

6-1-1992

The synthesis and characterization of  
poly[oxo(2-chloro-1, 4-phenylene) oxy  
terephthaloyl-co-(2chloro-1, 4-oxy carbonyl  
methylene oxo terephthayoly-co oxy(2-chloro-1,  
4-phenylene methylene oxy oxy terephthaloyl]

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## ABSTRACT

## CHEMISTRY

THUO, NJERI

B.S. MORGAN STATE UNIVERSITY, 1987

**THE SYNTHESIS AND CHARACTERIZATION OF POLY[OXO  
(2-CHLORO-1,4-PHENYLENE) OXY TEREPHTHALOYL-CO-  
(2CHLORO-1,4-OXY CARBONYL METHYLENE OXO TERE-  
PHTHAYOLY-CO OXY (2-CHLORO-1,4-PHENYLENE  
METHYLENE OXY OXY TEREPHTHALOYL)].**

Advisor: Professor Malcom B. Polk

Thesis dated June 1992

Two copolyesters were prepared in the melt from terephthalic acid, 1,4-phenylenediacetic acid, 2-chloro-1,4-phenylenediacetate and  $\alpha\alpha$ -diacetoxy-1,4-phenylene. Neither polymer is observed to exhibit liquid crystalline properties. Polymer 1 has an inherent viscosity of 0.39g/dl while polymer 2 has an inherent viscosity of 0.64g/dl. The Thermal properties of both polymers are obtained. Thermogravimetric analysis result indicate that polymer 1 starts to loose weight at

275°C, while polymer 2 which is more thermally stable only losses less than 5% of it's weight at 350° C.

Both polymers were characterized by FT-IR, <sup>1</sup>H NMR and <sup>13</sup>C NMR, POM, DSC, TGA and viscosity.

**THE SYNTHESIS AND CHARACTERIZATION OF POLY[OXY (2-CHLORO-  
1,4-PHENYLENE) OXY TEREPHTHALOYL-CO- (2-CHLORO-1,4,-OXY  
CARBONYL METHYLENE 1,4-PHENYLENE METHYLENE OXY  
TEREPHTHALOYL-CO-OXY (2-CHLORO-1,4-PHENYLENE )  
OXY TEREPHTHALOYL].**

**A THESIS**

**SUBMITTED TO THE FACULTY OF CLARK ATLANTA UNIVERSITY  
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS  
FOR THE DEGREE OF MASTER OF SCIENCE**

**BY**

**NJERI THUO**

**DEPARTMENT OF CHEMISTRY**

**ATLANTA GEORGIA**

**JUNE 1992**

*A = VII P = 50*

## ACKNOWLEDGEMENTS

For suggesting this project and advice and help in it's development I am deeply grateful to Dr. Malcolm B Polk.

Special thanks to Dr. Henry C. Mcbay for the incentive and the encouragement he gave to me during this period.

Special thanks to Daniel Pambi for providing me with a lot of the experimental equipment and for his advice and guidance. I am very grateful to Dr. Abotsi for ordering some of the chemicals for me.

I would also like to thank Dr. Venkatasubramanian for his guidance and help. To my fellow students and friends, my most sincere and deepest thanks.

My deepest thanks to my mother, Theresa Wanjiru, to my sister, Wangui, to my brothers Wachiuri, Rwigi and Gikiri and to my good friend Kimani Karangu, all of who encouraged me to pursue higher education.

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## INTRODUCTION

Polymers are macromolecules composed of small repeating units. They have strong intermolecular forces and thus they form strong fibers, plastics, rubbers, adhesives and coatings. In general, they are classified either from their finished product; linear or crosslinked, or from their polymerization process; addition or condensation.

Polymers can also be classified either as homopolymers or copolymers. A homopolymer is a macromolecule derived from a single monomer, whereas a copolymer is derived from the polymerization of two or more monomers.

Copolymers can further be subdivided into four groups: random, alternating, graft and block, whereby, a random copolymer is one in which the structural units are located randomly in the polymer, ABBBAAABABBA; while in an alternating polymer each monomer of one type is joined to another monomer of the other type, ABABABABAB. On the other hand, graft copolymers are formed by growing a homopolymer of one type on the main chain and then growing the homopolymer of the other monomers on the side chain, for example;

```
AAAAAAAAAAAAAAAAAAAAAAAAAAAAA
  B           B           B
  B           B           B
  B           B           B
  B           B           B
  B           B           B
```

Block copolymers are made up of long sequences of one monomer followed by a long sequence of the other monomer, for example, AAAAAAAAAAABBBBBBBBBB---

Genetically, polymers are named from their source. They are given a prefix 'poly' followed by the monomer(s) name. For example, poly(ethylene terephthalate), polystyrene, poly(vinyl chloride) and polyethylene. They are also grouped from their source, whereby the prefix 'poly' is followed by the functional group name, for instance, polyethers, polyamides, polysilicones and polyesters.

Polyesters are macromolecules composed of a stiff

carboxylate ester group,  $-\overset{\text{O}}{\underset{\text{||}}{\text{C}}}-\text{O}-$ , in their repeat units. They are usually produced by the reactions of diols with diacids or by the reaction of their derivatives. Since a variety of alcohols and acids can be used, different types of polyesters with various properties, depending on the geometry, the polarity and the mobility of the repeat unit, can be synthesized. Systems with aliphatic cyclic and aromatic carboxylate units have been produced. However, more emphasis has been put on the aromatic polyesters because they have a variety of applications<sup>1-3</sup>.

Moreover, some of these aromatic polyesters have an interesting property and that is they are capable of exhibiting liquid crystalline characteristics<sup>4-6</sup>.

The existence of liquid crystals was first discovered in 1888, by F. Reinitzer who noted that cholesteryl benzoate appeared to have two distinct melting points, whereby the crystals of this compound melted at  $145^{\circ}\text{C}$  giving a turbid liquid which then gave an ordinary clear liquid at  $179^{\circ}\text{C}$ <sup>7</sup>. Unlike most compounds which melt from the solid phase to the liquid phase through a single transition, liquid crystals do not melt directly from the solid phase to the isotropic liquid. Instead, one or more liquid crystalline phases exist in an intermediate temperature range. These liquid crystalline phases are termed mesophases. Therefore, liquid crystalline polymers or mesomorphic polymers are macromolecules that display a structure that is intermediate between the three dimensional ordered crystalline state and the disordered isotropic fluid. The word mesomorphic is derived from Greek with the prefix meso meaning middle and the suffix morphic meaning form. Thus mesomorphic implies some form or order which is in the middle.

In order for polymers to exhibit this liquid crystalline characteristic, they must possess an appreciable amount of stiffness, such as, aromatic rings interconnected in their para position, and more importantly, the molecule must be asymmetrical in shape<sup>8</sup>. A generalized structure of a liquid crystal is shown in figure 1.

Liquid crystalline behavior can be exhibited either in solution, due to a change in concentration which is termed lyotropic or in the melt due to a change in temperature

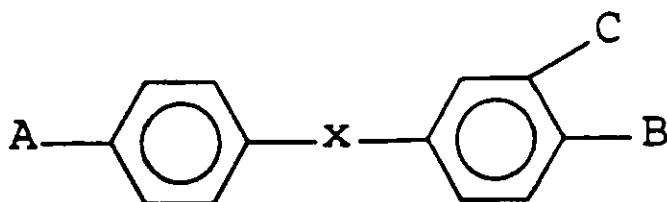


Fig.1. a generalized liquid crystal structure

which is termed thermotropic. Both in the solution and in the melt, there are a limited number of chains which can be accommodated in a random arrangement. When this limit is exceeded a highly oriented liquid crystalline phase separates out.

Lyotropic liquid crystalline polymers are of particular interest because they form fibers with high strength and ultra-high modulus. These polymers are dissolved in solvents and as the amount of the solvent is increased an isotropic solution is formed followed by a liquid crystalline solution. Included in this group of polymers are Dupont's <sup>R</sup>Kevlar<sup>9</sup> and poly(1,4 benzamide)<sup>10</sup>. The fibers of these polymers can be prepared directly during polymerization or by dissolving the isolated polymer in an appropriate solvent. However, due to the low solubility of the stiff carboxylate ester group, attempts to prepare lyotropic polyesters have not been very successful except in rare cases. For instance, Polk and co-

workers have synthesized a series of lyotropic block copolyesters containing cyclohexane and benzene rings<sup>11</sup>. The work reported here concerns only thermotropic liquid crystals, so there will be no further discussion of lyotropic mesophases.

In the thermotropic transition, the crystal goes through a first-order transition to the liquid crystal state and at yet a higher temperature goes through another first-order transition to the isotropic liquid state. The importance of this class of materials is increasing because they can be melt spun or injection molded to form oriented fibers or plastics of high strength in the liquid crystalline state<sup>12</sup>. During the injection molding of these polymers, an anisotropic structure which varies from location to location is introduced. It is proposed that this anisotropic property is due to a skin/core morphology, which has a distinct molecular orientation<sup>13</sup>. These polymers also form films which have superior properties<sup>14</sup>. Included in this class are copolyesters derived from 1,4-hydroxybenzoic acid, terephthalic acid and 2,6-naphthalenediol<sup>15</sup> and also poly(3-chloro-4-oxybenzoate-co-ethylene terephthalate)<sup>16</sup>.

Mesomorphicity may be achieved due to the main chain component which is characterized as a main chain polymeric liquid crystal (MPLC) or due to the nature of the side chain.

Main chain liquid crystalline polymers can further be subdivided into three groups: nematic, smectic and cholesteric. The subdivision arises from the nature of the

mesogenic groups and the interactions giving rise to these mesomorphic behaviors. From the generalized liquid crystalline structure (Fig.1.), the X, A and B, and C are respectively the central, terminal and lateral substituents. Mesomorphic properties, such as thermal stability, the mesophase type, and the mesophase numbers, depend on the nature of these groups. All these substituents have an effect on the magnitude of the terminal and the lateral cohesions. Terminal cohesions are those attractions between neighboring groups and they depend on the nature of A and B. On the other hand, lateral cohesion are between the faces of neighboring molecules and they depend on the nature of C and X.

The mesophases of a liquid crystal can be more clearly understood when one considers the stepwise melting process from the solid phase to the isotropic phase. At the crystalline to the smectic transition, the terminal cohesions are disrupted, and the layers are free to slide over one another. At the smectic to nematic transition, the lateral cohesions are disrupted and the molecules are free to undergo translation. Finally at the nematic to isotropic transition the thermal vibrations are sufficient in intensity to destroy the remaining structural order. Since smectic phases are more highly ordered than nematic phases (Fig. 2. vs Fig.3.) some mesogenic groups can exhibit only nematic mesophases depending on the substituents and the nature of the linking group, X.



The nematic mesophase is characterized by rigid relatively polar worm-like chains that tend to orient their long axes parallel<sup>17</sup>. They have long persistence lengths and their preferred direction,  $n$ , in space is arbitrary (fig. 2.)<sup>18</sup>. When heated, they form birefringent anisotropic liquids, in which adjoining molecules lie parallel, and on further heating the mesophases form an isotropic liquid. Among such polymers are poly(1,4-phenylene terephthalate)<sup>19</sup> and polymers prepared from 2-methylhydroquinone, pyrocatechol bis-acetate and terephthalic acid<sup>20</sup>.

The smectic subgroup is rod-like and they are interconnected by flexible spacers. In order for them to exhibit liquid crystalline properties, their axial ratio (which is the ratio of the molecular length to width) must be greater than 3<sup>21</sup>. Also, the spacer must be sufficiently large so that each rod-like molecule has complete directional independence of its neighbor<sup>22</sup>. Furthermore, the mesogenic phases pack in organized stacks or layers giving rise to eight different smectic phases characterized by the relative organization of each layer to the main layer. However, only three of these phases denoted as smectic A, B, and C are more widely studied.

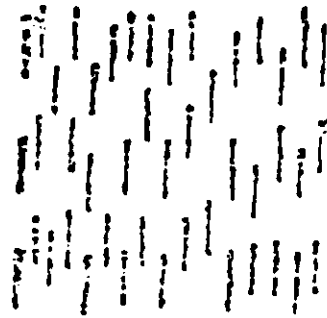


Fig.2. Structure of nematic phase

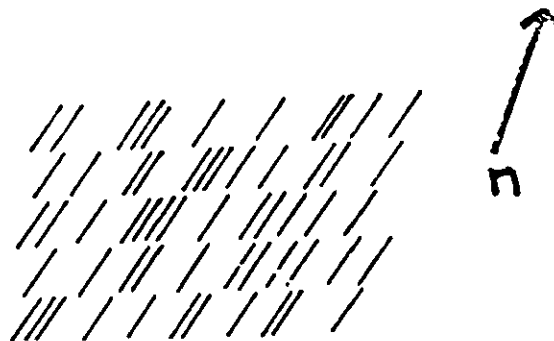


Fig.3a. Structure of smectic A phase

The layers in smectic A phases are aligned parallel to the main layer. They are individually fluid and each layer's thickness is identical to the full molecules' thickness (Fig. 3a.). Unlike the smectic A phases, smectic B layers are arranged in cubic arrays. Smectic C layers are also fluid but they are tilted at an angle (Fig. 3c.). Included in this group of smectic A, B, and C systems are polymers prepared from bis(4-hydroxybenzoyloxy)methylene and terephthaloyl chloride<sup>23</sup>, polyesters synthesized from bis(4-hydroxyphenoxy)-1,4-xylene with a series of dibromoalkanes<sup>24</sup> and poly(1,4-biphenylacrylate)<sup>25</sup>, respectively.

