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AFML-TR-68-130

Part II

AD0991316

SYNTHESIS OF POLYSPIROCYCLOBUTANES AND RELATED SPIROPOLYMERS

Part II. Poly(trispiro[3.1.1.3.1.1]dodecane-1,3-dione)
and Poly[3,3-Bis(methylene)cyclobutane-1,1-dicarboxylate]

Clay M. Sharts
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San Diego State College

TECHNICAL REPORT AFML-TR-68-130, PART II

December 1970

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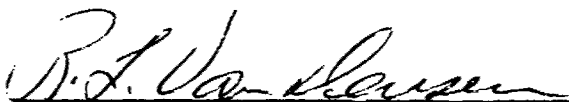
FOREWORD

This report was prepared by San Diego State College Foundation, San Diego State College under USAF Contract No. F33615-67-C-1560, "Research on Synthesis of Polyspirocyclobutanes and Related Polymers." The contract was initiated under Project No. 7342, "Fundamental Research on Macromolecular Materials and Lubrication Phenomena," Task No. 734201, "Basic Factors in the Synthesis of Macromolecular Materials." The work was administered under the direction of the Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio, with Dr. Harold Rosenberg (AFML/LNP) as Project Scientist.

Work on this contract was performed by Dr. Clay M. Sharts, the principal investigator, and Mr. Derril L. Steele.

This report covers work conducted during the period of 1 March 1968 to 1 June 1970. It was submitted by the authors in July 1970.

This technical report has been reviewed and is approved.



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Acting Chief, Polymer Branch
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ABSTRACT

Dispiro[3.1.1.3.1.1]decane-2,8-dicarboxylic acid was converted to the corresponding diacid chloride. Dehydrohalogenation of the diacidchloride gave a bis-ketene intermediate which polymerized to poly(trispiro[3.1.1.3.1.1]dodecane-1,3-dione) (I).

Polymer I was fluorinated with sulfur tetrafluoride to a new fluorinated polyspirocyclobutane. Attempts to convert Polymer I into polyspirocyclobutane failed.

Diethyl and diisoamyl 3,3-bis(hydroxymethyl)cyclobutane were synthesized by different methods. These monomers were polymerized under various conditions to a polymer believed to be a spiropolymer, poly[3,3-bis(hydroxymethyl)cyclobutane-1,1-dicarboxylate].

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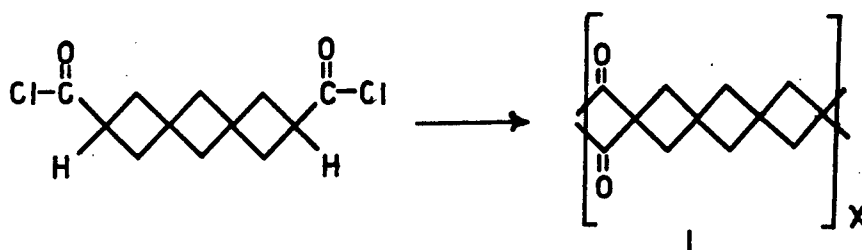
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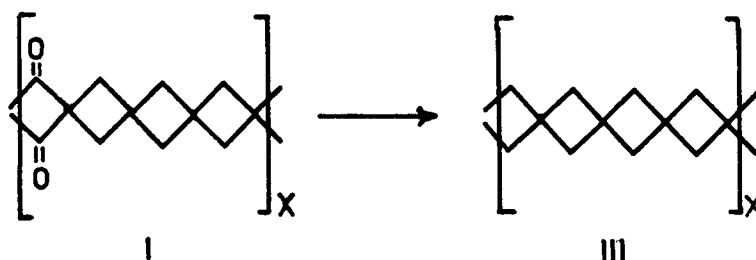
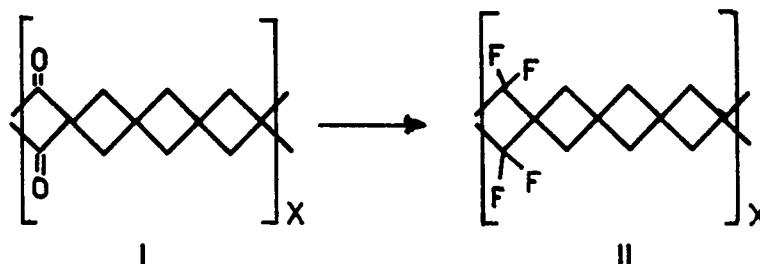
SECTION I

INTRODUCTION

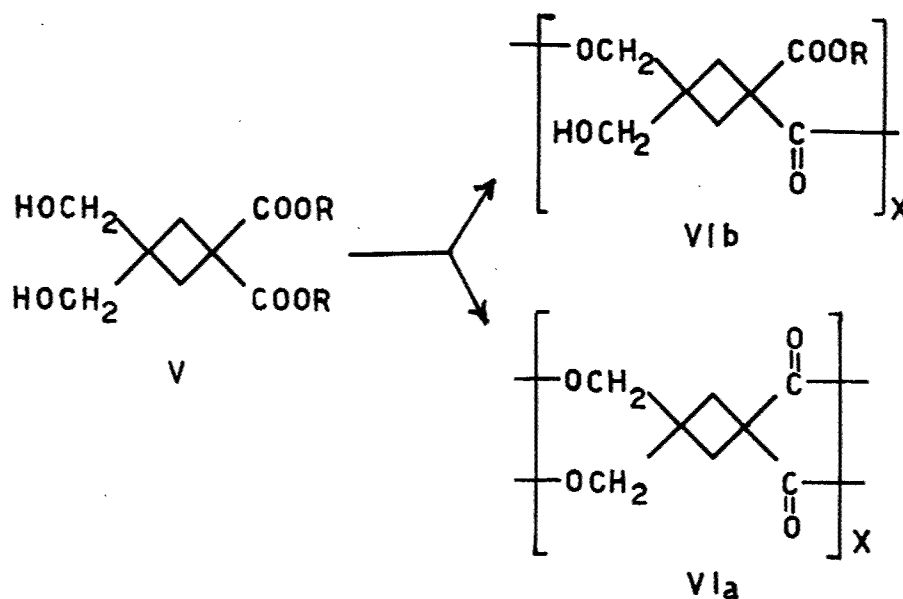
In the previous annual report (Reference 1) the synthesis of poly(trispiro[3.1.1.3.1.1]dodecane-1,3-dione), structure I, was reported. The objective of the work reported herein was improvement in the synthesis of Polymer I and conversion of Polymer I into



poly(1,1,3,3-tetrafluorotrispiro[3.1.1.3.1.1]dodecane), structure II, and into poly(trispiro[3.1.1.3.1.1]dodecane), structure III. Polymer III can also be called poly(spirocyclobutane).



Also reported earlier (Reference 1) was the polymerization of diethyl 3,3-bis(hydroxymethyl)cyclobutane-1,1-dicarboxylate to give a polymer postulated to have structure VIa. The alternate structure VIb was not eliminated. Another objective of this work was improvement of polymerization techniques for synthesis of polymer IV.



SECTION II

RESULTS AND DISCUSSION

A. Dispiro[3.1.3.1]decane-2,8-dicarboxylic Acid - Monomer for Poly-
(trispiro[3.1.1.3.1.1]dodecane-1,3-dione)

Synthesis of dispiro[3.1.3.1]decane-2,8-dicarboxylic acid was described earlier (References 1 and 2). Synthesis was carried out through the following sequence of compounds:

pentaerythritol

2,2-bis(bromomethyl)propane-1,3-diol

2-phenyl-5,5-bis(bromomethyl)-1,3-dioxacyclohexane

diisoamyl 7-phenyl-6,8-dioxaspiro[3.5]nonane-2,2-dicarboxylate

2,2-bis(hydroxymethyl)-7-phenyl-6,8-dioxaspiro[3.5]-nonane

1,1,3,3-tetrakis(hydroxymethyl)cyclobutane

1,1,3,3-tetrakis(hydroxymethyl)cyclobutane tetra-*p*-toluenesulfonate

tetraethyl dispiro[3.1.3.1]decane-2,2,8,8-tetracarboxylate

dispiro[3.1.3.1]decane-2,2,8,8-tetracarboxylic acid

dispiro[3.1.3.1]decane-2,8-dicarboxylic acid

The critical step in the synthesis is the double ring-closure of 1,1,3,3-tetrakis(hydroxymethyl)cyclobutane tetra-*p*-toluenesulfonate with diethyl malonate to form tetraethyl dispiro[3.1.3.1]decane-2,2,8,8-tetracarboxylate. Although this double ring-closure has been accomplished several times on a 0.02-molar scale, all efforts to scale up the reaction have failed. As a result the monomer diacid was in short supply during polymerization studies.

B. Poly(trispiro[3.1.1.3.1.1]dodecane-1,3-dione) (I) by Polymerization of Dispiro[3.1.3.1]decane-2,8-dicarbonyl chloride

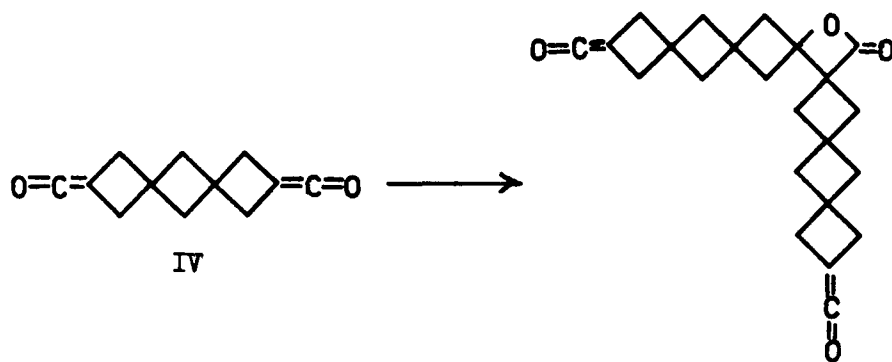
Efforts were made to improve the procedure for forming Polymer I, poly(trispiro[3.1.1.3.1.1]dodecane-1,3-dione) as given in Reference 1. Table I in the Experimental Section summarizes the results. No improvement was made even when the reaction was run in a nitrogen atmosphere. Synthesis of high quality Polymer I remains unreliable. The best Polymer I has a single sharp cyclobutanone carbonyl absorption at 5.78 microns. Lower quality Polymer I has a significant carbonyl absorption at 5.91 microns in addition to the 5.78 micron absorption. (See Figures 1 and 2, pages 24-25, of Reference 1)

In the polymerizations best results were obtained on a one-gram scale. A sample of Polymer I was prepared in a four-gram reaction and forwarded to Battelle Memorial Institute for further evaluation by Dr. K. A. Boni (See Figures 1 and 2). The results of the evaluation were published in Reference 3. Elemental analyses on Polymer I were not satisfactory and cast doubt on the assigned structure. The polymer was soluble to greater than 0.1% in aniline and pyridine and was partially soluble in hexamethylphosphoramide and N,N-dimethylaniline. Thermal gravimetric analysis indicated the polymer did not have good thermal stability; Dr. K. A. Boni reported initial decomposition at about 200° with carbon dioxide evolution.

The best sample of Polymer I prepared in a one-gram run was decomposed in our laboratory in a Stanton Thermal Balance. When heated under nitrogen at a rate of 7°C/min., initial decomposition was observed at 260°; at 300°C the weight loss was very rapid, over 50% weight loss having occurred.

The insolubility of best Polymer I prevented measurement of molecular weight. A poor sample of Polymer I containing infrared observable carboxylic acid groups was soluble in benzene. Soluble fractions gave molecular weights in the range of 800-1100 as determined by a Mechrolab Osmometer. This corresponds to tetramer or pentamer. By comparing the infrared spectrum of best Polymer I with low-grade Polymer I, it is estimated that the best Polymer I is a decamer or higher.

The failures to obtain high yields of high-quality Polymer I raises concern about possible side reactions. The diketene intermediate, structure IV, is expected to react with water, oxygen, primary or secondary amines, and possibly carbon dioxide. Presumably, proper experimental conditions can prevent these undesired side reactions. Although dimethyl ketene dimerizes cleanly to give only 1,1,3,3-tetramethylcyclobutane-1,3-dione (Reference 4) and the ketene derived from cyclobutanecarbonyl chloride is reported to give only dispiro-[3.1.3.1]decane-5,10-dione (Reference 5), the possibility exists that dimerization might occur to some extent through the carbonyl group rather than the methylene linkage.



The consistent formation of large amounts of benzene-soluble polymer might be due to this side reaction rather than the presence of impurities.

C. Poly (1,1,3,3-tetrafluorotrispiro[3.1.1.3.1.1]dodecane)- A
Fluorinated Derivative of Poly(spirocyclobutane)

Poly(1,1,3,3-tetrafluorotrispiro[3.1.1.3.1.1]dodecane (II) was obtained by reaction of sulfur tetrafluoride and Polymer I at 150°C. The infrared spectrum of Polymer II (Figure 3) confirmed the formation of a fluorinated polymer and complete reaction of Polymer I. New intense absorptions in the 10-14 micron region confirm the formation of carbon-fluorine bonds; complete disappearance of carbonyl absorption at 5.78 microns confirms total reaction of the cyclobutane carbonyl groups.

Polymer II was brown in color. The reason for the color is not certain but is probably associated with the poor quality of sulfur tetrafluoride which was used; the sulfur tetrafluoride was red-orange in color rather than water-white.

When Polymer II was heated in a Stanton Thermal Balance at a rate of 7°/min. under helium, the first observable weight loss occurred at 380°C. Weight loss was very rapid at 410°C. When a 21.0 mg. sample of Polymer II was heated at 300°C under nitrogen for sixteen hours a weight loss of 1.6 mg. occurred. The infrared spectrum of Polymer II was unchanged at this point. When the temperature was raised to 350°C for an additional sixteen hours, an additional 14 mg. of weight

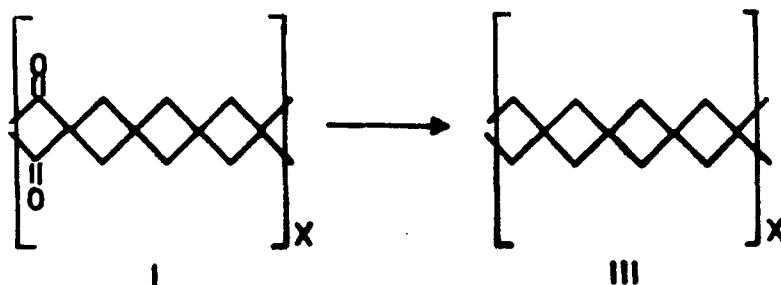
was lost. The infrared spectrum of the residue was featureless (carbon?). Intense carbon-fluorine absorption had completely disappeared.

On the basis of studies and calculations of O'Neal and Benson (Reference 5) the most probable initial step in decomposition of Polymer II is through elimination of difluorocarbene.

The clear success in converting Polymer I into Polymer II led to a decision to suspend further work until other exploratory goals had been achieved. The scarcity of Polymer I required rigid priorities on work scheduling.

D. Attempted Wolff-Kishner Reduction of Poly(trispiro[3.1.1.3.1.1]-dodecane-1,3-dione) (I)

Reduction of Polymer I to form poly(trispiro[3.1.1.3.1.1]dodecane) (III) or, more simply, poly(spirocyclobutane) was the ultimate synthetic objective of this research.



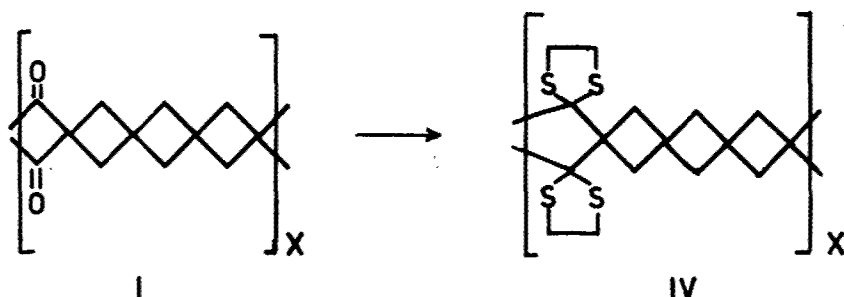
Several attempts were made to reduce Polymer I to Polymer III by the Huang-Minlon modification of the Wolff-Kishner reduction. When products were obtained they contained nitrogen. Decomposition of Polymer I under the strongly basic conditions was apparent. In many respects the results were similar to those of Buchman and Deutsch (Reference 5)

except that they succeeded in making the reduction occur on dispiro-[3.1.3.1]decane-5,10-dione.

Some of the experimental results are summarized in Table II in the Experimental Section.

E. Attempted Synthesis of Poly(spirocyclobutane) via the Bis-(Thioketal) of Poly(trispiro[3.1.1.3.1.1]dodecane-1,3-dione) (I)

Synthesis of poly(spirocyclobutane) was attempted by converting Polymer I into Polymer IV, a bis(thioketal) derivative of Polymer I.



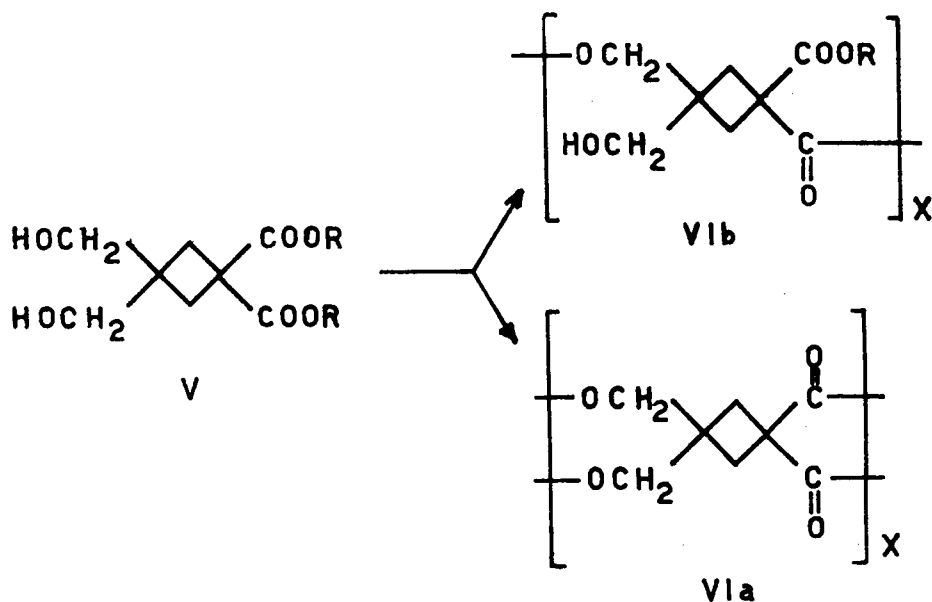
Methods similar to those of Buchman and Deutsch (Reference 5) did not convert Polymer I into Polymer IV. After several attempts using the method of Buchta and Ahne (Reference 7), a sample of low-grade Polymer I reacted with ethane-1,2-dithiol in boron trifluoride-etherate to give a sulfur-containing polymer designated as Polymer IV. The elemental analysis was poor and indicated incomplete incorporation of sulfur into the structure. The infrared spectra clearly showed that carbon-sulfur bonds had formed and that carbonyl groups had disappeared. In Figure 4 the infrared spectrum of Polymer I used for reaction is shown while Figure 5 shows the infrared spectrum of Polymer IV with the clear carbon-sulfur absorption at 9.5 microns and

greatly diminished carbonyl absorption at 5.85 microns. Figures 6 and 7 show the spectrum of Polymer IV in tetrachloroethylene and Kel-F oil mulls; these spectra more clearly show the diminished carbonyl absorption by permitting comparison with the carbon-hydrogen absorptions.

When Polymer IV was treated with Raney nickel to effect desulfurization, no reaction occurred. Recovered Polymer IV had almost the same percentage of sulfur as it had before attempted desulfurization.

F. Poly[3,3-bis(methylene)cyclobutane-1,1-dicarboxylate] by Polymerization of Diethyl 3,3-bis(hydroxymethyl)cyclobutane-1,1-dicarboxylate (V)

The polymerization of 3,3-bis(hydroxymethyl)cyclobutane-1,1-dicarboxylate (V) to poly[3,3-bis(methylene)cyclobutane-1,1-dicarboxylate] (VI) was reported previously (Reference 1). The structure of Polymer VI was suggested as the spiropolymer VIa but the single chain structure VIb was not ruled out. Polymer VI varied in properties



from experiment to experiment. In some experiments a tough clear film was obtained which was soluble in acetone over a long period of the polymerization process. In other experiments a brittle foamed polymer formed which was insoluble shortly after polymerization was started. A systematic study was started to determine the variables affecting the polymerization.

1. Initial Search for Conditions for Polymerization of Diethyl 3,3-bis(hydroxymethyl)cyclobutane-1,1-dicarboxylate

The sample of 3,3-bis(hydroxymethyl)cyclobutane-1,1-dicarboxylate (V) used in these polymerization studies was the best available at the time. It is known now that some impurities were present. These impurities were probably a moniodo derivative from incomplete malonic ester condensation to form the cyclobutane ring and some unhydrolyzed diethyl 6-oxaspiro[3.3]heptane-2,2-dicarboxylate.

Five 5.0-gram samples of monomer V were polymerized under the following set of conditions:

1. No catalyst; heated 25° to 200° over 2-hr. period.
2. Antimony(III) oxide-calcium acetate dihydrate catalyst; heated 25° to 200° over 2-hr. period.
3. Antimony(III) oxide-calcium acetate dihydrate catalyst; heated 25° to 250° over 5-hr. period.
4. p-Toluenesulfonic acid catalyst; heated 25° to 250° over 5-hr. period.
5. Hexamethylphosphoramide solvent; heated 25° to 250° over 5-hr. period.

In runs 1, 3, and 4 solid polymers insoluble in benzene or acetone were obtained. Solid polymer from run 2 was partially soluble in acetone. No solid polymer was obtained in run 5. In run 1 both water and ethanol were evolved; evolution of water indicated formation of ether linkages. In runs 2 and 3 only ethanol was evolved. The mixed catalyst substantially reduced ether formation.

The polymers were brittle and it was presumed that they were cross-linked. Infrared spectra showed two kinds of carbonyl absorptions and residual hydroxyl absorption. It is reasonable to say that the polymers just described existed with some kind of cross-linked structure VIb. At this point in the investigation it was concluded that Monomer V was not sufficiently pure for polymerization studies.

2. Polymerizations on Low Purity Diethyl 3,3-bis(hydroxymethyl)-cyclobutane-1,1-dicarboxylate (V)

It was recognized that diethyl 3,3-bis(hydroxymethyl)cyclobutane-1,1-dicarboxylate used in polymerizations was insufficiently purified. The problem had to be attacked at two points;

- a. the condensation reaction between diethyl malonate and 3,3-bis(iodomethyl)oxetane.
- b. the hydrolysis of diethyl 6-oxaspiro[3.3]heptane-2,2-dicarboxylate.

The problem in point "a" is to assure complete ring closure and total elimination of iodide ion. The moniodo compound cannot be separated by distillation from diethyl 6-oxaspiro[3.3]heptane-2,2-dicarboxylate. The problem in point "b" is to assure complete hydrolysis of the oxetane ring without hydrolyzing the ester groups. A subsequent

problem that was discovered was the difficulty in removing the last traces of sulfuric acid from Monomer V which will be discussed later.

While experimental work was underway to improve the quality of Monomer V, samples of Monomer V from these experiments were polymerized under a variety of conditions. These experiments will not be enumerated here because they did not lead to polymers with desirable properties.

3. Improved Synthesis of Diethyl 3,3-bis(hydroxymethyl)cyclobutane-1,1-dicarboxylate (V)

The diethyl malonate reaction with 3,3-bis(iodomethyl)oxetane was made to go to completion by use of potassium metal as the base and refluxing xylene as the reaction medium. By heating the reaction mixture under reflux for an extended time period, all iodide was displaced. The product, diethyl 6-oxaspiro[3.3]heptane-2,2-dicarboxylate, was obtained free of the previously contaminating side-reaction products. Yields were raised from 60% to 75%. More importantly, the temperatures required for polymerization were reduced to less than 100°C.

The hydrolysis of the oxetane ring of diethyl 6-oxaspiro[3.3]-heptane-2,2-dicarboxylate proved to be more of a problem. Careful control of temperature and sulfuric acid concentration gave Monomer V of variable purity. Sometimes Monomer V polymerized at temperatures as low as 50°C; at other times a temperature of 100°C was required. The hydrolysis procedure finally developed was to treat the oxetane with 1M sodium bisulfate solution for 24 hours at 60°C. This procedure minimized the hydrolysis of the ester groups. Equally important was simplification of removal of residual acid from Monomer V. As the

next section will show, removal of acid from monomer was found to be very important.

4. The Effect of Acid on the Polymerization of Diethyl 3,3-bis-(hydroxymethyl)cyclobutane-1,1-dicarboxylate (V)

Inspection of samples of polymers of Monomer V that had stood in the atmosphere at room temperature for several months showed beads of liquid on the surface of the polymer. The liquid was identified as sulfuric acid. It was apparent that all acid was not being removed from Monomer V that was produced by sulfuric acid hydrolysis. Apparently the ether solvent and Monomer V were sufficiently strong bases to prevent complete removal of sulfuric acid by routine washes with sodium bicarbonate solution.

A large sample of diethyl 6-oxaspiro[3.3]heptane-2,2-dicarboxylate was prepared by condensing diethyl malonate and 3,3-bis(hydroxymethyl)-cyclobutane-1,1-dicarboxylate using sodium in xylene as the base and reaction medium as described on page 45 of the Experimental Section. The oxetane was hydrolyzed in two parts with 2.0 N sulfuric acid at room temperature over a 3-day period. One part was exhaustively washed to remove all acid; the other part was washed only with water to assure that residual acid would remain. Samples of acid-free and acid-containing Monomer V were then polymerized under various conditions. Table II in the Experimental Section summarizes the experimental conditions of the polymerizations. The results are clear. Acid-containing Monomer V polymerized at temperatures as low as 40°C and consistently gave a brittle polymer which was insoluble in all solvents at an early stage of polymerization. In contrast, acid-free Monomer V gave a

tough polymer which remained soluble for a longer time period during polymerization.

5. Partial Polymerization of High Purity Diethyl 3,3-bis(hydroxymethyl)-cyclobutane-1,1-dicarboxylate

Diethyl 6-oxaspiro[3.3]heptane-2,2-dicarboxylate was prepared by condensing diethyl malonate and 3,3-bis(iodomethyl)oxetane using potassium as the base in refluxing xylene. The product oxetane was hydrolyzed with 10% sodium bisulfate solution at 60°. The experimental procedures are described on pages 44-45 of the Experimental Section. The polymerization was carried out over a 14-day period at a maximum temperature of 130°C as described on page 49. The infrared spectrum of this polymer is shown as Figure 8. Considerable hydroxyl absorption is evident. A sample of this polymer was forwarded to Air Force Materials Laboratory for evaluation as a sample that had not been completely polymerized.

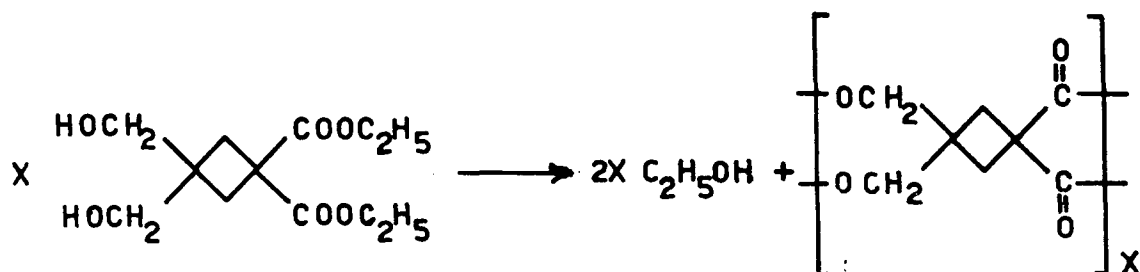
6. Polymerization of High Purity Diethyl 3,3-bis(hydroxymethyl)-cyclobutane-1,1-dicarboxylate

A center cut of the highest purity diethyl 6-oxaspiro[3.3]heptane-2,2-dicarboxylate was redistilled and a center cut used (see infrared spectrum, Figure 9, and nmr spectrum, Figure 10) to prepare monomer I, diethyl 3,3-bis(hydroxymethyl)cyclobutane-1,1-dicarboxylate (see infrared spectrum, Figure 11). An eighteen-gram uncatalyzed sample and an eighteen-gram catalyzed sample of monomer I were polymerized over a 17-day period with programmed heating from 90° to 213°. By 130° the samples were significantly polymerized as shown by their infrared spectra (see infrared for uncatalyzed, Figure 12, and infrared for

catalyzed polymer, Figure 13) when compared with the infrared spectrum for monomer I (Figure 11). For eighteen-gram samples the final weight of the polymers should have been 11.20 grams if complete polymerization occurred. After heating to 130° the uncatalyzed sample weighed 12.14 grams; the catalyzed sample weighed 9.81 grams. These weight losses will be discussed later. Results are interpreted to indicate that nearly complete polymerization had occurred by 130° to give a double-chained structure or a cross-linked structure.

When heated to 213° to complete the heating cycle, both samples were yellow-brown hard, brittle polymers. The infrared spectra of both samples were essentially free of hydroxyl absorption (see Figures 14 and 15). The final weight of the uncatalyzed sample was 10.74 grams (0.46 excessive weight lost over theoretical); the catalyzed sample weighed 9.35 grams (theoretically 1.85 grams excess weight lost).

The weight losses up to 130° were not due solely to evolution of ethanol by the polymerization reaction. Because of the method of preparing monomer I, there was some solvent left in the sample. This



has been shown earlier by analysis for chlorine when dichloromethane was used for the solvent. In addition, monomer I was contaminated with some unhydrolyzed oxetane which volatilized onto the walls of the oven at temperatures in the range of 100-130°. For these reasons

weight loss can be used only as an indication as to how far the polymerizations have gone. Above 179° a liquid of unknown structure was evolved in addition to ethanol. Less than 0.5 grams of this liquid was obtained. The infrared spectrum of the liquid showed the presence of ester and alcohol groups. The uncatalyzed and catalyzed polymers obtained at 213° had infrared spectra which showed them to be almost completely free of hydroxyl absorptions. Neither polymer melted when heated in a capillary to 330° nor did they show obvious signs of decomposition. Neither polymer was soluble in common solvents at elevated temperatures.

Elemental analysis can give some information about the extent of polymerization of monomer V. If monomer V (C = 55.40, H = 7.75) were completely polymerized to a doubly-linked infinite polymer, the final polymer would have a composition of C = 57.14% and H = 4.80%. The uncatalyzed polymer had C = 57.66% and H = 5.81%. The catalyzed polymer had C = 58.56 and H = 6.09%. In agreement with other data, the uncatalyzed polymer seems to be closer to the desired polymer. The carbon percentage is 0.52% high and the hydrogen percentage is 1.0% high for the uncatalyzed polymer. This result would be caused either by crosslinking by loss of water to form an ether crosslink or by decarboxylation and elimination of ethylene from a carbethoxy group. Both processes are reasonable. The higher discrepancies in the catalyzed polymer can also be caused by these side reactions.

Samples of the polymers described above were designated as samples 96A-catalyzed and 96B-uncatalyzed and forwarded to Air Force Materials Laboratory, Wright-Patterson Air Force Base for evaluation.

7. Detailed Study of the Polymerization of Diethyl 3,3-bis-
(hydroxymethyl)cyclobutane-1,1-dicarboxylate (V)

Irreproducibility in the polymerization of diethyl 3,3-bis-(hydroxymethyl)cyclobutane-1,1-dicarboxylate (V) plagued the polymerization work. Most difficulties were believed to be due to impurity of Monomer V and to traces of acid not removed in the hydrolysis of the oxetane precursor to monomer V. Even after the synthetic precautions described earlier were taken, there was still uncertainty in the purity of monomer V. The reason was, of course, the ease with which the monomer could be polymerized. Last traces of solvent could not be safely removed from monomer V without risking polymerization. Successful polymerization at temperatures below 100°C finally became the criterion for assessing monomer purity.

Monomer V was carefully prepared using potassium in xylene as the base for condensing diethyl malonate with 3,3-bis(iodomethyl)-oxetane and using 1M sodium bisulfate solution at 60°C to hydrolyze the condensation product. This carefully prepared monomer V was designated as sample 40 and contained 1.49% residual dichloromethane solvent. Six samples of this Monomer V were polymerized in the presence of antimony(III) oxide-calcium acetate dihydrate catalyst for varying time periods as presented in Table IV. Individual samples of polymer (40-1 to 40-6) were analyzed for the following properties:

Weight Loss

Molecular Weight (by a Mechrolab Osmometer).

Nmr Spectra (by a Varian A-60 Spectrometer).

IR Spectra (by a Perkin-Elmer Model 621 Grating Spectrometer).

Elemental Analyses (by Geiger Laboratories).

Viscosity (in acetone and sulfuric acid solutions).

Samples 40-1 to 40-4 were completely soluble in acetone and dichloromethane.

Table IV summarizes the data obtained in the polymerization studies and should be consulted at this point. Sample number is given in column 1. Columns 2-4 give the time, temperature, and pressure used for a polymer sample. Columns 5-6 give the gravimetric data on the polymer sample. Column 6, which gives the percentage weight lost, provides valuable information on the extent of polymerization of a polymer sample. In column 5 the initial weight of the monomer sample is given corrected for 1.49% dichloromethane; also given is the corrected weight lost by the sample. If you consider that a singly-linked trans polymer will have a maximum weight loss of 17.7% before cross-linking and a doubly-linked cis polymer can lose a maximum of 35.4%, then the data of column 6 can be interpreted as supporting a doubly-linked cis polymer. It should be noted also that samples 5 and 6 were identical initially except for the amount of sample, and that they were treated identically in polymerization. These two samples, which differed completely in physical properties when polymerized, will be discussed later.

Molecular weights for samples are given in column 7. The osmometer-measured molecular weight for sample 40 is high because of dichloromethane impurity. Because of the possible mixed-type polymers that can be present, it is hard to say what these number-averaged molecular weights mean. Sample 40-4 was the last sample completely soluble in acetone and had a molecular weight of 980. If weight distribution

within the polymer is ignored, a molecular weight of 980 corresponds to a doubly-linked cis polymer of five monomer units (theoretical MW = 932) and there should be a corresponding weight loss of 27.4% (observed 25.8%). In contrast, a singly-linked trans polymer with four monomer units (theoretical MW = 902) would have a weight loss of 13.3%. The combination of acetone solubility, percentage weight lost, and molecular weight data strongly indicates that the sample 40-4 is a short spiro polymer.

Elemental analyses are presented in column 8 for each sample. Without exception, all carbon analyses are too low to make sense. Except for the trend of increasing percentage carbon, the elemental analyses cannot be correlated with the other data in Table II. Sample 40 (monomer I) gave C = 53.87%, H = 7.34%, and Cl = 1.24%. If dichloromethane is assumed as an impurity, this corresponds to 1.49% dichloromethane in the sample. If the analysis is corrected for dichloromethane, then sample 40 would analyze for C = 54.7% and H = 7.46%. This value is very close to the analysis for sample 40-1 which is still essentially monomer but should have lost dichloromethane. Since the theoretical analysis for monomer I is C = 55.3% and H = 7.74%, it is presumed that water was also present in the monomer.

Possibly the only value the elemental analyses have is to confirm that the polymerization is going in the right direction as far as percentage carbon is concerned. Percentage carbon for monomer I, doubly-linked cis pentamer, and infinite spiro polymer are theoretically 55.36%, 56.65% and 57.15%. The change in percentage carbon is 1.29% from monomer to pentamer. When samples 40 and 40-4 are compared the observed change is 54.7% (corrected for dichloromethane) to 55.7%, a

change of 1.0%. If a singly-linked trans polymer is considered for monomer I singly-linked trans tetramer, and infinite polymer, the theoretical analyses are C = 55.36%, C = 55.86% and 56.07%. The theoretical change from monomer to tetramer is 0.5%.

