



Rincon Guerrero, America (1984) *Preparation and thermal degradation of polycarbonates*. PhD thesis.

<http://theses.gla.ac.uk/2092/>

Copyright and moral rights for this thesis are retained by the author

A copy can be downloaded for personal non-commercial research or study, without prior permission or charge

This thesis cannot be reproduced or quoted extensively from without first obtaining permission in writing from the Author

The content must not be changed in any way or sold commercially in any format or medium without the formal permission of the Author

When referring to this work, full bibliographic details including the author, title, awarding institution and date of the thesis must be given

PREPARATION AND THERMAL DEGRADATION OF POLYCARBONATES

by

AMERICA RINCON G

A Thesis submitted in partial fulfilment  
of the requirements for the degree of  
PHILOSOPHIAE DOCTOR in the Faculty of  
Science at the University of Glasgow,  
Scotland.

May 1984

Supervisor : Dr. I.C. McNeill

# **TEXT BOUND INTO THE SPINE**

## Foreword

The work described was carried out between October 1980 and January 1984 in the Physical Chemistry Department, which is under the general supervision of Professor G.A. Sim, and was supported during this period by a Grant award to the author by the University of Los Andes, Faculty of Science, Merida, Venezuela.

## ACKNOWLEDGEMENTS

I should like to express my gratitude to my supervisor, Dr. I.C. McNeill, for his guidance and moral support during the course of the work in this study.

I should also like to thank Professor N. Grassie for allowing me to work in his polymer group, and for his friendly support throughout the period of this work.

I should like to thank Mr. J. Gorman and Mr. G. McCulloch for their sound technical assistance.

I am most grateful to the University of los Andes, Merida, Venezuela, for the grant awarded to me, enabling me to study at the University of Glasgow.

I would like to express grateful thanks to Miss E. Forbes in the Department of Chemistry, for her friendship and encouragement during the period of my stay in Glasgow.

Finally, I should like to thank both Mrs. J. Anthony and Mrs. J. Rodgers for their kindness and efficiency in the preparation of this thesis, also the many other people in the Department who were always very willing and helpful.

## CONTENTS

	Page
CHAPTER ONE - INTRODUCTION	1
1.1 Historical Development	1
1.2 General Aspects of Polymer Degradation	2
1.3 Thermal Degradation	3
1.4 Preview of the Thermal Degradation of Polycarbonates	5
1.4.1 Thermal degradation of aliphatic polycarbonates	6
1.4.2 Degradation of aliphatic-aromatic polycarbonates	8
1.4.3 Degradation of aromatic polycarbonates	9
1.5 Aim of This Work	11
CHAPTER TWO - THERMAL AND ANALYTICAL TECHNIQUES	12
2.1 Thermal Analysis Techniques	12
2.1.1 Thermal volatilisation analysis (TVA)	13
2.1.2 Differential condensation TVA	13
2.1.3 The oven assembly	15
2.1.4 Sub-ambient thermal volatilisation analysis (SATVA)	17
2.1.5 Product collection	21
2.1.6 Quantitative analysis for standard compounds	22
2.1.7 Thermogravimetry (TG)	24
2.1.8 Differential scanning calorimetry (DSC)	24

	Page
2.2	Analytical Techniques 25
2.2.1	Infrared spectroscopy 25
2.2.2	Gas liquid chromatography-mass spectroscopy 25
2.2.3	Nuclear magnetic resonance (nmr) spectroscopy 25
2.2.4	Vapour pressure osmometry (VPO) 26
2.2.5	Mass spectrometry 26
2.2.6	Elemental analysis 26
2.2.7	End-group analysis 26
CHAPTER THREE - PREPARATION OF MONOMERS AND POLYMERS	27
3.1	Introduction 27
3.1.1	Aliphatic polycarbonates 27
3.1.2	Aliphatic-aromatic polycarbonates 31
3.1.3	Aromatic polycarbonates 33
3.2	Preparation of Aliphatic Polycarbonates 35
3.2.1	Preparation of monomers 35
3.2.2	Preparation of starting material - 2-phenyl- 1,3-propane-diol 37
3.2.3	Preparation of polymers 39
3.2.3.1	Poly(trimethylene carbonate) 39
3.2.3.2	Poly(neopentylene carbonate) 42
3.2.3.3	Poly(2-phenyl-trimethylene carbonate) 44
3.3	Characterisation of Monomers and Aliphatic Polycarbonates 45
3.4	Preparation of Aliphatic-Aromatic Polycarbonates 58
3.4.1	Poly(p-xylylene carbonate) 58
3.4.2	Characterisation of poly(p-xylylene carbonate) 64



	Page
3.5	Preparation of Aromatic Polycarbonates:
	Bisphenol A Polycarbonate 66
3.6	Characterisation of Bisphenol A Polycarbonate 68
CHAPTER FOUR -	EXPERIMENTAL RESULTS AND DISCUSSION 72
4.1	Programmed Degradations for Aliphatic Polycarbonates 72
4.1.1	Poly(trimethylene carbonate) 72
4.1.2	Poly(neopentylene carbonate) 78
4.1.3	Poly(2-phenyl-trimethylene carbonate) 84
4.2	Isothermal Degradations for Aliphatic Polycarbonates 91
4.2.1	Poly(trimethylene carbonate) 91
4.2.2	Poly(neopentylene carbonate) 94
4.2.3	Poly(2-phenyl-trimethylene carbonate) 95
4.3	Rates of Thermal Degradation for Aliphatic Polycarbonates 96
4.4	Thermal Stability of Acetylated Aliphatic Polycarbonates 105
4.5	Thermal Fragmentation by Mass Spectrometry of Aliphatic Polycarbonates and their Cold Ring Fractions 105
4.5.1	The mass spectrum of degraded poly(trimethylene carbonate) and its cold ring fraction 108
4.5.2	The mass spectrum of degraded poly(neopentylene carbonate) and its cold ring fraction 114



		Page
4.5.3	The mass spectrum of degraded poly(2-phenyl-trimethylene carbonate) and its cold ring fractions	120
4.6	Discussion	125
4.7	Programmed Degradation for Aliphatic-Aromatic Polycarbonates	137
4.8	Isothermal Degradations for Aliphatic-Aromatic Polycarbonates	156
4.8.1	Production of condensable gases	156
4.8.2	Characterisation of cold ring fractions	156
4.8.3	Spectral changes for polymer residue	163
4.9	Rates of Thermal Degradation for Poly(p-xylylene carbonate)	163
4.10	Hydroxyl End-Groups Determination	164
4.11	The Mass Spectrum of Degraded Poly(p-xylylene carbonate) and its Cold Ring Fraction	164
4.12	Discussion	173
4.13	Programmed Degradation for Aromatic Polycarbonates: Bisphenol A Polycarbonate (Laboratory and Commercial Samples)	181
4.14	Isothermal Degradation for Aromatic Polycarbonates	193
4.15	Rates of Thermal Degradation of Bisphenol A Polycarbonate	194

	Page
4.16	Thermal Degradation of Bisphenol A Polycarbonate in the presence of 1,4-Diamino-Anthraquinone (DAA)
	199
4.17	The Mass Spectra of Degraded Bisphenol A Polycarbonate and its Cold Ring Fraction
	202
4.18	Discussion
	207
CHAPTER FIVE -	QUANTITATIVE DETERMINATION OF DEGRADATION PRODUCTS
	221
5.1	General Procedure for Quantitative Degradation of Polymer in TVA System
	221
5.2	Aliphatic Polycarbonates
	222
5.2.1	Programmed degradadation for poly(trimethylene carbonate)
	222
5.2.1.1	Analysis of solid products
	222
5.2.1.2	Analysis of carbon dioxide
	222
5.2.2.	Isothermal degradation for poly(trimethylene carbonate)
	223
5.2.2.1	Analysis of solid products
	223
5.2.3	Programmed degradation for poly(neopentylene carbonate)
	228
5.2.3.1	Analysis of solid products
	228
5.2.3.2	Analysis of carbon dioxide
	228
5.2.4	Isothermal degradations for poly(neopentylene carbonate)
	229

	Page
5.2.4.1	Analysis of solid products 229
5.2.4.2	Analysis of carbon dioxide 232
5.2.5	Programmed degradation for poly(2-phenyl- trimethylene carbonate) 232
5.2.5.1	Analysis of solid products 232
5.2.6	Isothermal degradations for poly(2-phenyl- trimethylene carbonate) 232
5.2.6.1	Analysis of solid products 232
5.2.6.2	Analysis of carbon dioxide 234
5.3	Aliphatic-Aromatic Polycarbonates 234
5.3.1	Programmed degradation for poly(p-xylylene carbonate) 234
5.3.1.1	Analysis of solid products 234
5.3.1.2	Analysis of condensable products 237
5.3.2	Isothermal degradations for poly(p-xylylene carbonate) 237
5.3.2.1	Analysis of solid products 237
5.4	Aromatic Polycarbonates 238
5.4.1	Programmed degradation for bisphenol A polycarbonate 238
5.4.1.1	Analysis of solid products 238
5.4.1.2	Analysis of carbon dioxide 240
5.4.2	Isothermal degradations for bisphenol A polycarbonate (laboratory and commercial samples) 240

	Page
5.4.2.1      Analysis of solid products	240
CHAPTER SIX - GENERAL CONCLUSIONS	243
Suggestions for Further Work	245
APPENDIX A - Activation Energy for Bisphenol A Polycarbonate	
Degradation	246
REFERENCES -	257

## SUMMARY

This study is concerned with the preparation, characterisation and subsequent thermal degradation of three different classes of polycarbonates, viz. aliphatic, aliphatic-aromatic, and aromatic polycarbonates.

Five different polycarbonates were prepared and characterised: poly(trimethylene carbonate), poly(neopentylene carbonate), poly(2-phenyl-trimethylene carbonate), poly(p-xylylene carbonate) and bisphenol A polycarbonate. Polymerisations were carried out by using ring-opening polymerisation and transesterification reactions.

The second major part of the work deals with the thermal degradation of these polymers. Most of the thermal degradations have been performed using two approaches, programmed and isothermal heating.

The basic thermal technique used was thermal volatilisation analysis (TVA), with fractionation of the products of degradation by subambient TVA. Thermogravimetry and differential scanning calorimetry were used to provide additional information to complement the TVA data.

The analysis of the degradation products was carried out using mainly infrared spectroscopy and mass spectrometry.

The principal degradation route of aliphatic polycarbonates is via an ester interchange mechanism with the formation of cyclic oligomers. The polymerisation-depolymerisation equilibrium is affected by the presence of substituents such as phenyl groups which displace the equilibrium in favour of the formation of short chain fragments via a random chain scission.



Aliphatic-aromatic polycarbonates degrade via a random chain scission at the carbonate groups.

Aromatic polycarbonates degrade via a random chain scission at the carbonate groups at the first stage of the process. The removal of the volatile products was found to favour condensation reactions. The thermal rearrangement at the carbonate group leads to branching and eventually gelation.

The characteristic feature in the degradation of polycarbonates is that the most reactive group in the macromolecule is the carbonate group.

## CHAPTER ONE

### INTRODUCTION

#### 1.1 HISTORICAL DEVELOPMENT

Natural occurring polymers have been used by man for thousands of years. However, the structure of polymers was not understood until the late 1920's. The assertion that materials such as starch, rubber or proteins had high molecular weight was regarded with scepticism by most scientists. The more generally accepted view was that these apparently large molecules were colloidal aggregates of smaller molecules held in a micellar structure by secondary forces. The basic units in both cellulose and rubber were known, but cellulose was thought to be a cyclic tetrasaccharide and rubber merely a ring composed of two isoprene molecules. However, it was not until 1920 that Staundinger<sup>1</sup> put forward the idea of covalently bonded macromolecular structures for polystyrene, rubber and polyoxymethylene, and began the process of providing convincing evidence in favour of this structure. In 1925, the X-ray studies by Katz revealed a fibre-like diagram for stretched rubber and similar work led Meyer and Mark (1928) to propose a semicrystalline structure for long chain molecules in cellulose. The development of methods for measuring molecular weights and molecular weight distribution of polymer by ultracentrifugation (Svedberg, 1926) and viscosity (Staundinger, 1928) helped the acceptance of the macromolecular hypothesis. For instance, the narrow molecular distributions found for proteins were particularly



difficult to explain by the colloidal theory. By 1930, the macromolecular theory was beginning to be accepted. In 1929 Carothers and co-workers<sup>2</sup> began the classical series of attempts to prepare high polymers from well-characterised, low-molecular-weight compounds. The success of these studies provided a major advance in the understanding of the dependence of polymer properties on structure and led to the final verification of the macromolecular theory. From 1930 onwards the foundations of modern polymer science and the plastics industry had been laid, leading eventually to the polymer-based way of life we have today.

## 1.2 GENERAL ASPECTS OF POLYMER DEGRADATION

Ever since polymer became a commercially important material, it has been particularly important to understand the nature of the degradative processes.

From the 1940's pure scientists<sup>3-5</sup> began to take an interest in the fundamental chemistry underlying polymer degradation as one of the most important areas of polymer chemistry in both scientific and technological respects. In recent years this has been stimulated by the fact that the microstructural polymer properties have become better understood and by the developments of new applications for synthetic polymeric materials in which they must be stable to a wide variety of chemical, physical and mechanical agencies.

The term "degradation" is a collective name given to various processes which degrade polymers, i.e., cause the properties which make them useful to deteriorate, or ruin the outward appearance, for example, by discolouration.

Degradation may happen during every phase of the life of a polymer, i.e., during its synthesis, processing and use.

Depending on polymerisation conditions, during polymer synthesis, depolymerisation may take place. Depolymerisation is the reverse of polymerisation.

During processing, the material is subjected to a very high thermal and mechanical stress. These drastic stresses may initiate a variety of polymer degradation processes leading to a deterioration of properties.

During use, some agencies, such as sunlight (uv light) and moisture, may cause polymer degradation.

Polymer degradation is mainly caused by chemical bond scission reactions in macromolecules. For practical reasons, however, it is useful to subdivide this broad field according to the various modes of initiation. These comprise thermal, photochemical, mechanical, chemical, biological, high energy radiation, etc.

### 1.3 THERMAL DEGRADATION

Thermal degradation refers to the case when the polymer, at elevated temperatures, starts to undergo chemical changes without the involvement of another compound. The study of this process is important in revealing a variety of information about these changes and how they are affected by choice of temperature.

Various methods of analysis can be used and the simultaneous use of two or more thermal techniques provides complementary data which

be used to evaluate properties such as the relationship between the stability of a polymer and detailed aspects of its chemical structure, the pattern of degradation products evolved during the heating of the polymer and the weight loss of a substance as it is heated.

It is convenient to classify thermal degradation reactions into two groups:

- (i) Reactions which result in depolymerisation to the monomer unit and main chain scission.
- (ii) Reactions which modify or remove active groups attached to the backbone of the macromolecule.

Depolymerisation is essentially a reversal of the polymerisation process. In the simplest case, depolymerisation consists of initiation at chain ends, depropagation and termination.

Depolymerisation has been studied in some detail.<sup>6,7</sup> It has been shown that it can be completely described by a free radical chain reaction which may also include inter or intramolecular transfer of radical activity. The formation of monomer is encouraged in systems which do not possess labile atoms in the polymer chain structure.

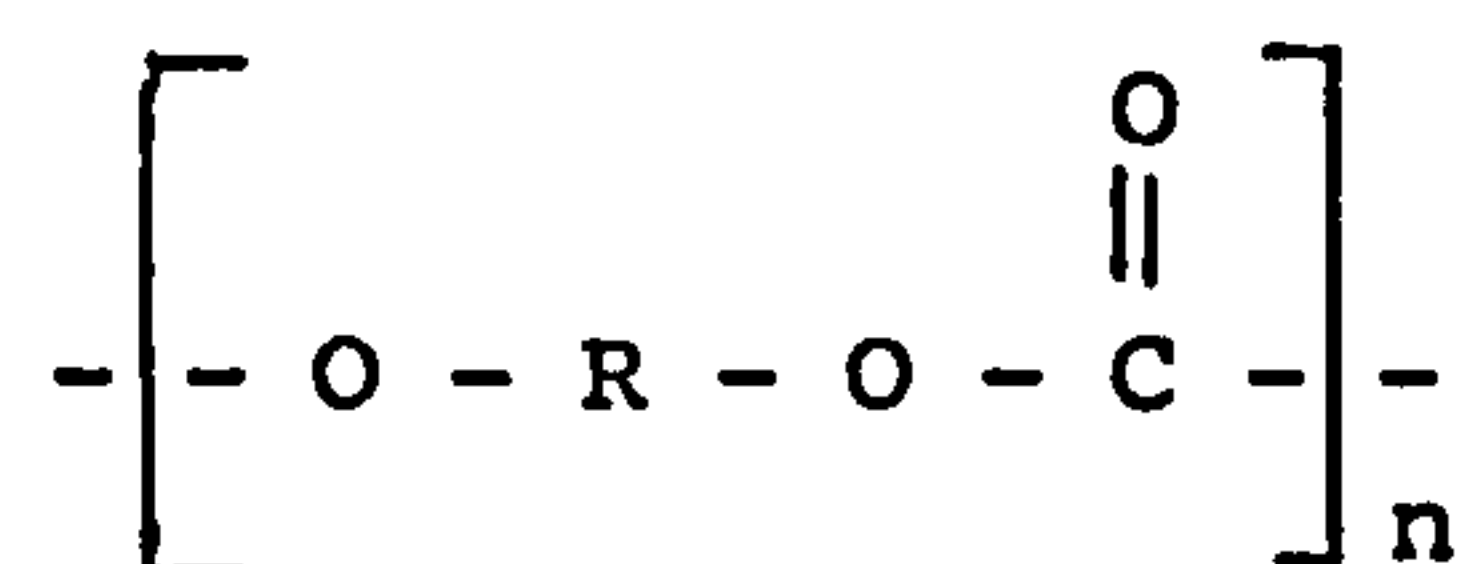
Substituent reactions<sup>8</sup> are another type of polymer degradation process which does not involve scission of the main polymer chain. These reactions will occur in a given system only if they can be initiated at temperatures lower than that at which main chain bonds are broken. Substituent reactions usually take place at relatively low temperatures. Thermal depolymerisation seldom takes place below 200°C, even if structural features are most favourable. Substituent reactions



if they take place at all, are frequently quite rapid at this temperature.

#### 1.4 PREVIEW OF THE THERMAL DEGRADATION OF POLYCARBONATES

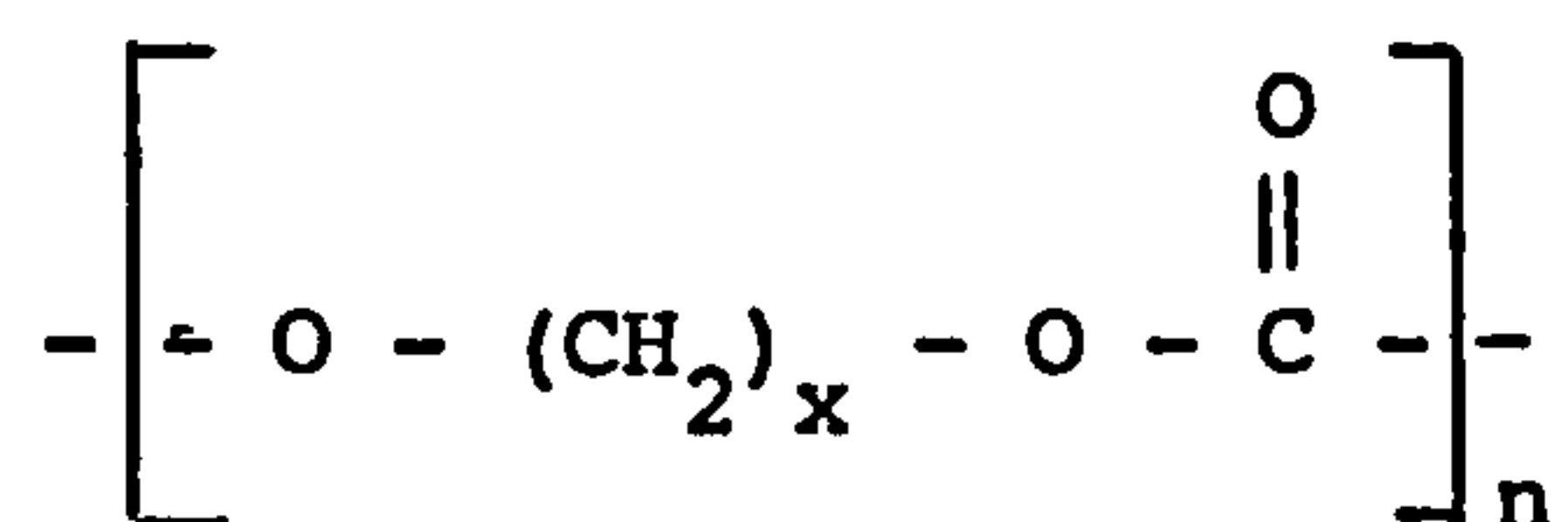
Polycarbonates are a special class of polyesters derived from the reaction of carbonic acid derivatives with aliphatic diols, aliphatic-aromatic diols, dihydroxy-benzenes or bisphenols. Their structures may be represented by the general formula



where

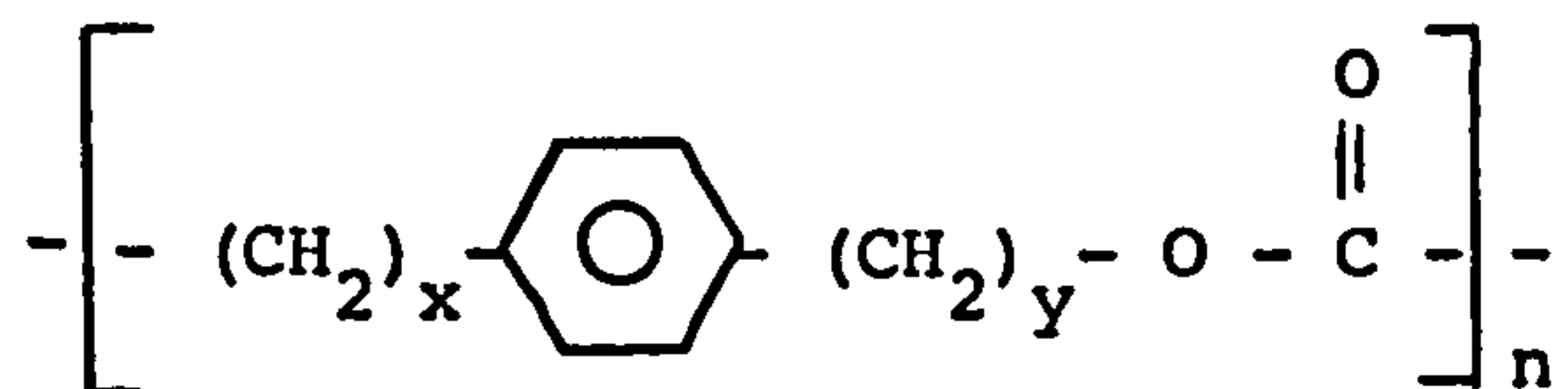
for aliphatic polycarbonates

R = alkyl group.



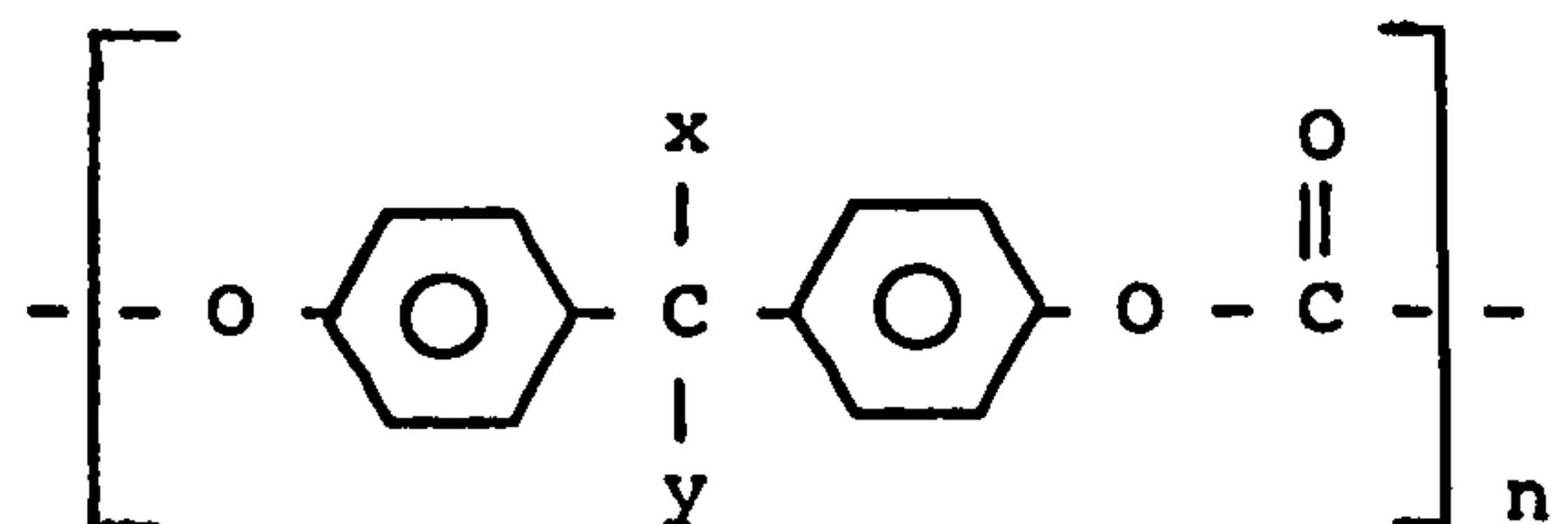
for aliphatic-aromatic polycarbonates

R = Arenes group.



for aromatic polycarbonates

R = phenyl group.



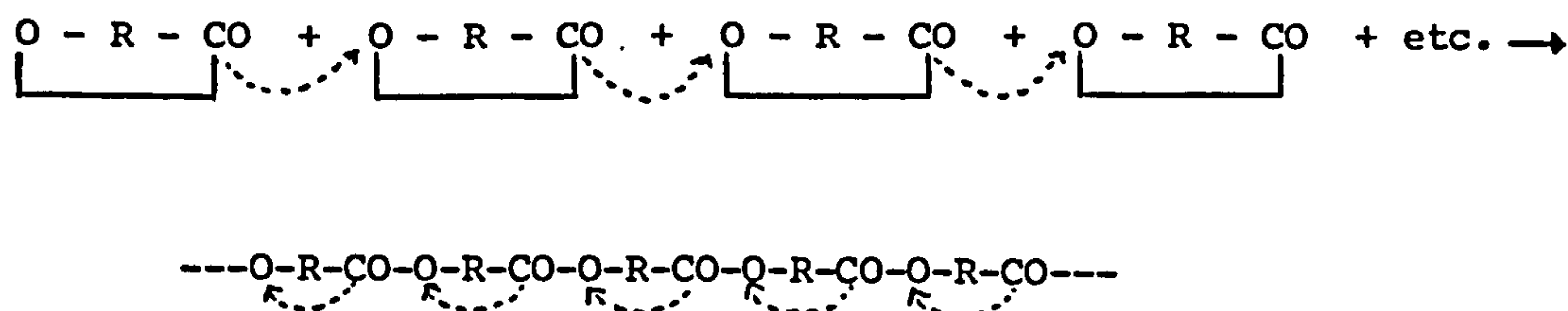
where x, y = H, alkyl or aryl group.

Most of the studies on thermal degradation of polycarbonates have been devoted mainly to aromatic polycarbonates, principally on bisphenol A polycarbonate. This is probably due to the fact that aliphatic polycarbonates and aliphatic-aromatic polycarbonates have found no technological applications due to their poor chemical and thermal stability.

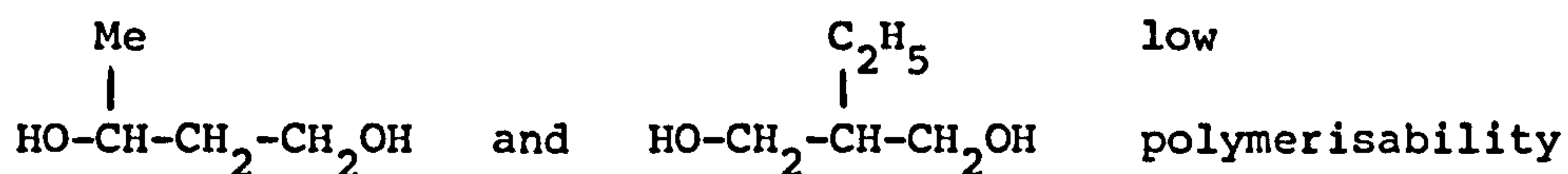
#### 1.4.1 Thermal Degradation of Aliphatic Polycarbonates

Among all the cyclic esters prepared by Carothers and co-workers<sup>9</sup> it was found that trimethylene carbonate and ethylene oxalate exhibit the property of reversible transformation between a monomeric and a polymeric form. They suggested that the ease of Polymerisation of the six-membered cyclic compounds appears to be related to their susceptibility to hydrolysis. In general, substitution increases the resistance to hydrolysis and diminishes the tendency to polymerise.

Carothers and van Natta<sup>9</sup> proposed that the polymerisation of these polymers and its reversal proceeds by a process of ester interchange reaction, indicated by the general equation:

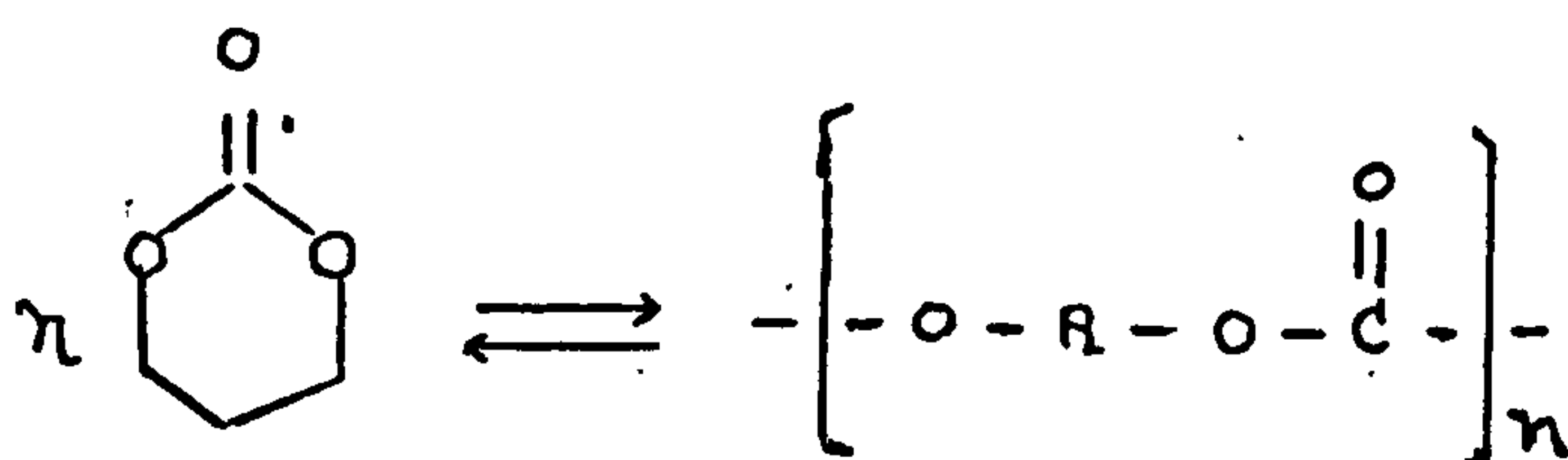


They suggested that due to stereochemical factors, rings of six atoms are strained (or may pass through positions of strain); rings of five atoms or more than ten are strainless. In the six-membered cyclic esters, strain can be relieved by the process of ester interchange which results in polymerisation. The polymers from the six-membered ester are easily depolymerised owing to the high probability of the close approach of atoms six apart atoms in the chain. Hall and Schneider<sup>10</sup> reported that the presence of substituents has a considerable effect on the polymerisability. 4-, 7- and 8-membered ring compounds polymerised in all cases, but in the case of 5- or 6-member carbonyl-containing monomers, polymerisability depends markedly on the classes of compounds involved. For instance, alkyl or aryl substituents on a ring always decrease polymerisability. They found that two methyl groups can be tolerated but ethyl or phenyl substituents prevented polymerisation. Sarel and Pohoryles<sup>11,12</sup> also reported that six-membered ring esters obtained from 1,3-propane diol substituted at carbon 1 or 2 showed different polymerisability properties. Thus methyl substituents at carbon 1 and ethyl substituents at carbon atom 2 do not favour the formation of polymeric carbonates. However, the introduction of methyl groups at carbon 2 has little effect on polymerisability



They explained that this behaviour is due to stereochemical and not kinetic factors because these substituted esters e.g. cyclic 4-methyl-trimethylene carbonate and cyclic 4,4-dimethyl trimethylene carbonate are hydrolysed by alkali at approximately the same rate.<sup>13</sup>

In the degradation of aliphatic polycarbonates, most of the authors support the view that the polymerisation-depolymerisation reversion mechanism is essentially the same, an intramolecular ester interchange reaction.

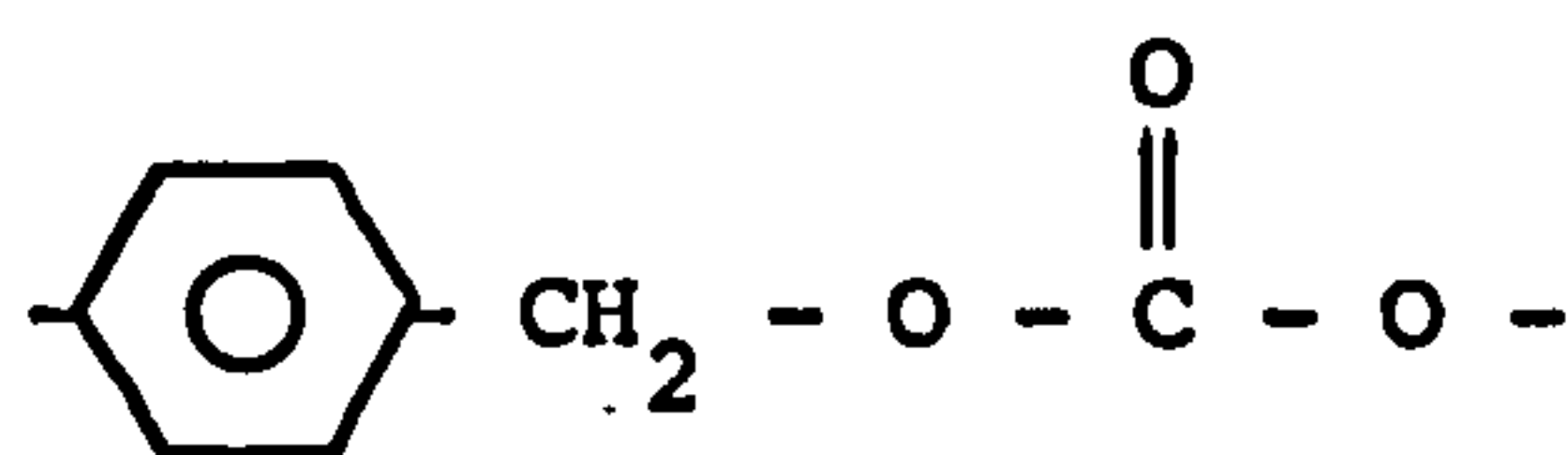


#### 1.4.2 Degradation of Aliphatic-Aromatic Polycarbonates

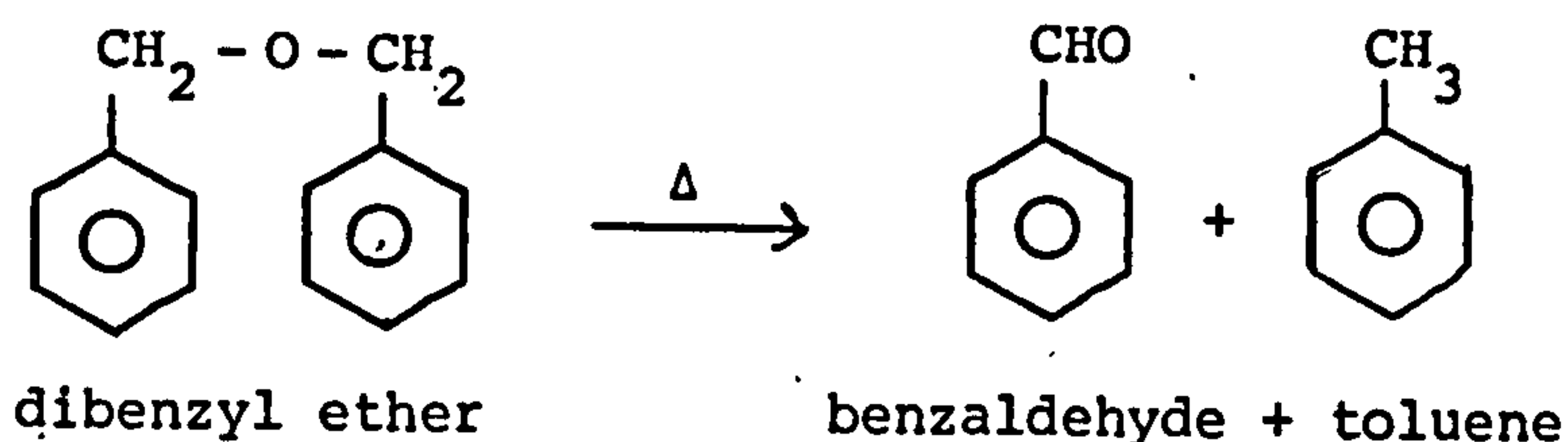
The aliphatic-aromatic polycarbonates are comparable to aliphatic polycarbonates in their thermal stability. They show a poor stability at high temperatures, especially in the presence of alkaline compounds.

Experiments with the model compound benzyl ethyl carbonate<sup>14</sup> suggested that polycarbonates produced from the structural unit





will thermally decompose to  $\text{CO}_2$ , poly benzyl ether, aromatic hydrocarbons and resins which are formed by secondary reactions of benzyl aldehyde groups. The pyrolysis of an aliphatic ether produces aldehyde compounds<sup>15</sup> and hydrocarbons, such as:



Little work has been done on the thermal degradation behaviour of aliphatic-aromatic polycarbonates.

#### 1.4.3 Degradation of Aromatic Polycarbonates

The previous studies of the thermal degradation of bisphenol A polycarbonate<sup>16-18</sup> had shown that, like most polyesters, it is also susceptible to hydrolysis, especially at elevated temperatures. Under dry conditions only limited degradation is observed below 250°C. The stability of bisphenol A polycarbonate has been the subject of a review by Davis and Golden<sup>19</sup> where the effects of different agencies are summarised.

Davis and Golden noticed a decrease in molecular weight during heat exposure in a sealed vessel and claimed that the polymer underwent random chain scission.<sup>17</sup> In studies carried out in a continuously

evacuated system, the polymer rapidly crosslinked and formed an insoluble gel.<sup>21</sup> The large discrepancies between the results from these two methods are due to the competition between condensation and hydrolysis reactions, as explained by Davis and Golden.

Lee<sup>22</sup> emphasised the sensitivity of the carbonic ester towards hydrolysis and alcoholysis.

Depolymerisation is enhanced by the presence of acidid or basic impurities, which may well be formed during the degradation reaction<sup>17,23</sup> and, consequently, hydrolysis results in a decrease in molecular weight.

The principal volatile products collected during degradation of bisphenol A polycarbonate are, carbon dioxide, phenol and bisphenol A. Smaller amounts of other compounds, like carbon monoxide, methane, 2-(p-hydroxy phenyl)-2-phenyl-propane and diphenyl carbonate, have also been observed. Davis and Golden<sup>20</sup> determined the rate of gas evolution in an evacuated system at 360°C to be  $2 \times 10^{-5}$  millimol. of gas per gram of polymer per sec. The volatiles consisted of 95% CO<sub>2</sub>, 3% CO and 2% CH<sub>4</sub>. The fact that CO<sub>2</sub> is the major volatile product indicates that the carbonate linkage is the most reactive group in the polymer. The amount of phenol formed increases with the increased moisture content in the sample.

Kovarskaya<sup>16</sup> found that a scission reaction occurred during Processing of polycarbonate, which may lead to deterioration of the mechanical properties.

Abbas<sup>24</sup> degraded bisphenol A polycarbonate in static conditions and evaluated the changes in molecular weight by gel permeation

chromatography. The activation energy of the overall process was found to be 26.7 kcal/mol.

Bisphenol A polycarbonate is one of the most versatile engineering plastics.<sup>14,25,26</sup> It has an attractive combination of mechanical properties and good heat stability.

#### 1.5 AIM OF THIS WORK

The main purpose of this work was to study the thermal degradation of three different classes of polycarbonates, in particular by applying the thermal volatilisation analysis technique and the complementary subambient TVA technique, in order to gain a more complete insight into the degradative processes of these polymers, and to try to ascertain the effect on the structural differences on the mechanism of the thermal degradation.

## CHAPTER TWO

### THERMAL AND ANALYTICAL TECHNIQUES

#### INTRODUCTION

The experimental techniques and apparatus used in this work are briefly described in this chapter.

As TVA was extensively employed throughout this work, it is appropriate to give a full description of the apparatus and operation. TVA and its application to polymer chemistry has given rise to a number of publications.<sup>27-29</sup> TVA and the further development differential condensation TVA are important, well established techniques, along with the complementary SATVA technique.

#### 2.1 THERMAL ANALYSIS TECHNIQUES

##### 2.1.1 Thermal Volatilisation Analysis (TVA)

In this technique devised by McNeill,<sup>30,31,32</sup> a polymer sample is subjected to heating within a continuously evacuated system and the pressure of the volatile products evolved recorded as they distil from the heated sample to a cold trap placed some distance away. The pressure, which is conveniently monitored by a Pirani gauge, is a measurement of the rate of volatilisation. A TVA curve is a record of Pirani response versus temperature for a sample subjected to linear increase of temperature with time. The pressures measured are in the range  $10^{-5}$  to  $10^{-1}$  mm Hg and the temperature is programmed from ambient to 500°C at a



heating rate of 10°C per minute. The TVA curve may have one or more peaks corresponding to maximum in the rate of decomposition of the polymer.

### 2.1.2 Differential Condensation TVA

This is an important development of the basic TVA technique,<sup>32-34</sup> which provides an indication of the volatility of the products evolved at each stage in the breakdown of the polymer. In the procedure described by McNeill,<sup>32</sup> the degradation products evolved are routed through four cold traps, all at different temperatures, which are situated in parallel between the heated sample and the main trap at -196°C. Depending on volatility, different quantities of gases pass through each trap i.e., more products pass through the trap at highest temperature. A Pirani gauge placed after each of the four traps measures the pressure of the volatiles which pass through them and one after the main trap measures the pressure of non-condensable gases. During the degradation process the Pirani gauge responses are recorded simultaneously, together with the oven temperature, as measured by a chromel-alumel thermocouple. The resulting TVA curve can yield much information about the nature of the degradation products.