The cholesteric subgroup comprises most biopolymers. These liquid crystals are characterized by exceptionally high optical rotatory power and their molecular arrangement is helical (Fig. 4.). They include acetyethyl cellulose<sup>26</sup> and acetoxypropyl cellulose<sup>27</sup>.

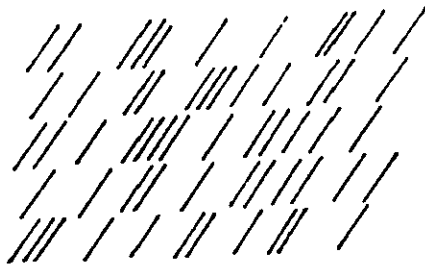


Fig. 3c. Structure of smectic C phase

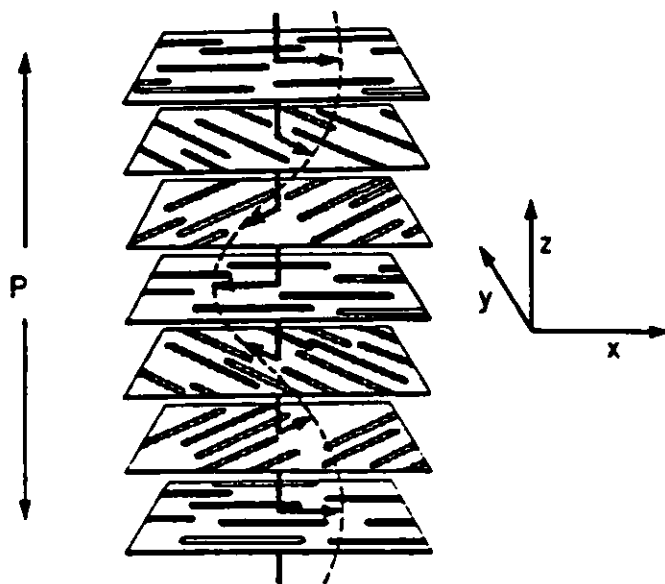


Fig. 4. Structure of a cholesteric phase

Further distinctions between these mesophases can be observed in polarized optical microscopy. Since mesophases are ordered, they are birefringent. Both the nematic and smectic phases exhibit characteristic structures when viewed between crossed polarizers. Typical textures of nematic and smectic phases are shown in figure 5 and figure 6, respectively. The nematic phase exhibits thread-like textures. The smectic phase exhibits a focal-conic texture. These two words nematic and smectic are derived from the Greek. Nematic means thread-like and smectic means soap-like.



Fig. 5. A nematic phase texture



Fig. 6. A smectic phase texture

The purpose of this research is to prepare and characterize two liquid crystalline high molecular weight copolyesters, with good mechanical properties and which can be spun into fibers. These polymers are synthesized by melt polymerization (acidolysis) so that high molecular weight polymers are obtained. The polymers were characterized by infrared spectroscopy (IR), nuclear magnetic resonance (NMR), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), polarizing optical microscopy (POM), solubility, and inherent viscometry. The monomers were characterized by melting point detection, IR, NMR, and Gas chromatography-mass spectroscopy (GC-MS)

## CHARACTERIZATION

The thorough characterization of these polymers is essential. Thus the following tests were performed.

### FOURIER-TRANSFORM INFRARED SPECTROSCOPY (FT-IR).

The FT-IR spectrum may be used to determine the chemical structure of the polymer. The carbonyl group peak, at approximately 1740 indicates the formation of the polyester.

### NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY (NMR)

The NMR spectrum may also be used to provide the chemical structure of the polymer.

### DIFFERENTIAL SCANNING CALORIMETRY (DSC)

The DSC provides values for the transition temperatures of the polymers; including melting transition temperature, glass transition temperature, and the liquid crystalline to isotropic transition temperature.

### THERMOGRAVIMETRIC ANALYSIS (TGA)

The TGA provides information about the sample's weight loss when the sample is exposed to a specific heating rate. This can be related to the thermal degradation properties of the polymer.

### INHERENT VISCOSITY

This provides an "idea" of the molecular weight of the polymer. These values cannot be used to determine the molecular weight of the polymers because the Mark-Howink parameters are unknown.



Inherent viscosities were measured at 30°C and 40°C with a calibrated Cannon-Fenske viscometer at concentrations of 0.5 g/dl of the polymer in DMF, and p-chlorophenol.

The thermal properties were determined under a nitrogen atmosphere and in air using the Dupont 990 DSC, and Dupont 9000 TGA. The Leitz Laborlux 12 Pol Microscope with a Leitz 350 heat stage was used to determine the visual thermal transitions.

Deuterated DMF was used to obtain the proton NMR spectrum of polymer 1 and the  $^{13}\text{C}$  NMR spectrum was obtained using the solid state NMR technique. The other polymer was characterized by solid state NMR spectroscopy. All the solution spectra were obtained on a Virian EM. 360 60 MHz NMR spectrometer.

The IR spectra were obtained on KBr discs using the Beckman 4240 IR spectrometer.

The solubility tests of the polymers were done using a variety of solvents.

## EXPERIMENTAL SECTION

### PREPARATION AND PURIFICATION OF MONOMERS

#### 2-CHLORO-1,4-PHENYLENEDIACETATE

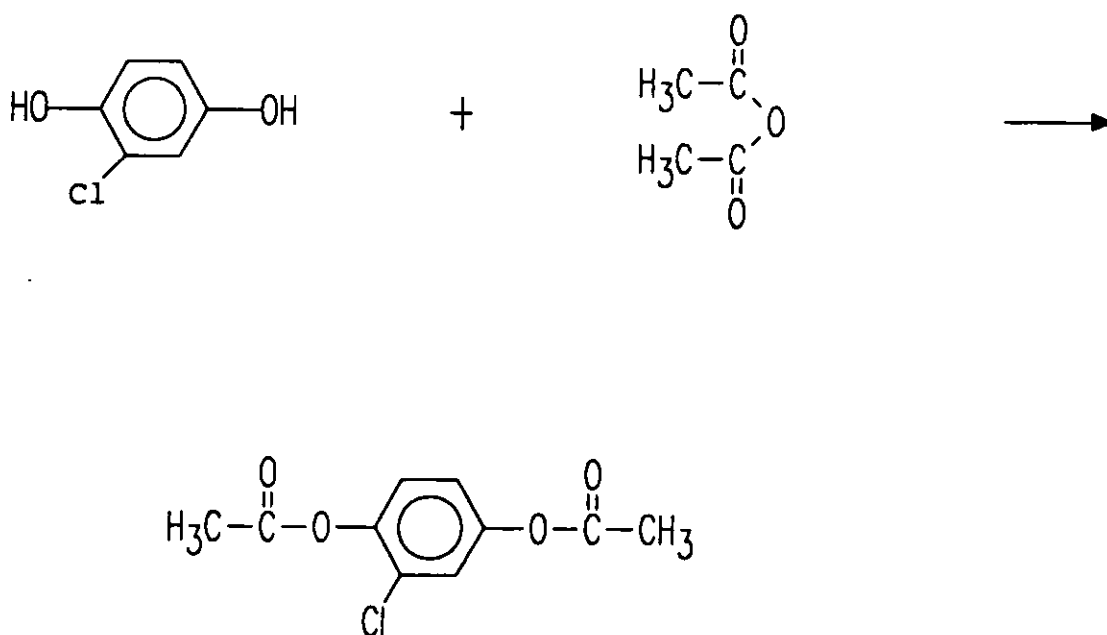
Chlorohydroquinone was obtained from Aldrich and it was purified by sublimation. Then in a 250ml erlenmeyer flask, 30g of the purified chlorohydroquinone was combined with excess distilled acetic anhydride(150ml), and 8 drops of sulfuric acid were added. The reaction was heated for 45 minutes at 80°C, and then the reaction mixture was allowed to cool to room temperature. It was then, slowly, poured over ice. The white precipitate that was formed, 2-chloro-1,4-phenylenediacetate, (scheme 1) was filtered and washed once in dilute aqueous potassium hydroxide solution and then several times in deionized water. The product was recrystallized three times in absolute ethanol. The melting point was obtained (67-69°C)<sup>28</sup>, and for further identification the IR(fig. 7.), H-NMR(fig. 9.), and GC-MS (fig. 11.) were obtained. The monomer was dried in a vacuum oven for 24 hours prior to polymerization.

#### αα'-DIACETOXY-1,4-XYLENE

1,4-Benzenedimethanol was obtained from Aldrich and recrystallized in hexane. The monomer (10g) was reacted with excess acetic anhydride under the above conditions. The αα'-diacetoxy-1,4-xylene (scheme 2) was purified by recrystallization in hexane and its melting point (48-49°C),

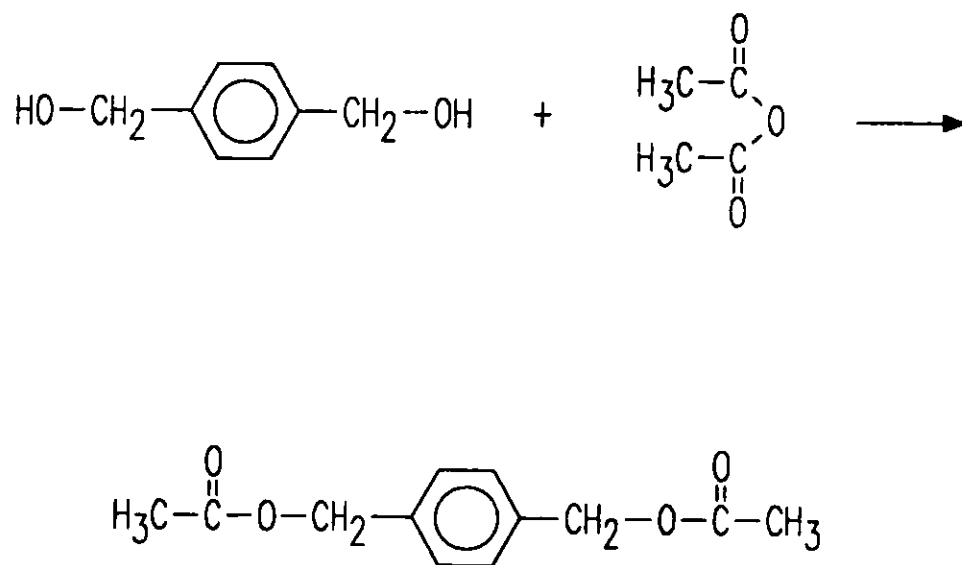
IR (fig. 8.), H-NMR (fig. 10.), and GC-MS (fig. 12.) were obtained. The monomer was dried in a vacuum oven.

