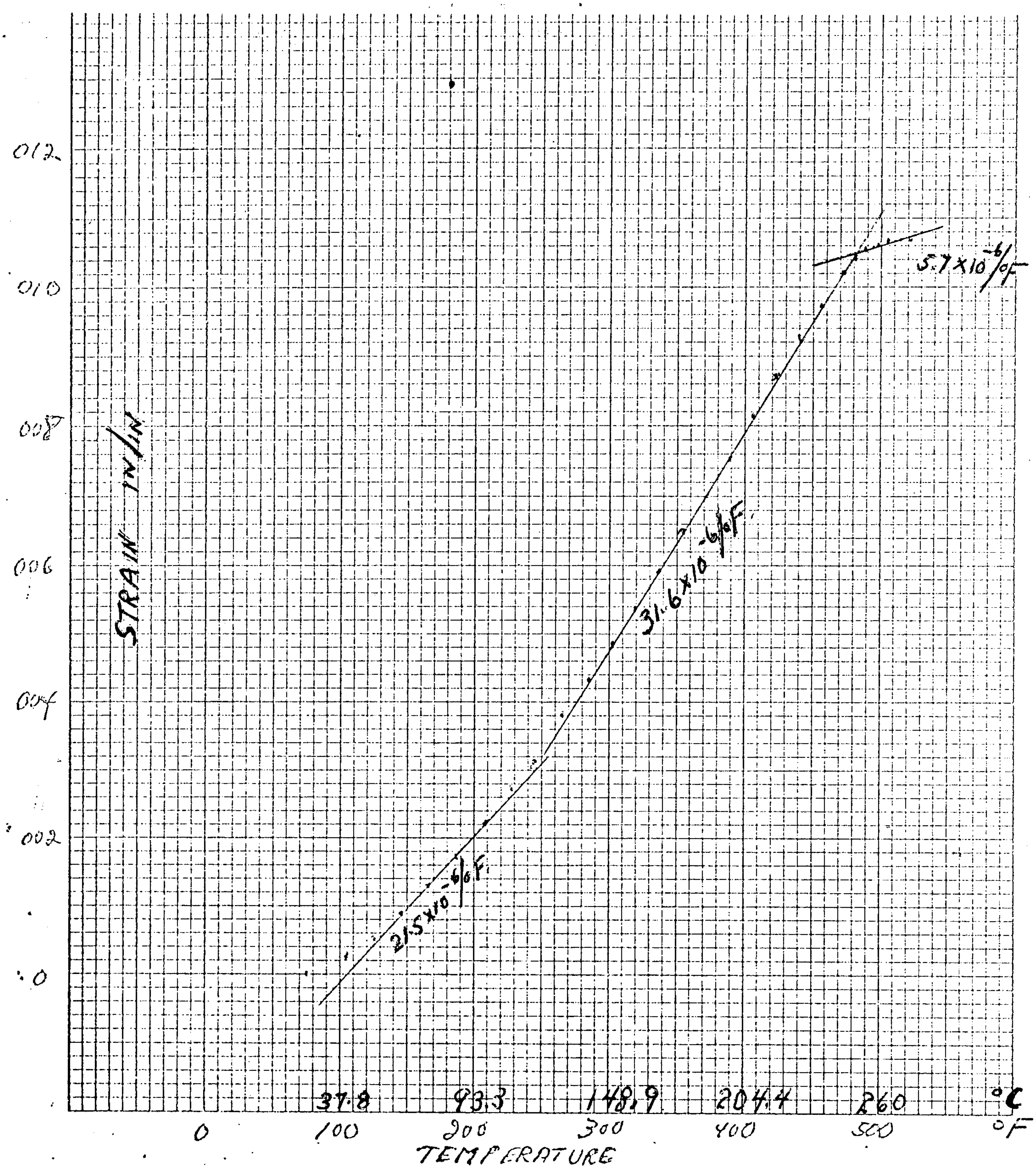


Figure 21. Coefficient of Linear Thermal Expansion of Polymer II as a Function of Temperature.

Subtask C: Polymer Cross-Linking Studies

1.13 Reaction Conditions for Cross-Linking Polyquinoxalines by Quaternization

Reaction conditions for cross-linking Polymer I by quaternization with p-bis(chloromethyl)benzene were sought first by studies of polymer films by infrared spectrophotometric analysis and then by model compound investigation.

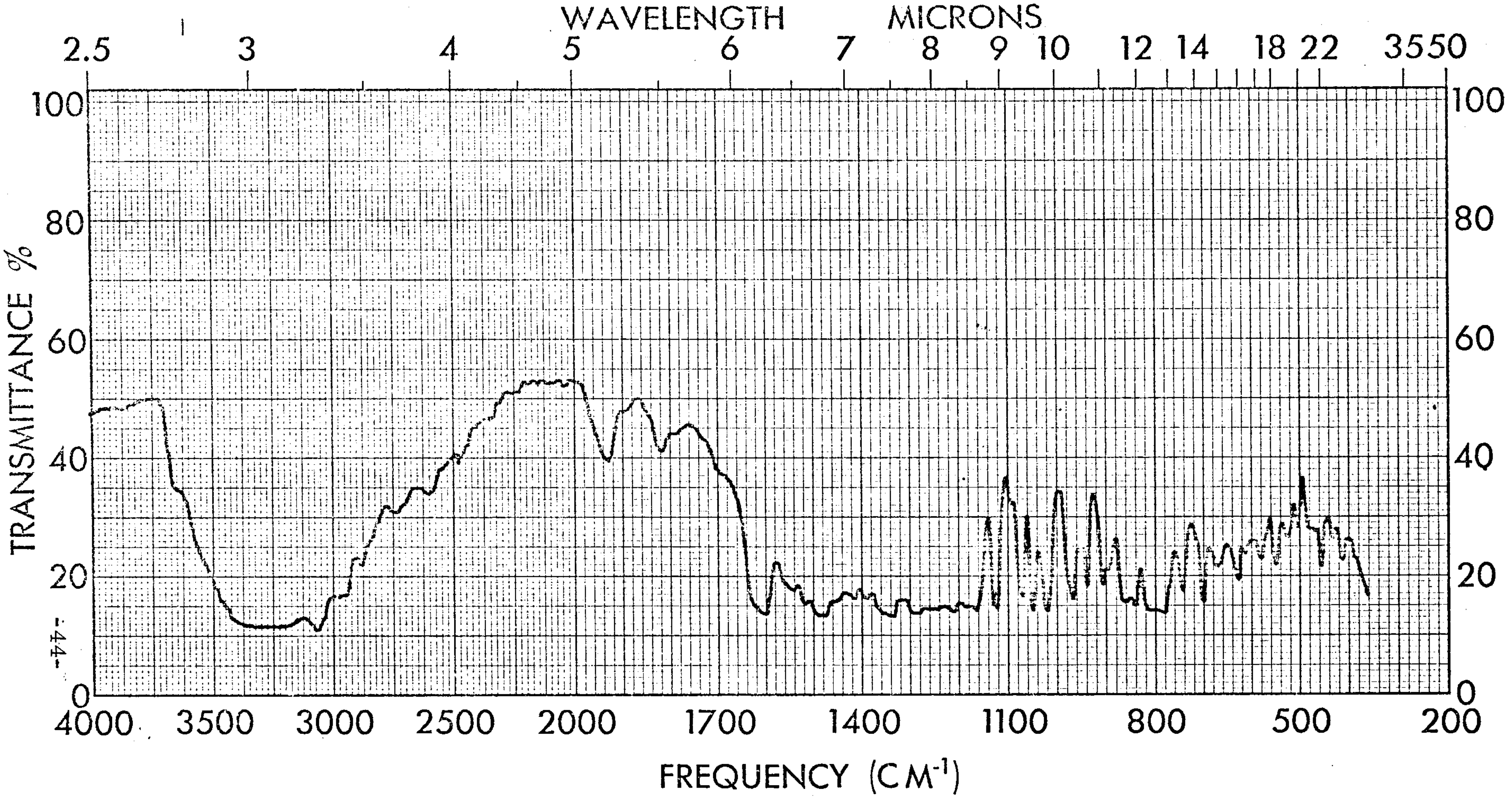
1.13.1 Polymer Film Studies

A solution of 0.148 g p-bis(chloromethyl)benzene in 1 g m-cresol was dispersed in 18 g of a solution of Polymer I in m-cresol. This produced a solution containing 5% of p-bis(chloromethyl)benzene based on the resin present. The solution was cast onto a glass plate for specimen preparation for infrared spectrophotometric analysis.

Figure 20, the infrared spectrum of Polymer I, shows absorption at 1285 cm $^{-1}$. Figure 22, the infrared spectrum of Polymer I containing 5% p-bis(chloromethyl)benzene, shows an additional shoulder at 1270 cm $^{-1}$ in which region chloromethylaryl compounds have been observed to absorb (cf. Figure 9). However, the close proximity of the two absorption bands leads to uncertainty in the interpretation of the results. Therefore, conditions for quaternization were sought with the use of model compounds.

1.13.2 Quaternization of Model Compounds

2,3-Diphenylquinoxaline was prepared by an adaptation of the method of Bost and Towell [54] and when recrystallized from methanol melted at 125-7 °C. Its infrared spectrum is shown in Figure 23 and may be compared with the spectrum for p-bis(chloromethyl)benzene (Figure 24). Although the spectra differs in many aspects, the key differences lie in the absence of absorption in Figure 23 at 1420, 1270, 850, 680 and 520 cm $^{-1}$ at which frequencies absorption is noted in Figure 24. Figure 25 is the infrared absorption spectrum for an equimolar mixture of the two compounds and Figure 26 is the infrared absorption spectrum for the mixture which had been heated for 30 minutes at 85°C. Absorption at 1420, 1270, 850, 680 and 520 cm $^{-1}$ may be noted. Figure 27 is the infrared absorption spectrum of the mixture after being heated at 150°C for 90 minutes (411-100-2). (The mixture changed to a brittle glass after being heated). The absence of absorption at 1420, 1270 850, 680 and 520 cm $^{-1}$ may be noted. The presence of chloride ion in 411-100-2 was demonstrated by the addition of silver nitrate; the precipitate which formed was soluble in aqueous ammonia. It is reasonable,



SPECTRUM NO. 2557

SAMPLE 411-95-3

ORIGIN

PURITY

THICKNESS

LEGEND

1.

2.

OPERATOR [illegible]

REMARKS

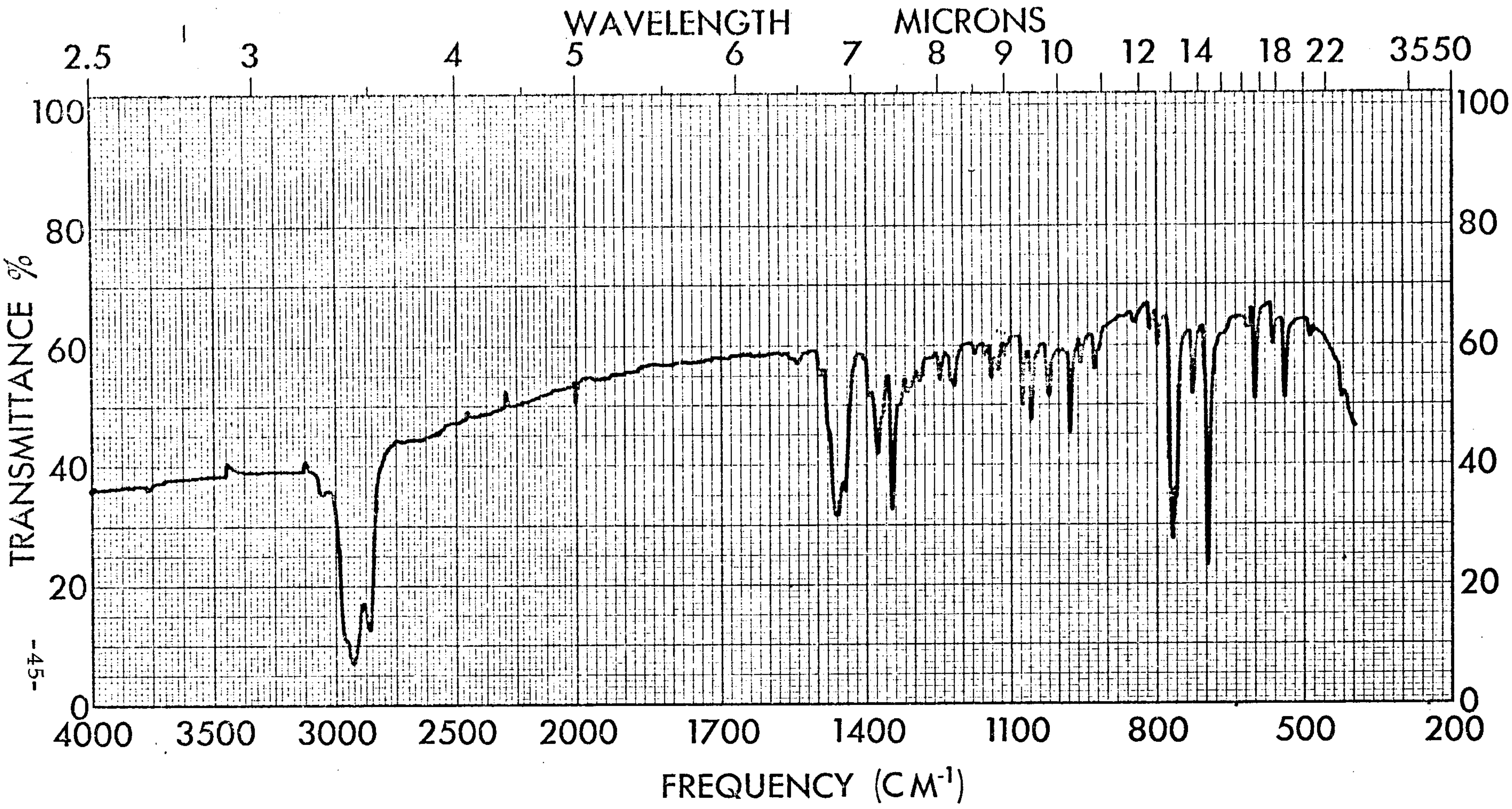
Figure 22. Infrared Spectrum of Polymer I Containing 5% p-Bis(chloromethyl)benzene.

SPECTRUM NO.

SAMPLE

PART NO. 221-1617

THE PERKIN-ELMER CORPORATION NORWALK, CONN.



SPECTRUM NO. 7863

SAMPLE 411-99-1

2,3-Diphenylquinoxaline

ORIGIN

PURITY

THICKNESS

LEGEND

1.

2.