The theoretical elemental analysis for the precursor to monomer V (diethyl 6-oxaspiro[3.3]heptane-2,2-dicarboxylate) is C = 59.49% and H = 7.49%. Elemental analysis as well as the nmr spectra indicate that unhydrolyzed oxetane was not the contaminant. The low analyses for carbon and hydrogen are not explained and cast a question mark over other data.

Infrared spectra were observed of samples 40 to 40-6 with a Perkin-Elmer Model 621 Infrared Grating Spectrophotometer. Spectra were obtained for neat liquids, dichloromethane solutions, or in potassium bromide pellets as appropriate for each sample. Dichloromethane solutions and potassium bromide pellets were prepared quantitatively. Table V summarizes the integrated intensities obtained gravimetrically on paper cutouts for the hydroxyl absorption at 3410 cm^{-1} (2.94 microns) and the carbonyl absorption at 1730 cm^{-1} (5.78 microns). The important column is the ratio of the hydroxyl absorption to the carbonyl absorption which provides a measure of the number of ethanol units lost. The assumption is made that the extinction coefficient of the carbonyl group is the same in monomer and polymer.

For sample 40-4 the hydroxyl/carbonyl ratio is 1.65 which corresponds to 52.7% of the theoretical ethanol to be lost. The ratio of 0.591 in sample 40-5 corresponds to 83% weight loss. These numbers by infrared analysis do not correspond with the gravimetric results suggesting caution in interpreting the infrared spectra. If it is

noted that there is a large change in elemental analysis for hydrogen for these two samples ($H = 7.75\%$ for 40-4 and $H = 6.42$ for 40-5), it can be suggested that residual water is being evolved when the temperature was raised from 80° to 110° . It is believed that infrared spectra support a spiro polymer.

The nuclear magnetic resonance (nmr) spectrum of neat monomer I (sample 40) is shown in Figure 16. The hydroxyl absorption lies under the quartet methylene group of the carbethoxy function. The nmr spectra of samples 40-1 to 40-4 are given in Figures 17-20 and were observed in dichloromethane solution. It should be noted that due to a solvent effect, the hydroxyl absorption is shifted under the methylene absorption of the hydroxymethyl group. In Table VI the gravimetrically obtained integrated intensities of each of the peaks is presented in tabular form. At the top of Table VI is a coded structure to identify what are called Peaks 1, 2, 3 and 4. The integrated intensity of the cyclobutane peak has been corrected in all cases by a factor of 1.07.

Peak 1 is a quartet. Its intensity is due to the $-\text{CH}_2-$ in the $-\text{COOC}_2\text{H}_5$ group of the monomer plus $-\text{CH}_2-$ in the $-\text{COOCH}_2\text{-cyclobutane}$ in the polyester. The growing spike in the center of the quartet should be noted.

Peak 2 is a single peak which contains the $-\text{OH}$ and $-\text{CH}_2-$ of the $-\text{CH}_2\text{OH}$ group. This peak is steadily disappearing as polymer forms.

Peak 3 is the cyclobutane hydrogens. It has a constant value during polymerization and is the reference point for analysis of the nmr spectra. Note carefully that the ratio of peak 1 to peak 3 should remain constant at 1.00 as the polymerization proceeds because every

disappearing methylene group from the carbethoxy group is replaced by a methylene group forming as an ester to link the polymer.

Peak 4 is the triplet methyl group of the carbethoxy function. It disappears continuously during polymerization. The ratio of peak 4 to peak 3 measures how much ethanol is lost.

Nmr spectra are interpreted as supporting a spiro polymer.

Viscosities of the samples were measured in acetone and sulfuric acid. The results are summarized in Table VII.

Samples 40-5 and 40-6 have not been discussed. Initially they were identical materials. The only difference in polymerization was that 40-5 weighed only 3.00 grams and 40-6 weighed 13.9 grams. The large amount of the latter was used to try to provide Air Force Materials Laboratory with a large sample for characterization. When removed from the oven, sample 40-5 was a very viscous, tacky liquid which solidified on cooling. While it was warm, fibers could be drawn. It was partially soluble in solvents. In contrast, 40-6 was a hard, brittle, insoluble foamed solid when removed from the oven. Weight loss and infrared spectra indicate that sample 40-5 lost the most amount of ethanol. Sample 40-6 is thought to be cross-linked. Apparently the bulk of the sample prevented sufficiently rapid diffusion of ethanol and heat. The observation of the effect of mass on the polymerization of V has resulted in adopting Teflon-covered cookie pans as the vessel for polymerizations.

TABLE IV

Polymerization of Diethyl 3,3-bis(Hydroxymethyl)cyclobutane-1,1-dicarboxylate

(1) Sample Number	(2) Time, Days	(3) Temp., °C	(4) Press., mm-Hg	(5)* Init. Wt. and Wt. lost, grams	% Weight Lost	Mol. Wt.	Elemental Anal., %	Appearance and Comments
40	0	Room	1.6	--	--	289	C, 53.87 H, 7.34 Cl, 1.24	clear viscous liquid. sol. acetone, dichloromethane.
40-1	3	60	1.6	2.969 .226	7.60	291	C, 54.87 H, 7.35	clear viscous liquid. sol. acetone, dichloromethane.
40-2	3 4	60 80	1.6 1.6	2.979 .560	18.8	485	C, 54.41 H, 7.20	clear very viscous liquid. sol. acetone, dichloromethane.
40-3	3 8	60 80	1.6 1.6	2.962 .738	24.9	810	C, 54.86 H, 6.65	soft solid. sol. acetone, dichloromethane.
40-4	3 12	60 80	1.6 1.6	2.959 .763	25.8	980	C, 55.68 H, 7.75	soft solid. surface appears to have crystal boundaries. sol. acetone, dichloromethane.
40-5	3 12 2	60 80 110	1.6 1.6 1.6	2.976 .956	32.0	--	C, 55.74 H, 6.42	hard solid. can draw fibers from melt. partly soluble acetone.
40-6	3 12 2	60 80 110	1.6 1.6 1.6	13.643 4.11	30.1	--		hard, brittle, foamed solid. insoluble.

*Weights corrected for dichloromethane.

TABLE V

Infrared Spectra of Polymers from Diethyl 3,3-bis(Hydroxymethyl)cyclobutane-1,1-dicarboxylate

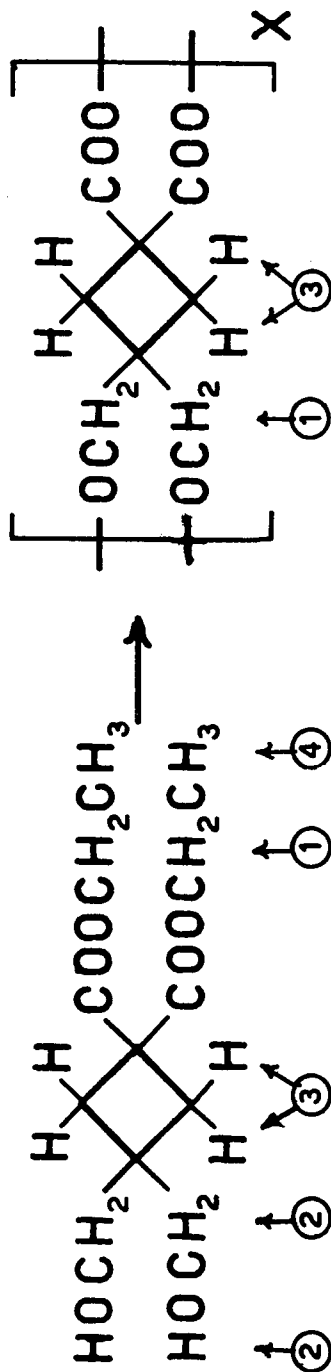
Sample Number	Phase for Spectrum	Intensity of		Ratio of Hydroxyl to Carbonyl Abs.	Observed Molecular Weight
		Hydroxyl Abs. at 3410 cm^{-1} , grams	Carbonyl Abs. at 1730 cm^{-1} , grams		
40	Neat	0.3734	0.1068	3.49	289*
40-1	Neat	0.2695	0.0881	3.06	291
40-2	Neat	0.3018	0.1412	2.14	485
40-3	CH_2Cl_2 **	--	--	--	--
40-4	KBr	0.1990	0.1214	1.65	980
40-5	KBr	0.0573	0.0970	0.591	--
40-6	KBr	0.0869	0.1306	0.675	--

*High due to residual dichloromethane.

**Dichloromethane absorptions interfere with the hydroxyl absorption.

TABLE VI

Nuclear Magnetic Resonance Spectra of Polymer From Diethyl
3,3-bis(Hydroxymethyl)cyclobutane-1,1-dicarboxylate



Sample Number Phase	Peak No.	Wt. of Peak, grams	Ratio 4/3	Ratio 1/3	Ratio 2/3	Ratio 2/1	Ratio 1/4
40 ^a Neat	1	0.0674	1.50	-- ^a	-- ^a	-- ^a	-- ^a
	2	0.0414					
	3	0.0455*					
	4	0.0685					
40-1 ^b CH ₂ Cl ₂ solution	1	0.0309	1.49	1.00	1.28	1.28	0.671
	2	0.0394					
	3	0.0308*					
	4	0.0461					
40-2 ^b CH ₂ Cl ₂ solution	1	0.0468	1.21	1.00	0.983	0.99	0.828
	2	0.0462					
	3	0.0468*					
	4	0.0566					

Table VI (continued)

Sample Number— Phase	Peak No.	Wt of Peak, grams	Ratio 4/3	Ratio 1/3	Ratio 2/3	Ratio 2/1	Ratio 1/4
40-3 ^b CH ₂ Cl ₂ solution	1	0.0649	0.892	1.00	0.766	0.765	1.12
	2	0.0496					
	3	0.0647*					
	4	0.0578					
40-4 ^b CH ₂ Cl ₂ solution	1	0.0631	0.876	1.00	0.534	0.534	1.14
	2	0.0337					
	3	0.0632*					
	4	0.0554					
Limiting value trans-polymer			0.750	1.00	0.750	0.750	1.33
Limiting value cis-polymer			0.000	1.00	0.000	0.000	infinity

*Cyclobutane hydrogen areas have been multiplied by 1.07 to give the tabulated values.

^aIn the neat sample the hydroxyl hydrogen falls under the carboxy methylene quartet. The ratios cannot be compared with ratios for dichloromethane solutions.

Peak 1 - carboxy methylene quartet plus hydroxyl.

Peak 2 - methylene of hydroxymethyl group.

Peak 3 - cyclobutane methylene.

Peak 4 - carboxy methyl triplet.

^bIn dichloromethane solution the hydroxyl hydrogen falls under the methylene group of the hydroxymethyl group.

Peak 1 - carboxy methylene quartet plus methylene of polymer ester linkage.

Peak 2 - hydroxyl and methylene of hydroxymethyl group.

Peak 3 - cyclobutane methylene.

Peak 4 - carboxy methyl triplet.

TABLE VII

Viscosity Measurements at 25° on Poly[3,3-bis(hydroxymethyl)cyclobutane-1,1-dicarboxylate]^a

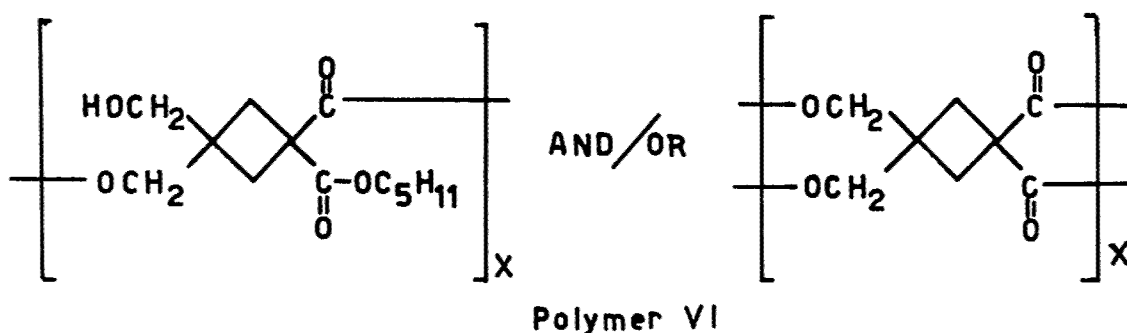
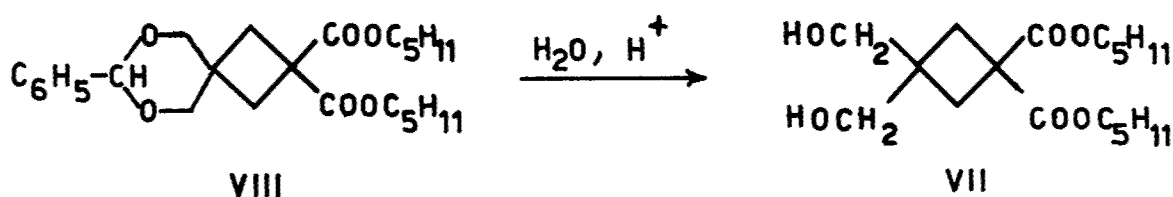
Sample Number ^a	Mol. Wt. ^b	Solvent	Conc. (C) in g/100 ml.	t ₀ , sec.	t _s , sec.	$\frac{t_s}{t_0}/C$	$\ln \frac{t_s}{t_0}/C$
40	260	acetone	.5485	110.1	111.4	1.843	0.612
40-1	290	acetone	1.000	110.1	112.4	1.021	0.028
			.500	110.1	111.3	2.022	0.704
			.333	110.1	110.8	3.019	1.102
		sulfuric acid	1.005	105.1	108.2	1.024	.024
			.503	105.1	106.4	2.015	.704
			.335	105.1	105.8	3.005	1.100
40-2	485	acetone	1.000	110.1	113.1	1.027	0.027
			.500	110.1	111.7	2.029	0.696
			.333	110.1	111.1	3.027	1.101
		sulfuric acid	1.077	105.1	108.5	.959	--
			.538	105.1	106.7	106.7	.633
			.359	105.1	106.1	106.1	1.030
40-3	810	acetone	.993	110.1	114.2	1.045	0.044
			.497	110.1	112.1	2.051	0.718
			.331	110.1	111.5	3.038	1.110
		sulfuric acid	1.001	105.1	108.6	1.033	.032
			.500	105.1	106.4	2.024	.704
			.333	105.1	105.8	3.022	1.105
40-4	-- ^c	sulfuric acid	1.007	105.1	110.1	1.041	0.040
			.503	105.1	107.5	2.033	0.710
			.336	105.1	106.6	3.023	1.105
40-5	-- ^c	sulfuric acid	1.007	105.1	110.1	1.041	.040
			.503	105.1	107.1	2.025	.705
			.336	105.1	106.2	3.012	1.099
40-6	-- ^c	sulfuric acid	1.102	105.1	111.4	.962	--
			.551	105.1	108.6	1.875	.628
			.367	105.1	107.1	2.774	1.020

^aSee reference 2 for data on these samples.^bMolecular weights measured in acetone with Mechrolab Osmometer.^cSamples insoluble in acetone.

G. Poly[3,3-bis(methylene)cyclobutane-1,1-dicarboxylate] by
Polymerization of Diisoamyl 3,3-bis(hydroxymethyl)cyclobutane-
1,1-dicarboxylate (VII)

1. Initial Studies

Difficulties encountered in purifying diethyl 3,3-bis(hydroxymethyl)-cyclobutane-1,1-dicarboxylate prompted (V) investigation of an alternate route to the desired polymer, poly[3,3-bis(methylene)cyclobutane-1,1-dicarboxylate], (VI). Diisoamyl 7-phenyl-6,8-dioxaspiro[3.5]nonane-2,2-dicarboxylate (VIII) is a white crystalline solid which has been synthesized many times in conjunction with other work (Reference 1). Because VIII is a solid, it may be purified to a much greater purity than liquid V. Further, acid hydrolysis of VIII should be easier than hydrolysis of V since an acetal is expected to hydrolyze easier than an oxetane. The reaction sequence envisioned is shown below.



The polymerization was carried out with programmed heating to a final temperature of 252°C. Below 213°C only isoamyl alcohol was obtained as volatile material. Elemental analysis and infrared spectra of the 213°C polymer suggested that polymerization occurred well beyond the singly-linked polymer; Table V and Figure 21-24 should be consulted to understand this conclusion.

When the polymer was heated from 213° to 252° very little isoamyl alcohol was evolved. Instead a liquid which was not volatile at 25°C at 1 mm-Hg pressure was evolved. The infrared spectrum of the liquid (Figure 25) showed hydroxyl and carbonyl absorption. The nmr spectrum (Figure 26) suggest an intact isoamyl group in the compound. Monomer VII has an elemental composition of C = 62.76% and H = 9.36%. The 213°C polymer had a composition of C = 59.37% and H = 5.95%. The 252° polymer had a composition of C = 60.92% and H = 7.86%. The 252°C polymer had a higher percentage of both carbon and hydrogen than did the 213°C polymer. The infrared spectrum of the 252°C polymer was free of hydroxyl absorption. A reasonable deduction is that pendant unreacted hydroxymethyl and carboamyloxy groups are lost when the polymer is heated from 213°C to 252°C.

Samples of 213°C- and 252°C polymer were forwarded to Air Force Materials Laboratory for evaluation.

2. Detailed Study of the Polymerization of Diisoamyl 3,3-bis-(hydroxymethyl)cyclobutane-1,1-dicarboxylate (VII)

The initial success in polymerizing diisoamyl 3,3-bis(hydroxymethyl)-cyclobutane-1,1-dicarboxylate prompted a more thorough study of the polymerization. Unfortunately some difficulty was encountered in the

hydrolysis of diisoamyl 7-phenyl-6,8-dioxaspiro[3.5]nonane-2,2-dicarboxylate. In contrast to the first experiments, hydrolysis of ester groups occurred as shown by isolation of isoamyl alcohol. The experiments were carried out with some reluctance because of doubts as to the quality of monomer VII.

Monomer VII was divided into four-gram samples and into one large thirty-four gram sample. A rather complicated polymerization procedure was used which is summarized in Table VI. The polymerization was followed by removing samples at various times. However, up to a certain point all samples experienced the same environment. Table VI should be consulted at this point.

Up to 110°C the samples were chloroform- and acetone-soluble. Samples heated at 110°C and above did not dissolve in chloroform. However, chloroform did extract a soluble material from the polymers heated to 110°C and higher. The soluble material was identified as compound VIII, the precursor to monomer VII. Compound VIII amounted to 5.4% of monomer VII. Discovery of low-molecular-weight VIII in the polymers caused abandonment of planned viscosity measurements.

Samples of polymer heated to 130°C were extracted with chloroform, dried at 147° and submitted to Air Force Materials Laboratory for evaluation. The sample submitted had a composition of C = 58.67 and H = 6.53. This approaches the theoretical limit for a doubly-linked spiro polymer; the theoretical values are C = 57.14, and H = 4.80. For a singly-linked polymer the limit is C = 60.92% and H = 7.87% (monomer VII; C = 62.76%, H = 9.36%). Except for the solubility to 100°C and the physical properties of toughness rather than brittleness,

TABLE VI

Date on Polymerization of Diisoamyl
3,3-bis(Hydroxymethyl)cyclobutane-1,1-dicarboxylate

Sample ^a Designation	Infrared Spectrum	Heating Cycle, °C and Time	Weight of Sample 134SP, Grams	Percentage ^b Weight Lost	Elemental ^c Analysis, %	Comment
Monomer 133 ^d	Figure 13	None	33.78	--	C, 63.21 H, 9.20	Monomer contains water plus isoamyl alcohol.
133-56	Figure 14	48°-16 hr., 56°-48 hr.	30.96	0.00	C, 63.26 H, 9.23	Lost 2.02 g at 48° and 0.80 g at 56°.
134A-80	Figure 15	As for 133-56 plus 80°-16 hr.	30.63	1.1	C, 63.46 H, 8.84	Viscous liquid; less than 0.3 g isoamyl alcohol in traps.
134A-90	Figure 16	As for 134A-80 plus 90°-24 hr.	27.32	11.7	C, 62.34 H, 7.94	Very viscous liquid; 7.7 g isoamyl alcohol in traps.
134B-100	Figure 17	As for 134A-90 plus 100°-48 hr.	24.86	19.7	C, 62.31 H, 8.10	Tough, highly viscous, sticky gum; 4 g isoamyl alcohol in traps.
134C-110	Figure 18	As for 134B-100 plus 110°-60 hr.	22.12	28.5	C, 60.61 H, 7.28	Solid film; 5 g isoamyl alcohol in traps.
140A	Figure 19	Identical to 134C-110	n.a.	n.a.		This sample is 134C-110 after extraction with chloroform which removes monomer precursor ^d . Sample did not melt when heated to 300°.
134-DEF-115	Figure 20	As for 134C-110 plus 115°-60 hr.	21.28	30.3		Less than 1 g isoamyl alcohol in traps.
143A	Figure 21	Identical to 134 DEF-115	n.a.	n.a.		This sample is 134-DEF-115 after extraction with chloroform which removes monomer precursor ^d .
145A-179	Figure 22	Sample 143A heated 147°-24 hr. 179°-24 hr.			C, 58.41 H, 5.66	A 1.001-g sample lost .118 g. Only isoamyl alcohol found in traps.

Table VI (Continued)

Sample ^a Designation	Infrared Spectrum	Heating Cycle, °C and Time	Weight of Sample 134SP, Grams	Percentage ^b Weight Lost	Elemental ^c Analysis, %	Comment
145A-213	Figure 23	As for 145A-179 plus 213°-60 hr.	n.a.	(39.2) ^e	C, 58.18 H, 5.57	An initial 6.89 g sample of 143A lost 0.90 g.
134-SP-130	Figure 24	48°-16 hr., 56°-48 hr., 80°-16 hr., 90°-24 hr., 100°-24 hr., 110°-60 hr., 115°-60 hr., 130°-60 hr.	20.38	34.2	Not received	Polymer is a clear flexible sheet. Work on this material is still in progress.
Theoretical Double-strand Polymer	--	--	(16.49)	51.2	C, 57.14 H, 4.80	
Theoretical Single-strand Polymer			(25.14)	25.6	C, 60.92 H, 7.87	

a. All polymer samples are derived from Monomer-133

b. Determined on the assumption that sample 133-56 is free of entrained solvents. Calculation made by subtracting final weight from initial weight and dividing by initial weight.

c. Elemental analyses for samples monomer-133, 133-56, 134A-80, 134A-90, 134B-100, 134C-110 have an error associated with the inclusion of monomer precursor in the polymer.

d. Monomer precursor is diisoamyl 7-phenyl-6,8-dioxaspiro[3.5]nonane-2,2-dicarboxylate.

e. Calculated figure based on weight loss.

there is no compelling evidence to support a doubly-linked structure in preference to a cross-linked single-chain polymer.

SECTION III

EXPERIMENTAL

All temperatures in this report are in degrees centigrade. Melting points were determined in capillary tubes. Infrared spectra were observed with a Perkin-Elmer Infracord Spectrophotometer or, where indicated, on a Perkin-Elmer Model 621 Infrared Spectrometer. Nuclear magnetic resonance spectra were observed with a Varian A-60 Spectrometer. Unless otherwise indicated, chemicals were the best grade commercially available for normal chemical synthesis.

A. Synthesis of Dispiro[3.1.3.1]decane-2,8-dicarboxylic acid

This key monomer was prepared by the synthetic sequence described in References 1 and 2.

B. Poly(trispiro[3.1.1.3.1.1]dodecane-1,3-dione) (I) by Polymerization of Dispiro[3.1.3.1]decane-2,8-dicarboxylic Acid:

1. Purification of Reagents

- a. Dispiro[3.1.3.1]decane-2,8-dicarboxylic acid. This diacid was purified by sublimation at 160° (1 mm), recrystallization from distilled water, and sublimation at 160° (1 mm).
- b. Triethylamine. The amine (Eastman Catalog No. 616) was purified by heating 24 hours under reflux with p-toluenesulfonyl chloride to remove primary and secondary amines. Triethylamine was then distilled onto sodium, distilled from sodium under nitrogen and stored over sodium. Prior to use, triethylamine was freshly distilled from sodium under nitrogen.

- c. Thionyl chloride. Thionyl chloride (Matheson, Coleman and Bell, Catalog No. TX-535) was heated under reflux for 24 hours with triphenyl phosphite and then distilled at a constant boiling point of 76°C according to the procedure described by Fieser and Fieser (Reference 8).
- d. Benzene. Thiophene-free benzene was distilled from sodium and stored over lead-sodium alloy.

2. Poly(trispiro[3.1.1.3.1.1]dodecane-1,3-dione) (I)

Synthesis of this polymer has been described earlier (Reference 1). In some of the work, experimental procedures were carried out in a Fischer Isolator Box containing a dry nitrogen atmosphere. Initial results were unsatisfactory due to incorrect experimental technique. Eventually results were obtained equivalent to, but not better than, those reported in Reference 1.

Typically 1.0 g. of dispiro[3.1.3.1]decane-2,8-dicarboxylic acid was reacted with 5.0 g. of thionyl chloride at 40° until a clear solution formed. Excess thionyl chloride was removed under reduced pressure (< 1 mm) to a final temperature of 40°. Benzene (10 ml), freshly distilled from sodium inside the Isolator Box, was added. Then triethylamine (5 ml), freshly distilled from sodium inside the Isolator Box, was added. The benzene solution was brought to reflux for several hours. Polymer I was separated by filtration and washed with water to remove triethylamine hydrochloride.

Inside the Isolator Box the atmosphere of dry nitrogen was maintained by a continuous input of dry nitrogen which was bubbled first through sulfuric acid and then passed over sodium hydroxide

pellets. Inside the box a dish of diphosphorus pentoxide and another dish of sodium hydroxide were continuously exposed. In this way any triethylamine or thionyl chloride which escaped reaction vessels was absorbed.

In Table VII some experimental runs are summarized.

A polymerization which gave poor Polymer I was carried out as follows and is described because the material was used for reaction with ethane-1,2-dithiol. Dispiro[3.1.3.1]decane-2,8-dicarboxylic acid was twice crystallized from water and then resublimed. This diacid (0.90 g) was treated with 5 ml of thionyl chloride (purified by distillation from triphenyl phosphite). After the mixture remained at 40° for 24 hours, excess thionyl chloride was removed under vacuum. Onto the dispiro[3.1.3.1]decane dicarbonyl chloride was distilled purified benzene which was distilled from sodium. To the resulting solution was added 8 ml of triethylamine which had been purified by refluxing with *p*-toluenesulfonyl chloride and distilling twice from sodium.

Polymer formed immediately. After heating to reflux the mixture was filtered. Polymer (0.60 g) was washed with water and dried. The infrared spectrum showed a doublet carbonyl peak indicative of relatively short chain length (see References 1 and 2).

The sample was analyzed for carbon, hydrogen and chlorine. The theoretical and found C, H and Cl values are as follows:

Monomer: C, 63.87%; H, 7.15%

Dimer with terminal-COOH: C, 70.0%; H, 6.7%

Trimer with terminal-COOH: C, 76.0%; H, 7.1%

TABLE VII

Polymerizations of Dispiro[3.1.3.1]decane-2,8-dicarboxylic Acid
to give Poly(trispiro[3.1.1.3.1.1]tridecane-1,3-dione)^a

Expt.	Reactants ^b	Conditions ^b	
1.	0.840 g. (3.75 mmole) monomer ^c 10 ml. thionyl chloride 75 ml. benzene 2.0 g. (20 mmole) triethylamine	Refluxed 48 hours	50 mg. of high-grade polymer whose infrared spectrum did not show significant C=O due to COOH. Strong 5.78 micron C=O absorption. 45.0 mg. of low-grade polymer with 5.91 and 5.78 micron bands of about equal intensity.
2.	1.00 g. (4.46 mmole) monomer ^c 10 ml. thionyl chloride 150 ml. benzene 4.0 g. (39 mmole) triethylamine	Refluxed 24 hours; N ₂ Atm.	108 mg. of high-grade polymer whose infrared spectrum had a strong 5.78 micron absorption with a very, very weak shoulder. Assumed to be reasonably high molecular weight polymer. 600 mg. of polymer with significant 5.78 micron absorption.
3.	1.00 g. (4.46 mmole) monomer ^c 10 ml. thionyl chloride 75 ml. para-xylene 4.0 g. (39 mmole) tripropylamine	Refluxed 4 hours; N ₂ Atm.	Intractable colored material.
4.	1.00 g. (4.46 mmole) monomer ^c 10 ml. thionyl chloride 75 ml. toluene 4.0 g. (39 mmole) tripropylamine	Refluxed 4 hours; N ₂ Atm.	Viscous red oil with very complex infrared spectrum. Intractable material.

Table VII (Continued)

Expt.	Reactants ^b	Conditions ^b	
5.	1.00 g. (4.45 mmole) dispiro-decane diacid ^c 10 ml. thionyl chloride 75 ml. benzene 4.0 g. (39 mmole) triethylamine	Refluxed 72 hours; N ₂ Atm.	Hot spots on flask walls gave yellow lower molecular weight (<i>vide infra</i>) polymer. Material not in contact with walls was white and had a clean infrared spectrum corresponding to low-grade polymer (5.91 micron absorption).
6.	0.90 g. monomer 5 ml. thionyl chloride 5 ml. triethylamine	Heated 16 hours under reflux in Isolator Box under N ₂ Atm.	No polymer precipitated. Low molecular weight benzene polymer was obtained which was discolored. Reagents were not distilled just before use.
7.	Identical to Expt. 6	Identical to Expt. 6	No satisfactory polymer. Reasons unknown.
8.	Identical to Expt. 6	Identical to Expt. 6	No satisfactory polymer. Reasons unknown. It was suspected that the atmosphere within the Isolator Box might have been at fault.
9.	0.92 g. monomer ^c 5 ml. thionyl chloride 8 ml. triethylamine 90 ml. benzene	Heated 16 hours under reflux in Isolator Box under N ₂ Atm.	Obtained 0.35 g. white Polymer I. Appeared to be equal in quality to polymer obtained earlier: 0.43 g. of benzene-soluble material, mw 900, estimated as timer and tetramer. Had open dishes of diphosphorus pentoxide and sodium hydroxide in Isolator Box.

Table VII (Continued)

Expt.	Reactants ^b	Conditions ^b	Results
10.	0.86 g. monomer ^c 8 ml. thionyl chloride 8 ml. triethylamine 80 ml. benzene	Warmed at 40° for two days in Isolator Box under N ₂ Atm.	Obtained 0.24 g. white Polymer I. 0.50 g. of yellow polymer soluble in benzene. mw 800-1000.
11.	4.00 g. (17.8 mmole) monomer ^c 25 ml. thionyl chloride 40 ml. triethylamine 600 ml. benzene	Heated 3 days under reflux under N ₂ Atm.	Obtained 1.0 g. of reasonably good polymer which was sent for evaluation. (See Figure 1 for infrared spectrum). Elemental analysis was unsatisfactory for the proposed structure. Anal. Found: C, 73.95; H, 6.87; O, 19.18. Calc: C, 78.00; H, 6.00; O, 16.00.
12.	1.00 g. monomer ^c 5 ml. thionyl chloride 5 ml. triethylamine 70 ml. benzene	Heated 24 hrs. under reflux	Poor sample. Doublet carbonyl in infrared spectrum. Anal. Found: C, 73.77%; H, 7.25%; Cl, 0.56%.

-
- a. Experiments which were obvious failures and not worked up are omitted.
b. Diacid converted to diacid chloride by thionyl chloride. Excess thionyl chloride removed at
reduced pressure, solvent added and then triethylamine added.
c. Dispiro[3.1.3.1]decane-dicarboxylic acid.

Found: C, 73.77%; H, 7.25%; Cl, 0.56%

The analysis confirms the conclusion based on the infrared spectrum.

The polymer has a low molecular weight.

C. Poly(1,1,3,3-tetrafluorotrispiro[3.1.1.3.1.1]dodecane) (II) by
Reaction of Poly(trispiro[3.1.1.3.1.1]dodecane-1,3-dione)
with Sulfur Tetrafluoride

A small pressure reaction vessel designed to hold 5000 p.s.i. at 200°C was fabricated from a 8-cm piece of 1/2" stainless steel tubing, Swagelok Cap, Swagelok Tube-to-Pipe adapter, and a Whitey Teflon-packed stainless steel valve. In this small pressure reactor was placed 0.228 g. of poly(trispiro[3.1.1.3.1.1]dodecane-1,3-dione) (I). Approximately 1.0 g. of sulfur tetrafluoride (Peninsular Chem Research) was then condensed into the reactor. The reactor was heated in 25° steps to 150° over a 4-hr. period and held at 150° for 16 hr. After venting, the contents of the flask were washed with water and dried. A brown powder remained.

The brown polymer II had an infrared spectrum (see Figure 3) free of carbonyl absorption. Absorptions typical for carbon-fluorine bonds appear in the range of 10-14 microns.

When the polymer was heated in a Stanton Thermal Balance at a rate of 7°/min. under helium the first weight loss occurred at 380°. Weight loss was very rapid at 410°. When a 21.0 mg sample of II was heated at 300° under nitrogen for 16 hr. a weight loss of 1.6 mg occurred. The infrared spectrum of II appeared unchanged. When the temperature was raised to 350° for an additional 16 hr., 14 mg of weight was lost. The infrared spectrum of the residue was featureless

(carbon?). All evidence of carbon-fluorine absorptions had disappeared. The sample was not soluble in any conventional solvent.

In a reaction between Polymer I and sulfur tetrafluoride at 125° only partial replacement of carbonyl groups occurred as shown by infrared analysis.

D. Attempted Wolff Kishner-Reduction of Poly(trispiro[3.1.1.3.1.1]-dodecane-1,3-dione)

The procedure described by Vogel was used (Reference 9). Some results are summarized in Table VIII.

E. Reaction of Ethane-1,2-dithiol and Poly(trispiro[3.1.1.3.1.1]-dodecane-1,3-dione) (I) to give Thioketal Polymer IV

Conversion of Polymer I to Polymer IV was accomplished by a modification of a procedure used by Buchta and Ahne (Reference 6). To 5.0 ml of 96% boron trifluoride etherate was added 0.20 g. of low-grade Polymer I. The mixture was vigorously stirred and 0.50 ml of ethane-1,2-dithiol added. The resulting mixture was stirred and heated 3 days at 60°C. The mixture was poured into 20 ml of isopropyl alcohol and the product filtered off. Additional washings were made with isopropyl alcohol.

The product Polymer IV had a different infrared spectrum (see Figure 5) from the starting Polymer I (see Figure 4). Most of the carbonyl group absorption had disappeared. A carbon-sulfur absorption at 9.5 microns appeared in the product. Comparison of the carbon-hydrogen absorptions to carbonyl absorptions can be made more easily in the infrared spectrum shown in Figures 6 and 7. These spectra were

observed in tetrachloroethylene and Kel-F oil mulls. The residual carbonyl absorptions are probably due to carboxyl end-groups.

Temperature was found to be important. At reflux temperature a red oil formed. At room temperature only partial reaction occurred. Order of addition was important. When Polymer I and ethane-1,2-dithiol were mixed initially, a red oil was obtained.

In another experiment Polymer IV was prepared from polymer I by treating 0.49 g of polymer I in 12.5 ml of boron-trifluoride etherate with 1.5 ml of ethane-1,2-dithiol. When heated to 60° the reaction became a clear solution. After 48 hours a tar was present which formed a solid when triturated with sodium methoxide in methanol. After considerable difficulty, 0.39 g of solid was obtained.

Elemental analysis of the sample was not encouraging. The analysis confirmed that a low molecular weight product was obtained and, that complete reaction of carbonyl groups had not been achieved. The infrared spectrum confirmed this and showed the presence of carboxylic acid groups (end groups) as well as some carbonyl assigned to cyclobutanone absorption. Anal. Calc. for Dimer ($C_{28}H_{36}S_4O_4$) with -COOH end group: C, 59.5%, H, 6.4%; S, 22.6%; O, 11.3%. Found: C, 63.4%; H, 6.84%; S, 17.36%.

F. Attempted Desulfurization of Thioketal Polymer IV

1. Preparation of Raney Nickel (W-2)

Catalyst was prepared as described by R. Mozingo (Reference 10). In a trial desulfurization the thioketal from cyclohexanone and ethane-1,2-dithiol was converted into cyclohexane.