A four limb parallel line system is shown in fig. 2.1. In this arrangement the four lines are so arranged that the sample to gauge distance does not differ from one line to another. In normal operation, the four lines are all open and the initial traps are kept at 0°, -45°, -75° and -100°C ( $\pm 2^\circ\text{C}$ ). Volatile products may be collected at the points 26, 27, 28 and 29, using minimum volume gas cell for infrared

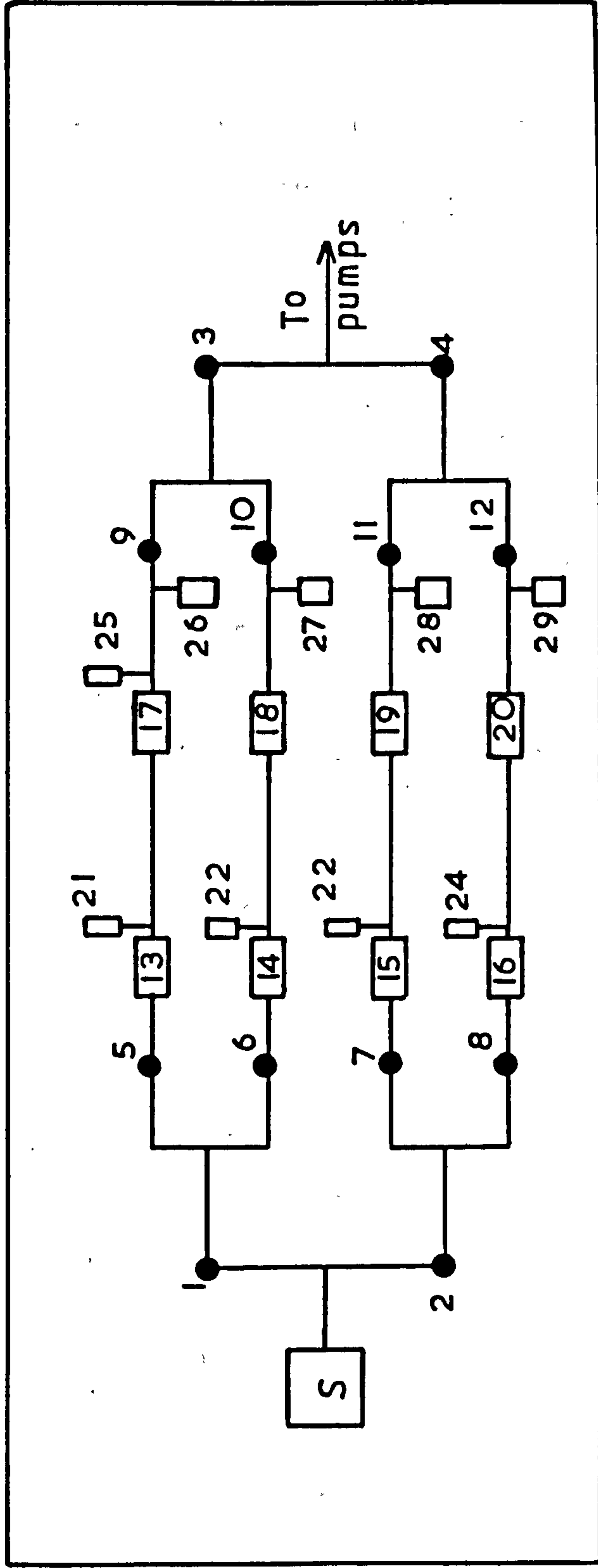


Fig 2.1 Parallel line differential condensation TVA system  
 s= heated sample; 1-4 = stopcocks (large bore, right angle type);  
 5-12 = stopcocks  
 (HV 8mm); 13-16 initial cold taps; 17-20 - common traps at -196°C;  
 21-25 = Pirani gauge heads; 26-29 = collection points

spectroscopy, or collection tubes and then removed for analysis.

The pressure measurements were made using a G5C-2 Pirani head connected via a multihead switch unit to an Edwards Model 8-2 Pirani gauge control unit. A Leeds-Northrup "Speedmax w" 12 point stripchart recorder with high gain amplifier was used with a reversed range card, -10 to 0 mv or -2 to 0 mv. A chromel-alumel thermocouple made from 20 gauge wire was used to monitor the oven temperature, using a cold junction at 0°C as reference point. A 100  $\Omega$  variable resistor was connected between the oven thermocouple and the recorder, as the oven temperatures were greater than those capable of being recorded using a -10 to 0 mv range card. Thermocouple output in mv was converted to temperature in °C by using standard conversion tables. When five Pirani gauge heads are used at the same time, the response for a given pressure may vary slightly. For this reason it is necessary to bring the responses into coincidence. This was done periodically, as required, using the procedure described by McNeill.<sup>31</sup>

Samples used were either in powder or film form in the weight range 25 to 150 mg. The system was evacuated by means of an Edwards type EO1 oil diffusion pump and an Edwards rotary pump Model ED100.

### 2.1.3 The Oven Assembly

Degradations were performed in the oven assembly<sup>32</sup> shown in fig. 2.2. The oven and linear temperature programmer used was a slightly modified Perkin-Elmer F-11 gas chromatography system. The oven can be used for temperatures up to 500°C and different heating rates are available.



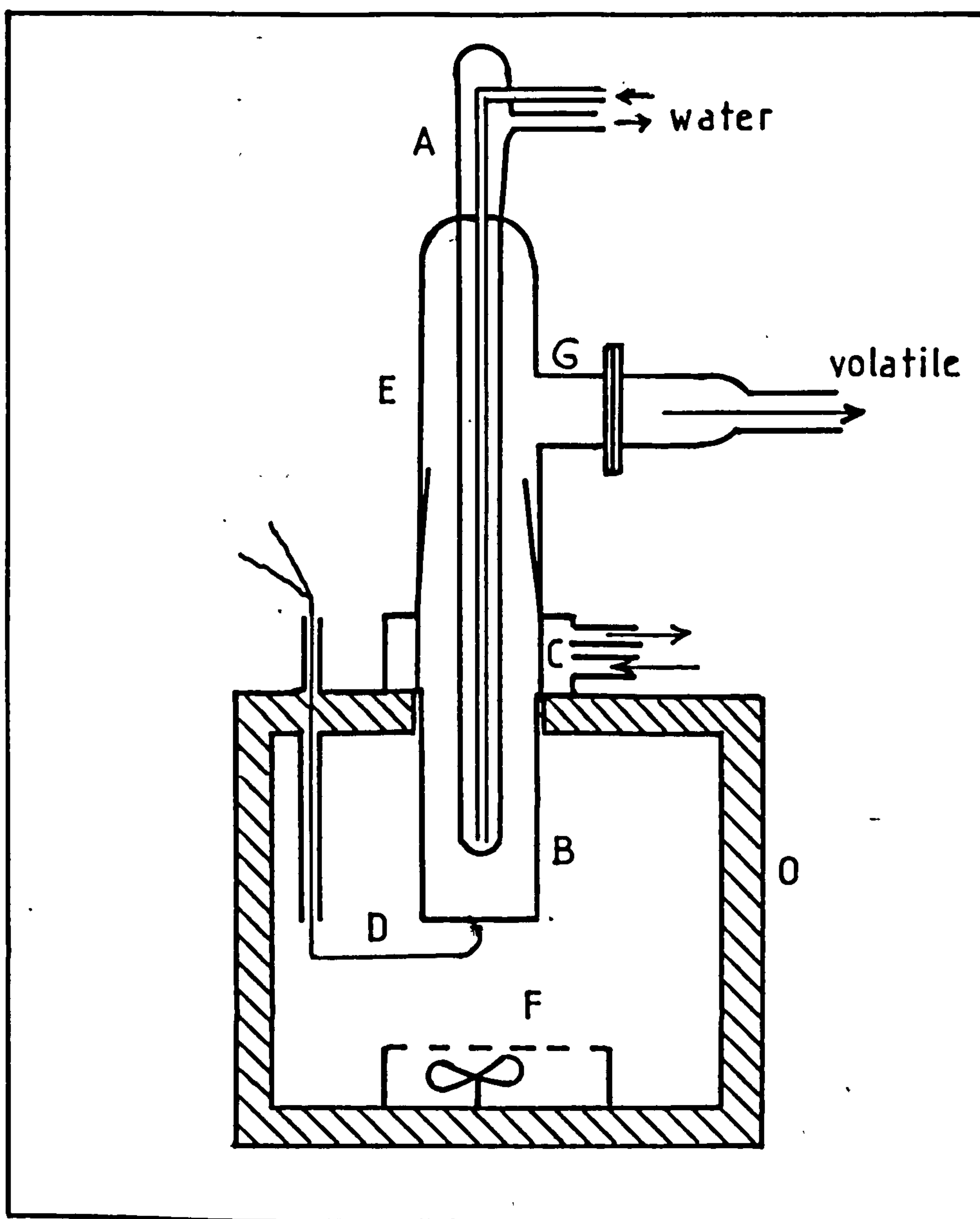


Fig.2.2 A: cold finger B: sample tube C: water jacket  
 D: thermocouple E: lid F: fan G: outlet to  
 trap system. O: OVEN  
 Oven assembly with cold finger incorporated

The degradation tubes used were 25 cm long and 38 mm diameter and made of pyrex glass. The lid inserted on the top connected the tube to the vacuum system by means of an FC flange. A B19 socket in the lid was used for two alternative purposes, firstly for insertion of a cold finger to assist in the collection of the cold ring fraction during the degradation process and, secondly, for insertion of a thermocouple used for calibration of the sample temperature.

The sample temperature is always lower than the oven temperature because of a temperature gradient across the base of the degradation tube. Using the calibration method described by McNeill,<sup>31</sup> sample temperatures can be accurately determined. Calibration curves determined using ice as reference point are shown in fig. 2.3.

#### 2.1.4 Sub-ambient Thermal Volatilisation Analysis (SATVA)

Sub-ambient TVA is a technique developed by McNeill and coworkers<sup>28,35,36</sup> in which a condensable volatile mixture may be selectively separated according to the volatility of the components. The degradation products formed during degradation are condensed in a trap at  $-196^{\circ}\text{C}$  and the trap is then allowed to warm gradually. The products which distil are collected into another trap at  $-196^{\circ}\text{C}$ , placed some distance away. The pressure of the products evolved is monitored by a Pirani gauge head located between the two traps. The sub-ambient trap temperature and the pressure of the products are simultaneously recorded to give a SATVA curve which consists of distinct peaks corresponding to the different condensable degradation products.

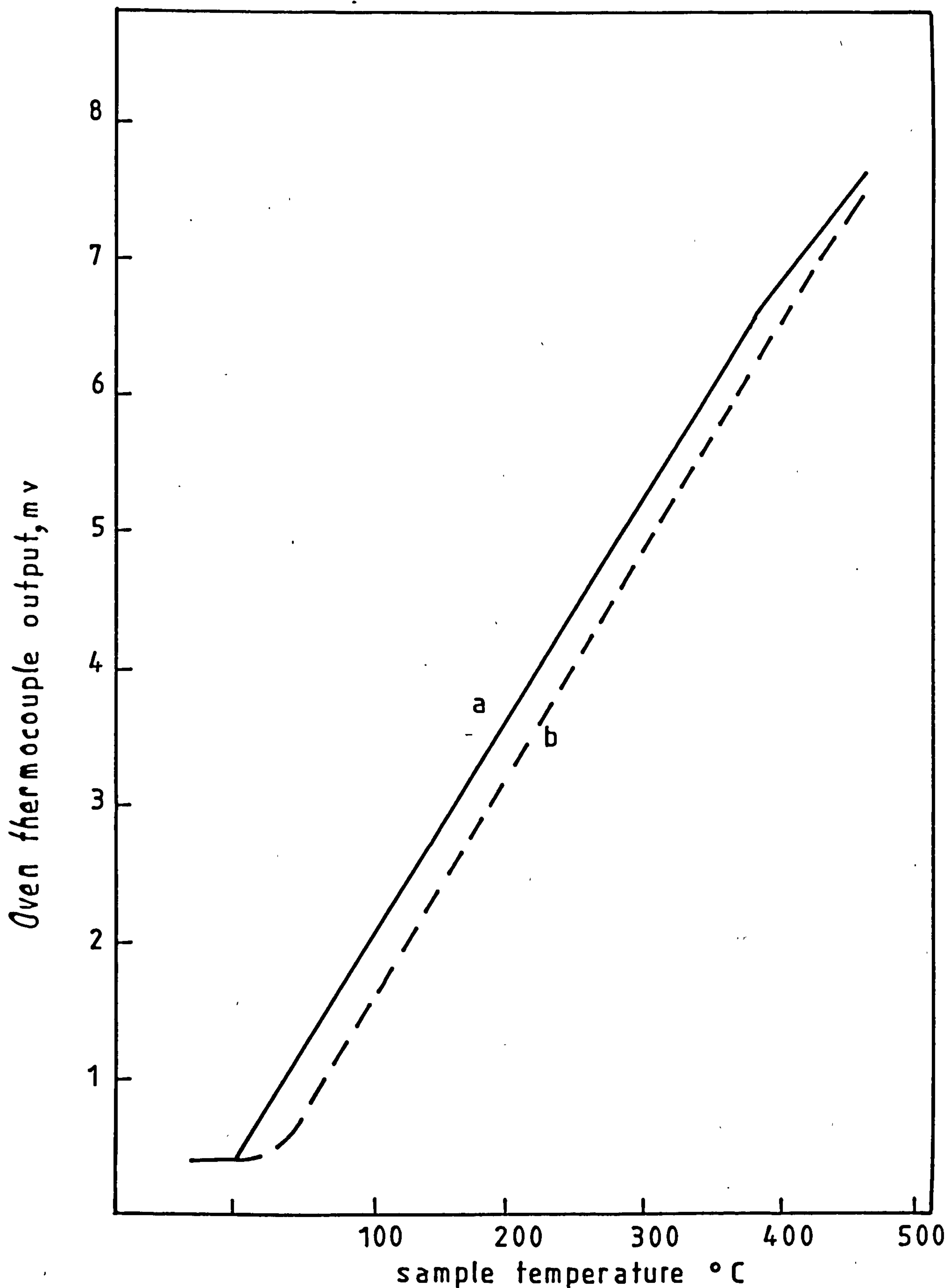


Fig. 2.3 Sample calibration curves with glass sample bottle at 10°C/min. a = oven thermocouple curve  
b = sample thermocouple curve

The separation of products can be hindered by the presence of hydrogen bond effects or by almost identical volatility.

The SATVA assembly is illustrated in fig. 2.4. The sample U tube of diameter 1.5 cm is surrounded by a jacket flask 10 cm in diameter which is filled by p-xylene (m.p. 13.3°C) or boiling stones (diameter = 4 mm). The efficiency of separation can often be improved by reducing the heating rate, which depends on the diameter of the jacket. The usual procedure in this technique is to evacuate the system and the bottom (5 cm) of the liquid in the jacket is then surrounded by liquid nitrogen. Once the temperature, which is monitored by means of a thermocouple, has reached -196°C, the degradation products are allowed to distil into the sample tube. When the transfer of products is complete, the degradation section is isolated and the rest of the jacket liquid completely frozen.

The sub-ambient separation and subsequent fractionation of the products can be performed in the same system used for differential condensation TVA. It is possible to separate the products evolved in SATVA which are responsible for the different peaks by permitting each to distil by a different route. The schematic diagram of the apparatus used for this fractionation is shown in fig. 2.5. The apparatus has four equivalent routes, AB, AC, AD and AE and in each line a collection point at R where can be attached a minimum volume infrared gas cell or a collection tube in which the products are collected and removed for analysis.

The Pirani gauge head at P records the pressure of gases as they distil from the main trap, while the heads at G are used only to



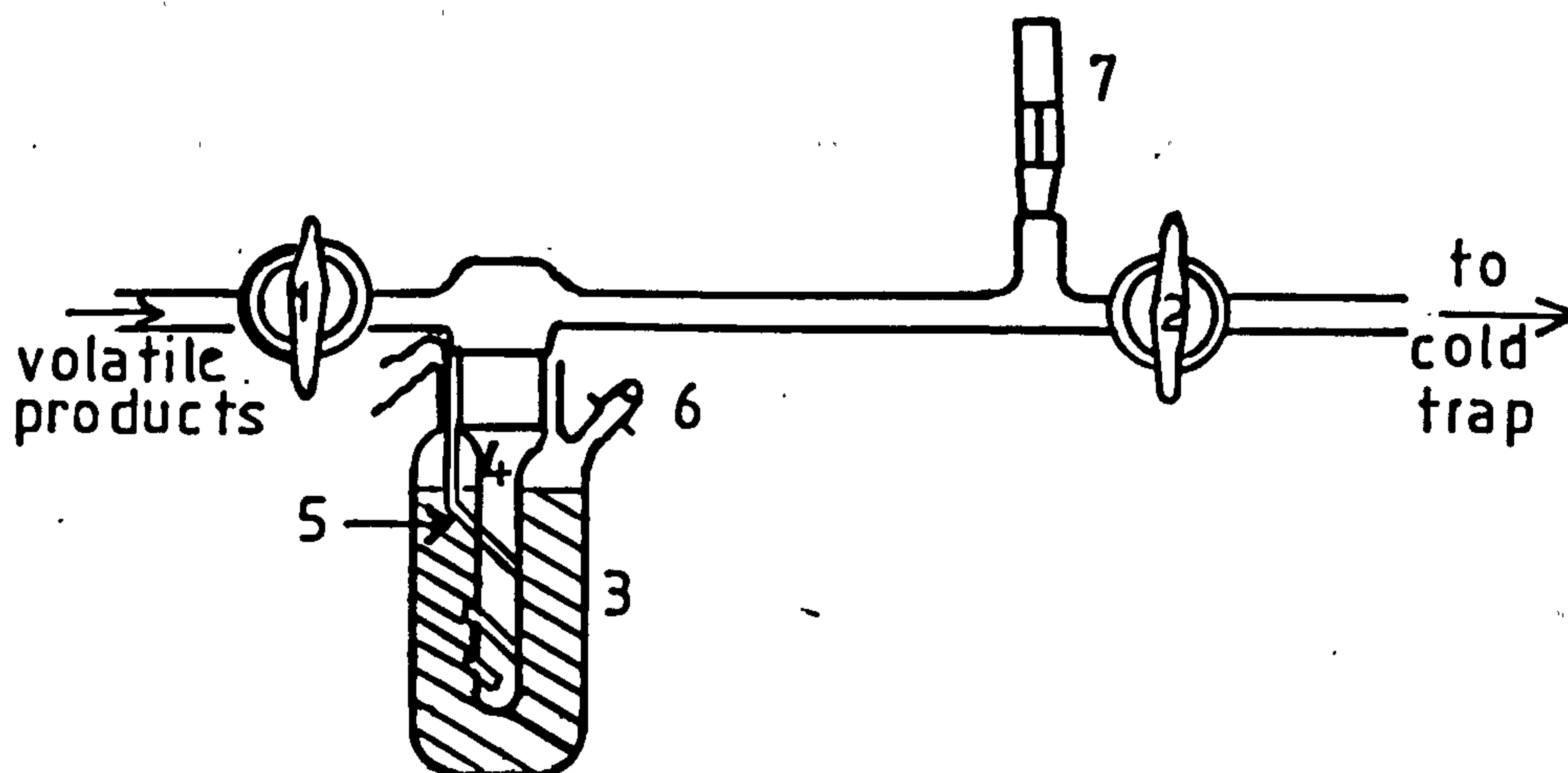


Fig. 2.4 Arrangements for sub ambient TVA system  
1-2=stopcocks; 3=jacket 4= sample tube; 5 =  
thermocouple; 6 = filler port; 7=Pirani gauge  
head.

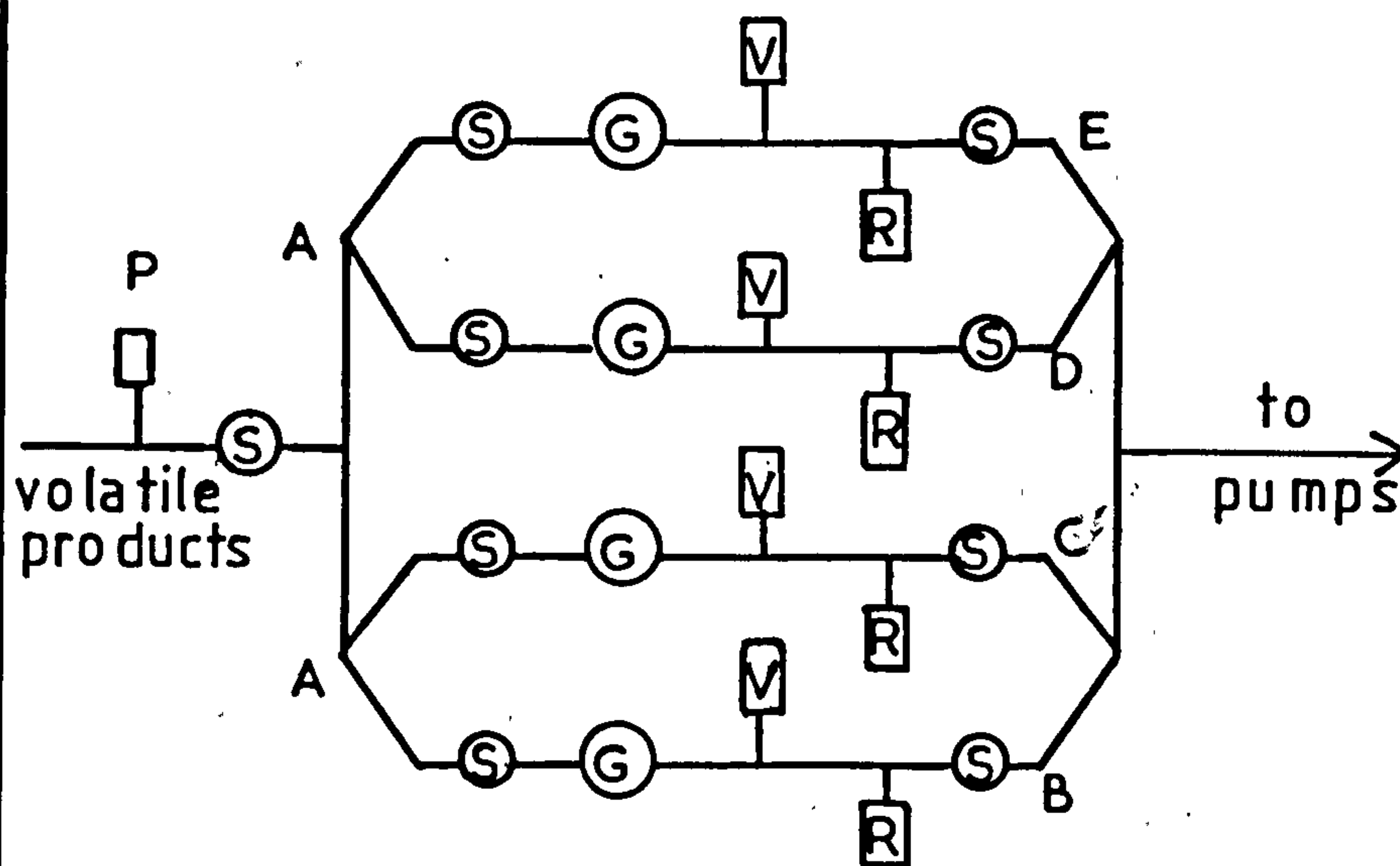


Fig 2.5 Assembly for collection of fractions in  
subambient TVA. P and v = Pirani gauge heads  
S = stopcocks G = traps at  $-196^{\circ}\text{C}$ , A B, AC, AD,  
AE geometrically equivalent routes  
R = collection points.

monitor distillation from the U tube traps to the collection points.

As in TVA the Pirani output is non-linear and is more sensitive at the low pressures of the scale.

#### 2.1.5 Product Collection

In a TVA experiment, products of degradation are separated according to their volatility.<sup>28</sup>

I. Residue: This is the material which remains after degradation, which can be analysed by spectroscopy and elemental analysis.

Molecular weight changes in partially degraded samples can also be studied.

II. Cold ring fraction (CRF) - comprises products which are volatile at degradation temperatures but involatile at ambient temperature. In the TVA apparatus it is collected in the water-cooled upper part of the degradation tube and placed outside the oven.

This fraction is removed from the inner wall of the tube by dissolving in a solvent and analysed by spectroscopy and elemental analysis.

III. Volatile fraction - consists of products which are volatile at ambient temperature and can be divided into two fractions.

- (a) Condensable products. These are products condensable at  $-196^{\circ}\text{C}$ , which can be collected at the specified points in the system after degradation and sub-ambient separation, and subsequently analysed.

- (b) Non-condensable products. Permanent gases such as carbon monoxide, hydrogen and methane, which do not condense at  $-196^{\circ}\text{C}$ , can be analysed on production by mass spectrometry via an on line VG Micromass QX200 mass spectrometer attached to the TVA system.

#### 2.1.6 Quantitative Analysis for Standard Compounds

In this work the amount of volatile products formed was estimated by using calibration curves for standard known compounds. The qualitative distillation technique, SATVA, previously described, was adapted for quantitative determination.<sup>35,36</sup> A recorder range of 2 mv was used so the Pirani output was within the linear region (2 to 0 mv).

##### Calibration curve for carbon dioxide

Carbon dioxide was obtained by heating small amounts (0.1 - 0.6 mg) of sodium hydrogen carbonate which decomposes, giving  $\text{CO}_2$  as the only volatile product.

The carbon dioxide formed was distilled according to the already described SATVA technique. The area of the peak was measured. A calibration curve (fig. 2.6) was made, plotting area of the peak versus moles of carbon dioxide evolved.

##### Calibration curve for p-tolualdehyde

p-Tolualdehyde (Aldrich) 99% purity was employed. The calibration curve obtained is shown in fig. 2.7.



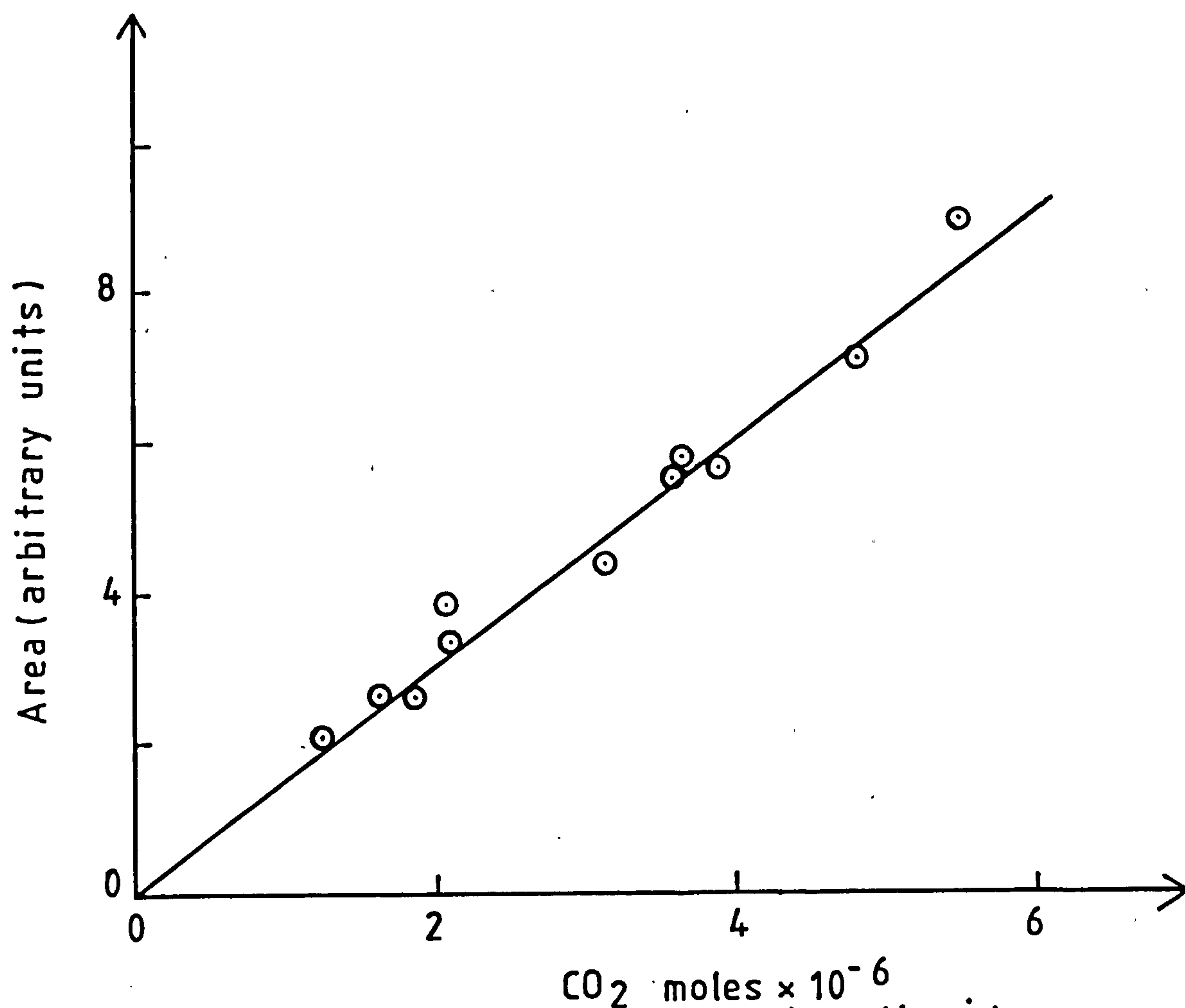


Fig.2.6 Calibration graph for carbon dioxide.

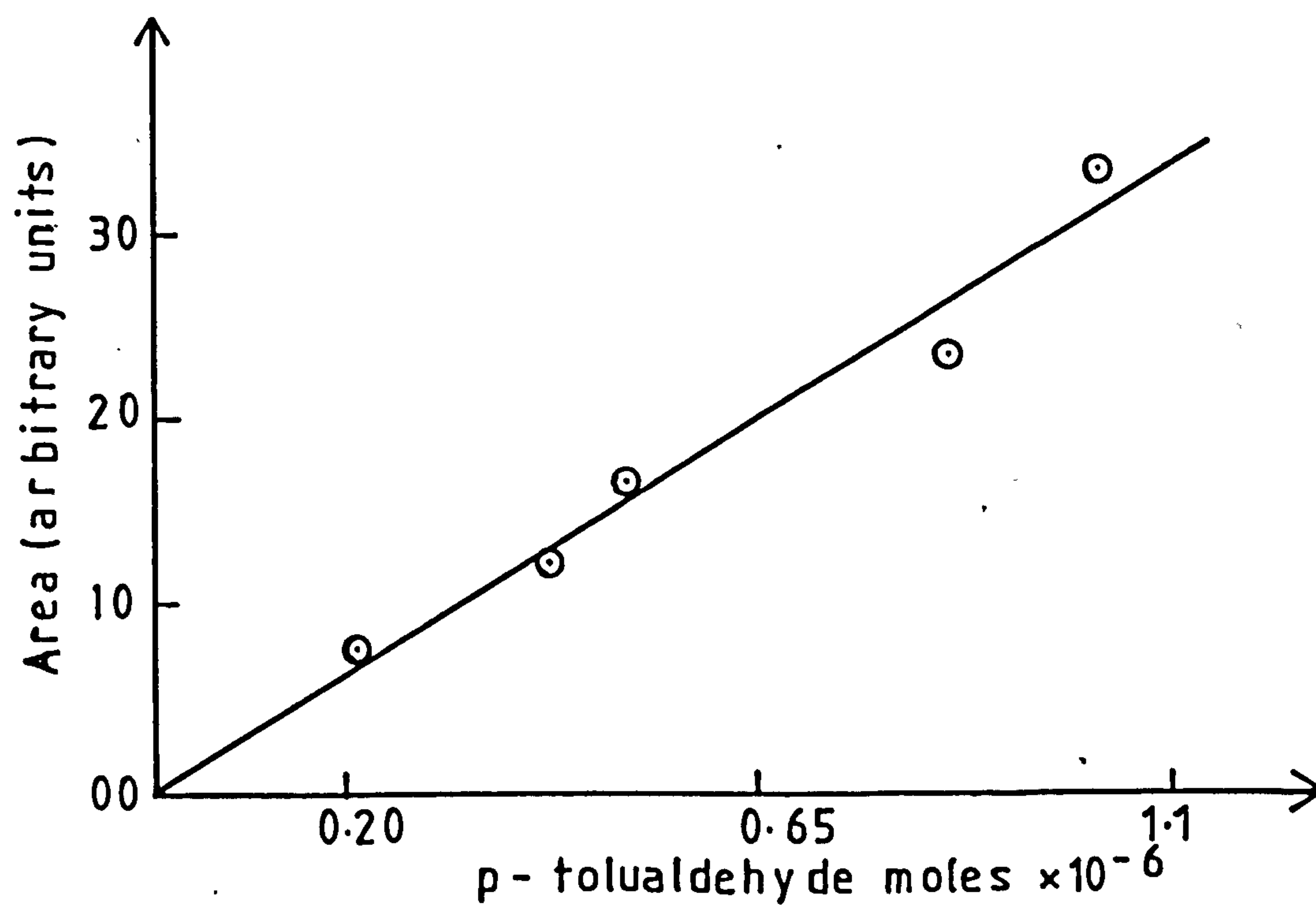


Fig. 2.7 Calibration graph for p-tolualdehyde

### 2.1.7 Thermogravimetry (TG)

This technique measures the loss or gain of weight of a sample as a function of temperature. The equipment used in this work was a Du Pont 990 Thermal Analyser incorporating a temperature programmer and chart recorder in conjunction with a Du Pont 951 Thermogravimetry Analyser which included a furnace and an amplifier. The transducer is a photo-sensitive null detector positioned at one end of the balance. Samples for analysis were contained in a boat-shaped platinum sample pan of dimensions (1 x 0.5 x 0.25 cm), and were located approximately 0.1cm below the temperature-measuring thermocouple. The weight change is displayed on the y-axis of the recorder, while the x-axis reads temperature. Programmed degradations were carried out at a heating rate of 10°C per minute from ambient to 500°C. All samples weighed were in the range 2-10 mg. The derivative TG curve was recorded simultaneously. Isothermal measurements in a dynamic nitrogen atmosphere (50 ml/min) or in vacuum were also obtained.

### 2.1.8 Differential Scanning Calorimetry (DSC)

DSC is a technique in which the difference in energy input into a substance and a reference material is measured as a function of temperature while the substance and the reference material are subjected to a controlled temperature program. The instrument employed in this work was a Du Pont 990 Thermal Analyser in conjunction with a Du Pont 910 Differential Scanning Calorimeter.

The temperature range used was from ambient to 500°C, at a heating rate 10°C per minute, and all runs were under nitrogen atmosphere (50 ml/min) with sample sizes between 1-6 mg.

## 2.2 ANALYTICAL TECHNIQUES

### 2.2.1 Infrared Spectroscopy

Infrared spectra were obtained using a Perkin-Elmer Model 257 grating infrared spectrometer. The undegraded polymer and products of degradation were analysed by the KBr disc technique or in the form of a film.

The KBr disc technique consists of grinding a mixture of 1-2 mg of sample with 300 mg of KBr salt and pressed to form a circular disc. Using a pressure of 8 tons per square inch, a disc of 13 mm diameter and 1.5 mm thick, was obtained. Thin films cast on a NaCl plate were prepared by dissolving a small amount of sample in a suitable solvent, e.g. dichloromethane, which was allowed to evaporate, forming a thin film of sample on the NaCl plate. Gaseous samples were studied using minimum volume infrared gas cells.

### 2.2.2 Gas Liquid Chromatography - Mass Spectrometry

Analyses of the degradation products were carried out on a Kratos MS-30 mass spectrometer coupled to a Pye-Unicam 104 gas chromatograph via a glass jet separator. Samples of a few milligrams were dissolved in ethyl acetate or a mixture of ethyl acetate and chloroform. Analyses were made using helium as a carrier gas (40 ml/min) and a 9 feet x 1/4" 10% OV-17 column.

### 2.2.3 Nuclear Magnetic Resonance (nmr) Spectroscopy

Most nmr spectra were obtained using a Perkin-Elmer R32 90 MHz spectrometer. A few milligrams of sample were dissolved in deuterated

chloroform and placed in a thin quartz tube. The spectra were obtained on 0-10 (ppm) scale using tetramethylsilane as reference (TMS = 0 ppm). Some nmr spectra were obtained using a Perkin-Elmer XL-100 A Varian Spectrometer.

#### 2.2.4 Vapour Pressure Osmometry (VPO)

Number average molecular weight of polymers and monomers were obtained on a Mechrolab Model 3001 A vapour pressure osmometer.

Solutions of the samples (1-2g sample/100g solvent) using chloroform or toluene were used.

#### 2.2.5 Mass Spectrometry

Original polymer and solid products of degradation were analysed on a A.E.I. MS 12 mass spectrometer. All other gaseous samples were analysed using a VG Micromass QX 200 mass spectrometer.

#### 2.2.6 Elemental Analysis

Elemental analysis of one milligram of sample was carried out after combustion in a CARLA-ERBA CHN Elemental Analyser Model 1106.

#### 2.2.7 End Group Analysis

A mixture of a small amount of the polymer and acetic anhydride was refluxed by six hours at 50°C, at the end of which time the acetic anhydride in excess was evaporated by vacuum. The thermal stability of the acetylated samples was assessed by thermogravimetry.



## CHAPTER THREE

### PREPARATION OF MONOMERS AND POLYMERS

Since none of the cyclic carbonates, nor the reagent 2-phenyl-1,3-propane diol were commercially available, synthesis and characterisation was carried out. In this chapter, preparation, purification and characterisation of both monomers and polymers are described.

#### 3.1 INTRODUCTION

Most research on preparation of polycarbonates has been focussed on the aromatic homopolymer and copolymer. Less attention has been given to aliphatic-aromatic homopolymers and copolymers. Even less research has been devoted to the aliphatic polycarbonates.

##### 3.1.1 Aliphatic Polycarbonates

Since the classical research by Carothers and coworkers<sup>2,9</sup> on cyclic carbonates and aliphatic polycarbonates, a number of methods of preparation have been described in various patents and other publications.

Cyclic carbonates are obtained in good yield by phosgenation in the presence of tertiary amines of 1,2- 1,3- and 1,4-diols which are capable of forming 5- or 6-membered cyclic carbonates. Sarel, Pohoryles and Ben-Shoshan<sup>37</sup> obtained the 7- and 14-membered cyclic carbonates besides low molecular weight polycarbonates, when they added a solution of phosgene in toluene to a dilute solution of 1,4-butanediol



(HO-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-OH) and antipyrine (2,3-dimethyl-1-phenyl-3-pyrazolin-5-one, phenazone) in chloroform at 40-50°C.

Aliphatic polycarbonates can also be prepared by phosgenation of diols at low temperatures in the presence of pyridine and tertiary amines. Krzikalla and Merkel<sup>38</sup> obtained low molecular weight polycarbonates by adding 1,4-butanediol to a solution of the chlorocarbonic ester of 1,4-butanediol at 75°C and 35 mm Hg, in the presence of pyridine in inert solvents such as toluene or xylene. A wax-like polymer mp = 62-65°C with MW over 2000 is obtained. The same route has been used to prepare copolymers with alternating monomer units.<sup>14</sup>

Carothers, Van Natta and Hill<sup>9</sup> prepared the cyclic carbonate by the transesterification reaction of diol OH-(CH<sub>2</sub>)<sub>n</sub>-OH, where n = 2 to 14 excluding the 10th derivative, with diethyl carbonate or dibutyl carbonate at temperatures between 120° to 160°C, using sodium as catalyst. They obtained the 5 or 6-membered cyclic carbonate for n = 2, 3, whereas for n ≥ 3, the reaction resulted in polycarbonates with molecular weights below 3000. Sarel and coworkers<sup>11</sup> investigated the influence of reaction conditions and the structure of the diol on the formation of cyclic carbonates or polycarbonates during the transesterification with diethyl carbonate. Only polycarbonates are obtained when 2,2-dimethyl-2-methyl-2-n-propane, and 2-methyl-2-isoamyl-1,3-propane diol are reacted with diethyl carbonate in the presence of small amounts of sodium methoxide. If large amounts of catalyst are used the 6-membered cyclic carbonate is also obtained. By using diols such as 2,3-diethyl-1,3-propanediol, 2-ethyl-2-phenyl-1,3-propanediol, 2,4-pentanediol and 1,3-butanediol, only 6-membered cyclic carbonates are obtained.

The reaction conditions and the structure of the diol determine whether the monoester forms cyclic carbonate or polycarbonate. Higher temperatures and use of the dilution principle favour <sup>2</sup> the formation of cyclic compounds. The formation of cyclic carbonates from 1,3-propanediol derivatives can also be favoured by bulky substituents on  $C_2$  or substituents on  $C_1$  or  $C_3$ .

Peterson <sup>39</sup> modified the transesterification procedure used by Carothers to eliminate the effect of the sodium methoxide in the last stages of the reaction, which prevents formation of high molecular weight polycarbonates, by using the catalytic action of an acid, e.g. lauric acid, in the later stages. After the elimination of NaOMe in the reaction medium by washing with a dilute solution of hydrochloric acid, the low molecular weight polycarbonate is dissolved in an inert solvent, e.g. toluene. After distilling off the solvent, the transesterification reaction is finished under the catalytic action of the carboxylic acid. Polycarbonates which are film or fibre-forming are obtained using diol compounds with  $n > 3$ . Piepenbrink <sup>40</sup> prepared aliphatic polycarbonates by reaction of diols ( $n = 6$ ) with diphenyl carbonate in the absence of catalyst. The poly(hexamethylene carbonate) obtained had a melting point of  $55^{\circ}\text{--}60^{\circ}\text{C}$  and a  $T_g$  of  $-5^{\circ}\text{C}$ . Phenol was eliminated as by-product. Reynolds and Van den Berghe <sup>41</sup> produced aliphatic polycarbonates from penta- hexa- and decamethylene diols by polycondensation of the bis-alkyl and bis-aryl carbonates of the corresponding diol which form polycarbonates by splitting off dialkyl or diaryl carbonates.

Carothers and Van Natta <sup>9</sup> obtained poly(trimethylene carbonate) by the ring-opening polymerisation reaction of trimethylene

carbonate in the presence of an alkaline catalyst, e.g. potassium carbonate. Hill and Carothers<sup>9</sup> also obtained polycarbonates by the ring-opening polymerisation reaction of cyclic carbonates of deca-, dodeca-, trideca-, and tetradecamethylene diol and from the cyclic carbonate dimers of hexa- and decamethylene diol.