OPERATOR WSF

REMARKS

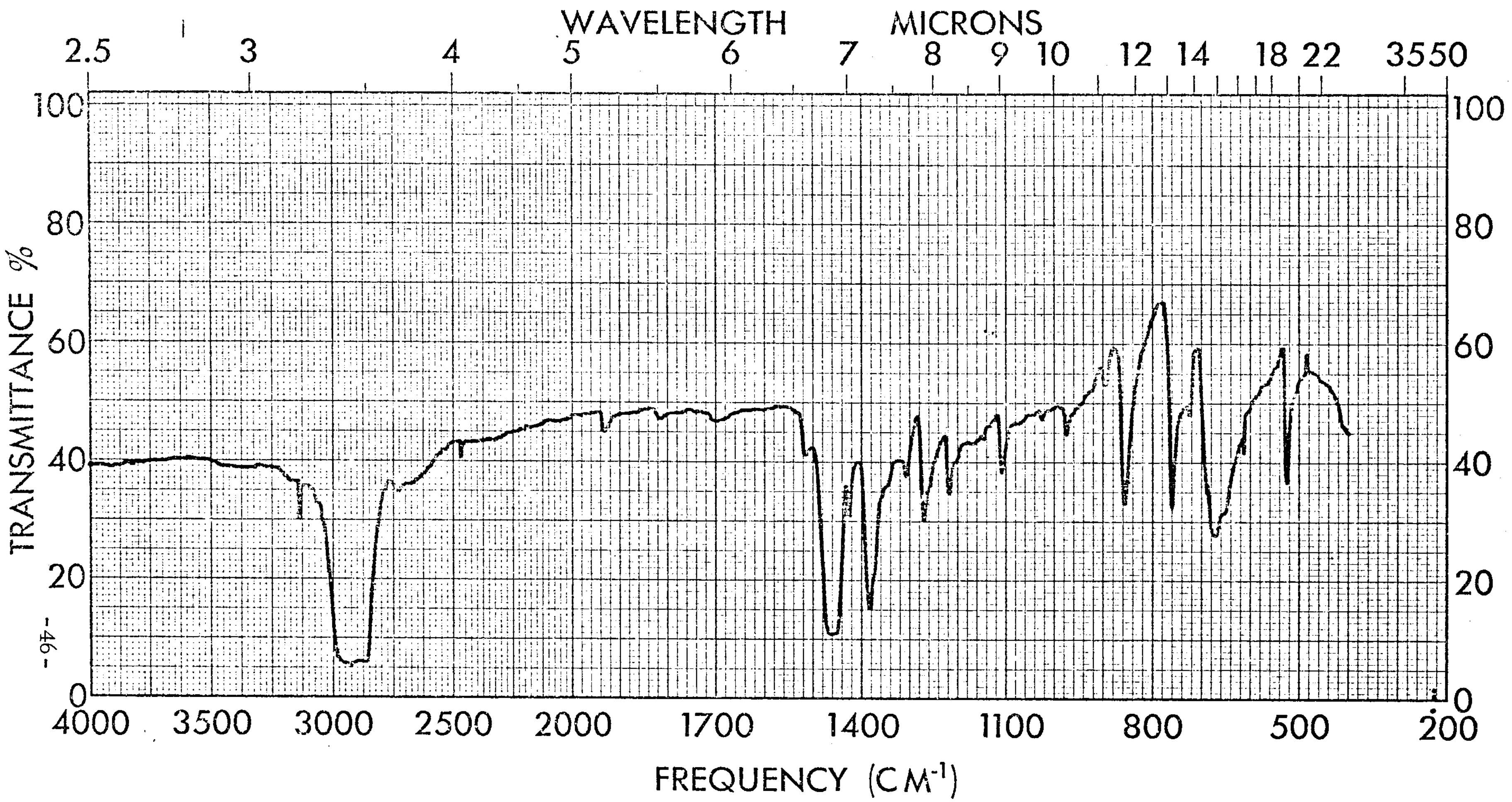
SPECTRUM NO.

SAMPLE

Figure 23. Infrared Spectrum of 2,3-Diphenylquinoxaline.

PART NO. 221-1617

THE PERKIN-ELMER CORPORATION NORWALK, CONN.



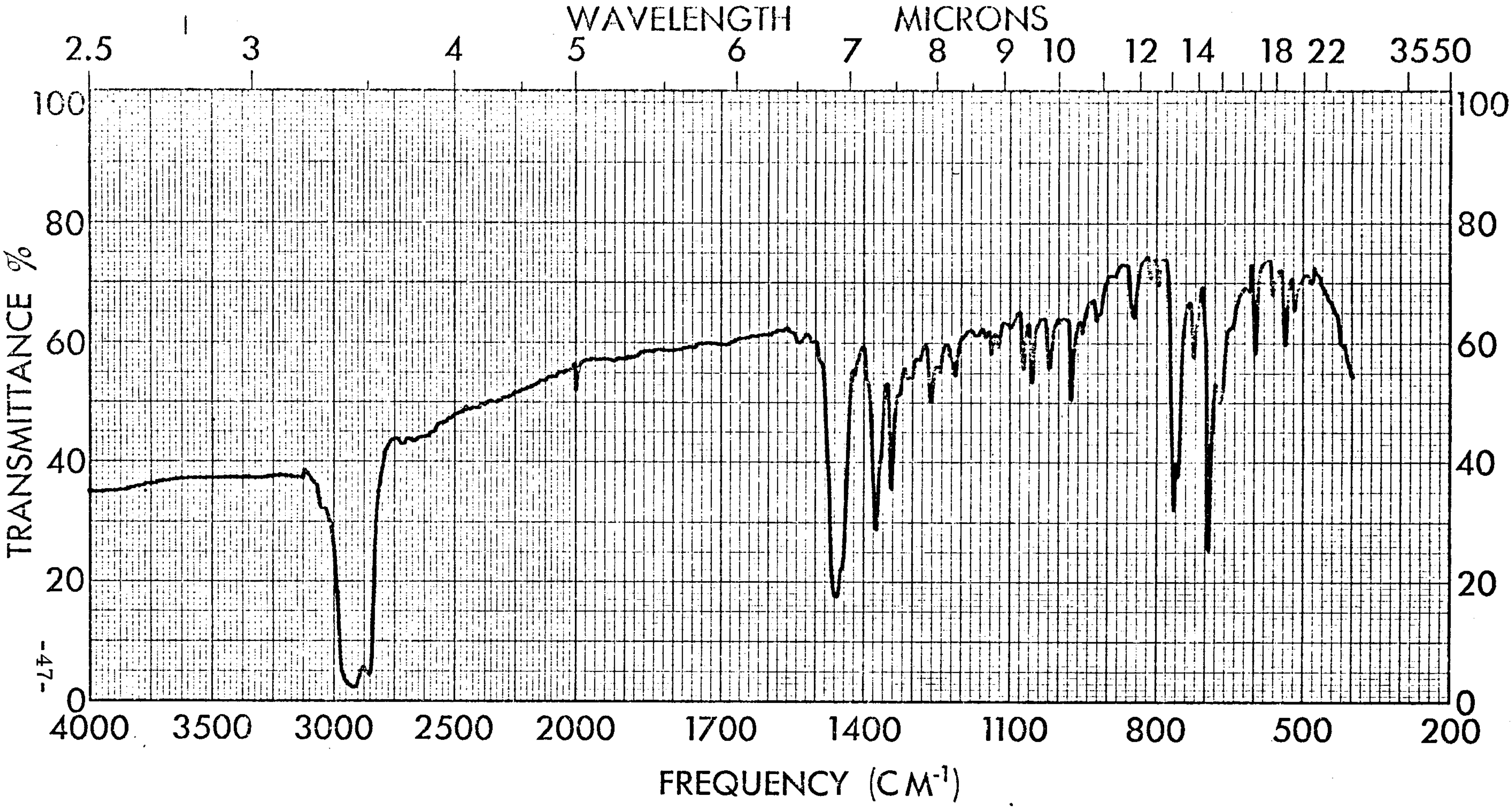
SPECTRUM NO. 7865
SAMPLE 1,4-Bis-(chloromethyl) benzene
ORIGIN Aldrich
PURITY
THICKNESS
LEGEND
1.
2.
OPERATOR WJP
REMARKS

Figure 24. Infrared Spectrum of p-Bis(chloromethyl)benzene.

SPECTRUM NO.
SAMPLE

PART NO. 221-1617

THE PERKIN-ELMER CORPORATION NORWALK, CONN.



SPECTRUM NO. 7867

SAMPLE 411-100

ORIGIN

PURITY

THICKNESS

LEGEND

1.

2.

OPERATOR [illegible]

REMARKS

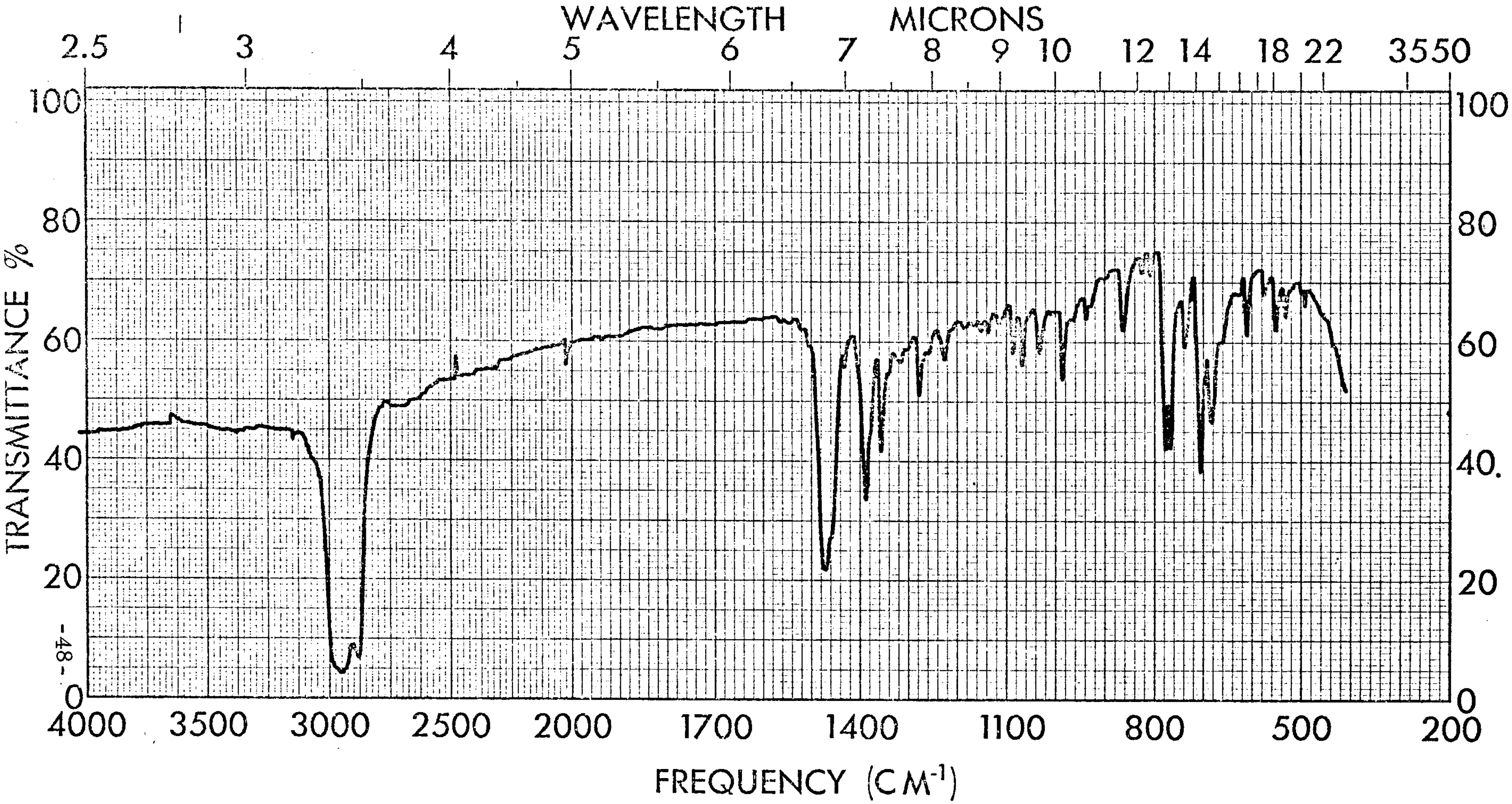
SPECTRUM NO.

SAMPLE

Figure 25. Infrared Spectrum of an Equimolar Mixture of 2,3-Diphenylquinoxaline and p-Bis(chloromethyl)benzene.

PART NO. 221-1617

THE PERKIN-ELMER CORPORATION NORWALK, CONN.



SPECTRUM NO. 7854
SAMPLE 411-100-1
ORIGIN
LEGEND
1.
REMARKS

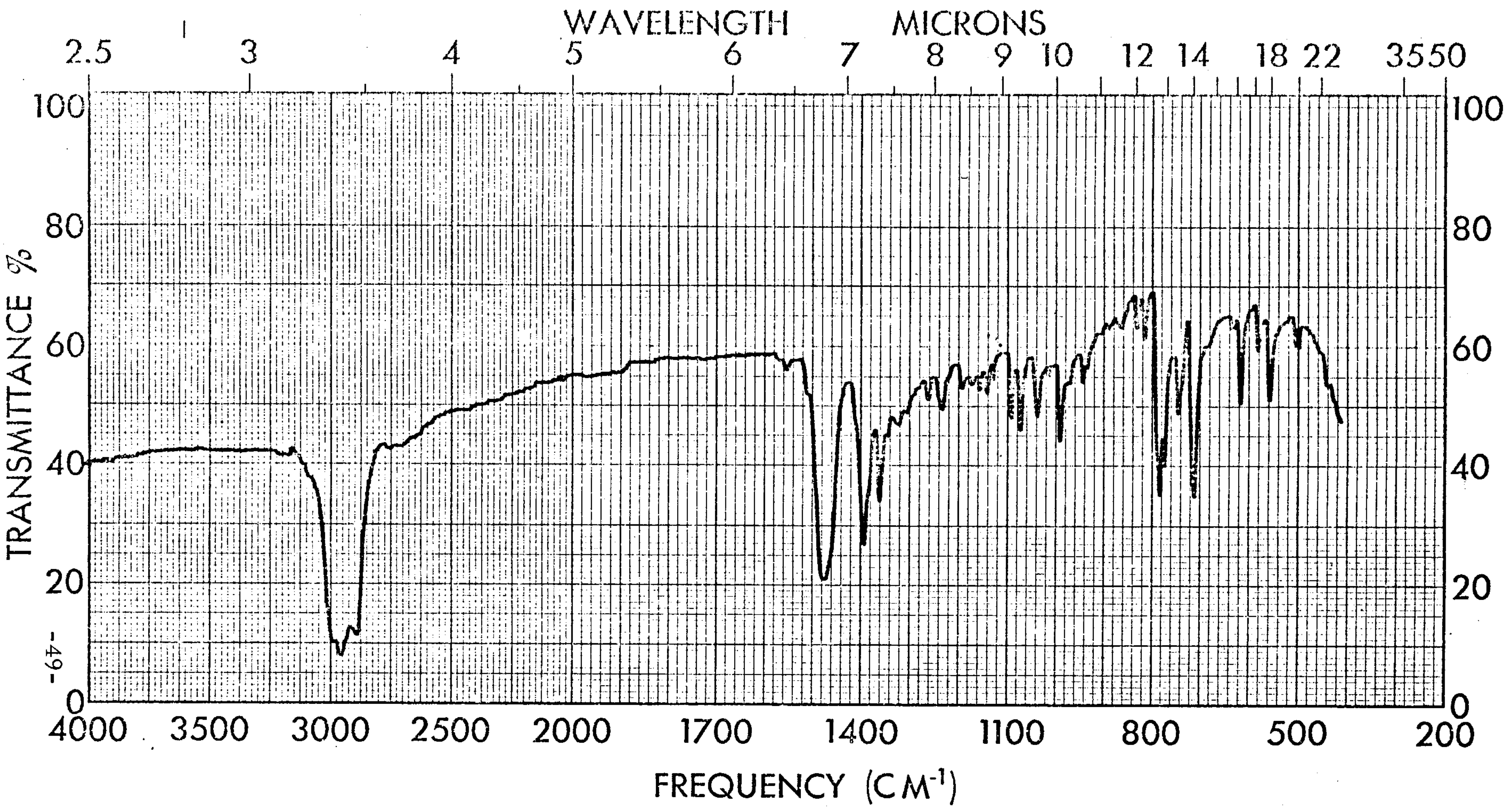
Figure 26. Infrared Spectrum of an Equimolar Mixture of 2,3-Diphenylquinoxaline and p-Bis(chloromethyl)benzene after Being Heated at 85°C for 30 minutes.