SCHEME 1



Synthetic route to 2-chloro-1,4-phenylenediacetate

SCHEME 2



Synthetic route to  $\alpha\alpha'$ -diacetoxy-1,4-xylene

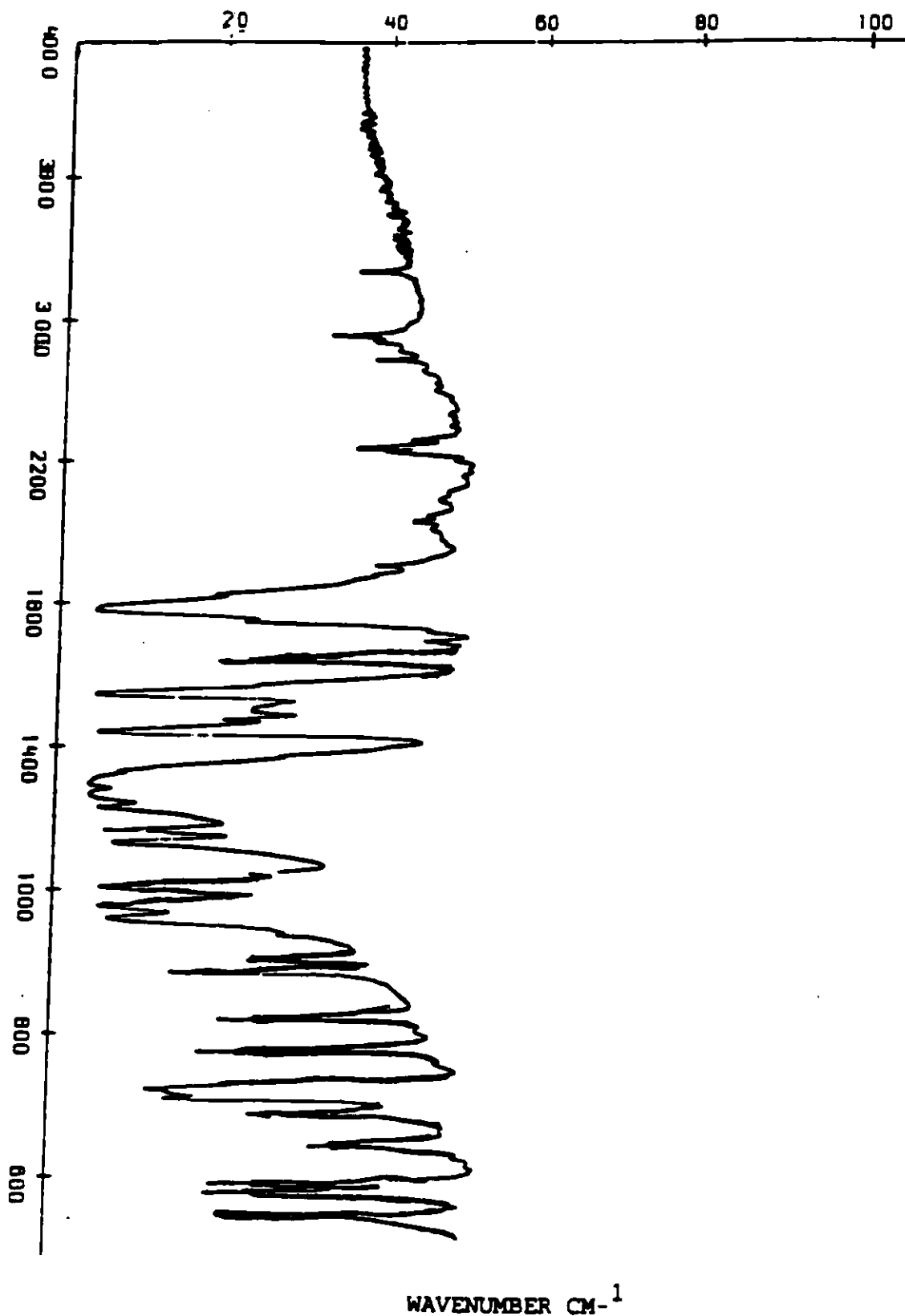
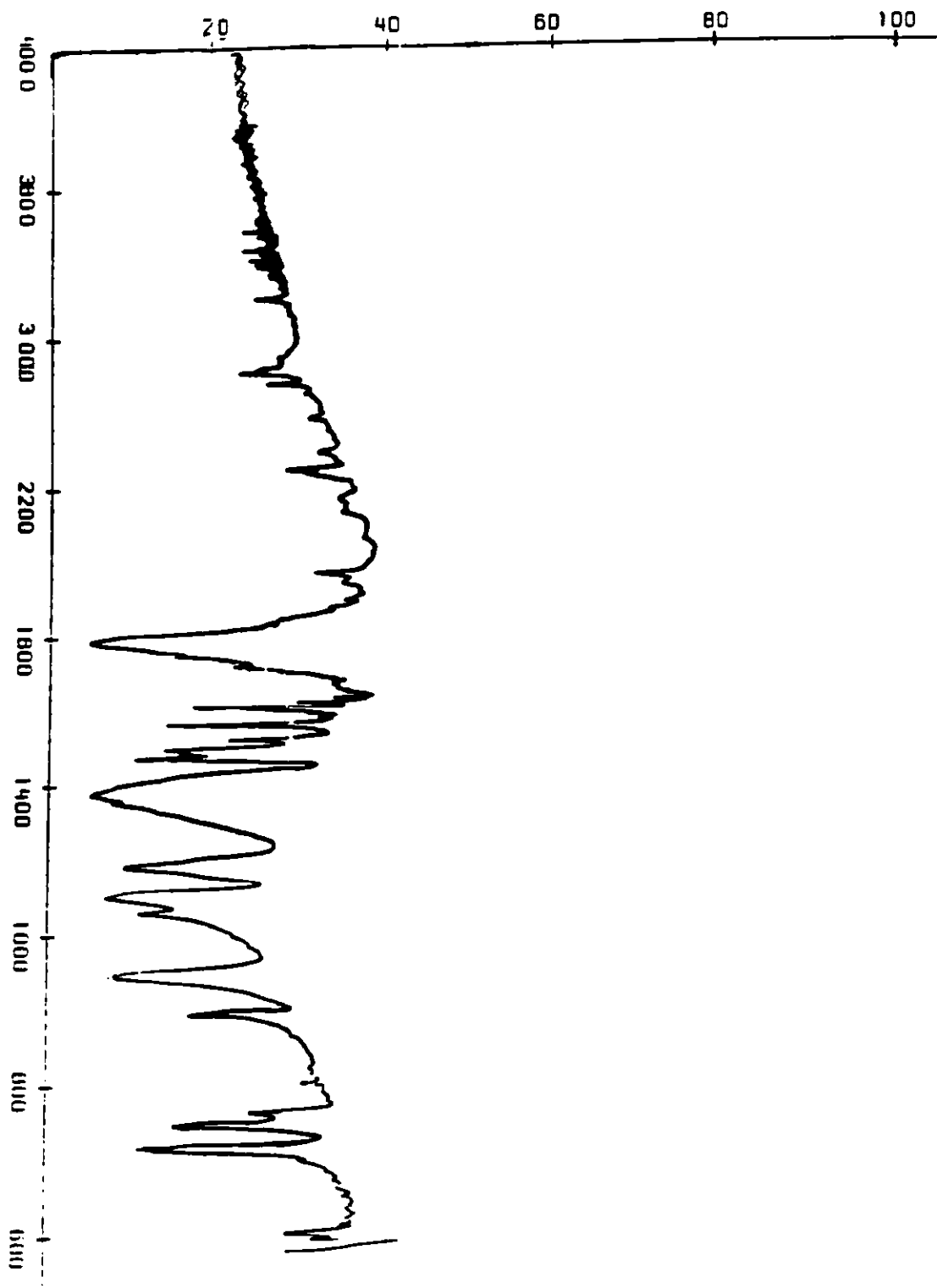


Fig. 7. IR spectrum of 2-chloro-1,4-phenylenediacetate.



WAVENUMBER CM<sup>-1</sup>

Fig. 8. IR spectrum of  $\alpha\alpha'$ -diacetoxy-1,4-xylene.

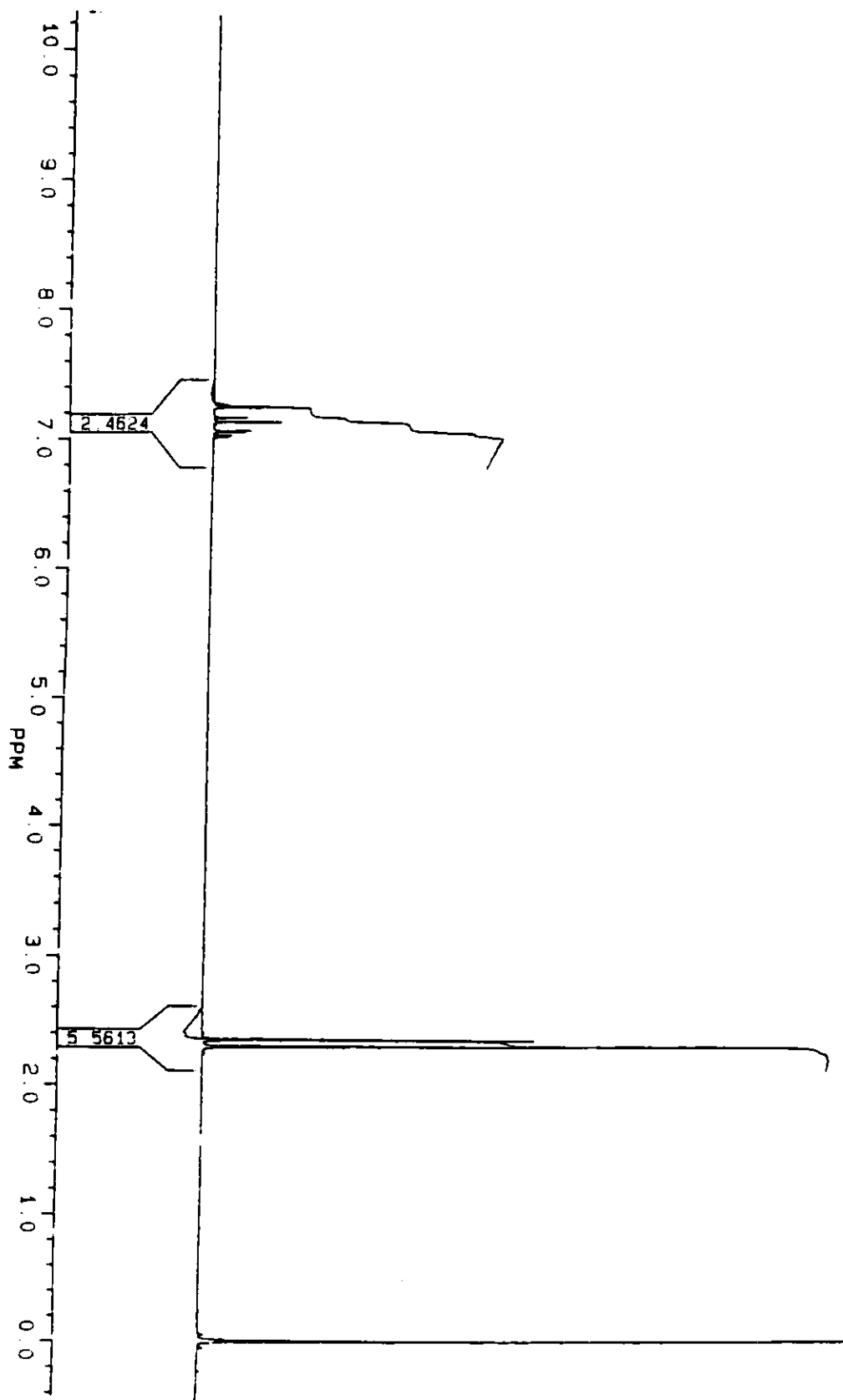


Fig. 9.  $^1\text{H}$  NMR spectrum of 2-chloro-1,4-phenylenediacetate

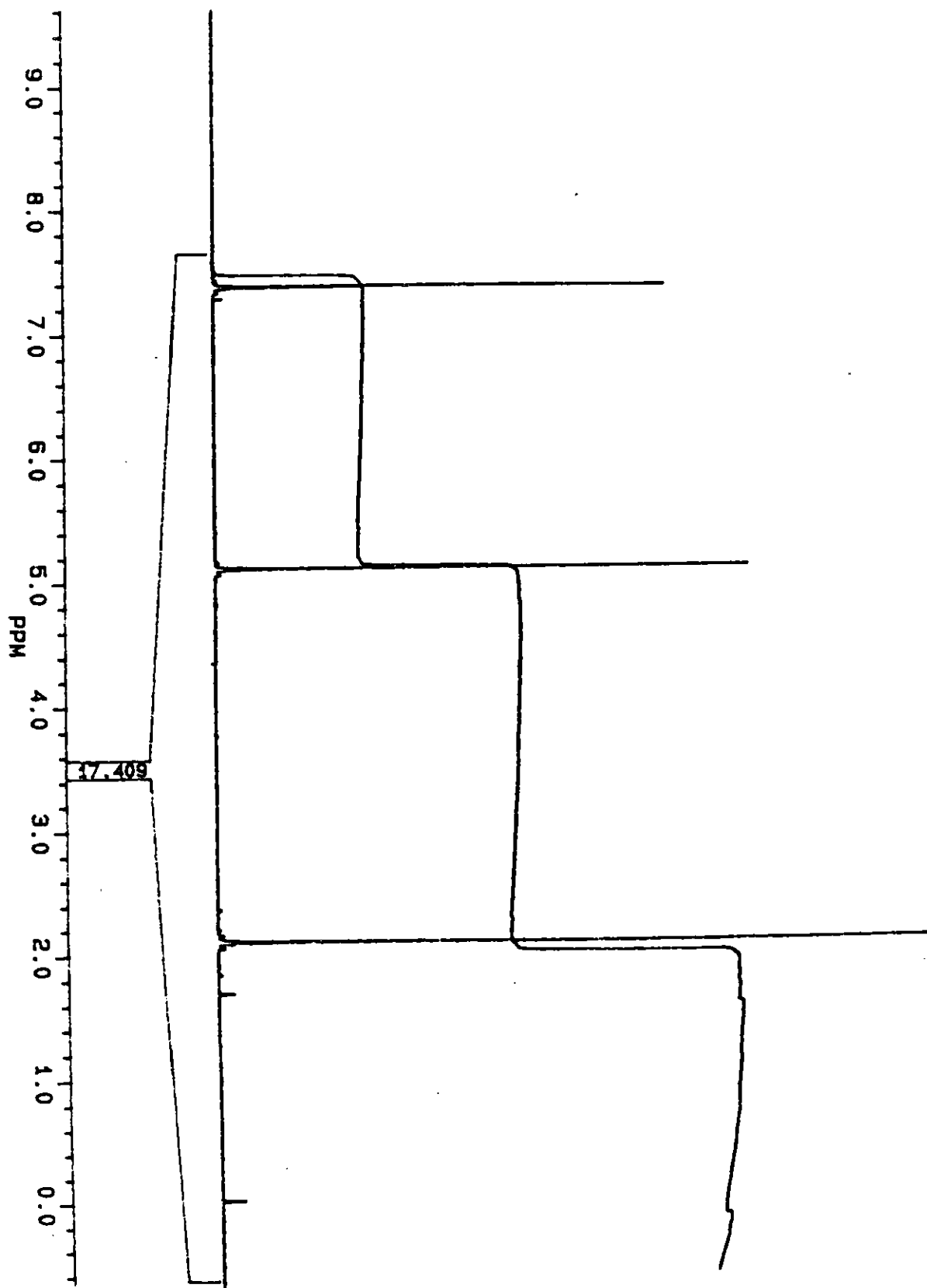


Fig. 10.  $^1\text{H}$  NMR spectrum of  $\alpha'$ -diacetoxy-1,4-xylene.