#### Properties of aliphatic polycarbonates

Aliphatic polycarbonates at room temperature are generally viscous liquids or microcrystalline, due to the low polarity of the carbonate group in the backbone of the polymer. Most aliphatic polycarbonates melt below 120°C, e.g. poly(trimethylene carbonate) has m.p. 47°C and poly(neopentylene carbonate) has m.p. 119°C. Most of the aliphatic polycarbonates which are solids at room temperature can be crystallised. On cooling from a melt opaque solids can be obtained. The melting points of crystallised compounds depend on the degree of crystallinity and therefore on their thermal history. Thus poly(neopentylene carbonate), if rapidly cooled from its melt, will melt at 107° to 109°C. If the same polymer is conditioned by heating at 100°C for a long period of time (one week) the melting point increases to 117° to 119°C by conversion from the  $\alpha$ -form to a more stable  $\beta$ -form of the polymer.<sup>37</sup> Polycarbonates made from symmetrically branched diols such as 2,2-dimethyl-1,3-propane diol and from the cis- and trans-isomers of 2,2-4,4-tetramethyl cyclobutane-1,3-diol, have higher melting points. Apparently, the melting point increment in these polycarbonates may be due to a stiffer polymer backbone and a lowered flexibility due to the pendant methyl groups. Aliphatic polycarbonates



are solubles in common organic solvents such as acetone, benzene, dichloromethane, chloroform and insoluble in ethanol, diethyl ether and petroleum ether. Aliphatic polycarbonates are affected by water vapour because of their hydrophilic nature. Little has been reported on the mechanical or electrical properties of these polymers.<sup>14</sup>

### 3.1.2 Aliphatic-Aromatic Polycarbonates

Carothers and Van Natta<sup>2</sup> prepared an aliphatic-aromatic polycarbonate, poly (p-xylylene carbonate), by the transesterification method using p-xylylene diol and diethyl carbonate with sodium as catalyst. They obtained an inhomogeneous microcrystalline polymer of low molecular weight, which was partially soluble in ethylene dichloride. The soluble portion melted at 137°-138°C and the insoluble portion at 177°-185°C. Reinholds and Van der Berghe<sup>42</sup> studied the transesterification reaction of p-xylylene glycol with different catalysts. They demonstrated that strongly alkaline catalysts such as lithium aluminium ethylate decompose the benzyl carbonate groups in the backbone making it difficult to obtain high molecular weight poly(p-xylylene carbonate). They prepared high molecular weight poly(p-xylylene carbonate) by polycondensation of the bisalkyl or bisaryl carbonate of the p-xylylene diol in the presence of titanium containing catalysts, e.g., tetrabutyl titanate or titanium tetrachloride. At temperatures of the reaction up to 250°C these catalysts slightly degrade the starting material or the polycarbonate formed. Other catalysts of the type  $(M)OR_2 \cdot Ti(OR)_4$  where M = Mg, Ca, Sr, R = alkyl ( $C_1$ - $C_{18}$ ) are also used to produce poly(p-xylylene carbonate) and other polycarbonates.

Caldwell <sup>43</sup> prepared several aliphatic-aromatic polycarbonates by reacting bis-hydroxyethyl ether of an aromatic glycol with dialkyl carbonate in the presence of bimetal complexes of magnesium, calcium, or strontium, with aluminium or titanium, of the general formula



where M = Ca, Sr, Mg, R = alkyl with C<sub>1</sub>-C<sub>6</sub>. Aliphatic-aromatic polycarbonates have been prepared by the transesterification reaction<sup>14</sup> of the bis-hydroxy alkyl ether of an aromatic glycol with diaryl carbonate without catalyst.

Aliphatic-aromatic polycarbonates have also been prepared by phosgenation<sup>14</sup> of a solution of the bis-hydroxy alkyl ether of an aromatic diol in the presence of pyridine.

Soga et al. <sup>44</sup> obtained a poly(p-xylylene carbonate) by the reaction of p-xylylene dibromide with potassium carbonate using an 18-Crown-6-ether (1,4,7,10,13,16-hexaoxacyclooctadecane) catalyst. They obtained a white solid, which melted at 195°C, insoluble in common organic solvents and soluble only in hot ortho-dichlorobenzene, dimethyl sulfoxide or dimethyl formamide. The same reaction when conducted at higher temperature (160°C) gave a polymer somewhat different from the others in nature. It was a yellow-coloured solid which was insoluble in hot dimethyl sulfoxide and stable even at 300°C when assessed by DSC technique.

#### Properties of aliphatic-aromatic polycarbonates

In these polymers, the melting range increased considerably compared to the aliphatic polycarbonates due to the presence of the aromatic ring in the backbone. However, it is considerably lower than



the melting range of aromatic polycarbonates.<sup>14</sup> This is explained by the presence of  $-\text{CH}_2-$  groups between the aromatic groups, which increases the mobility of the macromolecules. Aliphatic-aromatic polycarbonates are crystalline solids. From the melt they solidified to an opaque and, in most cases a brittle, microcrystalline solid. They dissolve in fewer common organic solvents. Fibres can be drawn from the melt and can be orientated by stretching due to the higher degree of crystallinity. Little is known about electrical and mechanical properties of aliphatic-aromatic polycarbonates.

### 3.1.3 Aromatic Polycarbonates

The preparation of aromatic polycarbonates has been known since 1898, when Einhorn<sup>45</sup> reported the preparation of a polycarbonate by phosgenation reaction with hydroquinone and with resorcinol and Bischoff and Hedenstroem<sup>46</sup> in 1902 reported also the preparation by transesterification reaction with resorcinol and diphenyl carbonate, but these polymers were insoluble and intractable, because of which no interest arose in the preparation of these materials for the next 50 years. Schnell<sup>47</sup> in 1956 reported the preparation of bisphenol-A polycarbonate, one of the aromatic polycarbonates widely used because of good thermal stability and outstanding mechanical properties. Since then preparation and characterisation of aromatic polycarbonates and copolymers has been extensively studied and reported in patents, technical articles and other publications.<sup>48-54</sup>

Aromatic polycarbonates can be prepared by three main methods: phosgenation of phenols in solution with pyridine, interfacial poly-

condensation and transesterification. Other methods reported in the literature are variations of these three main routes of preparation.

Phosgene in the presence of pyridine is more reactive with phenols than the aromatic carbonate derivative. The reaction must take place in the absence of water and with a large excess of pyridine in order to maintain the reaction in liquid phase. High molecular weight aromatic polycarbonates are obtained, if they are soluble in pyridine or other inert solvents, e.g. benzene, toluene. Aromatic polycarbonates are also prepared by the reaction of aqueous alkaline solutions of phenol with phosgene or bis-chloro carbonic ester of phenol in the presence of inert solvents. Bottenbruch and Schnell<sup>14</sup> found that by using small quantities of tertiary amines, such as triethylamine, N,N-dimethylcyclohexylamine, the reaction of interfacial polycondensation is accelerated with the advantage that chlorine-free polycarbonates are obtained because the remaining chlorocarbonic ester end groups are rapidly hydrolysed at the end of the reaction. The preparation of aromatic polycarbonates by phosgenation of phenol or interfacial polycondensation, results in products of useful mechanical properties only when the polycarbonate is soluble in inert solvents. The transesterification process can be applied for all aromatic polycarbonates, which can be melted below their decomposition temperature. Transesterification of phenols with diaryl carbonates in the absence of catalyst proceeds slowly at temperatures up to 280°C, accompanied by the formation of volatile phenols, e.g. phenol, but the reaction is accelerated markedly by alkaline catalyst.<sup>14</sup> In this study the latter method of preparation is employed to prepare bisphenol A polycarbonate.

### Properties of Aromatic Polycarbonates: Bisphenol A Polycarbonate

Bisphenol-A polycarbonate is soluble in chloroform, dichloromethane, pyridine. It swells in many other solvents, such as toluene. The melting range is within 218° to 265°C depending on the degree of crystallinity, e.g. the highly crystalline state has higher melting range temperature. The carbonate group contributes little to the intermolecular forces. This follows from the comparatively low melting point of aliphatic polycarbonates, as well as from the fact that reducing the percentage of  $\text{O}-\overset{\text{O}}{\underset{\text{||}}{\text{C}}}-\text{O}$  groups in the total polymer from 23.6% to 16.1% in comparable macromolecules raises the melting range temperature. In general thermal properties appear to be affected by the presence of aromatic rings and the degree of mobility of the macromolecule within the solid substance. Bulky substituents in the central atom of the bisphenol residue restrain the rotation of the phenyl groups with regard to the central atom, and thereby cause a further stiffening of the macromolecule, which adds to the inherent rigidity resulting from the close approximation of aromatic rings in the crystal. A review on preparation and properties of polycarbonates has been carried out by Schnell<sup>14</sup> and Christopher.<sup>55</sup>

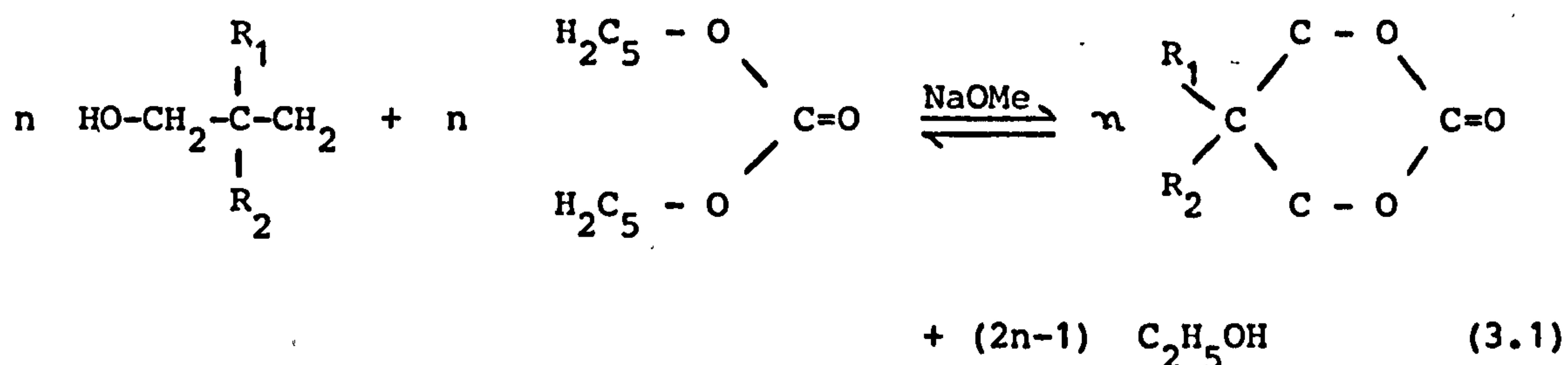
## 3.2 PREPARATION OF ALIPHATIC POLYCARBONATES

### 3.2.1 Preparation of Monomers

Trimethylene carbonate and neopentylene carbonate were prepared by the transesterification reaction of the corresponding diol and diethyl carbonate. The preparative method used was based on that of Carothers and coworkers<sup>2</sup> as modified by Sarel and Pohoryles.<sup>37</sup> The general



equation which describes the process is:



where

$\text{R}_1$  and  $\text{R}_2 = \text{H}$  (trimethylene carbonate)

$\text{R}_1$  and  $\text{R}_2 = \text{CH}_3$  (neopentylene carbonate)

The general procedure used was: a mixture of the starting material was placed in a three-necked round-bottomed flask which was fitted with a fractionating Vigreux column, a distillation head and condenser, a thermometer and a nitrogen inlet. Dry sodium methoxide (Aldrich) was added to the mixture as catalyst. The vessel was then gradually heated to 120°C by means of an oil bath and continuously stirred with a magnetic stirrer. Ethanol distilled off as by-product after a period of two hours; the rate of production fell and the pressure was gradually reduced to 20 mm Hg until distillation of ethanol and the reagent in excess was completed. The resulting oily residue was dissolved in benzene, washed with water, dried with anhydrous calcium chloride (Aldrich) and purified by distillation under reduced pressure (2-0.4 mm Hg). Initially, the monomer which distilled over was a thin colourless liquid, which completely crystallised in the receiver. After a while the distilling residue became more viscous and at this stage the distillation was stopped. The monomer was further purified by recrystallisation from diethyl ether and vacuum

sublimation. The amount of reactants and properties of the monomers are detailed in Table 3.1.

### 3.2.2 Preparation of Starting Material - 2-phenyl-1,3-propane diol

In the absence of the commercial product, 2-phenyl-1,3-propane diol was prepared by the selective reduction of carbonyl groups using lithium aluminium hydride as reducing agent. The methods of preparation reported by Adkins,<sup>56</sup> Searles<sup>57</sup> and Marshall<sup>58</sup> were slightly modified as follows: 10.8 g ( $4.5 \times 10^{-2}$  mole) of diethyl phenyl malonate (Aldrich) of 98% purity was slowly added to an ice-cooled, stirred suspension of 4.9 g lithium aluminium hydride in 150 ml of tetrahydrofuran under nitrogen atmosphere. After the resulting mixture had been stirred for one hour, the temperature was gradually increased up to 130°C (the original method used a reaction temperature of approximately 25°C) and continuously stirred for 18 hours. At the end of this period the mixture was cooled, and 100 ml of a 20% v/v of hydrochloric acid solution and 100 ml of water was slowly added. The  $\text{Al}(\text{OH})_3$  and  $\text{Li}(\text{OH})$  were dissolved. The resulting solution was extracted with 25 ml (3 portions) of diethyl ether. The combined ethereal extracts were washed with sodium carbonate solution (10% w/v) then with water and dried with magnesium sulphate. The solvent was removed by distillation and the pale yellow oily residue distilled at reduced pressure (0.5 mm Hg) at 119°-120°C, giving a colourless oily liquid which solidified as colourless needles with m.p. 48.5°-49°C. The yield was 50% after purification, microanalysis gave C = 71.20%, H = 8.04% in good agreement with the theoretical values C = 71.05%, H = 7.90% for  $\text{C}_9\text{H}_{13}\text{O}_2$ . The nmr spectrum



TABLE 3.1

Preparation and properties of trimethylene carbonate  
and neopentylene carbonate

(a) Trimethylene carbonate					(b) Neopentylene carbonate				
Reagents	g	mol	mol % alcohol		Reagents	g	mol	mol % alcohol	
(1) 1,3-propane-diol	15.2	0.2			(4) neopentylene-1,3- -propane diol	20	0.2		
(2) diethyl carbonate	2.6	0.22			diethyl carbonate	30	0.25		
(3) sodium methoxide	1.4	0.012	6		sodium methoxide	6.6	0.056	7	
Properties of monomer					Properties of monomer				
yield	bp	mp	solubility		yield	bp	mp	solubility	
%	°C	°C	W	Alc. Eth.	%	°C	°C	W	Alc. Eth.
80	-	49.8	+	+	-	-	107.5-108.5	+	+

(1) purified by distillation 110°C/15 mm Hg, Aldrich

(2) purity 99% used as supplied, Aldrich

(3) Aldrich

(4) purified by recrystallisation with benzene, Aldrich.

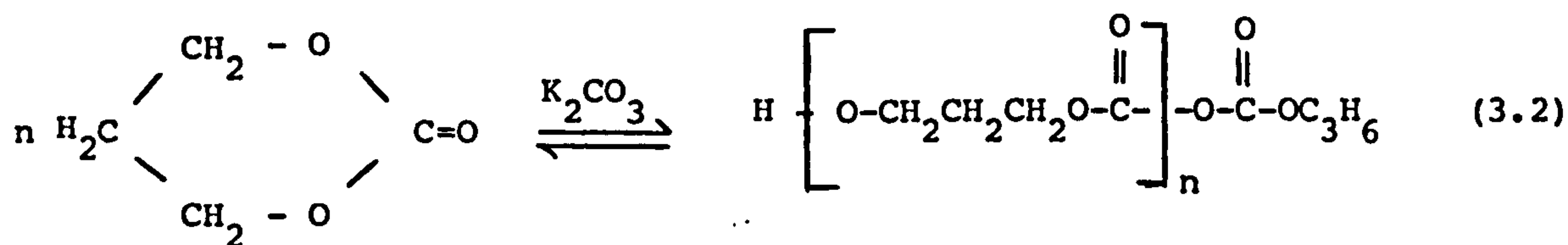
of the compound showed peaks at 7.27  $\delta$  (ppm) assigned to aromatic protons, a multiplet at 3.89  $\delta$  (ppm) assigned to the protons of the hydroxyl groups and a multiplet at 3.12  $\delta$  (ppm) assigned to  $-\text{CH}_2-$  groups. These values are in good agreement with those reported by Hiromichi Ohta et al.<sup>59</sup>

### 3.2.3 Preparation of Polymers

The method employed in the preparation of poly(trimethylene carbonate) and poly(neopentylene carbonate) was the ring opening reaction of the corresponding monomer.<sup>2,37</sup> Poly(2-phenyl-trimethylene carbonate) was prepared by the transesterification of the corresponding diol with diphenyl carbonate.

#### 3.2.3.1 Poly(Trimethylene Carbonate)

Poly(trimethylene carbonate) was prepared by the ring opening reaction of trimethylene carbonate



During this work, it was observed that monomer purified by recrystallisation can be polymerised by heating without the use of catalyst. On the other hand, it was found that polymerisation does not occur in the case of monomer purified by vacuum sublimation. Although the melting points and infrared spectra of both monomer samples were identical, the absence of polymerisation in the latter case may be due to the fact that adventitious impurities present in the monomer, which

can act as initiator, are removed by the further purification by sublimation. A variety of catalysts can be used in the polymerisation of trimethylene carbonate, e.g., sodium methoxide, potassium carbonate, zinc oxide, zinc acetate and a reaction temperature within the range 70° to 170°C. It was observed that potassium carbonate and zinc oxide produced a brown coloured polymer. This was purified by continuous extraction with methanol, which resulted in a colourless polymer. When zinc acetate was used no colouration was observed. The purified poly(trimethylene carbonate) was a colourless sticky resin which, after long standing (one week), solidified and became opaque (crystallisation). This solid (m.p. 47°C) was soluble in acetone, benzene and chloroform, and insoluble in methanol, water, diethyl ether and petroleum ether.

All polymerisations were carried out using a three-necked, round-bottomed flask which was fitted with a nitrogen inlet and a thermometer. The vessel was heated with an oil bath. In the polymerisation procedure, the monomer was gradually heated under nitrogen atmosphere and continuously stirred. When catalyst was used, this was added after the monomer melted. The resulting polymer was purified by dissolving in acetone, reprecipitated with methanol and dried under vacuum to constant weight. The thermal stability of the polymer was studied by thermogravimetry. The number-average molecular weight was determined by vapour pressure osmometry. Data are presented in Table 3.2.

The results suggest slightly lower stability for the lowest MW. samples, although more work in polymerisation under different conditions is necessary in order to establish the relationship between

TABLE 3.2

Thermal stability of poly(trimethylene carbonate)  
Polymers prepared under different reaction conditions

Polymerisation without catalyst				Polymerisation using catalyst $K_2CO_3$					
				150°C			100°C		
Reaction time h	Reaction temp °C	Temp. rate max.°C	$\bar{M}_n$	Reaction time h	% w/w	Temp. rate max.°C	Reaction time h	% w/w	Temp. rate max.°C
15	100	277	3354	12	0.1	288	6	0.13	275
19	135	250	2100	7	0.05	288	6	1.03	265
6.5	150	275	3500	6	0.14	280	6	1.5	290
7.0	160	255	ND	6	0.16	290	6	2.0	270
-	-	-	-	6	0.95	275	-	-	-
-	-	-	-	6	1.97	270	-	-	-

ND - Not Determined



molecular weight of the polymer and the thermal stability, with temperature and amount of catalyst.

#### 3.2.3.2 Poly(neopentylene carbonate)

It was observed during this work that neopentylene carbonate does not undergo polymerisation without a catalyst. Polymerisations were carried out over a range of temperatures of 120° to 165°C, using anhydrous potassium carbonate as catalyst. The temperature of the reaction was gradually increased from ambient to a maximum of 165°C. The resulting product was a brown viscous melt, from which fibres can be drawn and which solidified as a cream coloured glassy substance. This was soluble in chloroform and benzene. It was purified by continuous extraction with methanol which gave a microcrystalline solid. Polymerisations at different temperatures and at different concentrations of catalyst were carried out and the thermal stability of the different polymers obtained were assessed by thermogravimetry. The number-average molecular weights of some of the polymers were obtained by vapour pressure osmometry.

The variation of the thermal stability of poly(neopentylene carbonate) with temperature of reaction and percentage of catalyst used is indicated in Table 3.3.

The results show some variation of stability for the different samples. There is a variation in the rate maximum over a range from 272° to 331°C, but in general no clear relationships to temperature or catalyst concentration is apparent.



TABLE 3.3

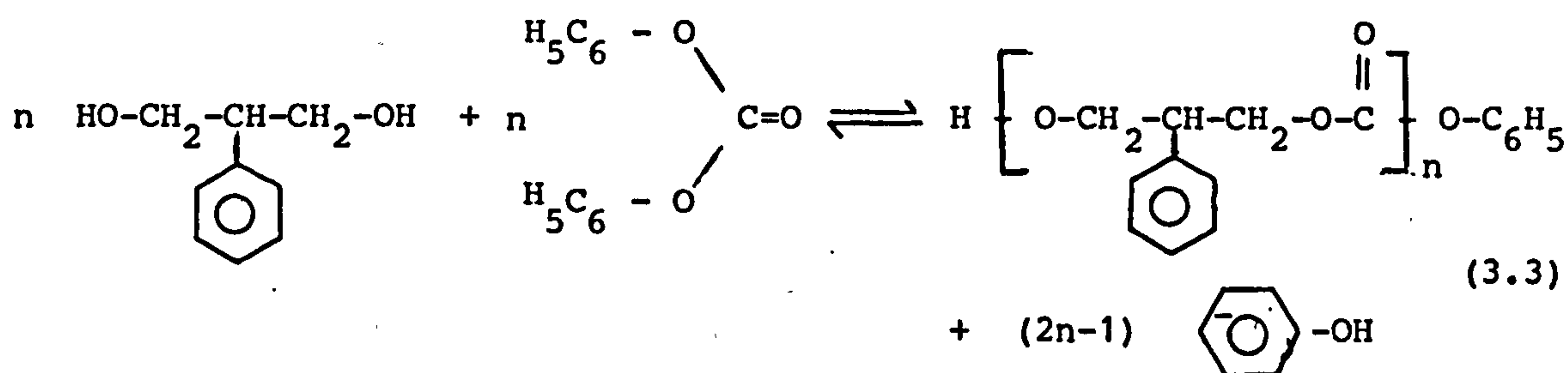
Thermal stability of poly(neopentylene carbonate)  
Polymers prepared under different reaction conditions

Reaction Temperatures									
150°C					165°C				
Reaction time h	Catalyst % w/w	Temp. rate max °C	$\bar{M}_n$		Reaction time h	Catalyst % w/w	Temp. rate max °C	$\bar{M}_n$	
10	0.30	330	ND		6	0.06	302	3445	20
10	0.72	297	ND		6	0.10	313	ND	-
10	0.96	272	ND		-	-	-	-	-
10	1.88	310	ND		-	-	-	-	-
20	1.30	317	3945		-	-	-	-	-
48	0.05	331	4332		-	-	-	-	-

ND - Not Determined

### 3.2.3.3 Poly(2-phenyl-trimethylene carbonate)

No specific method of preparation for this polymer has been reported. The method employed was the transesterification reaction of 2-phenyl-1,3-propane diol with diphenyl carbonate in the presence of potassium carbonate as catalyst. The chemical equation which describes the reaction is:



In the present work it was observed that the transesterification reaction proceeds without the use of catalyst. This behaviour may be due to the presence of impurities which act as catalyst in the reaction. The use of diethyl carbonate was impracticable since the reaction rate was too slow. When diphenyl carbonate was used the phenol which is formed as by-product was distilled off under reduced pressure (20 mm Hg). During the reaction, the diol which is volatile also tends to distil. This leads to the continuous decrease of diol in the mixture, which as a result decreases the yield of the reaction. On the other hand, the presence of phenol in the reaction medium inhibits the polymerisation reaction which probably explains the low molecular weight obtained. The product was a brown viscous liquid from which fibres could be drawn. It was purified by dissolution in acetone and precipitated with methanol giving a white sticky resin which solidified as colourless glassy material.

This was soluble in acetone, benzene, toluene and chloroform, but insoluble in methanol, diethyl ether and water. The number-average molecular weight was determined by vapour pressure osmometry,  $\bar{M}_n = 3500$ , and the thermal stability determined by thermogravimetry.

The reagents employed and conditions of polymerisation are detailed in Table 3.4.

### 3.3 CHARACTERISATION OF MONOMERS AND ALIPHATIC POLYCARBONATES

#### 3.3.1 Trimethylene Carbonate

a. The elemental analysis for trimethylene carbonate gave the following results: C = 46.9%, H = 5.30% and O = 47.8%. These are in good agreement with the theoretical values for the molecular formula  $C_4H_6O_3$ : C = 47.06%, H = 5.92% and O = 46.02%.

b. The infrared spectrum of a thin film is shown in fig. 3.1. Various overlapping bands can be seen at 3008, 2980, 2955 and 2920  $\text{cm}^{-1}$ , assigned to the stretching of  $-\text{CH}_2-$  groups which appear at higher frequency for 6-membered cyclic structures, the band at 1745  $\text{cm}^{-1}$  corresponds to the carbonyl group stretching vibration. The group of strong bands in the region 1250 to 1120  $\text{cm}^{-1}$  can be assigned to the C-O-C bond stretching absorption and carbonyl group in the carbonate group  $\text{O}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{O}$ . The two extensively overlapped bands at 780 and 765  $\text{cm}^{-1}$  are assigned to bending vibration of the carbonate and the band at 680  $\text{cm}^{-1}$  is assigned to the out-of-plane carbonate group vibration.

TABLE 3.4

Poly(2-phenyl-trimethylene carbonate)  
preparation conditions and properties

Starting material		Polymerisation conditions			Properties			
	mass (g)	mole	% w/w	Reaction time h	Reaction temp °C	Yield %	mp °C	Solubility
								bz CHCl <sub>3</sub> CH <sub>3</sub> OH H <sub>2</sub> O
(1) 2-phenyl propane glycol	8.78	0.058	-	18	165	35	~45	+ + - -
(2) diphenyl carbonate	13.7	0.0638	10% excess	8.0	150	45	~45	+ + - -
(3) K <sub>2</sub> CO <sub>3</sub>	0.44		0.5					

- (1) purified by distillation - mp = 49.8°C, Aldrich
- (2) recrystallised with ethanol - mp = 78°C, Aldrich
- (3) Analar, anhydrous, Aldrich



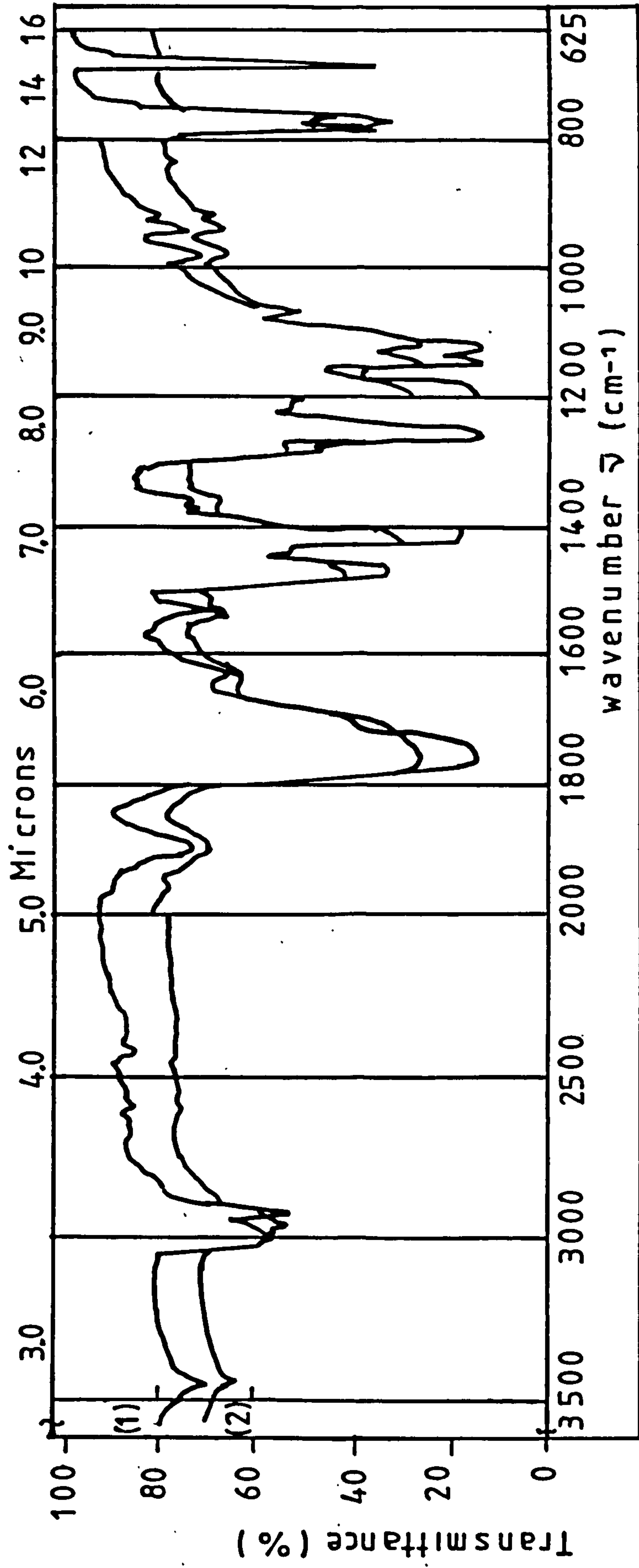


Fig. 3.1 Infrared spectrum from (3500 - 625 cm<sup>-1</sup>) for trimethylene carbonate crystals neat (1) purified vacuum distillation and recrystallisation (2) purified by vacuum distillation and sublimation.

c. The nmr spectrum (fig. 3.2) of trimethylene carbonate presents a multiplet at 1.90, 1.96, 2.02, 2.07 and 2.13  $\delta$  (ppm) which is due to the coupling protons on the  $C_3$ , and a triplet at 4.26, 4.32 and 4.38  $\delta$  (ppm) arising from the coupling of the protons of the equivalent methylene groups ( $C_2$  and  $C_4$ ) on the ring. No reference spectrum was found in the literature.

d. The mass spectrum presents a molecular ion peak at  $m/e$  102, which corresponds to the molecular weight of the trimethylene carbonate.

### 3.3.2 Poly(trimethylene carbonate)

a. The elemental analysis for poly(trimethylene carbonate) gave: C = 47.25%, H = 5.43% and O = 47.23%. These results agree well with the calculated values for  $(C_3H_6O_3)_n$ : C = 47.05%, H = 5.88% and O = 47.07%. The small discrepancies between the two sets of values may be due to the presence of chain ends, which were not taken into account when the theoretical values were calculated.

b. The infrared spectrum of a thin film of poly(trimethylene carbonate) is illustrated in fig. 3.3. This spectrum shows two extensively overlapped bands at  $2970\text{ cm}^{-1}$  and  $2900\text{ cm}^{-1}$ , attributed to  $-CH_2-$  group stretching vibration. The strong band at  $1745\text{ cm}^{-1}$  is assigned to the carbonyl group stretching vibration. The strong and broad band in the region  $1280 - 1220\text{ cm}^{-1}$  arising from overlapping of several vibrations may be attributed to the absorption of  $-C-O-C-$  links and carbonyl group in the carbonate group linkage. The strong and sharp band at  $785\text{ cm}^{-1}$  may be attributed to the carbonate group out-of-plane vibration.

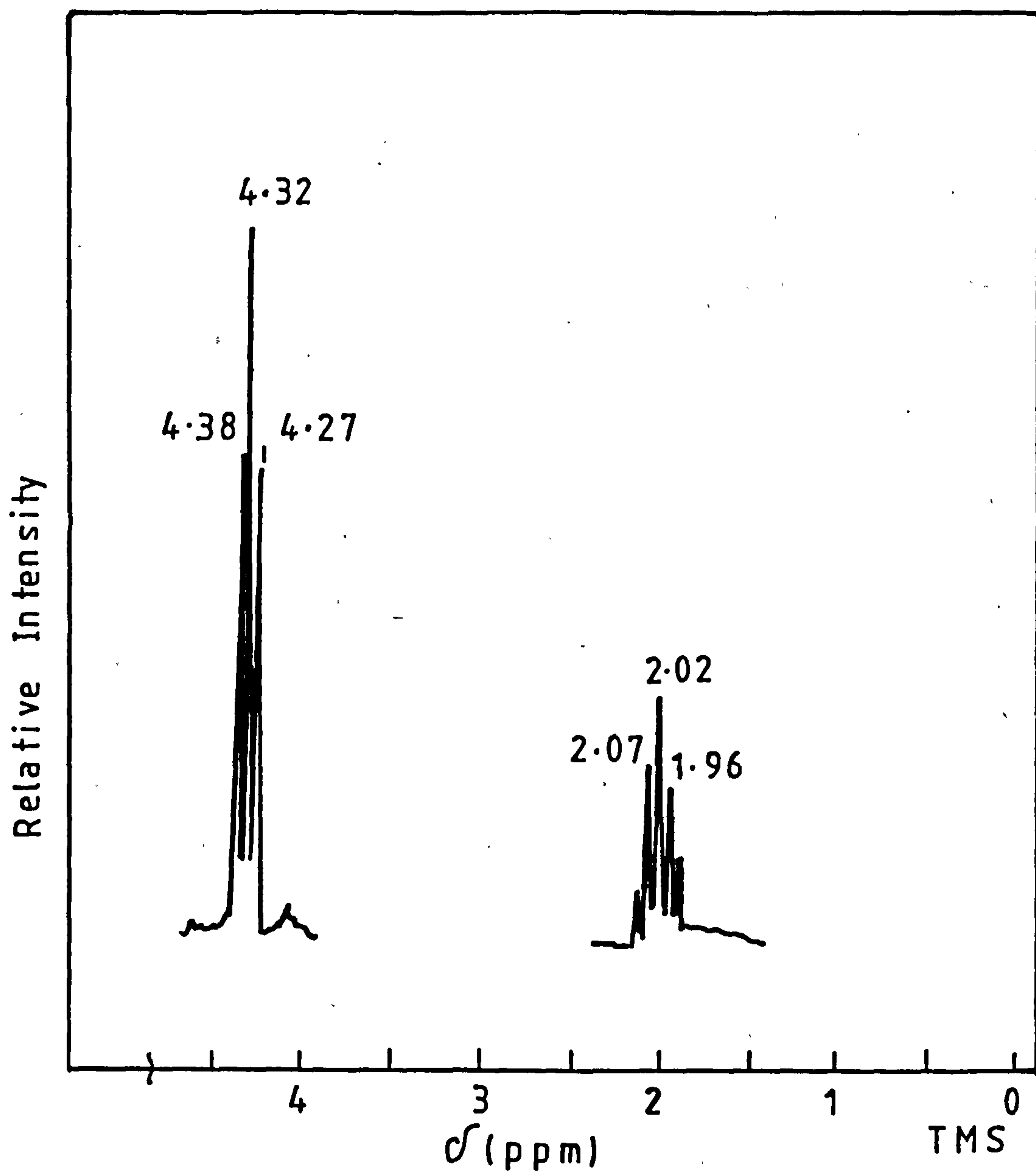


Fig. 3.2 n.m.r. spectrum for trimethylene carbonate,  $\text{CDCl}_3$ , temp. ambient  $^{\circ}\text{C}$

c. The nmr spectrum is shown in fig. 3.4. It shows a multiplet with peaks at 1.91, 1.98, 2.05, 2.11, 2.18  $\delta$  (ppm) corresponding to the resonance of the protons on the methylene groups on carbon 2 and a triplet at 4.18, 4.24 and 4.30  $\delta$  (ppm) arising from the protons on the methylene groups linked to the carbonate group.

### 3.3.3 Neopentylene Carbonate

a. The elemental analysis of neopentylene carbonate gave the following results: C = 55.32%, H = 7.69% and O = 36.99%. These results are comparable with the theoretical values for the molecular formula  $C_5H_{10}O_3$ : C = 55.39%, H = 7.69% and O = 36.92%.

b. The infrared spectrum is shown in fig. 3.5. The band assignments are: 2970 and 2880  $cm^{-1}$  due to the C-H stretching vibration in methyl groups; 2940 and 2918  $cm^{-1}$  due to C-H stretching vibration in methylene groups; 1761  $cm^{-1}$  due to C=O stretching vibration of the carbonyl group in the six-membered ring; 1195 and 1122  $cm^{-1}$  corresponding to C-O stretching in the carbonate linkage for six-membered ring. This spectrum agrees well with that reported by Sarel and Pohoryles.<sup>37</sup>

c. The nmr spectrum of neopentylene carbonate is shown in fig. 3.6. This presents a singlet at 4.13  $\delta$  (ppm) arising from the resonance of the protons of the methylene groups on the ring and another singlet at 1.05  $\delta$  (ppm) arising from the methyl group on the carbon 3 on the ring. Katzhendler et al.<sup>60</sup> reported a singlet at 4.10  $\delta$  (ppm) and a singlet at 1.10  $\delta$  (ppm).

d. A molecular ion peak at m/e 130 corresponding with the molecular weight of the monomer is present in the mass spectrum.



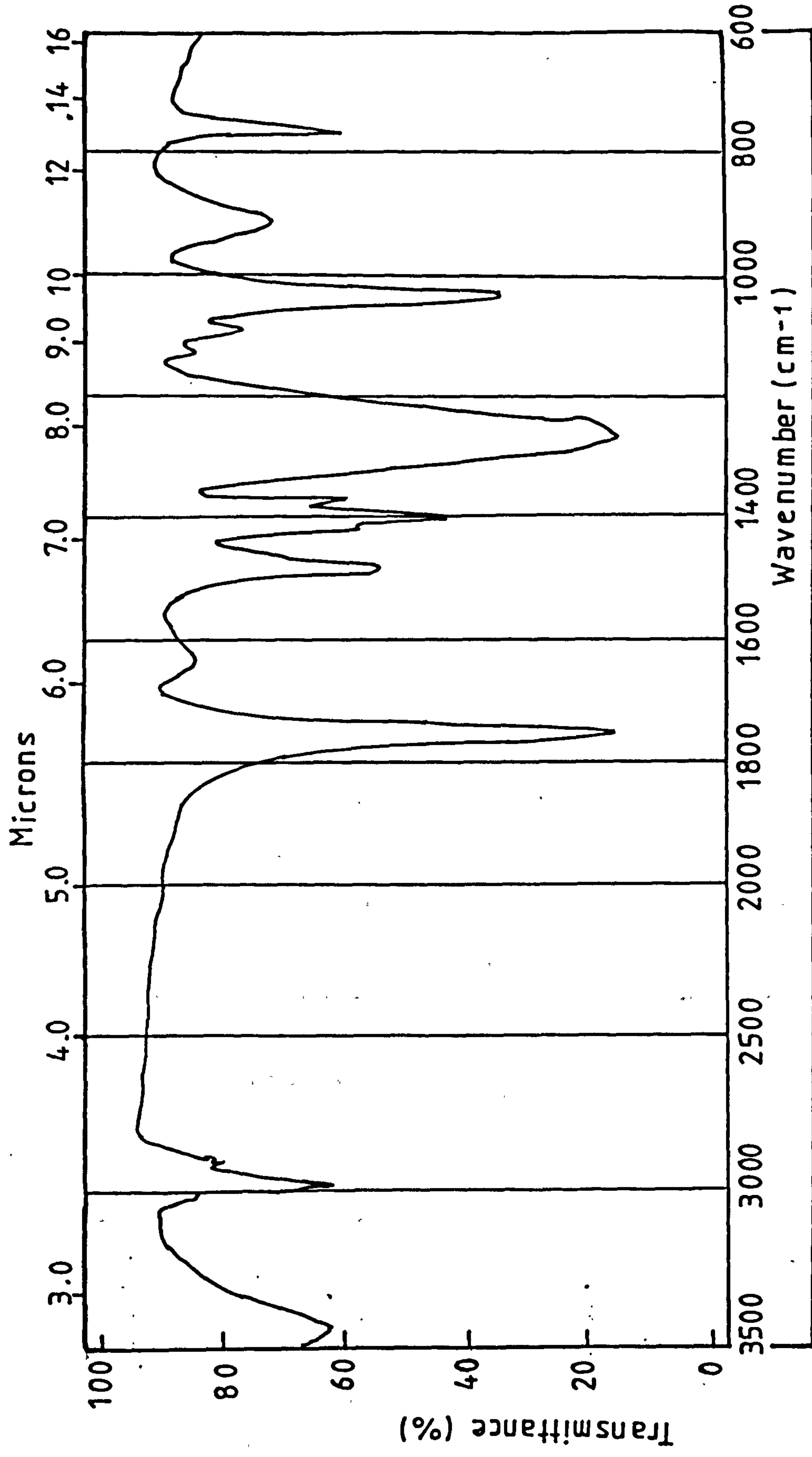


Fig. 3.3 Infrared spectrum from 3500 - 600 cm<sup>-1</sup> for poly(trimethylene carbonate) film

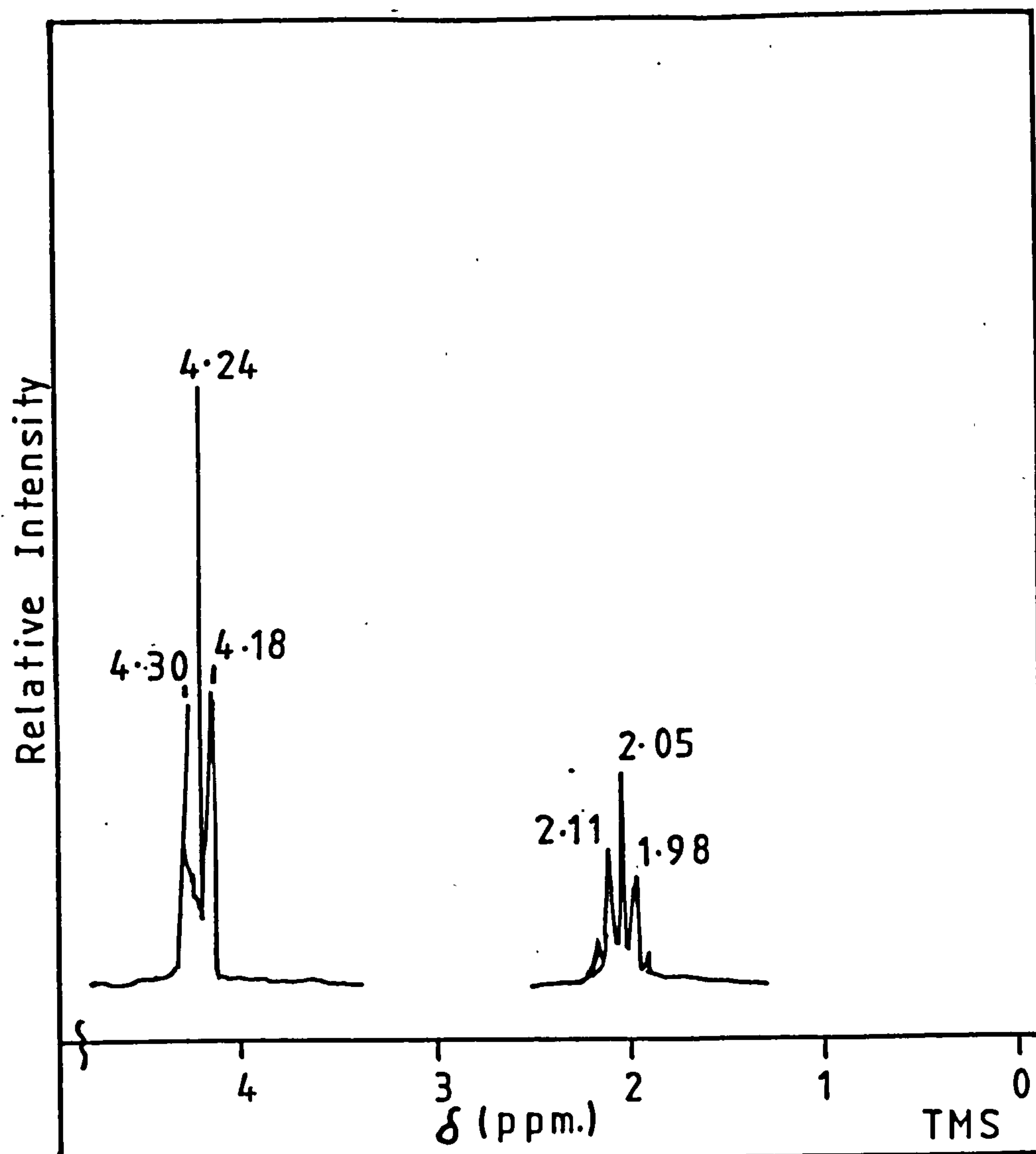


Fig. 3.4 n.m. r. spectrum for poly(trimethylene carbonate),  $\text{CDCl}_3$ , temp. ambient  $^{\circ}\text{C}$

### 3.3.4 Poly(neopentylene carbonate)

a. Poly(neopentylene carbonate) gave an elemental composition: C = 55.46%, H = 7.87% and O = 36.67% which agrees well with the theoretical values for  $(C_6H_{10}O_3)_n$ : C = 55.3%, H = 7.7% and O = 37.0%. Sarel and Pohoryles<sup>37</sup> had reported the values C = 55.4% and H = 7.7% for a similar polymer.

b. The infrared spectrum is shown in fig. 3.7. It shows a band at  $2970\text{ cm}^{-1}$  attributed to C-H stretching vibration of methyl groups and extensively overlapped bands at 2940, 2900 and  $2968\text{ cm}^{-1}$  assigned to the C-H stretching vibration of methyl and methylene groups. The strong band at  $1740\text{ cm}^{-1}$  corresponds to the C=O stretching vibration in carbonyl groups. The strong band in the region  $1308\text{--}1230\text{ cm}^{-1}$  arising from the overlapping of various absorptions is attributed to the stretching vibration of C-O-C and C=O group on the carbonate group. The band at  $968\text{ cm}^{-1}$  is also attributed to the stretching vibration of carbonate groups. The band at  $790\text{ cm}^{-1}$  could be attributed to the out-of-plane vibration of carbonate group.