THICKNESS
OPERATOR kjf

SPECTRUM NO.
SAMPLE

PART NO. 221-1617

THE PERKIN-ELMER CORPORATION NORWALK, CONN.



SPECTRUM NO. 7868	ORIGIN	LEGEND	REMARKS
SAMPLE 4111/100-2		1.	
	PURITY	2.	
	THICKNESS	OPERATOR LWSP	

Figure 27. Infrared Spectrum of an Equimolar Mixture of 2,3-Diphenylquinoxaline and p-Bis(chloromethyl)benzene after Being Heated at 150°C for 90 Minutes.

SPECTRUM NO.
SAMPLE

PART NO. 221-1617

THE PERKIN-ELMER CORPORATION NORWALK, CONN.

therefore, to conclude that quaternization may have occurred.

1.13.3 Transition Temperatures of Cross-Linked Polyquinoxalines

Samples of films of Polymer I and of Polymer I containing 5% p-bis(chloromethyl)benzene were heated at 160°C for 6 hours. The second-order phase transition temperatures of these samples were then determined from stress-relaxation measurements by plotting the shift factor, log (1/K) as a function of the reciprocal of the absolute temperature and noting the temperature at which the slope of the shift function, $d[\log(1/K)/d(1/T)]$ changes (see Section 1.10). Figure 17 is the master curve for Polymer I from which values for log (1/K) were obtained and plotted as a function of the reciprocal of the absolute temperature in Figure 18. The break in the curve in Figure 18, which occurs at 263°C, is the transition temperature. Figures 28 and 29 are respectively the master curve for Polymer I cross-linked with 5% p-bis(chloromethyl)benzene and the plot of log (1/K) vs. 1/T for this material. From the latter curve, the transition temperature for "cross-linked" Polymer I was determined to be 257°C. It is evident, therefore, that no change in the transition temperature occurred. It was observed that the film specimens of Polymer I containing 5% p-bis(chloromethyl)benzene were clouded, which is indicative of incompatibility of the cross-linking agent. The additional breaks (at 112 and 168°C) in the curve observable in Figure 29 may be due to volatilization of the cross-linking agent.

411-95-3

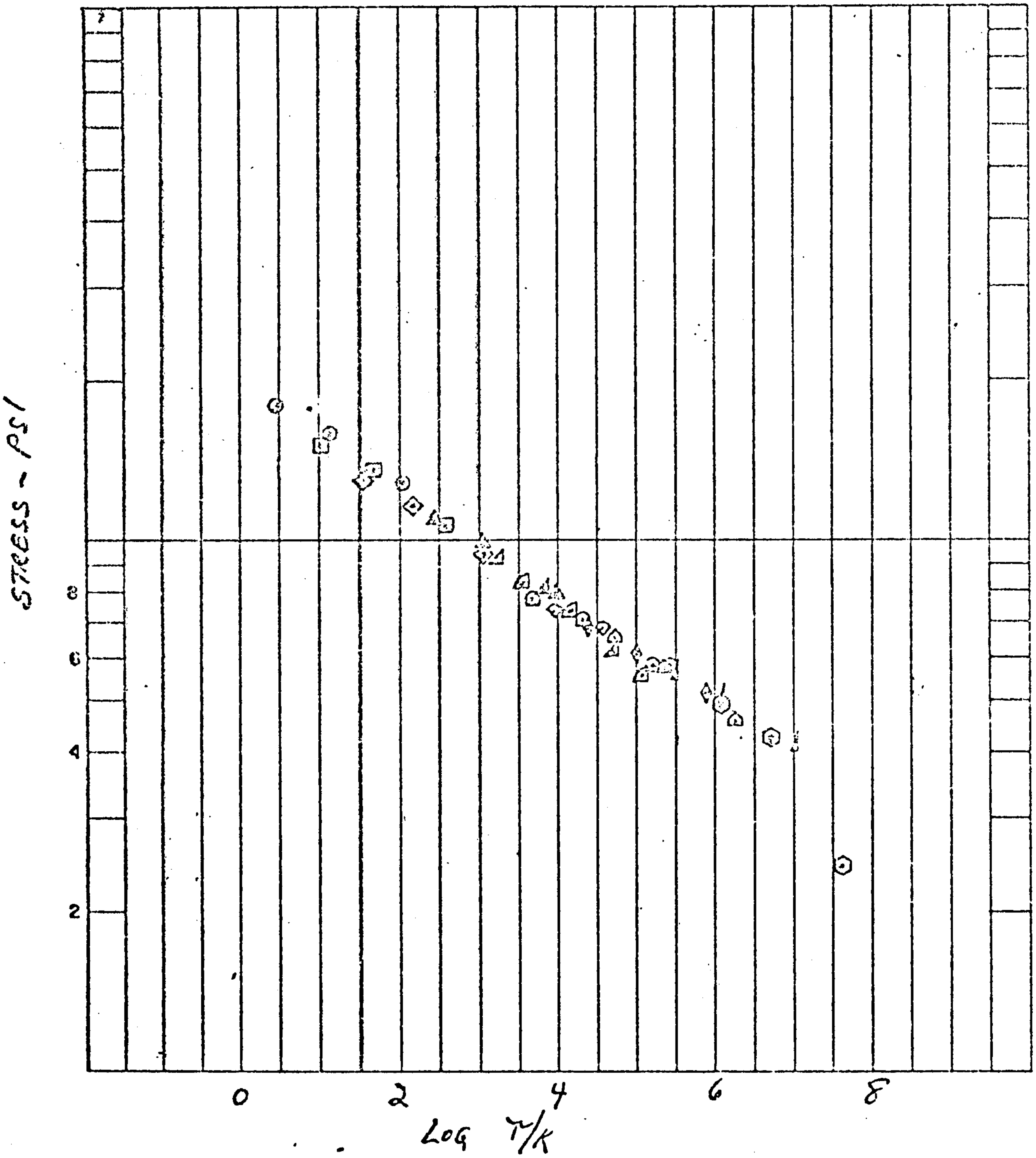


Figure 28. Master Modulus Curve for Polymer I "Crosslinked" with p-Bis(chloromethyl)benzene.

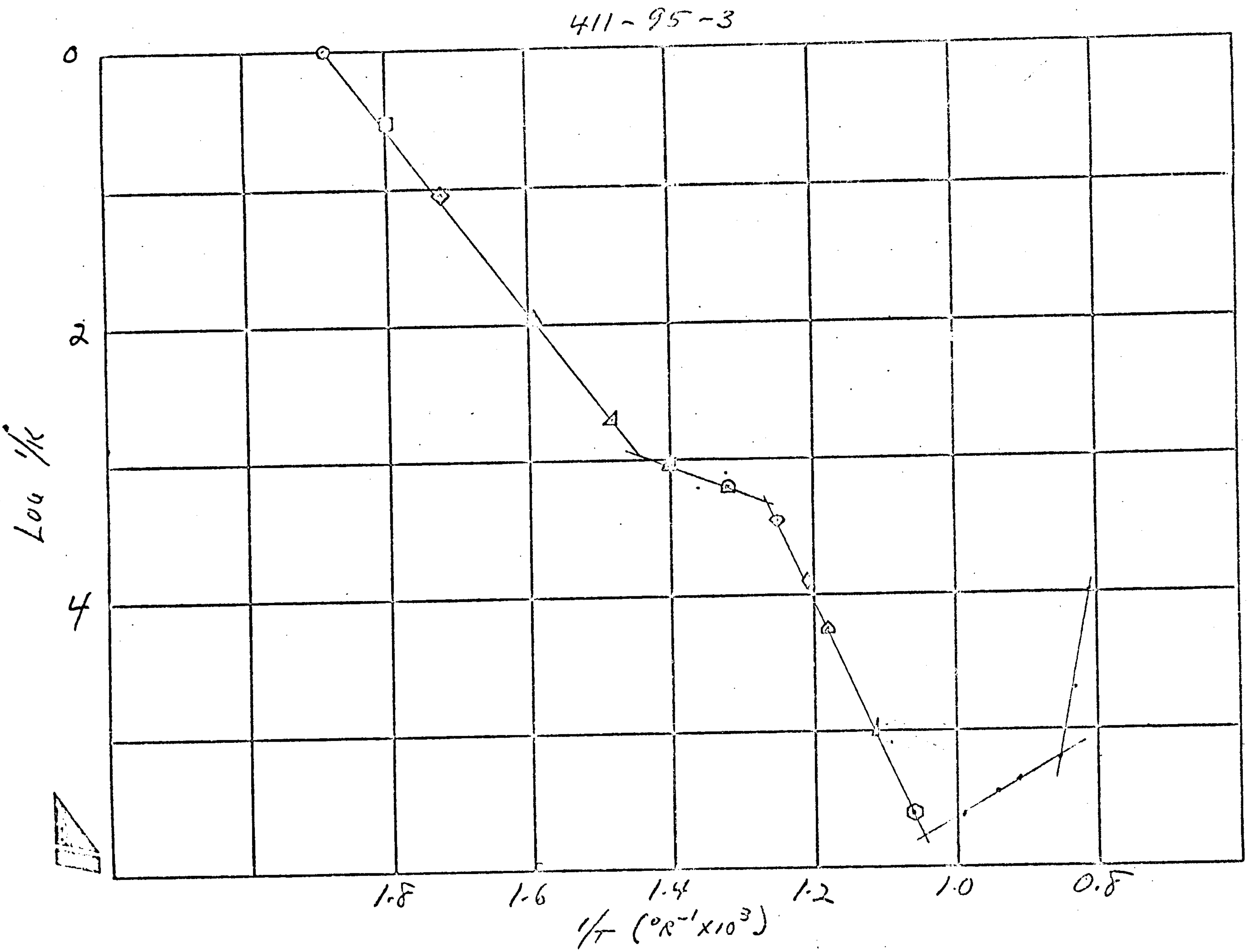


Figure 39. Determination of Second-Order Transition Temperature from Log 1/K vs. 1/T Plot for "Crosslinked" Polymer I.

TASK II: GRAPHITE/POLYQUINOXALINE FABRICATION AND EVALUATION

Subtask A: Preliminary Composite Fabrication and Evaluation

Preliminary experiments were performed to establish conditions suitable for preparation of undirectional prepregs and for fabrication of undirectional composites of graphite tow and Polymers I and III, respectively. In addition, test data were obtained on the interlaminar shear strength of samples of these composites to demonstrate suitability of these materials for more extensive evaluation.

2.1 Development of the Composite Fabrication Process

Techniques were sought for impregnation of Hercules HMS graphite tow (10,000 filaments per tow) with PPQ polymer solution, for removal of solvent from the prepreg and for molding sheets for prepreg into test panels. Preformed m-cresol solutions containing approximately 16.5% of Polymers I and III, respectively, were used for impregnation.

2.1.1 Development of the Impregnation Procedure

The impregnation process for the preparation of the PPQ prepreg went through several iterations (with variations) before the desired combination of resin content (35-40%) and volatiles level (3-7%) was obtained. The first attempt consisted of wrapping the dry fiber onto a dry cylindrical mandrel (a Kapton film was used as a release sheet). Approximately six wraps per inch were used which gave some space between succesive tows in order to permit complete impregnation of the tows to be made readily. However, 60 minutes of "staging" under radiant heaters on the rotating mandrel resulted in only 10% resin pickup. Moreover, inspection showed that the cylinder side of the prepreg was unevenly impregnated and exhibited dryness. A second attempt was made with the radiant heaters closer to the mandrel (providing higher varnish temperature during impregnation and thus lower varnish viscosity), but the impregnation was only marginally improved. The mandrel side of the prepreg was less dry; however, the resin content was only 11% and the volatiles were very low at approximately 1.5%. Although a reimpregnation of these prepregs with additional varnish raised the resin content to the desired level (39%), the prepreg lost alignment during the oven staging used to reduce the volatiles content.

In the next process variation essayed, the Kapton film (covering the mandrel) was precoated with varnish which was heated by two 24" x 0.5" 110 watt Chromalox Radiant Heaters (one heater being set at a distance of one inch in front and the other at 0.75 inches behind the rotating mandrel) as the graphite tow was wound (6.15 tows/in.) into the heated varnish.

Heating was maintained at 40% of wattage capacity by the use of a transformer until sufficient solvent had evaporated for the varnish coating to recede into the tow. A second coating of varnish was then applied and worked into the wrapped fibers with a Teflon roller. The prepreg was staged for 5-10 minutes, and a third coating of varnish was applied which increased the total resin content to approximately 40%. The prepreg was staged on the rotating mandrel for 10 minutes at the same heater settings used during the coating operation. The transformer setting was increased to impress 90% of rated wattage, the rotating mandrel was enclosed with aluminum foil, and staging was continued for 95 minutes. The resulting prepreg had 41% resin content and 3.7% volatiles. Because the technique of precoating the mandrel with the resin varnish provided a prepreg which had the desired resin content and volatiles, the method was used throughout for prepreg preparation. Tests of five prepregs so prepared showed a range of 40-43% resin and 3.4 - 5.5% volatiles.

2.1.2 Molding Composite Panels

The conditions selected for molding sheets of the prepregs into composite panels were based on previous experience at Avco[55] with other PPQ resins and on a knowledge of the transition temperatures of the two polymers used. The following describes the procedure used for molding. A prepreg sheet was clicker-die cut into 103 cm^2 (4" x 4") or 413 cm^2 (8" x 8") squares as required. Ten squares were then placed into a steel closed-mold with two peel ply layers between the prepreg stack and the mold plugs. The mold was covered with a Kapton polyimide film vacuum bag, and bag and mold were placed into a press preheated to 204.4°C (400°F). Full vacuum was drawn on the vacuum bag, and the press was loaded to 3.45×10^6 newtons/m^2 (500 psi). The temperature was raised to 287.8°C (550°F), and the pressure was then increased to 6.89×10^6 newtons/m^2 (1000 psi). Finally, the temperature was advanced to 398°C (750°F, which is above the T_g for the polymers) and held at that temperature and pressure for one hour. The finished molding was cooled under pressure to $<$ 204.4°C ($<$ 400°F) before being removed from the mold. Table VII lists the molding conditions for the panels fabricated.

Specimens for flexure and shear tests were obtained from the panels by rough sawing and grinding to size. The specific gravity of each panel was determined from the weight of representative specimens in air and water. The resin contents (weight percent) of the panels were calculated from chemical analysis for nitrogen or, by difference, from the measured weight of the panel and the weight of the graphite fiber. From the measured density of the panel, the void content and the volume percent of the fiber and resin were calculated (Table VIII).

TABLE VII

MOLDING CONDITIONS FOR POLYQUINOXALINE/GRAPHITE COMPOSITES

Panel Number[a]	Polymer Type	Pressure Conditions					
		Initial[d]		Intermediate[e]		Final[f]	
		newtons/m^2 x 10^{-6}	psi	newtons/m^2 x 10^{-6}	psi	newtons/m^2 x 10^{-6}	psi
1144-25A[b]	I	3.45	500	6.89	1,000	6.89	1,000
1144-25B[b]	I	1.38	200	6.89	1,000	6.89	1,000
1144-25C[b]	I	1.38	200	6.89	1,000	6.89	1,000
1144-27[b]	I	6.89	1,000	6.89	1,000	13.78	2,000
1144-23[c]	III	1.38	200	6.89	1,000	6.89	1,000

[a] All prepreg sheets 103 cm^2 (4" x 4") except 1144-27 413 cm^2 (8" x 8").