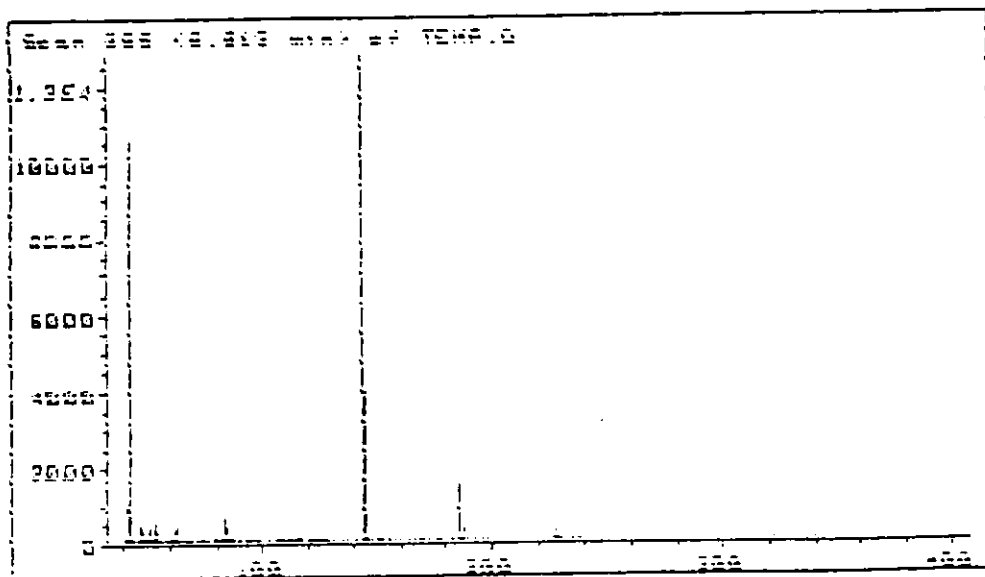
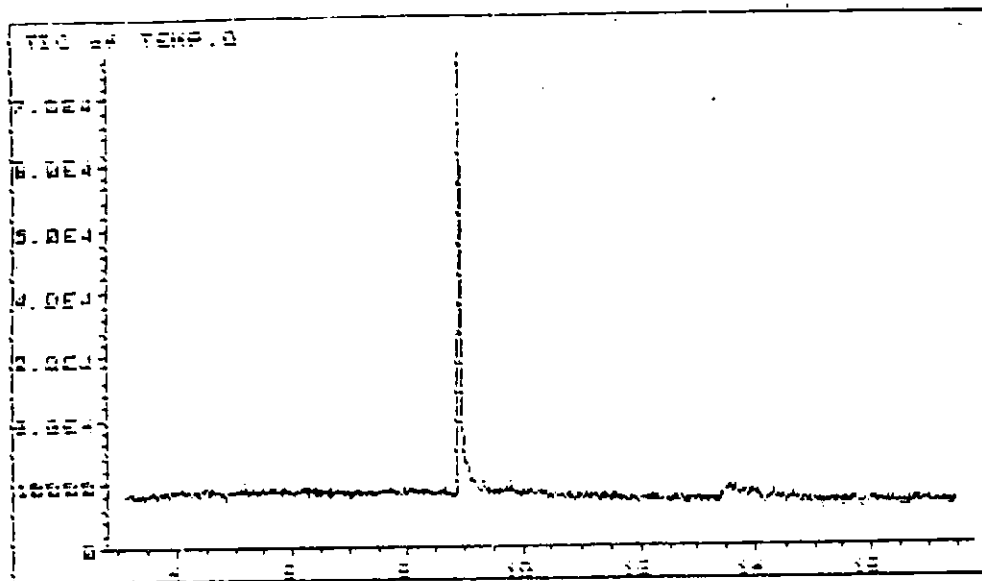


Fig. 11. GC-MS of 2-chloro-1,4-phenylenediacetate

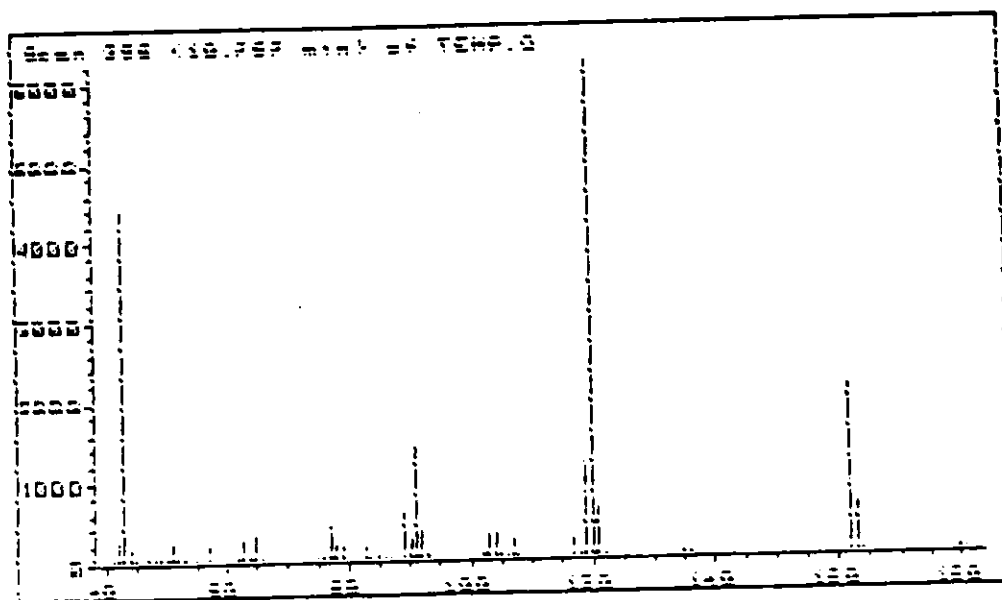
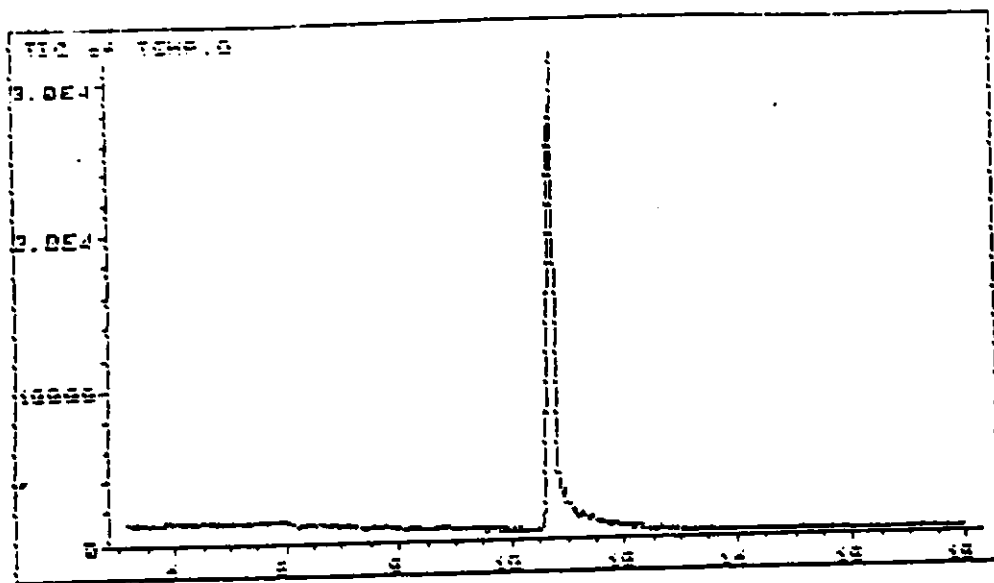


Fig. 12. GC-MS of  $\alpha\alpha'$ -diacetoxy-1,4-xylene.

### TEREPHTHALIC ACID

Practical grade terephthalic acid was obtained and used without further purification.

### 1,4-PHENYLENEDIACETIC ACID

This monomer was obtained from Aldrich and it was recrystallized three times from absolute ethanol. The melting point was 249<sup>o</sup>-251<sup>o</sup>C. The monomer was dried in a vacuum oven prior to polymerization.

### POLYMER 1

(Poly[oxy (2-chloro-1,4-phenylene) oxy terephthaloyl-co-oxy (2-chloro-1,4-phenylene oxy carbonyl methylene 1,4-phenylene methylene carbonyl])).

A 500ml three necked flask equipped with a mechanical stirrer, a nitrogen inlet, distillation column, and an acetic acid trap was purged with nitrogen for 15 minutes. Then terephthalic acid (0.0335 mole, 6.50g), 2-chloro-1,4-phenylenediacetate n(0.0670 mole, 15.37 g), and 1,4-phenylene diacetic acid (0.0335 mole, 5.68g) were introduced in the reaction flask. The equipment and it's contents were flushed with nitrogen for 10 minutes. The mixture was heated for 1 hour at 240<sup>o</sup>C with a steady flow of nitrogen and with stirring. The temperature was then raised and maintained at 285<sup>o</sup>C for 45 minutes under reduced pressure, of 1 torr. During this interval the nitrogen flow was stopped, while the

stirring was only employed for the first 15 minutes at a slower rate. The polymer formed was cooled down to room temperature, and washed once in deionized water, once in acetone and several times in deionized water. The copolyester was dried in a vacuum oven for 24 hours at 110°C. The polymer was then characterized. (n=1, 2, 3 for the first, second, and third experiment, respectively).

## POLYMER 2

(Poly[oxy methylene 1,4-phenylene methylene oxy terephthaloy-co-oxy (2-chloro-1,4-phenylene) terephthaloyl]).

A 250ml three necked round-bottom flask, equipped with a mechanical stirrer, a nitrogen inlet, a reflux condenser, and an acetic acid trap was charged with terephthalic acid (0.0394 mole, 6.45g), 2-chloro-1,4-phenylenediacetate (0.0237 mole, 5.39g),  $\alpha\alpha'$ -diacetoxy-1,4-xylene (0.0158 mole, 3.50g), and sodium acetate. Prior to the monomers being introduced to the reaction flask, the equipment was purged with nitrogen for 10 minutes and another 10 minutes after the monomers were introduced. The temperature was raised and held at 285°C for 1 hour. During this period there was a steady flow of nitrogen and the reaction was stirred steadily. Then, the temperature was raised to 300°C and held there for 45 minutes. During this interval the nitrogen flow was stopped and the mechanical stirring was only applied for the first 15

minutes, at a slower rate. However at this interval the reaction was under reduced pressure. The polymer obtained was allowed to cool down to room temperature, and then it was washed once in deionized water, then once in acetone, and finally several times in deionized water. The polymer was then dried in a vacuum oven at 110° C. for 24 hours. The dried polymer was then characterized.

Both polymers are prepared from the melt following the synthetic route used in the preparation of poly(chloro-1,4-phenylene trans hexahydroterephthalate)<sup>28</sup>. The equipment used for the polymerization is shown in figure 13.