2. Attempted Desulfurization of Thioketal Polymer IV

A mixture of 0.30 g of IV and 3.0 g of Raney nickel (W-2) was heated under reflux in ethanol for 48 hours. After filtration the reaction mass was treated with hydrochloric acid to dissolve nickel and with hydrogen peroxide-hydrochloric acid to dissolve nickelous sulfide. The residue was isolated.

The product was free of nickel as shown by oxidation of the solid with nitric acid followed by ammonia.

The solid had an infrared spectrum which showed carbonyl absorption at 5.82 microns. Possible sulfone absorption occurred at 8.6 microns (1160 cm^{-1}). The analysis gave C, 46.47%, H, 4.13% and S, 13.80% which also indicated incorporation of oxygen into the compound.

G. Polymerization of Diethyl 3,3-bis(Hydroxymethyl)cyclobutane-1,1-dicarboxylate (V)

1. Improved Synthesis of Diethyl 3,3-bis(Hydroxymethyl)cyclobutane-1,1-dicarboxylate (V)

Recrystallized 3,3-bis(iodomethyl)oxetane was prepared from 3,3-bis(chloromethyl)oxetane by a procedure described previously (References 1 and 11).

To 1500 ml. of dry xylene was added 322 g. (2.00 moles) of diethyl malonate. The mixture was heated to reflux and a few ml. of solvent distilled to remove any last traces of water. To this was added 46 g. (2.0 moles) of sodium metal over a 2-hr. period. 3,3-bis(Iodomethyl)-oxetane (321 g., 0.95 moles) was added and the reaction mixture was filtered, washed with 800 ml. of saturated sodium bicarbonate solution, and then with water. The xylene solution was dried over calcium

chloride and distilled. Crude product was distilled under reduced pressure over a broad temperature range, 110-135° (0.35 mm). Redistillation, b.p. 107-115° (0.15 mm-Hg), gave 158 g (0.68 mole, 64%) of diethyl 6-oxaspiro[3.3]-heptane-1,1-dicarboxylate. No impurities could be detected by analysis of the nmr spectrum.

A higher yield was obtained when potassium was used in place of sodium. To a flask containing 3 l. of xylene and 161 g. (1.00 mole) of diethyl malonate at a gentle reflux was added 80.0 g. of potassium metal over a 3-hour period. To this was added 338 g. (1.00 mole) of 3,3-bis(iodomethyl)oxetane. The resulting mixture was heated and stirred under reflux for 10 days. Solids were filtered off and the filtrate washed with 500 ml. of saturated sodium bicarbonate solution. Solvent was distilled off from the organic phase. The product was distilled at 115° (0.1 mm). Product amounted to 190 g. (0.785 mole, 78.5%). Distilled diethyl 6-oxaspiro[3.3]heptane-2,2-dicarboxylate had MW 243 (theoretical 242) as determined by a Mechrolab osmometer. The proton nmr spectrum was free of absorptions not associated with the product. The parent peak of the product in a mass spectrogram was 242.

2. Synthesis of Diethyl 3,3-bis(Hydroxymethyl)cyclobutane-1,1-dicarboxylate (V)

Several methods for hydrolysis of diethyl 6-oxaspiro[3.3]heptane-2,2-dicarboxylate were investigated. Acid strength was varied from 0.1 to 3.0 N and temperature from 25° to 100°. The procedure described here gave III which was most easily polymerized and which could be

polymerized into a polymer which was acetone soluble through an extended part of the polymerization.

Equal amounts of 2 N sulfuric acid (50.0 ml) and diethyl 6-oxaspiro-[3.3]heptane-2,2-dicarboxylate were mixed at room temperature and stirred for 24 hours. The initial two phases almost became one phase. The smaller phase (~ 5.0 ml) was separated and set aside. The larger phase was extracted with ten 50-ml. portions of diethyl ether. Combined extracts were treated with anhydrous sodium carbonate. The sodium carbonate was separated. Ether was removed by blowing dry nitrogen over the surface of the solution. As much of the residual ether as was possible was removed at 50° (1.0 mm).

3. Comparison Polymerizations of Low-purity Monomer V

Two 5.0-g. samples of V were purged for 1.0 hour with dry nitrogen. To one sample was added .010 g. of calcium acetate dihydrate and 0.003 g. of antimony(III) oxide. Both samples were heated at the same rate according to the following schedule:

<u>Time, Minutes</u>	<u>Temp., °C</u>
0	23
20	105
35	170
45	198
120	200

Nitrogen was bubbled through the samples continuously. The uncatalyzed sample became viscous more rapidly. From the uncatalyzed sample was evolved water and ethanol as shown by nmr. The sample with catalyst was partially soluble in acetone. Both polymers were insoluble in benzene. In the text these polymerizations are described in Section II-F-1.

In a parallel set of experiments (designated runs 3, 4, and 5 in the text) three 5.0 g. samples of V were polymerized in the presence of p-toluenesulfonic acid, (run 3), antimony(III) oxide and calcium acetate dihydrate catalyst (run 4), and in hexamethylphosphoramide solvent (run 5). Nitrogen was bubbled through polymerization mixtures and the reaction vessels were heated according to the following schedules:

<u>Time, Minutes</u>	<u>Temp., °C</u>
0	25
20	95
35	140
45	165
55	205
75	205
120	225
150	250
300	250

Solid brown polymers were obtained from run 3 and 4. No solid formed in run 5. The solid polymers were insoluble in benzene and acetone. They were not further investigated because it was concluded that monomer V used in the work was of too low purity to give meaningful results.

4. Controlled Polymerization of Acid-containing and Acid-free
Diethyl bis-3,3-(Hydroxymethyl)-cyclobutane-1,1-dicarboxylate
(V)

A modification of the procedure given in Section III-F-2 was used to hydrolyze diethyl 6-oxaspiro [3.3]heptane-2,2-dicarboxylate to give monomer V. A mixture of 30.0 g. of oxetane and 30.0 g. of 2.0 N sulfuric acid was stirred for 3 days at 35°C. The solution was neutralized with sodium bicarbonate and monomer V extracted with four 50-ml. portions of methylene chloride. The extracts were treated

with activated charcoal, filtered through sodium bicarbonate, and evaporated under a stream of nitrogen. Residual solvent was removed with a rotary evaporator at 1 mm. A property of the monomer was slow polymerization at 60°C without foaming or brittleness. See Table III for polymerization data. The nmr spectrum of this sample of monomer V did not show the presence of unreacted oxetane.

In another controlled preparation of VII, the procedure was similar to the above. However, in the work-up the reaction solution was not neutralized. The methylene chloride extracts were not treated to remove residual traces of acid. This monomer V polymerized rapidly at 60°C with foaming and gave a brittle foamed polymer. See Table III for polymerization data.

Polymerization of monomer V was carried out in Teflon-covered cupcake pans. Into each cupcake hole was placed 2.0 g. of monomer. Acid-containing V prepared by eliminating bicarbonate washes was used for samples labeled 34-A-(-). Neutral monomer V was used for samples labeled 34-B-(-). In Table III the conditions used for polymerizing samples are described. The key observation was that polymer formed from acid-containing monomer V was brittle and foamed. Polymer from acid-free monomer was clear, tough, and flexible. In addition the polymer from acid-free monomer V remained soluble over a greater degree of polymerization than did the polymer from acid-containing monomer V.

Figures 27-33 are infrared spectra of samples of polymer from acid-free monomer V.

5. Partial Polymerization of Higher Purity Diethyl 3,3-bis-(Hydroxymethyl)cyclobutane-1,1-dicarboxylate (V)

A modified procedure for synthesizing monomer V was developed. Sodium bisulfate was substituted for sulfuric acid in the hydrolysis of diethyl 6-oxaspiro[3.3]heptane-2,2-dicarboxylate (oxetane). The oxetane was prepared according to the procedure described in Section III-G-1, using potassium for the base.

In a 1-liter Erlenmeyer flask was placed 100 g (.413 mole) of diethyl 6-oxaspiro[3.3]heptane-2,2-dicarboxylate and 400 ml of 10% sodium bisulfate solution. The flask was heated and shaken for 3 days at 60°. After 3 days the initial two phases were one. The reaction mixture was cooled and washed with two 100-ml portions of diethyl ether to remove residual water-insoluble material. The water solution was neutralized with sodium carbonate and water was then removed with a rotary evaporator. Acetone was distilled from potassium permanganate and then used to extract organic material. The acetone solution was filtered and dried overnight over calcium chloride. The acetone solution was filtered and then acetone was removed with a rotary evaporator.

Residual 3,3-bis(hydroxymethyl)cyclobutane-1,1-dicarboxylate amounted to 93 grams (0.37 mole, 90%). When analyzed by nmr spectroscopy it was free of all impurities except acetone.

A mixture of 18.0 grams of diethyl 3,3-bis(hydroxymethyl)-cyclobutane-1,1-dicarboxylate and 0.020 g of a 1:4 mixture of antimony(III) oxide and calcium acetate dihydrate was divided into six three-gram portions and placed into a Teflon cupcake pan. These

TABLE III

Controlled Polymerization of Acid-Containing and Acid-free Diethyl

3,3-bis(Hydroxymethyl)-cyclobutane-1,1-dicarboxylate (I)

Sample (2.0 g)	Monomer Used	Time Under N ₂	Temp., °C	Physical Characteristics
34-A-1	Acidic*	8 hr.	40	Insoluble, foamed, soft and spongy at room temperature.
34-A-2	Acidic	8 hr.	60	Insoluble, foamed, extremely brittle at room temperature.
34-A-3	Acidic	8 hr.	80	Insoluble, foamed, brittle at room temperature.
34-A-1	Acidic	15 days	40	All samples showed no significant change in physical characteristics on continuous heating.
34-A-2	Acidic	15 days	60	No change.
34-A-3	Acidic	15 days	80	
34-B-1	Neutral**	6 days	30	
34-B-1	Neutral	3 days	80	
34-B-1	Neutral	4 days	80	Residual OH absorption in infrared spectrum. See Figure 27.
34-B-1	Neutral	5 days	120	Insoluble, hard brown solid at room temperature.
34-B-1	Neutral	5 days	200	Identical with 34-B-7. See Figure 33.
34-B-2	Neutral	6 days	40	No change.
34-B-2	Neutral	9 days	40	No change.
34-B-3	Neutral	6 days	60	No change.
34-B-3	Neutral	9 days	60	No change.
34-B-3	Neutral**	5 days	120	Hard brown solid at room temperature. See Figure 28.
34-B-3	Neutral	5 days	200	Figure 29.
34-B-3	Neutral	5 days	200	Insoluble. Identical with 34-B-7. See Figure 33.
34-B-4	Neutral	3 days	80	Slight increase in viscosity.

Table III (Continued)

Sample (2.0 g)	Monomer Used	Time Under N ₂	Temp., °C	Physical Characteristics
34-B-4	Neutral	9 days	80	Insoluble, hard brown solid at room temperature with residual OH absorption in the infrared spectrum.
34-B-4	Neutral	5 days	120	Insoluble, hard brown solid at room temperature with less OH absorption in the infrared spectrum. See Figure 30.
34-B-4	Neutral	5 days	200	Identical with 34-B-7. See Figure 33.
34-B-5	Neutral with Sb ₂ O ₃ / Ca(O ₂ CCH ₃) ₂ . 2H ₂ O Catalyst	3 days	80	Extremely viscous liquid at room temperature.
		9 days	80	Insoluble, hard brown solid at room temperature with residual OH absorption in the infrared spectrum.
		5 days	120	Insoluble, hard brown solid at room temperature with less OH absorption in the infrared spectrum. See Figure 31.
		5 days	200	Insoluble, tacky brown solid at room temperature.
34-B-6	Neutral with p-toluene- sulfonic acid catalyst	3 days	80	Insoluble, hard brown solid at room temperature. See Figure 32.
		4 days	120	Insoluble, hard brown solid at room temperature.
34-B-7	Neutral	12 days	80	Insoluble, hard brown solid at room temperature.
		5 days	120	Insoluble, hard brown solid at room temperature with residual OH absorptions in the infrared spectrum.
		4 days	200	Insoluble, strong-hard brown solid with small OH absorption in the infrared spectrum. See Figure 33.

*Monomer obtained from extraction of unneutralized hydrolysis mixture.

**Monomer obtained from extraction of sodium bicarbonate-neutralized hydrolysis mixture.

NOTE: Previous samples of polymer began to bleed small droplets of sulfuric acid on standing for long periods of time.

six samples were heated under vacuum according to the following schedule:

<u>Time, hrs</u>	<u>Temp., °C</u>	<u>Pressure, mmHg</u>
23	45	1
24	60	1
24	70	1
71	80	1
48	100	1
48	110	1
72	120	1
48	130	1

The final polymer showed a significant hydroxyl absorption clearly indicating incomplete polymerization.

This sample has been submitted to Air Force Materials Laboratory, Wright-Patterson Air Force Base as sample DIS-51.

6. High-Temperature Catalyzed and Uncatalyzed Polymerization of Diethyl 3,3-bis(Hydroxymethyl)cyclobutane-1,1-dicarboxylate (V)

To 5 liters of freshly-distilled xylene was added 840 g (5.23 moles) of diethyl malonate. The stirred solution was heated to just below reflux temperature and 245.5 g (6.30 moles) of potassium were added at a rate to maintain gentle reflux. When all potassium had dissolved the solution was heated to maintain gentle reflux. Then 1014 g (3.00 moles) of bis(iodomethyl)propane-1,3-diol were added at a rate that maintained reflux.

The mixture was heated and stirred for eight days under reflux. Work-up was by procedures described in Section III-F-1, and Reference 1. Distillation gave 550 g. (2.26 moles, 75.3%) of diethyl 6-oxaspiro-[3.3]heptane-1,1-dicarboxylate (oxetane). The oxetane was redistilled and a center cut taken for hydrolysis to monomer V. The infrared and

nuclear magnetic resonance spectra of the center cut of oxetane are shown as Figures 9 and 10.

A mixture of 100 g. of this oxetane and 400 ml. of 10% sodium bisulfate was heated at 60° and shaken continuously for 3 days. Traces of insoluble material were removed from the final aqueous solution by extraction with 100 ml of ether. The aqueous phase was neutralized with sodium carbonate and placed in a 1000-ml. round-bottomed flask. Water (300 ml) was removed at room temperature with a rotary evaporator. Acetone was added to precipitate inorganic salts. The resulting solution was permitted to stand overnight over calcium chloride. After filtering the remaining solution was placed in a rotary evaporator and all solvent removed. Monomer V remained as an oily viscous liquid and was used directly for polymerizations. The infrared spectrum of monomer V used for polymerization is shown in Figure 11.

Monomer V was divided into two 18-g. portions. To one of the 18-g. samples was added 0.040 g. of calcium acetate dihydrate and 0.012 g. of antimony(III) oxide. The catalyzed and uncatalyzed 18-g. samples were each divided into six 3.0-g. samples and placed in Teflon-coated cupcake pans. They were heated in the same oven to assure an identical temperature cycle.

<u>Time, Days</u>	<u>Temperature, °C</u>	<u>Conditions</u>
7	90	N ₂ atmosphere
4	130	N ₂ atmosphere
2	148	1 mm-Hg
2	179	1 mm-Hg
2	213	1 mm-Hg

After polymerization for 11 days (130°) the catalyzed sample (initial weight 18.00 g.) weighed 12.40 g.; after 17 days the weight was 10.74 g. Theoretically the lowest weight obtainable for complete

polymerization would be 11.20 g. Uncertainty in calculations is introduced because monomer V contains an unknown but real amount of solvent. Comparison of carbonyl and hydroxyl absorptions in the infrared spectra of the polymers taken after 11 and 17 days (Figures 12 and 14) permits an estimation of the amount of polymerization that had occurred at these times.

For the catalyzed sample (initial weight 18.00 g.) the weight was 9.81 g. after 11 days (130°) and 9.35 g. after 17 days (213°). The infrared spectra for these corresponding times are shown in Figures 13 and 15.

Anal. Found for Uncatalyzed Polymer: C, 57.66%; H, 5.81%.

Anal. Found for Catalyzed Polymer: C, 58.56%; H, 6.09%.

Both polymers were obtained as brittle solids, insoluble in common solvents.

7. Detailed Study of the Polymerization of Diethyl 3,3-bis-(Hydroxymethyl)cyclobutane-1,1-dicarboxylate (V)

The detailed polymerization is described in Section II-F-7 of this report.

Monomer V used in the polymerization was prepared as described in Section IV-F-2 of this report. Sulfuric acid was used to hydrolyze diethyl 6-oxaspiro[3.3]heptane-2,2-dicarboxylate.

H. Polymerization of Diisoamyl 3,3-bis(hydroxymethyl)cyclobutane-1,1-dicarboxylate (VII)

1. Preparation of Monomer VII Precursor, Diisoamyl 2,2-bis-(hydroxymethyl)-7-phenyl-6,8-dioxaspiro[3.5]nonane (VIII)

Diisoamyl 7-phenyl-6,8-dioxaspiro[3.5]nonane 2,2-dicarboxylate (IX) was prepared by the method described previously (Reference 1).

For polymerization work 200 g. of VII were recrystallized eight times from methanol to constant m.p. 50.9-51.1°.

2. Preparation of Diisoamyl 3,3-bis(Hydroxymethyl)cyclobutane-1,1-dicarboxylate (VII)

About 150 ml of water was brought to reflux. To this was added 54 g. of VIII. Then 6.0 g. of 97% sulfuric acid was very slowly added. Benzaldehyde was steam-distilled. Freshly boiled water was added to maintain at least 100 ml of aqueous phase. After all benzaldehyde had steam-distilled the aqueous phase was cooled. The organic phase was taken up in 200 ml of ACS reagent grade diethyl ether. The ether layer was washed 5-times with 100 ml of 10% sodium carbonate solution. After a water wash the ether was dried three times with anhydrous magnesium sulfate.

Ether was evaporated under vacuum to give 40 g. of VII. The infrared spectrum is shown as Figure 23.

3. Polymerization of 3,3-bis(Hydroxymethyl)cyclobutane-1,1-dicarboxylate (VII)

An eighteen gram sample of VIII was placed in a glass flask and heated under vacuum according to the following schedule:

<u>Time, hrs</u>	<u>Temp., °C</u>	<u>Pressure, mm-Hg</u>
24	90	1
24	110	1
24	130	1
24	147	1

As much sample as could be broken free from the glass was transferred to a drying pistol and heated for 24 hours at 179° and then 24 hours at 213°.

This sample has been submitted to Air Force Materials Laboratory as sample CMS-123A.

Another 18-g. sample was divided into 3-g. portions in a Teflon coated cupcake tin. These were heated under vacuum according to the following schedule:

<u>Time, hrs</u>	<u>Temp., °C</u>	<u>Pressure, mm-Hg</u>
24	80	1
24	100	1
24	130	1

The solid samples were then transferred to a drying pistol and heated as follows:

<u>Time, hrs</u>	<u>Temp., °C</u>	<u>Pressure, mm-Hg</u>
24	147	1
24	179	1
24	213	1

This sample was removed and analyzed. It is referred to as 213° polymer in Section II-G-1.

Analysis: Calcd. See Figure 35 and Table IX; Found: C, 59.37; H, 5.95.

This sample should be the same as sample CMS-123A as it was subjected to the same conditions. A small amount of this material has been submitted to Air Force Materials Laboratory as sample CMS-124A.

Only isoamyl alcohol was obtained as volatile material to this point in the polymerization.

The infrared spectrum of CMS-124A is shown in Figure 22.

The bulk of sample CMS-124A was heated at 252° for 24 hours. A liquid distilled from the sample which was not volatile at 25° and

1 mm-Hg. The infrared spectrum of this liquid is shown as Figure 25 the nmr spectrum appears as Figure 26. The liquid is unidentified.

From a 5.20 g sample of CMS-124A, 1.32 g of unknown liquid was evolved.

The clear brown polymer was submitted to Air Force Materials Laboratory as sample CMS-125A.

Analysis: Calcd. See Figure 35 and Table IX. Found: C, 61.42%; H, 6.00%.

4. Detailed Study of the Polymerization of Diisoamyl 3,3-bis-(Hydroxymethyl)cyclobutane-1,1-dicarboxylate (VII)

Monomer VII was prepared by the procedure described in the immediately-preceding pages from 7-times recrystallized diisoamyl 7-phenyl-6,8-dioxaspiro[3.5]nonane-2,2-dicarboxylate. The reaction did not proceed cleanly as in the earlier reaction (preceding pages). Isoamyl alcohol distilled with the benzaldehyde which indicated hydrolysis of ester groups in addition to the desired acetal cleavage. From 180 g. of benzaldehyde acetal was obtained only 62 g. of the desired title monomer.

Table VI in the discussion section (II-G-2) should be consulted for many aspects of the experimental work.

Into a 6-part Teflon-covered cupcake pan was placed 4.0 g. samples of monomer. The monomer was designated Monomer-133. The six parts of the pan were labeled A, B, C, D, E and F and the samples in each designated 134A, 134B, etc.

To a 6-inch square Teflon-covered cake pan was added 33.78 g. of Monomer-133. This sample was designated 134SP.

TABLE IX

Theoretical Elemental Compositions for Polymer from Diisoamyl3,3-bis(Hydroxymethyl)cyclobutane-1,1-dicarboxylate

	<u>Single strand</u>	<u>Double strand</u>
Monomer	$C_{18}H_{32}O_6$ C, 62.76% H, 9.36%	-- -- --
Dimer	$C_{31}H_{52}O_{11}$ C, 61.79% H, 8.72%	$C_{26}H_{40}O_{10}$ C, 60.95% H, 7.86%
Tetramer	$C_{57}H_{92}O_{21}$ C, 61.49% H, 8.33%	$C_{42}H_{56}O_{18}$ C, 59.43% H, 6.65%
Heptamer	$C_{96}H_{152}O_{36}$ C, 61.26% H, 8.14%	$C_{66}H_{80}O_{30}$ C, 58.57% H, 5.96%
Decamer	$C_{135}H_{212}O_{50}$ C, 61.16% H, 8.06%	$C_{90}H_{104}O_{42}$ C, 58.19% H, 5.64%
Infinite Chain	$C_{13}H_{20}O_5$ C, 60.92% H, 7.86%	$C_8H_8O_4$ C, 57.14% H, 4.80%

Both pans were placed in a vacuum oven at 1 mm and heated according to the cycle given below:

<u>Time, hrs</u>	<u>Temperature, °C</u>	<u>Comments</u>
16	48	Loss of 2.02 g. from 134 SP. This is solvent loss.
56	56	Loss of 0.80 g. from 134 SP. More solvent loss. The 30.96 g. left at this time is the reference point considered to be solvent-free monomer. Removed sample 133-56.
16	80	Wt. of 134 SP = 30.63 g. Removed part of 134A as sample 134A-80.
24	90	Wt. of 134SP = 27.32 g. Removed remainder of 134A as 134A-90.
48	100	Wt. of 134 SP = 24.86 g. Removed sample 134B as 134B-100.
60	110	Wt. of 134 SP = 22.12 g. Removed sample 134C as 134C-110.
60	115	Wt. of 134 SP = 21.28 g. Removed samples 134D, 134E, and 134F as 134-DEF-115.
60	130	Wt. of 134 SP = 34.2 g. Removed 134 SP as 134SP-130.

All samples not heated above 100° were soluble in acetone and chloroform.

When sample 134C-110 was treated with chloroform, the solid flexible plate disintegrated into a fine powder. The chloroform extracted out an impurity which was identified as monomer precursor, diisoamyl 7-phenyl-6,8-dioxaspiro[3.5]nonane-2,2-dicarboxylate. The white solid left was designated 140A. It did not dissolve in aliphatic hydrocarbon, aromatic hydrocarbon, ester, alcohol, or amide solvents. On heating to 300°C it did not melt and discolored only slightly.

Sample 134-DEF-115 was triturated with chloroform and combined with 140A. The combined materials were heated to 147° for 24 hrs. and then to 179° for 24 hrs. The sample was designated 145A-179. This sample was then heated at 213° for 60 hrs. and redesignated as 145A-213.

Table VI Section III-G-2 should be consulted for data on analysis and additional comments. Infrared spectra appear as Figures 36-47.

Sample 134SP was an approximate 9-cm square plate varying in thickness from 1/2 mm to 2 mm. It could be flexed about 1 cm without breaking. It was transparent. The plate was broken by cutting and snapping. Part of the sample was set aside. A 12.53 g. part of the plate was pulverized and then heated in 700 ml of refluxing chloroform for 18 hrs. After filtration there was obtained 10.70 g. of white solid. When the chloroform was evaporated the residue was primarily the monomer precursor but there was also a small amount, < 0.1 g., of polymer present. A careful check on this small amount of soluble polymer has not been completed.

On the basis of the extraction data, the upper limit on amount of monomer precursor in monomer-133 can be set as 1.83 g. in the initial 33.78-g. sample. If the results of Table I are used, then monomer-133

as used had a composition of:

> 30.96 g. of monomer

2.82 g. of solvent (water, isoamyl alcohol, benzene)

< 1.83 g. of monomer precursor.

On this basis, all data can be corrected at a later time if it seems desirable to do so.

IV ADDITIONAL COMMENTS

Although the contract period for research has expired, it is intended that research will be continued on the work described in this report. In particular, when more dispiro[3.1.3.1]decane-2,8-dicarboxylic acid is synthesized, it will be converted to Polymer I. This Polymer I will be reacted with sulfur tetrafluoride, and hopefully enough Polymer II will be prepared to forward a sample to Air Force Material Laboratory for evaluation.

Work on Polymer VI will also be continued.

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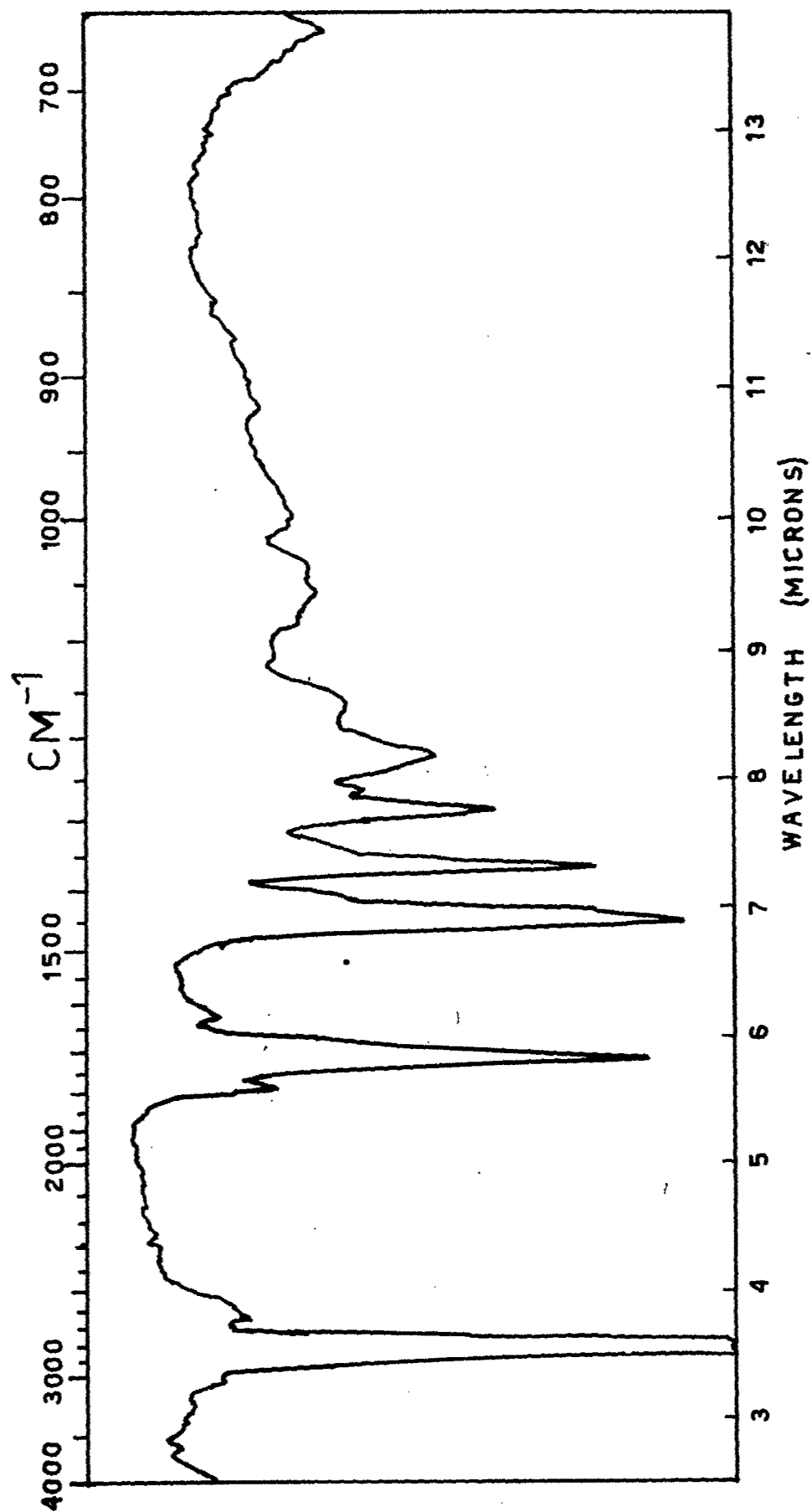


Figure 1. Infrared Spectrum of Poly(trispiro[3.1.1.3.1.1]dodecane-1,3-dione) in Paraffin Oil Mull.

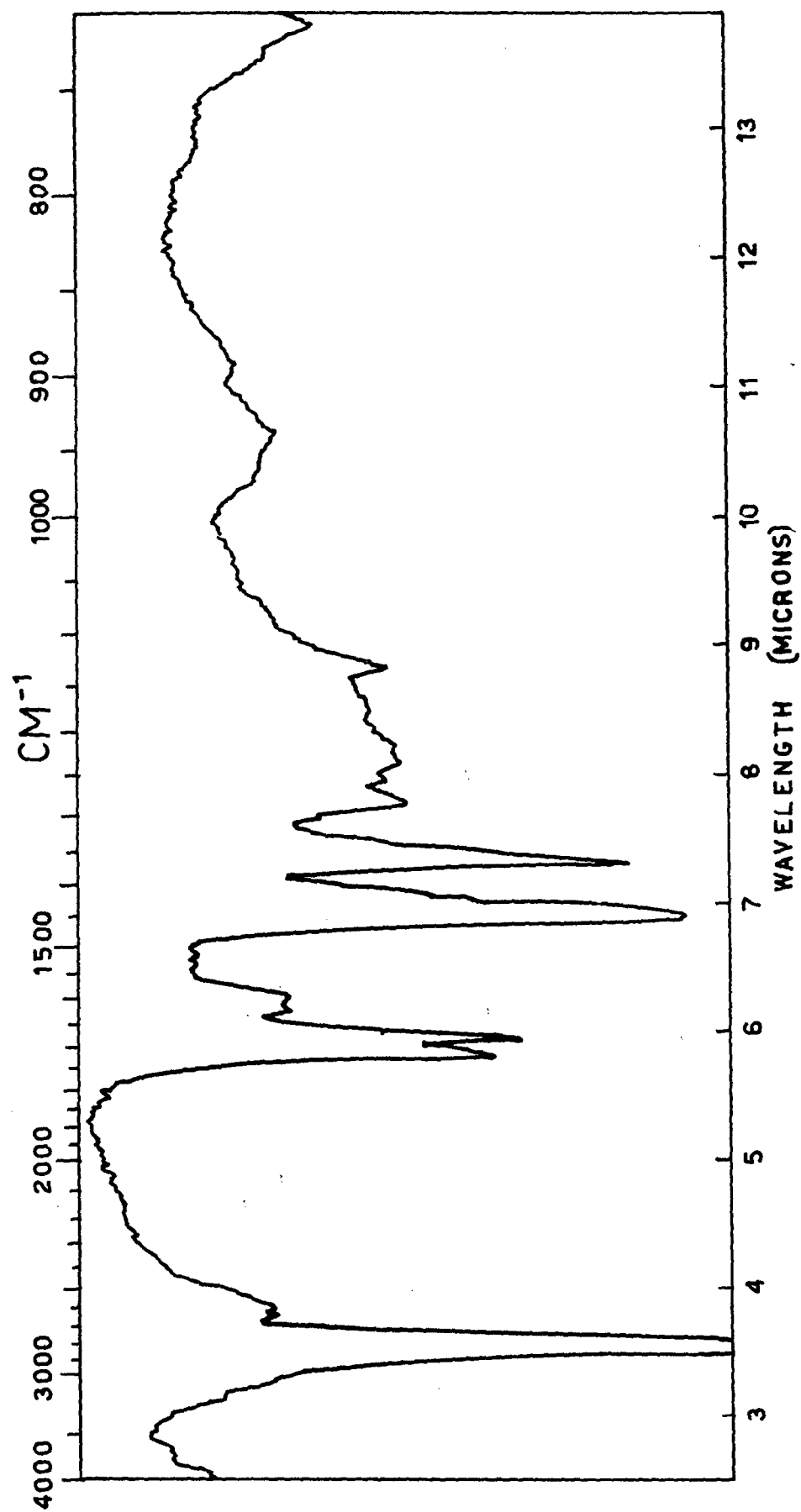


Figure 2. Infrared Spectrum of Low Quality Poly(trispiro[3.1.1.3.1.1.3.1.1.1]dodecane-1,3-dione) in Paraffin Oil Mull.

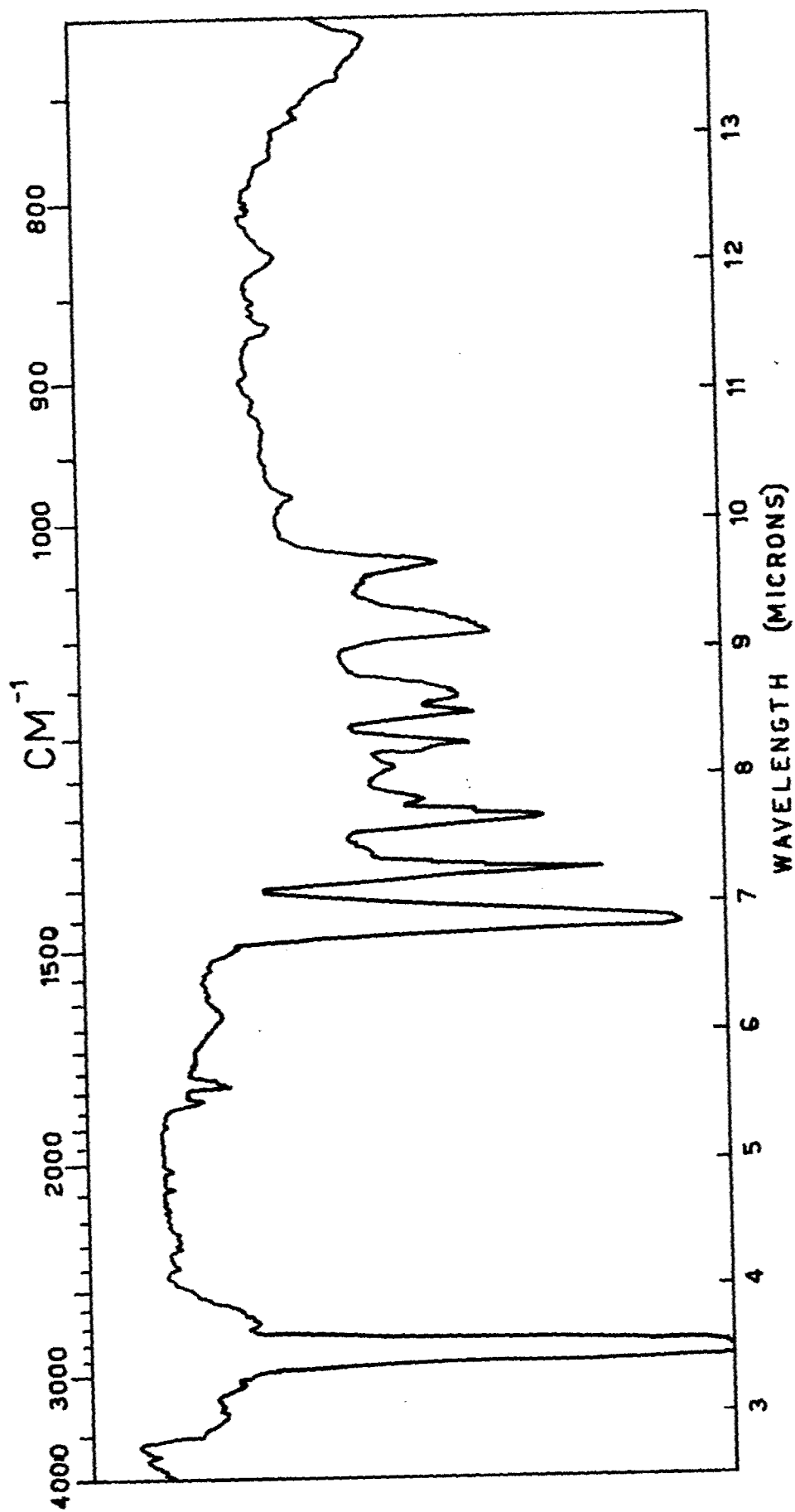


Figure 3. Infrared Spectrum of Poly(1,1,3,3-tetrafluorotrispiro[3.1.1.3.1.1.3.1.1]dodecane) in Paraffin Oil Mull.