[b] Average resin content of prepreg sheets 41.4%, average volatiles 4.68%.

[c] Resin content 42.75%, 3.75% volatiles.

[d] At 204.4°C (400°F).

[e] At 287.8°C (550°F).

[f] At 398.9°C (750°F); specimen held at pressure and temperature for 60 minutes.

TABLE VIII

PHYSICAL PROPERTIES OF POLYQUINOXALINE/HMS GRAPHITE COMPOSITE PANELS

Panel Number	Polymer	Density	Resin Content		Fiber Content	Voids
		g/cc	Weight %	Volume %	Volume %	Volume %
1144-25A	I	1.37	35.7[a]	42.2	48.9	8.8
1144-25B	I	1.38	37.6[b]	44.8	47.8	7.3
			37.1[a]	44.2	48.2	7.6
1144-25C	I	1.36	38.8[a]	45.6	46.2	8.2
1144-27	I	1.40	37.4[a]	45.1	48.8	6.1
1144-23	III	1.36	40.5[b]	49.3	44.2	6.5

[a] From weight of panels and weight of fiber used.

[b] From nitrogen analysis.

2.2 Preliminary Evaluation of Composites

Table IX lists preliminary test data of the interlaminar shear strength (at room temperature and after 30 minute exposure at 316°C) of composites of Hercules HMS graphite and respectively, Polymers I and III.

Subtask B: Final Composite Evaluation

The composite of Polymer I and Hercules HMS graphite tow was subjected to a more extensive evaluation comprising studies of its mechanical properties (flexural strength and modulus and interlaminar shear strength) and its isothermal aging characteristics (weight loss) at 260°C (500°F) and 315.6°C (600°F).

3.1 Mechanical Properties

3.1.1 Flexural Properties

Table X lists the flexural strength and modulus of the composite at 25°, and 315.6°C as a function of time. Each test was made after a 30 minute exposure at temperature. All specimens failed in a cleavage mode. The data (average values) are plotted in Figures 30-32. Figure 30 shows the change in flexural strength and modulus as a function of temperature. Figure 31 shows the effect of time of exposure on the flexural strength and Figure 32 the effect on the modulus of samples of the composite as aged respectively at 260° and 315.6°C. Specimens held at 315.6°C failed (delaminated) after 300 hours.

The increase in modulus at 260°C observed as a result of aging from 600 to 1000 hours appeared anomalous. However, test of a specimen held at 260°C for 1290 hours gave a value of 1.19×10^{10} n/m^2 (17.2×10^6 psi) and thus gave a measure of confidence to the observed increase in modulus with aging. Because of the statistically small samples size, the shape of the modulus-time curve is uncertain, and, therefore, no curve was drawn. It appears safe to say, however, that if the modulus did not actually increase with time of exposure, it, at least, remained relatively constant.

3.1.2 Interlaminar Shear Strength

Table XI lists the interlaminar shear strength of the composite at 25°, 260°, and 315.6° as a function of time. These data are represented graphically in Figures 33 and 34.

3.1.3 Assessment of Mechanical Property Data

The mechanical properties of the composite may be assessed from several considerations. Figure 35 shows the retention of interlaminar

TABLE IX

PRELIMINARY COMPOSITE EVALUATION

	Interlaminar Shear Strength[a]	
	Composite I	Composite III
Temperature °C (°F)	Newtons/m^2 x 10^{-6} (psi)	Newtons/m^2 x 10^{-6} (psi)
25 (77)	32.3 (4687)	39.0 (5663)
316[b] (600)	25.7 (3733)	26.7 (3870)

[a] Average of three values.

[b] Tested after 20 minutes exposure at temperature.

TABLE X

EFFECT OF AGING AT ELEVATED TEMPERATURES ON FLEXURAL PROPERTIES OF POLYMER I/GRAPHITE COMPOSITE

Test Temperature		Time at Temperature, Hours									
°C	°F	0.5		100		300		600		1000	
		Ultimate Stress									
		A[a]	B[b]	A	B	A	B	A	B	A	B
25	77	5.07 7.10 7.86	73.6 103.0 114.0								
		6.68 av.	96.9 av.								
260	500	4.73 4.84 4.62	68.6 70.2 67.0	6.15 4.89 5.36	89.2 70.9 77.7	4.29 4.47 5.35	62.2 64.8 77.6	3.70 4.06 5.57	53.6 58.9 80.8	4.05 3.55 -	58.7 51.5 -
		4.73	68.6	5.47	79.3	4.70	68.2	4.44	64.4	3.80	55.1
315.6	600	4.43 4.43 4.28	64.3 64.3 62.1	3.70 3.87 -	53.6 56.1 -	1.12 1.96 2.14	16.3 28.4 31.0	Specimens Failed			
		4.38	63.6	3.79	55.1	1.74	25.2				
		Modulus									
		C[c]	D[d]	C	D	C	D	C	D	C	D
25	77	1.11 1.20 1.16	16.1 17.4 16.8								
		1.16	16.8								
260	500	1.09 1.13 1.19	15.8 16.4 17.2	1.26 1.24 1.31	18.3 18.0 19.0	1.25 1.21 1.25	18.2 17.5 18.2	1.18 1.09 1.02	17.1 15.8 14.8	1.53 1.41 -	22.2 20.4 -
		1.14	16.5	1.27	18.4	1.26	18.0	1.10	15.8	1.47	21.3
315.6	600	1.03 1.08 1.05	15.0 15.7 15.3	1.28 1.23 -	18.6 17.8 -	5.52 8.21 9.31	8.0 11.9 13.5	Specimens Failed			
		1.05	15.3	1.26	18.2	7.68	11.1				

[a] newtons/$m^2 \times 10^{-7}$

[b] psi $\times 10^{-3}$

[c] newtons/$m^2 \times 10^{-10}$

[d] psi $\times 10^{-6}$

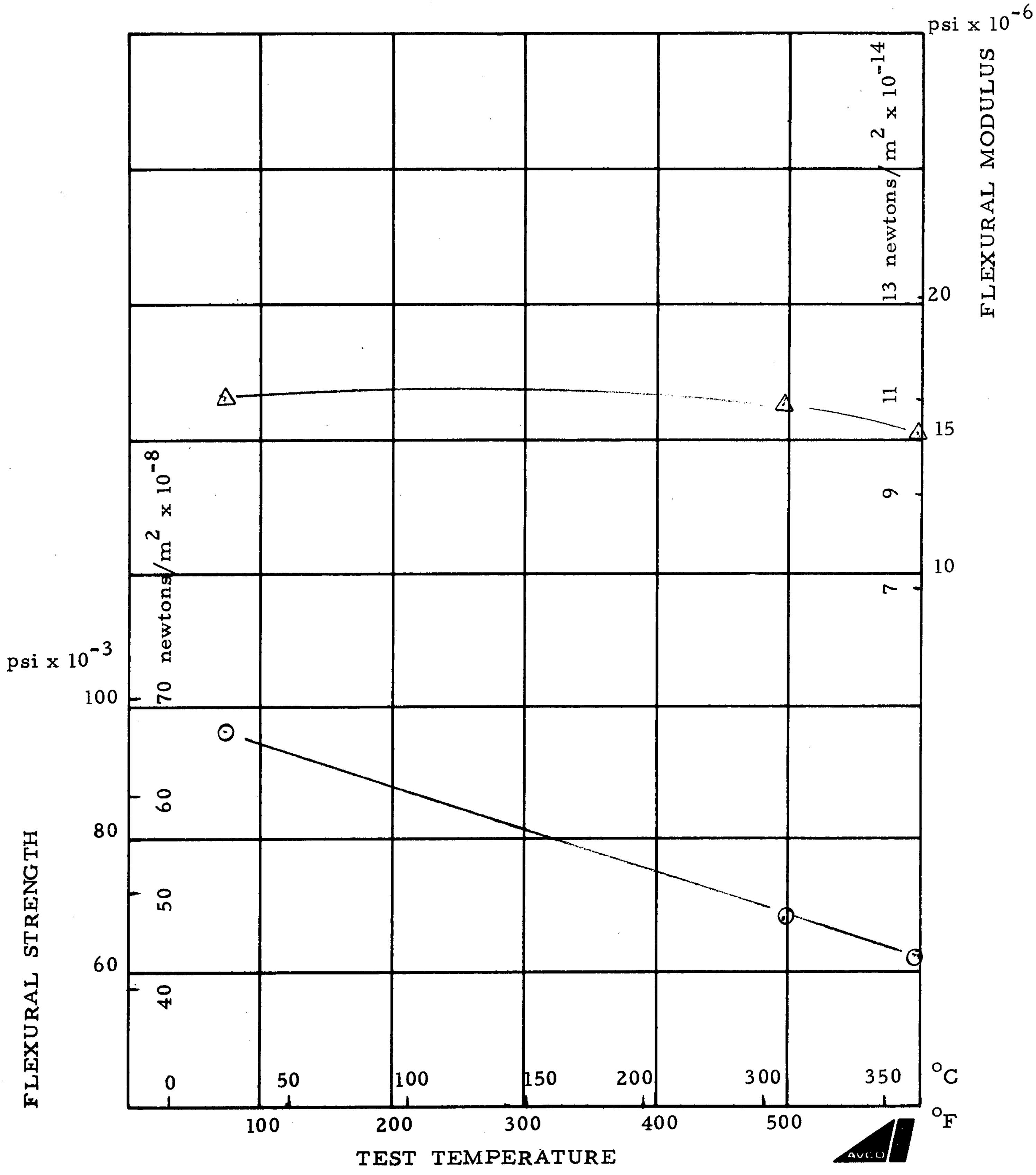


Figure 30. Effect of Temperature on Flexural Strength and Modulus of Polymer I/ Graphite Composite after 30 Minutes Exposure at Temperature.

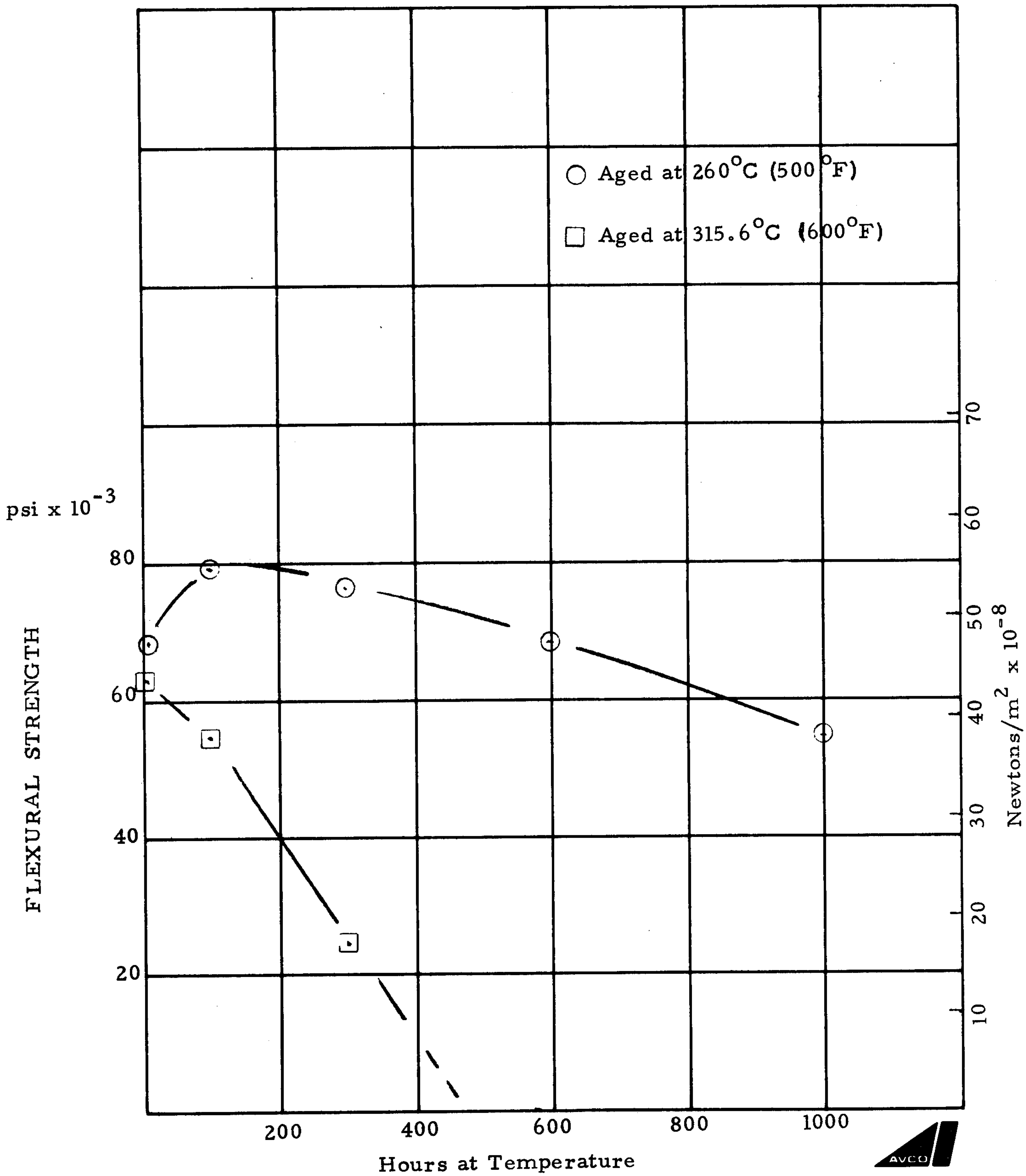


Figure 31. Effect of Aging at Elevated Temperatures on the Flexural Strength of Polymer I/Graphite Composite.