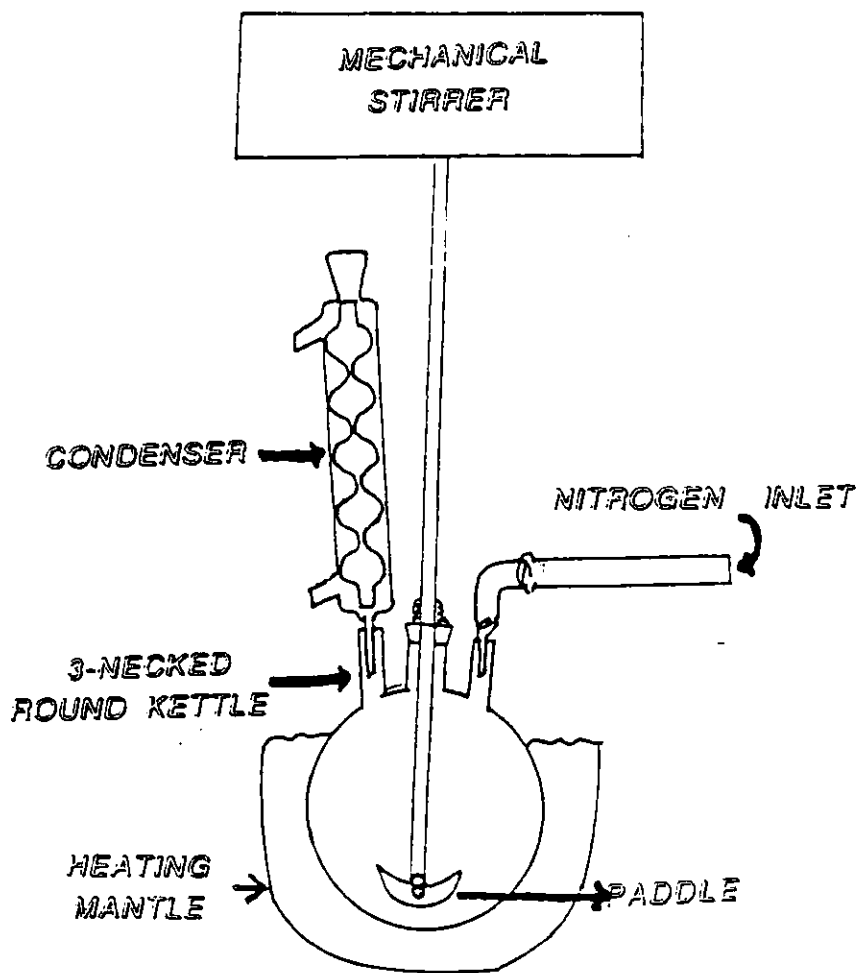
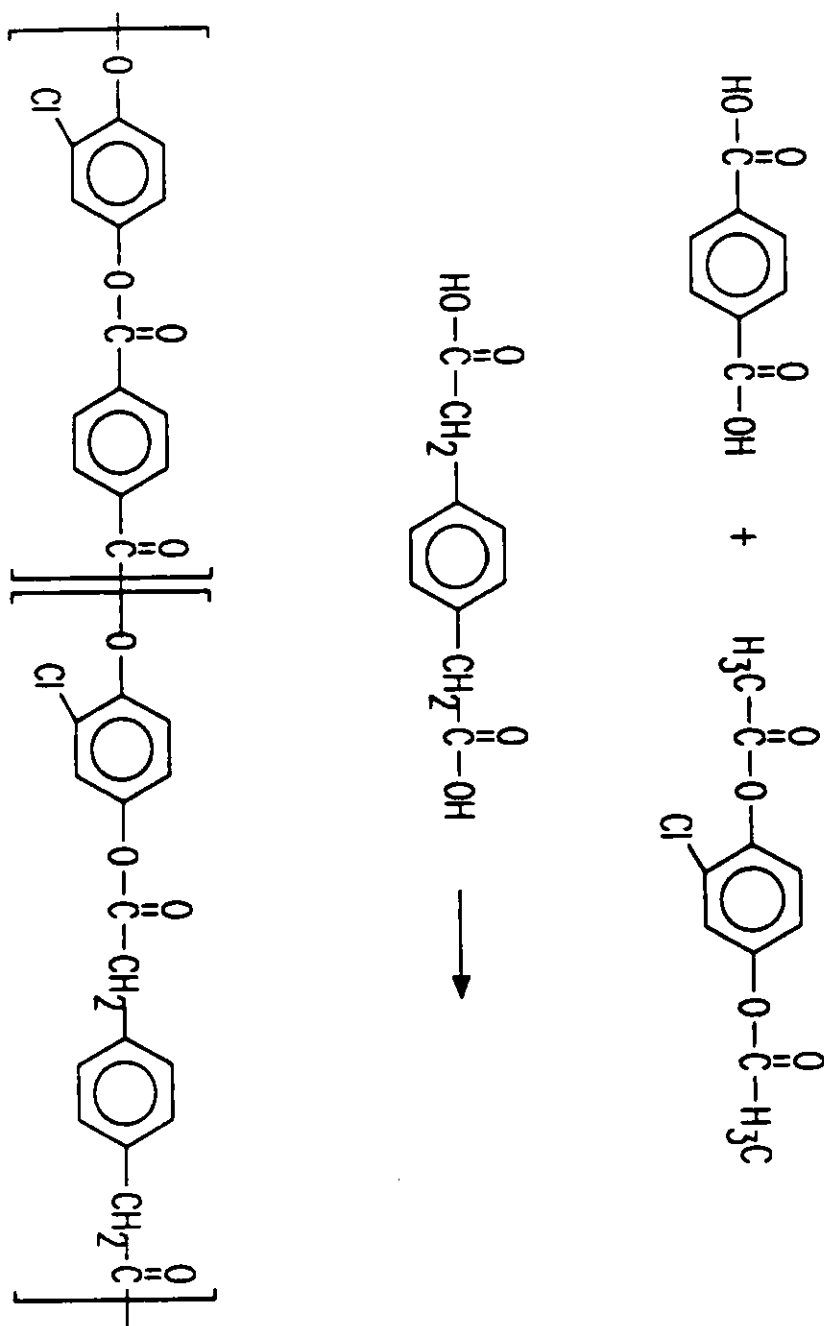


Fig. 13 Equipment used for polymerization

POLYMERIZATION

POLYMER 1

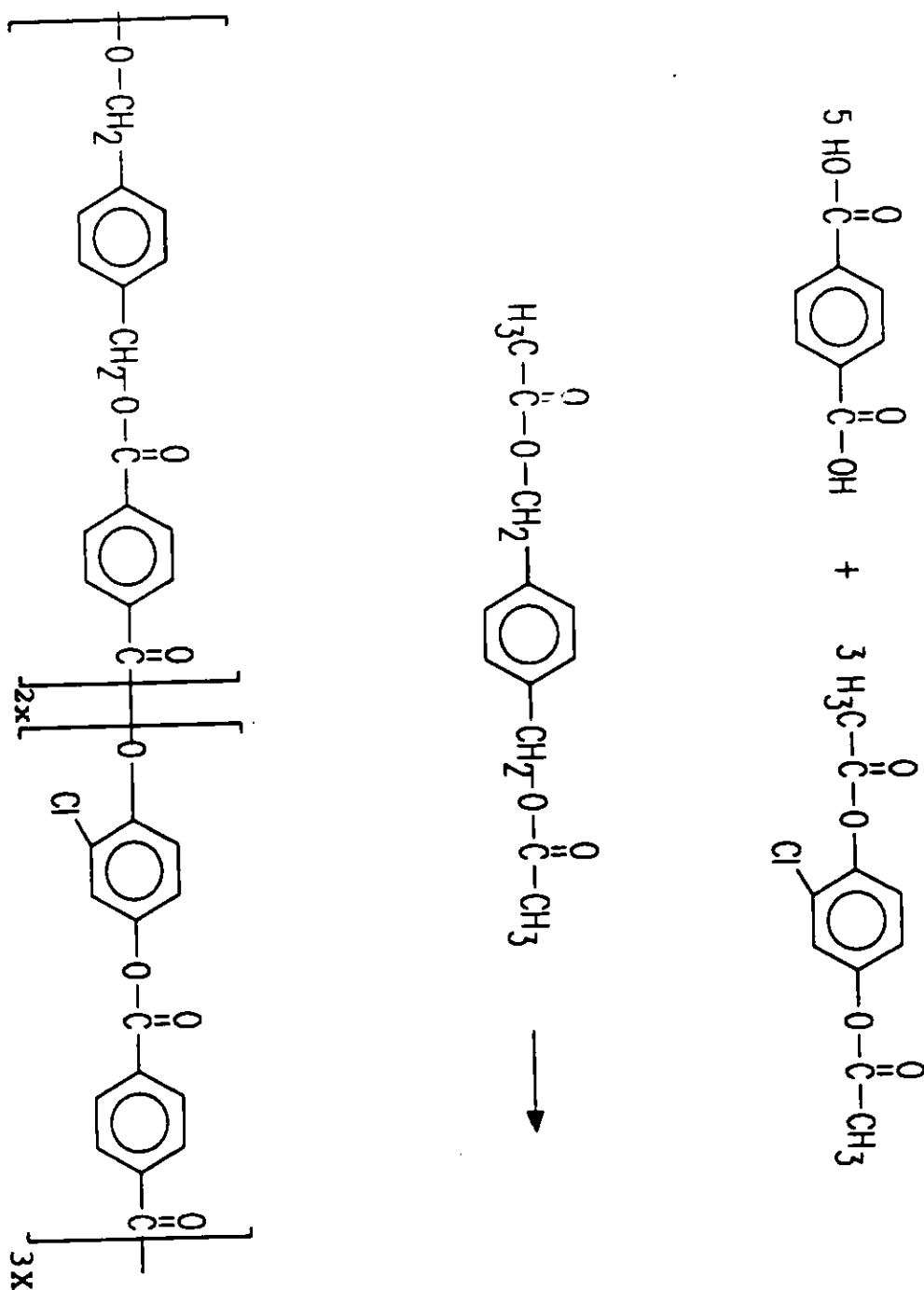
SCHEME 3



Synthetic route to poly[oxy (2-chloro-1,4-phenylene) oxy terephthaloyl-co-oxy (2-chloro-1,4-phenylene) oxy carbonyl methylene 1,4-phenylene methylene carbonyl].

POLYMERIZATION

POLYMER 2  
SCHEME 4



Synthetic route to poly[oxy methylene 1,4-phenylene methylene oxy terephthaloyl-co-oxy (2-chloro-1,4-phenylene) oxy terephthaloyl]



## RESULTS AND DISCUSSION

The synthetic routes for these two polymers are outlined in scheme 3 and 4. The polymers are prepared by acidolysis so that acetic acid is liberated. The liberation of the acetic acid shifts the equilibria of the reactions, as written, to the right.

### CHARACTERIZATION

#### FT-IR

The IR spectra (Fig. 14) of polymer 1 shows peaks at 3500-3300 $\text{cm}^{-1}$  (OH-stretch). This polymer also shows a peak at 1696 $\text{cm}^{-1}$  (C=O stretch of an acid). The two peaks are an indication that the reaction did not go to completion. The other peaks of this polymer are assigned in table 1. The IR spectrum of polymer 2 (fig. 15) is assigned in table 2. Both polymers have peaks at 1737 $\text{cm}^{-1}$  and 1236 $\text{cm}^{-1}$  which are characteristic of polyesters.

#### NUCLEAR MAGNETIC RESONANCE ANALYSIS

The proton NMR spectrum of Polymer 1 is presented in presented figure 16. This spectrum indicates the presence of aromatic protons at 7.0-8.0 ppm.

The of proton chemical shifts at 3.0 and 2.8 ppm for Polymer 1 (Fig. 16) represent the methylene units in the 1,4-phenylenediacetic acid monomer.