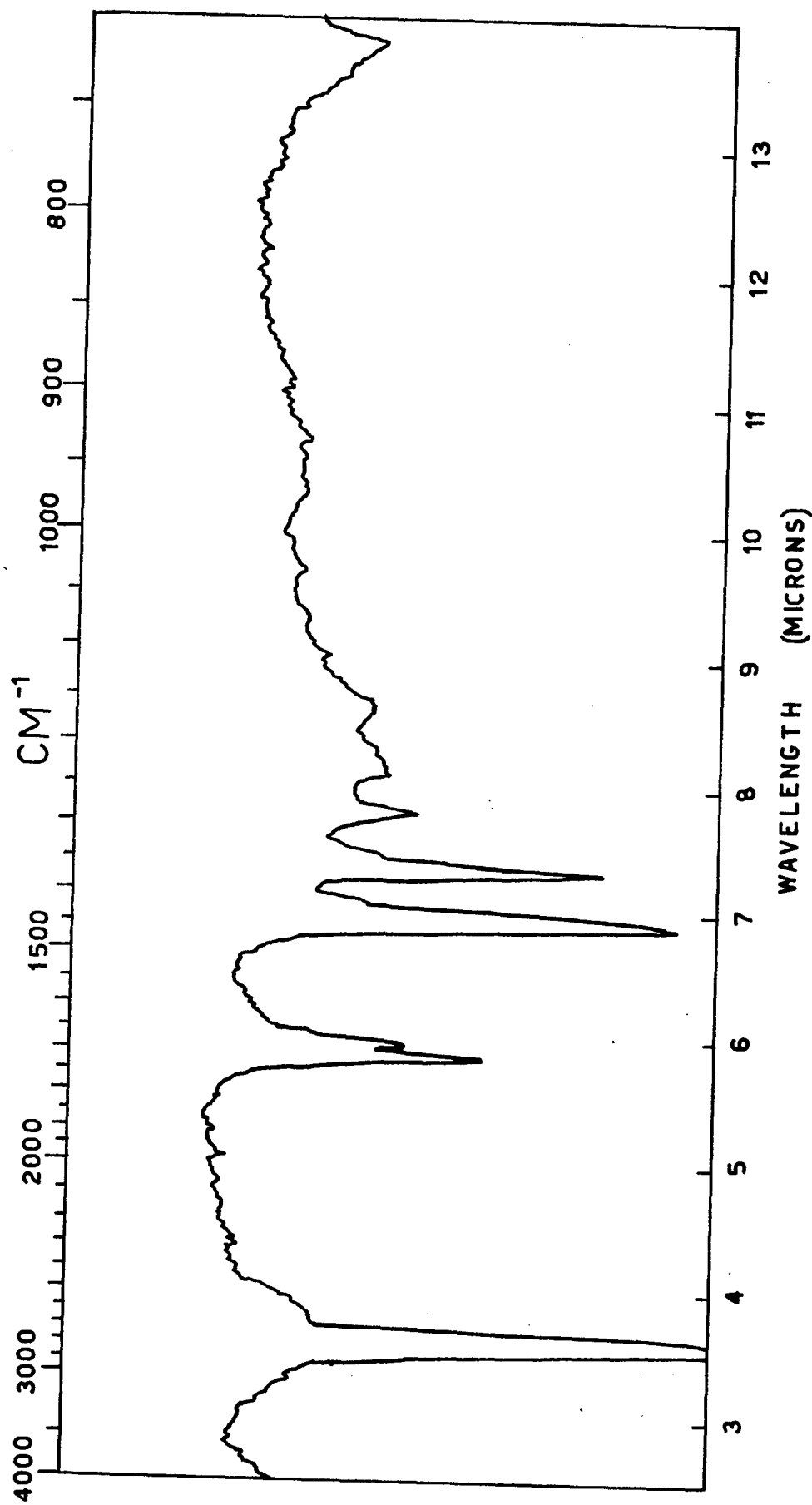


Figure 4. Infrared Spectrum of Poly(trispiro[3.1.1.3.1.1.3.1.1.1]dodecane-1,3-dione) Before Reaction With Ethane-1,2-dithiol in Paraffin Oil Mull.

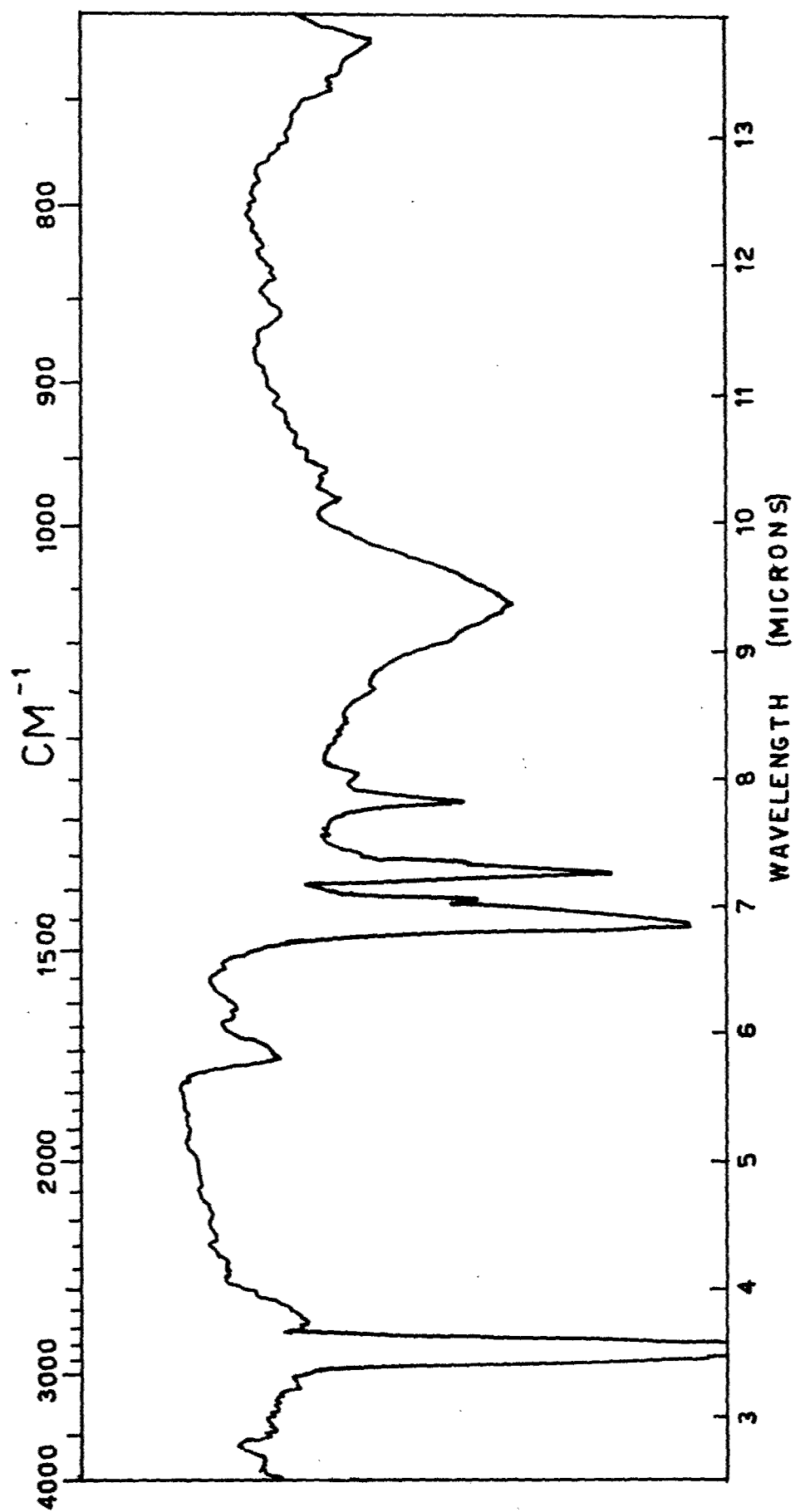


Figure 5. Infrared Spectrum in Paraffin Oil Mull of Polymer from Reaction of Poly(trispiro-[3.1.1.3.1.1]dodecane-1,3-dione) with Ethane-1,2-dithiol.

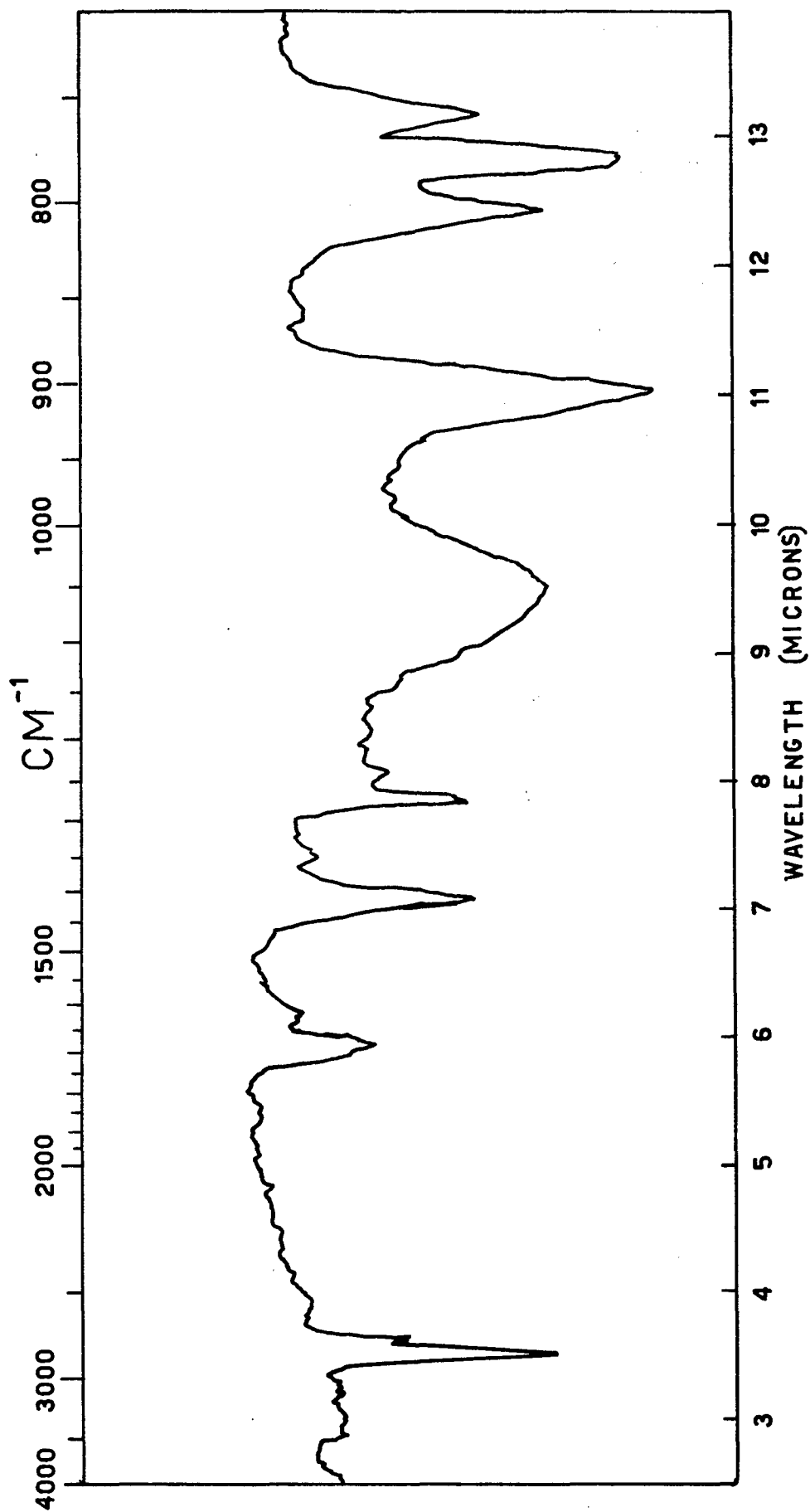


Figure 6. Infrared Spectrum in Tetrachloroethylene Mull of Polymer from Reaction of Poly(trispiro-[3.1.1.3.1.1]dodecane-1,3-dione) with Ethane-1,2-dithiol.

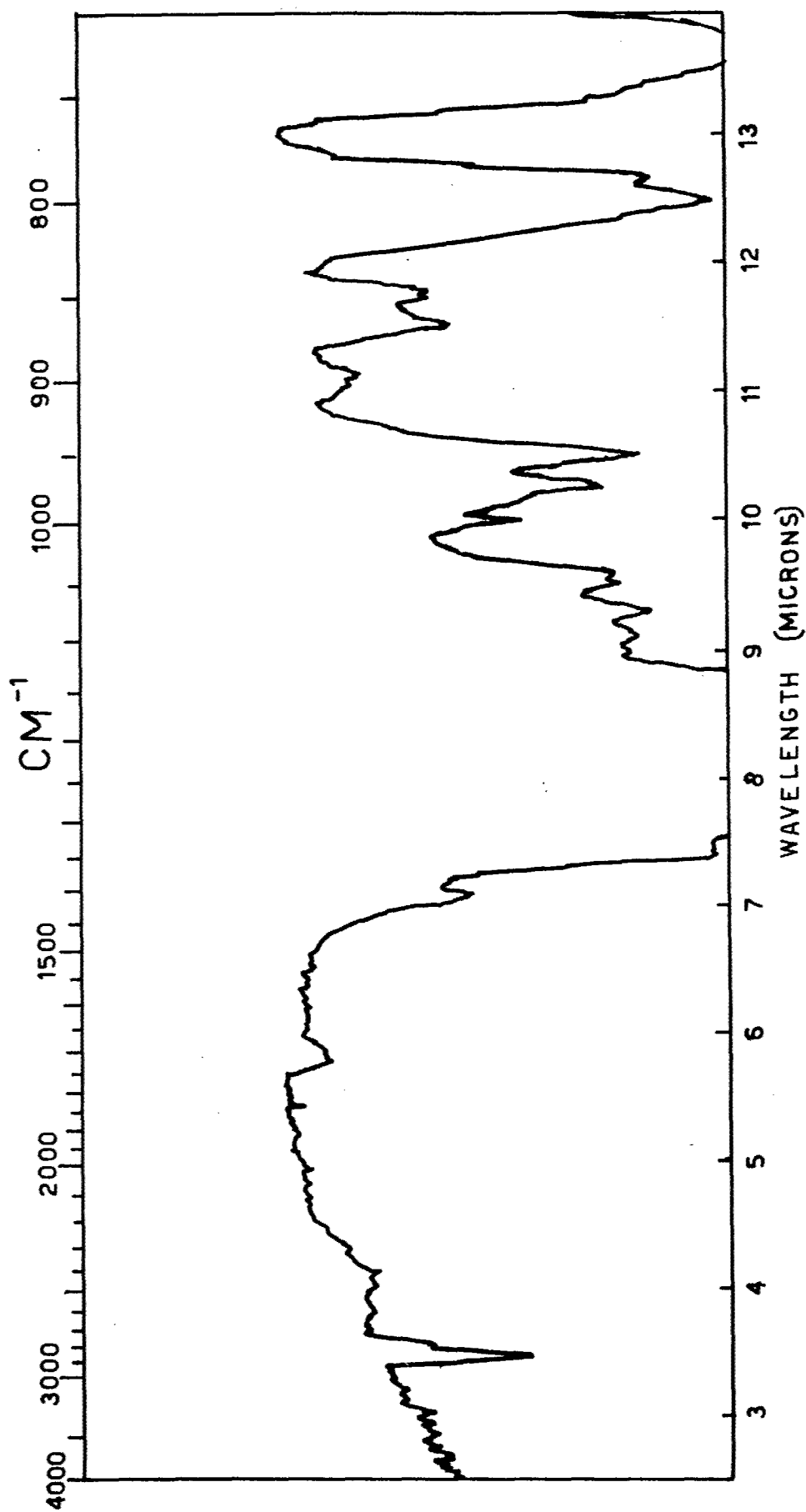


Figure 7. Infrared Spectrum of Polymer from Reaction of Poly[3.1.1.3.1.1]dodecane-1,3-dione) with Ethane-1,2-dithiol.

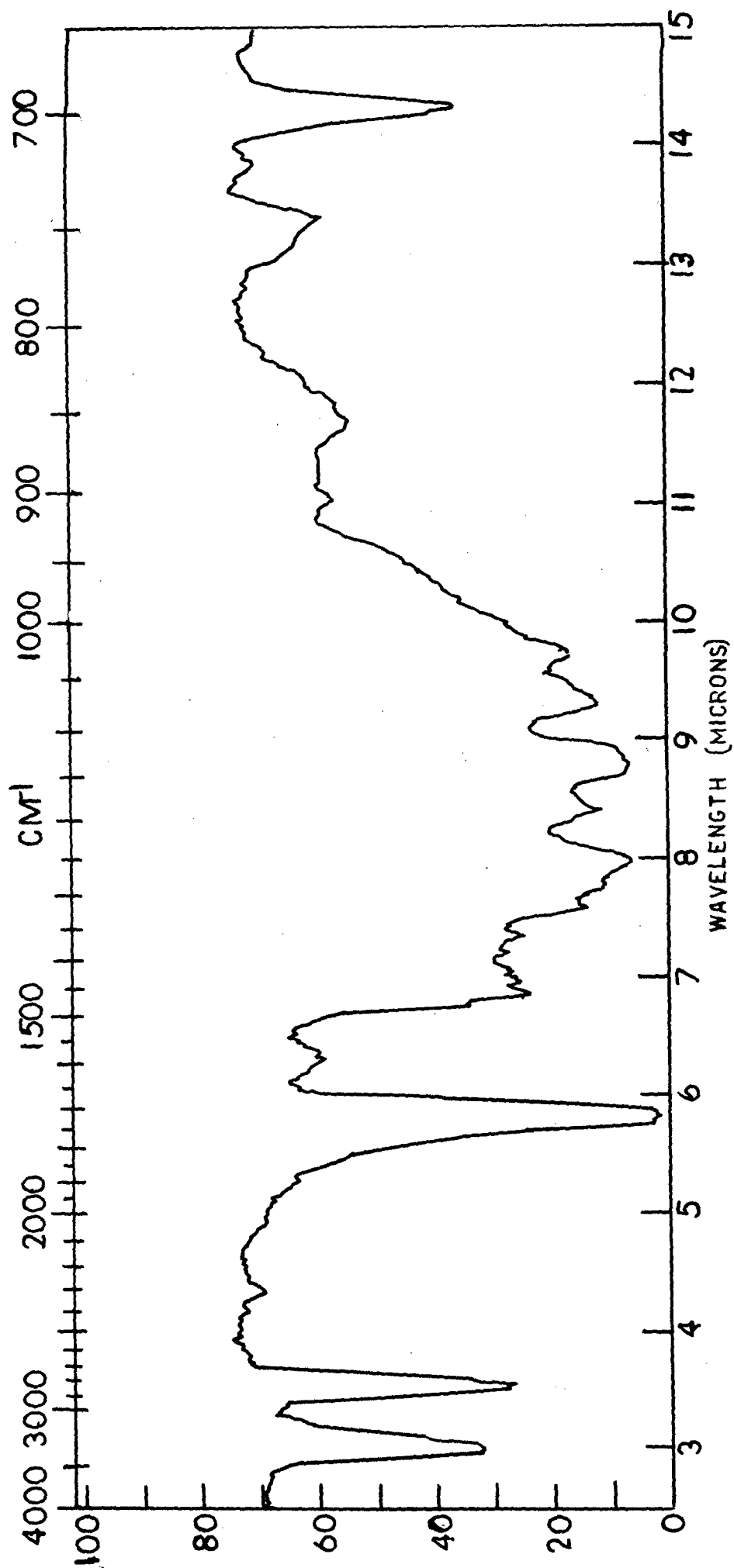


Figure 8. Infrared Spectrum of Poly[3,3-bis(hydroxymethyl)cyclobutane-1,1-dicarboxylate] formed at 130° from Diethyl 3,3-bis(hydroxymethyl)cyclobutane-1,1-dicarboxylate in the presence of $\text{Sb}_2\text{O}_3\text{-Ca}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ catalyst (in Nujol mull).

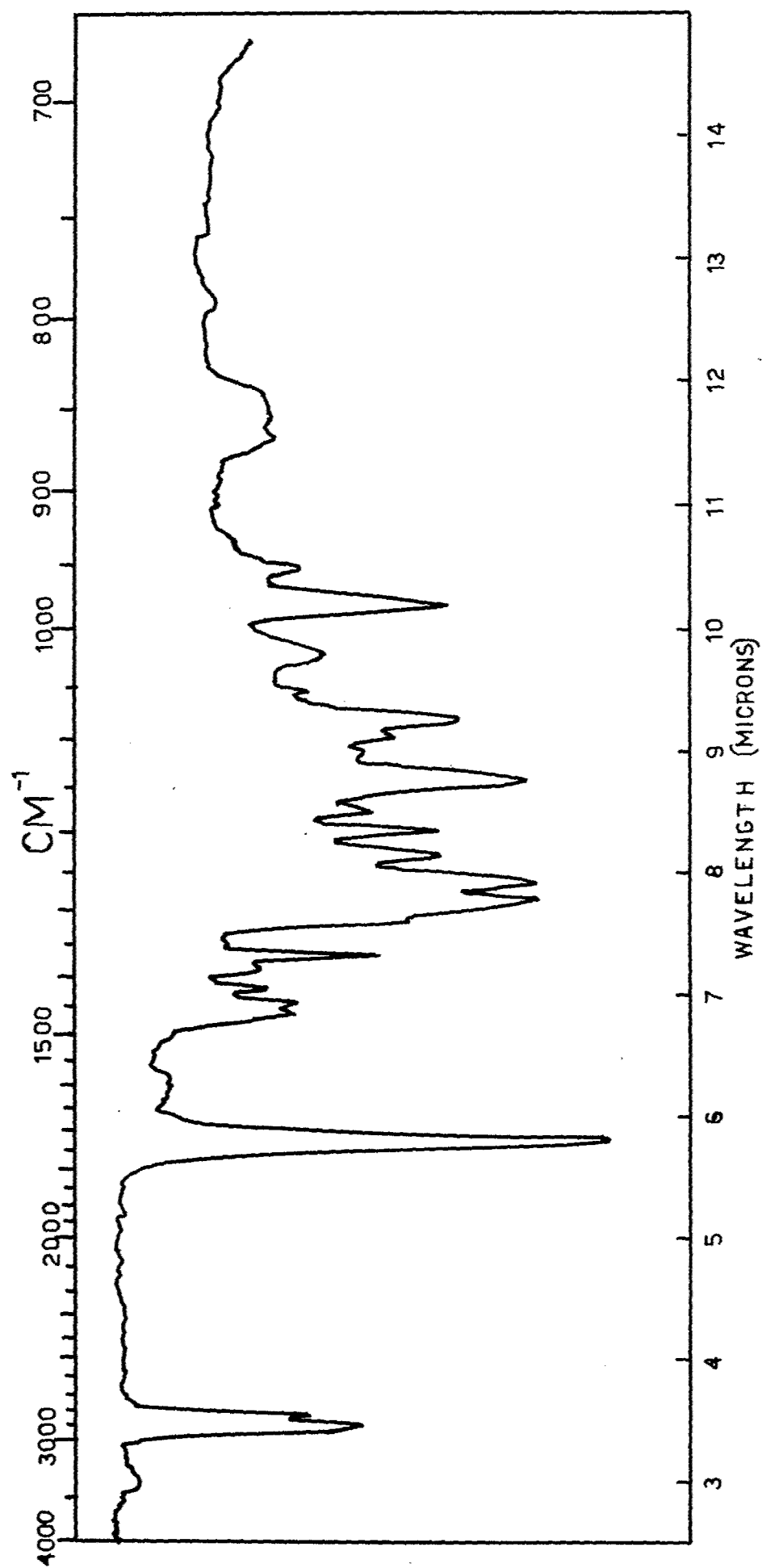


Figure 9. Infrared Spectrum of Diethyl 6-oxaspiro[3.3]heptane-2,2-dicarboxylate.

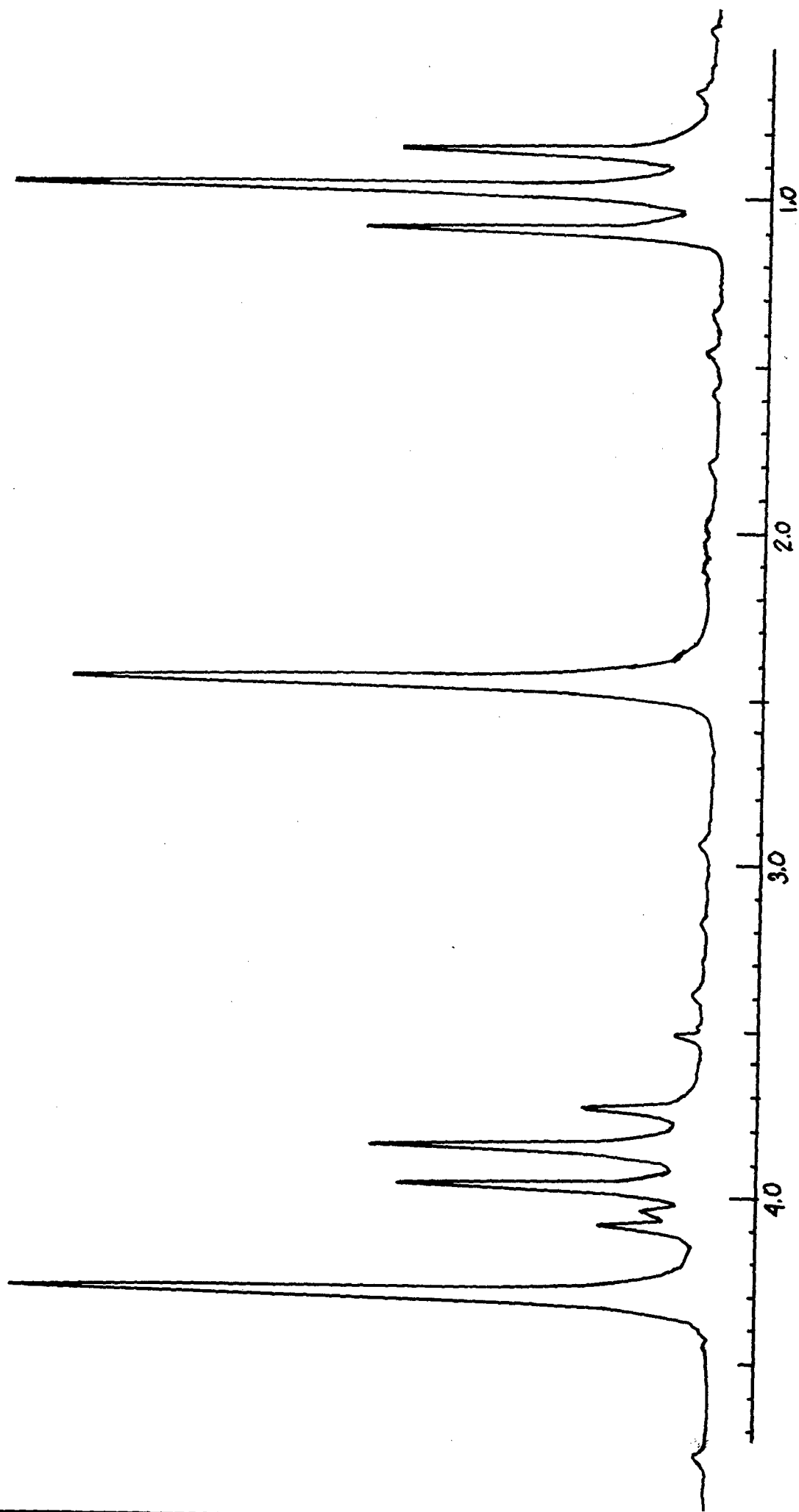


Figure 10. Nmr Spectrum of Diethyl 6-oxaspiro[3.3]heptane-2,2-dicarboxylate.

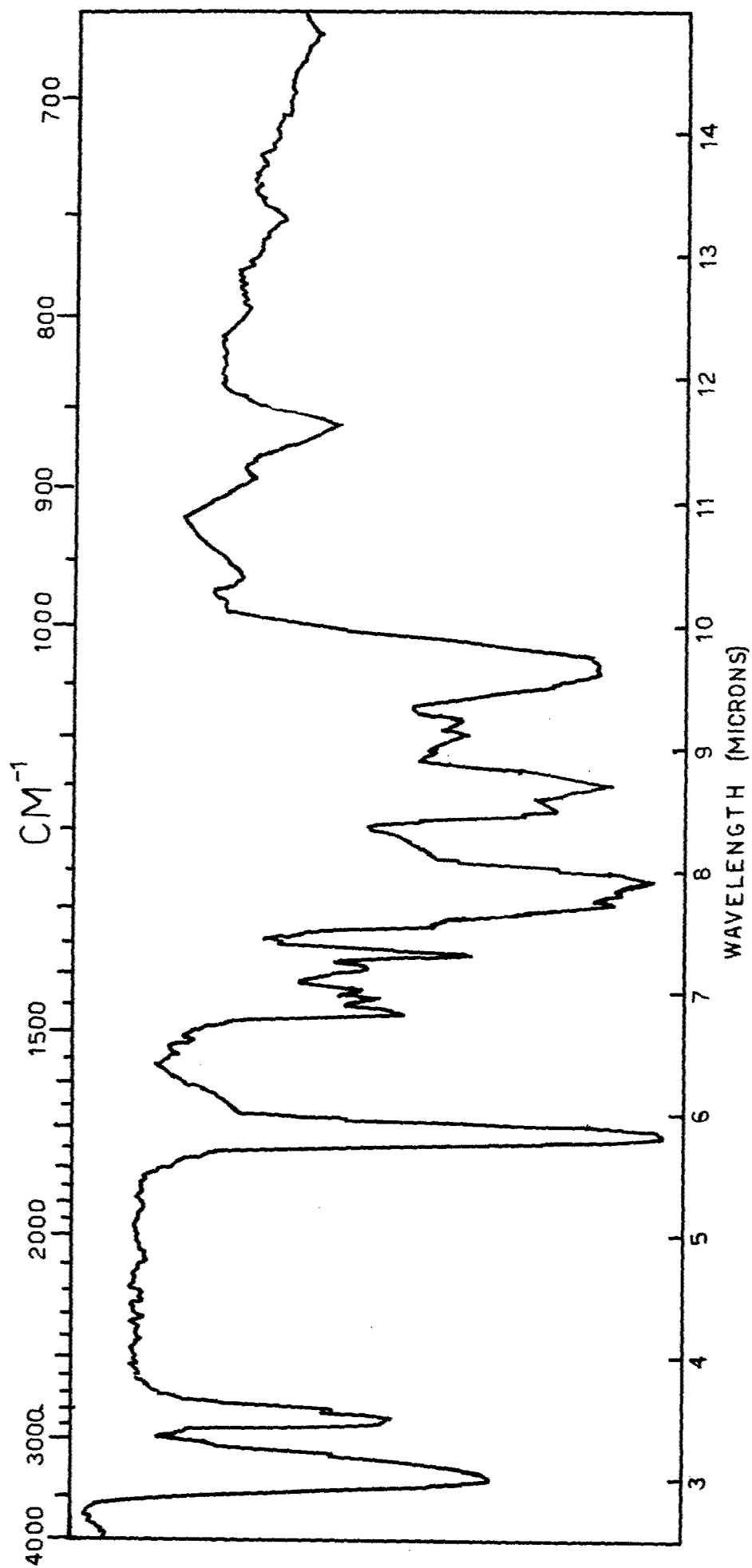


Figure 11. Infrared Spectrum of Diethyl 3,3-bis(hydroxymethyl)cyclobutane-1,1-dicarboxylate.

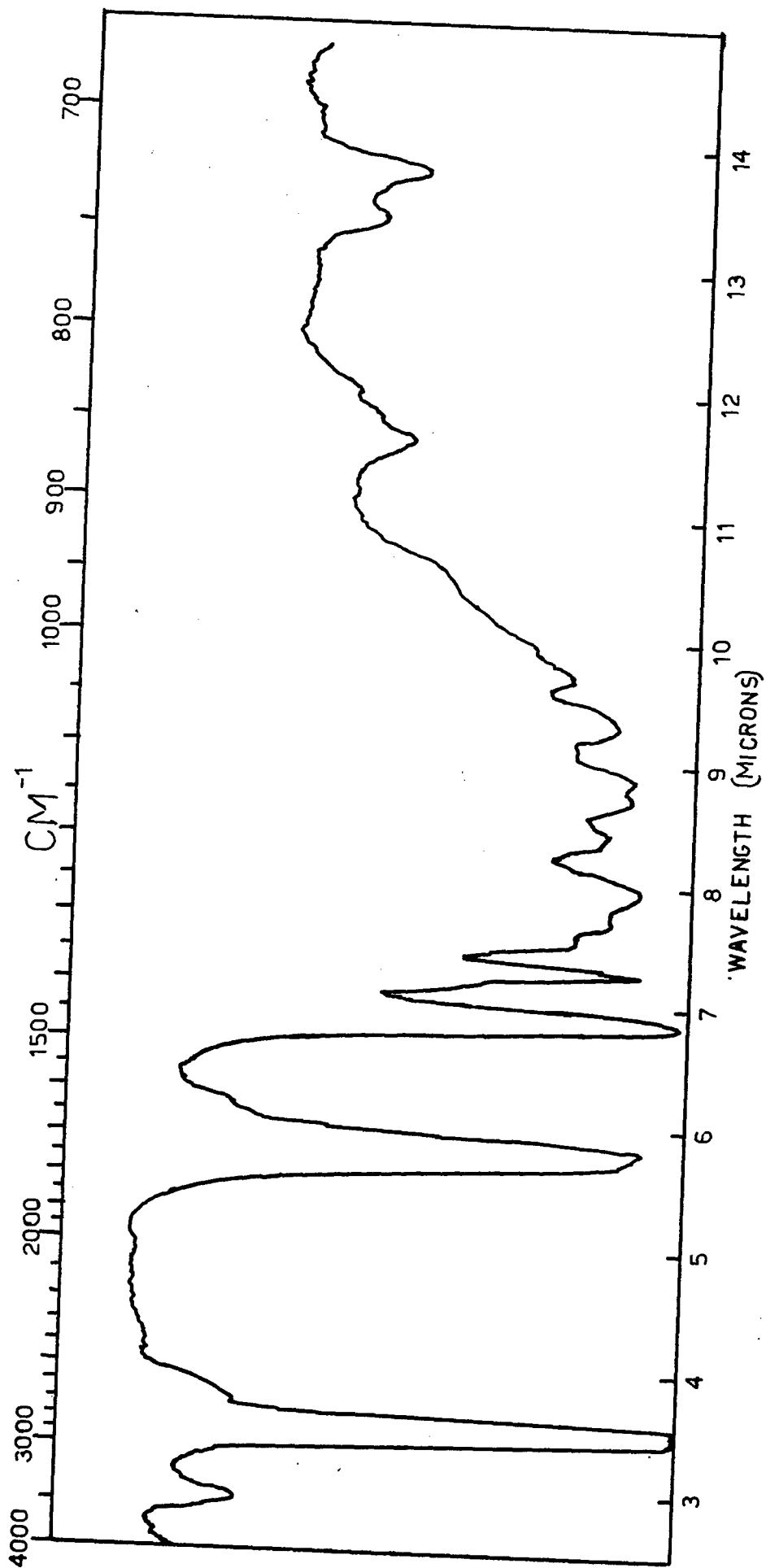


Figure 12. Infrared Spectrum of Uncatalyzed Polymer (130°) from Diethyl 3,3-bis(hydroxymethyl)-cyclobutane-1,1-dicarboxylate.