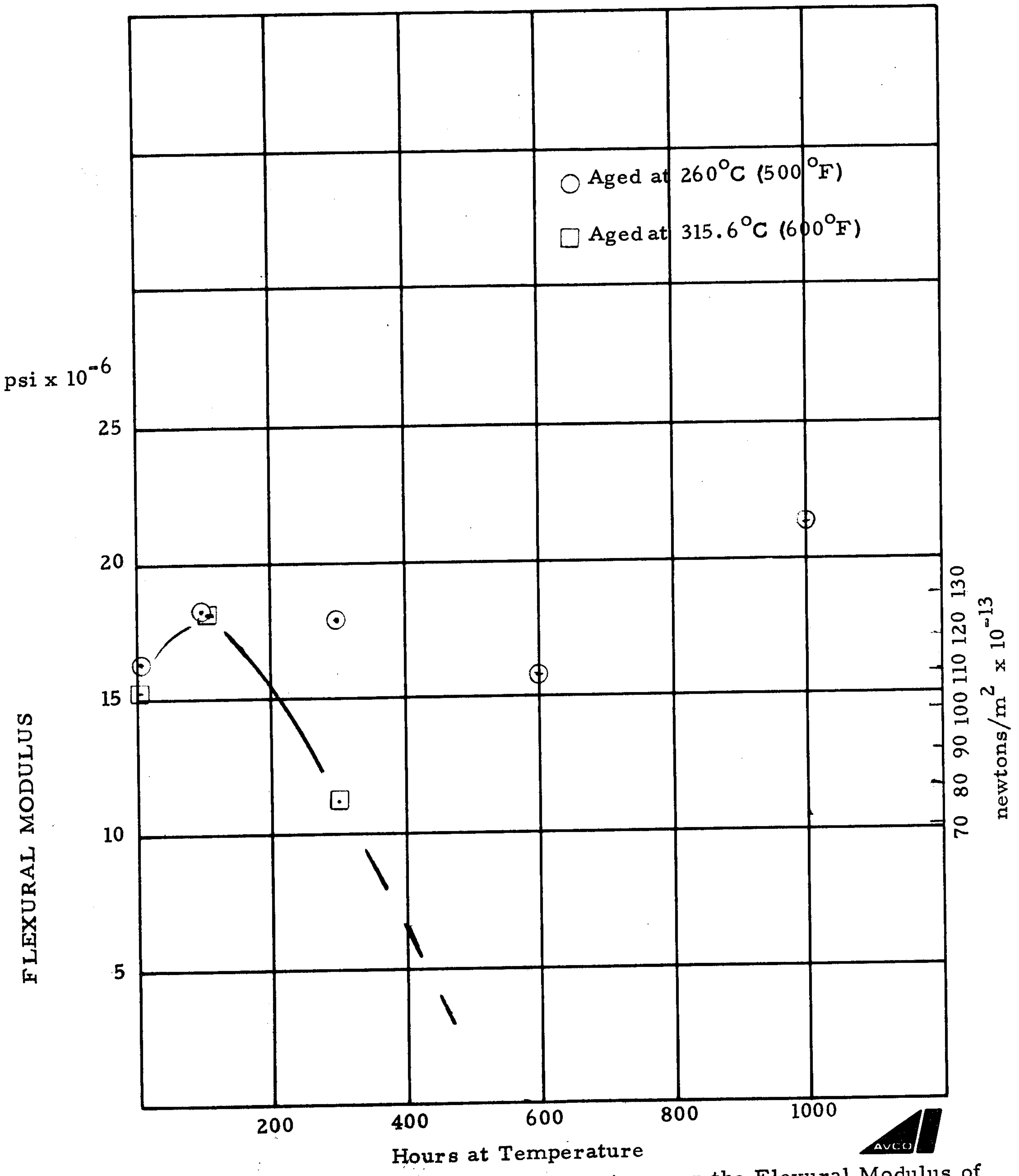


Figure 32. Effect of Aging at Elevated Temperatures on the Flexural Modulus of Polymer I/Graphite Composite.

TABLE XI

EFFECT OF AGING AT ELEVATED TEMPERATURES ON INTERLAMINAR SHEAR STRENGTH OF POLYMER I/GRAPHITE COMPOSITE

Test Temperature		Time at Temperature, Hours									
°C	°F	0.5		100		300		600		1000	
		A[a]	B[b]	A	B	A	B	A	B	A	B
25	77	3.37 2.98 3.34	4.89 4.32 4.85								
		3.23 av.	4.69 av.								
260	500	3.04 2.21 2.83	4.41 3.21 4.11	2.81 3.10 2.94	4.08 4.49 4.26	3.01 2.92 2.86	4.37 4.23 4.15	2.59 2.18 1.90	3.75 3.16 2.75	2.01 1.91 1.98	2.92 2.77 2.87
		2.69	3.91	2.95	4.28	2.93	4.25	2.22	3.22	1.97	2.85
315.6	600	2.59 2.56 2.58	3.75 3.71 3.74	2.25 2.17 2.13	3.26 3.15 3.09	1.23 1.57 1.71	1.78 2.28 2.48	Specimens Failed			
		2.58	3.73	2.18	3.16	1.50	2.18				

[a] newtons/m^2 x 10^{-6}

[b] psi x 10^{-3}

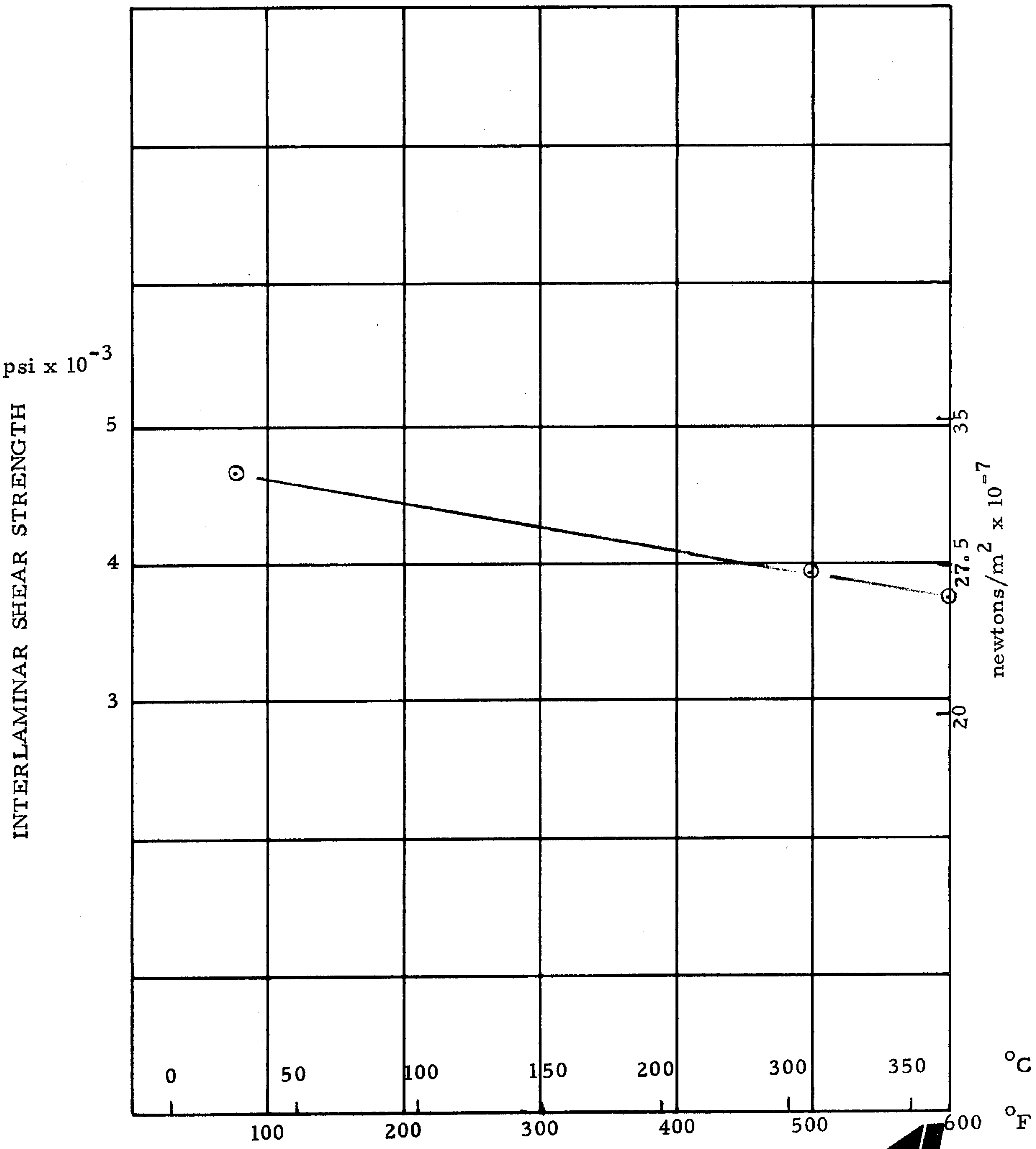


Figure 33. Effect of Temperature on Interlaminar Shear Strength of Polymer I/ Graphite Composite after 30 Minute Exposure at Temperature.

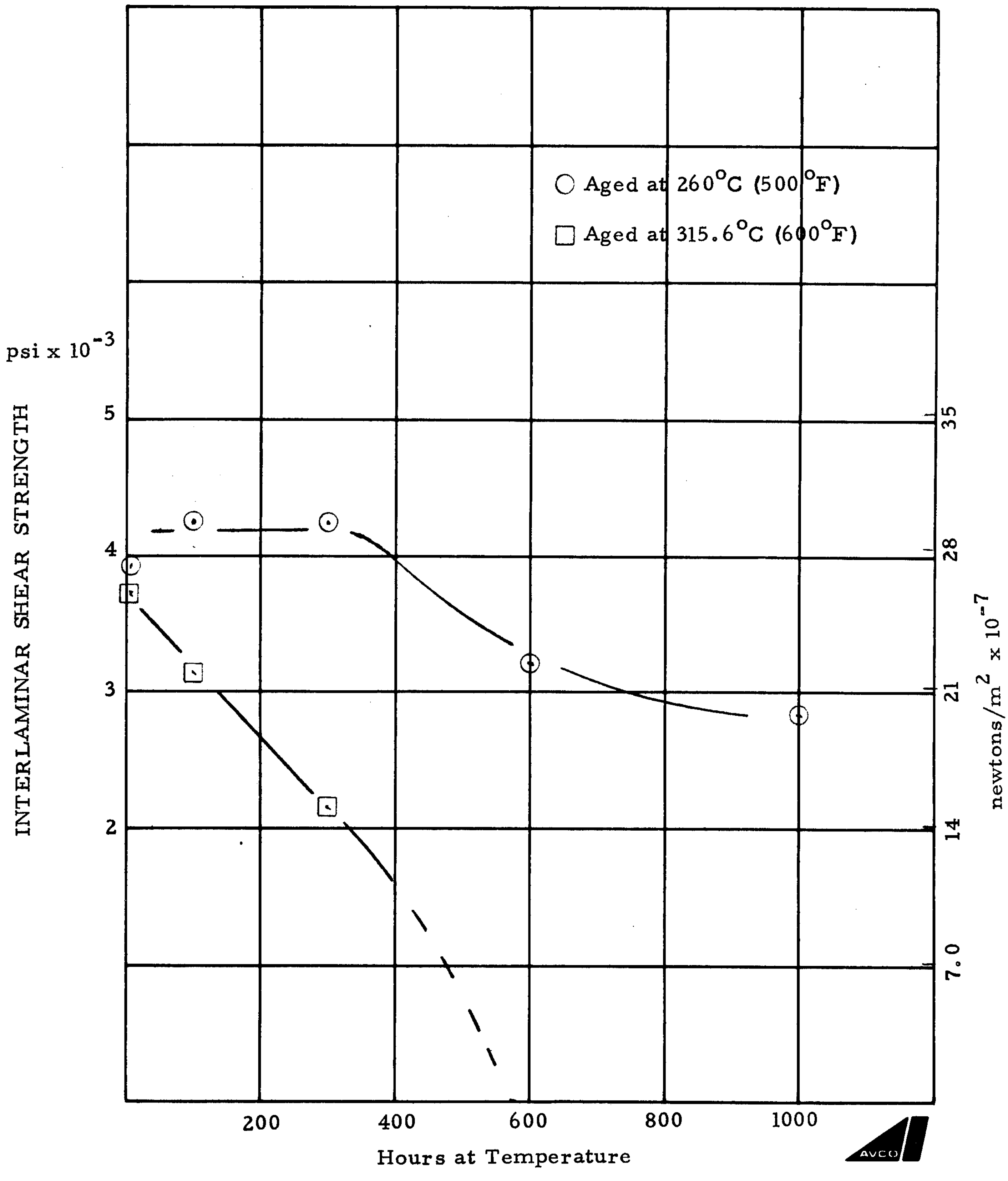


Figure 34. Effect of Aging at Elevated Temperatures on the Interlaminar Shear Strength of Polymer I/Graphite Composite.

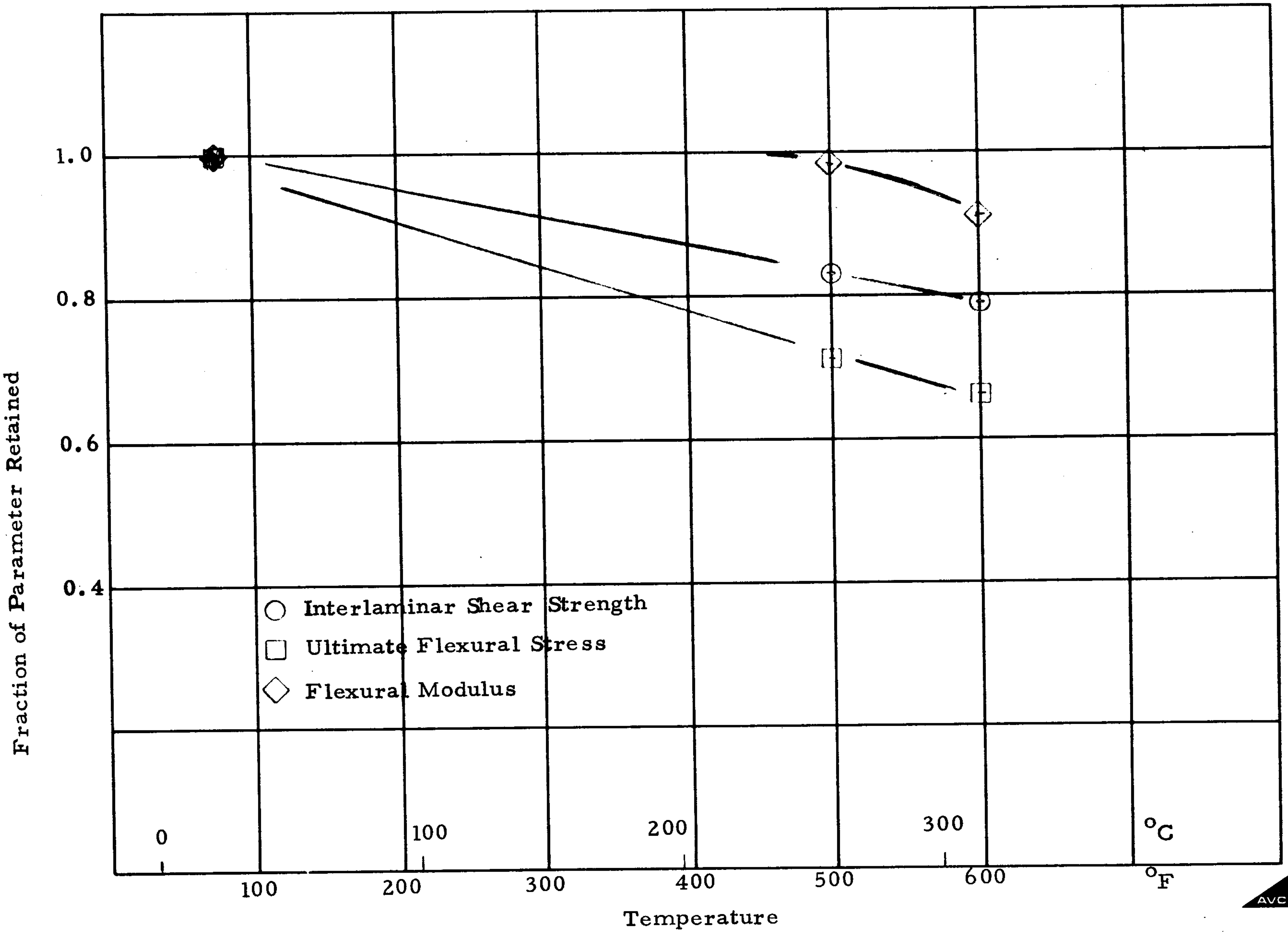


Figure 35. Effect of Temperature on the Fraction of the Value of Mechanical Properties Parameters Retained.

shear strength and flexural strength and modulus as a function of temperature expressed as the fraction of the corresponding room temperature mechanical property values. Aging a specimen for 1000 hours at 260°C reduces the value of the ultimate flexural stress to 80% of the initial value at that temperature. The modulus, as already noted, remains unchanged or increases. The interlaminar shear strength is also relatively well retained (72.5% of initial) at 260°C. Aging at 315.6°C, however, produces a marked decrease in the properties. After 300 hours exposure, the flexural strength declines to 39% and the interlaminar shear strength to 59% of the initial value; the flexural modulus decreases less-to 72% of the initial value.