The nmr spectrum is shown in fig. 3.8. It shows a singlet at  $3.96\delta$  (ppm) arising from the protons at the methylene groups and a singlet at  $1.00\delta$  (ppm) which corresponds to the protons of the methyl group on the carbon 3.

### 3.3.5 Poly(2-phenyl-trimethylene carbonate)

a. Microanalysis gave: C = 66.44%, H = 5.65% and O = 27.9% in good agreement with the calculated values for the structural formula  $(C_{10}H_{10}O_3)_n$  C = 67.42%, H = 5.62% and O = 26.96%.

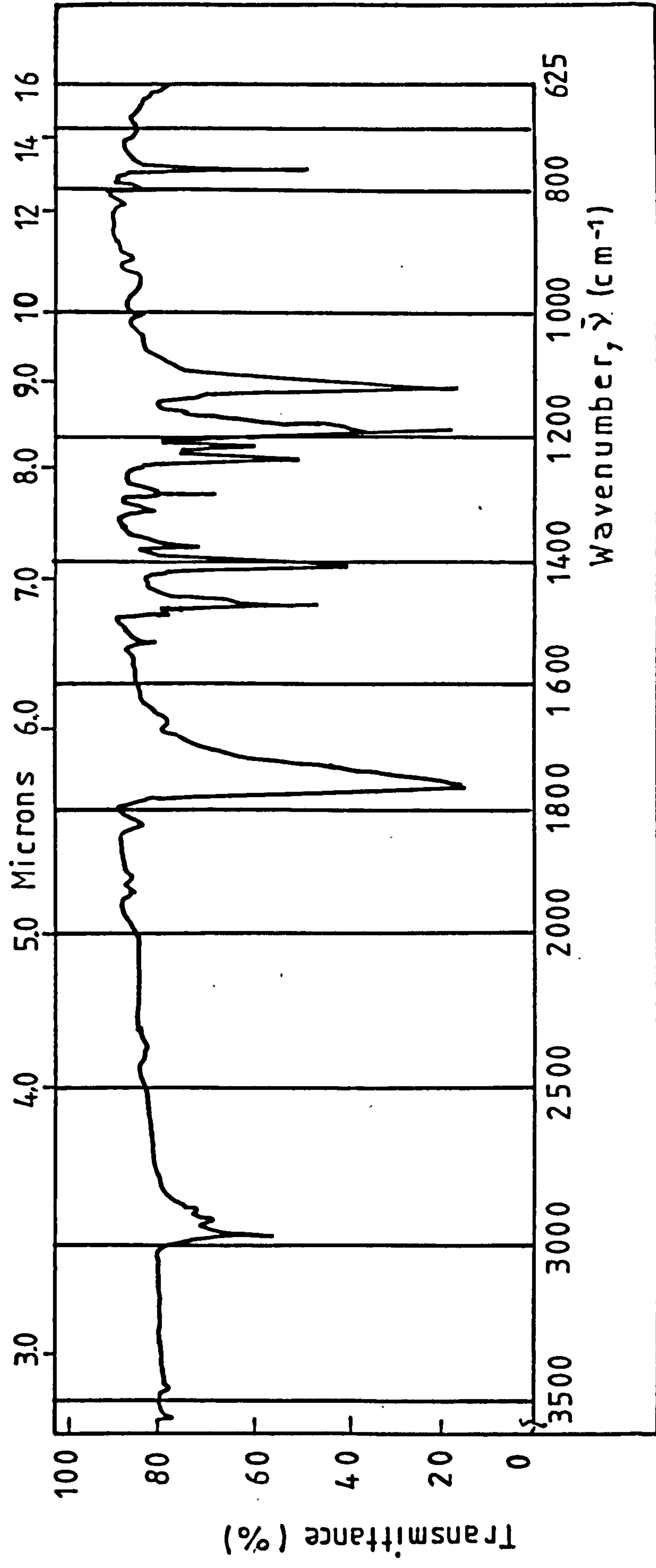


Fig 3.5 Infrared spectrum from 3500 - 625 cm<sup>-1</sup> for neopentylene carbonate; (crystals), purified by recrystallisation, neat.



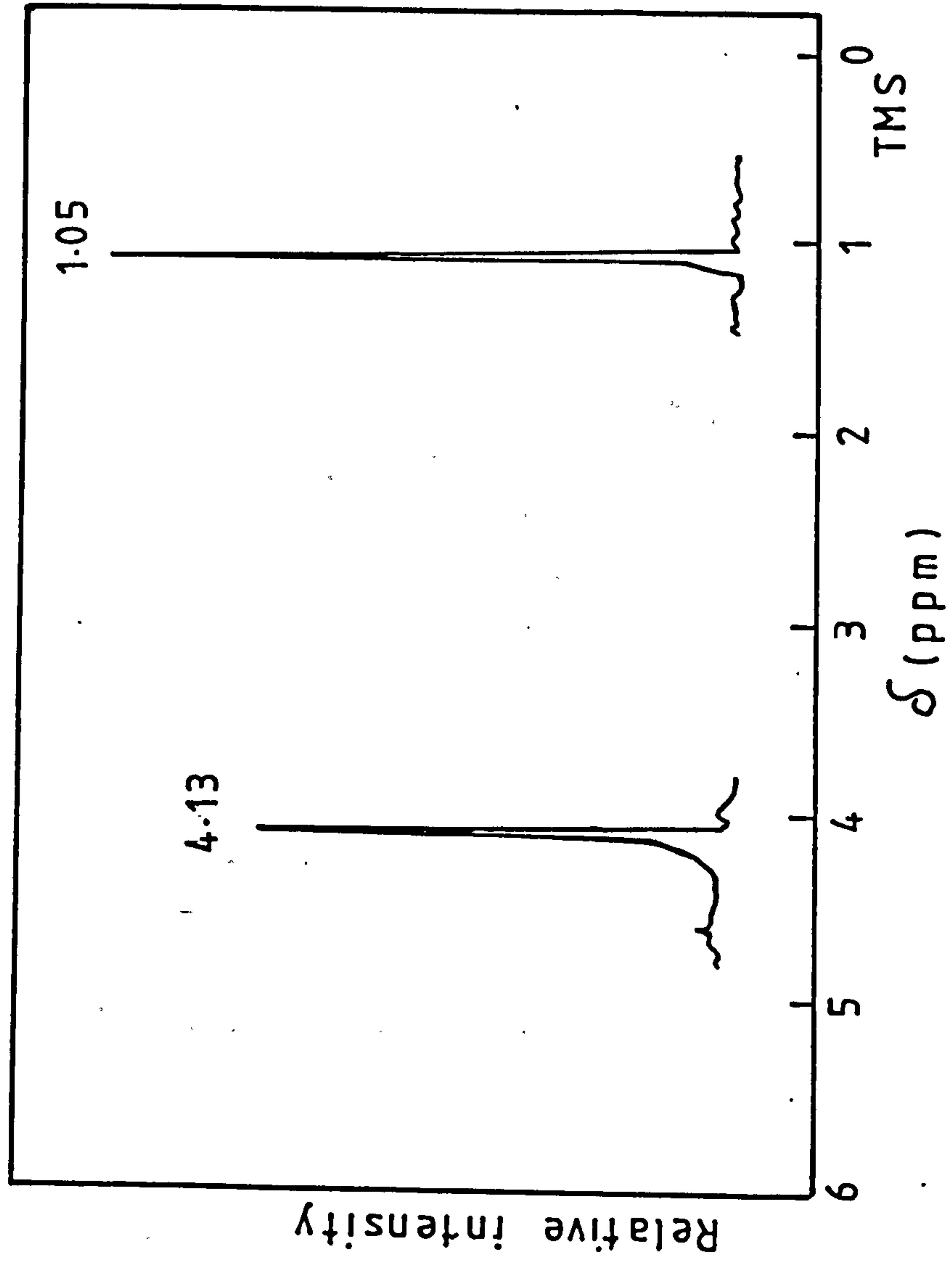


Fig.3.6. nmr spectrum for neopentylene carbonate

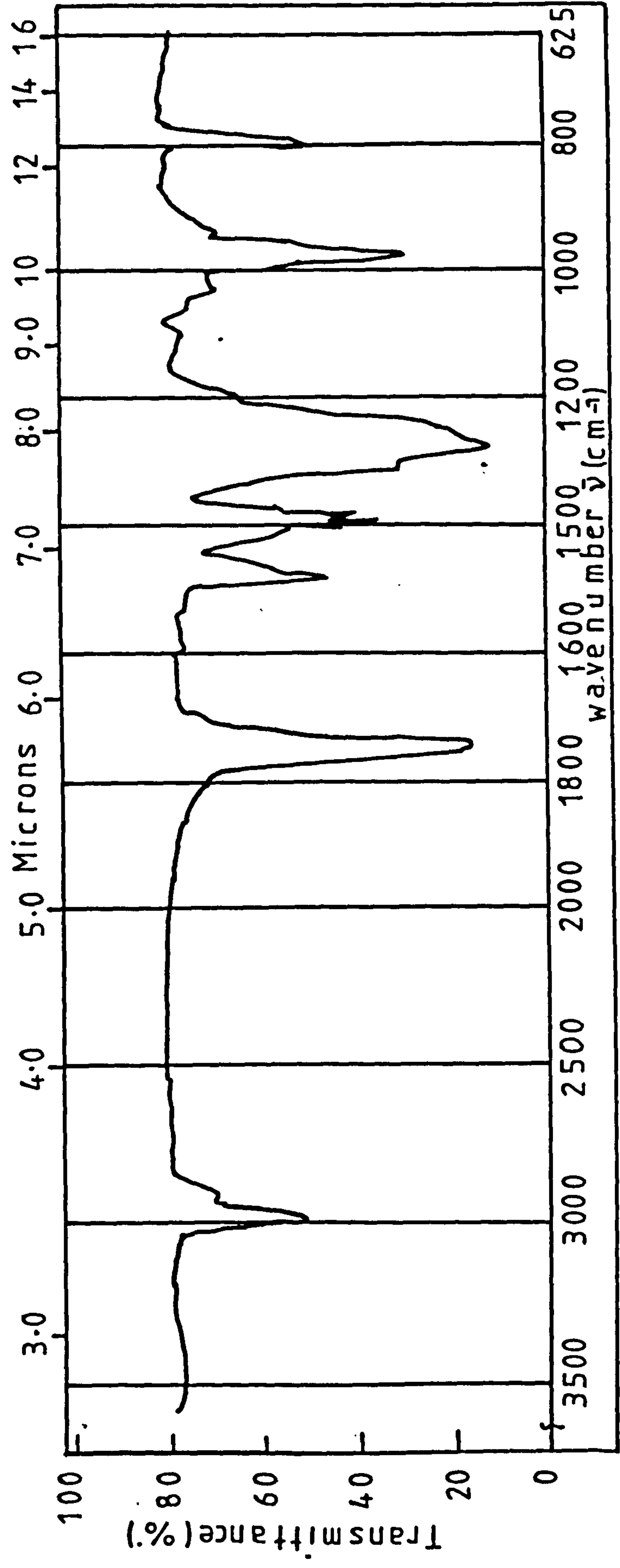


Fig.3.7 Infrared spectrum ( $3700 - 625\text{cm}^{-1}$ ) for poly (neopentylene carbonate)  
K(Br disc)

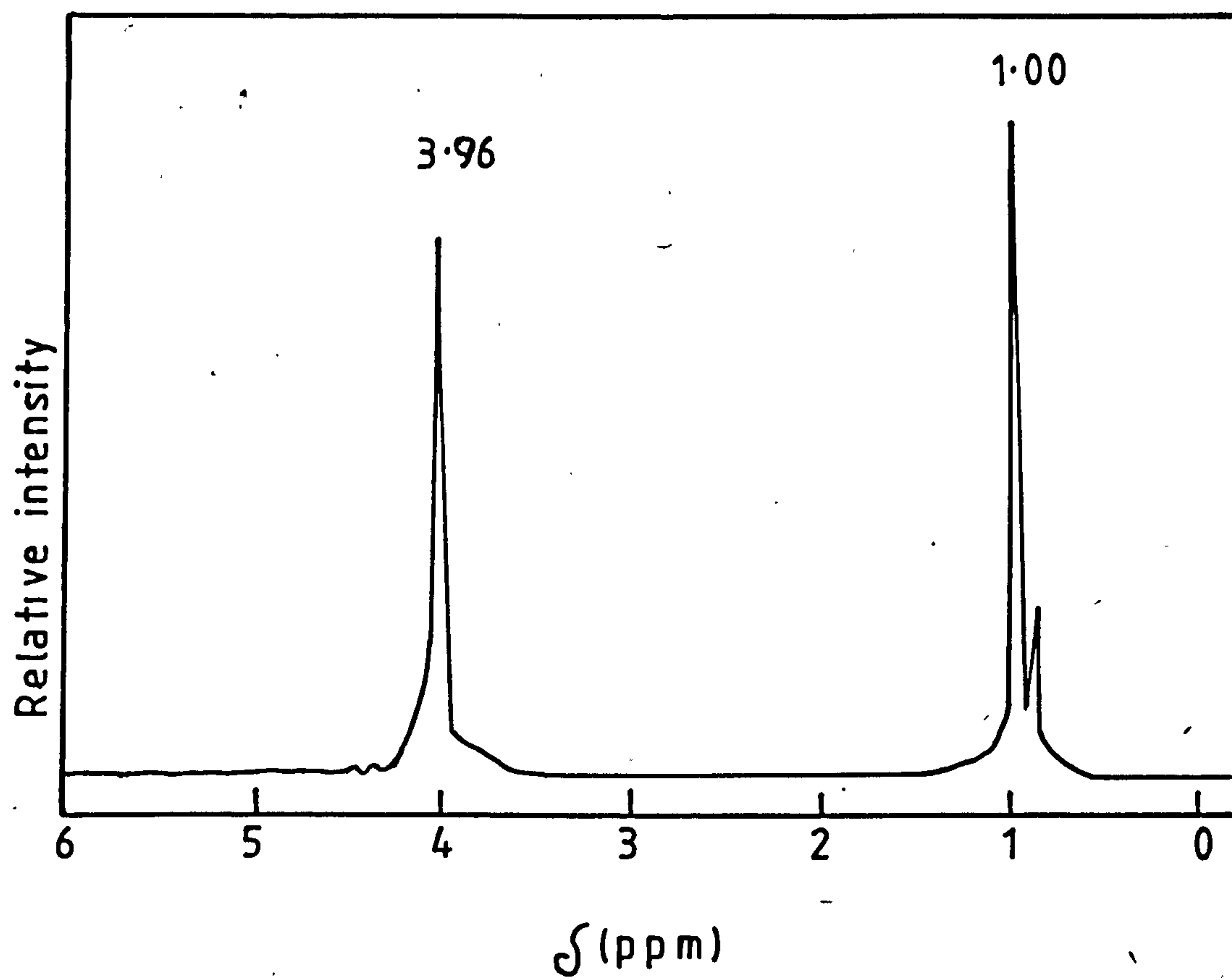


Fig. 3.8. nmr spectrum for poly(neopentylene carbonate)

b. The infrared spectrum (fig. 3.9) shows bands at 3080 and 3040  $\text{cm}^{-1}$  corresponding to the stretching of C-H in the aromatic ring. The bands at 2980 and 2810  $\text{cm}^{-1}$  correspond to the C-H stretching vibration of  $\text{CH}_2$  groups. A sharp, strong band at 1747  $\text{cm}^{-1}$  attributed to C=O stretching vibration. Extensively overlapped bands in the region 1270-1245  $\text{cm}^{-1}$  are assigned to stretching of the C-O-C linkage. Several extensively overlapped bands in the region 1090-1030  $\text{cm}^{-1}$  are assigned to the C-O-C and C=O stretching bands of the carbonate linkage. A sharp band at 760  $\text{cm}^{-1}$  is attributed to aromatic ring out-of-plane vibration. The strong, sharp band at 700  $\text{cm}^{-1}$  is attributed to carbonate group out-of-plane vibration.

c. The nmr spectrum (fig. 3.10) showed a poorly resolved multiplet at 7.36, 7.32, 7.29, 7.27 and 7.14  $\delta$  (ppm) which corresponds to the coupling of the protons on the aromatic ring. A doublet at 4.54 and 4.46  $\delta$  (ppm) assigned to the protons of the methylene groups neighbouring to the carbonate links and a multiplet centred on 3.42  $\delta$  (ppm) corresponding to the proton on carbon 2 linked to the aromatic ring.

### 3.4 PREPARATION OF ALIPHATIC-AROMATIC POLYCARBONATES

#### 3.4.1 Poly(p-xylylene carbonate)

In the present study, the method employed was the transesterification reaction of p-xylylene diol with diphenyl carbonate in the presence of potassium carbonate as catalyst. This method of ester interchange<sup>61</sup> is the most practical approach to the aliphatic-aromatic polycarbonates formation because of the faster reaction rate and ease of purification of the product. The chemical equation which describes the process is:



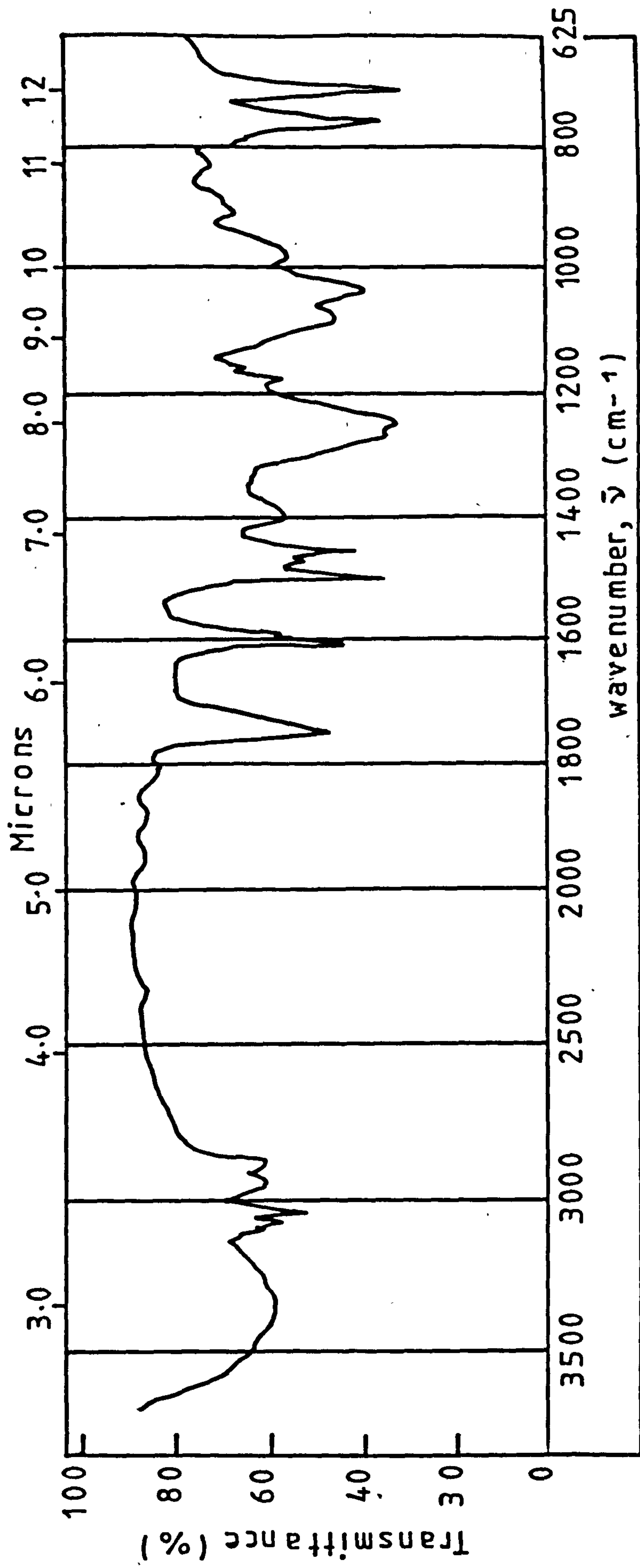


Fig. 3.9 Infrared spectrum (3700 - 625 cm<sup>-1</sup>) for poly(2-phenyl-trimethylene carbonate); neat; purified by precipitation.

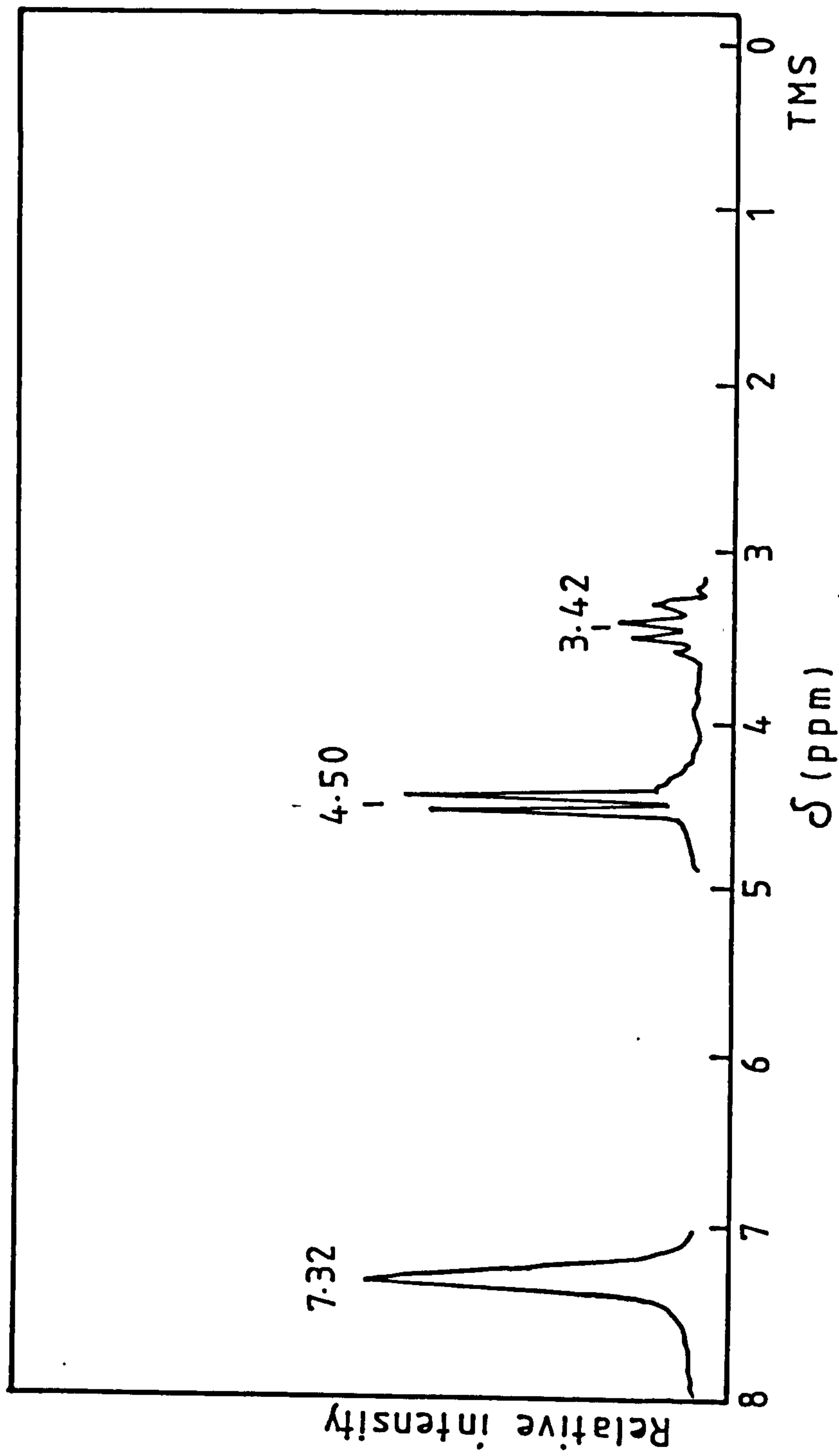


Fig. 3.10. nmr spectrum for poly(2- phenyl- trimethylene carbonate)







TABLE 3.5. Poly(p-xylylene carbonate).

Polymer A								
Reaction conditions								
Reagent	mass g	mole	catalyst %	yield %	Reaction temp °C	Reaction time h		
(1) p-xylylene diol	27.6	0.2	-	70	120	20		
(2) Diphenyl carbonate	47.2	0.22	-					
(3) Potassium carbonate	0.15	-	0.48					
Properties								
Colour	mp °C	temp rate max °C	Solubility					
White	<250	250	<u>CHCl<sub>3</sub></u> cold hot		<u>DMF</u> cold hot		<u>DMSO</u> cold hot	
		287	- -	- +	- +			

- (1) Purification by reprecipitation with ethanol/toluene,  
m.p. 114-115°C, Aldrich.
- (2) Purification by reprecipitation with ethanol,  
m.p. 78°C, Aldrich.

Preparation under different reaction conditions and properties

Polymer B								
Reaction conditions								
Reagent	mass g	mole	catalyst %	yield %	Reaction temp °C	Reaction time h		
(1) p-xylylene diol	27.8	0.2	-	65	150-260	8		
(2) Diphenyl carbonate	47.3	0.22	-					
(3) Potassium carbonate	0.16	-	0.49					
Properties								
Colour	mp °C	temp rate max °C	Solubility					
Yellow	-	347	<u>CHCl<sub>3</sub></u> cold hot		<u>DMF</u> cold hot		<u>DMSO</u> cold hot	
			-	-	-	+	-	+

(3) Analar, anhydrous, Aldrich.

### 3.4.2 Characterisation of poly(p-xylylene carbonate)

a. Microanalysis of poly(p-xylylene carbonate) for Polymer A gave: C = 67.04%, H = 4.88% and O = 28.19%. For Polymer B: C = 68.29%, H = 5.32% and O = 26.39%. The theoretical values for the molecular formula  $(C_9H_8O_3)_n$  are: C = 65.85%, H = 4.88% and O = 29.27%. Polymer A approximates to the theoretical composition; the small differences may be explained by the fact that the theoretical values take no account of end structures. Polymer B shows a larger deviation, which may be due to structural differences.

b. The infrared spectra for both polymers are shown in fig. 3.11. Absorptions due to the carbonate group occur at  $1745\text{ cm}^{-1}$  and in the region  $1280\text{--}1230\text{ cm}^{-1}$ . Slight differences in the spectra are evident, including for Polymer B, a broadening of the bands appearing in the region at  $3060\text{--}2815\text{ cm}^{-1}$  and the presence of two additional bands at  $1080$  and  $820\text{ cm}^{-1}$ . These features may be attributable to the presence of p-xylylene ether groups along with p-xylylene carbonate groups in the backbone of the polymer. These ether structures are most likely formed during the polymerisation process when active carbonate groups react with evolution of carbon dioxide due to the higher temperature of the reaction. This could also explain the foam-like texture of the polymer.

c. No nmr spectrum was obtained because of the insolubility of the polymer in the common solvents used in nmr spectroscopy.

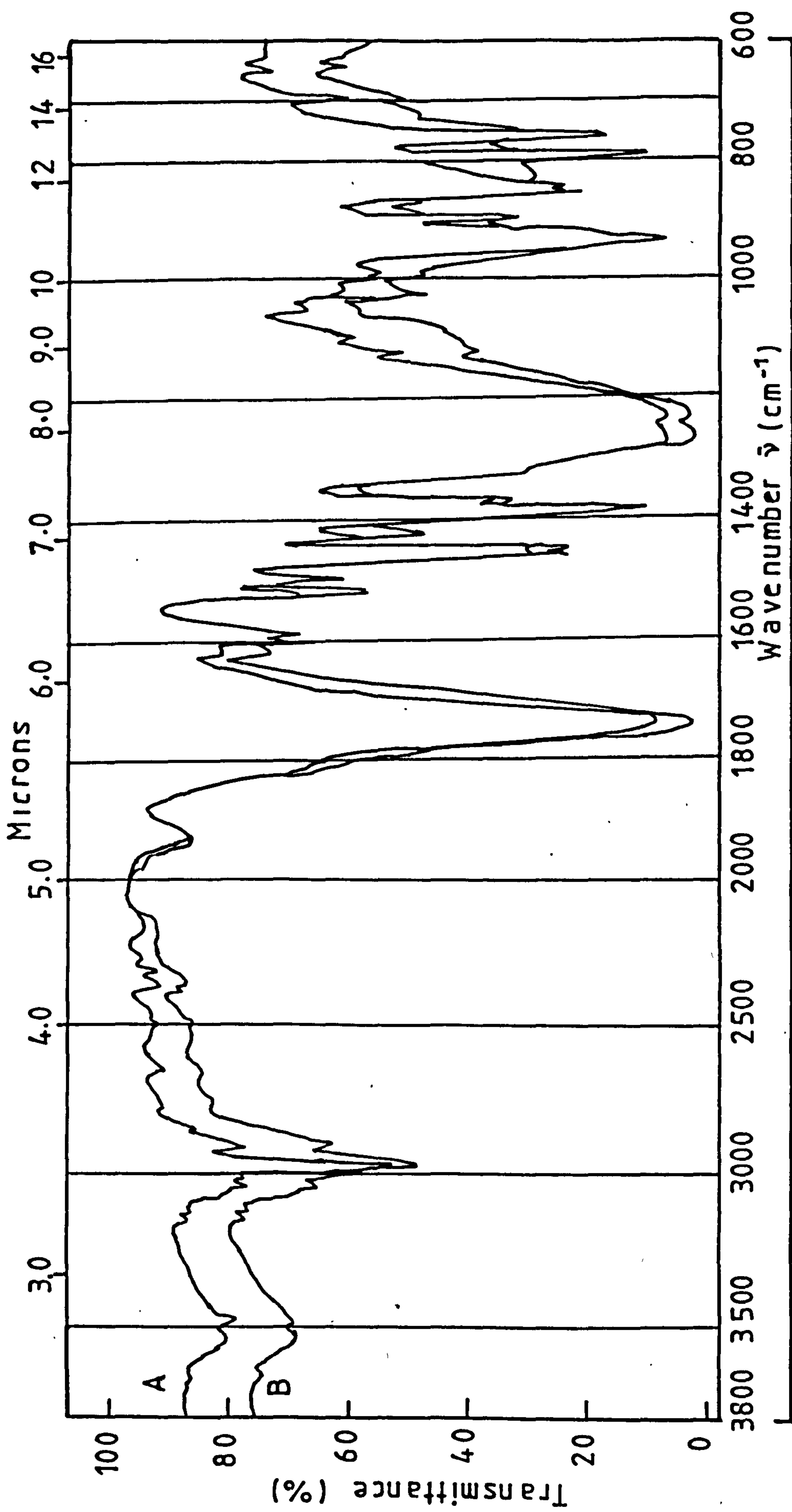
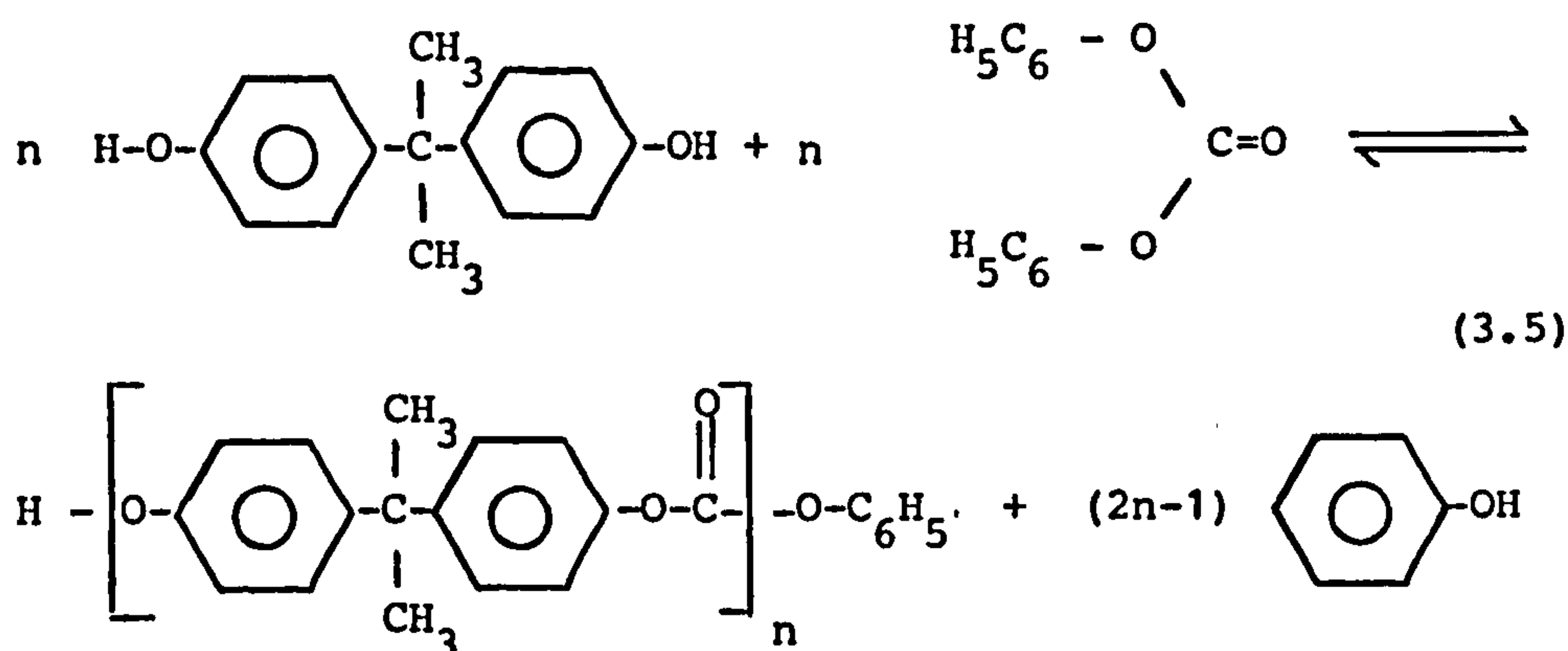


Fig. 3.11 Infrared spectrum (3800–600 cm<sup>-1</sup>) for poly (p-xylylene carbonate)  
A sample and B (K Br disc)

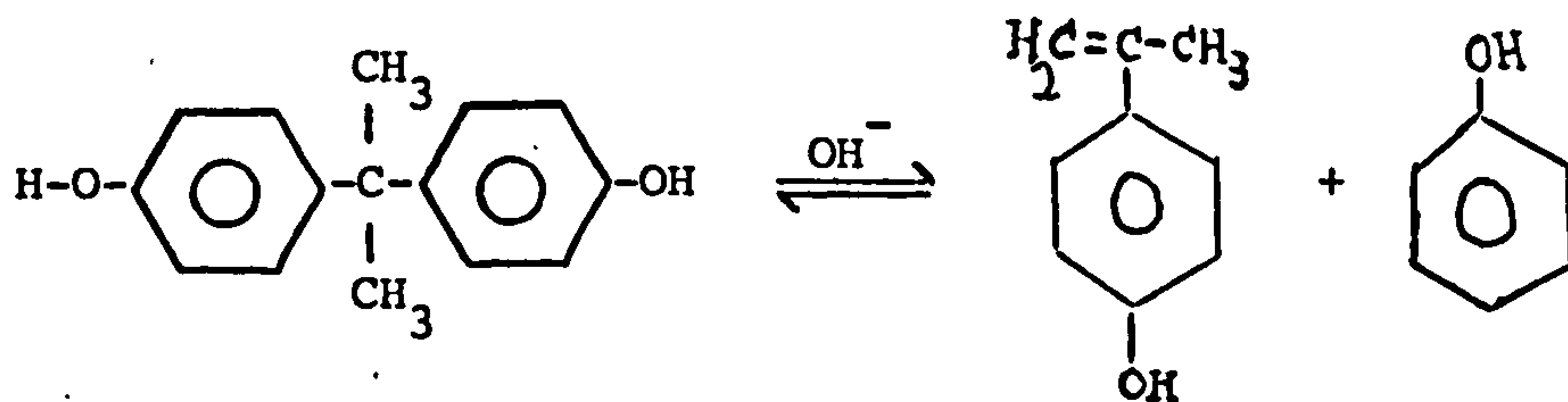


### 3.5 PREPARATION OF AROMATIC POLYCARBONATES BY TRANSESTERIFICATION: Bisphenol A polycarbonate

The preparation of aromatic polycarbonates by means of the transesterification process is a quantitative reaction which utilises equimolar quantities of reagents as follows:



The polycondensation is an equilibrium reaction. To obtain high yields and a high molecular weight almost complete removal of the by-product from the reaction mixture is required. In the absence of catalyst, reaction of phenols with diphenyl carbonate proceed slowly for temperatures up to 280°C. The transesterification is only slightly accelerated by acid catalyst and it is accelerated markedly by basic catalyst as potassium carbonate. It has been established<sup>62</sup> that 4,4'-dihydroxy-diphenyl alkanes, i.e., bisphenol-A, decompose into isopropenyl phenol and phenol in the presence of alkaline substances and at temperatures over 150°C. These unsaturated phenols undergo



polymerisation and addition reactions before they can be removed from the reaction mixture by distillation. Polymers or addition products of these phenols result in undesirable coloured products. In order to avoid this problem in the preparation of polycarbonates, it is necessary to carry out the transesterification with a slight excess of diphenyl carbonate rather than an equimolar quantity. It is possible to prepare, at temperatures between 150° and 200°C, low molecular weight polycarbonates terminated with phenyl carbonate end groups. At higher temperatures and greatly reduced pressures these low molecular weight polymers can undergo polycondensation converting to high molecular weight polycarbonates with the elimination of diphenyl carbonate. This second stage of the reaction of transesterification takes place only at temperatures over 250°C and is not accelerated as much by catalyst as the transesterification reaction, giving off phenol as by-product.

The reaction was performed in a three-necked round-bottomed flask, which was fitted with a distillation head, a condenser, a thermometer and a nitrogen inlet. A mixture of bisphenol-A (5 g) and diphenyl carbonate (5.2g) with potassium carbonate (0.02 g) (0.4% w/w) as catalyst, was added. The vessel was then gradually heated to 150°C by means of an oil bath and continuously stirred with a magnetic stirrer. The pressure was reduced to ~ 20 mm Hg by means of a water pump. Phenol was eliminated and after a period of three hours, the rate of phenol production fell. The temperature was then gradually increased over a period of six hours to 280°C until complete removal of phenol and the reagent in excess was achieved. The polymer obtained in a dry form was white pearl-like solid. It was purified by dissolution with chloroform

and precipitated with methanol and further continuous extraction with diethyl ether and methanol (24h), and dried under vacuum at 90°C for 7 hours. The polymer was soluble in chloroform, dichloromethane, and insoluble in benzene, cyclohexanone, methanol and diethyl ether. The molecular weight of the polymer was measured by vapour pressure osmometry  $\bar{M}_n = 9000$ , and the thermal stability was determined by thermogravimetry.

A commercial bisphenol A polycarbonate resin (ALDRICH)  $\bar{M}_n = 10,000$  was also analysed in this study.

The commercial product was subjected to purification by dissolution in chloroform and precipitated with methanol and further continuous extraction with diethyl ether and methanol for 24 hours and dried under vacuum at 90°C for 7 hours.