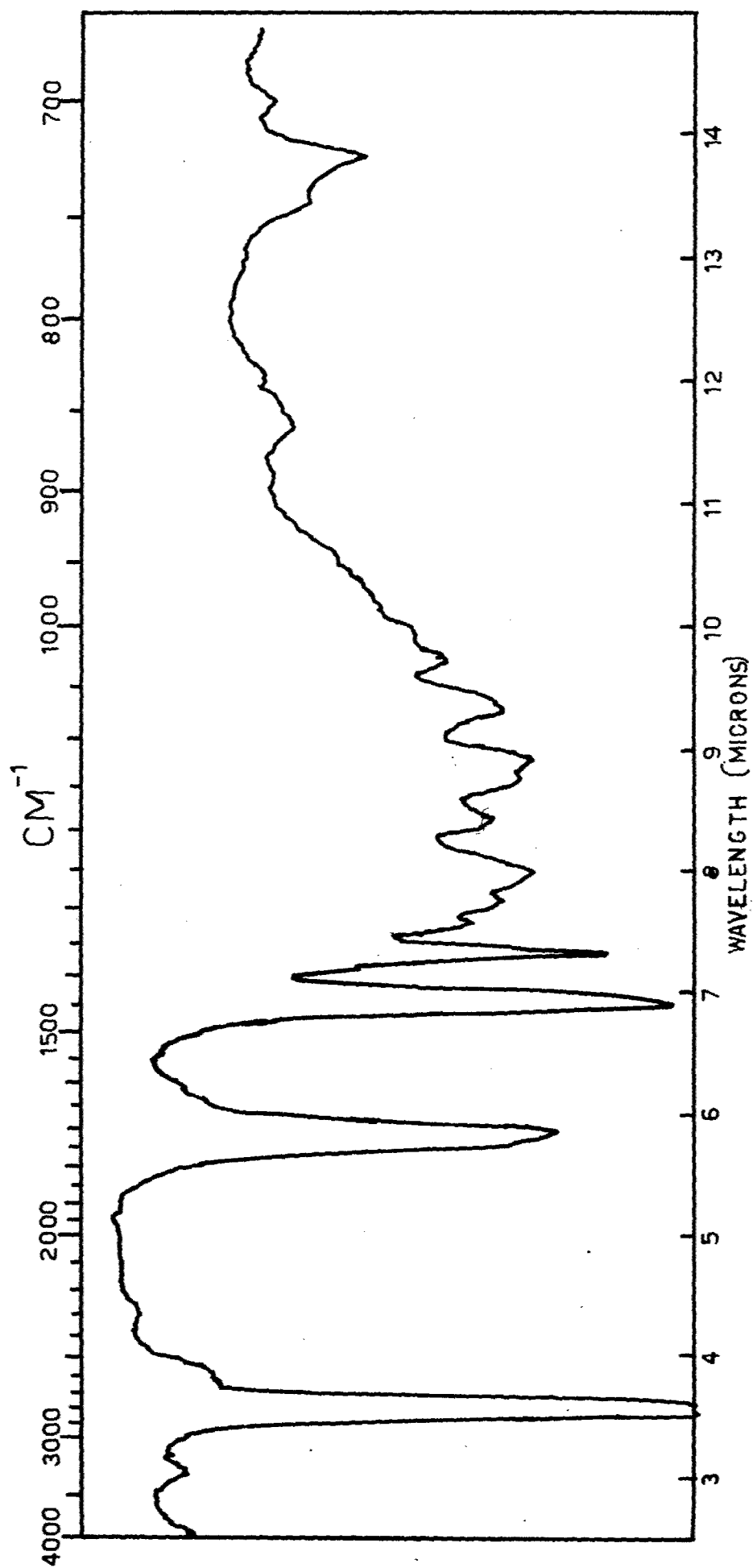


Figure 13. Infrared Spectrum of Catalyzed Polymer (130°) from Diethyl 3,3-bis(hydroxymethyl)-cyclobutane-1,1-dicarboxylate.

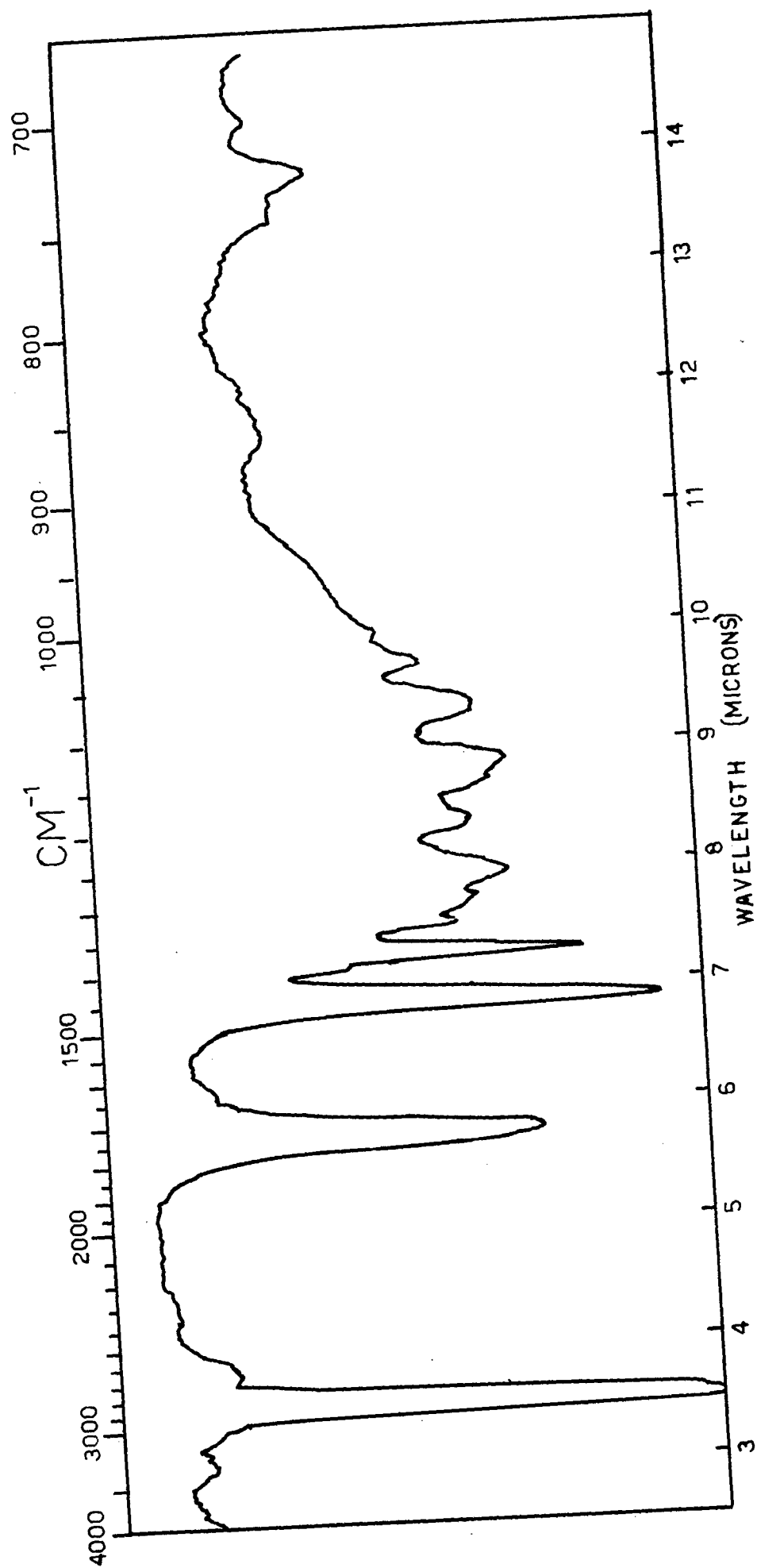


Figure 14. Infrared Spectrum of Uncatalyzed Polymer (213°) from Diethyl 3,3-bis(hydroxymethyl)-cyclobutane-1,1-dicarboxylate.

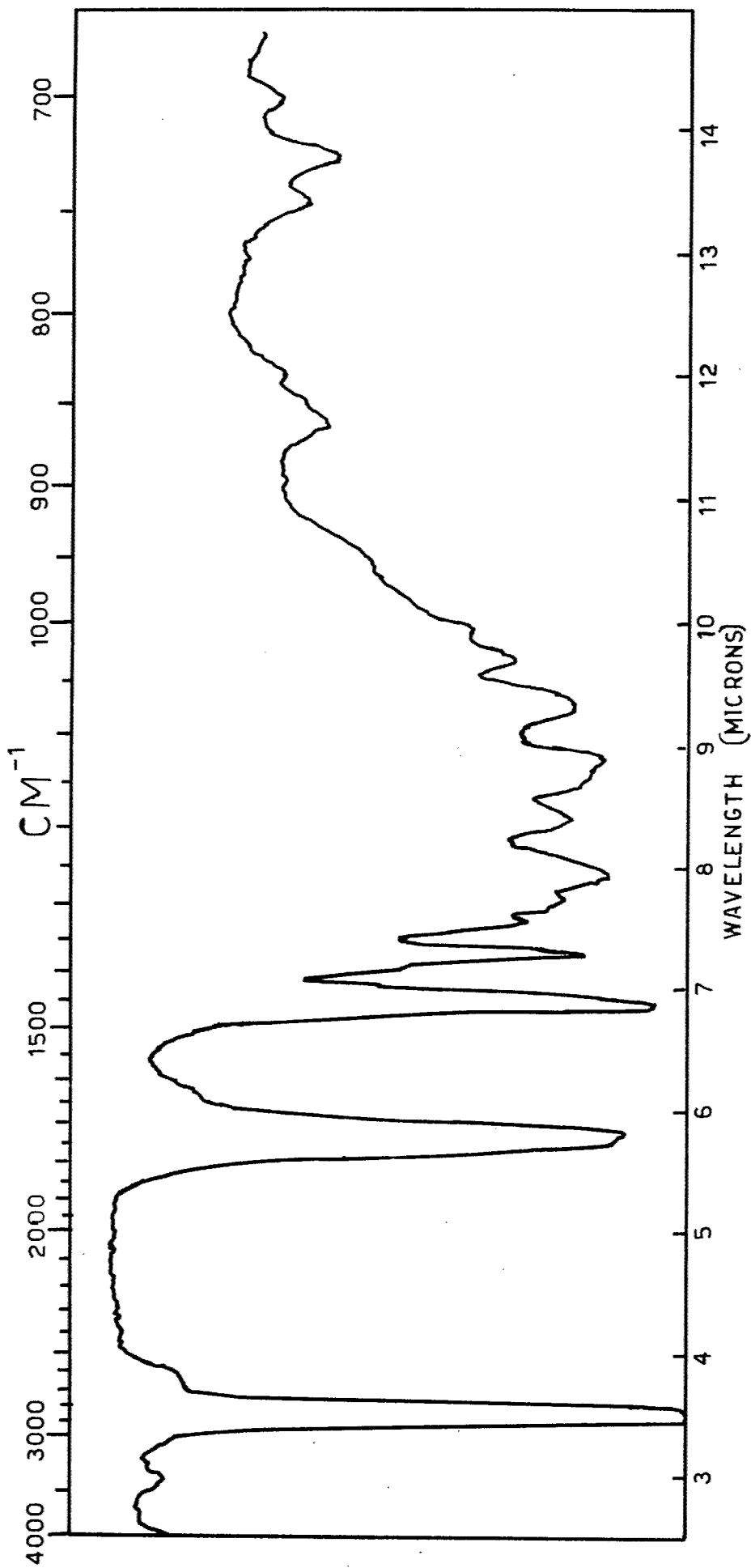


Figure 15. Infrared Spectrum of Catalyzed Polymer (213°) from Diethyl 3,3-bis(hydroxymethyl)-cyclobutane-1,1-dicarboxylate.

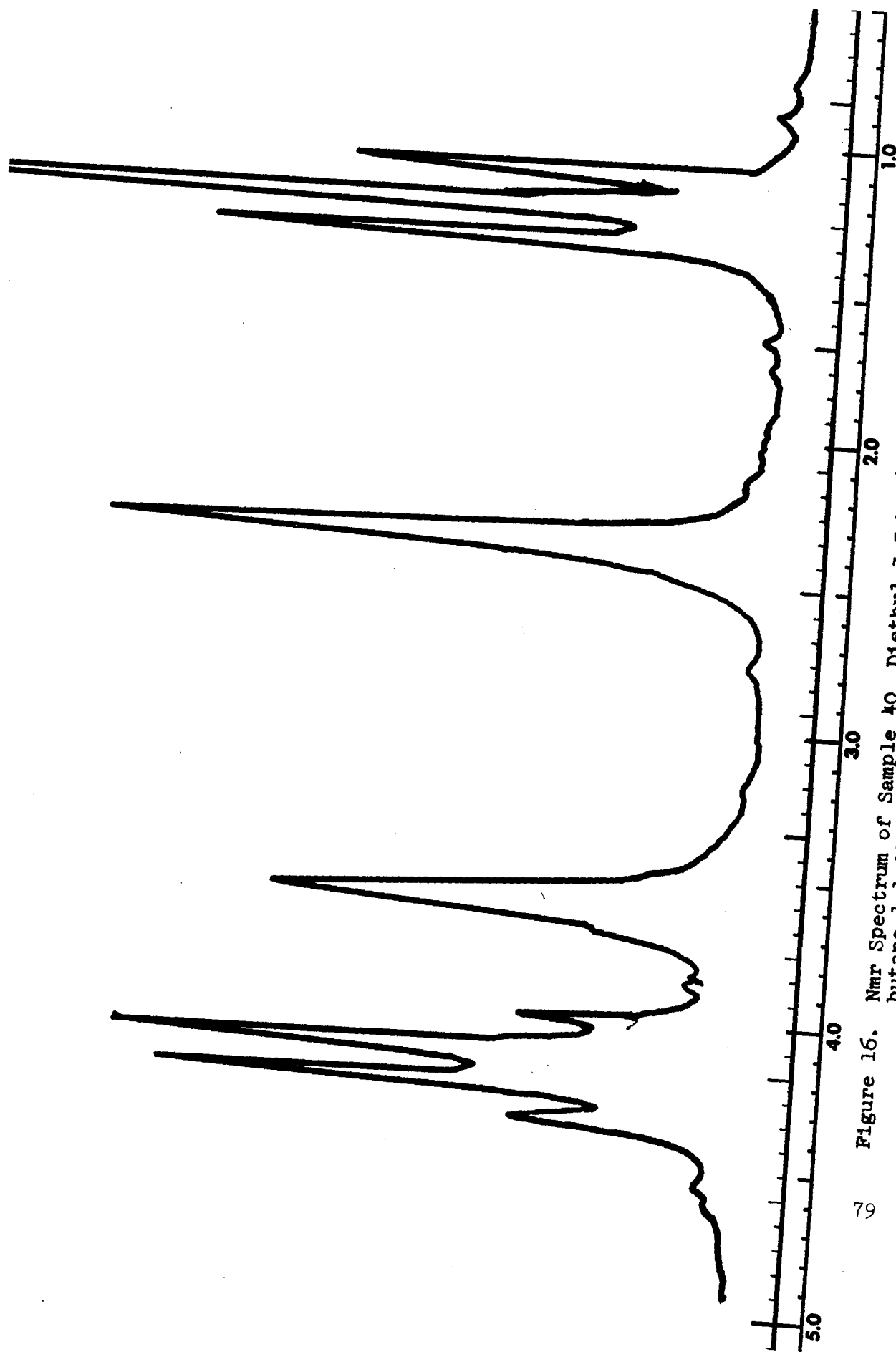


Figure 16. Nmr Spectrum of Sample 40, Diethyl 3,3-bis(Hydroxymethyl)cyclobutane-1,1-dicarboxylate. (Dichloromethane Solution)

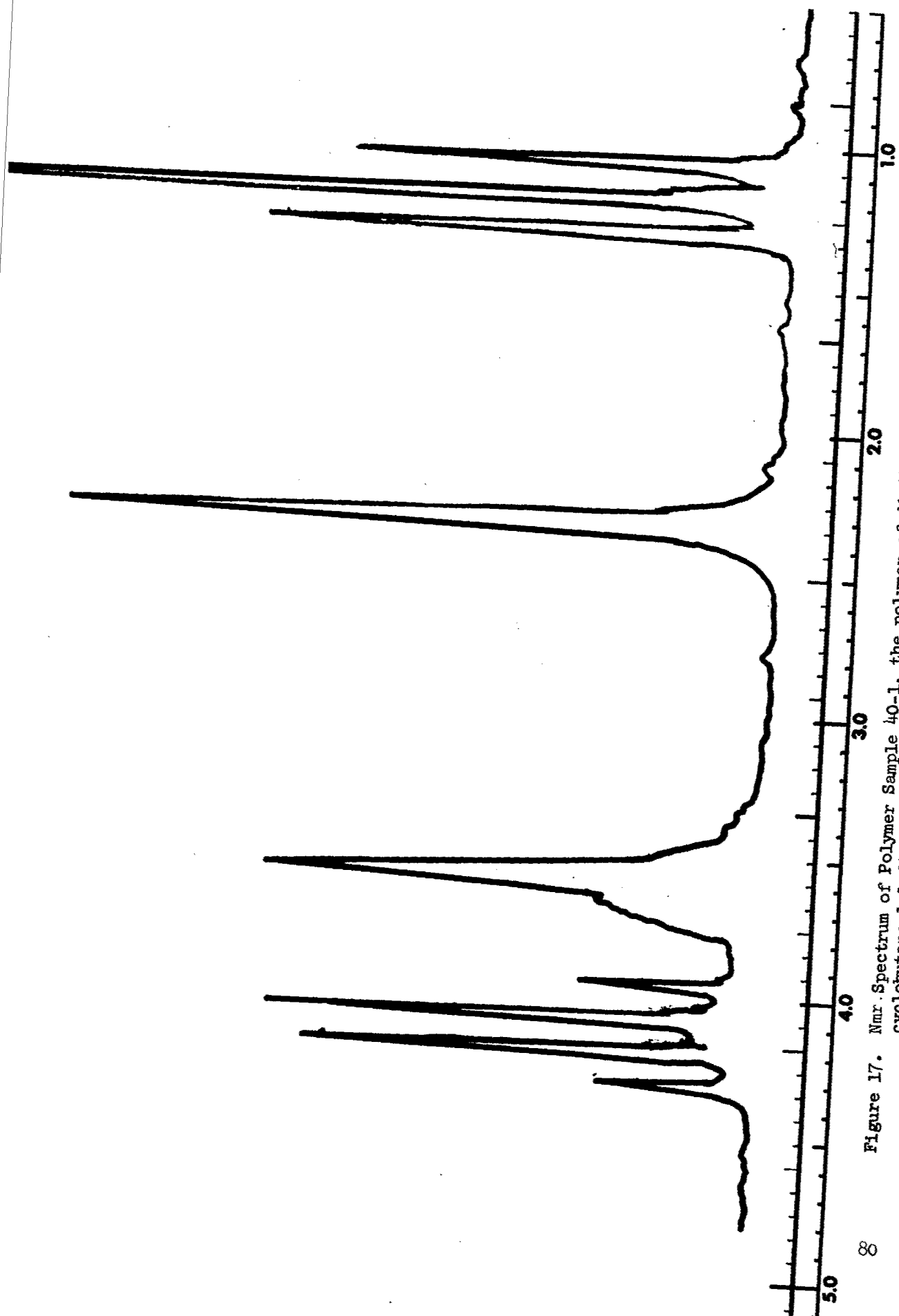


Figure 17. Nmr. Spectrum of Polymer Sample 40-1, the polymer of diethyl 3,3-bis(hydroxymethyl)-cyclobutane-1,1-dicarboxylate. (Dichloromethane Solution).

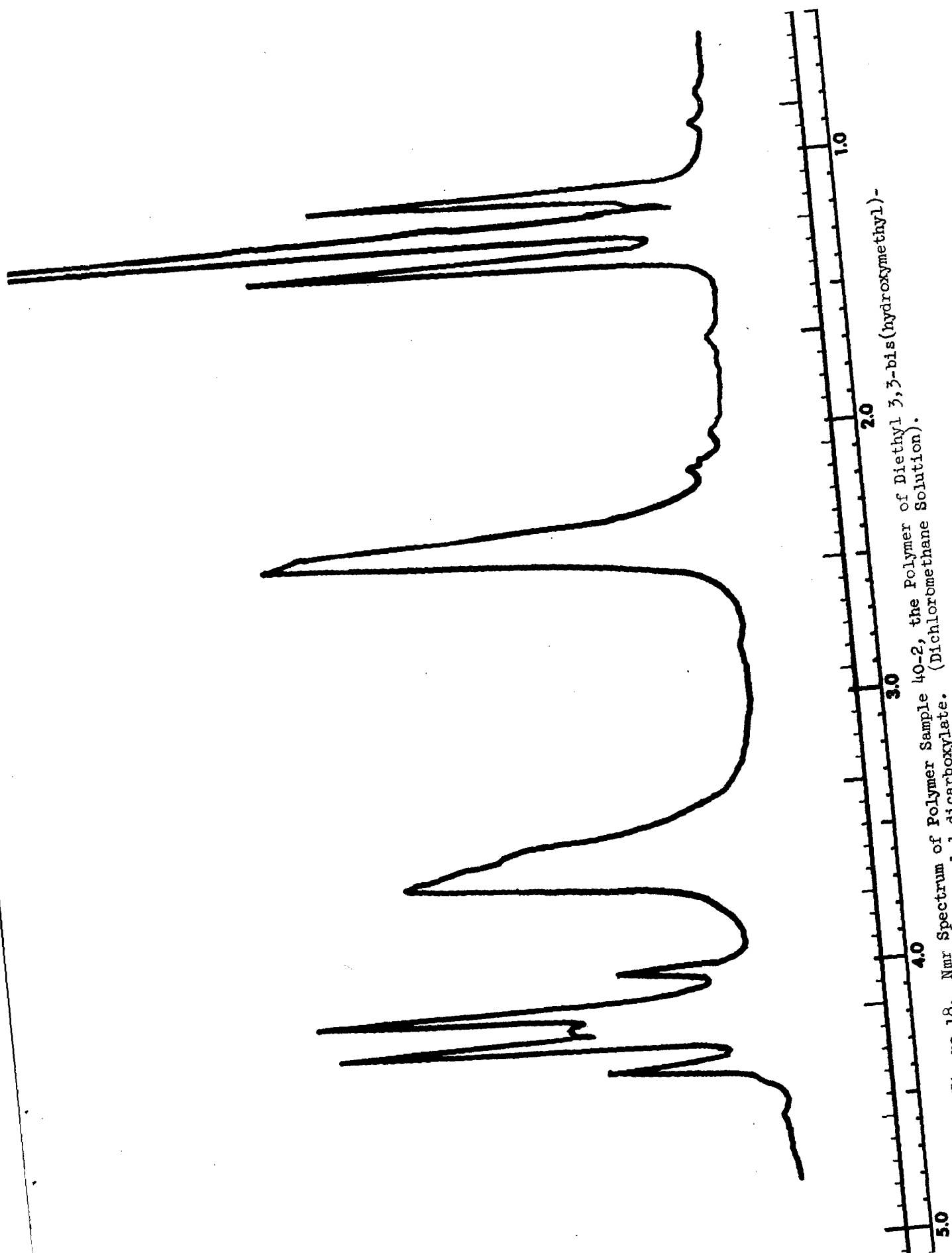


Figure 18. Nmr Spectrum of Polymer Sample 40-2, the Polymer of Diethyl 3,3-bis(hydroxymethyl)-cyclobutane-1,1-dicarboxylate. (Dichloromethane Solution).

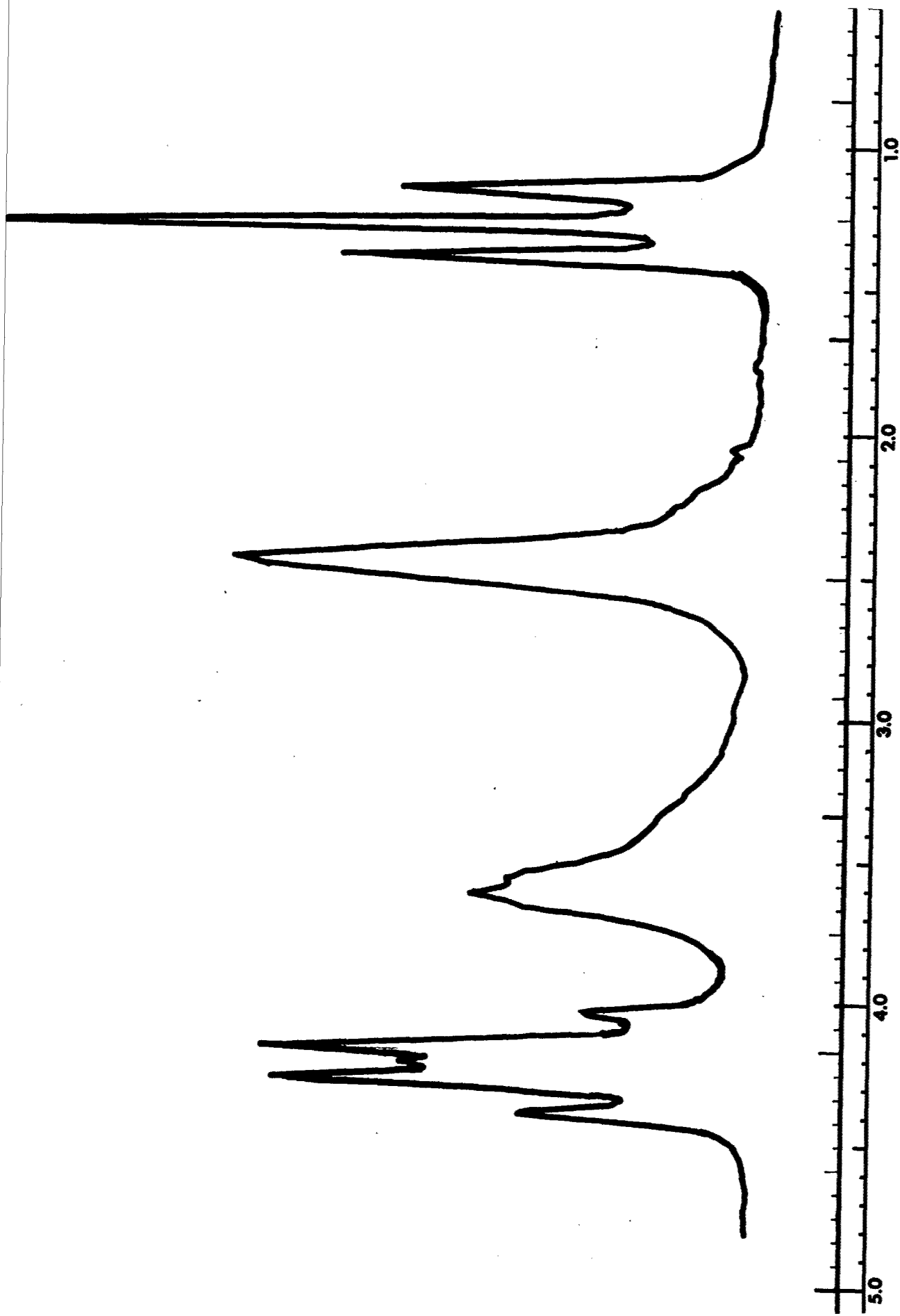


Figure 19. Nmr Spectrum of Polymer Sample 40-3, the Polymer of Diethyl 3,3-bis(hydroxymethyl)-cyclobutane-1,1-dicarboxylate. (Dichloromethane Solution).

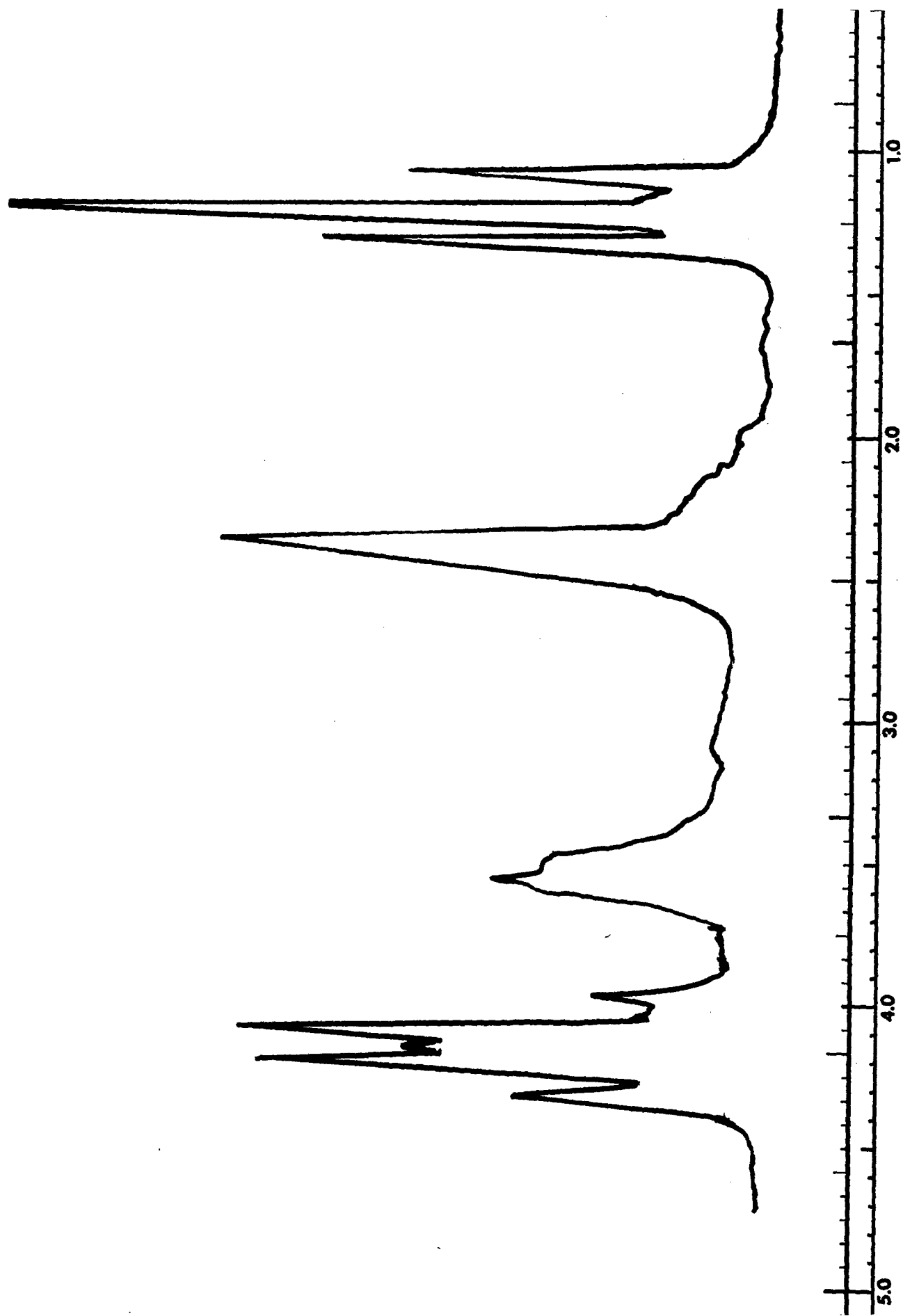


Figure 20. Nmr Spectrum of Polymer Sample 40-4, the Polymer of Diethyl 3,3-bis(hydroxymethyl)-cyclobutane-1,1-dicarboxylate. (Dichloromethane Solution).

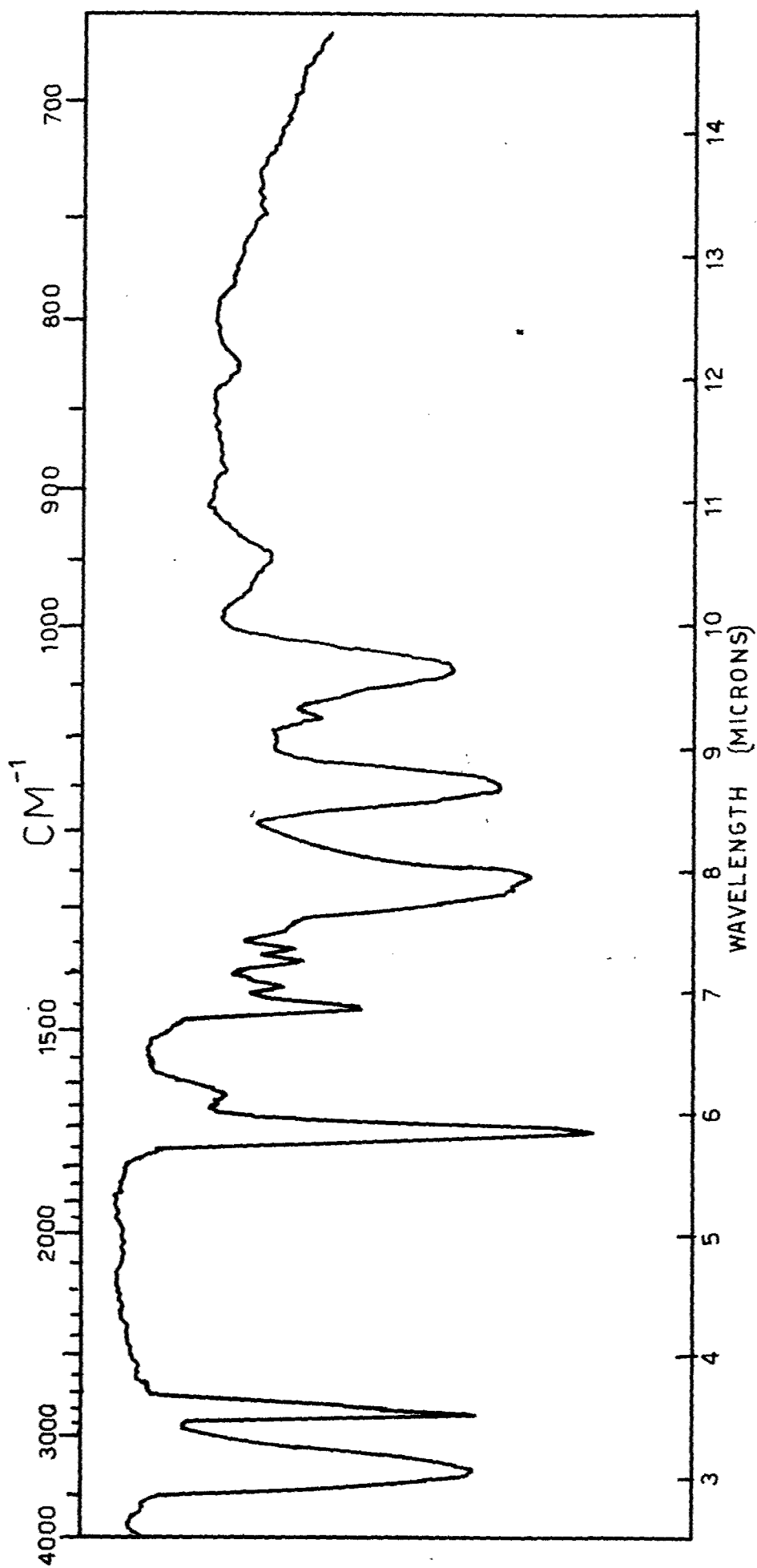


Figure 21. Infrared Spectrum of Diisoamy 3,3-bis(hydroxymethyl)cyclobutane-1,1-dicarboxylate.