These results may also be compared (Table XII) with the results obtained by Hoggatt, Hill and Shdo[48] who prepared and tested composites of poly {2,2'-(1,4-phenylene)-6,6'-bis(3-phenyl)quinoxalinyl} containing 70 volume percent of HMS graphite fiber. It is noteworthy that the flexural strength and interlaminar shear strength in short-time exposure are greater for composite A than for composite B in the temperature interval tested. No long-term exposure data was given in the cited work.

3.2 Isothermal Weight Loss Studies

Table XIII shows the cumulative weight loss as a function of time for samples of the composite which were aged at 260°C and 315.6°C, respectively. The weight loss at 260°C is slight even up to 1,152 hours, but at 315.6°C, the loss is extensive and becomes pronounced after 288 hours. This behavior probably accounts for the delamination of specimens exposed at 315.6°C for more than 300 hours (cf. Section 3.1.1).

TABLE XII

COMPARISON OF MECHANICAL PROPERTIES OF POLYQUINOXALINE/HMS GRAPHITE COMPOSITES

	Composite A[a]		Composite B[b]	
Polymer Type	Naphthalenyl	Naphthalenyl	Phenyl	Phenyl
Volume % Graphite	48.8	60[c]	60[c]	70
Flexural Strength, n/m^2 x 10^{-7}	6.68 (25°C)	8.21 (25°C)	4.29 (21°C)	5.00 (21°C)
			3.75 (204°C)	4.37 (204°C)
	4.73 (260°C)	5.82 (260°C)		
	4.38 (316°C)	5.39 (316°C)	2.96 (316°C)	3.45 (316°C)
% Retention at 316° from 25°C	65	65	69	69
Flexural Modulus, n/m^2 x 10^{-10}	1.16 (25°C)	1.43 (25°C)	0.99 (21°C)	1.16 (21°C)
			0.87 (204°C)	1.01 (204°C)
	1.14 (260°C)	1.40 (260°C)		
	1.05 (316°C)	1.29 (316°C)	0.85 (316°C)	1.00 (316°C)
% Retention at 316° from 25°C	91	91	86	86
Interlaminar Shear Strength, n/m^2 x 10^{-7}	3.23 (25°C)			1.94 (21°C)
				2.05 (204°C)
	2.69 (260°C)			
	2.58 (316°C)			1.65 (316°C)
% Retention at 316° from 25°C	80			85

---

[a] Composite of Poly {2, 2'-(1, 4-phenylene)-6, 6'-bis[3-(1-naphthalenyl)]-quinoxalinyl}.

[b] Composite of Poly {2, 2'-(1, 4-phenylene)-6, 6'-bis-(3-phenyl)quinoxalinyl.}

[c] Normalized (calculated values).

TABLE XIII

ISOTHERMAL AGING STUDIES OF POLYMER I/GRAPHITE HMS COMPOSITE

Time, hours	Cumulative Weight Loss, %							
	260°C (500°F)				315.6°C (600°F)			
	1	2	3	Average	1	2	3	Average
0	0	0	0	0	0	0	0	0
24	0.17	0.09	0.03	0.10	0.26	0.28	-	0.27
48	0.19	0.09	0.12	0.13	0.32	0.38	-	0.35
120	0.19	0.28	0.33	0.27	0.60	0.83	-	0.71
216	0.19	0.28	0.12	0.20	1.82	2.62	-	2.22
288	0.21	0.34	0.42	0.32	4.36	6.20	5.33	5.30
408	0.27	0.40	0.51	0.39	9.42	14.37	-	11.90
456	0.28	0.47	0.45	0.40	13.41	19.33	-	16.37
624	0.28	0.40	0.45	0.38	23.52	29.36	-	26.44
816	0.31	0.40	0.45	0.39	30.73	34.04	-	32.39
960	0.34	0.47	0.45	0.42	36.15	36.82	-	36.48
1,152	0.45	0.65	0.66	0.59	39.36	38.64	28.58	35.5

IV. CONCLUSIONS AND RECOMMENDATIONS

1. The method previously reported for synthesizing 1,4-bis[(1'-naphthalenyl)acetyl]benzene was extended to 1,3-bis[(1'-naphthalenyl)acetyl]benzene. The procedure, therefore, probably has value as a general method for synthesizing bis(arylacetyl)benzene compounds which are intermediates for monomers needed in the preparation of polyarylquinoxalines.

2. Poly{2,2'-(1,4-phenylene)-6,6'-bis[3-(1-naphthalenyl)]-quinoxalinyl} (Polymer I), the polyquinoxaline prepared from 1,4-bis[(1'-naphthalenyl)oxalyl]benzene and 3,3'-diaminobenzidine has excellent film-forming properties. However, the polymer poly{2,2'-(1,3-phenylene)-6,6'-bis[3-(1-naphthalenyl)]quinoxalinyl} derived from the isomeric tetracarbonyl monomer gave brittle films.

3. The glass transition temperature of Polymer I is comparable to that of the homologous poly 2,2'-(1,4-phenylene)-6,6'-bis(3-phenyl)quinoxalinyl (Polymer PPQ), a typical polyphenylquinoxaline. The use of bulky pendant groups in the polymer chain to increase the glass transition temperature, either does not apply to polyquinoxalines or the naphthalenyl group is not sufficiently bulky. It is recommended that the synthesis of monomers for polyquinoxalines derived from anthracene be investigated.

4. Polyquinoxalines prepared from poly-p-benzil had low molecular weights and were brittle. The low molecular weights may be ascribed to the low molecular weight of the poly-p-benzil which was prepared by oxidation of poly-p-benzoin synthesized from terephthalaldehyde. It is recommended that poly-p-benzil be prepared from poly(p-phenylethylene) which has been available commercially (e.g., as Parylene) or may be synthesized by several methods reported in the literature.

5. Conditions for quaternization of model quinoxalines with 1,4-bis(chloromethyl)benzene were determined, but the use of these conditions for crosslinking compositions of polyquinoxalines and 1,4-bis(chloromethyl)benzene did not increase the transition temperature.

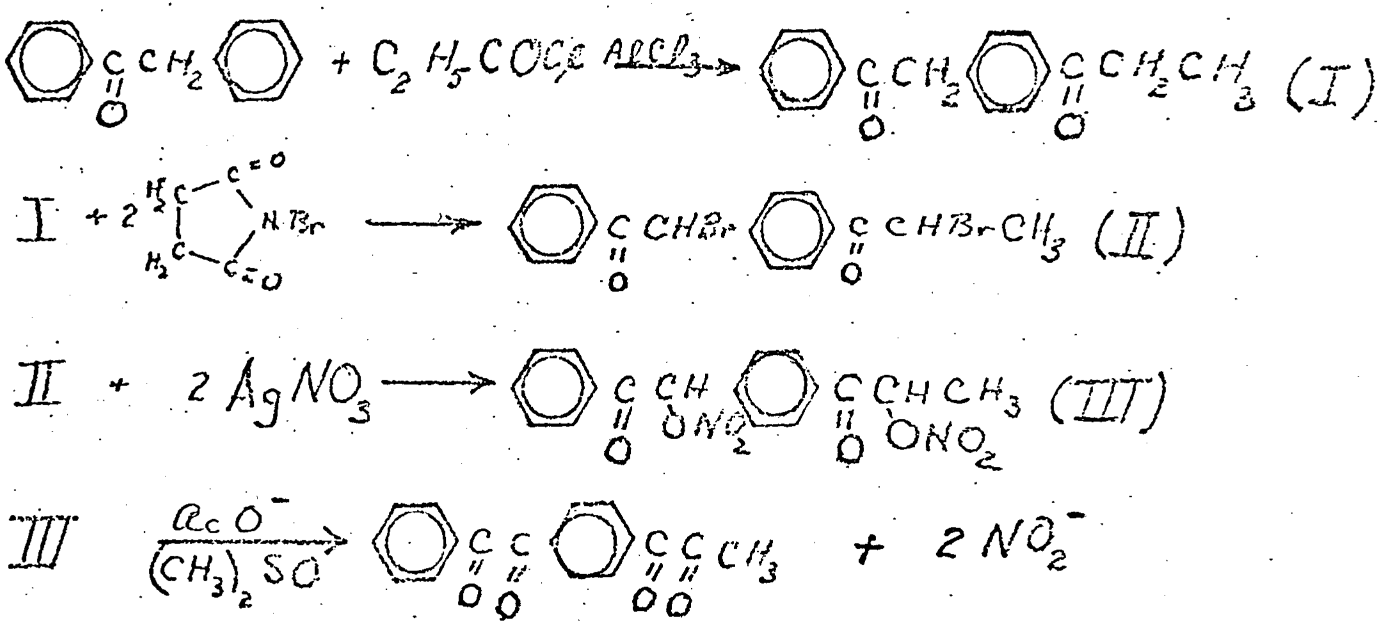
6. A composite fabricated from Polymer I and HMS graphite fiber exhibited considerably higher flexural properties than a composite

made from Polymer PPQ and HMS graphite fiber when normalized to 60% by volume. When tested at elevated temperatures after short-time exposure, the composite of Polymer I showed good retention of its room temperature mechanical properties. Retention was good after exposure in air for 1000 hours at 260°C, but at 316°C, the composite degraded markedly and failed by delamination after 300 hours of exposure.

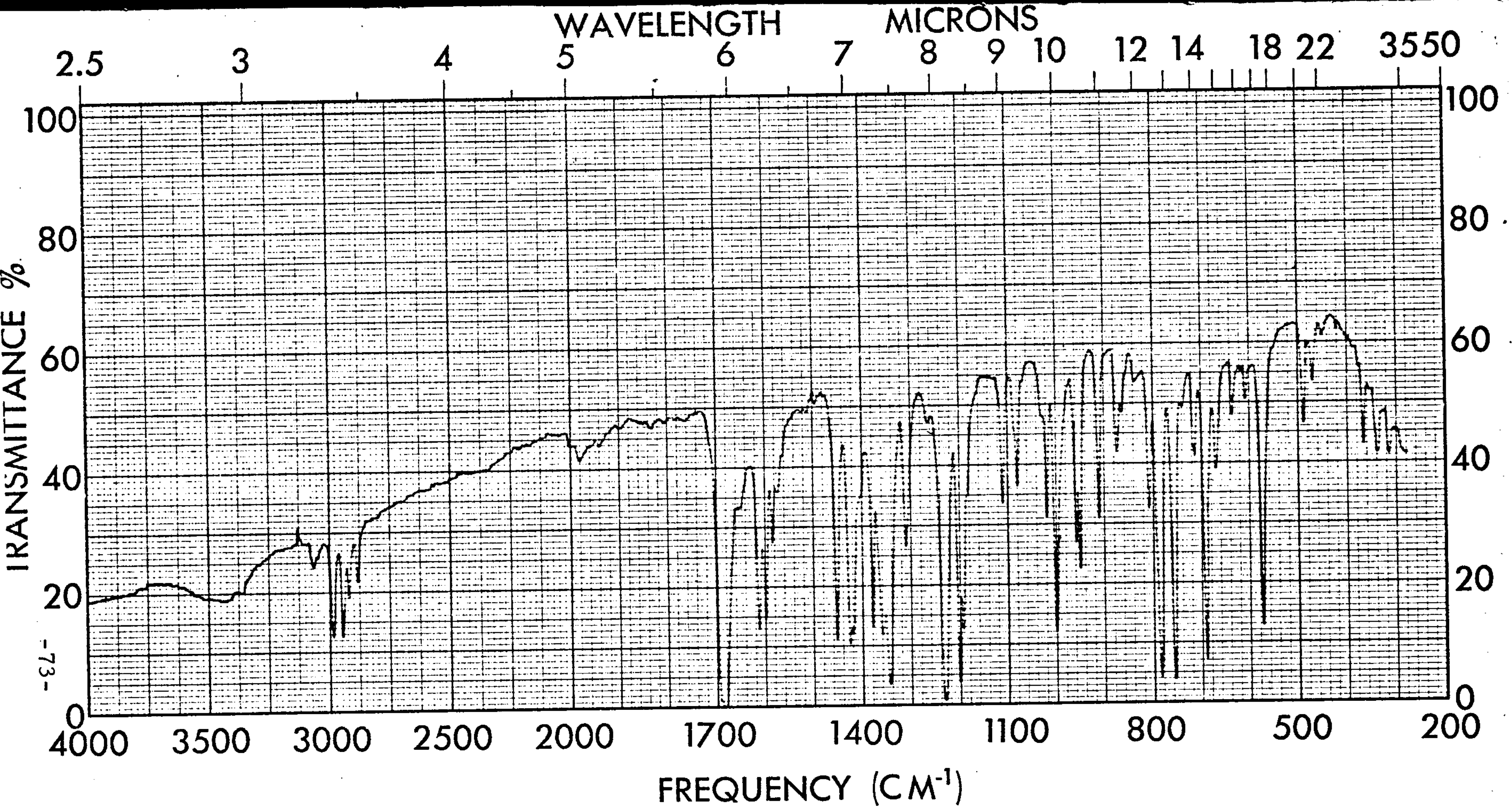
V. APPENDIX I

Attempted Synthesis of p-(Methyloxalyl)benzil from p-Phenacylpropiophenone

Kornblum and Frazier's[56] method of converting α-bromoketones to α-diketones was the basis of an attempted method for preparing p-(methyloxalyl)benzil from p-phenacylpropiophenone in accordance with the following scheme:



p-Phenacylpropiophenone was prepared by the Friedel-Crafts reaction between deoxybenzoin and propionyl chloride[42e]. Crude p-(β-bromophenacyl)- β-bromopropiophenone was prepared by the method of C. Djerassi[57]. A mixture of 10 g (0.04 mole) p-phenacylpropiophenone and 14.2 g (0.08 mole) N-bromosuccinimide in 250 cc carbon tetrachloride was refluxed for 3 hours under radiation from a heating lamp. During the course of the reaction, the solution changed color from yellow to bright orange to pale yellow. The succinimide was removed by filtering and the clear solution was evaporated to dryness yielding 18.1 g of a viscous amber liquid Evidence for bromination may be found by comparing the infrared absorption spectra for p-phenacylpropiophenone (Figure 36) with that for the amber liquid (Figure 37). The salient changes are the appearance in Figure 37 of absorption bands at 1250, 1130, 840, 820 and 640 cm^{-1} which are absent in Figure 36 and the absence of absorptions at 910 and 880 which are present in Figure 36. According to C.N.R. Rao[58a], C-Br stretching vibration appears in the region 700-500 cm^{-1}. L. J. Bellamy[46b] associates absorption due to



SPECTRUM NO. 7280

SAMPLE 206-65-2

p-Phenacylpropiophenone

ORIGIN

PURITY

PHASE

THICKNESS

LEGEND

1.

2.