### 3.6 CHARACTERISATION OF BISPHENOL A POLYCARBONATE

The characteristics of bisphenol A polycarbonate preparation are compared in this section with those of a commercial sample.

a. Microanalysis of bisphenol A polycarbonate prepared gave C = 75.2%, H = 5.5% and O = 19.3%. These results are in good agreement with the theoretical values for the structural unit  $(C_{15}H_{14}O_3)_n$  C = 75.59%, H = 5.51% and O = 18.9%.

b. The infrared spectrum shown in fig. 3.12 consisted of bands similar to the commercial sample. The assignments are: a band at  $3030\text{ cm}^{-1}$  corresponding to C-H stretching vibration of the aromatic ring; the strong sharp band at  $\sim 1786\text{ cm}^{-1}$  assigned to the C=O stretching vibration of the carbonate group; the strong sharp band at  $1500\text{ cm}^{-1}$ .

corresponding to bending absorption of methyl groups; the three strong bands extensively superimposed at 1235, 1193 and 1161  $\text{cm}^{-1}$  and the band at 1010  $\text{cm}^{-1}$  corresponding to the absorption of C-O-C bond and the carbonyl bond on the carbonate group; the absorption at 769  $\text{cm}^{-1}$  assigned to the out-of-plane vibration of the carbonate groups. These values are comparable to the infrared spectrum of the commercial sample.

c. The nmr spectrum for bisphenol A polycarbonate, (fig. 3.13) shows a multiplet with maxima at 7.22  $\delta$  (ppm) attributed to the resonance of protons in the aromatic rings and a singlet at 1.68  $\delta$  (ppm) assigned to the methyl groups. This agrees with a spectrum obtained for the commercial sample. The values obtained from the literature <sup>63</sup> are a singlet at 7.20  $\delta$  (ppm) and a singlet at 1.69  $\delta$  (ppm).



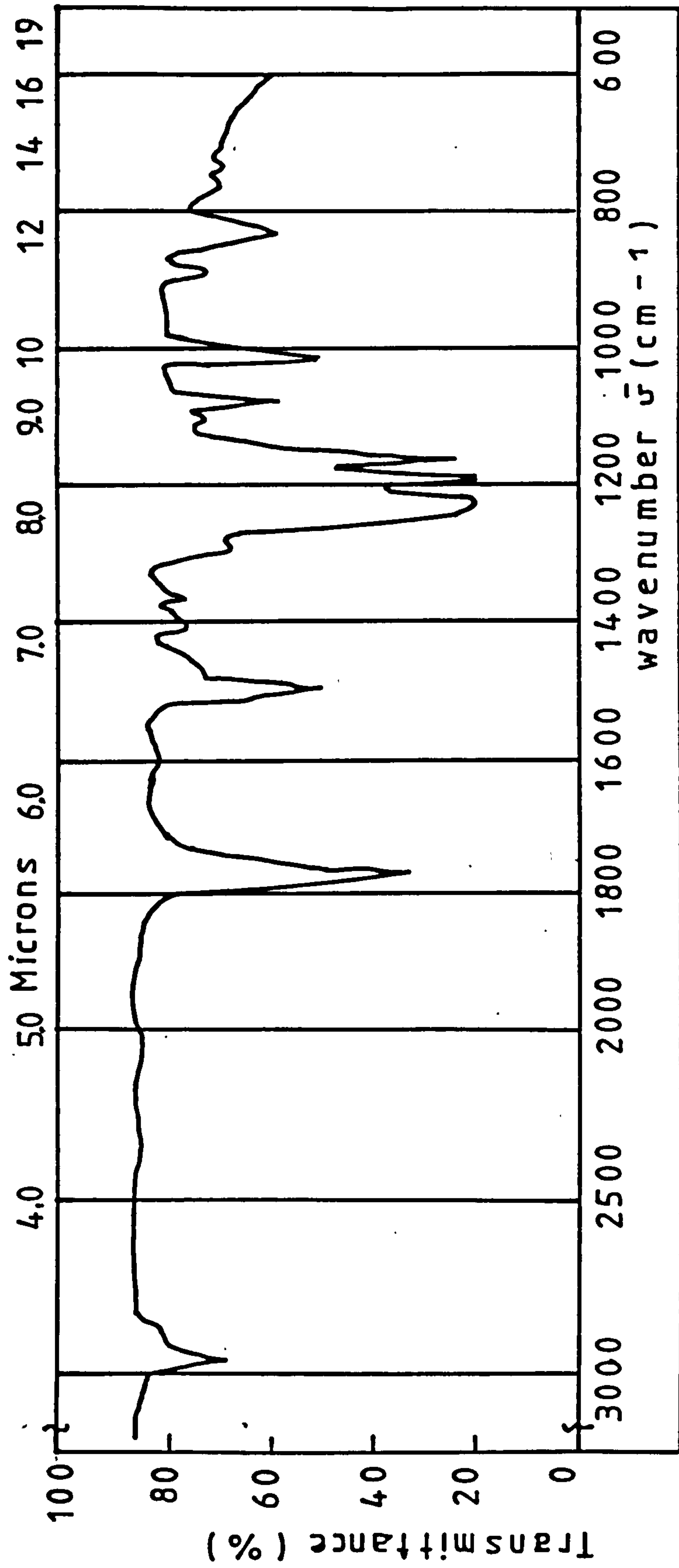


Fig. 3-12 Infrared spectrum from 3200 - 600 cm<sup>-1</sup>; for Bisphenol A polycarbonate, (laboratory sample), film onto NaCl disc.

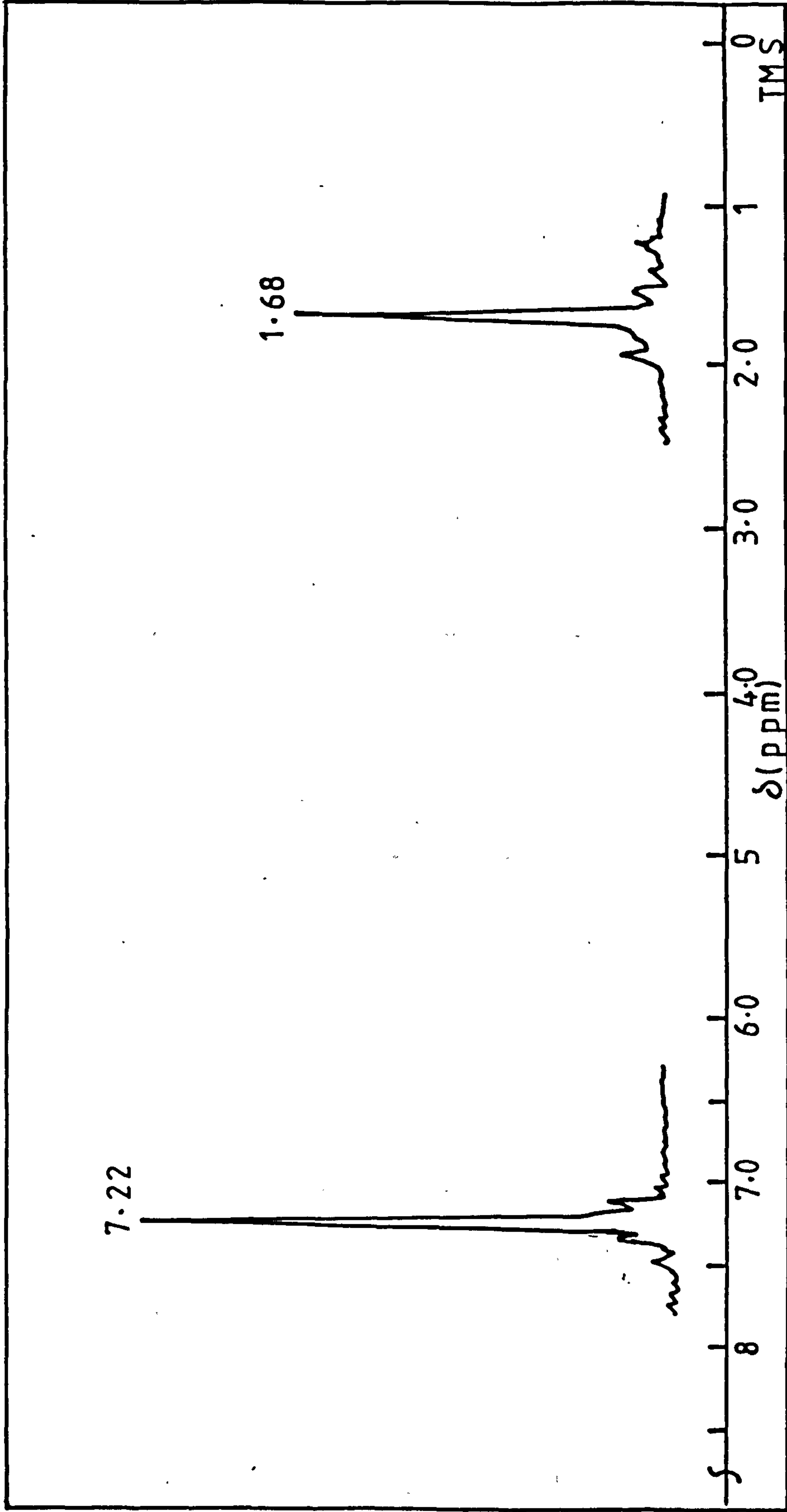


Fig. 3.13 n.m.r. spectrum for bisphenol a polycarbonate (laboratory sample)  
solvent  $\text{CDCl}_3$  temp. ambient  $^\circ\text{C}$

## CHAPTER FOUR

### EXPERIMENTAL RESULTS AND DISCUSSION

#### INTRODUCTION

In this Chapter the products of degradation of the prepared polycarbonates and a commercial sample of bisphenol A polycarbonate are given. Most of the thermal degradations have been performed using two approaches, programmed and isothermal heating, and under different environments, e.g. nitrogen atmosphere and/or vacuum. The different features of the thermal degradation with different techniques are described. The different fractions formed in the thermal degradation are analysed, e.g. cold ring fractions, volatile products and residue. Mechanisms of the degradation processes of the different classes of polycarbonates studied have been proposed.

#### 4.1 PROGRAMMED DEGRADATIONS FOR ALIPHATIC POLYCARBONATES

##### 4.1.1 Poly(trimethylene carbonate)

###### 4.1.1.1 Thermogravimetry (TG)

The TG curves for poly(trimethylene carbonate) heated in two different environments are shown in fig. 4.1. The derivative TG curve recorded for nitrogen atmosphere is also shown in the same figure.

A rapid weight loss occurs in both environments. In nitrogen atmosphere, this commences at 215°C, achieves a rate maximum at 288°C

and is completed at 312°C. The volatilisation process in vacuum starts at a lower temperature (198°C) and reaches a rate maximum at 247°C. The percentages of residue remaining are of the order of 0-1% and 4-6% respectively.

#### 4.1.1.2 Differential Scanning Calorimetry (DSC)

The DSC curve (fig. 4.2) shows an endothermic peak with minimum at 47°C attributable to the melting point of the polymer and a second endothermic peak which indicates a greater energy change with a minimum at 299°C. This large change in energy suggests that the decomposition process of the polymer occurs at this temperature.

#### 4.1.1.3 Thermal Volatilisation Analysis (TVA)

For poly(trimethylene carbonate) no variation of the pressure traces with temperature or time was observed. This indicates that the production of volatile products is not detectable within the sensitivity of the Pirani gauges (10 mv range). A very small amount of CO<sub>2</sub> is produced, however, and its formation will be discussed later in this chapter. A white crystalline solid (cold ring fraction) was obtained. No residue was observed after the degradation.

#### 4.1.1.4 Subambient Thermal Volatilisation Analysis (SATVA)

##### Poly(trimethylene carbonate) Products

Poly(trimethylene carbonate) was degraded to 500°C at a rate of 10°C per minute. The very small amount of volatile products collected in the -196°C trap was fractionated by SATVA. The SATVA



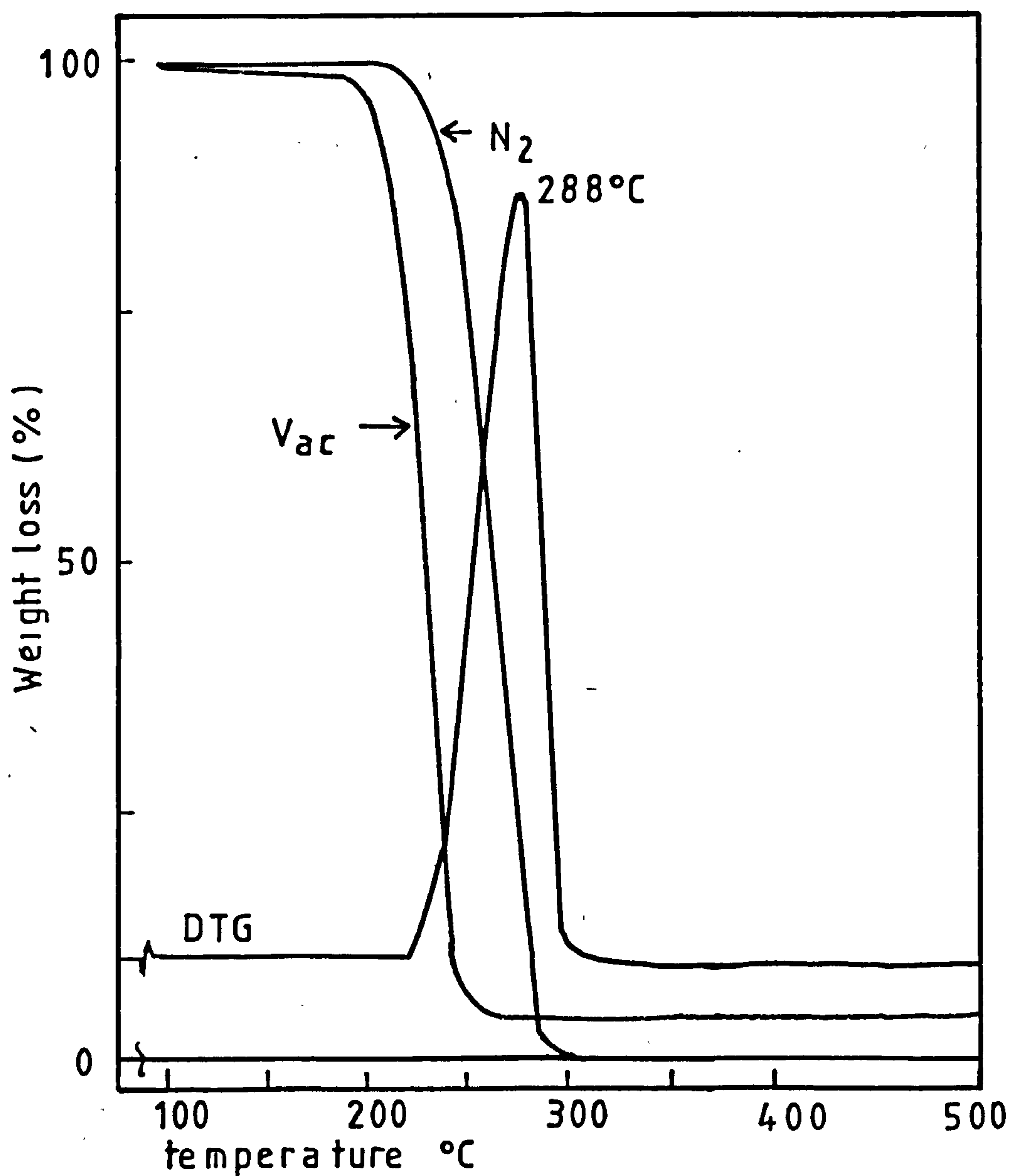


Fig 4.1. TG curves for poly (trimethylene carbonate) in Vac and N<sub>2</sub> atmosphere, heated to 500 °C at 10 °C/min. DTG curve in N<sub>2</sub>

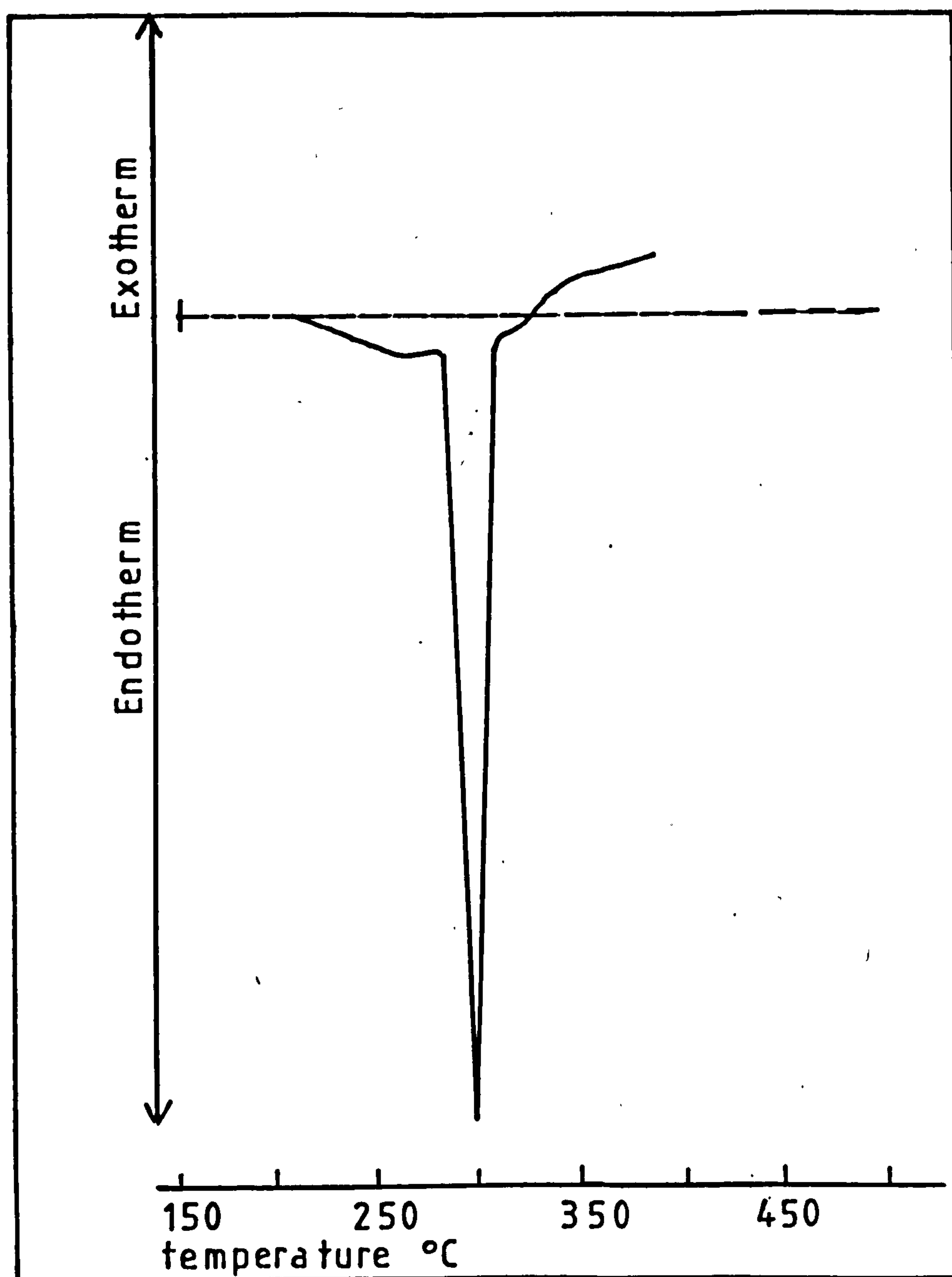


Fig.4·2 DSC curve for poly(trimethylene carbonate) in  $N_2$  atmosphere, heated at 500°C at 10°C/min.

curve indicated in fig. 4.3 shows four distinct peaks at  $-147^{\circ}$ ,  $-126^{\circ}$ ,  $-63^{\circ}$  and  $-5^{\circ}\text{C}$ , respectively. The first peak is assigned to carbon dioxide, the second peak corresponds to the solvent, acetone, the third peak corresponds to water and the fourth to monomer. The assignments are based upon infrared and mass spectrometric examination of each fraction.

The principal products of degradation are of low volatility and are collected as cold ring fraction.

#### 4.1.1.5 Characterisation of Cold Ring Fractions

After the polymer was degraded to  $500^{\circ}\text{C}$  the cold ring fraction obtained consisted of two different solid materials. The band which condensed further up in the tube (upper CRF) consisted of a colourless crystalline solid, whereas the lower band (lower CRF) consisted of a colourless sticky material. These different materials were analysed spectroscopically.

The upper CRF was collected separately from the lower CRF by wiping with a solvent-moistened tissue and dissolved with a suitable solvent. The amount was determined by weight after evaporation of the solvent. The lower CRF was collected by washing the degradation tube wall with a solvent. The amount was measured in the same way.

A GC-MS investigation was carried out of the total cold ring material. The first peak, with a retention time 4.1 min, showed a molecular ion at  $m/e$  102 which corresponds to the molecular weight of the monomer. The second peak, with a retention time of 24.1 min, showed a peak at  $m/e$  249 attributable to oligomeric product. Other

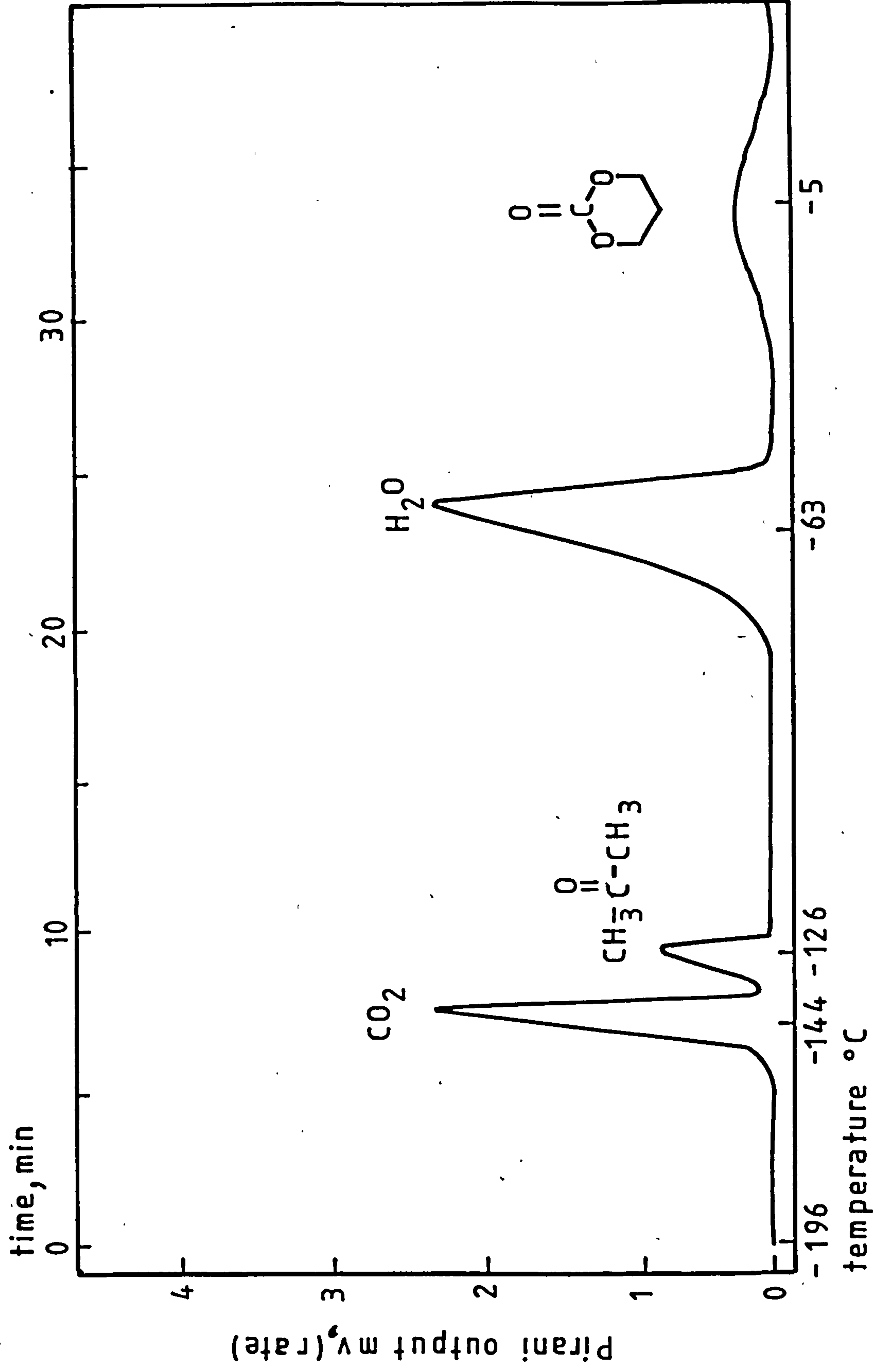


Fig.4. 3. SATVA curve of volatile products for poly(trimethylene carbonate) heated to 500 °C, at 10°C/min



minor GC peaks were observed at retention times of 14.9, 17.0, 22.5, 26 and 28 minutes which could be attributed to different short chain fragments produced during degradation.

Each fraction gave an infrared spectrum similar to that of monomer, except for some broadening of the bands and the additional presence of an absorption at  $3480\text{ cm}^{-1}$  due to water; these materials are hygroscopic.

It is concluded that the upper CRF consists of monomer, whereas the lower CRF contains less volatile short chain fragments. The difference in appearance of the two fractions is also indicative of the type of material present. Trimethylene carbonate is a colourless crystalline solid, whereas the sticky texture of the lower CRF resembles that of the polymer.

It can be concluded that the thermal degradation of Poly(trimethylene carbonate) produces carbon dioxide, monomer and polymer short chain fragments. There was no residue after degradation.

The relative proportions of the degradation products will be discussed in another chapter.

#### 4.1.2 Poly(neopentylene carbonate)

##### 4.1.2.1 Thermogravimetry (TG)

The TG curves for poly(neopentylene carbonate) heated in two different environments, are presented in fig. 4.4. The DTG curve recorded for nitrogen atmosphere is also shown. The volatilisation process for both environments occurs in one stage within a narrow range of temperature. In nitrogen the weight loss commences at  $288^{\circ}\text{C}$  and

reaches the rate maximum at 331°C. The onset of volatilisation in vacuum is at 285°C with a rate maximum at 341°C. The percentages of residue remaining after the degradation are of the order of 4-5% and 2-2.5%, respectively.

#### 4.1.2.2 Differential Scanning Calorimetry (DSC)

The DSC curve for poly(neopentylene carbonate) is indicated in fig. 4.5 and shows three endothermic peaks at 99°, 122° and 308°C. The second peak may correspond with a previously reported melting point of 117-119°C for the  $\beta$  form of a similar polymer. The first peak may be due to an  $\alpha$  solid- $\beta$  solid phase transition of the polymer. The third peak is attributed to the decomposition process of the polymer. This suggests that the breakdown of the polymer occurs in one stage, supporting the evidence already obtained from thermogravimetry. The fact that this decomposition is endothermic may suggest that the main route of degradation is depolymerisation.

#### 4.1.2.3 Thermal Volatilisation Analysis (TVA)

The TVA curve for poly(neopentylene carbonate) is presented in fig. 4.6. The volatile products are formed in a one-stage process indicated by a single very small peak extended over a wide range of temperature. The TVA traces at 0°, -45°, -75° and -100°C coincide, indicating volatile products which do not condense at these temperatures. The -196°C trace follows the baseline. This behaviour in the volatilisation process is indicative that the volatile products formed condense at -196°C but not at -100°C, consistent for example with the behaviour of CO<sub>2</sub>.

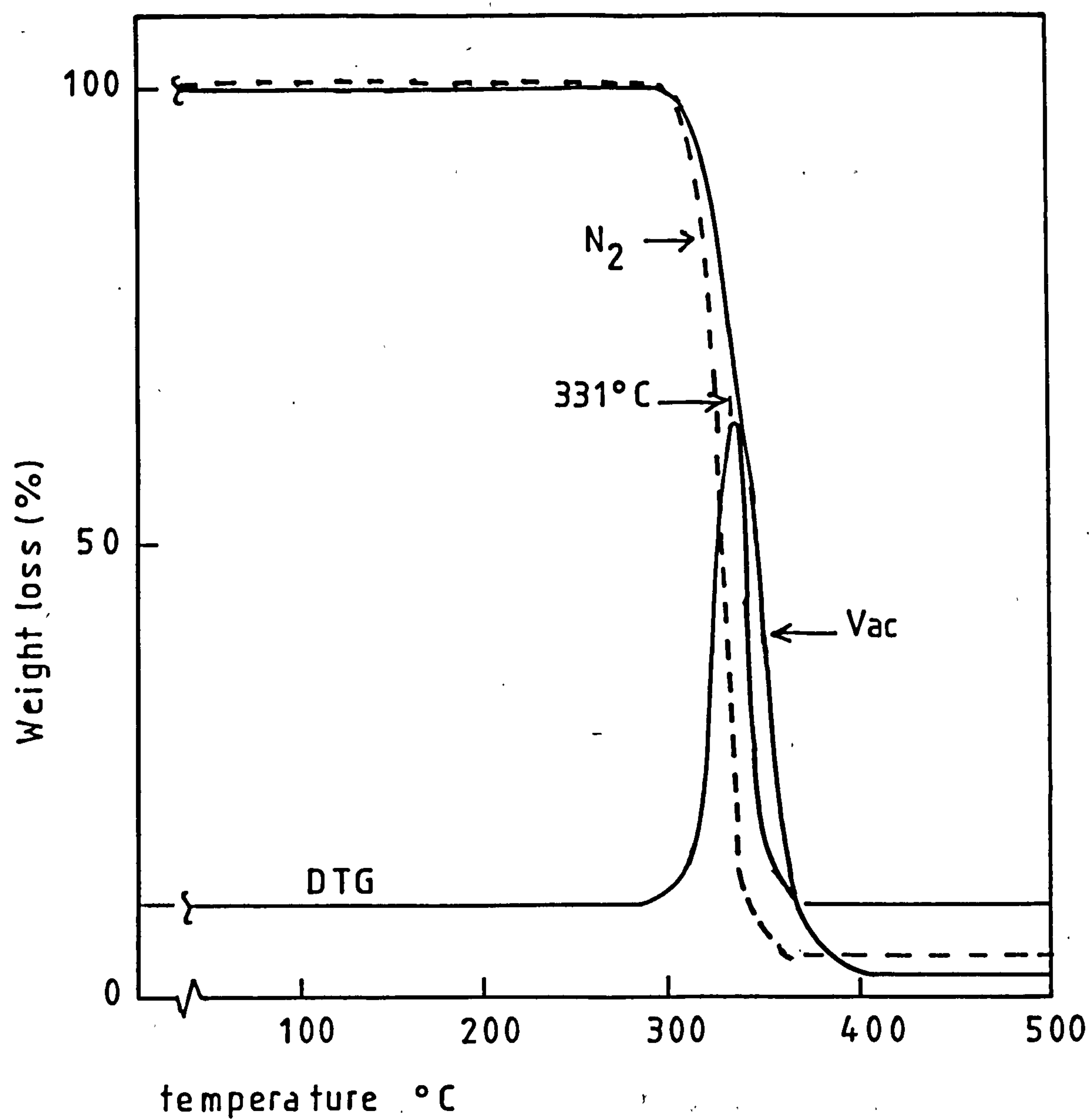


Fig. 4. 4' TG curves for poly(neopentylene carbonate) heated to 500°C for vacuum and N<sub>2</sub> atmosphere at a heating 10°/min.

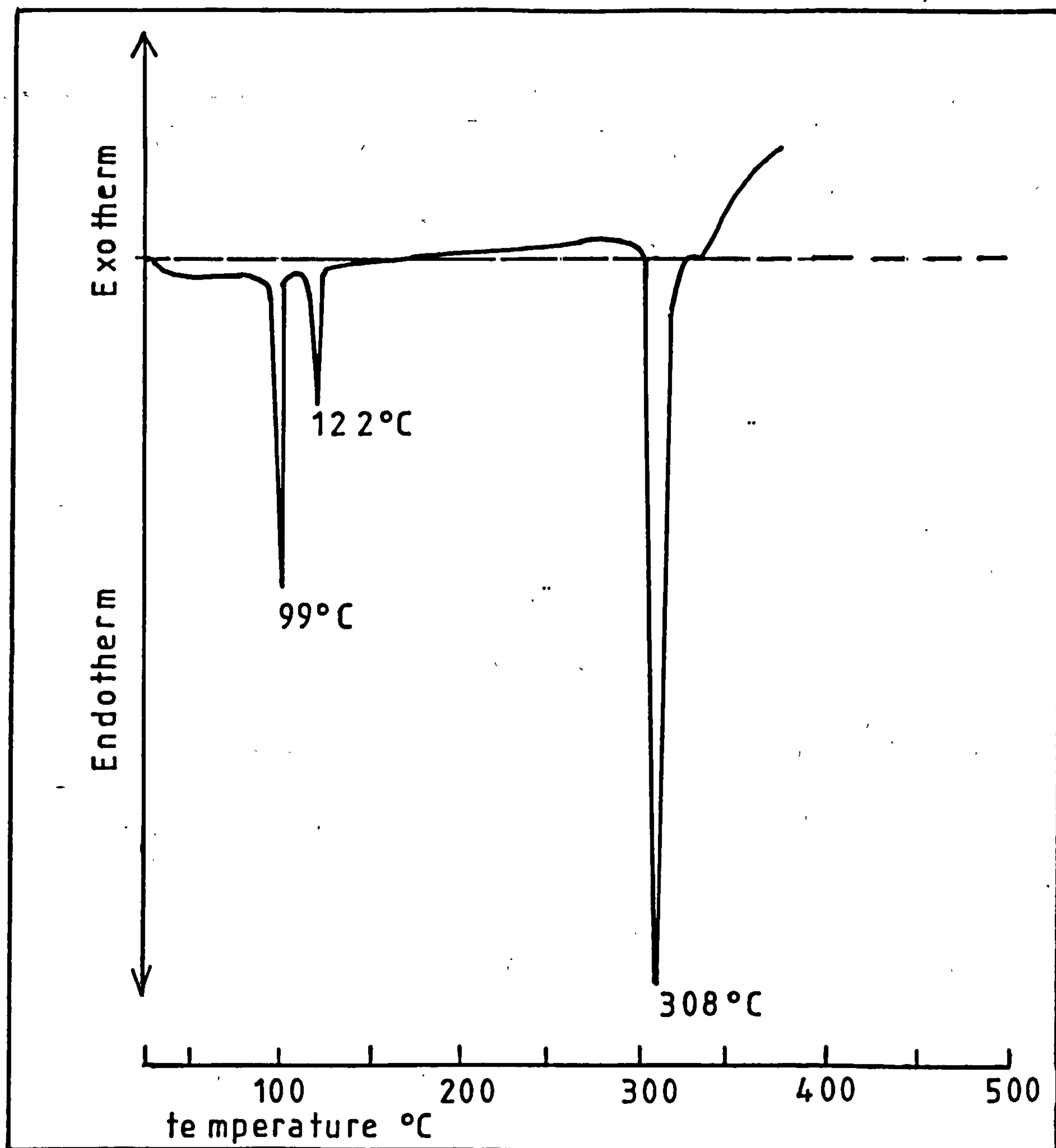


Fig.4.5 DSC curve for poly (neopentylene carbonate) in  $N_2$  atmosphere heated to 500° at 10°C/min

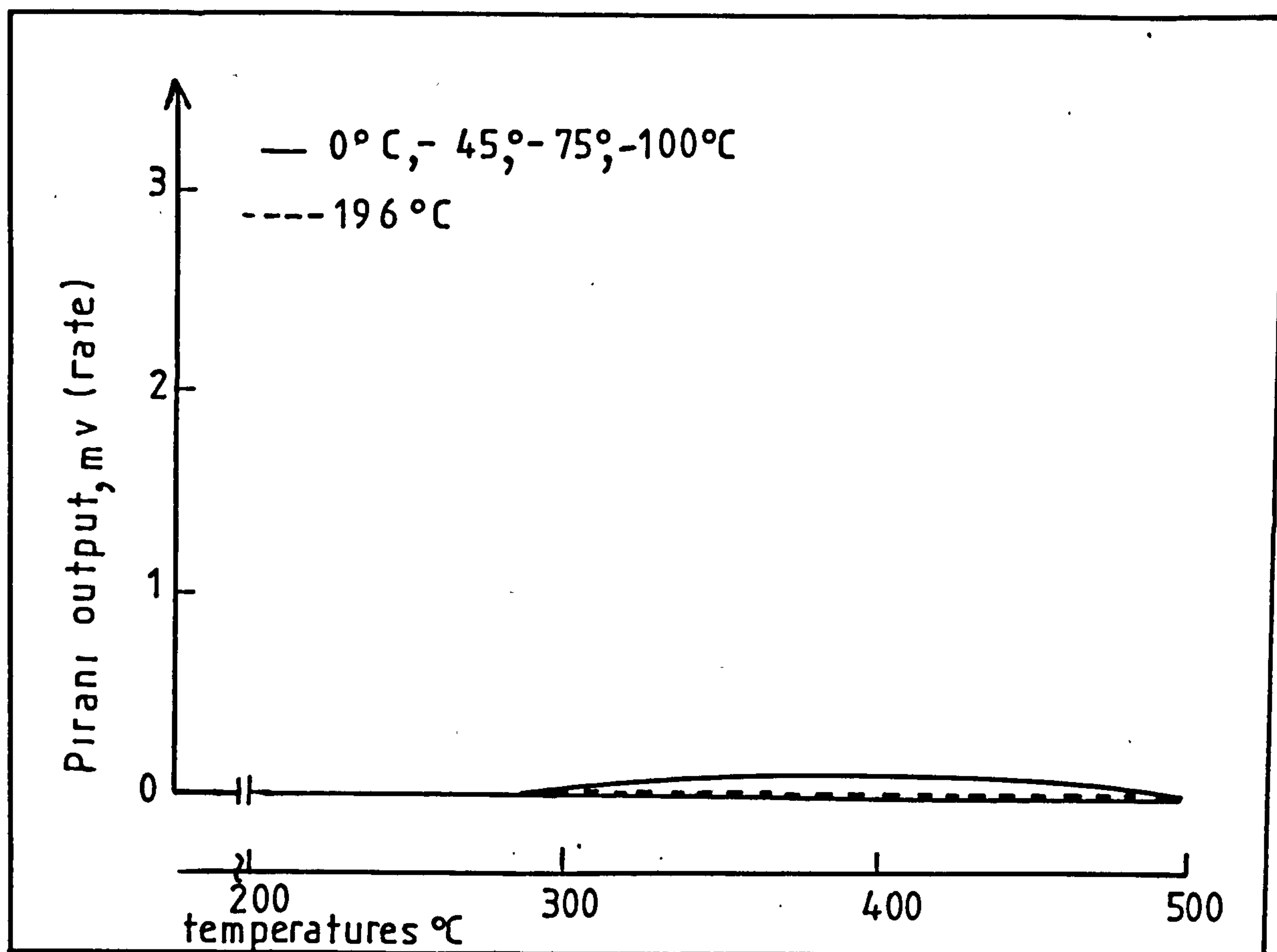


Fig 4.6 TVA curve for poly(neopentylene carbonate) heated to 500°C at 10°C/min



Subambient TVA, together with infrared and mass spectrometric analysis indicated the presence in the  $-196^{\circ}\text{C}$  trap of a small amount of carbon dioxide, together with traces of monomer and water; the latter are probably released from the polymer during evacuation prior to degradation. The principal products of degradation are of low volatility and are collected as cold ring fractions.

#### 4.1.2.4 Characterisation of Cold Ring Fractions

The cold ring fraction produced when poly(neopentylene carbonate) was heated to  $500^{\circ}\text{C}$  at a rate of  $10^{\circ}\text{C}$  per minute was collected and analysed spectroscopically. Two different bands of material were deposited in the inner wall of the degradation tube as cold ring fraction. The upper CRF was a colourless crystalline material and there was a thin lower CRF of powdered solid. Both were collected separately by washing with a suitable solvent which was then evaporated. The infrared spectrum for the upper CRF was identical with that of the monomer. The lower CRF had infrared bands characteristic of both monomer and polymer. In both cases a broad band at  $3445\text{ cm}^{-1}$  was observed, due to water, since the CRF is hygroscopic.

The separated bands were further analysed by GC-MS (column temp-programmed at  $10^{\circ}\text{C}/\text{min}$ ). The upper CRF gave a main peak with retention time at 8.4 min which showed a molecular ion  $m/e$  130 corresponding to the molecular weight of the monomer. A second small peak at the higher retention time of 17.3 minutes may be due to the presence of a small amount of oligomeric fragments.

Results for the lower CRF (column temp-programmed at 5°/min) showed several GC peaks. The two main peaks consisted of monomer and a second peak with retention time at 34.6 min. The latter showed a peak at m/e 228 which may be assigned to an oligomeric product.

It is most likely that the main mode of degradation under vacuum conditions is depolymerisation, which probably takes place at the lowest temperature and when the temperature is raised continuously, some reacting macromolecules volatilise when their length is lower than the volatilisation limit at the degradation temperature.

It may be concluded that the thermal degradation of poly(neopentylene carbonate) gives carbon dioxide, monomer and oligomeric fragments. There was no residue after degradation.

The relative proportions of the degradation products will be discussed in Chapter Five.

#### 4.1.3 Poly(2-phenyl trimethylene carbonate)

##### 4.1.3.1 Thermogravimetry (TG)

The TG curves for poly(2-phenyl trimethylene carbonate) obtained and the DTG curve for nitrogen atmosphere are shown in fig. 4.7.