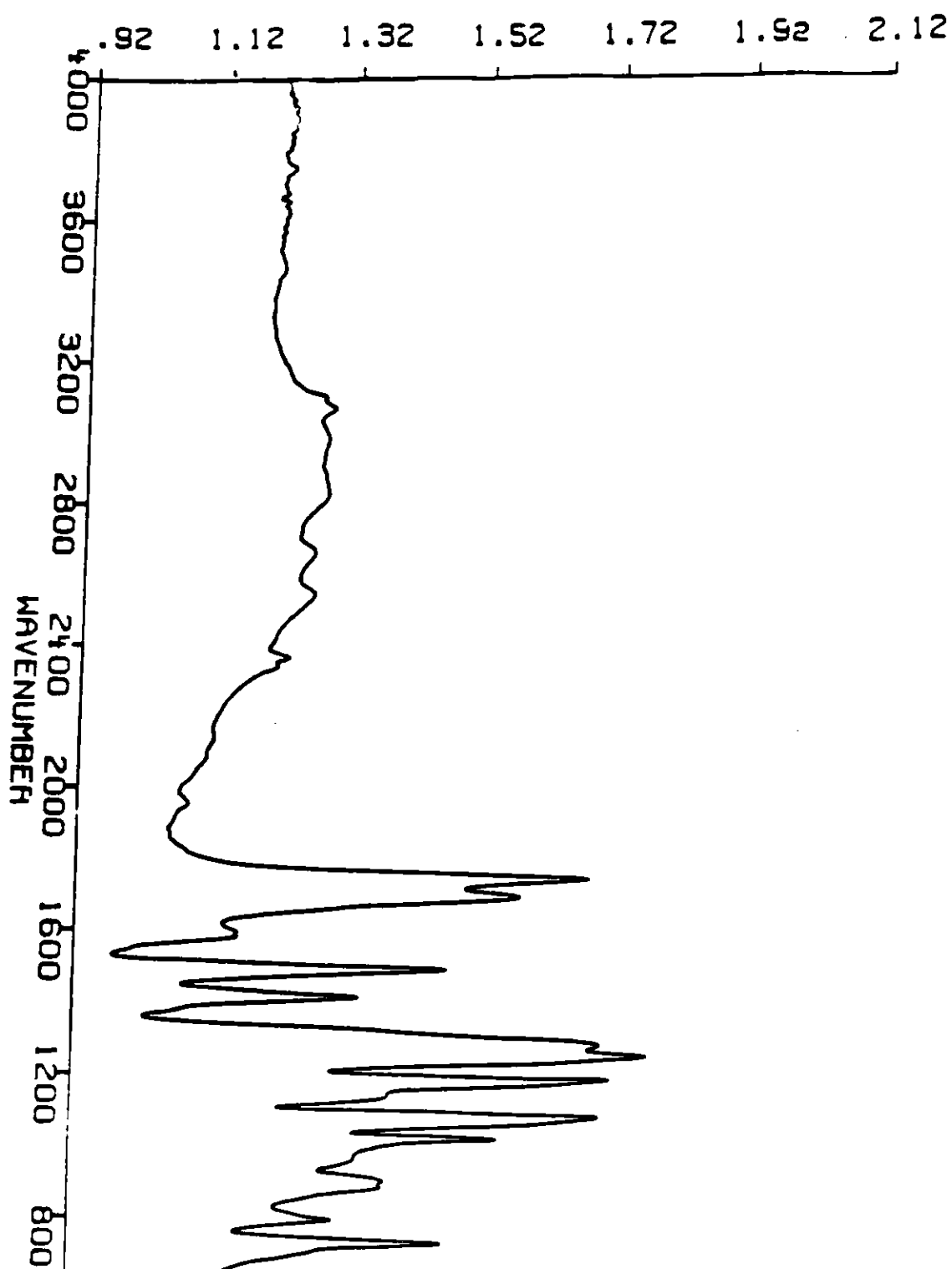
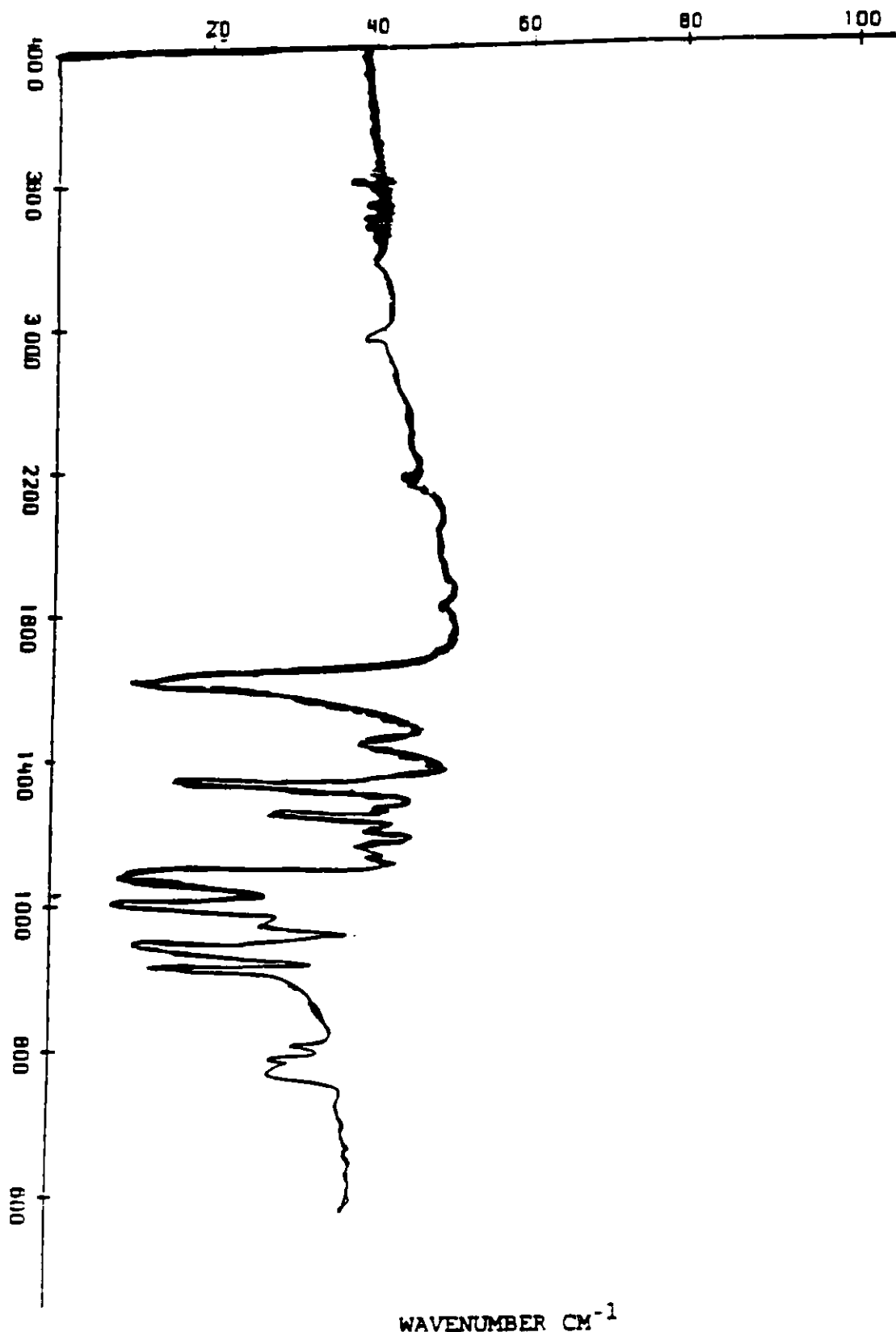


Fig. 14. IR spectra of polymer 1.



WAVENUMBER  $\text{CM}^{-1}$   
Fig. 15. IR spectrum of polymer 2.

Table 1. Absorption peaks and assignments of polymer 1

Functionality	Energy	Assignment	Remark
-OH	3500-3300	-OH stretch	broad
ester C=O	1737	ester C=O stretch	strong
carboxylic acid C=O	1696	acid C=O stretch	medium
C=C	1589	aromatic ring in plane vibration	medium
C-O	1236	C-O stretch	strong
aromatic 1,2,4 trisubstituted benzene	1072,1010	two adjacent hydrogens	weak
1,4-disubstituted benzene	900,860	1,4 disubstituted out-of-plane bending	medium
Ar-X	719	halogen substituted aromatic out-plane bending	strong

Ar = Aromatic ring

X = Halogen

Reference: Pasto, D. J.; Johnson, C. R. "Organic Structure Determination"; Prentice-Hall: Englewood Cliffs, 1969; Chapter 4.

Table 2. Absorption peaks and assignments of polymer 2

Functionality	Energy	Assignment	Remark
ester C=O	1737	ester C=O stretch	strong
C=C	1589	aromatic ring in plane vibration	medium
C-O	1236	C-O stretch	strong
aromatic 1,2,4 trisubstituted benzene	1072,1010	two adjacent hydrogens	weak
1,4-disubstituted benzene	900,860	1,4 disubstituted out-of-plane bending	medium
Ar-X	719	halogen substituted aromatic out-plane bending	strong

Ar = Aromatic ring

X = Halogen

Reference: Pasto, D. J.; Johnson, C. R. "Organic Structure Determination"; Prentice-Hall: Englewood Cliffs, 1969; Chapter 4.

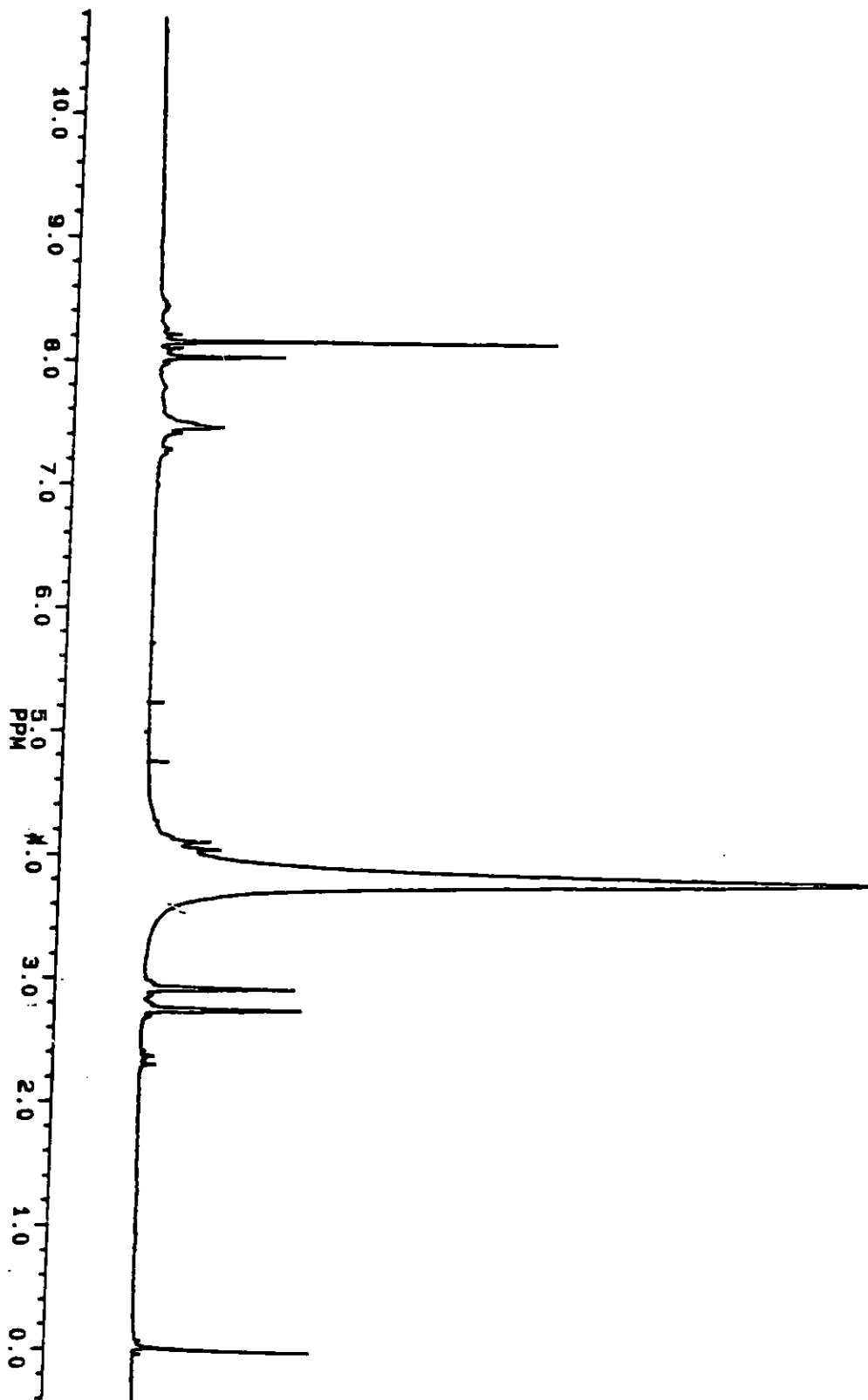


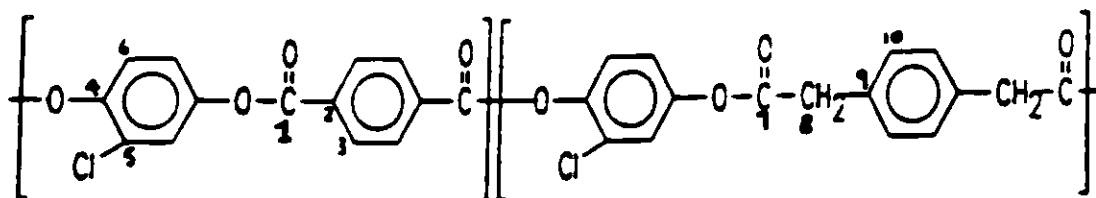
Fig. 16.  $^1\text{H}$  NMR spectrum of polymer 1.

The chemical shift at 4.0 ppm can be attributed to moisture in the deuterated DMF.

The carbon-13 NMR spectrum of Polymer 1 and 2 are presented in Fig. 17 and 18, respectively.

The carbon-13 NMR of polymer 1 is assigned in table 3. C-1 and C-7 represent the carbonyl carbons. The downfield shift of C-7 relative to C-1 indicates that both carbons are in different environments created by the methylene unit (C-8).

Table 3  $^{13}\text{C}$  NMR spectrum of polymer 1 showing carbon numbers and chemical shifts.