OPERATOR BWB

REMARKS

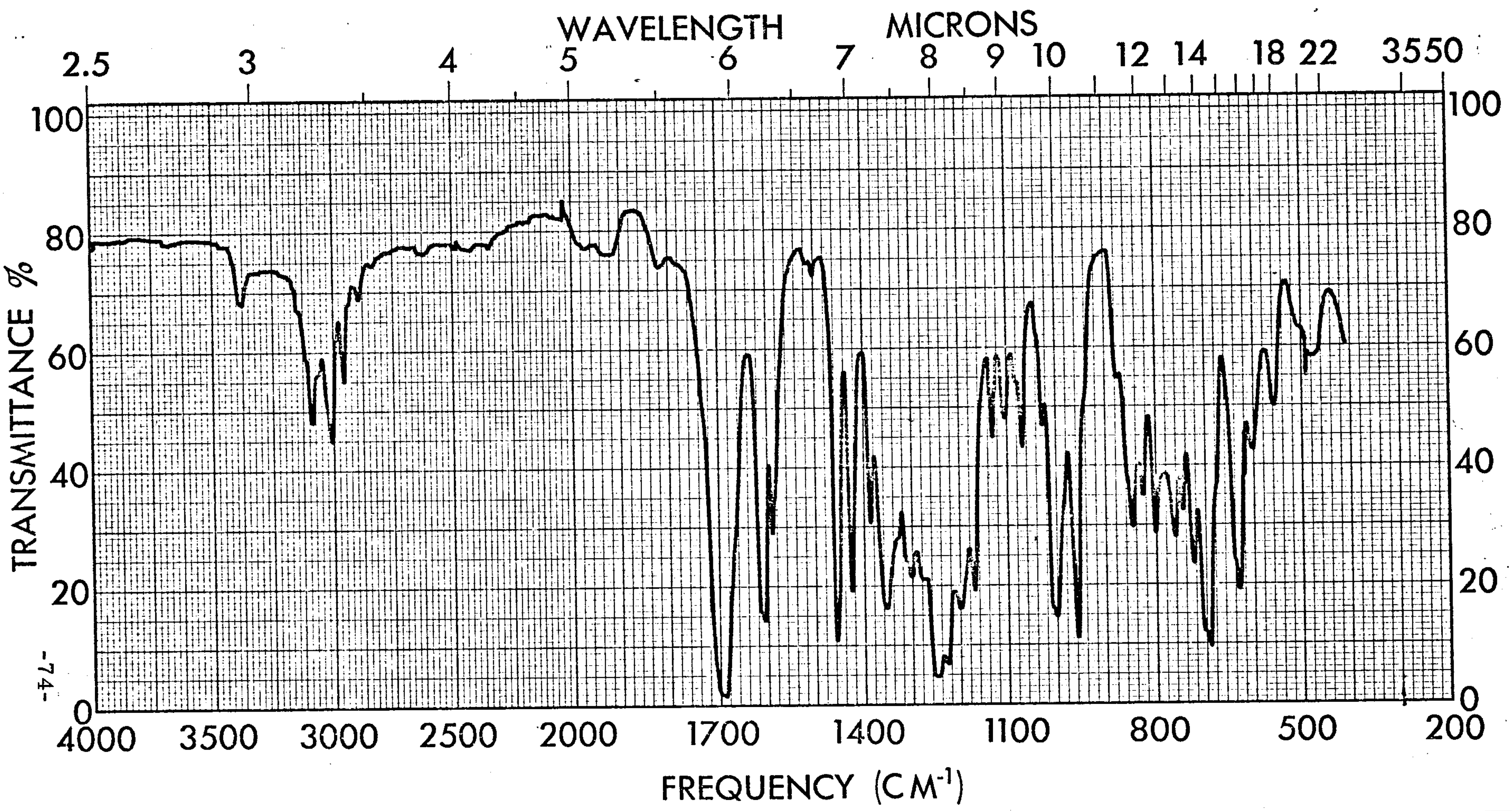
Figure 36. Infrared Spectrum of p-Phenacylpropiophenone.

SPECTRUM NO. 7280

SAMPLE

PART NO. 221-1617

THE PERKIN-ELMER CORPORATION NORWALK, CONN.



SPECTRUM NO. 7522

SAMPLE 1081-149-1

ORIGIN

PURITY

LEGEND

1.

2.

REMARKS

Figure 37. Infrared Spectrum of Bromination Product of p-Phenacylpropiophenone.

THICKNESS /

OPERATOR WJP

PART NO. 221-1617

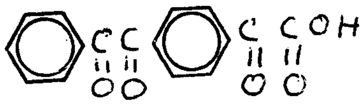
THE PERKIN-ELMER CORPORATION NORWALK, CONN.

SPECTRUM NO.
SAMPLE

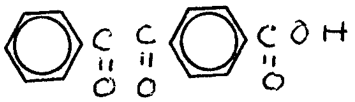
bromine in benzyl bromides with frequencies of 689-645 cm^{-1}.

A solution of 4.37 g (0.0107 mole) crude p-(β-bromophenacyl)-β-bromopropiophenone in 25 cc acetonitrile was treated at room temperature with 4.77 g (0.0281 mole, 32% molar excess) silver nitrate dissolved in 20 ml acetonitrile. The solution turned cloudy immediately and the mixture was stirred mechanically for 20 hours and was then filtered free from the silver bromide which was washed with ether. The filtrate and washings were combined and were evaporated to dryness yielding 7.0 g of a yellow fluid (94-59). Figure 38 is the infrared absorption spectrum of 94-59 and shows the presence of absorption at 1660, 1630, 1300, 1200cm^{-1}. Rao [58b] notes that "Covalent nitrates show the asymmetric and symmetric stretching vibrations of the NO_2 group in the regions 1650-1600 and 1300-1250 cm^{-1}."

A solution of 94-59 in 90 cc dimethyl sulfoxide was treated with a suspension of 0.286 g $NaO_2CCH_3 \cdot 3H_2O$ in 20 cc dimethyl sulfoxide and stirred mechanically for 30 minutes. The mixture was poured into 400 cc ice and water and saturated with sodium chloride. A yellow solid separated which was extracted with 200 cc ethyl ether. The ethereal solution was extracted with 100 cc saturated $NaHCO_3$ solution and dried over anhydrous calcium sulfate. The ether was distilled off and the residue 94-59-1A was recrystallized from toluene. The product (94-59-1A-1) was filtered off and washed on the filter with toluene. The melting point of 94-59-1A-1 was 227-231°C, and Figure 39 is its infrared spectrum. Figures 40 and 41 are proton nuclear magnetic spectra of 94-59-1A-1 in deuterated acetone. (Figure 41 shows a magnification of the phenyl region). p-Phenyl substitution and singly substituted phenyl are observed, but no methyl group is apparent. Figure 42 is the proton n.m.r. spectrum of 94-59-1A-1 in deuterated dimethyl sulfoxide and shows a carboxylic acid peak. The infrared spectrum (Figure 39) confirms the presence of the carboxylic acid group with absorption at 2660, 2560, 1680, 1300, and 940 cm^{-1}. Bellamy [46c] notes absorption due to OH stretching at 2700-2500 cm^{-1} and to C=O vibration in aryl acids at 1700-1680 cm^{-1}, and OH deformation at 950-900 cm^{-1}. The n.m.r. findings are consistent with the structures:

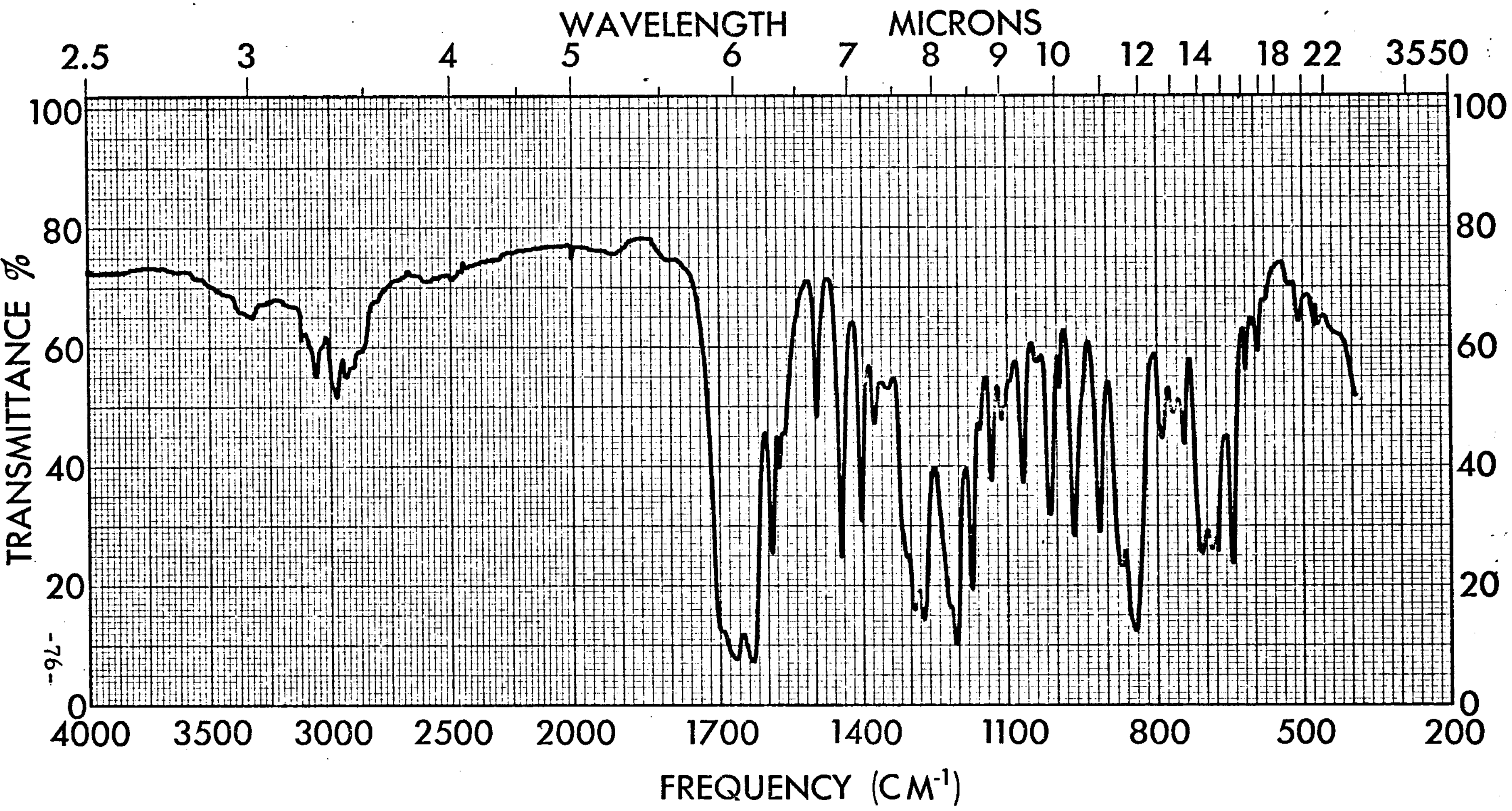


or



.

Weissberger, Salminen and Mader [59] reported a melting point for p-(phenyloxalyl)-benzoic acid as 228-30°C which appears to be the compound obtained in the present work. It is not clear, however, whether oxidation to the carboxylic acid occurred during the bromination step (since the pure compound was not isolated) or in any of the subsequent steps.



SPECTRUM NO. 7871
SAMPLE 94-59

ORIGIN

PURITY

THICKNESS

LEGEND
1.
2.

OPERATOR

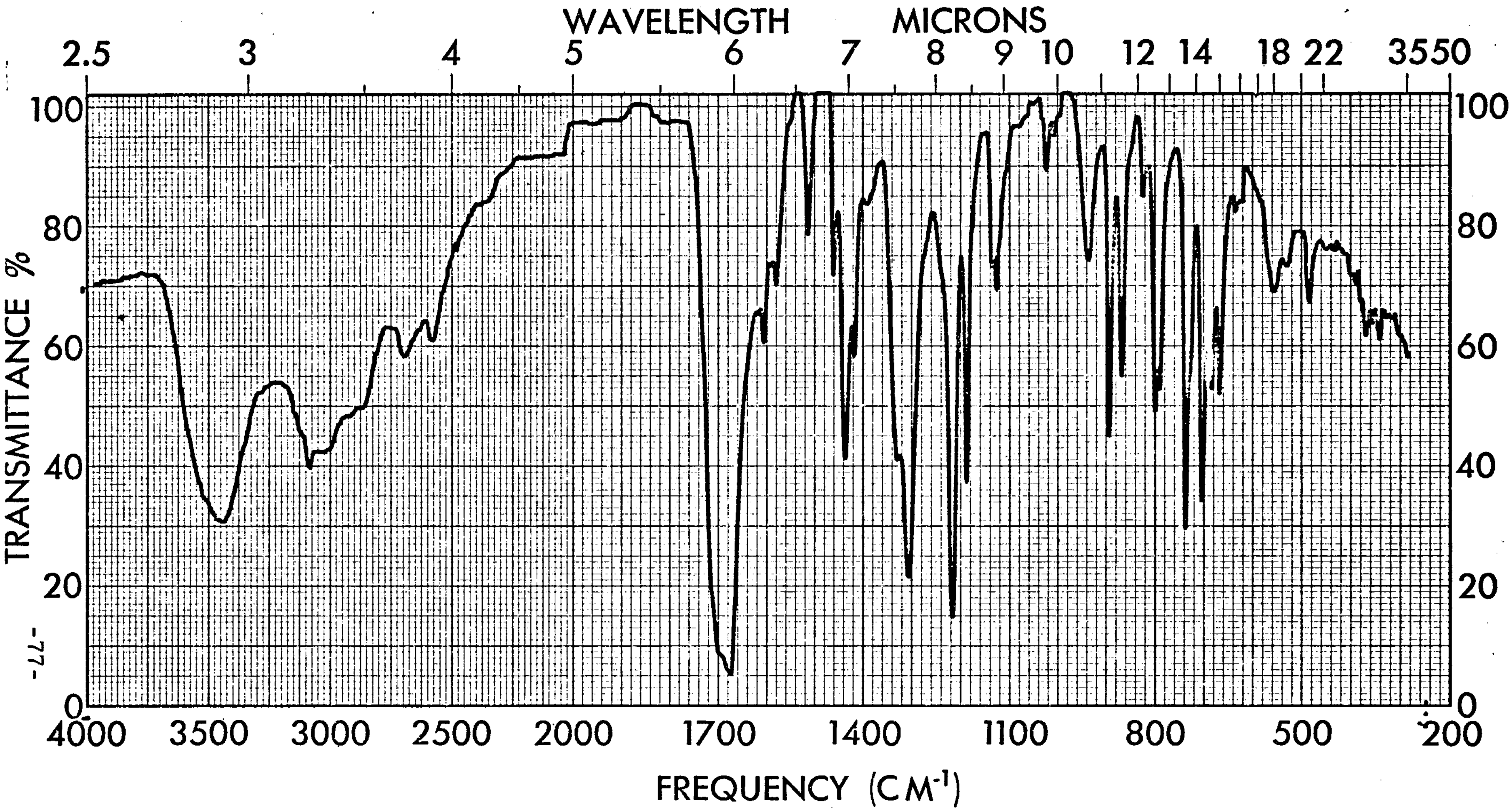
REMARKS

SPECTRUM NO.
SAMPLE

Figure 38. Infrared Spectrum of Nitrate Ester Derived from p-Phenacylpropiophenone.

PART NO. 221-1617

THE PERKIN-ELMER CORPORATION NORWALK, CONN.



SPECTRUM NO. 2874

SAMPLE 94-57-1A-1

ORIGIN

PURITY

THICKNESS

LEGEND

1.