For both environments, the weight loss occurs in one stage. In nitrogen a rapid weight loss commences at 262°C and achieves a rate maximum at 325°C. For vacuum the rapid decomposition process starts at a lower temperature (250°C) with a rate maximum at about 325°C. From the beginning a shift of the baseline is observed which in nitrogen

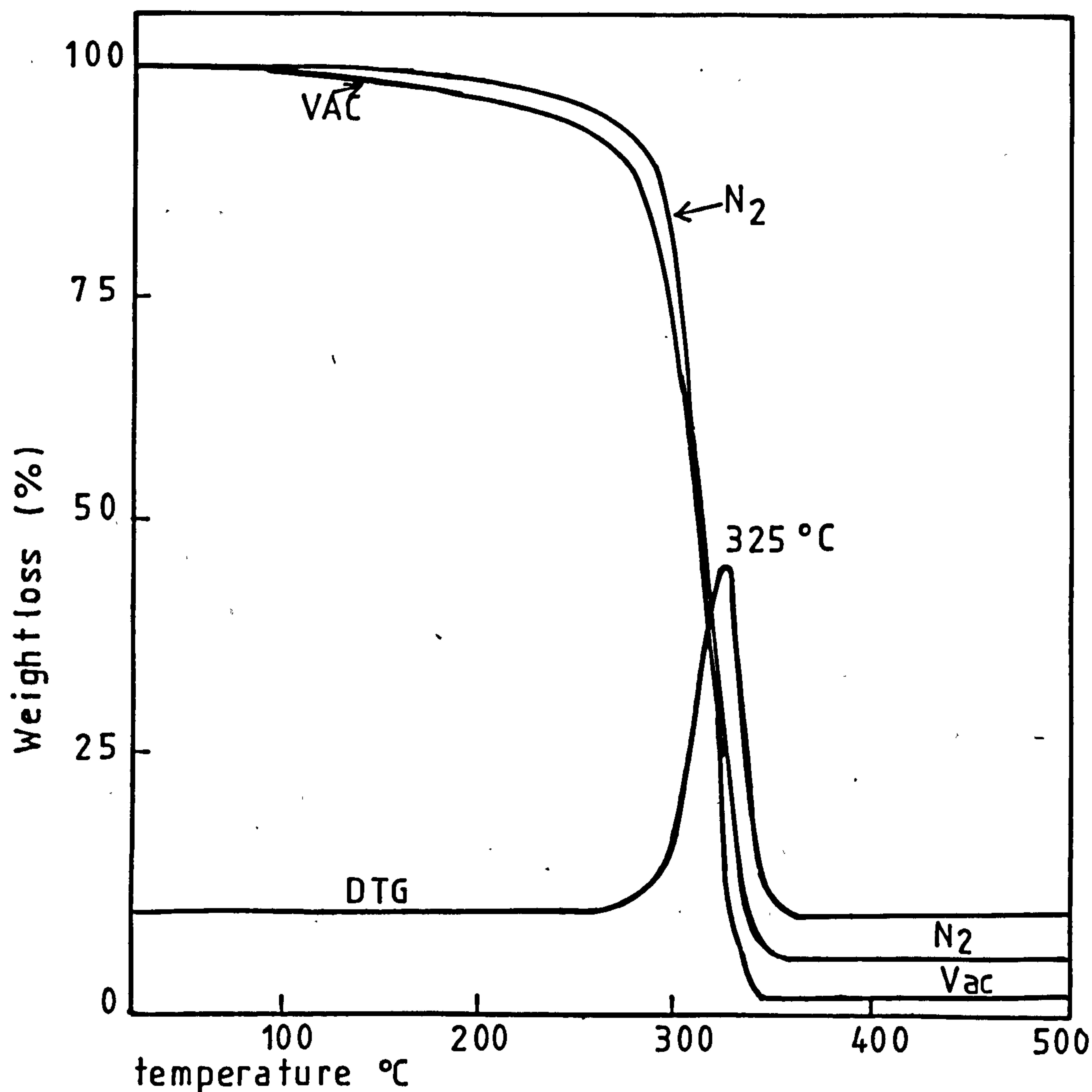


Fig.4.7 TG curves for poly (2-phenyl-trimethylene carbonate) heated at 500°C at 10°C/min. in vacuum and N<sub>2</sub> atmosphere. DTG curve in N<sub>2</sub>

is less pronounced. This may be due to slow release of trapped solvent which occurs more readily under vacuum.

#### 4.1.3.2 Differential Scanning Calorimetry (DSC)

The DSC curve (fig. 4.8) shows an endothermic peak with a minimum at 282°C. There is also observed a continuous upward shift (exothermic) of the base line. This behaviour may suggest a complex decomposition process occurring during heating.

#### 4.1.3.3 Thermal Volatilisation Analysis (TVA)

The TVA curve (fig. 4.9) shows essentially a one-step degradation process commencing at about 307°C, with rate maximum of volatilisation at 355°C and is completed at about 418°C. The non-coincidence of the 0°C trace and -100°C shows production of distinct products of different volatility. The -196°C curve indicates production of non-condensable gases at about 337°C, which were analysed by mass spectroscopy via an on-line Micromass QX200 spectrometer attached to the TVA apparatus. The mass spectrum showed a peak at m/e 28 assigned to carbon monoxide.

#### 4.1.3.4 Subambient Thermal Volatilisation Analysis (SATVA) for Poly(2-phenyl-trimethylene carbonate) products

Degradation of poly(2-phenyl-trimethylene carbonate) to 500°C under vacuum gave non-condensable and condensable volatile products. These latter substances were examined by SATVA. The trace (fig. 4.10) shows five separate peaks. The products corresponding to these peaks were also analysed by mass spectroscopy via an on-line Micromass QX200 spectrometer.

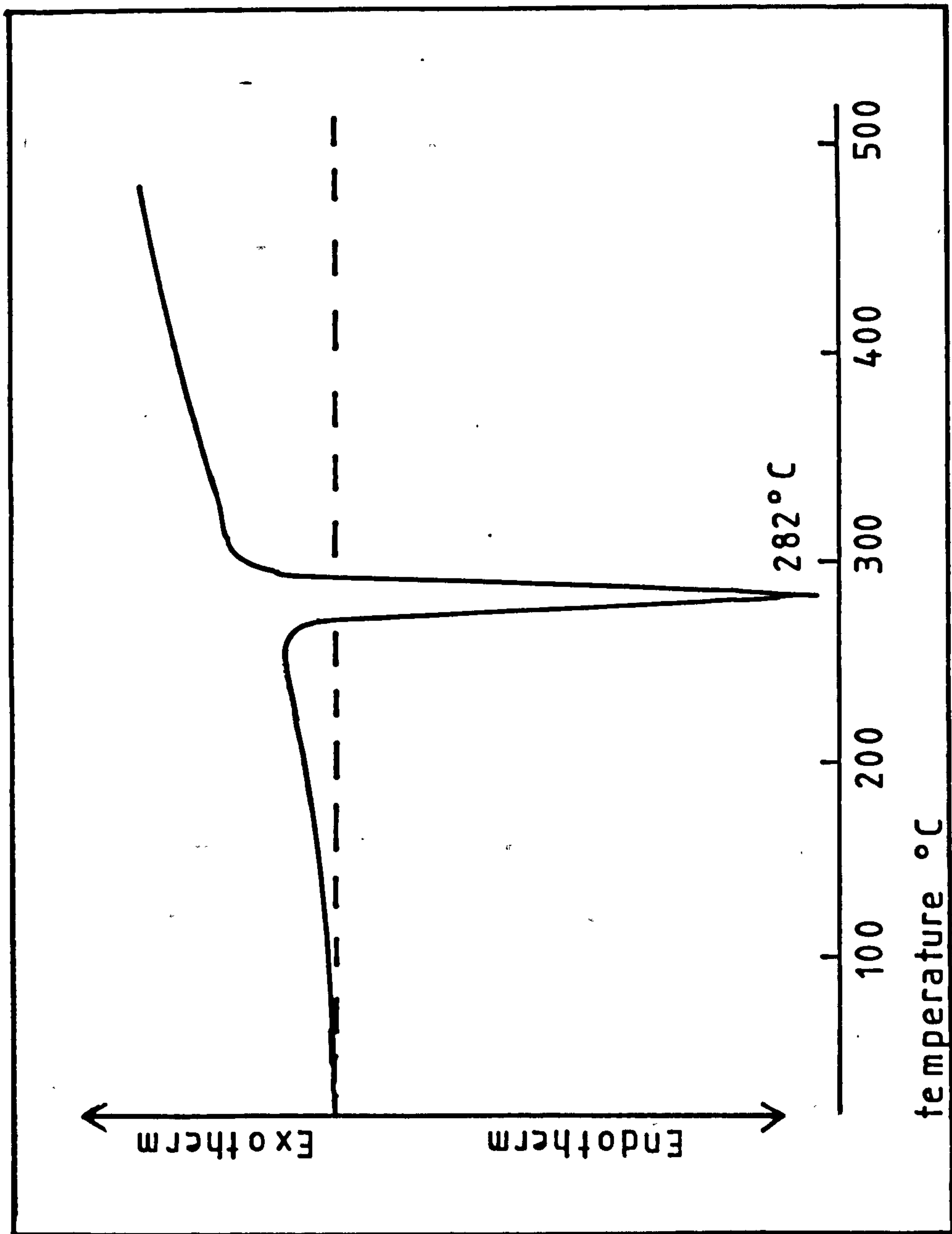


Fig. 4.8 DSC curve for poly (2- phenyl- trimethylene carbonate )  
in N<sub>2</sub> atmosphere, to 500°C at 10°C / min.



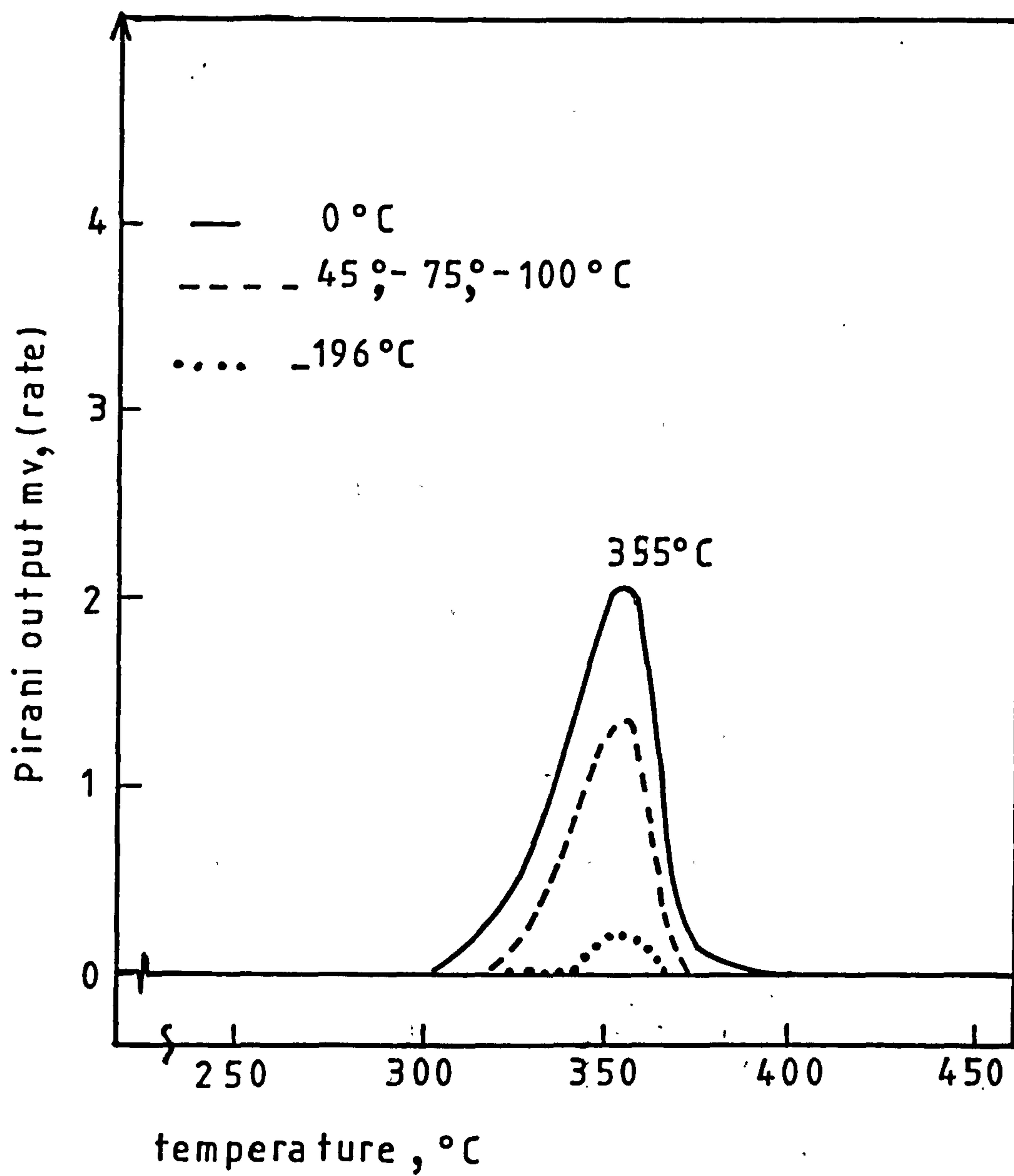


Fig. 4.9. TVA curve for poly(2-phenyl-trimethylene carbonate) heated to 450°C, at a rate 10°C/min.

The product at the first peak of the SATVA curve was identified by the molecular ion at  $m/e$  44 and other characteristic peaks as carbon dioxide. Identification was confirmed by infrared spectroscopy. These techniques were also applied to establish that the second peak was due to acetone, the third peak to  $\alpha$ -methyl styrene and the fourth to a mixture of water,  $\alpha$ -methyl styrene and phenol. The fifth peak was attributed to phenol. It is most likely that the source of the second peak is acetone trapped in the polymer. This was used as solvent during the purification process. Water may not be a genuine product of degradation, but may be absorbed by the polymer or released from the glassware. Phenol is a by-product in the polymerisation process and remains as an impurity in the polymer, despite continuous extraction with non-solvent diethyl ether.

It is concluded that the volatile products formed in small amounts during the breakdown of poly(2-phenyl-trimethylene carbonate) are carbon monoxide, carbon dioxide and  $\alpha$ -methyl styrene.

#### 4.1.3.5 Characterisation of Cold Ring Fraction

When poly(2-phenyl-trimethylene carbonate) was degraded to 500°C at a rate of 10°C per minute, a thin film of a sticky material condensed on the inner wall of the degradation tube as a cold ring fraction. The infrared spectrum of this material consisted of bands which are characteristic of the polymer, the only difference being a better resolution of the bands.

This suggests that in the degradation process of poly(2-phenyl-trimethylene carbonate) the principal route of degradation is chain

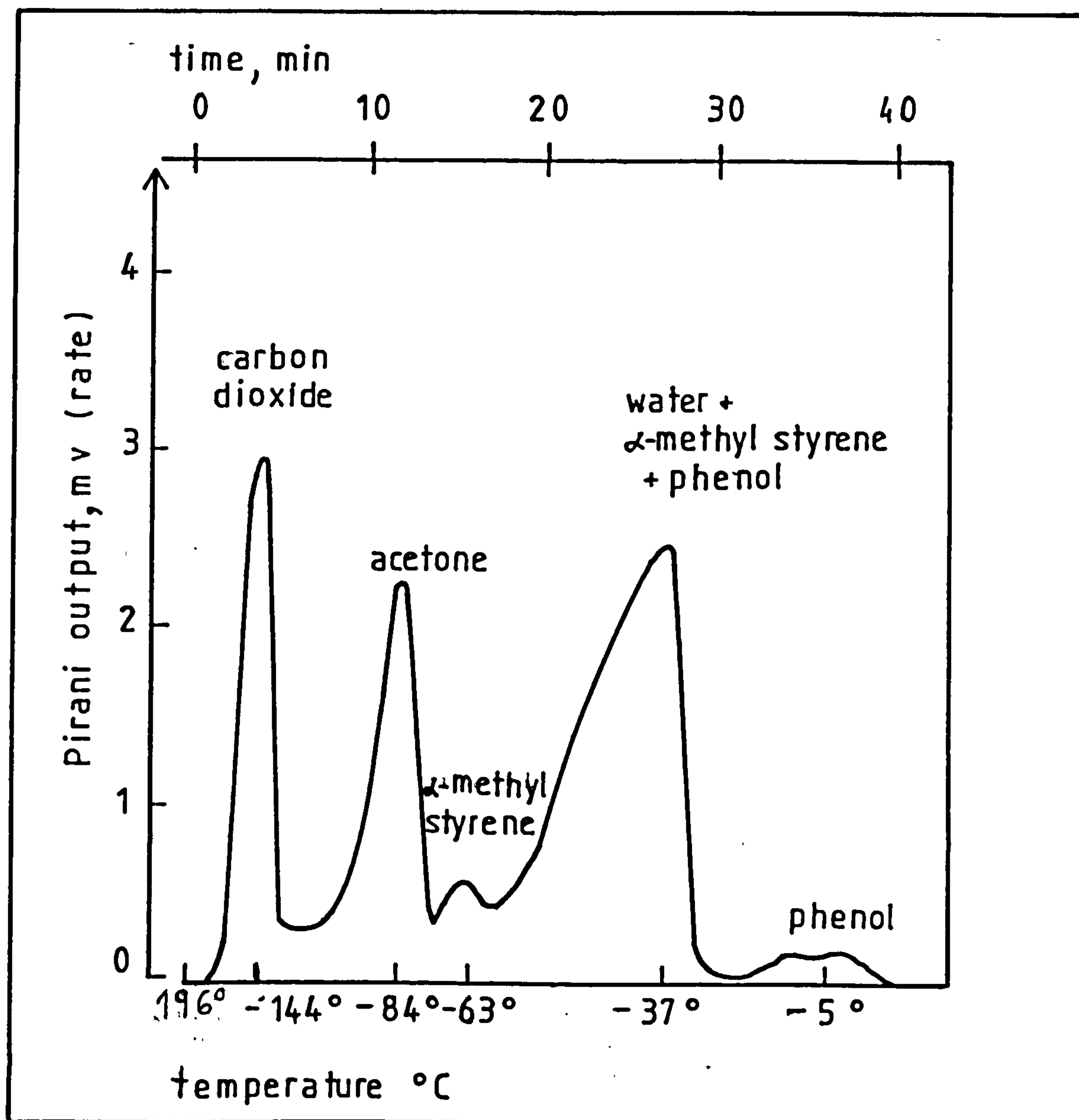


Fig. 4.10. SATVA curve for the products of degradation of poly(2-phenyl-trimethylene carbonated), heated to 500°C at 10°C/min.

scission to give polymer chain fragments of lower molecular weight.

## 4.2 ISOTHERMAL DEGRADATIONS FOR ALIPHATIC POLYCARBONATES

### 4.2.1 Poly(trimethylene carbonate)

#### 4.2.1.1 Carbon Dioxide Production

Samples of poly(trimethylene carbonate) were heated isothermally at 185°, 190°, 214° and 243°C in vacuum for one hour. A SATVA curve for the products of degradation was recorded.

It was observed that CO<sub>2</sub> started to be formed at 190°C. The peak corresponding to water was observed for all temperatures of degradation. Qualitatively, it is observed that the peak corresponding to CO<sub>2</sub> increases with temperature. This suggests that a greater amount of carbonate groups react giving the product CO<sub>2</sub>.

#### 4.2.1.2 Cold Ring Fraction Analysis

The cold ring fractions collected after the degradation of poly(trimethylene carbonate) at 200°, 243° and 300°C, respectively, were analysed by infrared spectroscopy.

The infrared spectrum corresponding to the cold ring products formed at 200° and 243°C showed bands characteristic of the monomer. At 300°C the texture of the CRF began to change. Further up in the tube a colourless crystalline solid was deposited and below this a thin film was observed. The infrared spectra for both fractions (fig. 4.11) consist mainly of peaks which are characteristic of trimethylene carbonate (monomer). In both spectra in the region 3020-2900 cm<sup>-1</sup>

four bands are present at 3018, 2980, 2960, 2923, together with shoulder at  $\sim 2918\text{ cm}^{-1}$ . The first three bands correspond to the stretching vibration of the C-H bond in the cyclic monomer, while the shoulder at about  $2918\text{ cm}^{-1}$  can be attributed to the C-H stretching of the  $-\text{CH}_2-$  groups of the polymer.

In the spectrum of the upper CRF (crystalline solid) the shoulder at  $1476\text{ cm}^{-1}$ , the band at 1330 and the small shoulder at  $1030\text{ cm}^{-1}$  are absent. All these bands are characteristic of the polymer and they are present in the lower CRF. This indicates that in the lower CRF there is a larger amount of polymer short chains. However, the main component in both fractions is monomer.

The predominance of monomer in the upper CRF may be explained because of higher volatility, due to its lower molecular weight. It is reasonable to assume that the polymer chain fragments present in the upper CRF are of lower molecular weight than those present in the lower CRF.

The different texture of the two fractions is consistent with the differences in the molecular weight of the substances deposited in the different region of the cold ring; the upper CRF is crystalline (monomer) whereas the lower CRF is not.



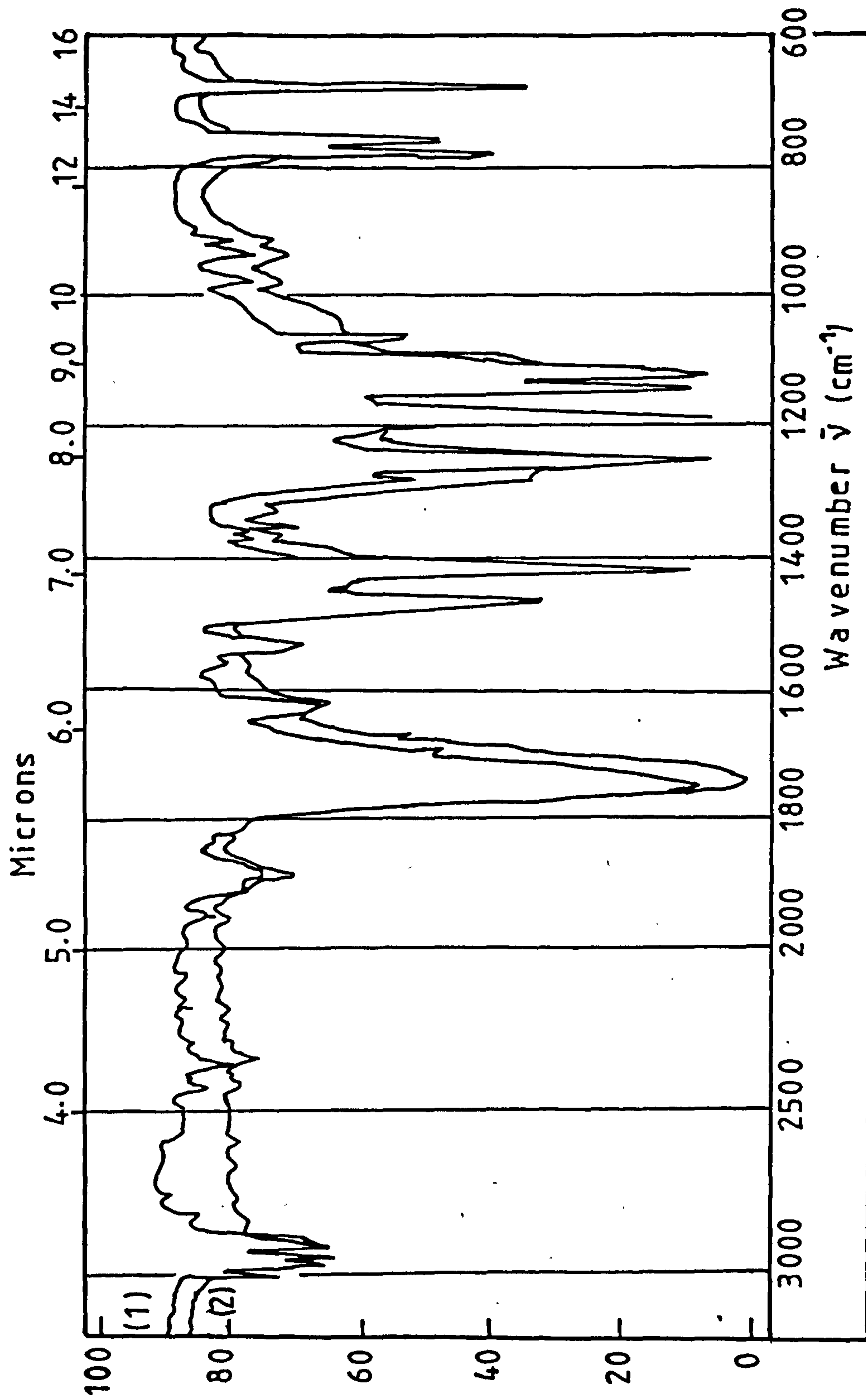


Fig. 4.11. Infrared spectrum from 3100-600  $\text{cm}^{-1}$  for the degradation products (cold ring fraction) for poly(trimethylene carbonate) heated up to 300°C for one hour. (1) Upper cold ring fraction (2) lower cold ring fraction.

#### 4.2.2 Poly(neopentylene carbonate)

##### 4.2.2.1 Carbon Dioxide Production

Poly(neopentylene carbonate) was heated isothermally at 290°, 300° and 350°C under vacuum for one hour and a SATVA curve of the degradation products for each temperature of degradation was recorded.

Carbon dioxide began to be produced when the temperature of degradation reached 300°C and was produced in greater amount at 350°C. It appears that at these temperatures some scission of the carbonate group occurs as well as depolymerisation to monomer.

##### 4.2.2.2 Cold Ring Fraction Analysis

Fifty milligrams of poly(neopentylene carbonate) were heated under vacuum at 275°, 290°, 300° and 350°C. The cold ring fraction, a colourless crystalline solid deposited on the wall of the degradation tube, was collected and analysed by infrared spectroscopy. The infrared spectrum corresponding to the CRF produced at 275° and 300°C consisted of bands which are characteristic of the monomer.

At 350°C the characteristics of the material began to change. Two different bands were deposited, a white crystalline solid in the upper part of the degradation tube and a lower band consisted of a thin film of a powdered solid. The spectroscopic analysis showed that the upper CRF consisted mainly of monomer. The lower CRF contained a mixture of monomer and polymer short chain fragments.

The difference in the nature of the two bands is also apparent from their appearance. Upper CRF resembled monomer and the lower CRF was similar to polymer.

#### 4.2.3 Poly(2-phenyl-trimethylene carbonate)

##### 4.2.3.1 Production of Condensable Gases

Samples of poly(2-phenyl-trimethylene carbonate) were subjected to isothermal heating at 200°, 225°, 254°, 275° and 305°C under vacuum for one hour and a SATVA curve of the degradation products for each temperature was recorded. The purpose was to determine the temperature at which carbon dioxide and  $\alpha$ -methyl styrene are produced.

The experimental results show that neither carbon dioxide nor  $\alpha$ -methyl styrene are produced at 200°C. At about 254°C carbon dioxide begins to be produced but  $\alpha$ -methyl styrene is still absent from the volatile products of degradation. It is formed when the temperature of degradation is increased to 275°C. At all temperatures of degradation, water is produced.

It can be concluded that the reaction leading to the production of  $\alpha$ -methyl styrene has higher activation energy than that giving carbon dioxide.

##### 4.2.3.2 Cold Ring Fraction Analysis

After samples of poly(2-phenyl-trimethylene carbonate) had been heated at 254°, 275°, 305° and 325°C, each for one hour under vacuum, the thin, sticky film formed as CRF was removed from the walls of the degradation tube and analysed by infrared spectroscopy. It showed similar bands to the spectrum of the polymer.



### 4.3 RATES OF THERMAL DEGRADATION FOR ALIPHATIC POLYCARBONATES

In order to obtain a better insight into the degradation process for aliphatic polycarbonates, the rates of thermal degradation by TG under vacuum were obtained.

#### 4.3.1 Poly(trimethylene carbonate)

Three isothermal TG experiments were performed under vacuum at 190°, 195° and 200°C respectively. Using these curves, plots of percentage of residue and the extent of degradation for various times were made (fig. 4.12). Using the data (residue %) from these curves the rates of thermal degradation versus percentage of volatilisation were obtained (fig. 4.13).

From the curves it can be seen that the low rates of degradation at low percentage conversions may suggest that the polymer degrades by depropagation to monomer, the main product as already found by TVA, by reaction probably initiated at the chain ends, the initiation step being rate determining. The depropagation may end either by complete unzipping of the macromolecule or by termination reactions yielding products of low molecular weight which may volatilise due to the vacuum conditions. The considerable increase in rate with temperature and the appearance of carbon dioxide as a minor volatile product may suggest that for higher temperatures than 190°C another initiation mechanism may occur, by scission of the carbonate groups with production of carbon dioxide and formation of two active chain ends, capable of depropagation to monomer or recombination. The decrease of the rates for each temperature may be due to the depletion of the polymer sample during the thermal degradation.

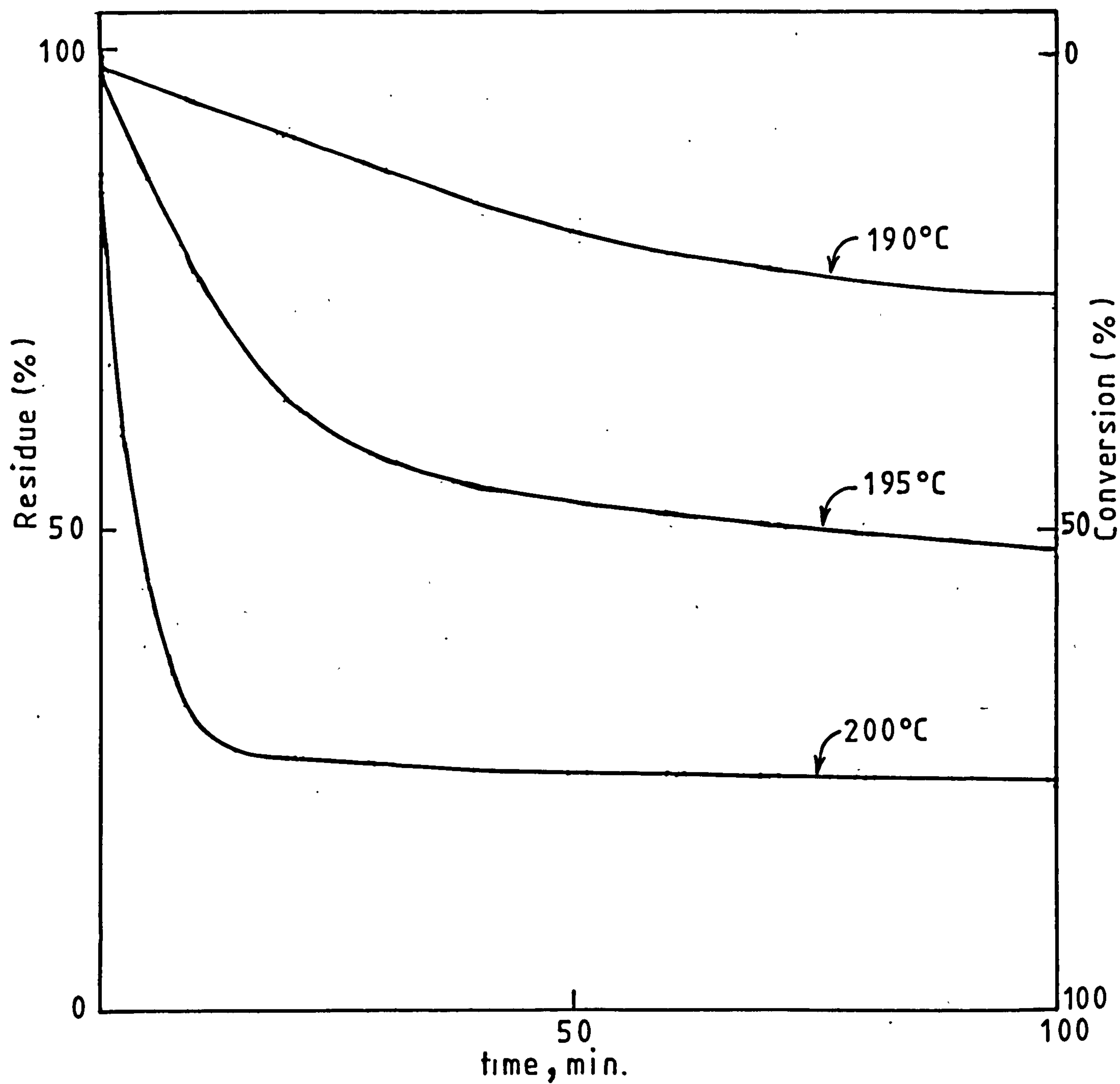


Fig.4.12. Percentages of residue and conversion  
For poly(trimethylene carbonate) by TG under vacuum  
heated for various times at 190°, 195° and 200°C  
respectively.



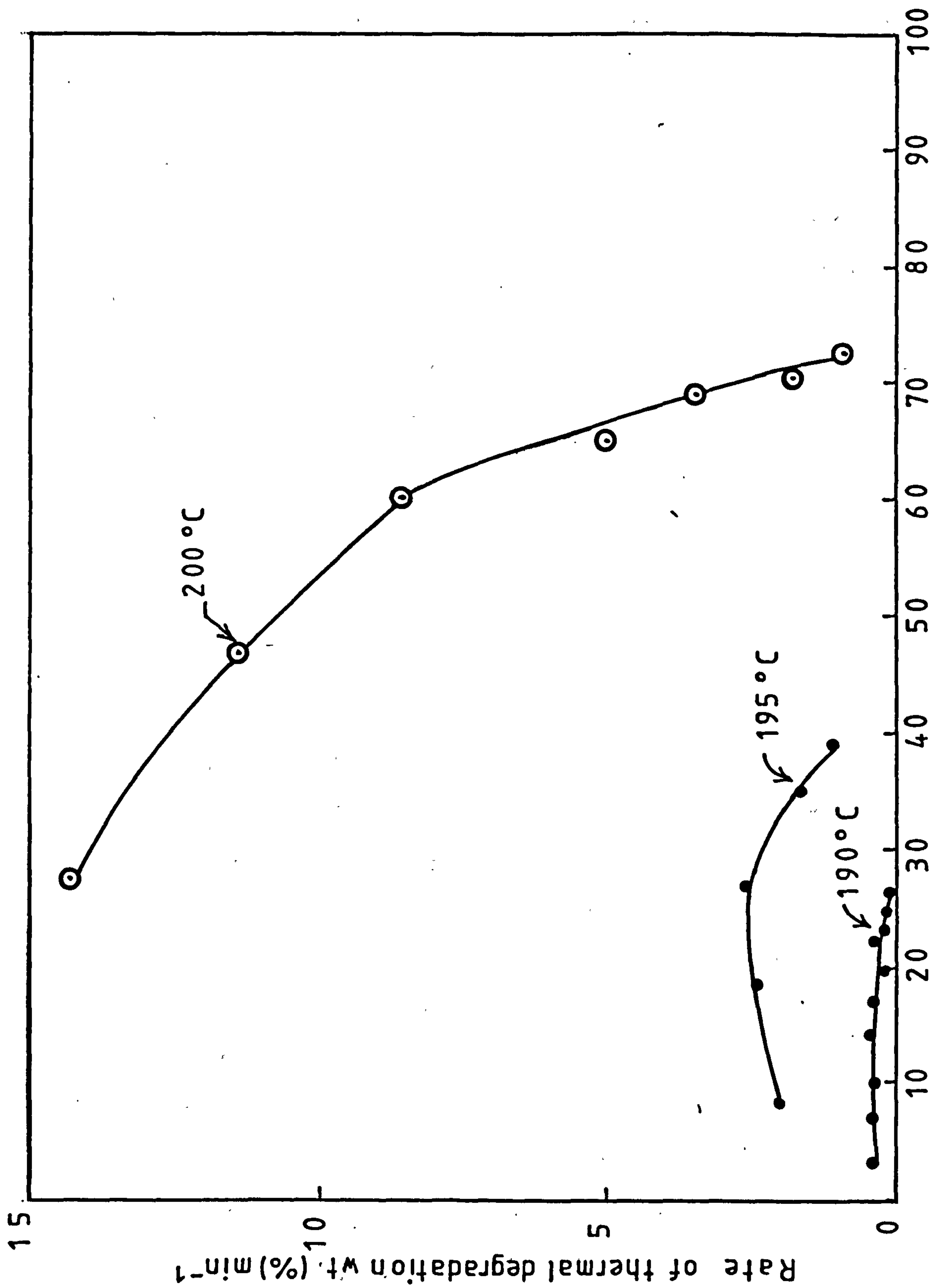


Fig.4.13. Rates of thermal degradation of poly (trimethylene carbonate) by T.G. at 190°C, 195°C and 200°C respectively

#### 4.3.2 Poly(neopentylene carbonate)

Isothermal TG curves for poly(neopentylene carbonate) were obtained at 205°, 215°, 225° and 235°C. Using these curves plots of percentage of residue and extent of degradation versus time were made (fig. 4.14).

Using the data obtained from these plots the rates of degradation for poly(neopentylene carbonate) versus percentage of volatilisation were determined (fig. 4.15).

From the examination of the curves, it can be observed that the rates of degradation increase with temperature. The low rates of degradation at low conversion may indicate that the polymer degrades to monomer by depropagation to monomer initiated at the chain ends, the initiation step being rate determining. The depropagation process may occur by an intramolecular interchange mechanism, ending by complete unzipping to monomer or by termination reaction yielding products of lower molecular weight which are either able to volatilise when the molecular weight is lower than the volatilisation threshold, at the temperature of degradation, or remain in the reaction medium to undergo further reaction. The decrease of the rates for each temperature may be due to the polymer sample being used up.

The considerable increase in rate with temperature and the appearance of carbon dioxide as a minor volatile product suggest that for higher temperatures than 300°C, the carbonate groups on the macromolecule are capable of undergoing reaction with the production of carbon dioxide. The splitting of a carbonate group gives very labile radicals which may readily react to produce polymer chain fragments and volatilise from the medium of the reaction.

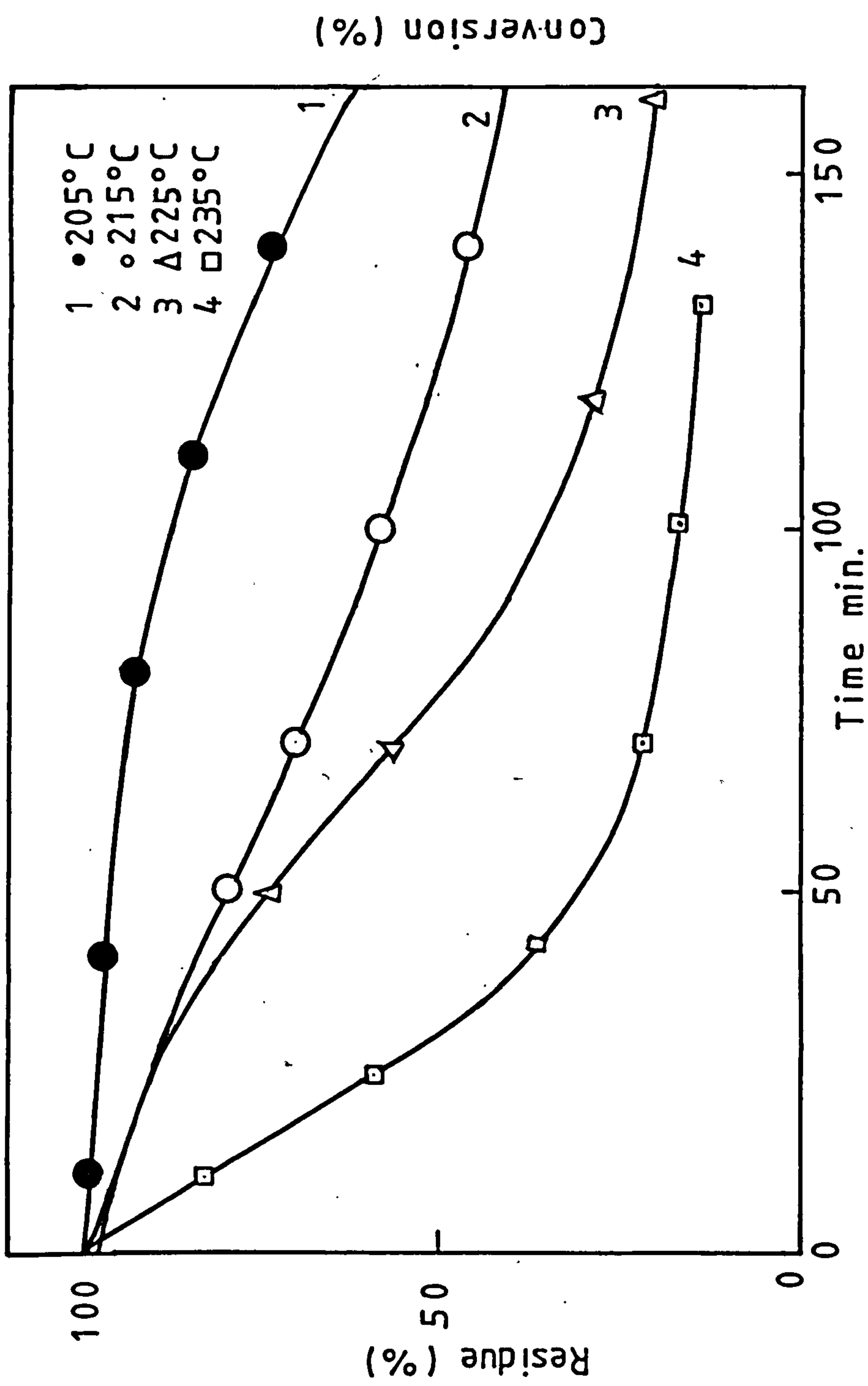


Fig.4.14 Percentages residue and conversion for poly(neopentylene carbonate) by TG in vacuum heated at different temperatures

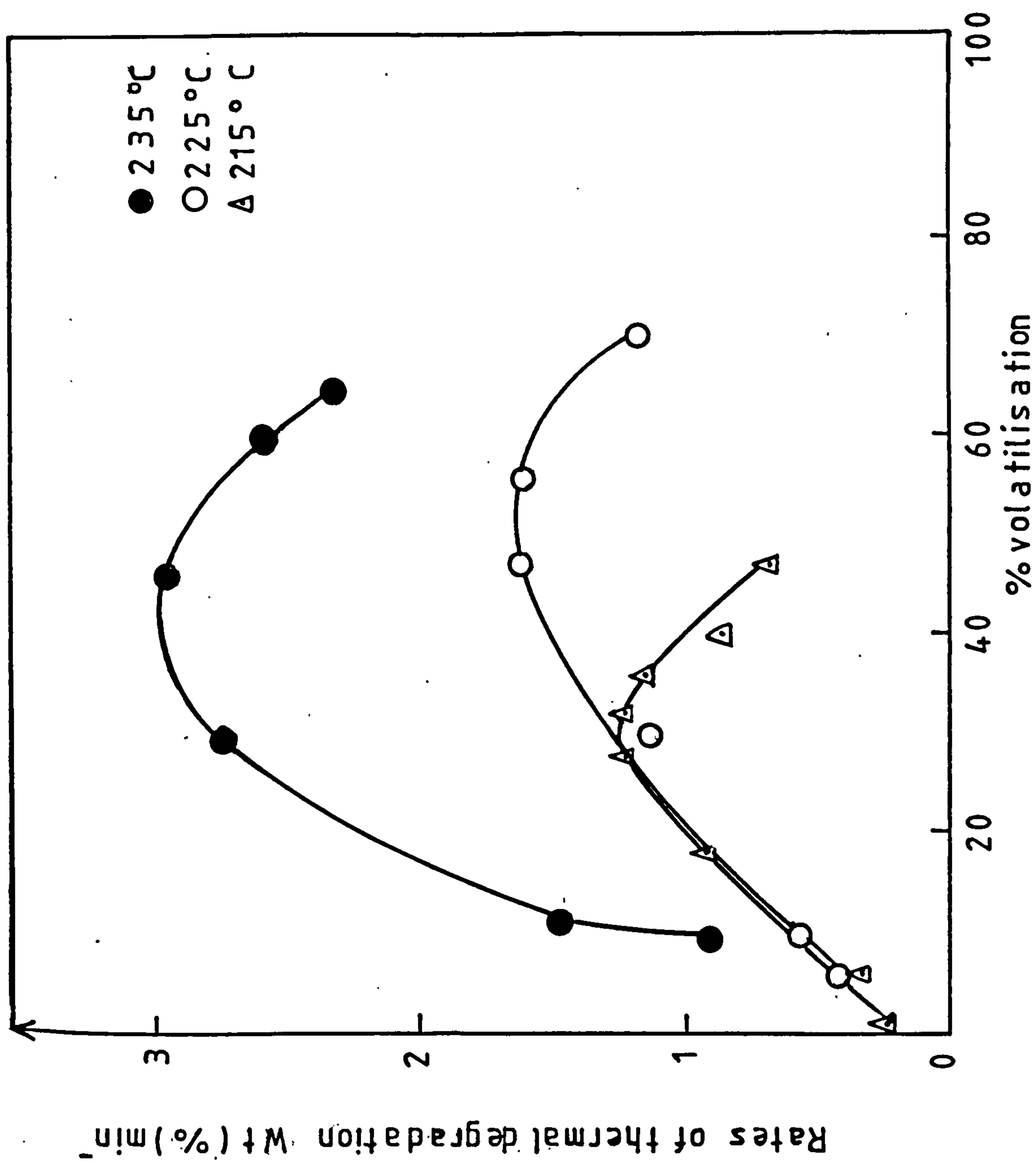


Fig.4.15 Rates of thermal degradation for poly (neopentylene carbonate) by TG in vacuum at 215° 225° and 235°C, respectively.