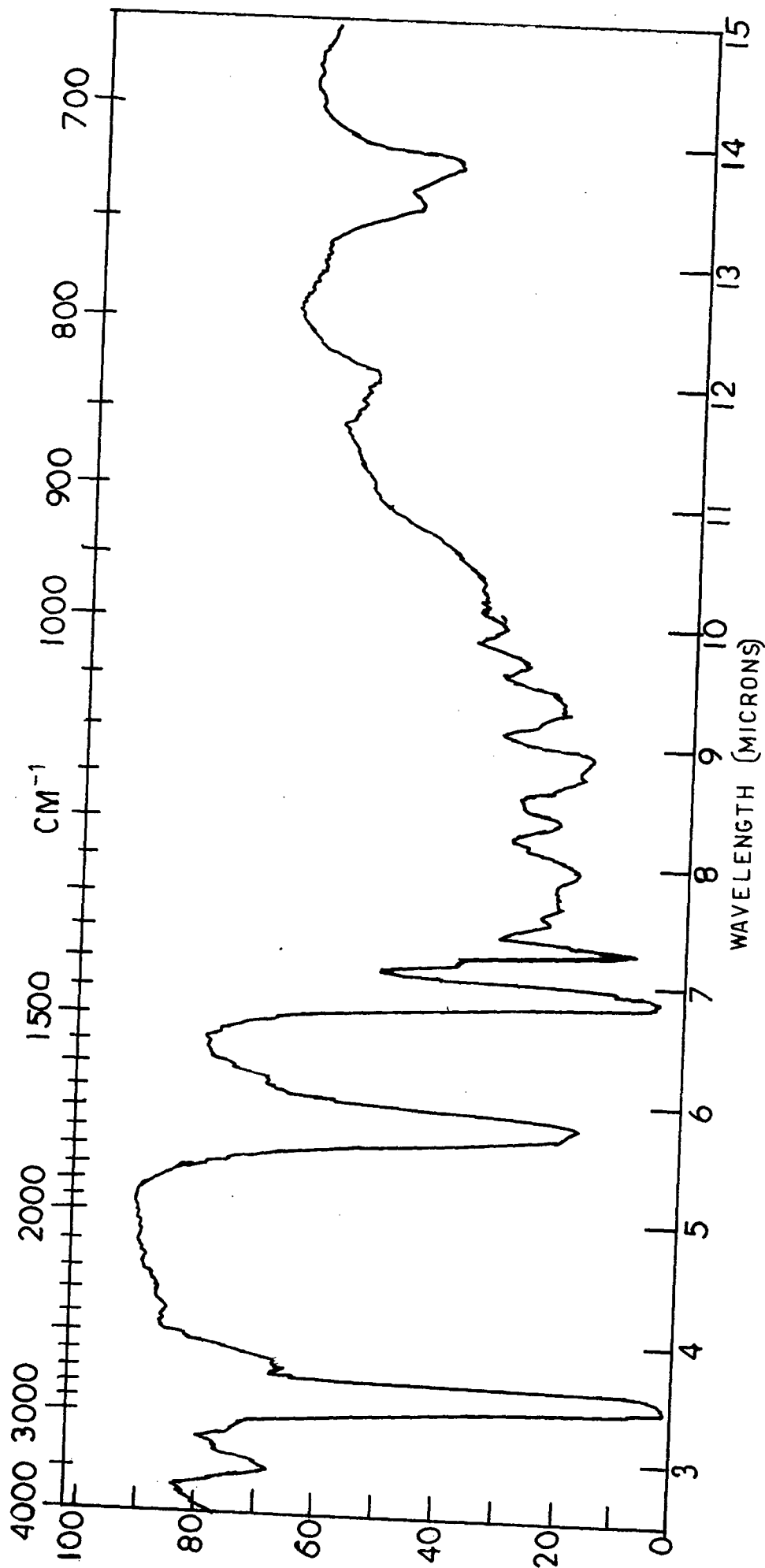


Figure 22. Infrared Spectrum of Poly[3,3-bis(hydroxymethyl)cyclobutane-1,1-dicarboxylate] formed at 213° from Diisoamyl 3,3-bis(hydroxymethyl)cyclobutane-1,1-dicarboxylate in the presence of $\text{Sb}_2\text{O}_3\text{-Ca(OAc)}_2 \cdot 2\text{H}_2\text{O}$ Catalyst (in Nujol mull).

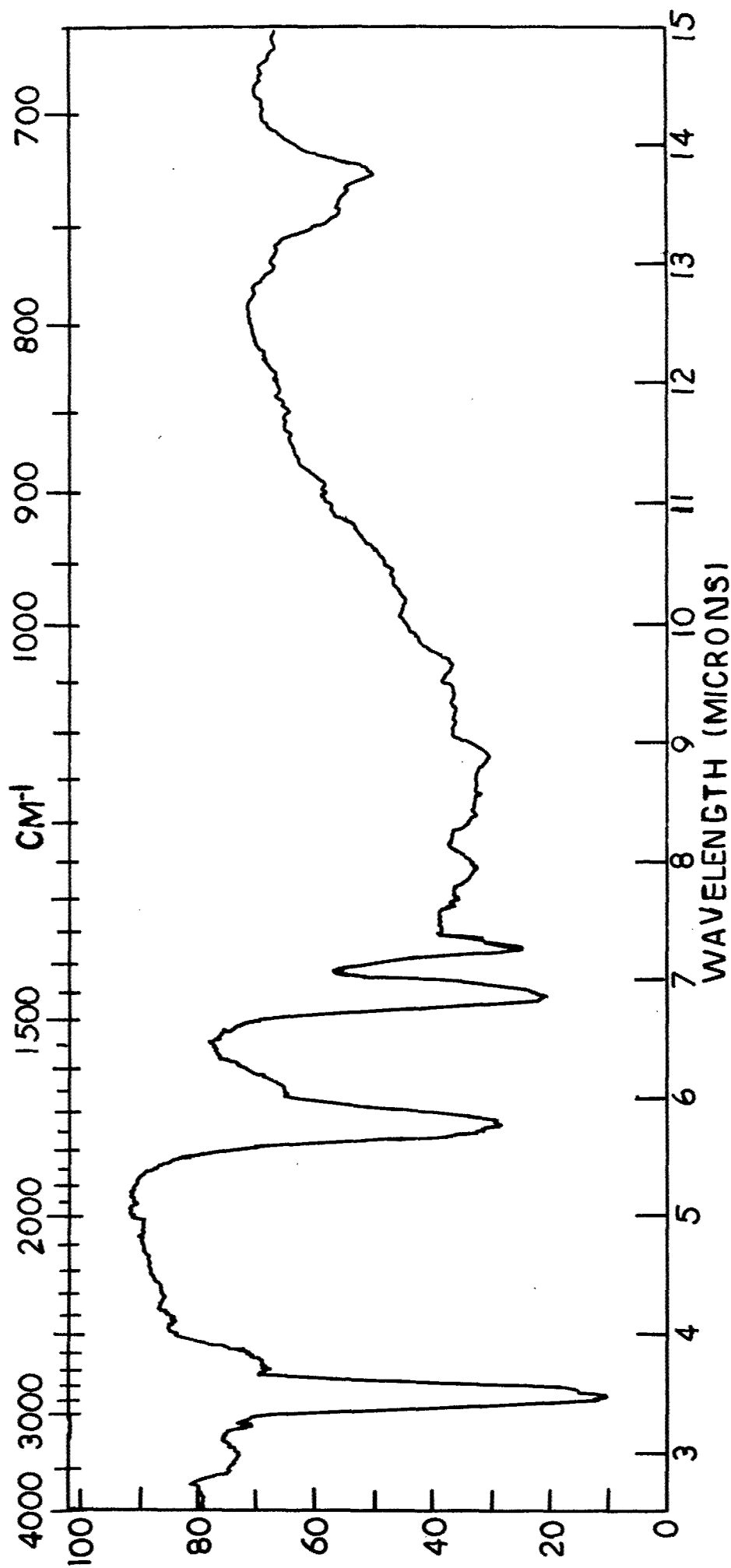


Figure 23. Infrared Spectrum of Poly[3,3-bis(hydroxymethyl)cyclobutane-1,1-dicarboxylate] formed at 252° in the presence of $\text{Sb}_2\text{O}_3\text{-Ca}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ Catalyst (in Nujol mull).

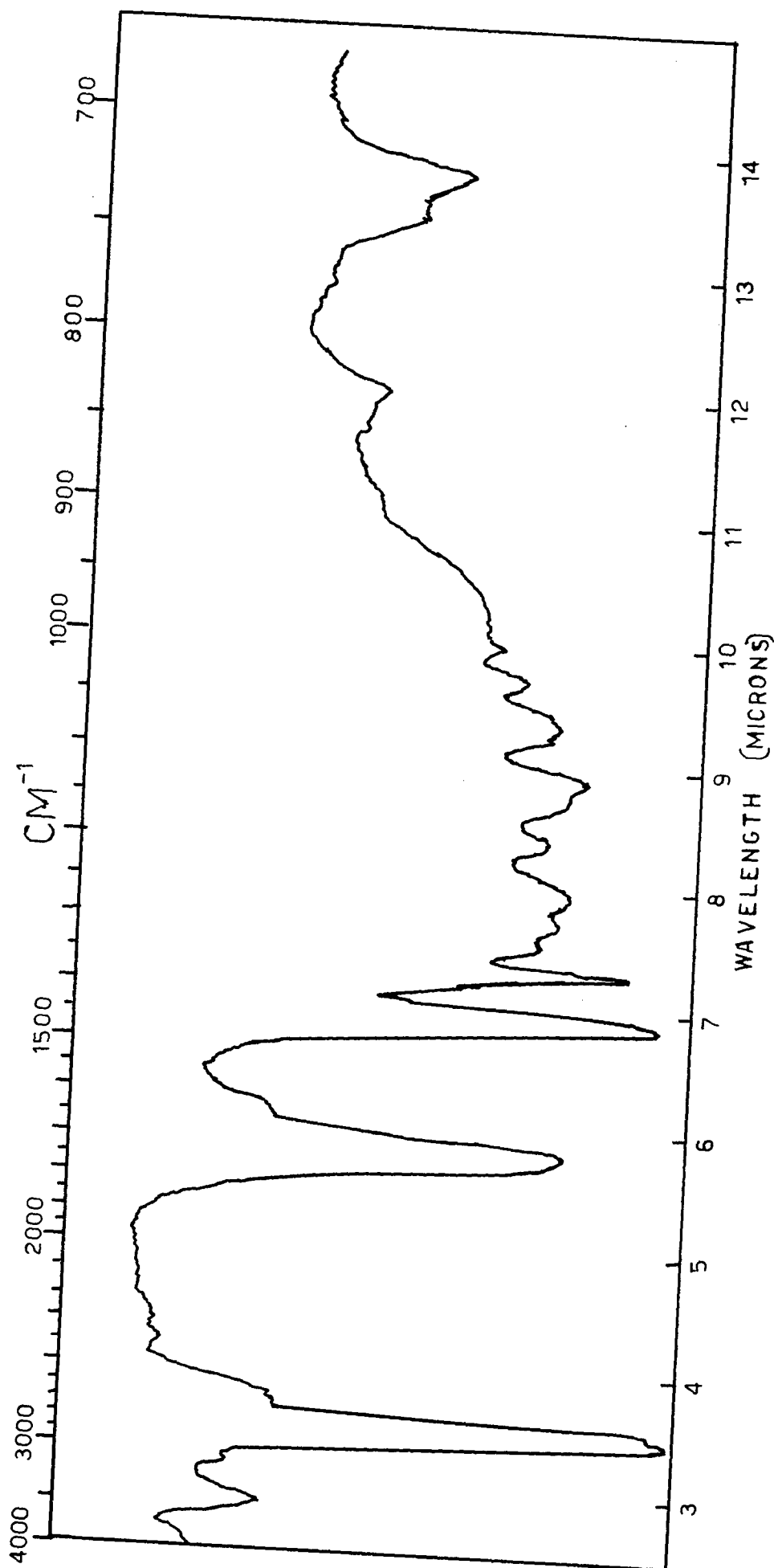


Figure 24. Infrared Spectrum of Poly 3,3-bis(hydroxymethyl)cyclobutane-1,1-dicarboxylate formed at 213° (no catalyst) in Nujol mull.

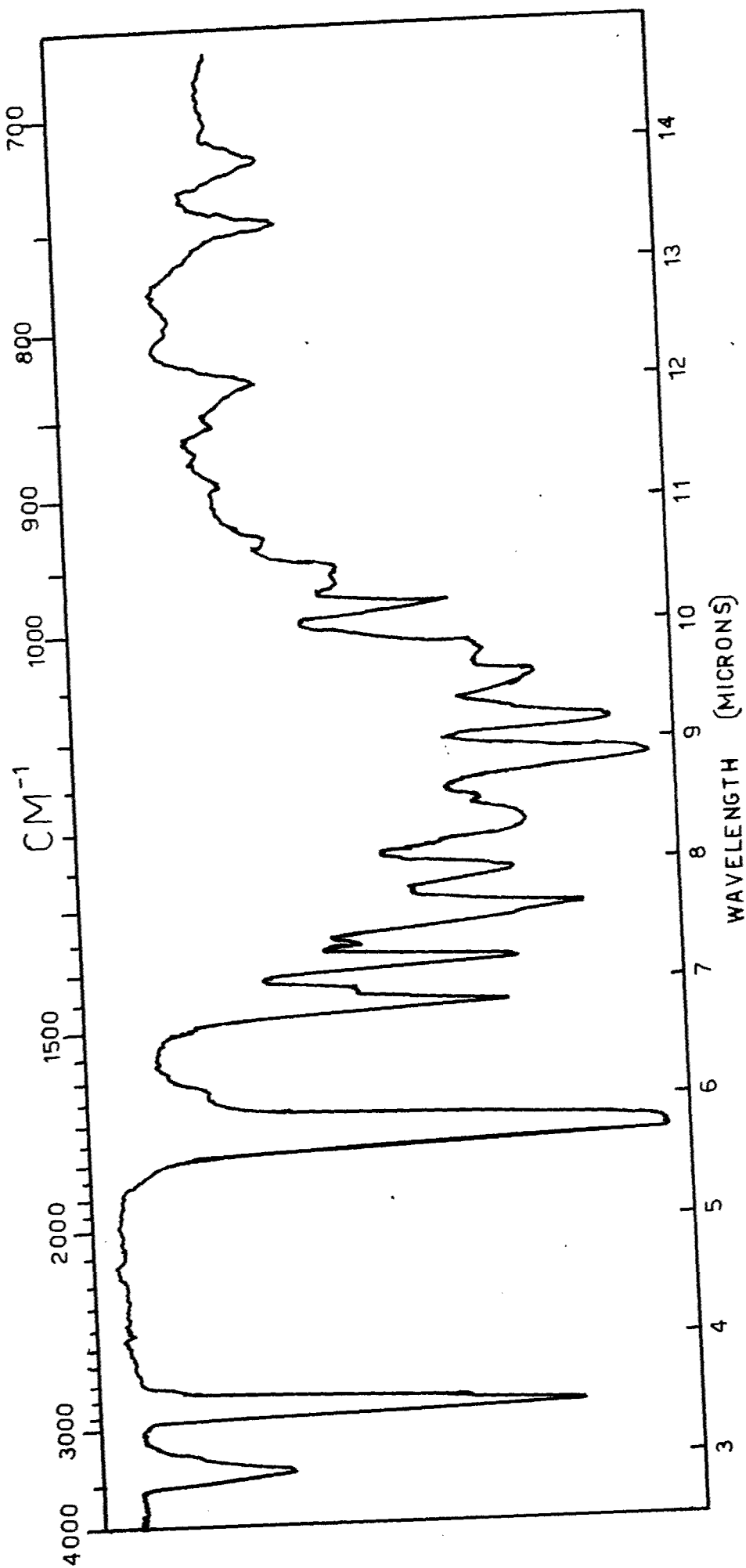


Figure 25. Infrared Spectrum of Unknown Liquid evolved in Polymerization of Diisoamyl 3,3-bis(hydroxymethyl)cyclobutane-1,1-dicarboxylate at 252°.

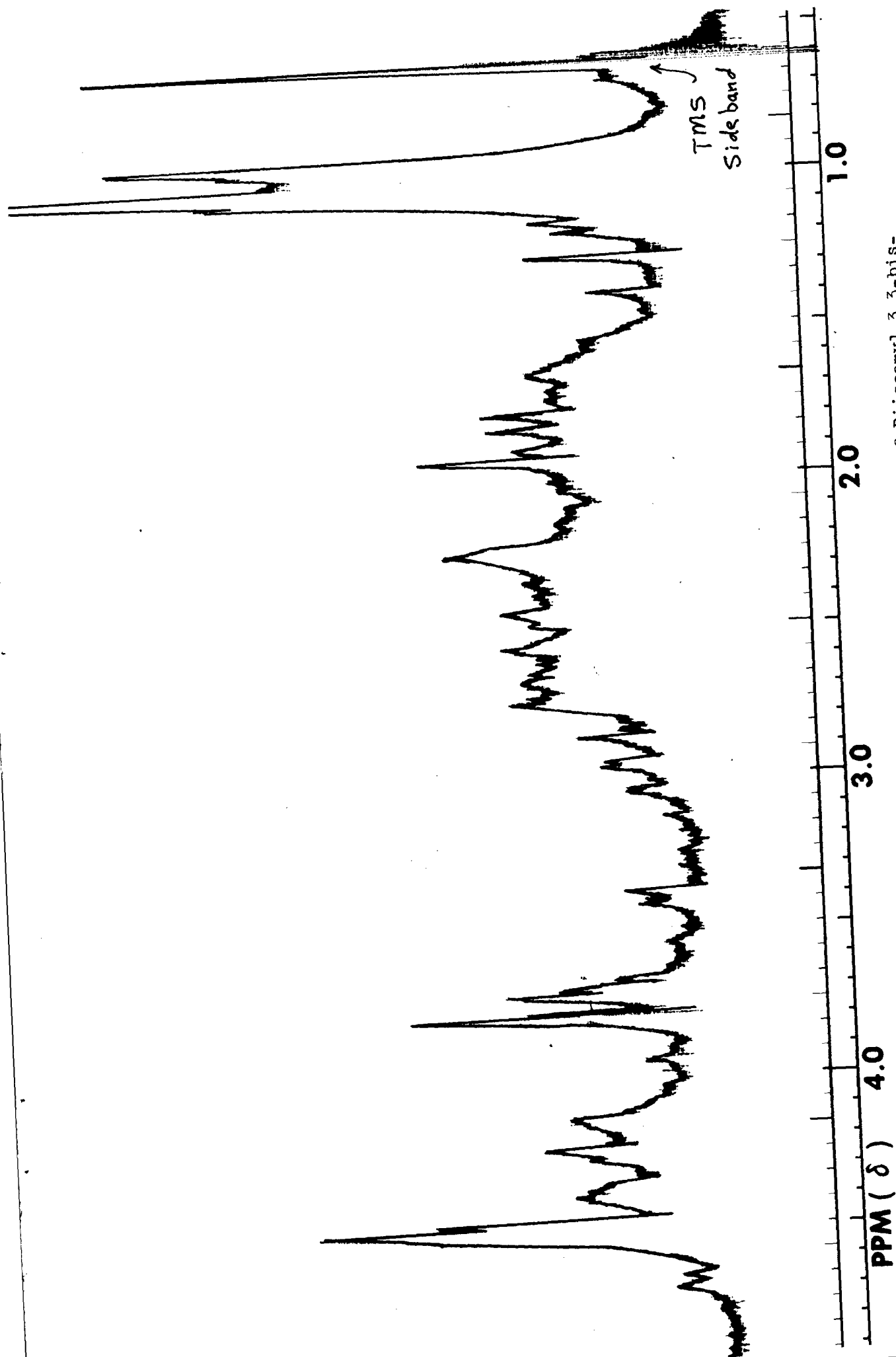


Figure 26. Nmr Spectrum of Unknown Liquid evolved in Polymerization of Diisoamyl 3,3-bis-(hydroxymethyl)cyclobutane-1,1-dicarboxylate at 252° as observed in chloroform.

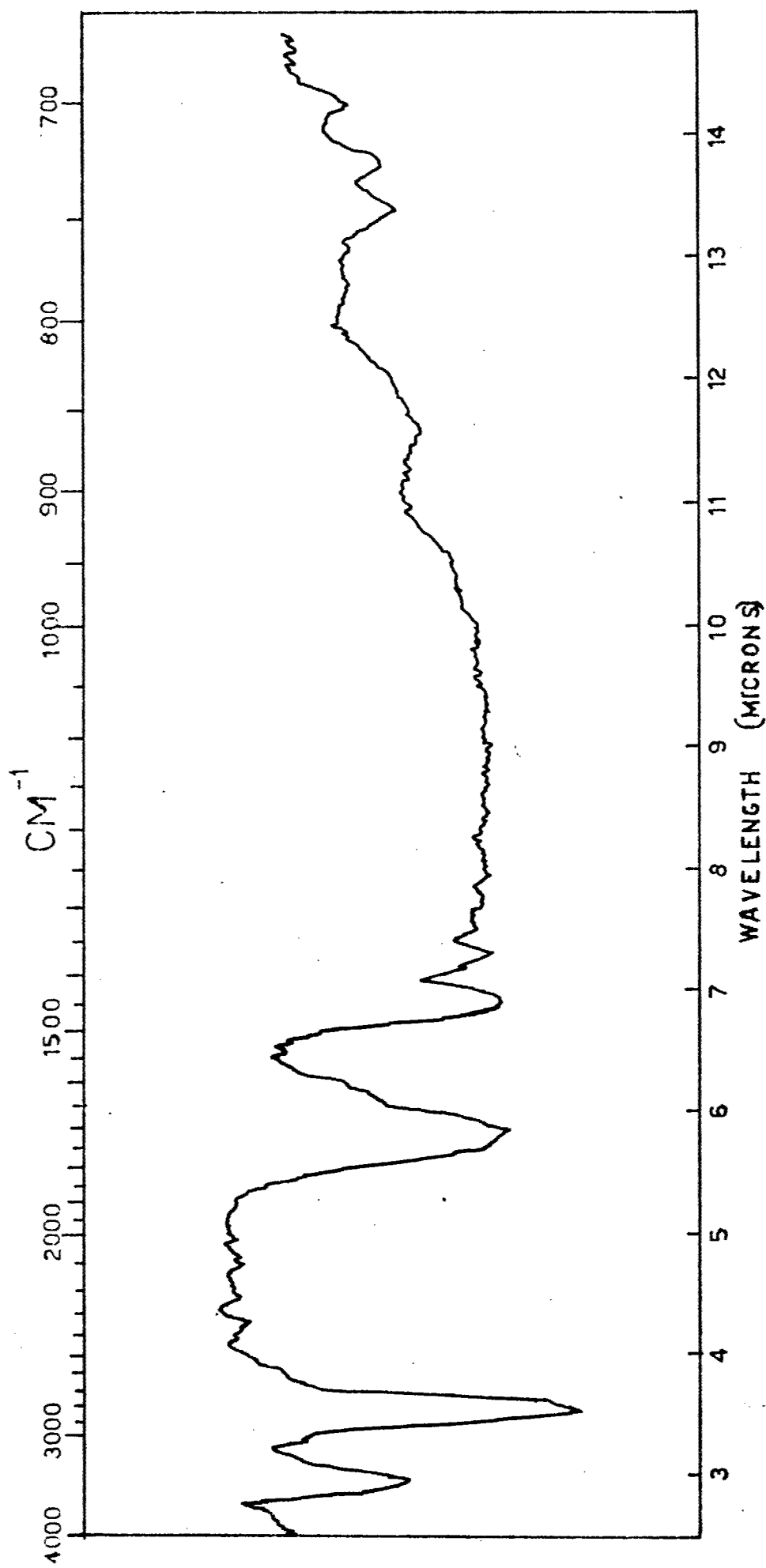


Figure 27. Infrared Spectrum of Polymer Sample 34-B-1, the Polymer from Diethyl 3,3-bis-(hydroxymethyl)cyclobutane-1,1-dicarboxylate.

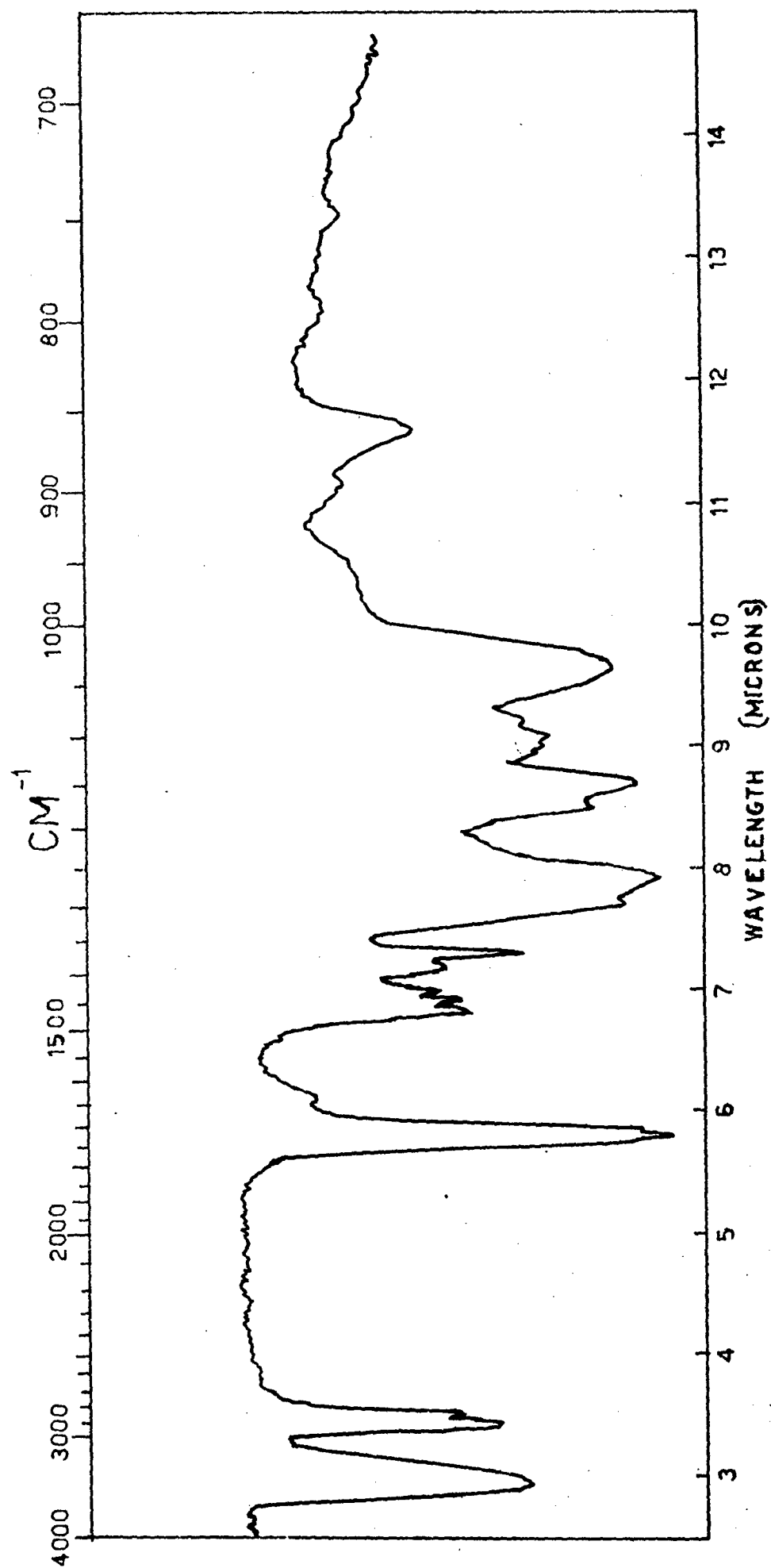


Figure 28. Infrared Spectrum of Polymer Sample 34-B-2, the Polymer from Diethyl 3,3-bis-(hydroxymethyl)cyclobutane-1,1-dicarboxylate.

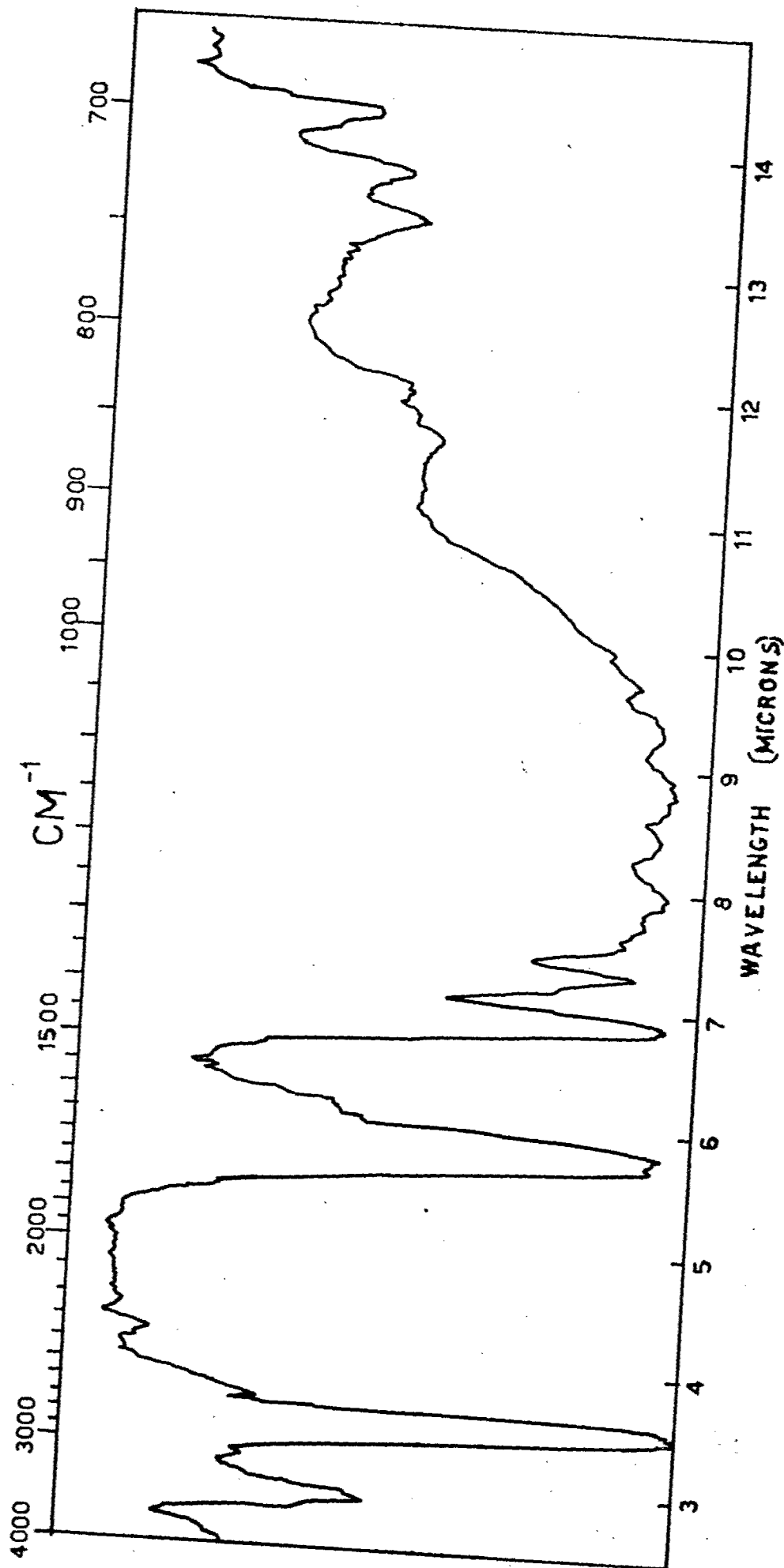


Figure 29. Infrared Spectrum of Polymer Sample 34-B-3, the Polymer from Diethyl 3,3-bis-(hydroxymethyl)cyclobutane-1,1-dicarboxylate.

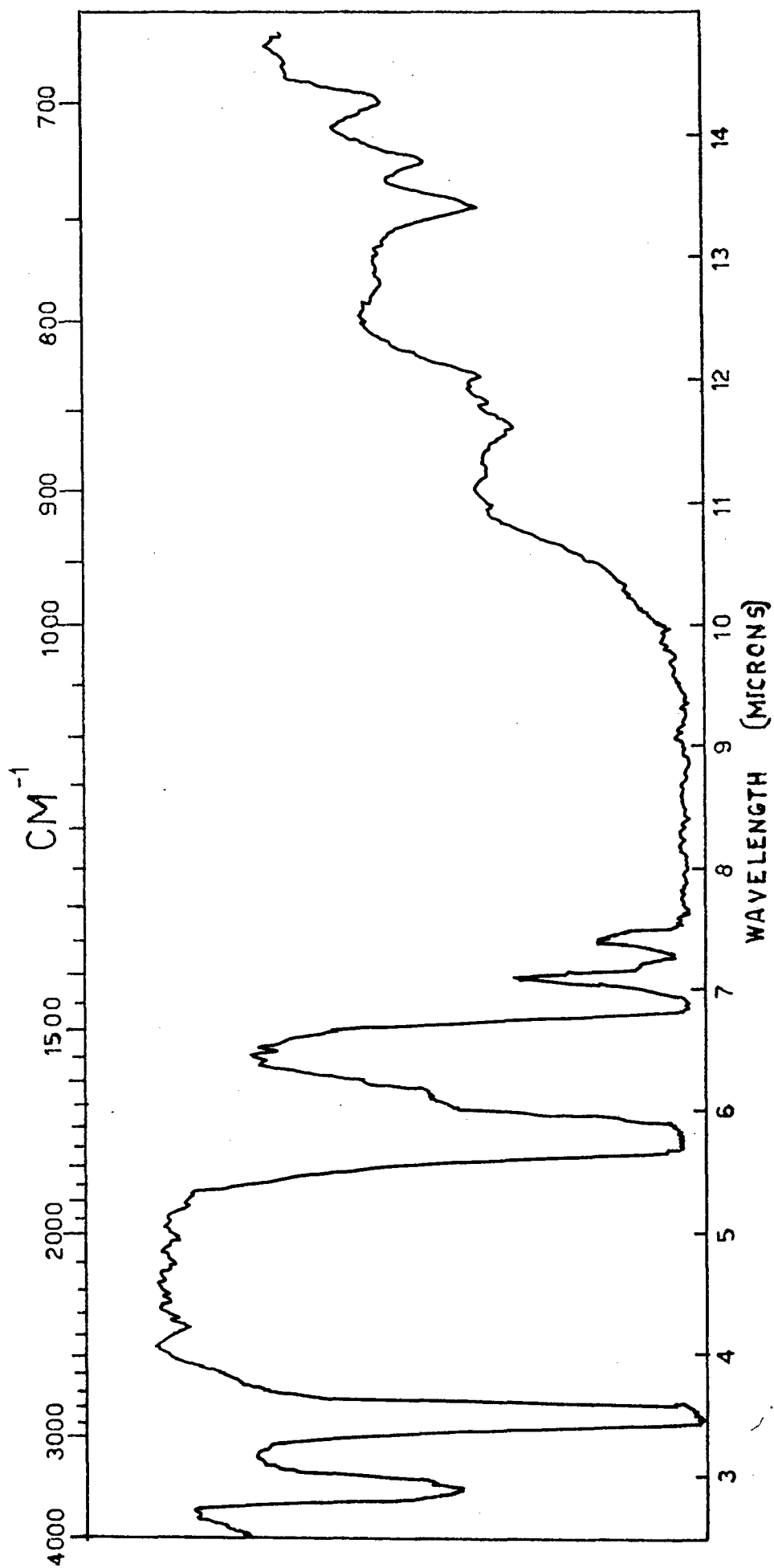


Figure 30. Infrared Spectrum of Polymer Sample 34-B-4, the Polymer from Diethyl 3,3-bis-(hydroxymethyl)cyclobutane-1,1-dicarboxylate.