2.

OPERATOR WJF

REMARKS

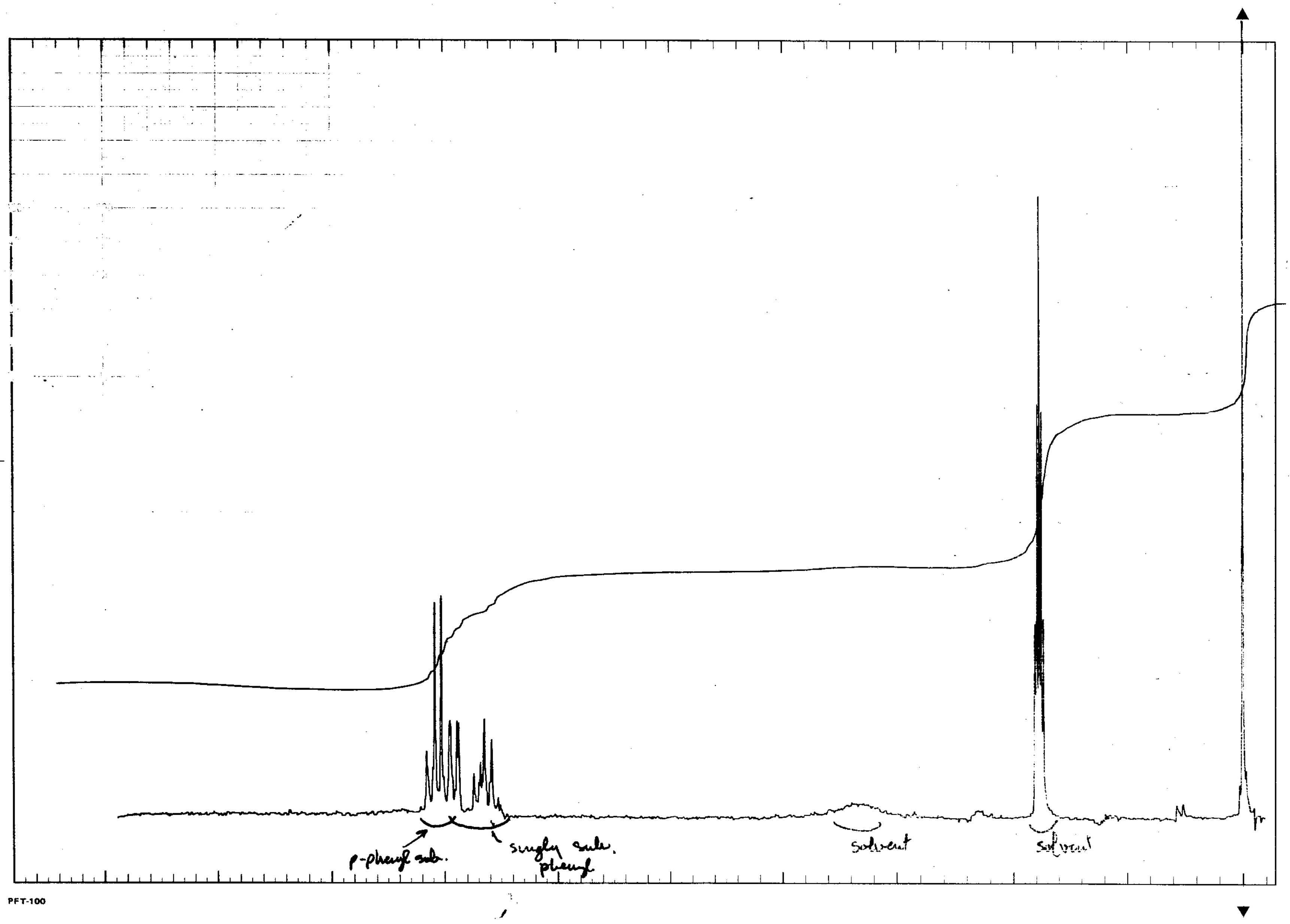
Figure 39. Infrared Spectrum of p-(Phenyloxalyl)benzoic Acid.

SPECTRUM NO.

SAMPLE

PART NO. 221-1617

THE PERKIN-ELMER CORPORATION NORWALK, CONN.



SPECTRUM NO. 3
SAMPLE 94-59-1A-1

SOLVENT Acetone-d6
CONC. ~.2 %
REFERENCE TMS
TEMP. 20 c°

OBSERVE
NUCLEUS ¹H
FREQ. ____ MHz
PULSE: ☐Sing. ☒Mult. 5
WIDTH 13 u sec.
INTERVAL – SEC
REPETITION 4.3 SEC
DATA POINTS 8191
WINDOW EXPONENTIAL T.C.=0
MODE FT
SPECTRUM WIDTH 1250 KHz
FILTER 1250 KHz
AMPL. RF MAX AF 8×10
NO. of SCANS 5

LOCK ☒INT. ☐EXT. ____
FREQ. ____ MHz. (____)
SIGNAL ²D
LEVEL RF 20dB AF ____

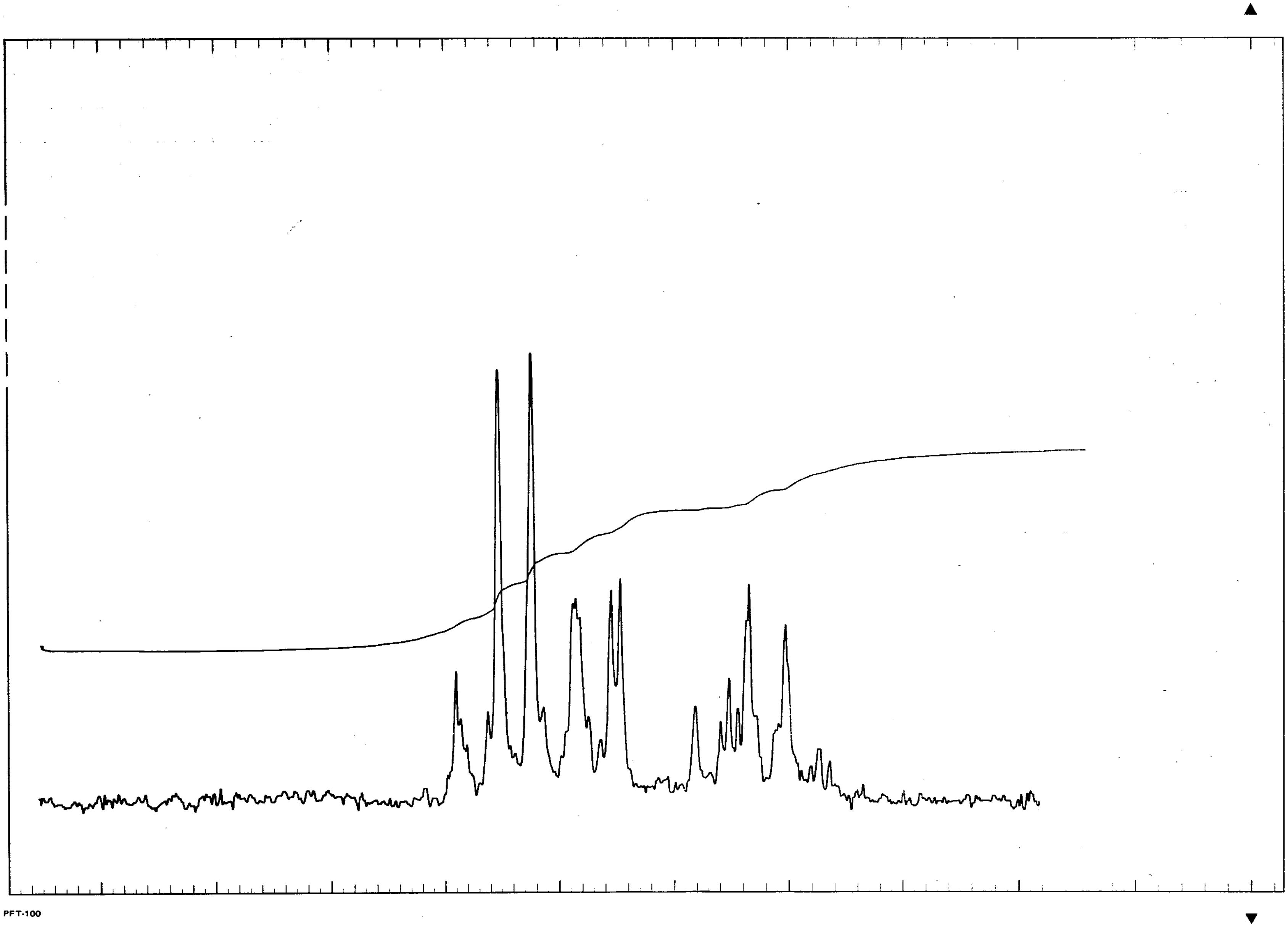
SPIN DECOUPLER
FREQ. ____ HZ (____)
POWER ____ B.W. ____ KHz
MODULATION ____
☐CW ☐Noise ☐EXT. ____

DATE Sept 19, 1975
OPERATOR RES
REMARKS:

Methyl should appear 2.2 – 2.4 ppm

JEOL

Figure 40 Proton Nuclear Magnetic Resonance Spectrum of p-Phenyloxalyl)benzoic acid



SPECTRUM NO. 5
SAMPLE 94-59-1A-1

SOLVENT ACETONE-d6
CONC. ~.2%
REFERENCE TMS
TEMP. 20 c°

OBSERVE
NUCLEUS 1H
FREQ. ______ MHz
PULSE: ☐Sing. ☒Mult. 5
WIDTH 13 u sec.
INTERVAL — SEC
REPETITION 4.3 SEC
DATA POINTS 8191
WINDOW EXPONENTIAL T.C.=0
MODE FT
SPECTRUM WIDTH 1250 KHz
FILTER 1250 KHz
AMPL. RF MAX AF 8×10
NO. of SCANS 5

LOCK ☒INT. ☐EXT. ______
FREQ. ______ MHz. (____)
SIGNAL 2D
LEVEL RF 20dB AF ______

SPIN DECOUPLER
FREQ. ______ HZ (______)
POWER ______ B.W. ______ KHz
MODULATION ______
☐CW ☐Noise ☐EXT. ______

DATE SEPT 19, 1975
OPERATOR RES
REMARKS: MAG: 3↕×5↔

JEOL

Figure 41 Expansion of Aromatic Region of Proton Nuclear Magnetic Resonance Spectrum of p-(Phenyloxalyl)benzoic Acid

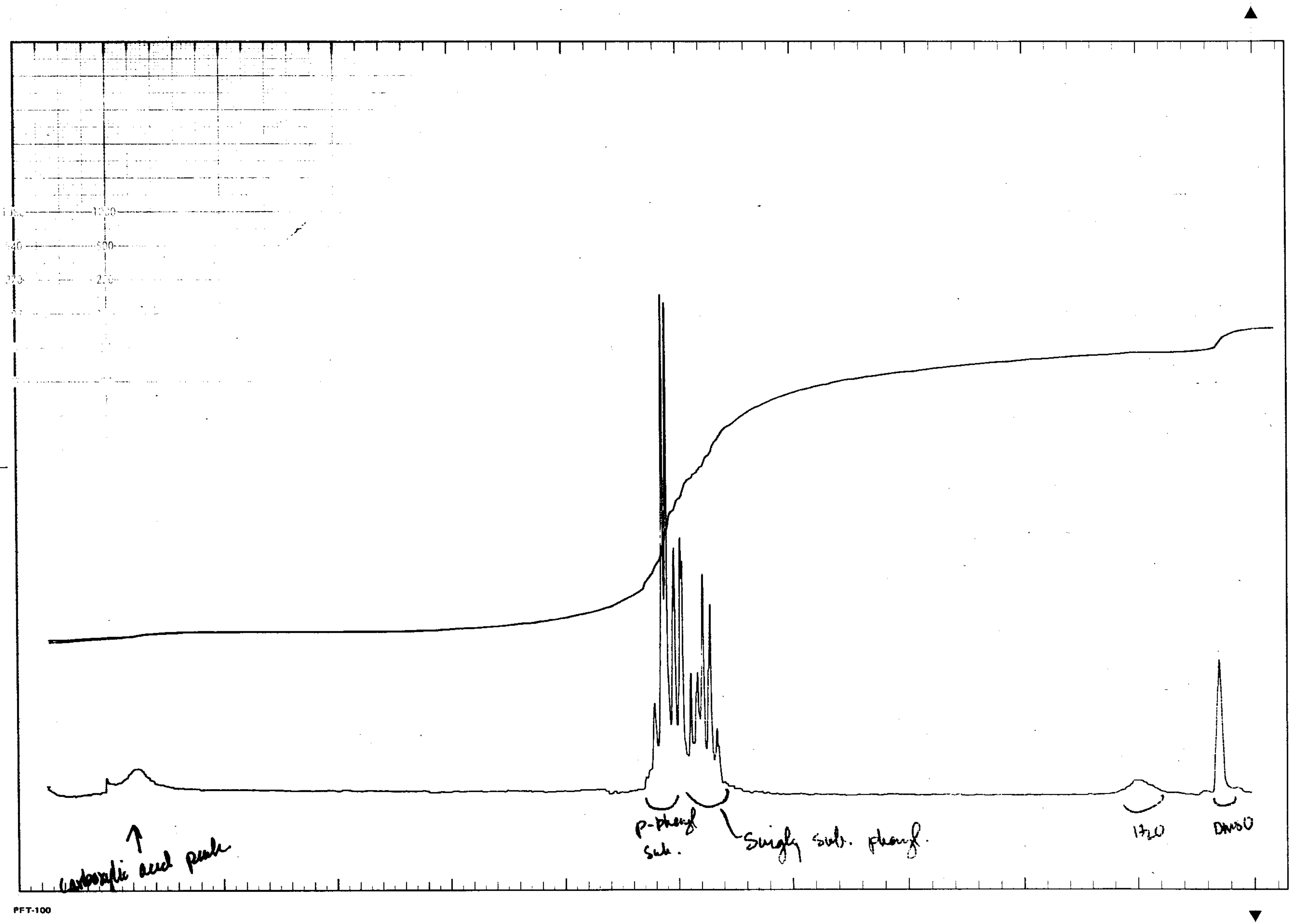


Figure 42 Proton Nuclear Magnetic Resonance Spectrum of p-(Phenyloxalyl)benzoic Acid in Deuterated Dimethylsulfoxide Showing Carboxylic Acid Resonance

SPECTRUM NO. 6
SAMPLE 94-59-1A-1

SOLVENT DMSOd_6
CONC.
REFERENCE
TEMP. R.T. C°

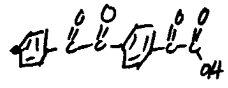
OBSERVE
NUCLEUS
FREQ. MHz
PULSE: ☐Sing. ☐Mult.
WIDTH u sec.
INTERVAL SEC
REPETITION SEC
DATA POINTS
WINDOW EXPONENTIAL T.C.=
MODE
SPECTRUM WIDTH 1250 KHz
FILTER 1250 KHz
AMPL.
NO. of SCANS 1

LOCK ☒INT. ☐EXT.
FREQ. MHz. ( )
SIGNAL
LEVEL RF AF

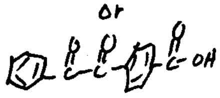
SPIN DECOUPLER
FREQ. HZ ( )
POWER B.W. KHz
MODULATION
☐CW ☐Noise ☐EXT.

DATE
OPERATOR
REMARKS:

carboxylic acid group present



or



JEOL

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