Carbon number	shift (ppm)
8	41.3
3, 10	124.5
5, 6	130.6
2, 9	144.8
4	148.7
7	187.4
1	191.6

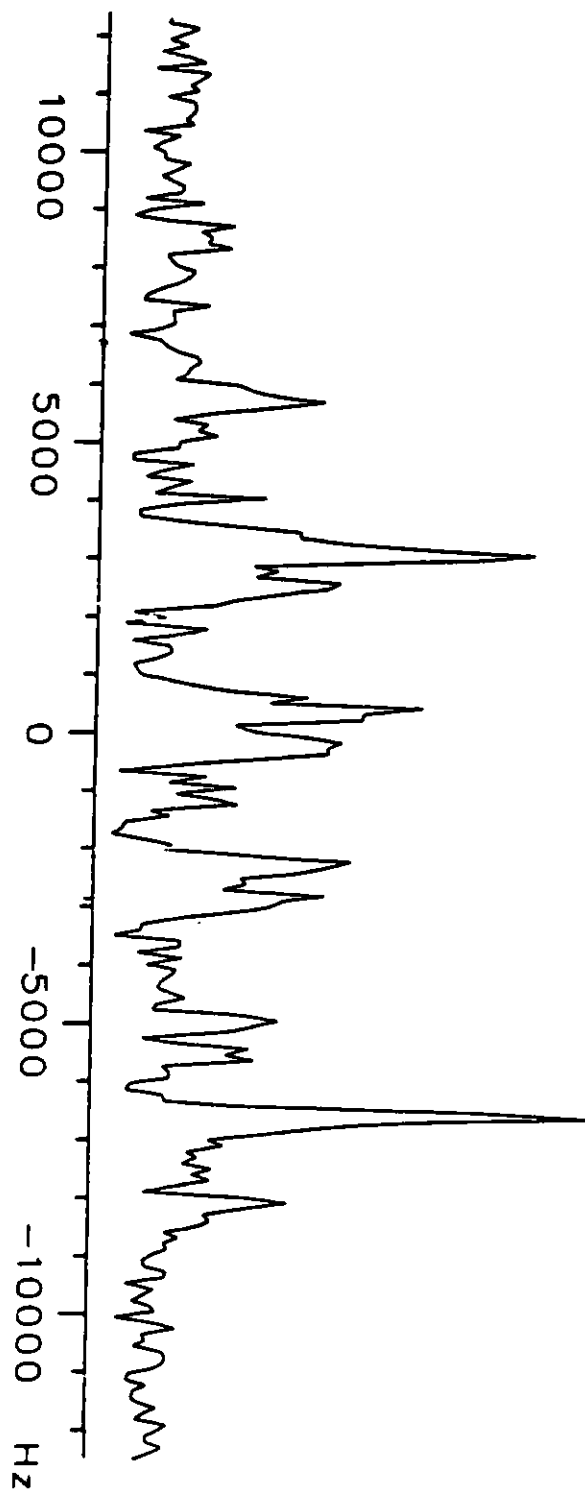


Fig.17.  $^{13}\text{C}$  NMR spectrum of polymer 1



## DSC

The DSC of Polymer 1 did not show any conclusive data.

The DSC of Polymer 2 under  $N_2$  is shown in Fig.19. The endotherms at  $345^{\circ}C$  and  $359^{\circ}C$  can be attributed to decomposition of the polymer since they coincide with the TGA thermogram decomposition profile.

The DSC of Polymer 2 in air is presented in Fig. 20. The polymer has a complex behavior under air and one observes endotherms at  $321^{\circ}$ ,  $345^{\circ}$  and  $359^{\circ}C$ . This complex behavior can be attributed to the polymer decomposition in air. All the DSCs were run at a heating rate of  $20^{\circ}/min$  and at cooling rate of  $-20^{\circ}/min$ . A second heating trace was measured to check the reproducibility of the phase transition. The DSCs represented here are of the second heating rate.

## POLARIZING OPTICAL MICROSCOPY

Under polarized light, Polymer 1 showed a complex behavior. When shear was applied on the cover slip, the polymer began to glow in small spots in the temperature range of  $320-350^{\circ}C$ . No evidence of liquid crystallinity was observed for this polymer.

After applying shear to the cover slip, Polymer 2 also begins to glow in small spots in the temperature range of  $290-320^{\circ}C$ . The crystals then begin to gradually darken at the temperature range of  $320-350^{\circ}C$ . This can be attributed to decomposition of the polymer in air.

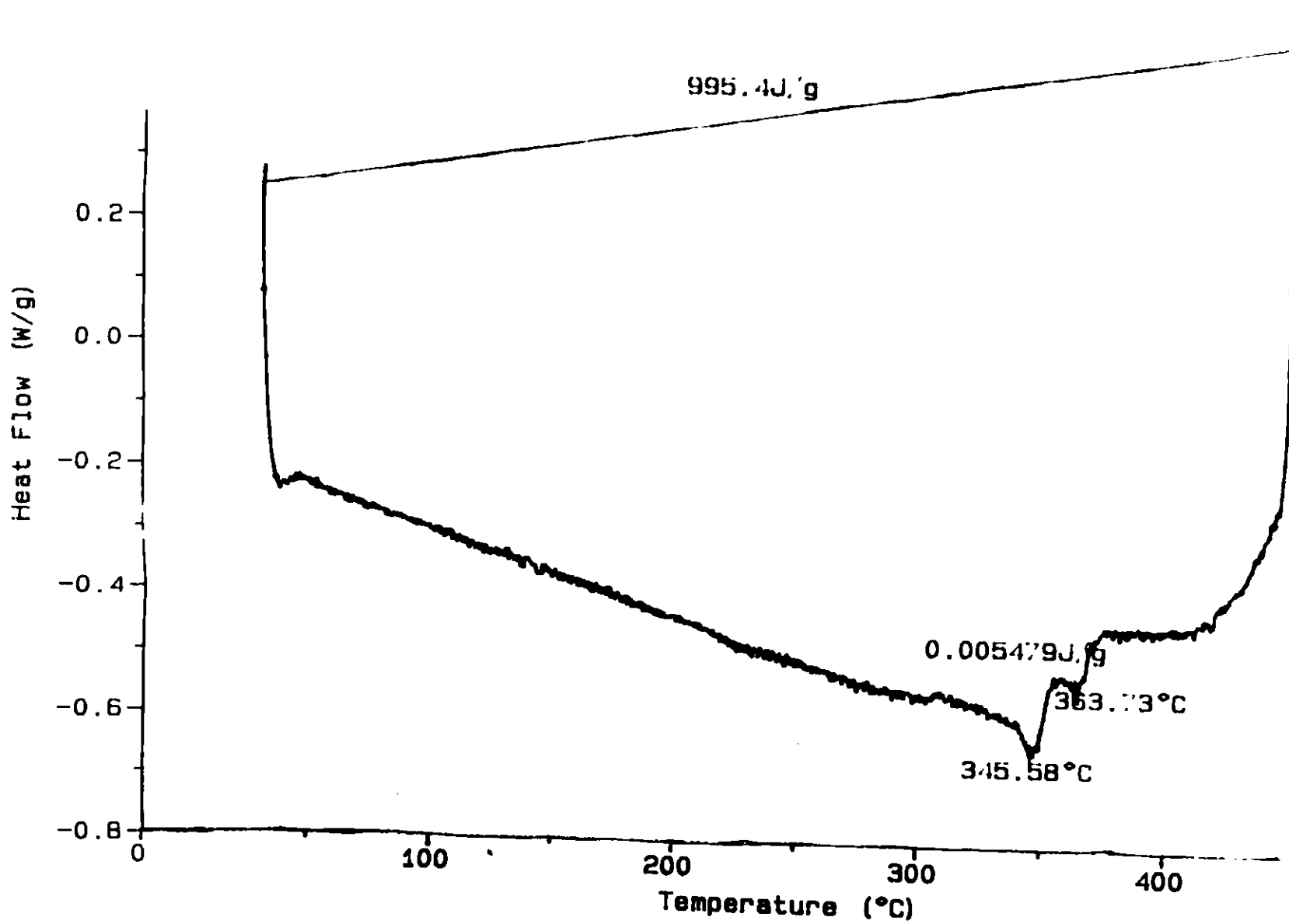


Fig. 18. DSC thermogram of polymer 1.

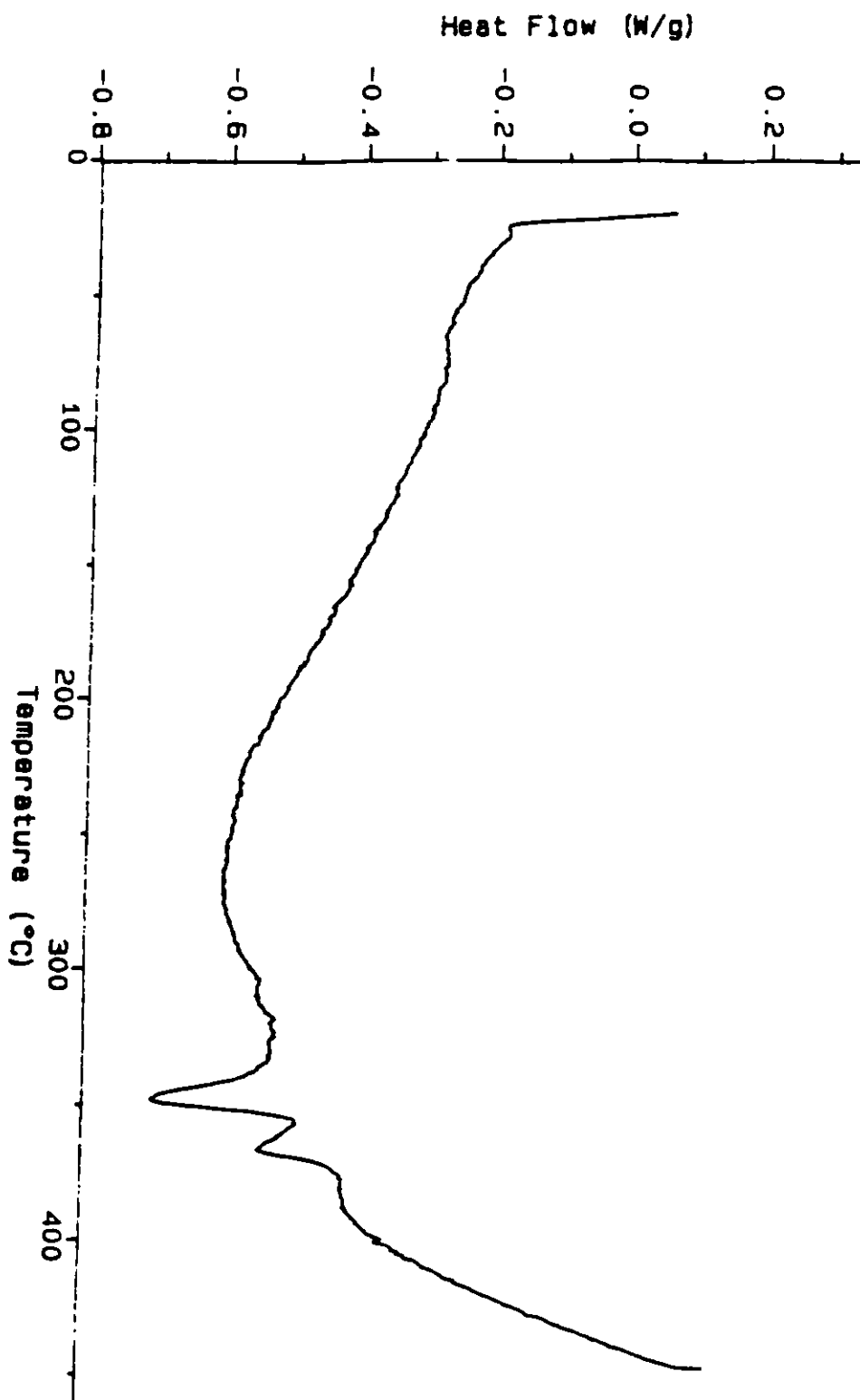


Fig. 19. DSC thermogram of polymer 2.

## TGA

The thermal stability of these two polymers in nitrogen was studied by TGA at heating rate of 20°C /min. Polymer 1 showed a small weight loss at about 275°C and at 325°C, (Fig 21) it had lost 50% of it's weight. However, polymer 2 is more thermally stable and it is observed to lose very little weight (-5%) at 350°C (Fig. 22). The temperature at which the highest weight loss rate was observed (for polymer 2) obtained from the differential thermogravimetry curve (Fig 23) was at 420°C.