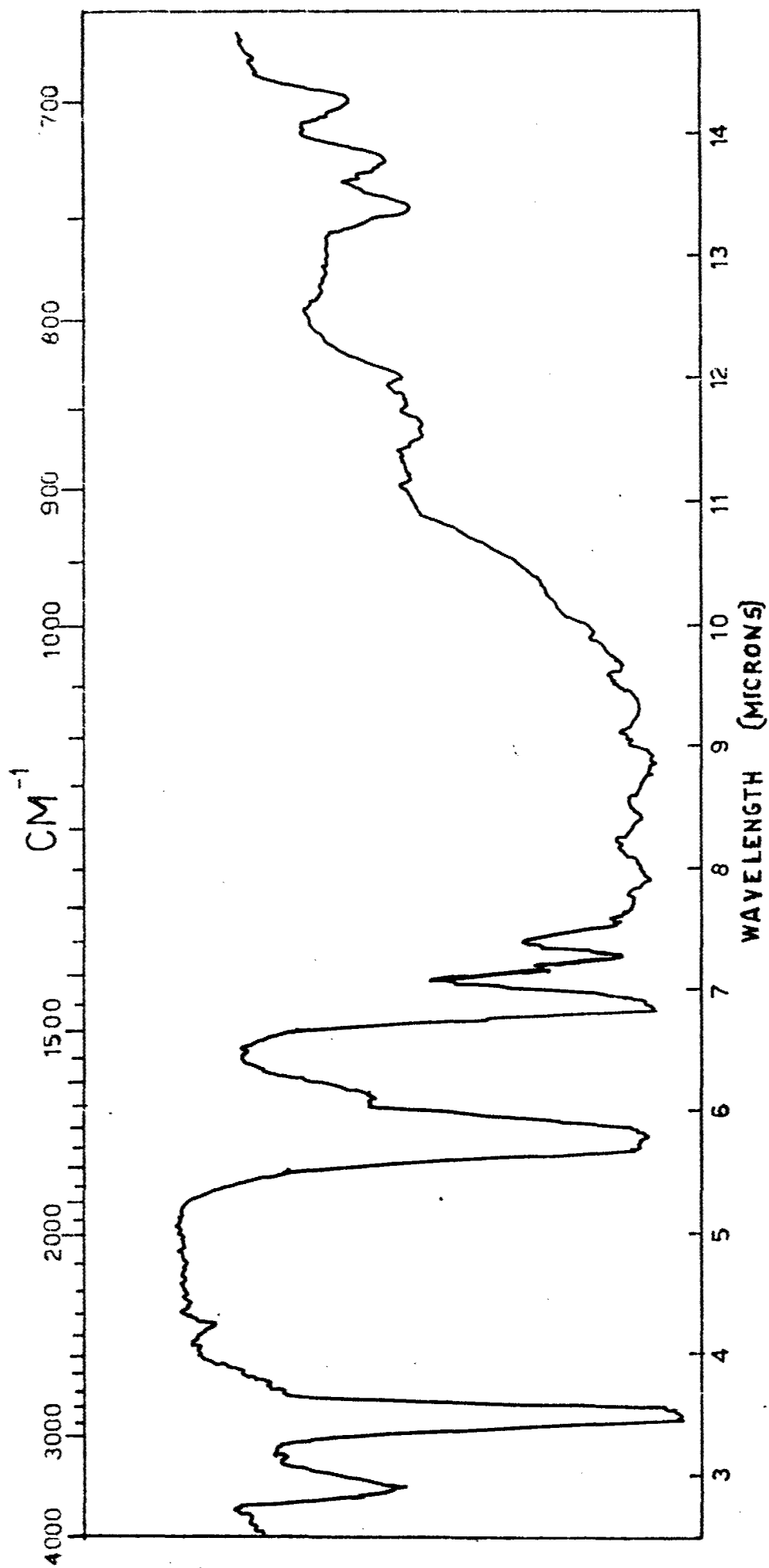


Figure 31. Infrared Spectrum of Polymer Sample 34-B-5, the Polymer from Diethyl 3,3-bis-(hydroxymethyl)cyclobutane-1,1-dicarboxylate.

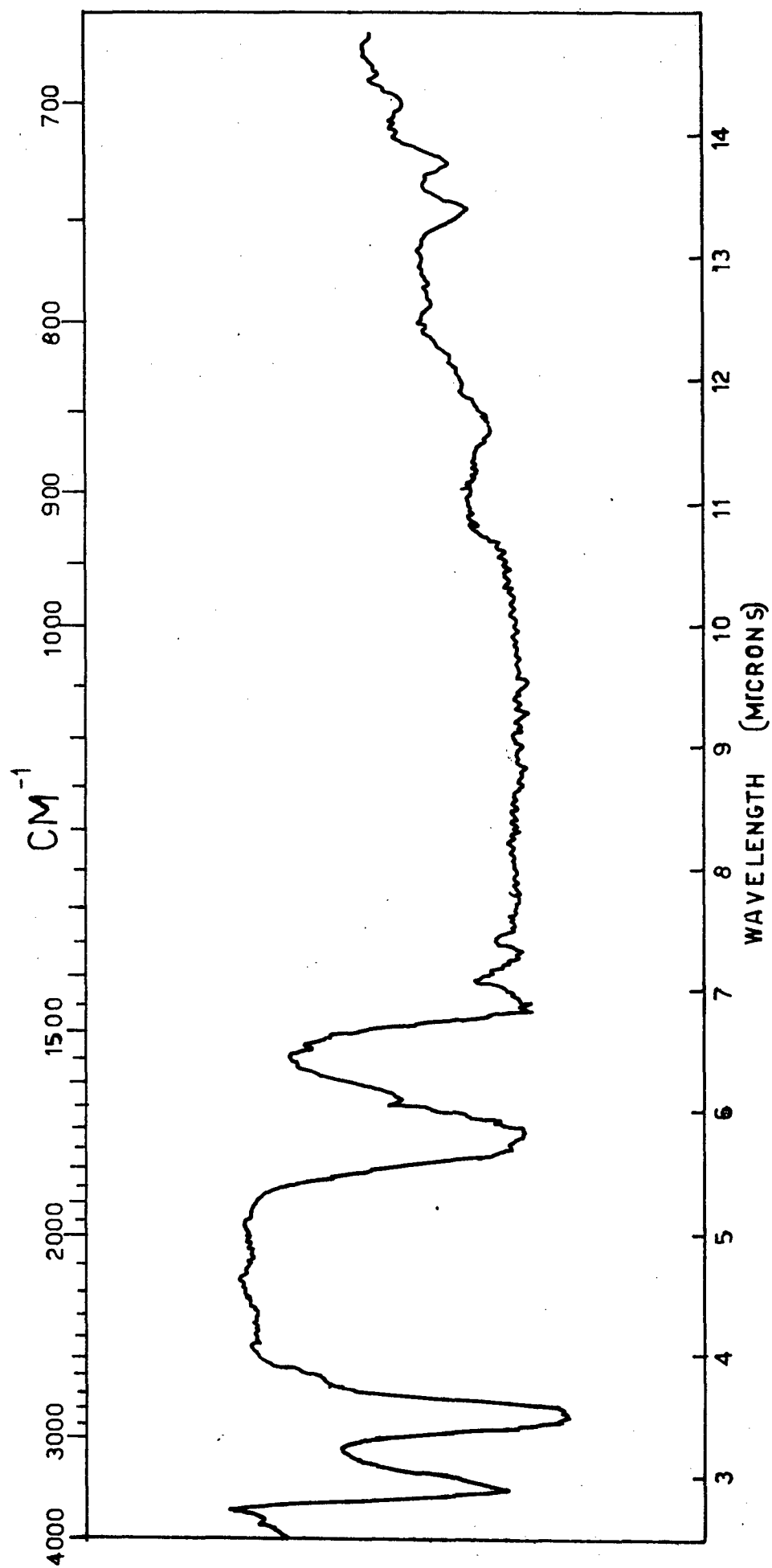


Figure 32. Infrared Spectrum of Polymer Sample 34-B-6, the polymer from Diethyl 3,3-bis-(hydroxymethyl)cyclobutane-1,1-dicarboxylate.

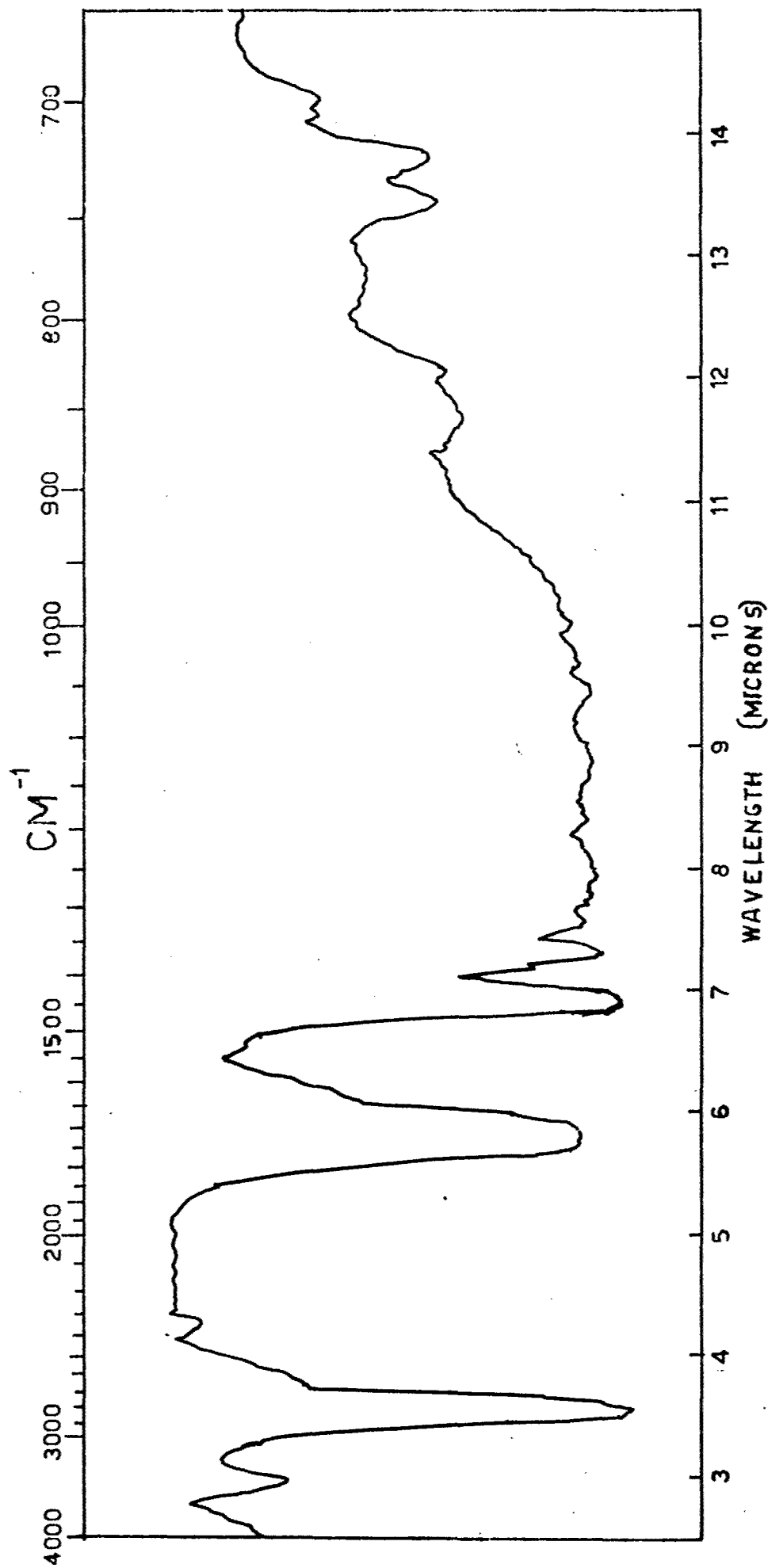


Figure 33. Infrared Spectrum of Polymer Sample 34-B-7, the Polymer from Diethyl 3,3-bis-(hydroxymethyl)cyclobutane-1,1-dicarboxylate.

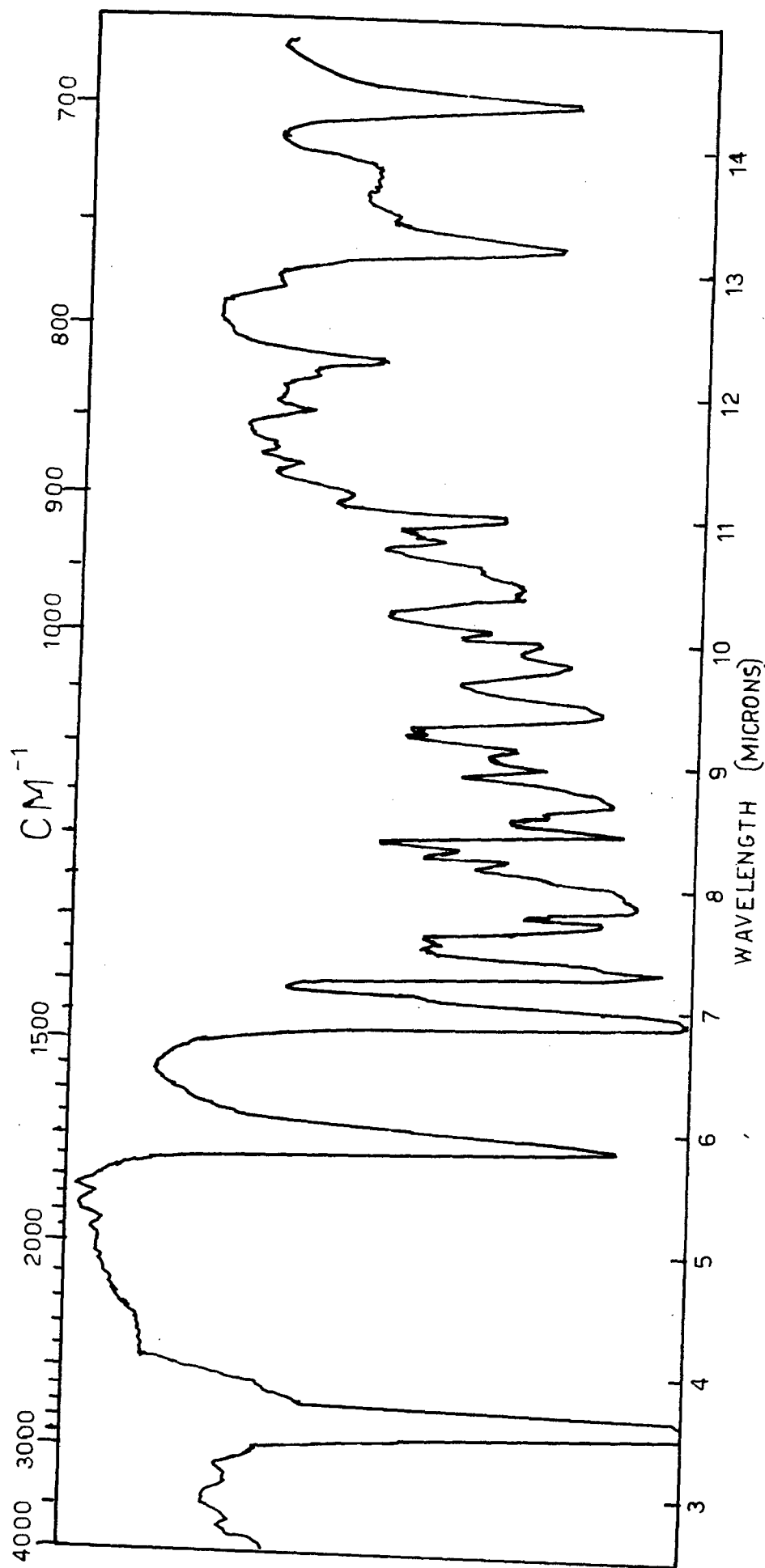


Figure 34. Infrared Spectrum of Diisoamyl 7-phenyl-6,8-dioxaspiro[3.5]nonane-2,2-dicarboxylate.

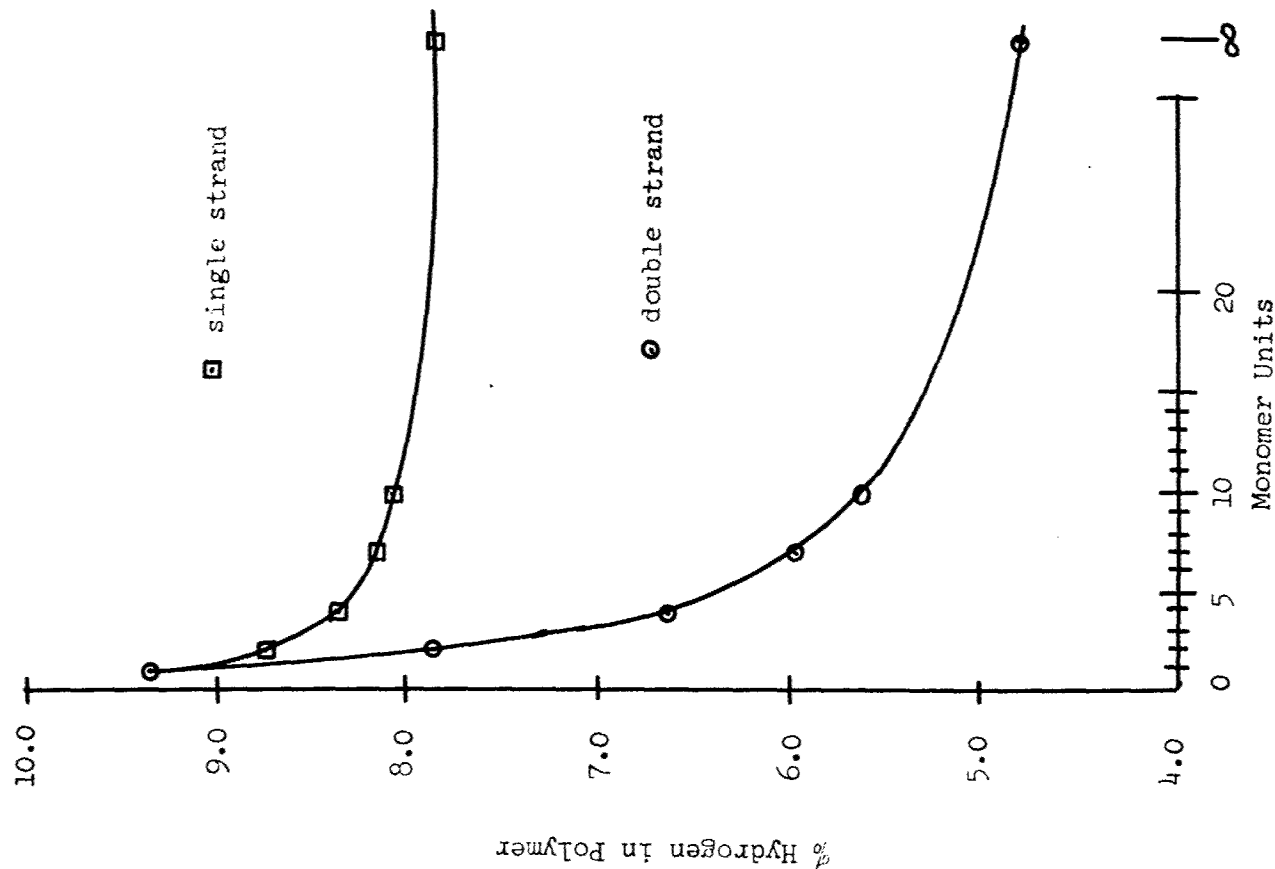
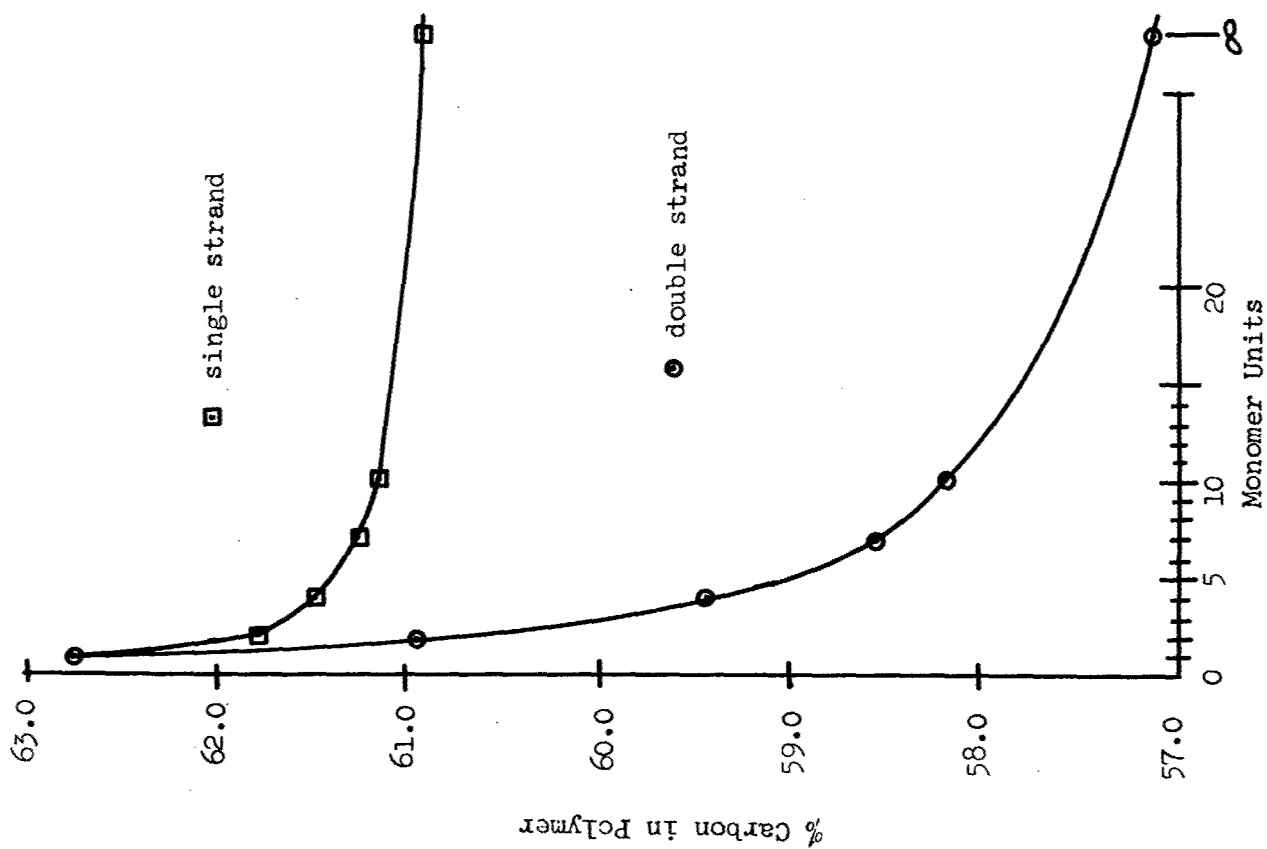


Figure 35. Theoretical % Carbon and % Hydrogen for Poly[3,3-bis(hydroxymethyl)cyclobutane-1,1-dicarboxylate of varied monomer units of Diisomyl 3,3-bis(hydroxymethyl)cyclobutane-1,1-dicarboxylate.

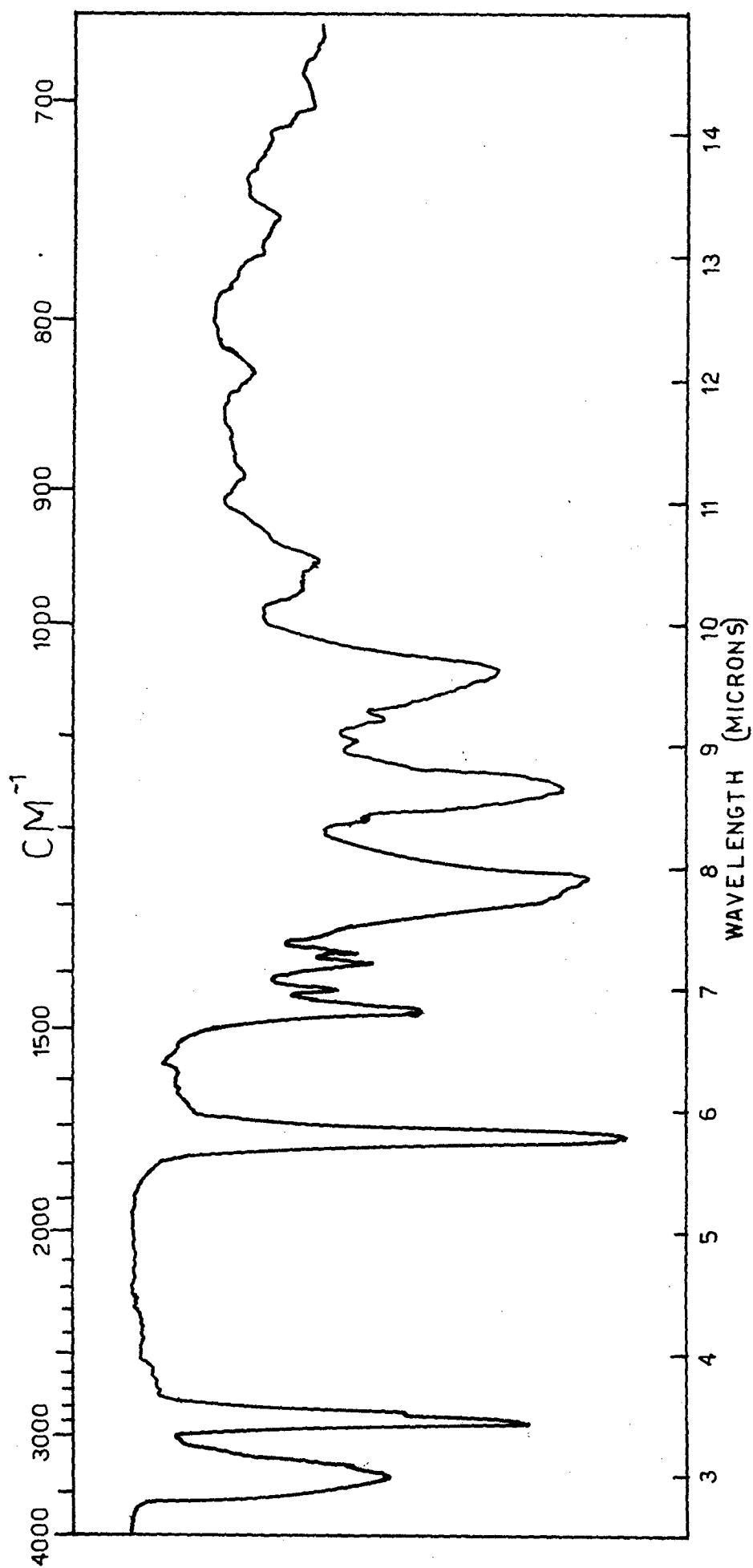


Figure 36. Infrared Spectrum of Sample Monomer 133 (Diisoamyl 3,3-bis(hydroxymethyl)cyclobutane-1,1-dicarboxylate).

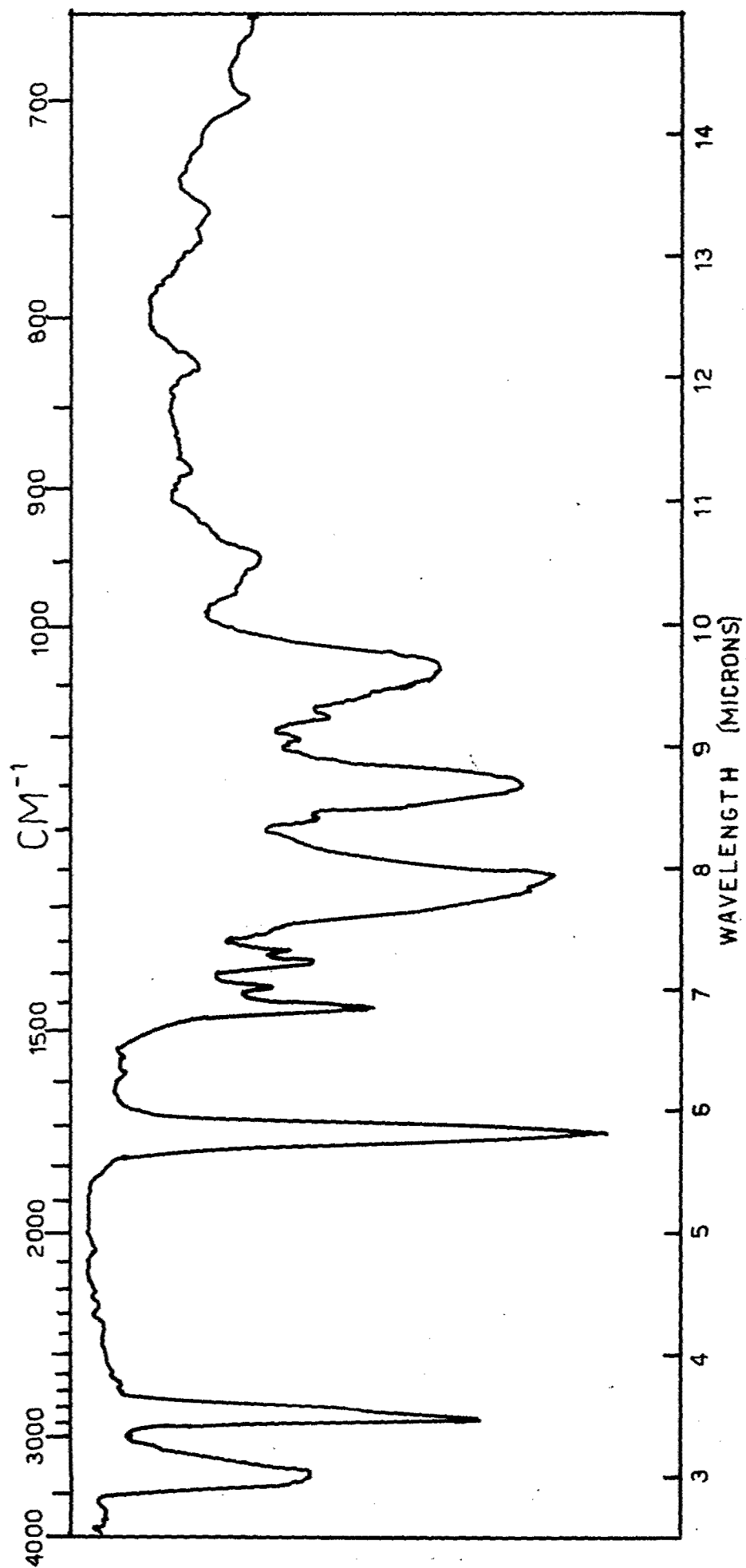


Figure 37. Infrared Spectrum of Sample 133-56 (Unpolymerized Diisoamyl 3,3-bis(hydroxymethyl)-cyclobutane-1,1-dicarboxylate).

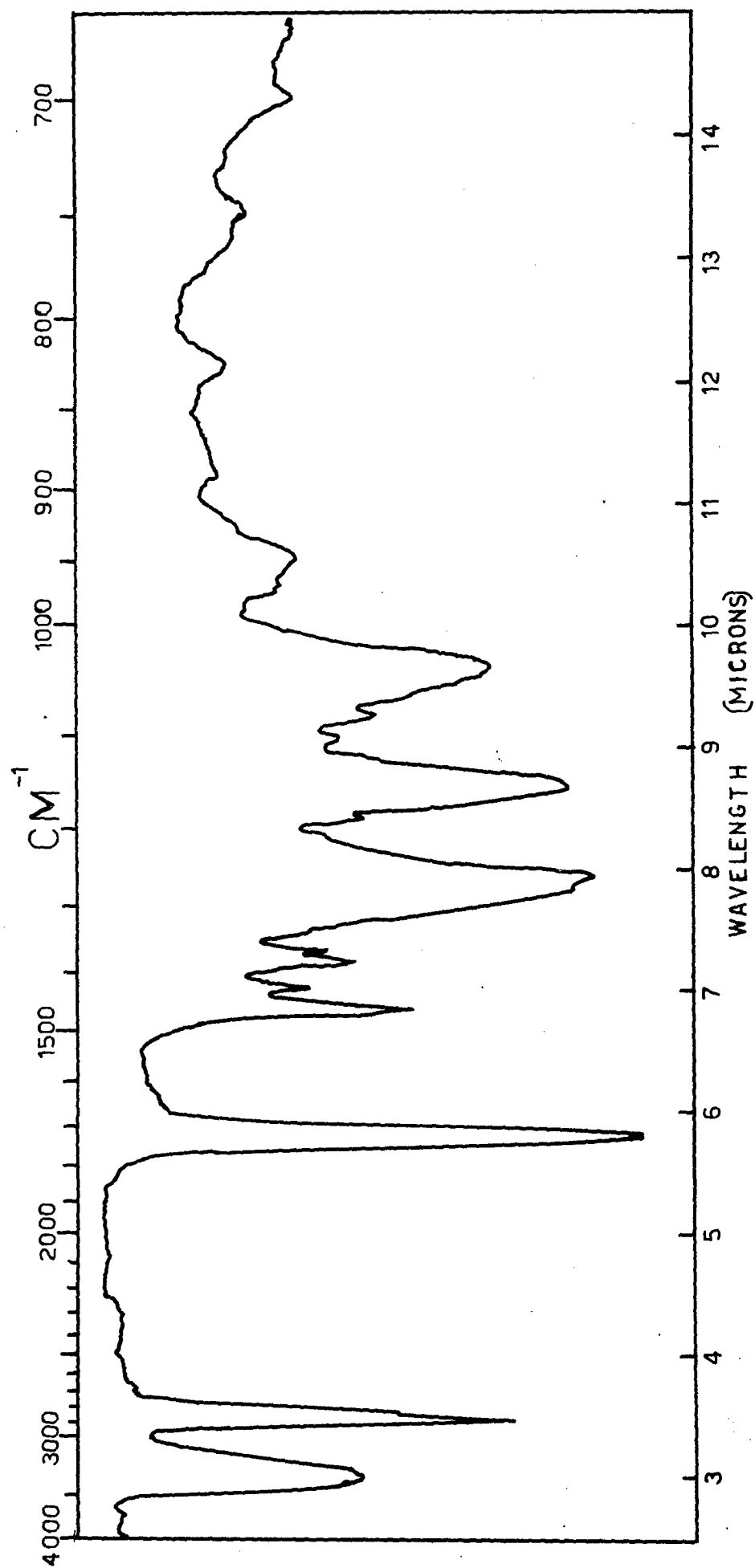


Figure 38. Infrared Spectrum of Sample 134A-80 (Unpolymerized Diisoamyl 3,3-bis(hydroxymethyl)-cyclobutane-1,1-dicarboxylate).