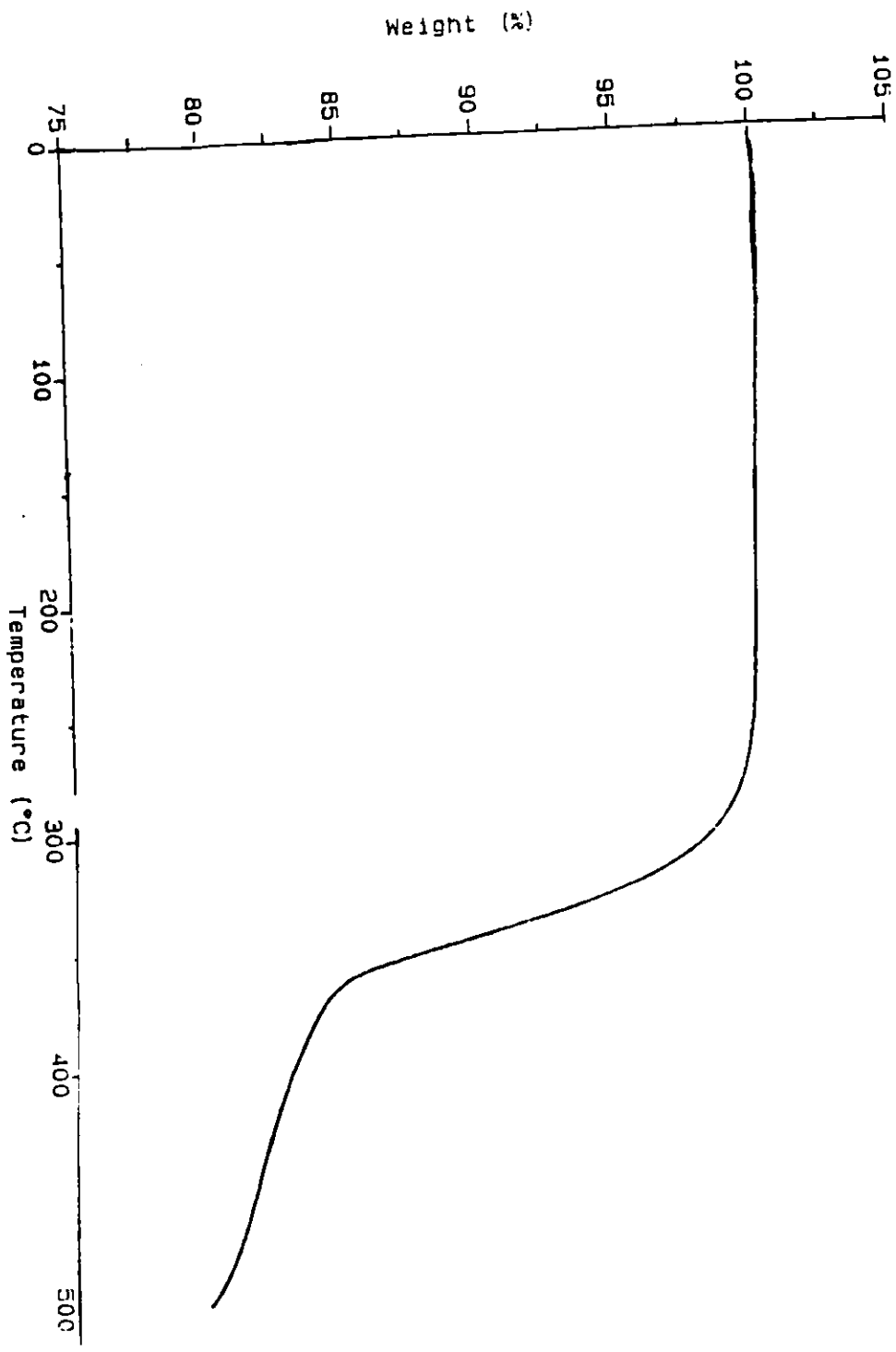


Fig. 20. TGA thermogram of polymer 1

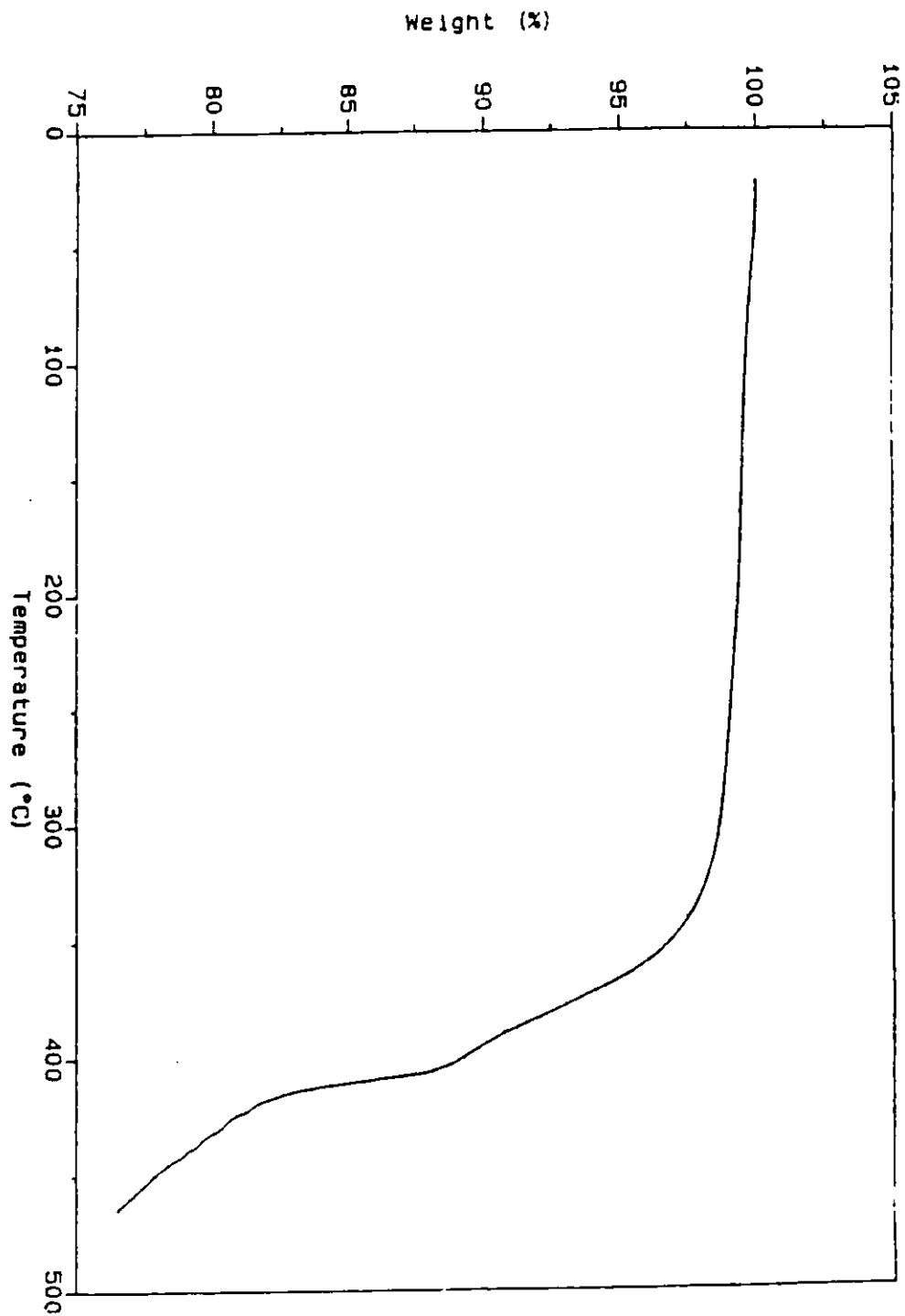


Fig. 21. TGA thermogram of polymer 2

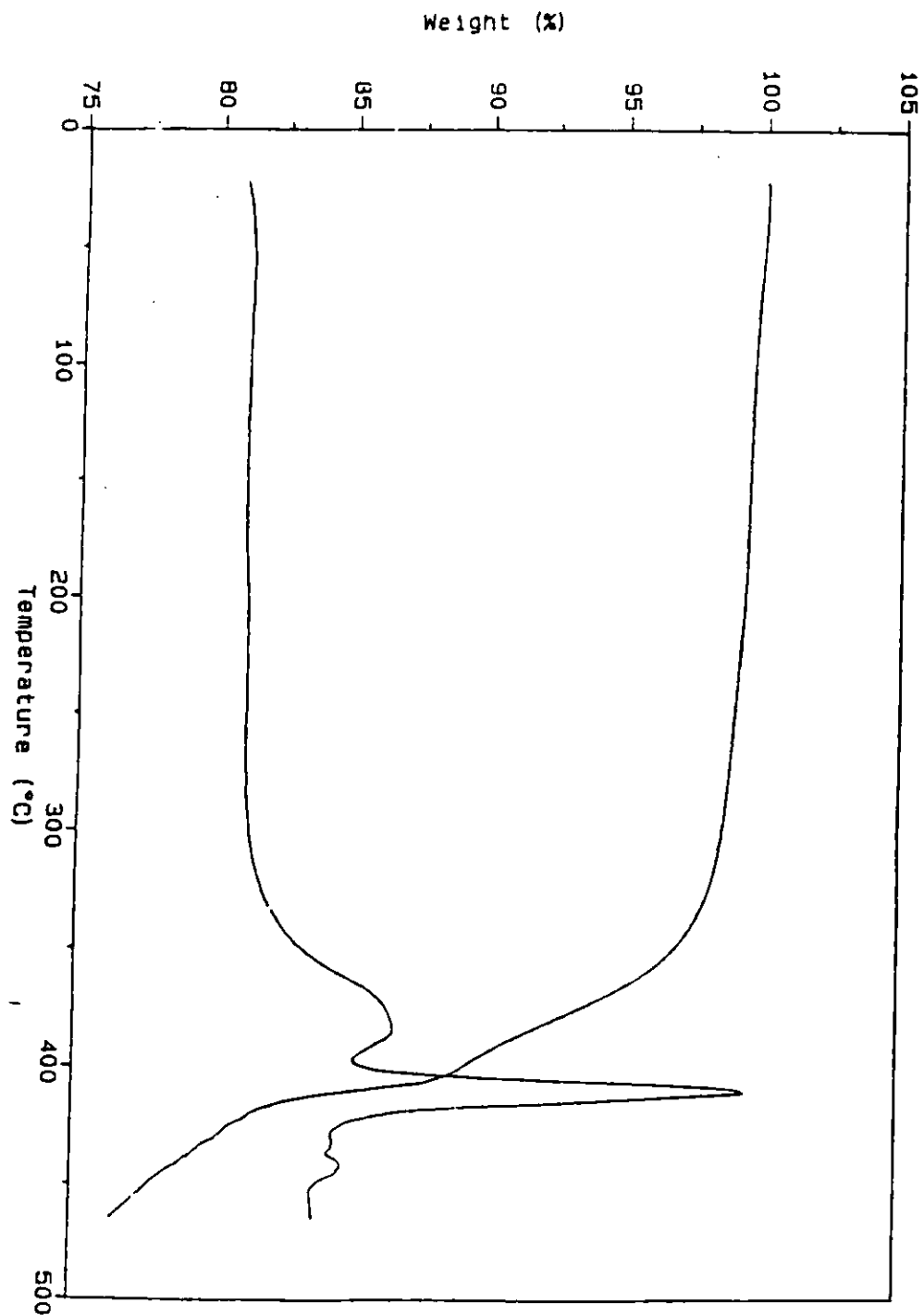


Fig. 22. Differential TGA thermogram of polymer 2

## SOLUBILITY

Polymer I is completely insoluble, both in cold and hot, chloroform, tetrahydrofuran(THF), carbontetrachloride( $\text{CCl}_4$ ), benzene and water. It is slightly soluble in hot m-cresol and 2-chlorophenol but insoluble in the cold. In trifluoroacetic acid and methanesulfonic acid, a chemical reaction was observed, and both solutions turned dark red. It was slightly soluble in p-dioxane, pyridine and 1-methyl-2-pyrrolidinone. The polymer was completely soluble in N,N-dimethylacetamide(DMA) and N,N-dimethylformamide (DMF). The requirement of a base to dissolve the polymer is attributed to the terephthalic acid in the polymer. Polymer 2 was completely insoluble in (cold and hot) chloroform, THF, DMF, pyridine, p-dioxane,  $\text{CCl}_4$ , methanesulfonic acid, toluene, benzene, 1-methyl-2-pyrrolidinone, and water. It was slightly soluble in cold m-cresol, 2-chlorophenol and trifluoroacetic acid, but completely soluble when heated. The polymer was soluble in p-chlorophenol.

The necessity of a very strong solvent, p-chlorophenol, to dissolve the copolymer is the result of the high molecular weight of the polymer.

## INHERENT VISCOSITY

The viscosity measurement indicated that Polymer I had an inherent viscosity of 0.39g/dl at 30°C in DMF. Polymer 2 had an inherent viscosity of 0.64g/dl at 40°C in p-chlorophenol.



## SUMMARY AND CONCLUSION

From the IR spectra of Polymer I, the peaks at  $3500-3300\text{cm}^{-1}$  and  $1696\text{cm}^{-1}$  indicate the presence of terephthalic acid. Thus, the polymerization did not go to completion. During polymerization, it was observed that some of the 2-chloro-1,4-phenylenediacetate sublimed and condensed on the collecting flask. Due to the high melting point of 1,4-phenylenediacetic acid ( $249^{\circ}\text{C}-251^{\circ}\text{C}$ ) and that of terephthalic acid which decomposes at  $300^{\circ}\text{C}$  it is observed that most of the 2-chloro-1,4-phenylenediacetate had already sublimed, before the other two monomers began to melt. Thus, as a result the end product still contains some amount of unreacted terephthalic acid.

This sublimation of one monomer has been reported by others such Guo and co-workers<sup>27</sup>. In their case they rectified this problem by increasing ratio of one monomer to the others to a ratio of 9:1:1. However, due to the large melting point difference between 2-chloro-1,4-phenylene-diacetate and 1,4-phenylenediacetic acid, increasing the ratio of the 2-chloro-1,4-phenylenediacetate did not solve this problem. Nevertheless one observes a progressive decrease of the intensity the terephthalic acid observed in the IR spectrum (Fig. 17) as the ratio of the 2-chloro-1,4-phenylenediacetate is increased from a ratio of 2:1:1, to 4:1:1, to 6:1:1.

To avoid this problem, Polymer 2 was prepared with sodium acetate, as the catalyst, and a monomer with a lower melting point  $\alpha\alpha'$ -diacetoxy-1,4-xylene (48-49°C).

In line with the stated purpose and the above observation, it can be concluded that polymer I was not successfully synthesized, and that polymer 2 has been synthesized successfully and it has a high inherent viscosity indicative of a high molecular weight. The TGA of polymer 2 indicates that this polymer has good thermal properties. However this polymer does not show liquid crystalline properties. It is suspected that if this polymer had increased spacer length it would have formed an isotropic melt.

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