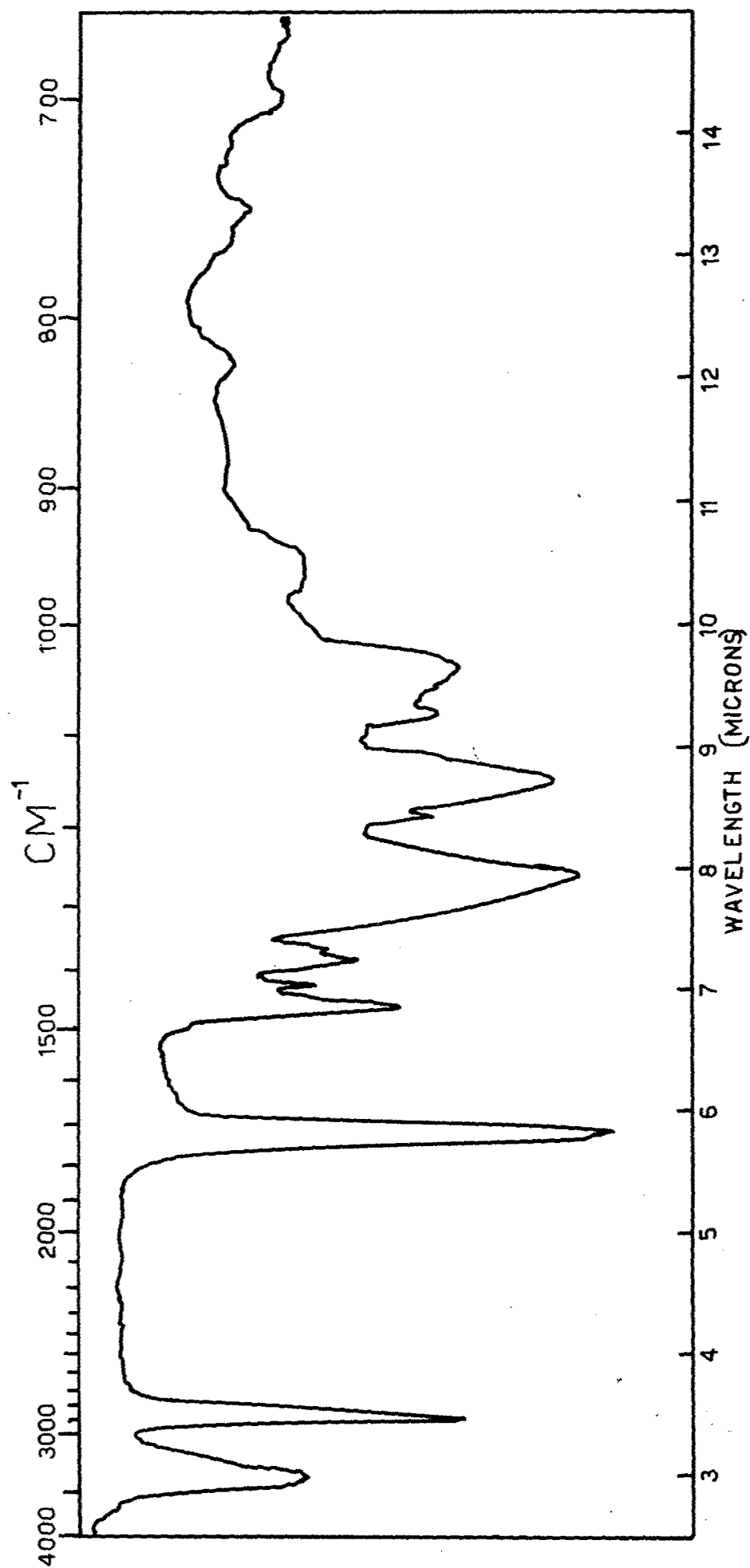


Figure 39. Infrared Spectrum of Sample 134A-90 (Polymerized Diisoamyl 3,3-bis(hydroxymethyl)-cyclobutane-1,1-dicarboxylate).

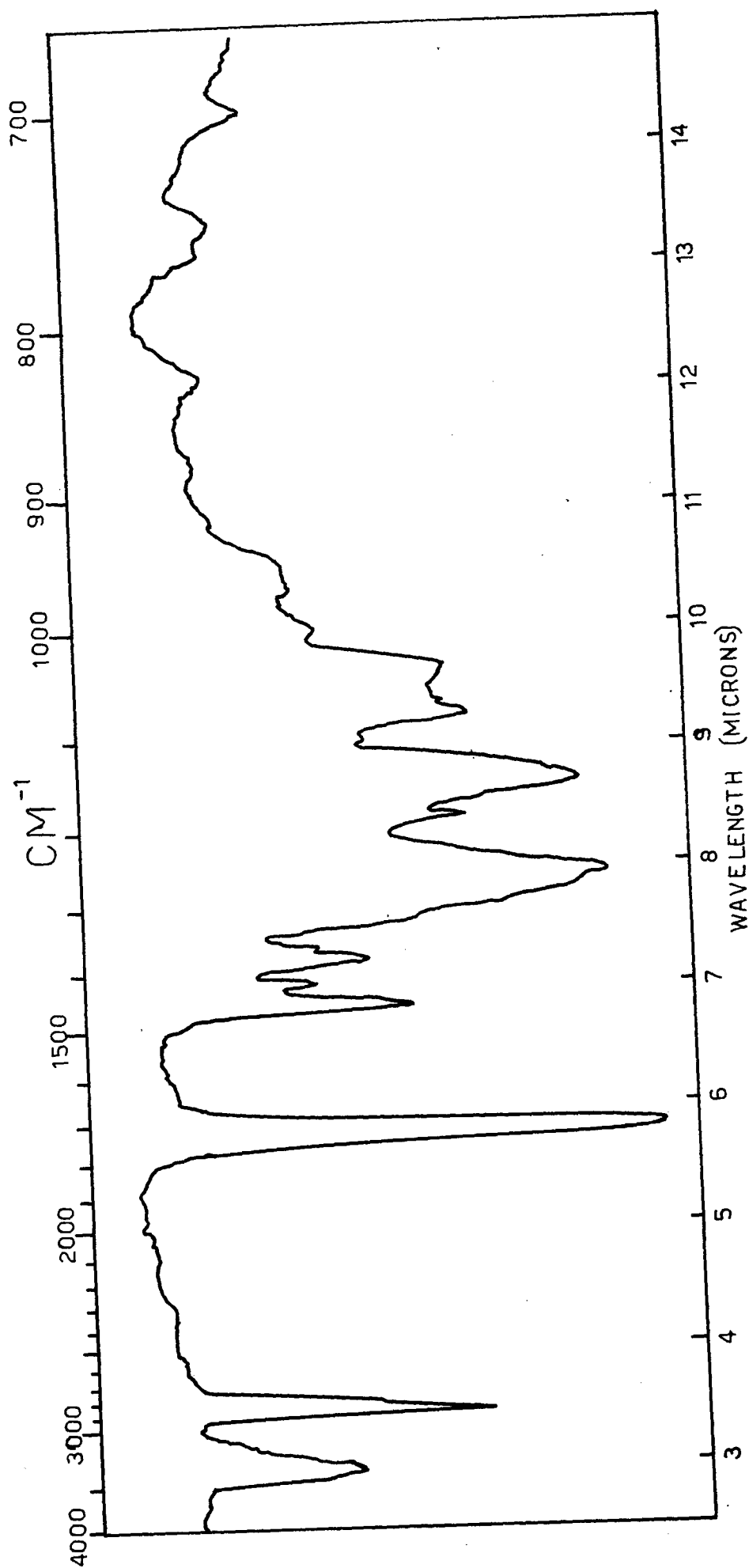


Figure 40. Infrared Spectrum of Sample 134B-100 (Polymerized Diisoamyl 3,3-bis(hydroxymethyl)-cyclobutane-1,1-dicarboxylate).

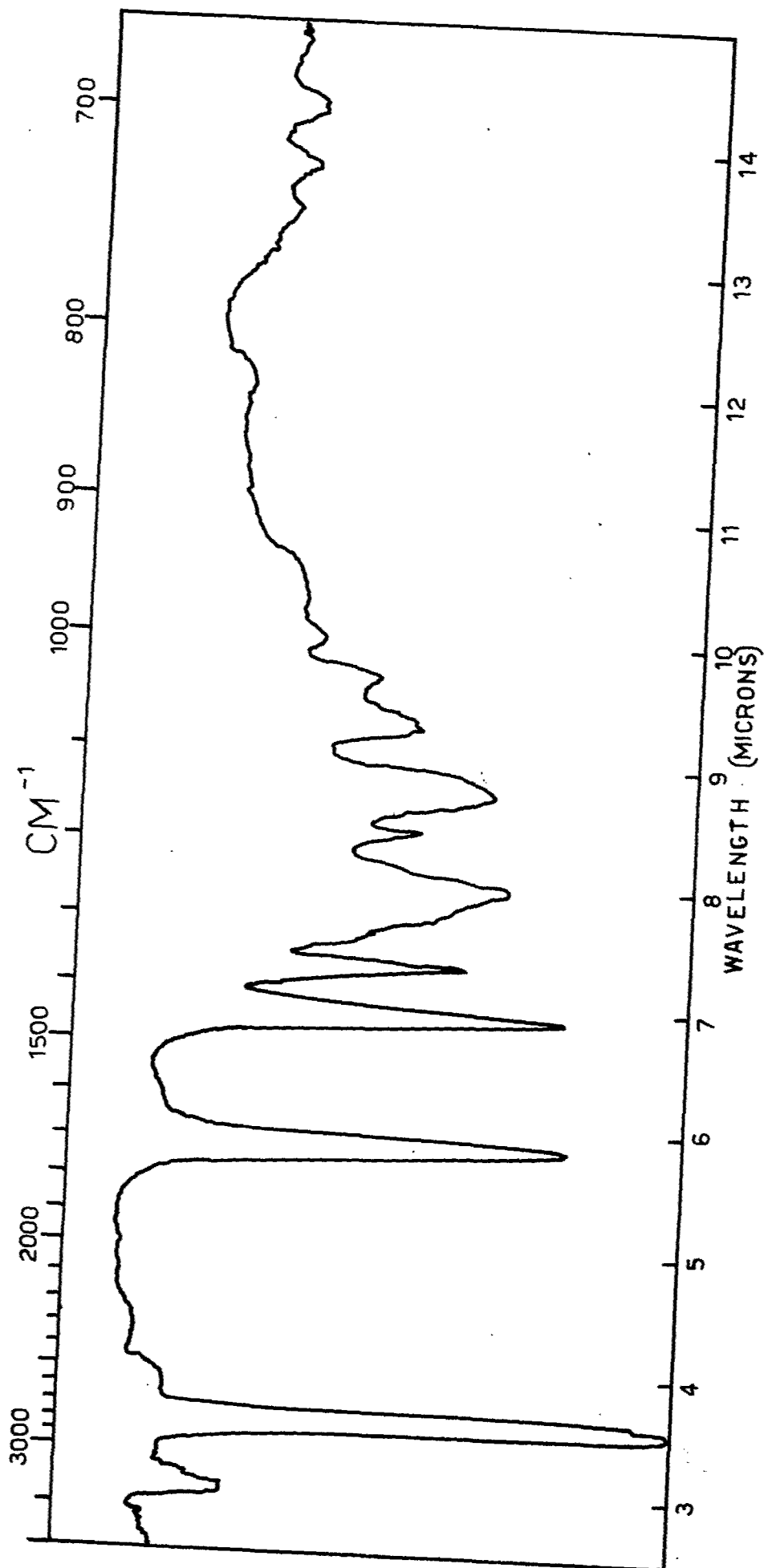


Figure 41. Infrared Spectrum of Sample 134C-110 (Polymerized Diisoamyl 3,3-bis(hydroxymethyl)-cyclobutane-1,1-dicarboxylate).

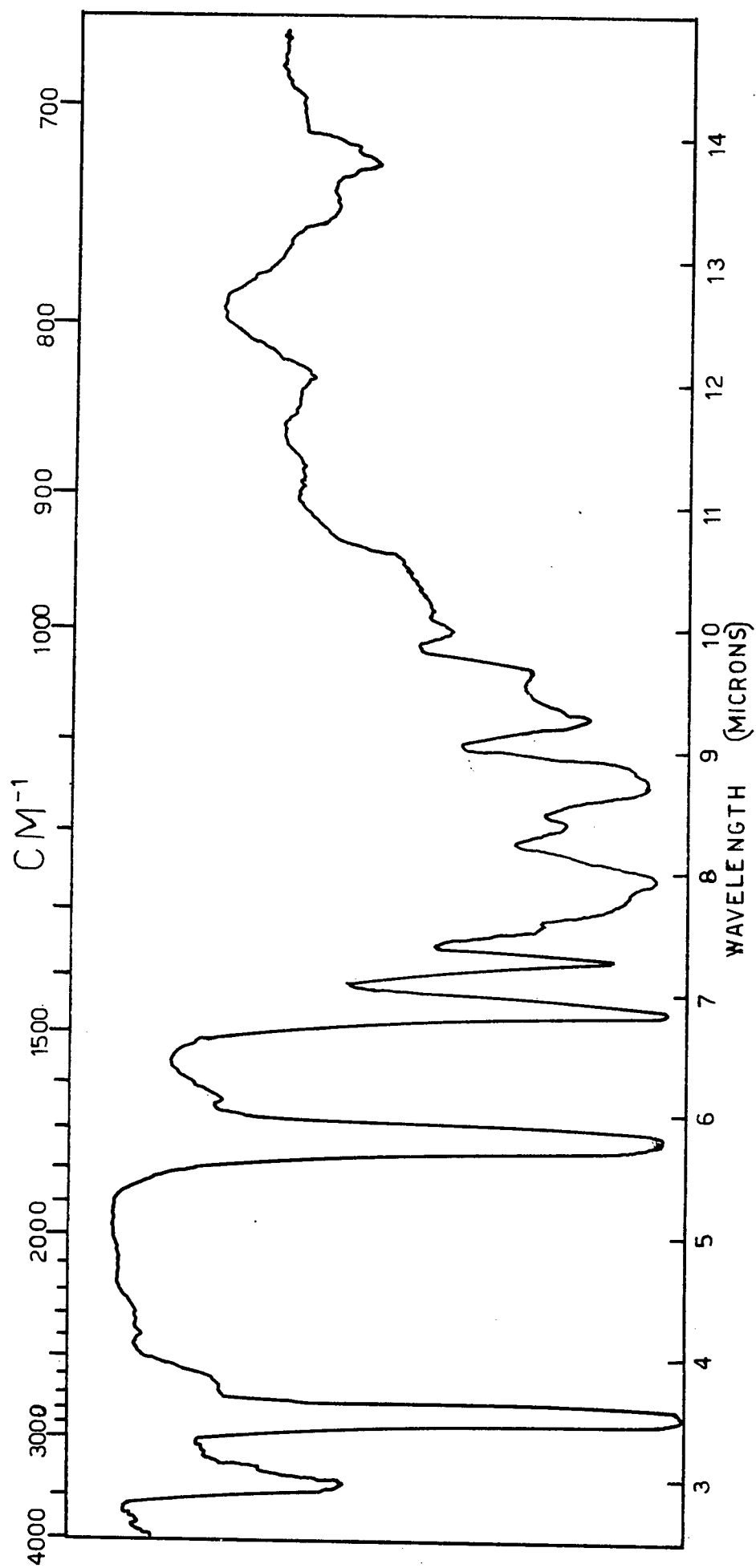


Figure 42. Infrared Spectrum of Sample 140A (Polymerized Diisocyanyl 3,3-bis(hydroxymethyl)-cyclobutane-1,1-dicarboxylate).

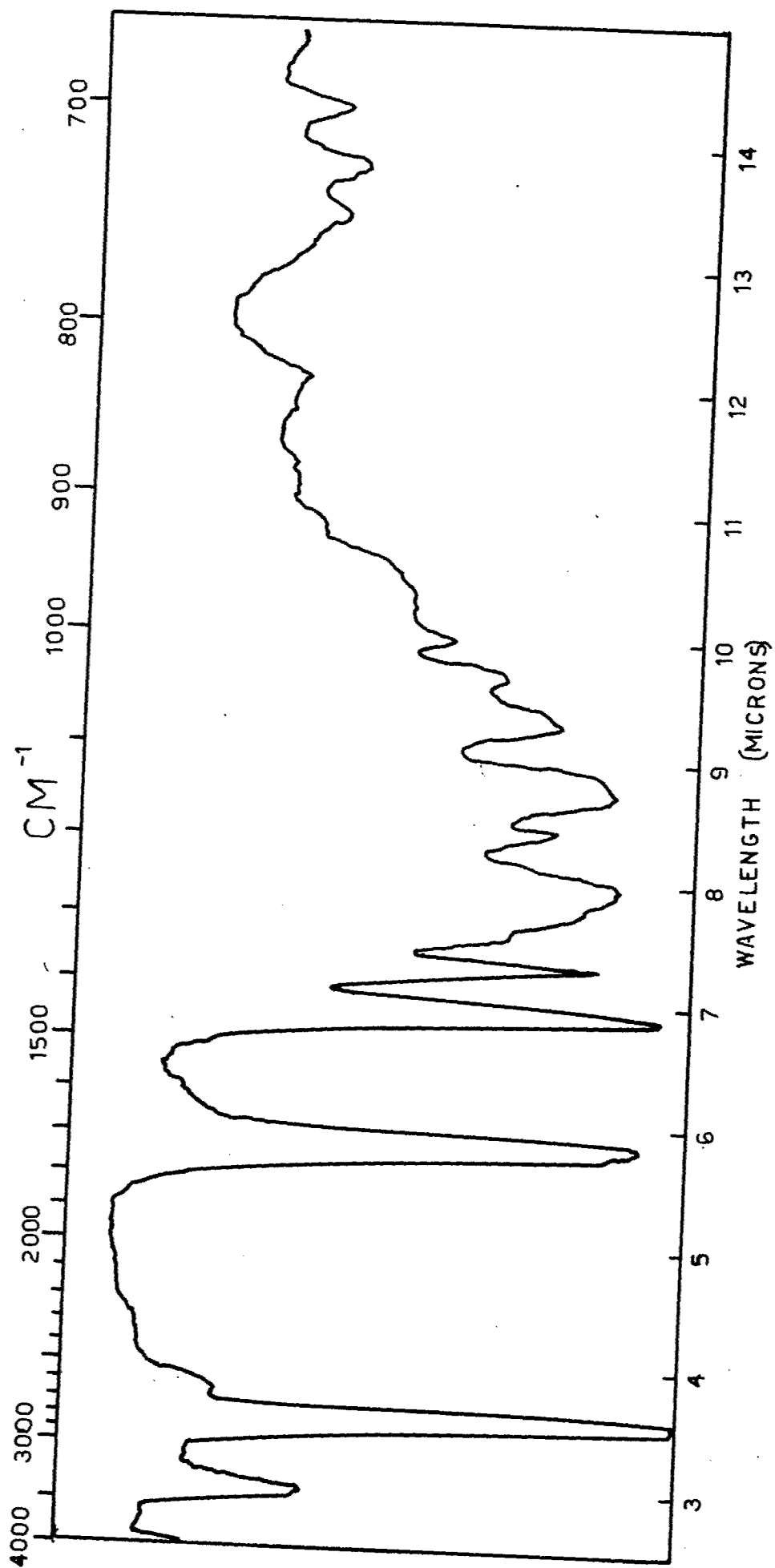


Figure 43. Infrared Spectrum of Sample 134-DEF-115 (Polymerized Diisocyanyl 3,3-bis(hydroxymethyl)-cyclobutane-1,1-dicarboxylate).

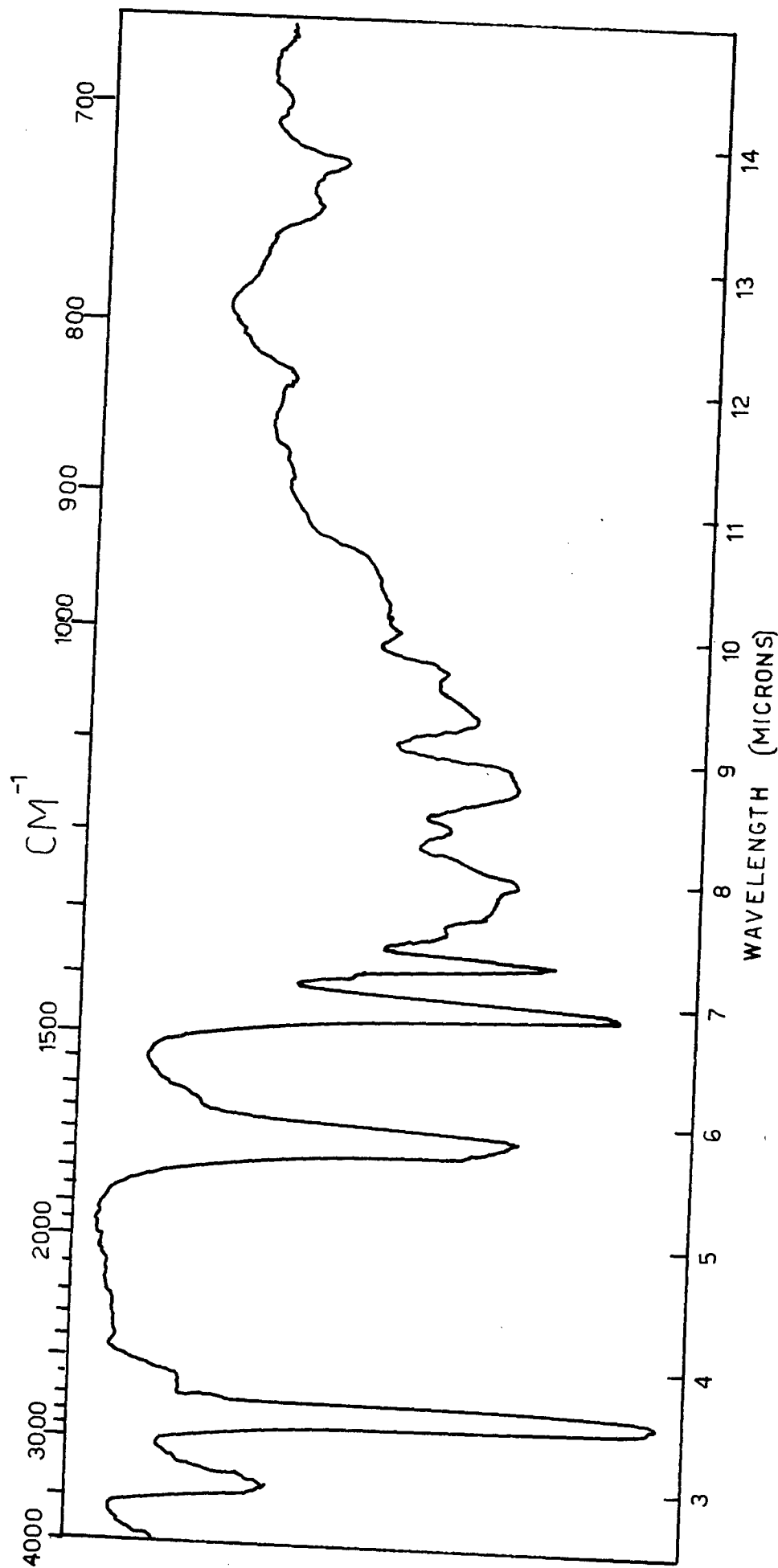


Figure 44. Infrared Spectrum of Sample 143A (Polymerized Diisoamyl 3,3-bis(hydroxymethyl)-cyclobutane-1,1-dicarboxylate).

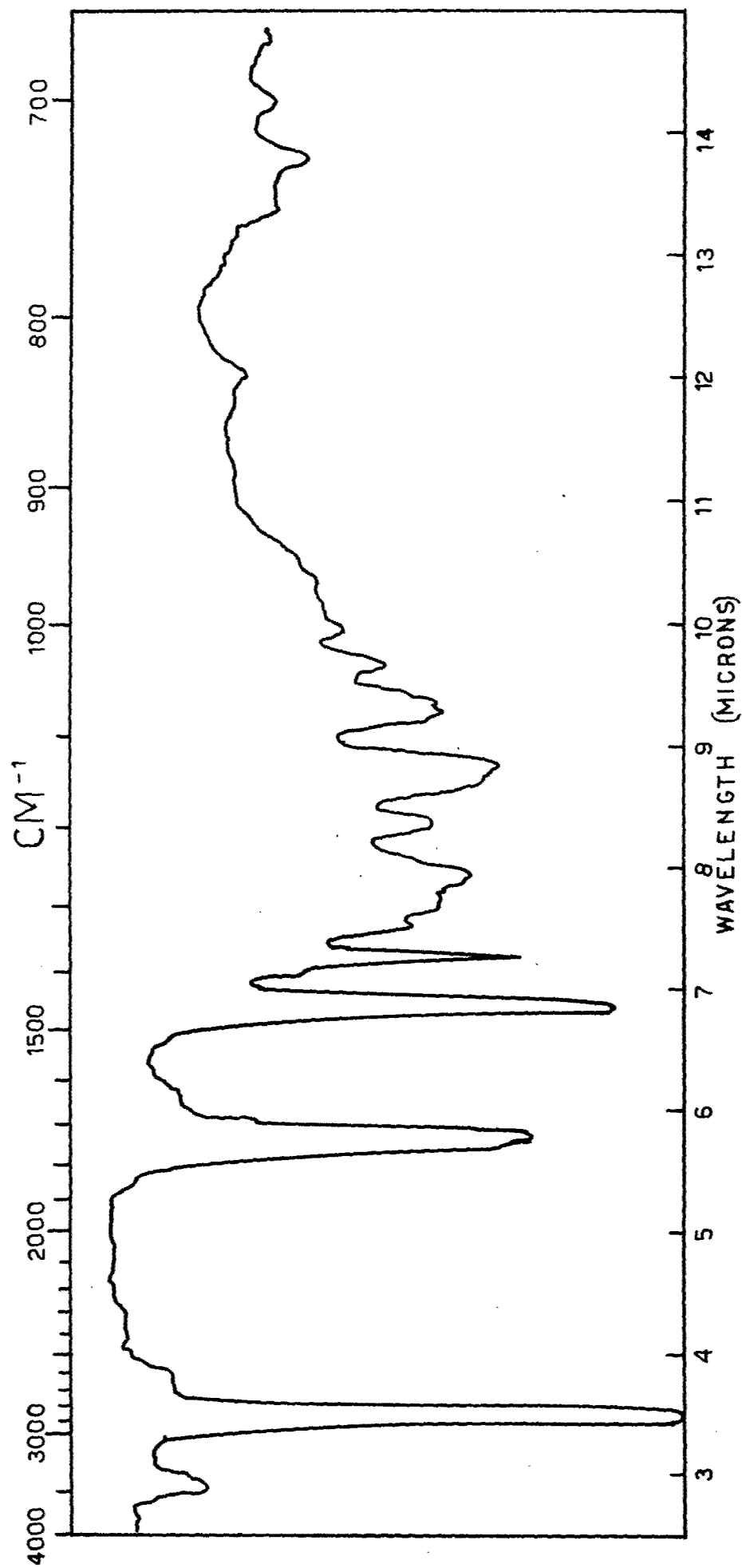


Figure 45. Infrared Spectrum of Sample 145A-179 (Polymerized Diisoamyl 3,3-bis(hydroxymethyl)-cyclobutane-1,1-dicarboxylate).

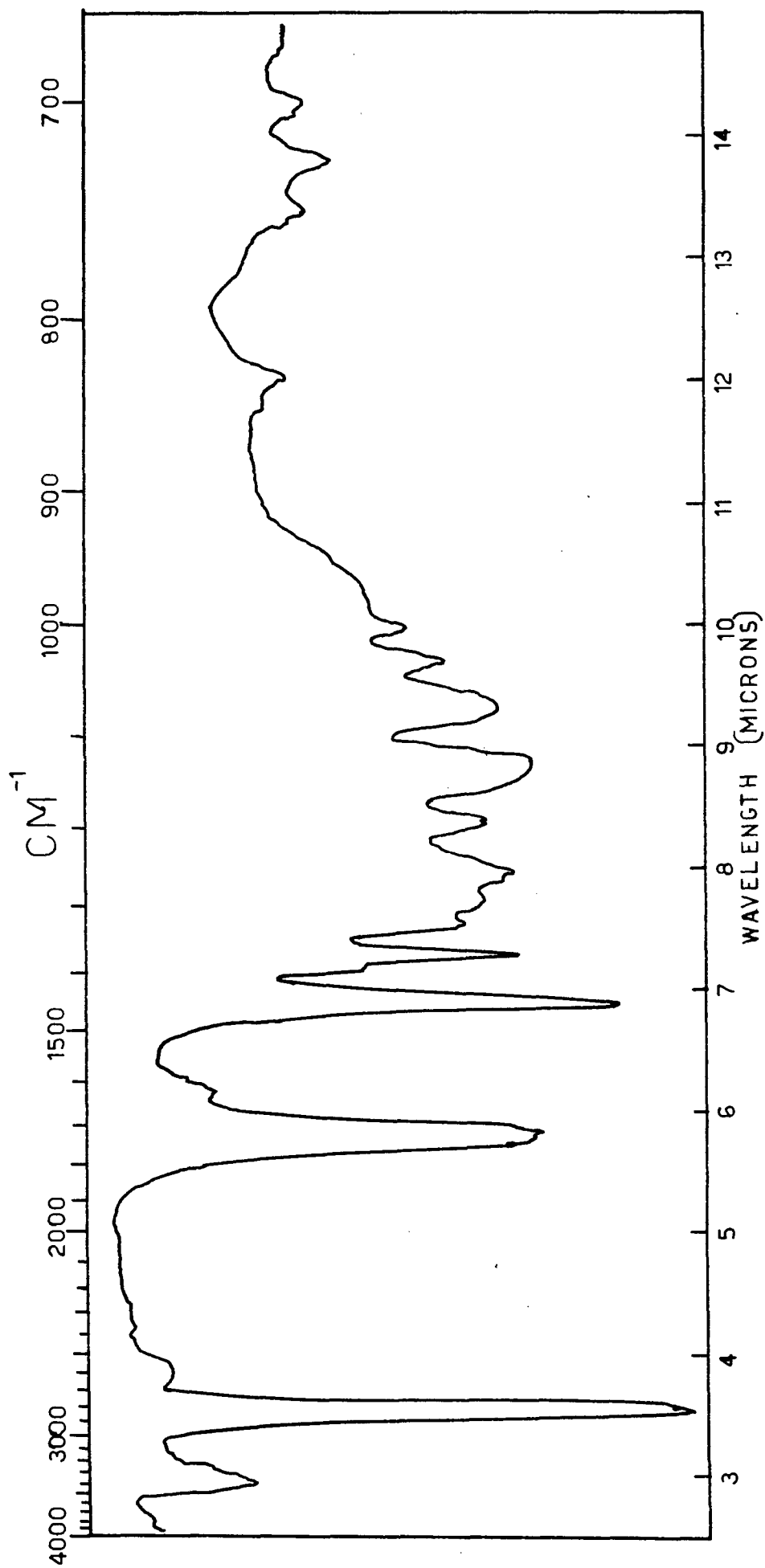


Figure 46. Infrared Spectrum of Sample 145A-213 (Polymerized Diisoamyl 3,3-bis(hydroxymethyl)-cyclobutane-1,1-dicarboxylate).

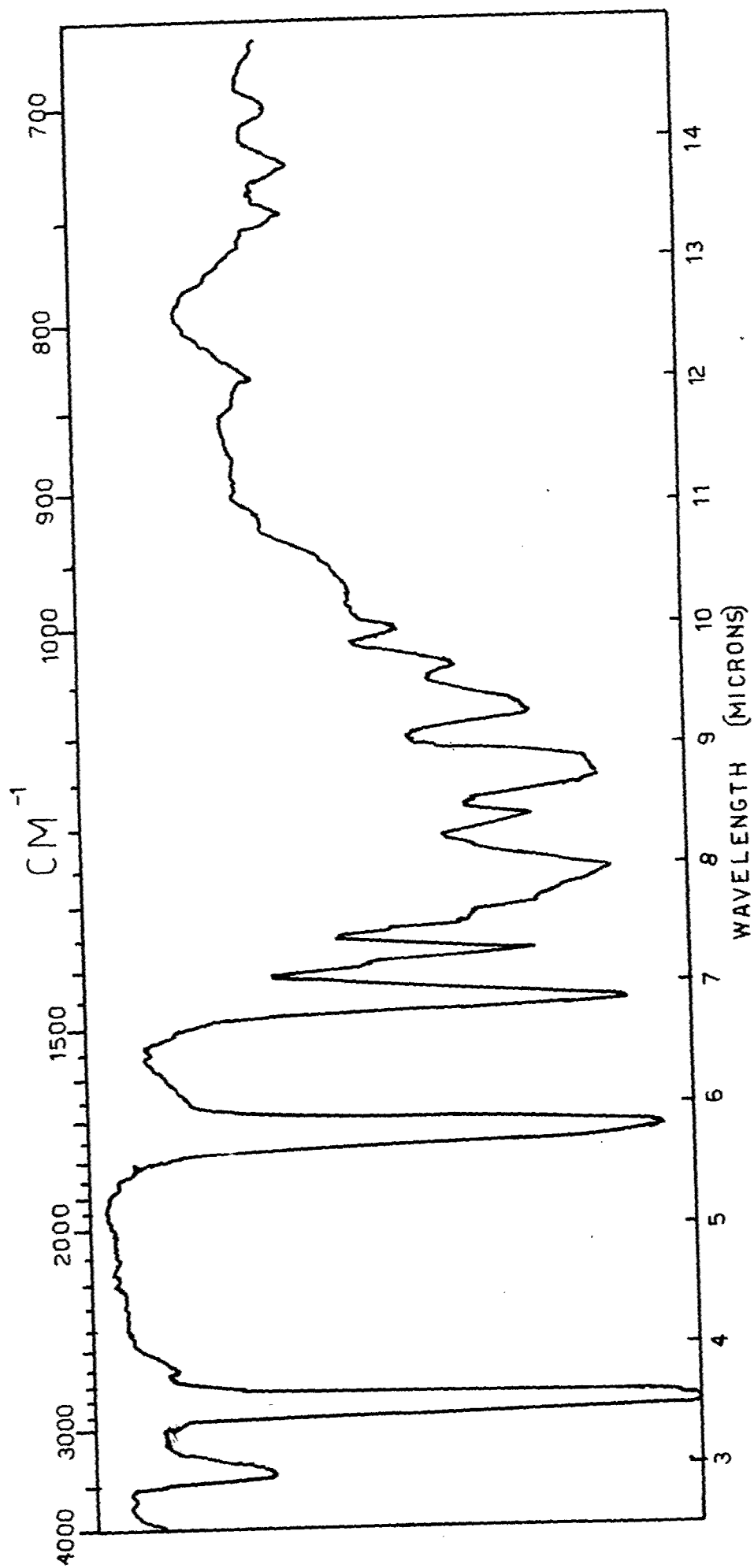


Figure 47. Infrared Spectrum of Sample 134-SP-130 (Polymerized Diisoamyl 3,3-bis(hydroxymethyl)-cyclobutane-1,1-dicarboxylate).

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Security Classification

DOCUMENT CONTROL DATA - R & D		
(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)		
1. ORIGINATING ACTIVITY (Corporate author) San Diego State College Foundation San Diego State College San Diego, California 92115		2a. REPORT SECURITY CLASSIFICATION Unclassified
		2b. GROUP
3. REPORT TITLE SYNTHESIS OF POLYSPIROCYCLOBUTANES AND RELATED SPIROPOLYMERS. Part II. Poly-(trispiro[3.1.1.3.1.1]dodecane-1,3-dione) and Poly[3,3-Bis(methylene)cyclobutane-1,1-dicarboxylate]		
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Technical Report (1 March 1968 to 1 July 1970)		
5. AUTHOR(S) (First name, middle initial, last name) C. M. Sharts D. L. Steele		
6. REPORT DATE December 1970	7a. TOTAL NO. OF PAGES 110	7b. NO. OF REFS 11
8a. CONTRACT OR GRANT NO. F33615-67-C-1560	9a. ORIGINATOR'S REPORT NUMBER(S) 250-020 Annual Report Number Two	
b. PROJECT NO. 7342		
c. Task No. 734201	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report) AFML-TR-68-130	
d.		
10. DISTRIBUTION STATEMENT This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of the Polymer Branch, Nonmetallic Materials Division, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio 45433.		
11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY Air Force Materials Laboratory Air Force Systems Command Wright-Patterson Air Force Base, Ohio 45433	
13. ABSTRACT Dispiro[3.1.1.3.1.1]decane-2,8-dicarboxylic acid was converted to the corresponding diacid chloride. Dehydrohalogenation of the diacidchloride gave a bis-ketene intermediate which polymerized to poly(trispiro[3.1.1.3.1.1]dodecane-1,3-dione) (I). Polymer I was fluorinated with sulfur tetrafluoride to a new fluorinated polyspirocyclobutane. Attempts to convert Polymer I into polyspirocyclobutane failed. Diethyl and diisooamyl 3,3-bis(hydroxymethyl)cyclobutane were synthesized by different methods. These monomers were polymerized under various conditions to a polymer believed to be a spiropolymer, poly[3,3-bis(hydroxymethyl)cyclobutane-1,1-dicarboxylate].		

DD FORM 1 NOV 65 1473

UNCLASSIFIED

Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Polymers Spiropolymers Spirocyclobutanes Pentaerythritol Oxetanes						