#### 4.3.3 Poly(2-phenyl-trimethylene carbonate)

Poly(2-phenyl-trimethylene carbonate) was heated by TG under vacuum at 250°, 255° and 260°C. Using these curves, plots of percentage of residue and extent of degradation versus time were made, fig. (4.16). By means of these plots the curves for degradation for poly(2-phenyl-trimethylene carbonate) versus percentage of volatilisation were derived (fig. 4.17).

It is evident that the rates of degradation increase with temperature. The initial low rates at low conversion may indicate that the polymer initially degrades at the chain ends, the initiation step being rate determining. As has already been observed by TVA, the main product of the degradation consists of short chain fragments which are likely to be formed by random chain scission of the polymer chains. The absence of depolymerisation to monomer in the case of Poly(2-phenyl-trimethylene carbonate) may be explained by the pendant phenyl group on the ring which probably hinders the formation of the six-membered ring. The continuous increase of the degradation rates can be explained by the volatilisation process of the lower molecular weight polymer chain fragments formed as the polymer sample is being degraded.

The considerable increase in rate with temperature and the appearance of volatile degradation products, e.g., carbon dioxide and  $\alpha$ -methyl styrene suggests that for higher temperatures than 307°C, the carbonate groupson the macromolecule are capable of undergoing reaction



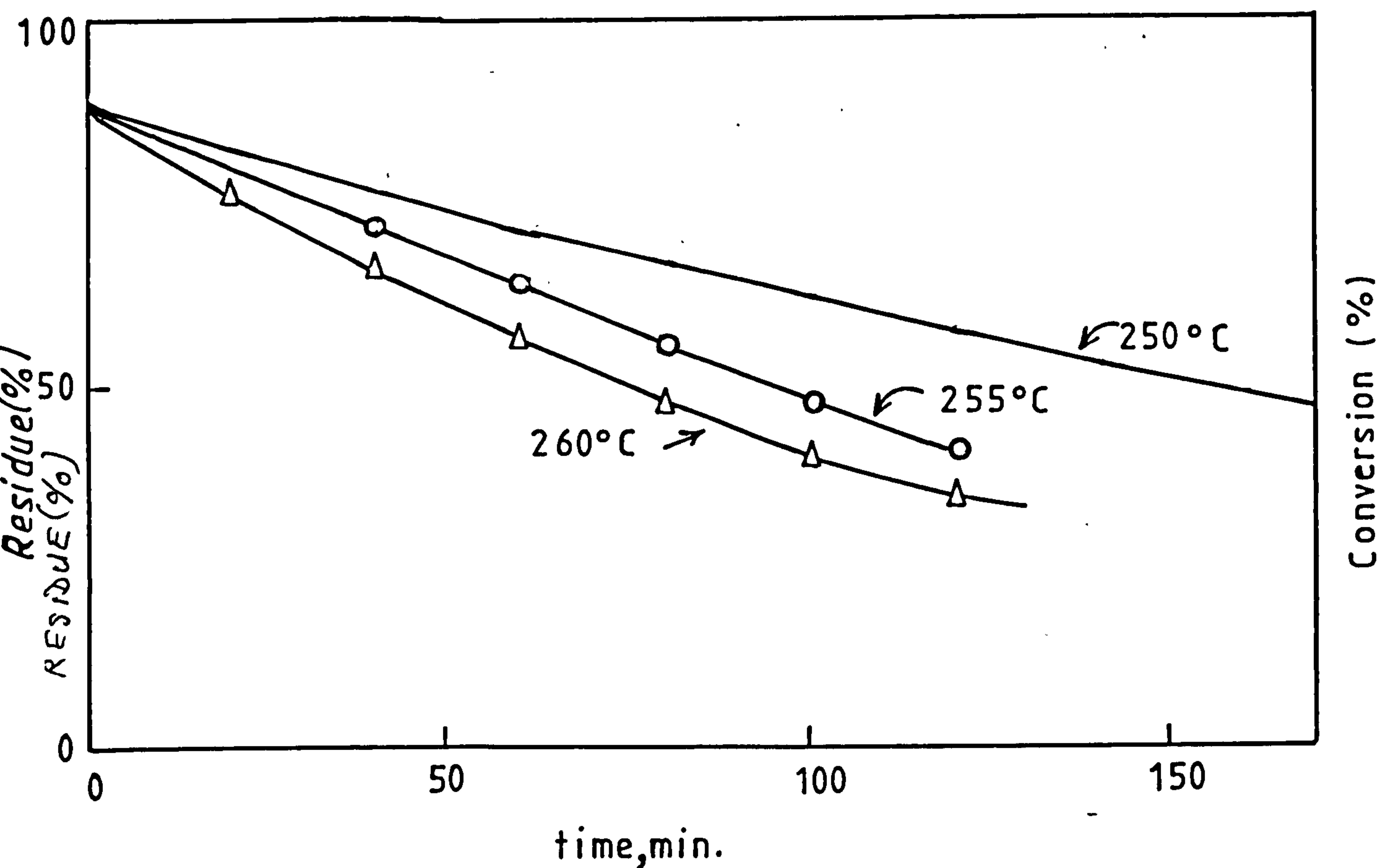


Fig. 4.16. Percentage of residue and conversion for poly (2-phenyl-trimethylene carbonate) by TG at 250°, 255° and 260°C respectively.

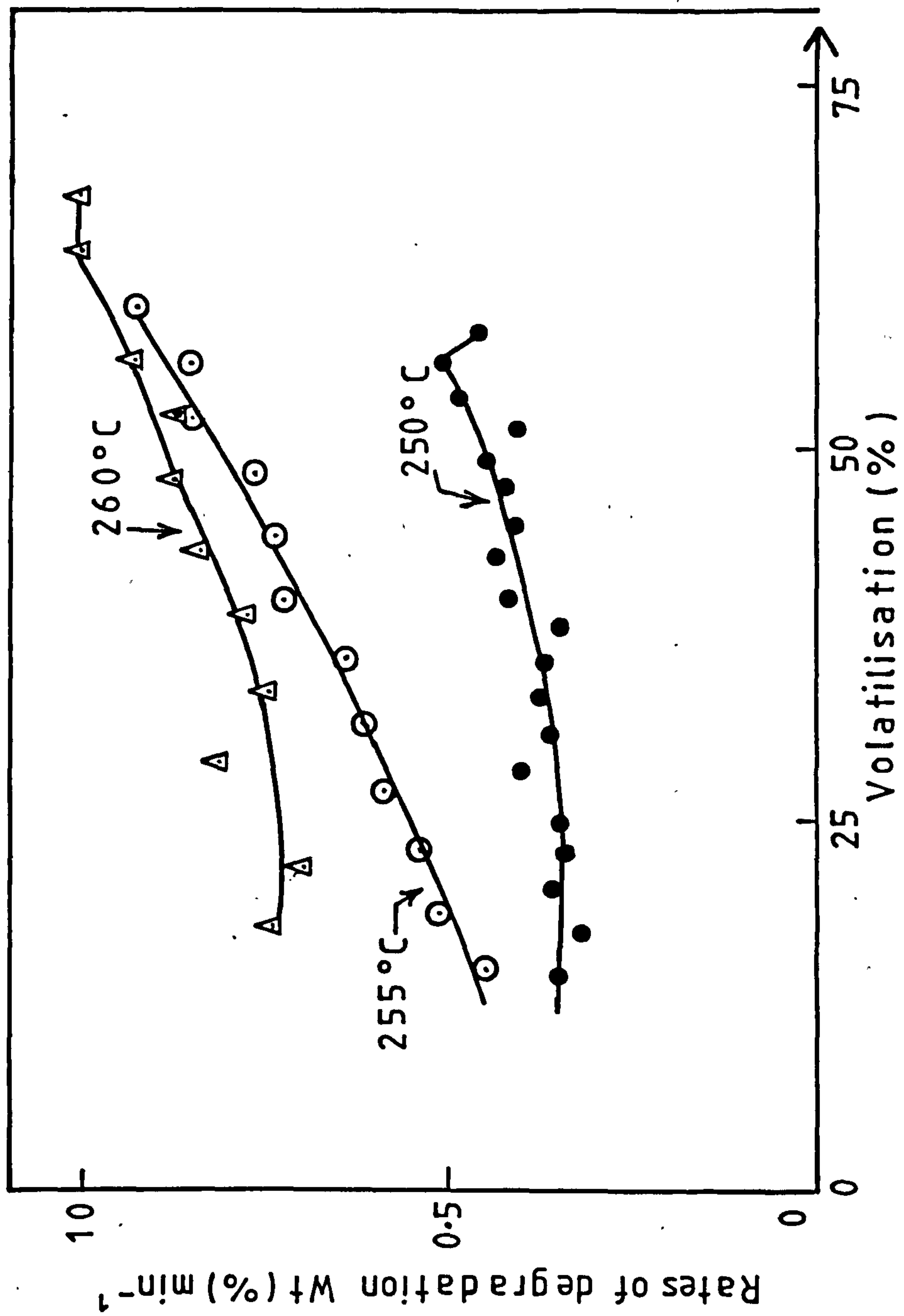


Fig. 4.17. Rates of thermal degradation for poly (2 - phenyl-trimethylene carbonate) by TG at 250°, 255° and 260°C respectively.

with the production of carbon dioxide, and  $\alpha$ -methyl styrene may be produced by secondary reactions of the reacting macromolecule.

#### 4.4 THERMAL STABILITY OF ACETYLATED ALIPHATIC POLYCARBONATES

Poly(trimethylene carbonate) and poly(neopentylene carbonate) were acetylated by the method described in Chapter 2 (see p.26). The thermal stability of the samples was assessed by thermogravimetry for  $N_2$  atmosphere. The TG curves for the original and acetylated polymers are shown in figs. 4.18 and 4.19.

For the acetylated poly(trimethylene carbonate) sample, the maximum rate of volatilisation is  $282^\circ C$ , about  $57^\circ C$  higher than for the original sample. For the acetylated poly(neopentylene carbonate) sample, the maximum rate of volatilisation is  $290^\circ C$  which is  $21^\circ C$  higher than the original sample.

Therefore, by acetylating the hydroxyl chain ends the polymer has a higher thermal stability.

This supports the view that degradation of poly(trimethylene carbonate) and poly(neopentylene carbonate) may be initiated at chain ends at low temperatures.

#### 4.5 THERMAL FRAGMENTATION BY MASS SPECTROMETRY OF ALIPHATIC POLYCARBONATES AND THEIR COLD RING FRACTIONS

The fragmentation pattern in the thermal decomposition of the aliphatic polycarbonates prepared and the solid degradation product obtained by TVA were studied by direct pyrolysis in the mass spectrometer ( $70\text{ ev}$  electron energy). Results, from the two techniques,

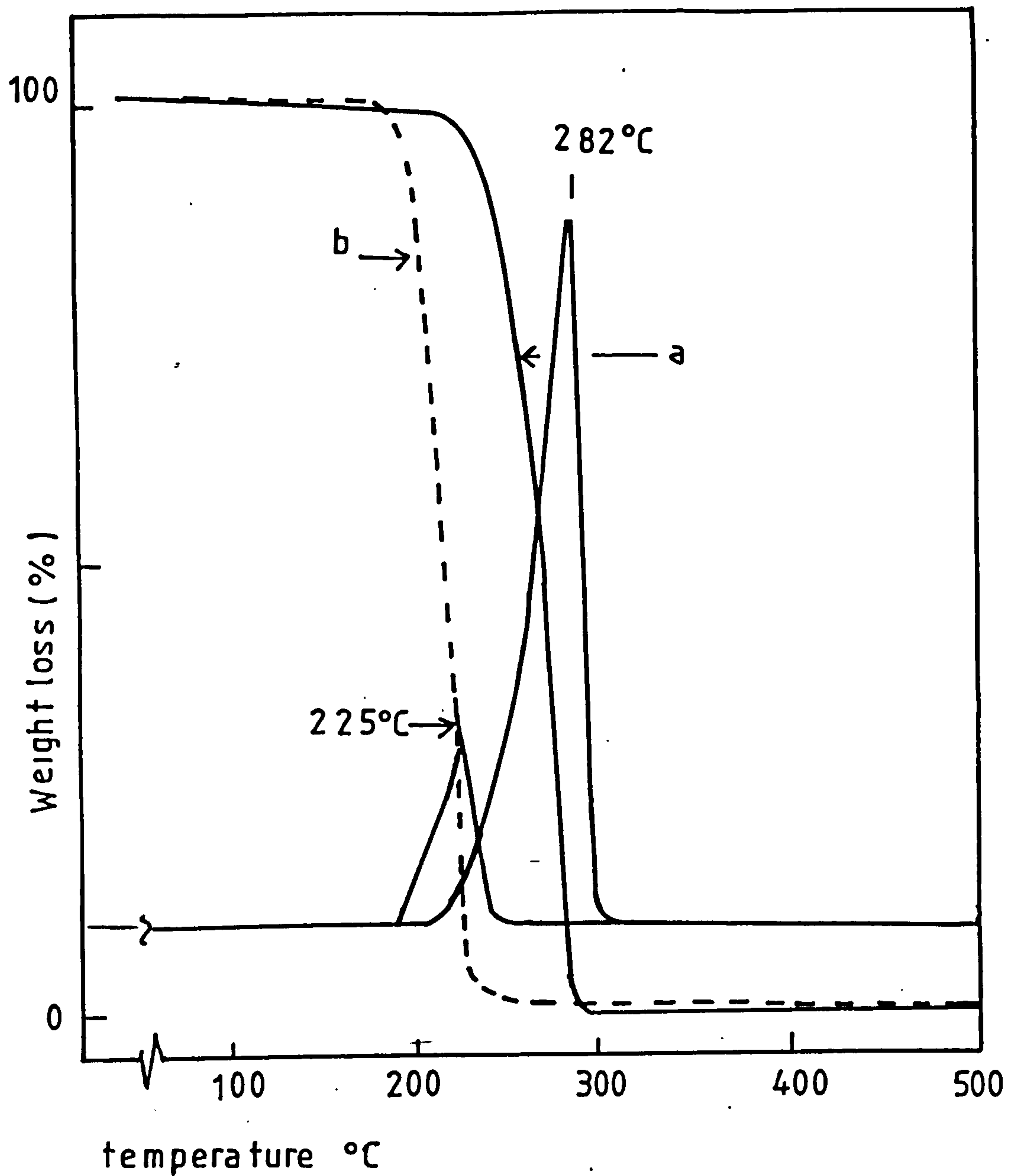


Fig. 4.18. TG curves for poly(trimethylene carbonate) heated to 500° in N<sub>2</sub> atmosphere  
(a) acetylated polymer (b) original polymer

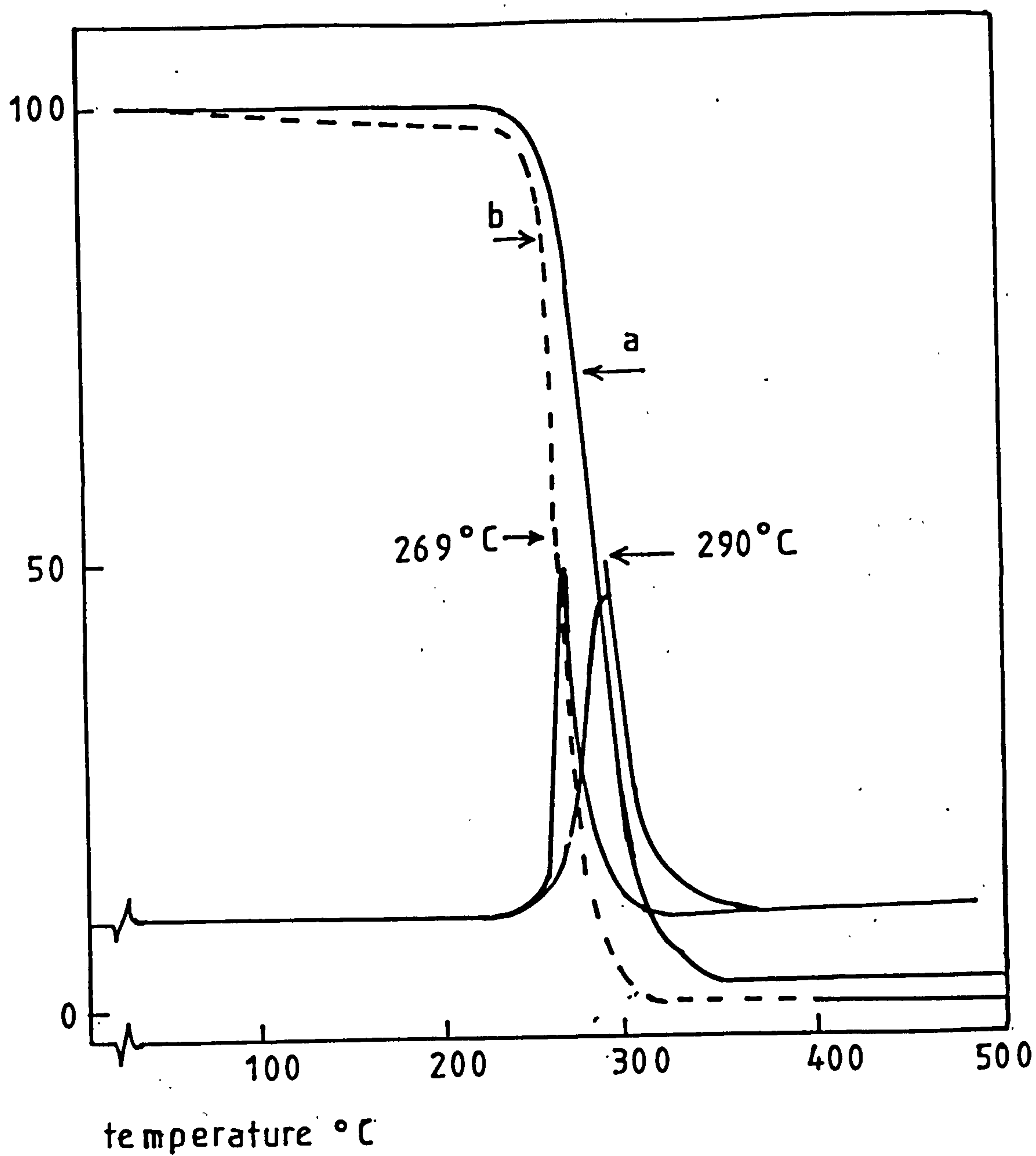


Fig.4.19. TG curves for poly (neopentylene carbonate) heated at 500°C at a heating 10°C/min  
(a) Acetylated sample (b) original sample



TVA and mass spectrometry, are compared.

#### 4.5.1 The Mass Spectrum of Degraded Poly(trimethylene carbonate) and its Cold Ring Fraction

The fragmentation pattern by electron impact for poly(trimethylene carbonate) (fig. 4.20) exhibits peaks up to  $m/e$  306. Other main peaks are at  $m/e$  205, 161, 102 (100%), 63, 59, 58, 57, 44, 41. The base peak at  $m/e$  102 is attributed to the presence of the cyclic monomer. The stability to electron impact of this structure accounts for the high relative intensity of the peak, which also indicates that it is the main decomposition product. The spectrum also gives evidence for the formation of short chain fragments (peak at  $m/e$  306, 206, 161). It is likely they are produced by random chain scission at the carbonate groups on the macromolecule. The smaller peaks at  $m/e$  69, 59, 58, 57, 44, 41 may be formed from the progressive further fragmentation of these short chain fragments.

The spectral data agree well with the evidence already obtained by thermal volatilisation analysis. The main product of degradation is the cyclic monomer. This indicates that the ester interchange mechanism is the main mode of degradation.<sup>2</sup> At higher temperatures in TVA, random chain scission is also observed, producing short chain fragments. It is likely that this occurs by cleavage of the carbonate group with the formation of carbon dioxide.

Brown and Djerassi<sup>64</sup> proposed a fragmentation mechanism for the compound di-n-propyl-carbonate which could also explain some peaks in the mass spectrum of poly(trimethylene carbonate).

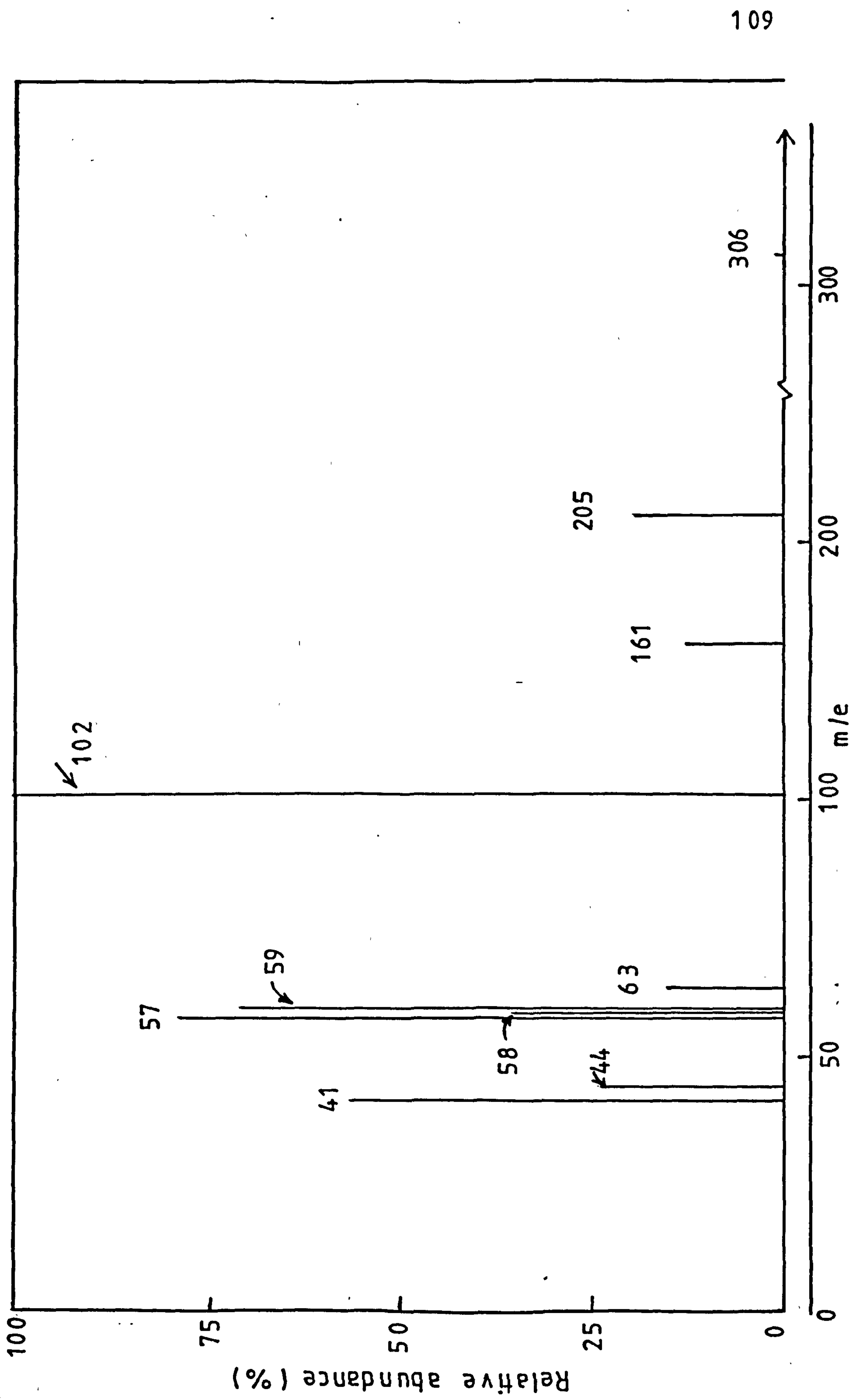
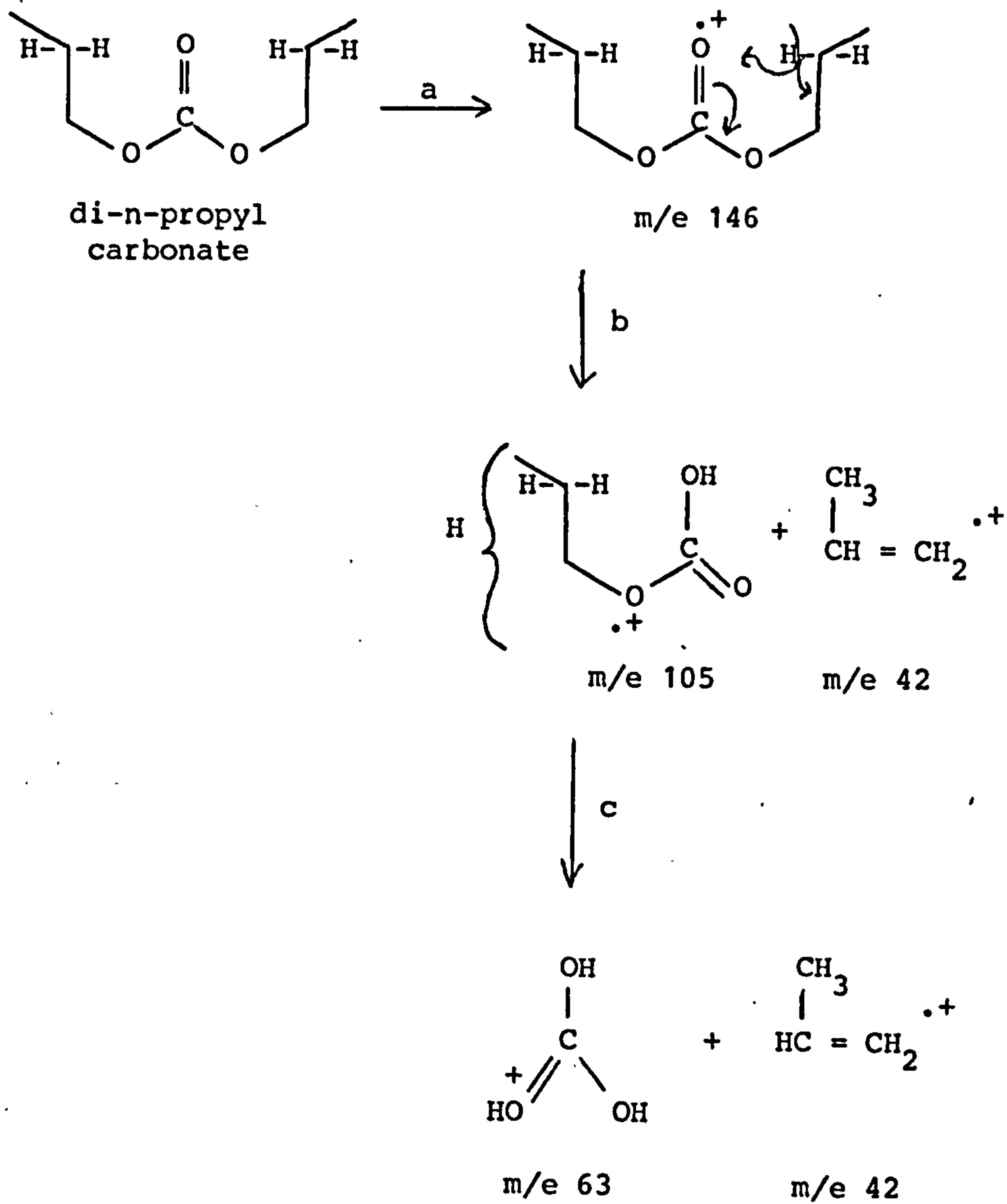
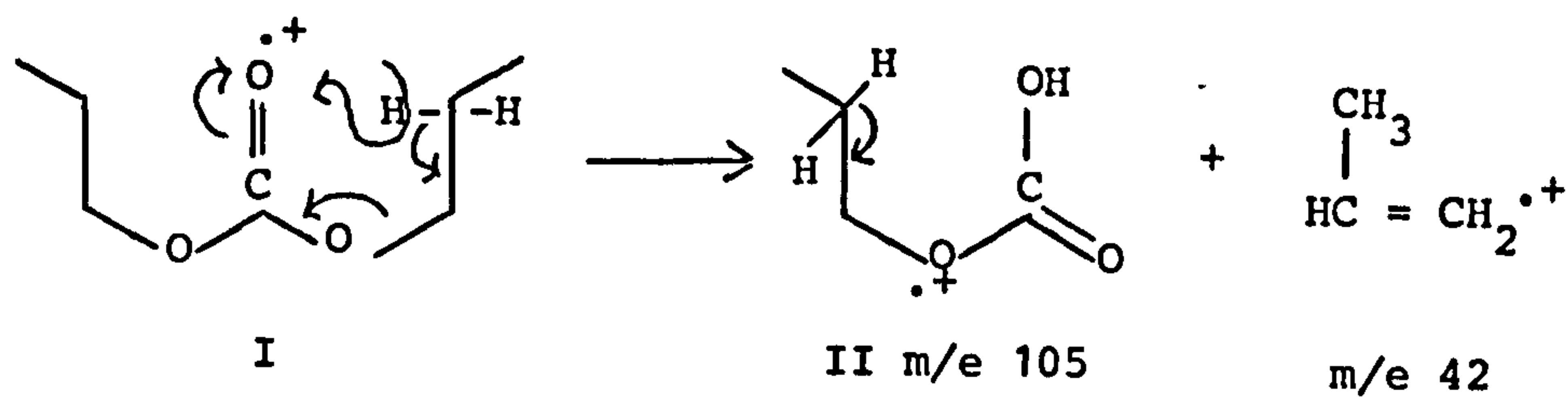


Fig 4.20 Mass spectrum (70 eV) of the products of the degradation for poly(trimethylene carbonate)

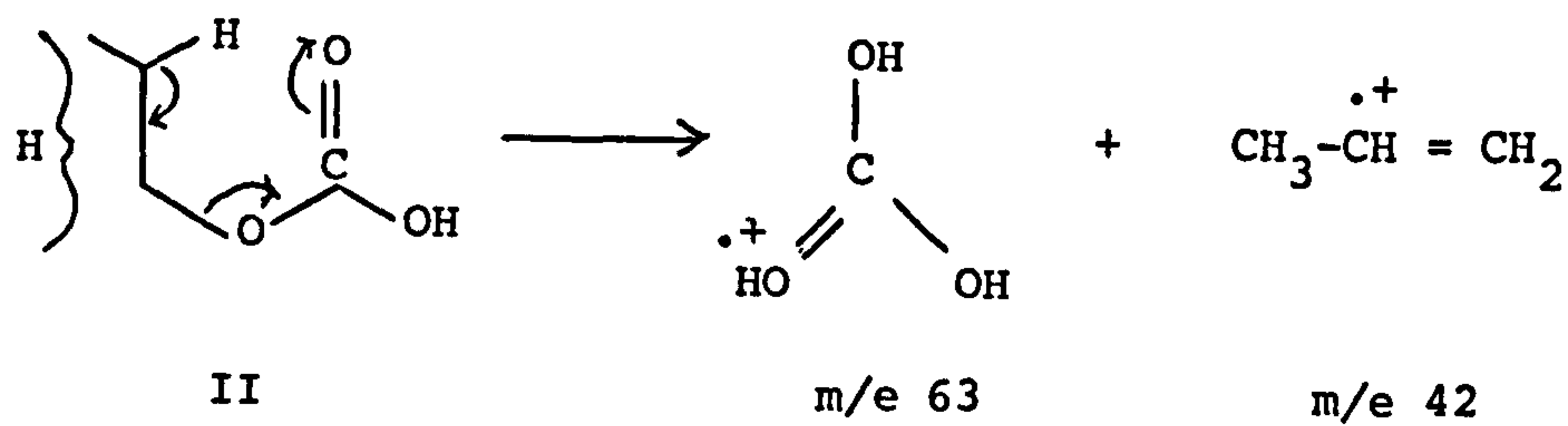
The fragmentation pattern of di-n-propyl carbonate is represented as:



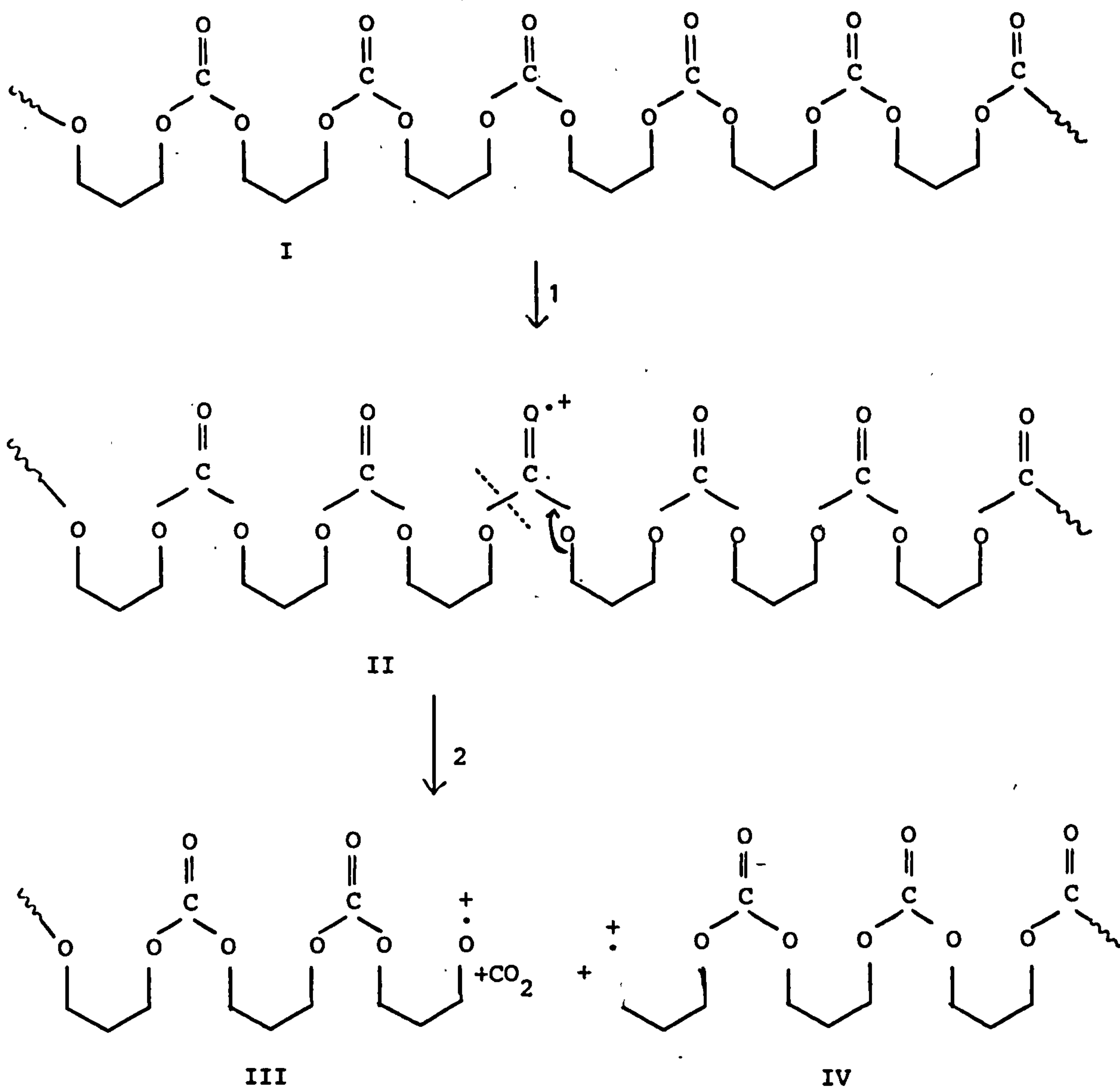
Another possible explanation may be a McLafferty rearrangement and a single hydrogen transfer,



the second step could be represented as an ether oxonium ion type of fragmentation of II

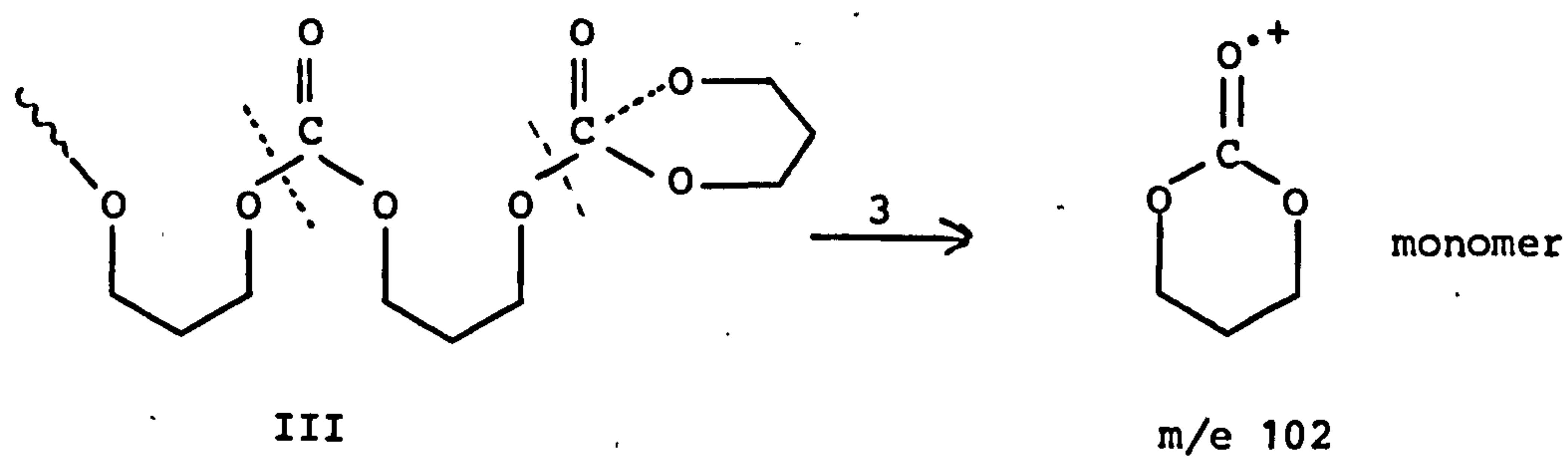


In the polymer the fragmentation to form the cyclic monomer and the short chain fragments may be represented as follows:

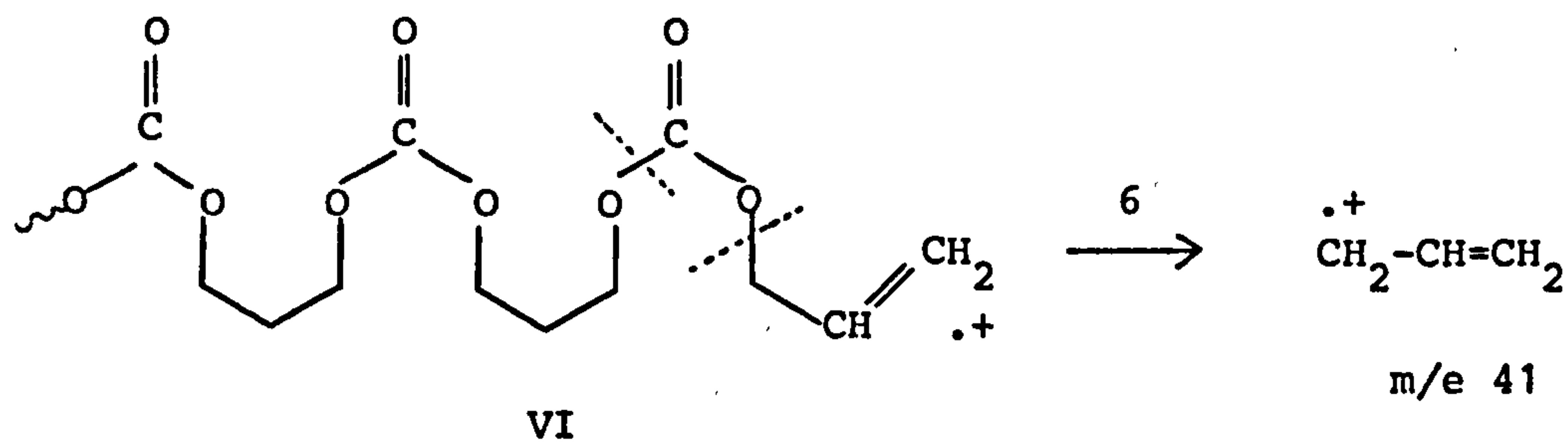
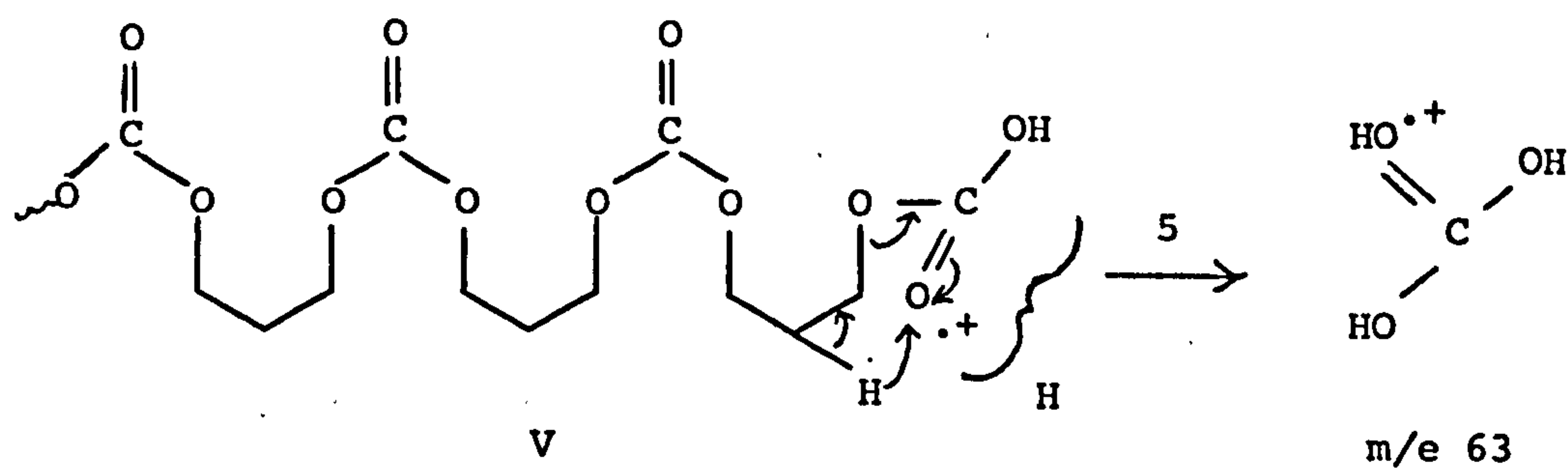
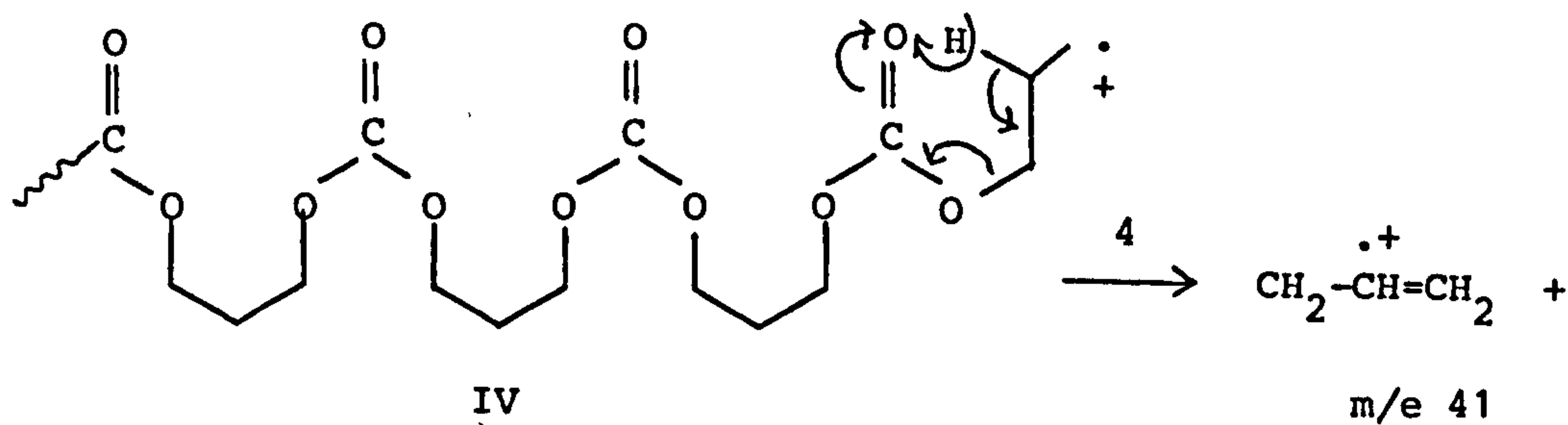


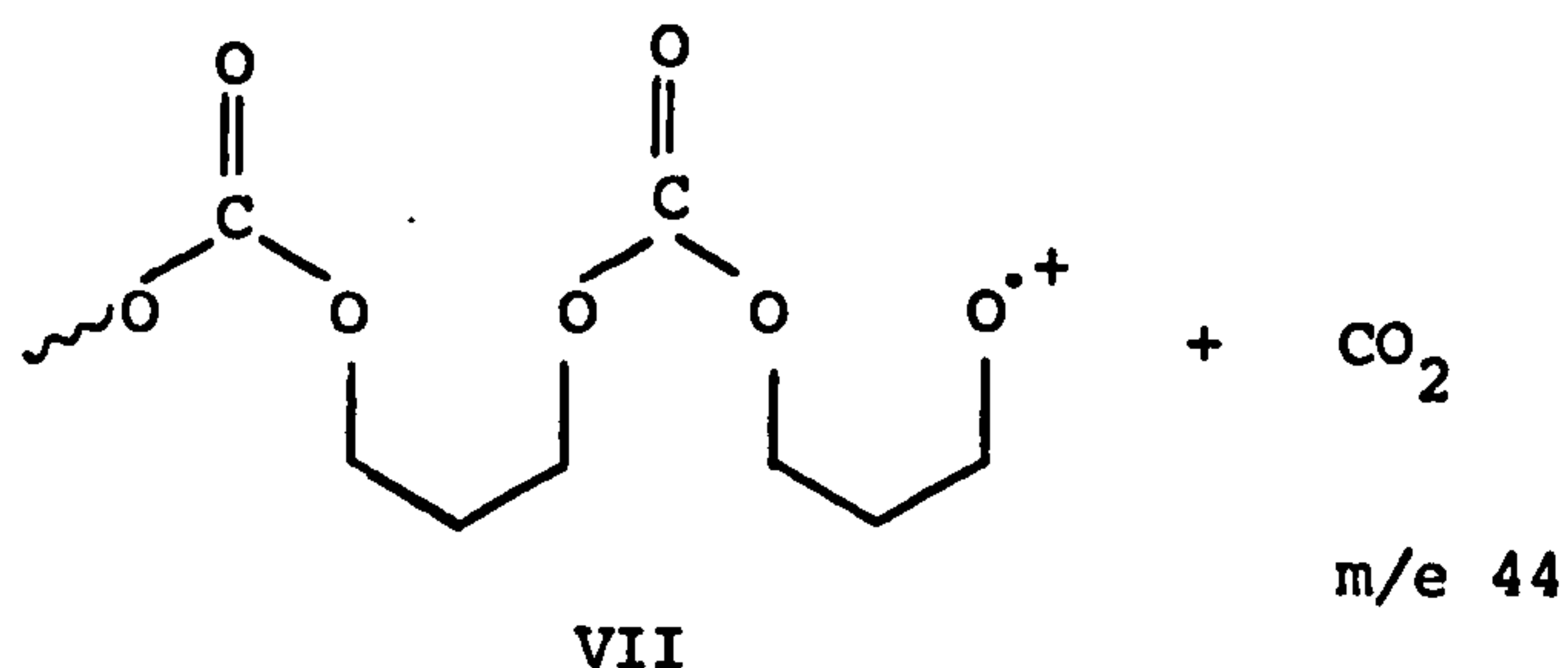
Short chain fragment ion III may be responsible for the formation of the cyclic monomer by an ester interchange mechanism.



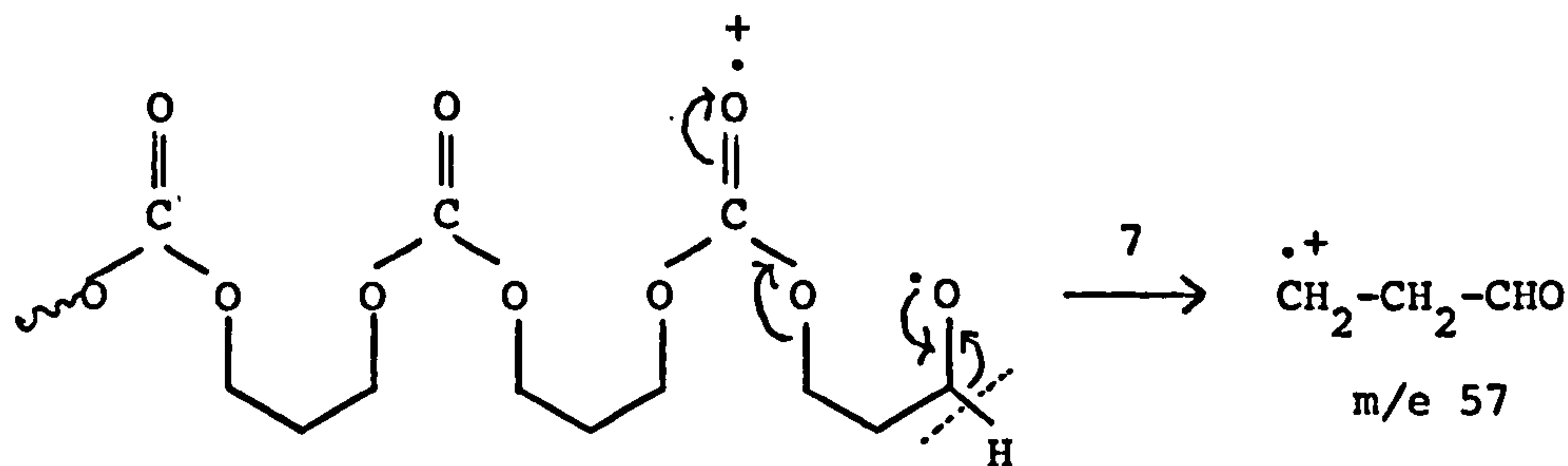


Short chain fragment ion IV may undergo a fragmentation similar to the model compound di-n-propyl-carbonate





Fragment ion VII could form cyclic monomer by ester interchange process, or may be responsible for the formation of other main fragment ion, m/e 57, through another type of fragmentation.



The mass spectrum of the solid degradation product (CRF) formed in TVA consists of peaks similar to those of the mass spectrum of the monomer. The most prominent peaks are at 102, 59, 58, 57 (base peak) 44, 43, 42, 41.

#### 4.5.2 The Mass Spectrum of Degraded Poly(neopentylene carbonate) and its Cold Ring Fraction

The mass spectrum for poly(neopentylene carbonate) (fig. 4.21) exhibits peaks up to m/e 279. Other main peaks are at m/e 149, 131, 130, 87, 73, 71, 69, 57, 56, 55, 44, 43, 41 (100%). The peak at m/e 130 is attributed to the presence of the monomer. The spectrum indicates

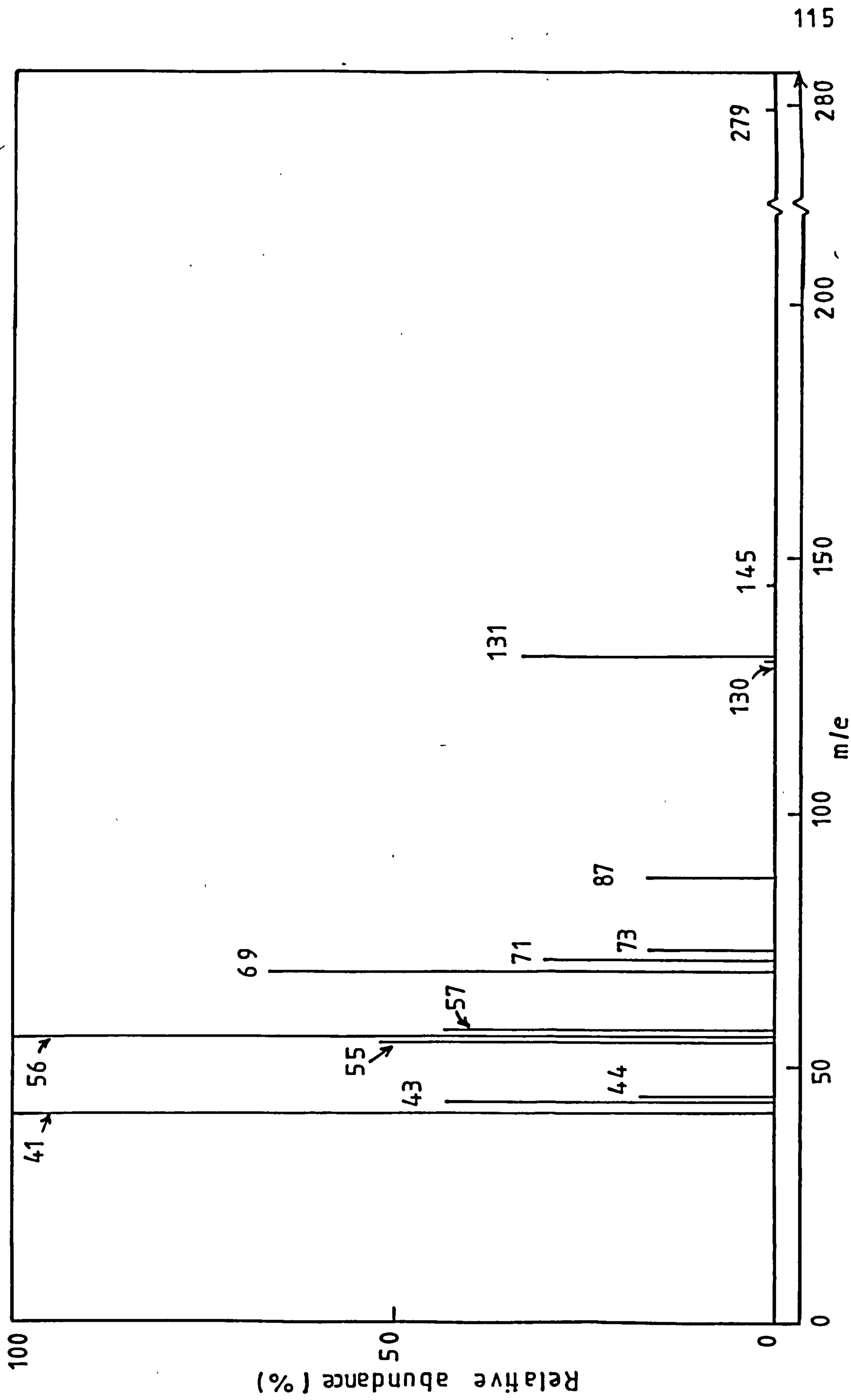


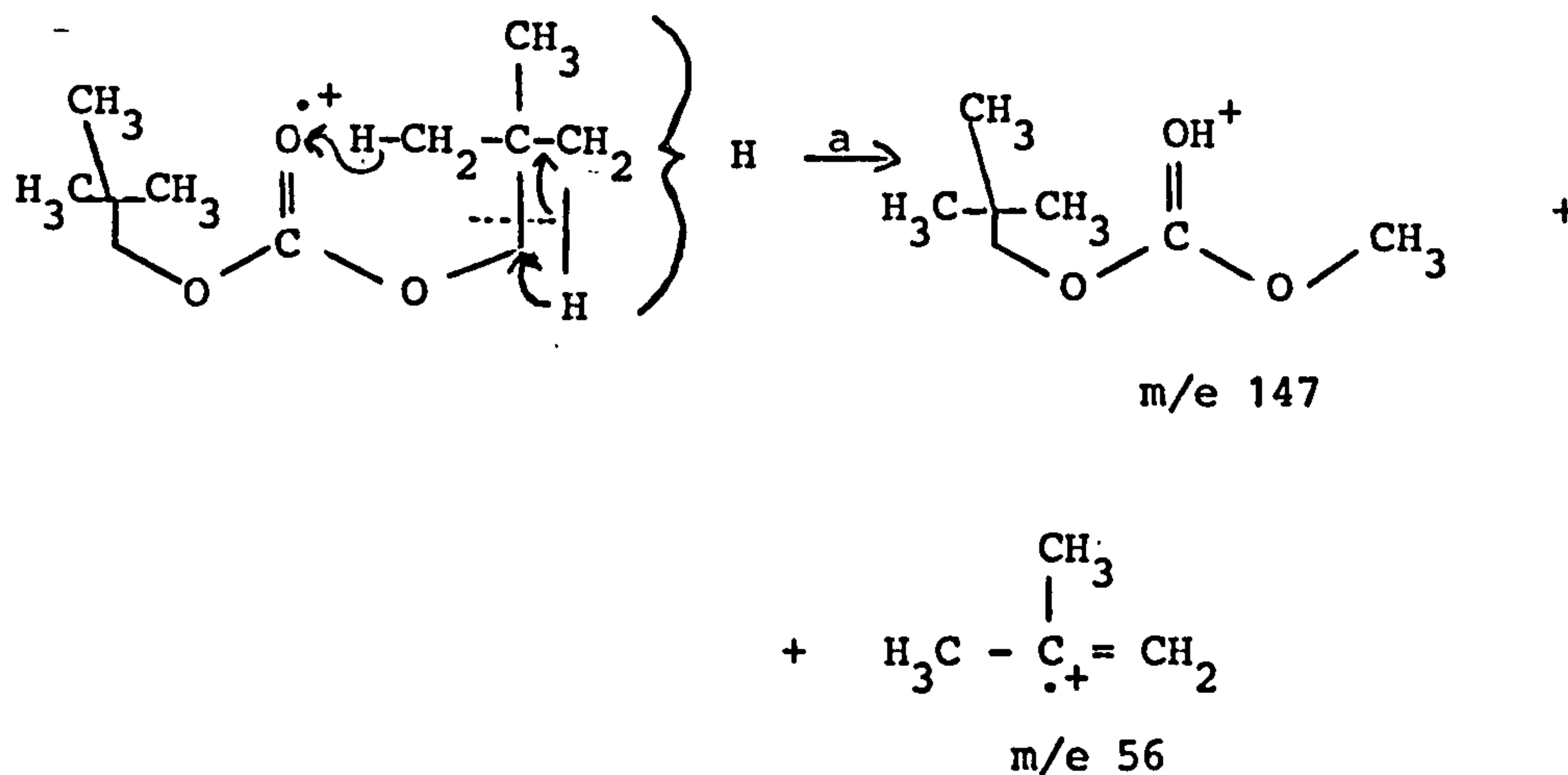
Fig. 4.21. Mass spectrum of the products of the thermal degradation for poly(neopentylene carbonate)

The presence of fragment ions which may be formed by progressive further fragmentation from short chain fragments.

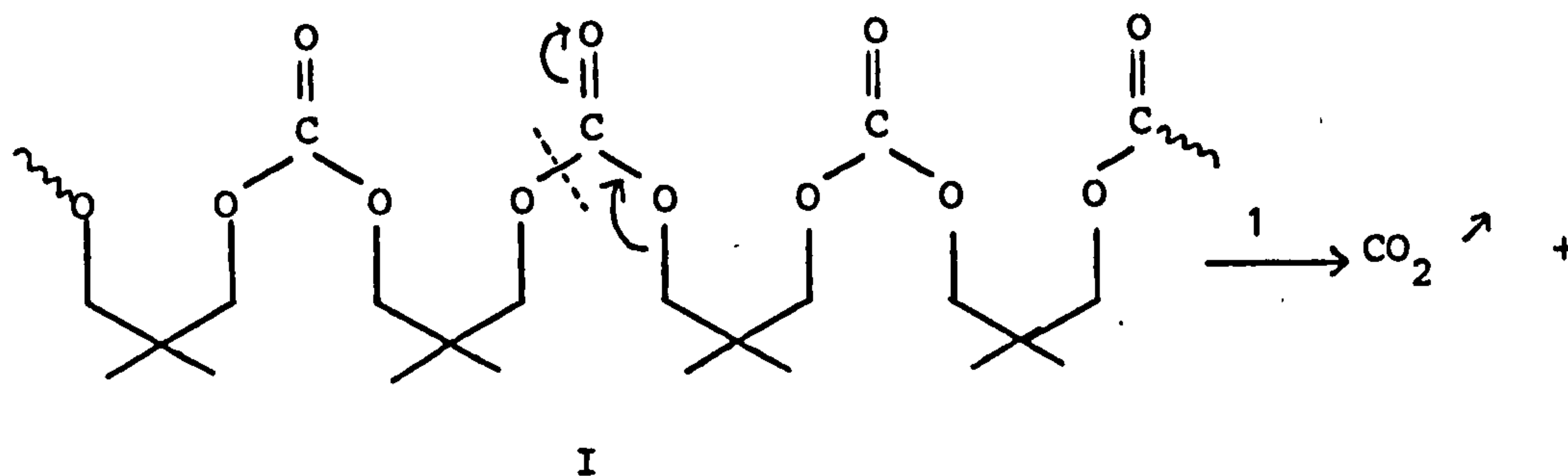
TVA showed the main degradation product to be the cyclic monomer, indicating that intramolecular ester interchange reaction is the main mode of degradation. At higher temperatures in TVA a random chain scission is also observed producing oligomeric fragments.

The spectral data for this polymer shows that the cyclic monomer is not an abundant fragment ion (1.07%). This indicates that possibly another mechanism of degradation may be involved when the polymer is degraded by electron impact in the spectrometer.

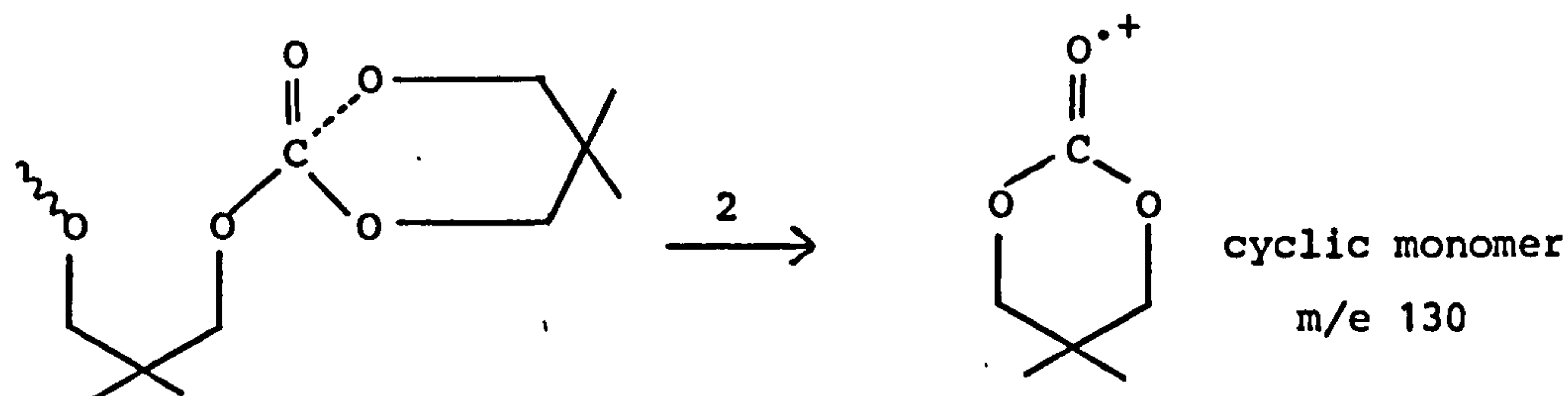
Brown and Djerassi<sup>64</sup> proposed a mechanism for the model compound di-neopentyl carbonate, represented as:



In the case of the polymer the mechanism of fragmentation of the polymer to give the cyclic monomer and fragment ions may be explained as follows:

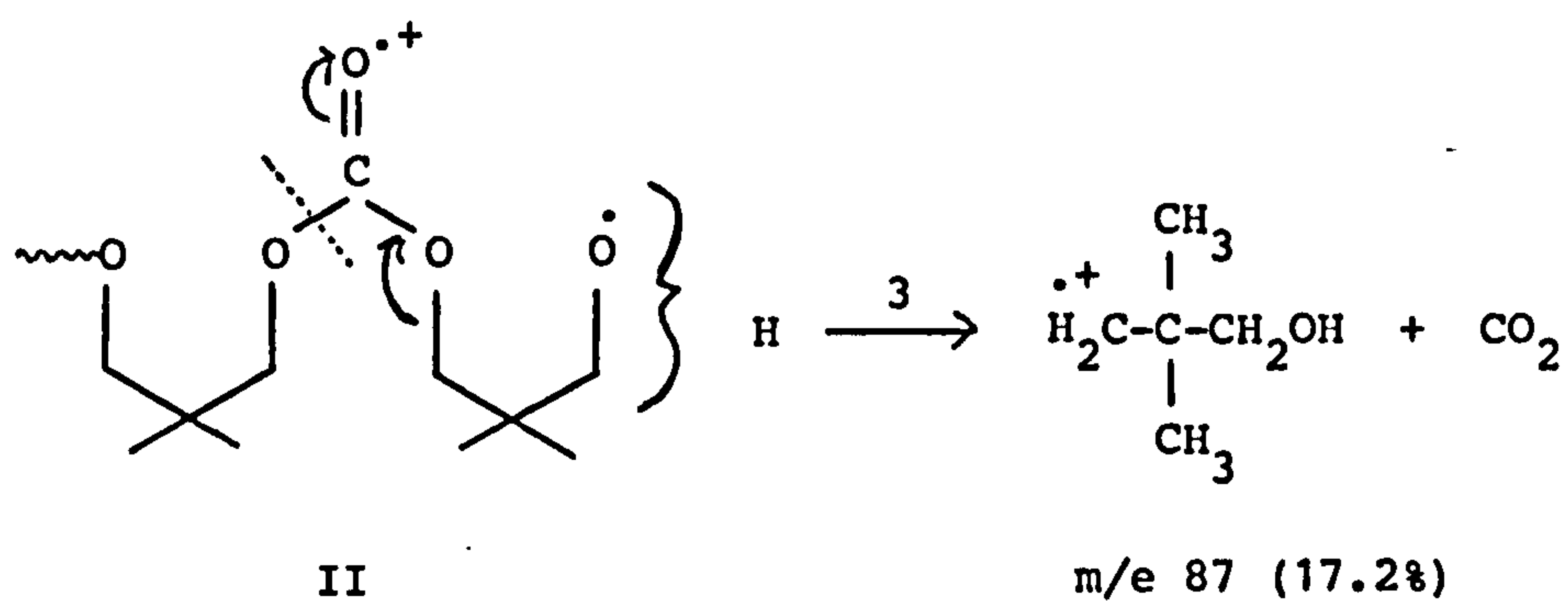


Short chain fragment ion II could undergo an ester interchange mechanism with formation of the cyclic monomer.

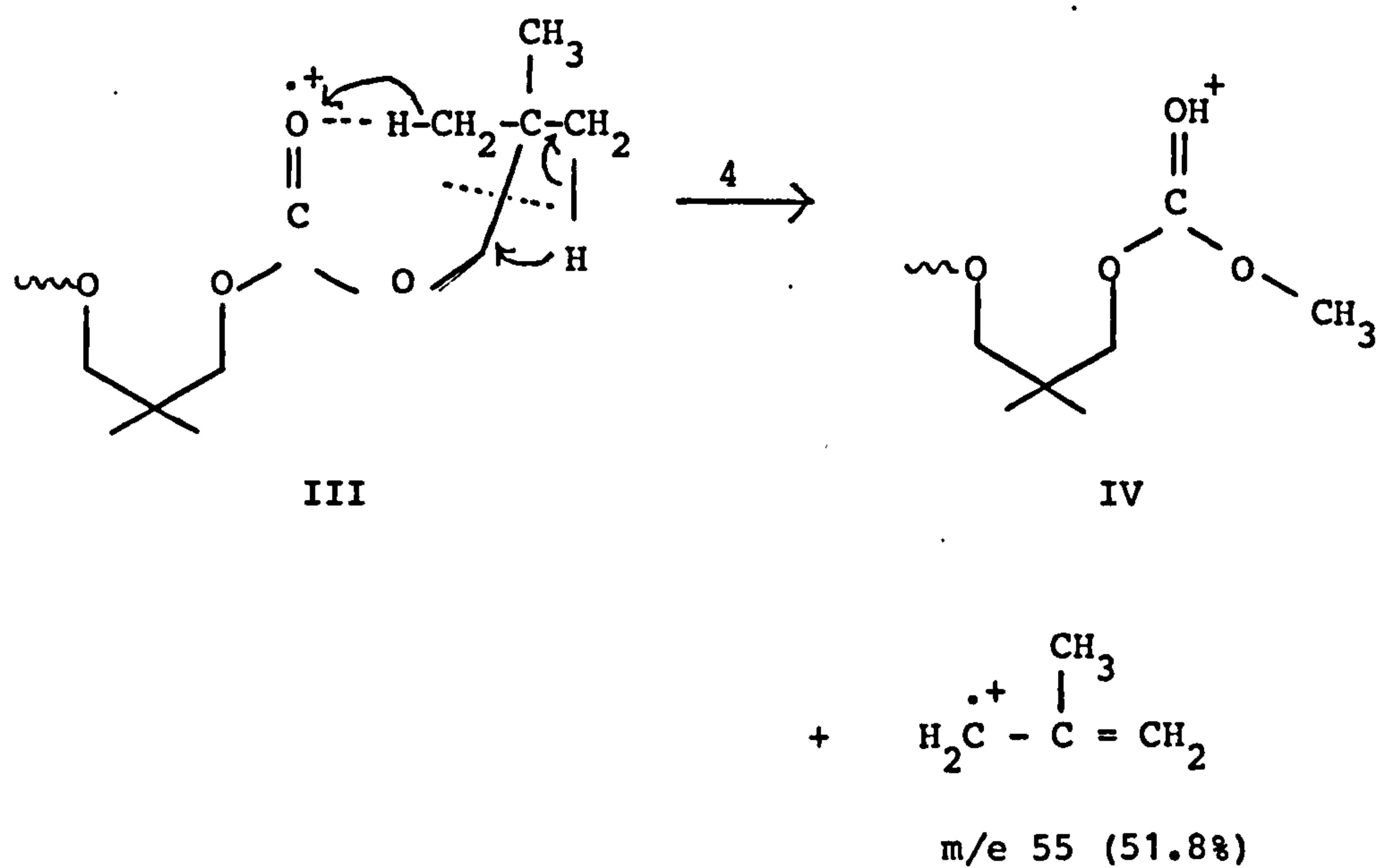


Short chain fragment ion II could undergo another type of fragmentation to give another fragment ion

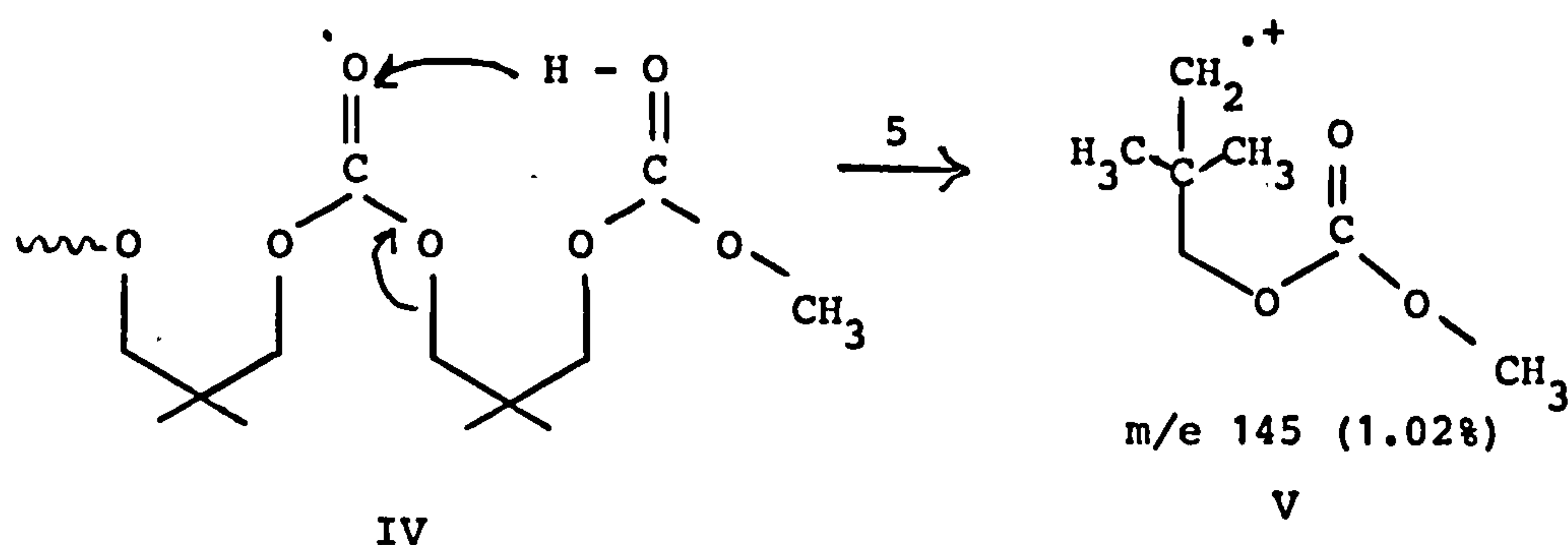




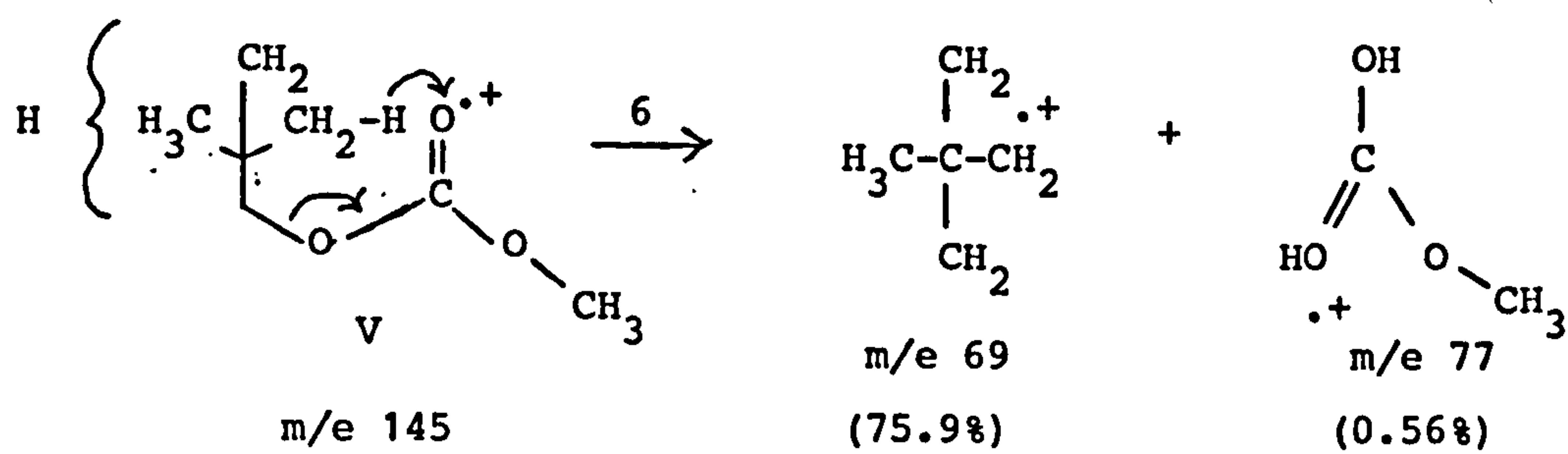
Short chain fragment ion III may be responsible for the formation of peak m/e 55



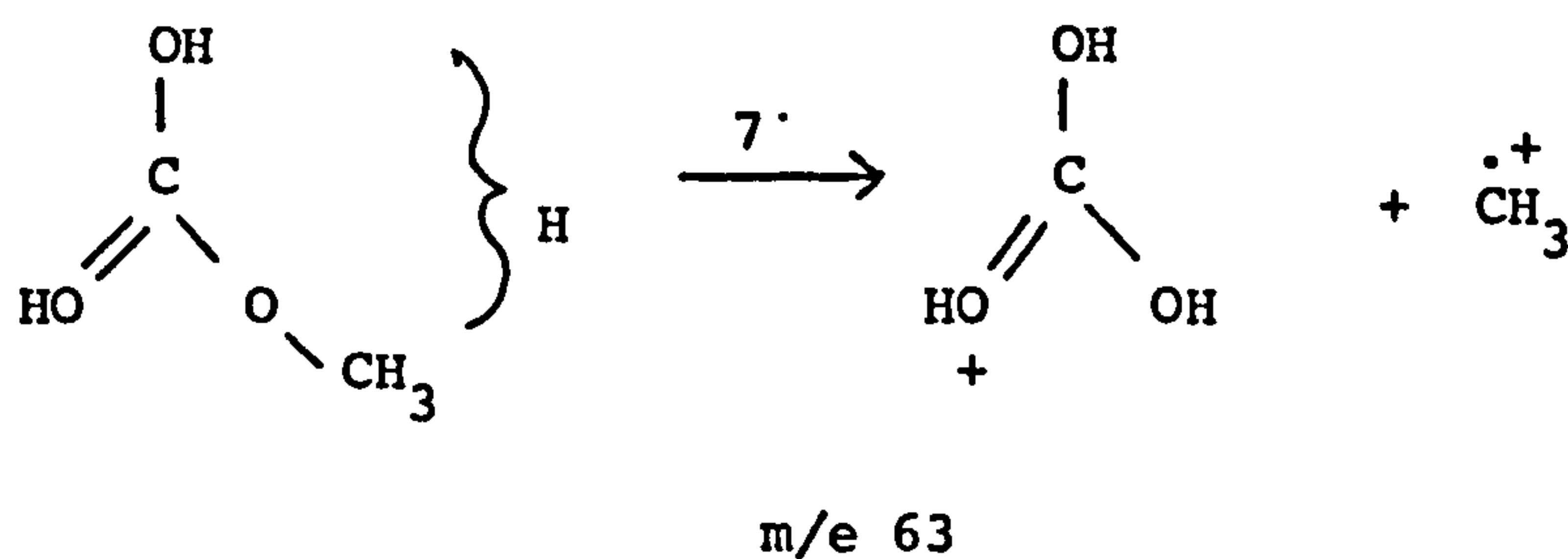
A further fragmentation of the short chain fragment ion IV could be represented as follows:



Fragment ion  $m/e$  145 could originate peak at  $m/e$  69 (75%)



Peak at  $m/e$  77 could undergo further fragmentation to give peak at  $m/e$  63

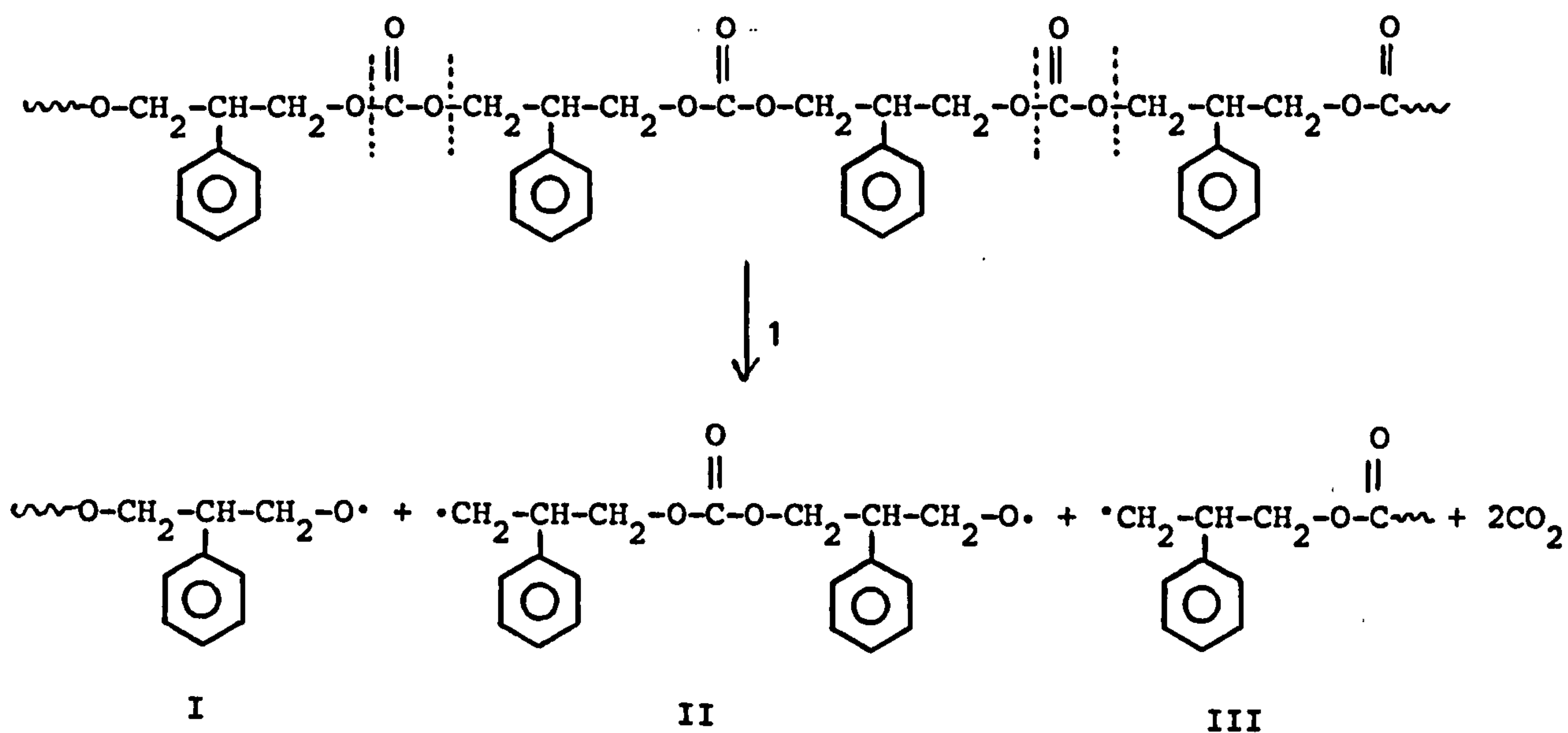


The fragmentation pattern of the solid product of degradation (CRF) obtained in TVA degradation exhibits peaks up to  $m/e$  131. Other prominent peaks are at 87, 85, 73, 72, 71, 69, 57, 56, 55, similar to the mass spectrum of the pure monomer.

#### 4.5.3 Mass Spectrum for Poly(2-phenyl-trimethylene carbonate)

The mass spectrum for the polymer degraded by electron impact (fig. 4.22) shows the largest peak at  $m/e$  215. Other major peaks are at  $m/e$  214, 178, 170, 169, 163, 142, 141, 118, 117, 105, 104 (base peak), 103, 91, 79, 78, 77, 65, 51, 44.

The fragmentation pattern obtained indicates that this polymer gives mainly by thermal decomposition fragment ions, probably formed from larger short chain fragments formed of 2, 3, 4 or more structural units. The molecular ions of these oligomers do not appear in the mass spectrum probably because of the instability of these partially aliphatic structures to E.I. From the TVA experiments, the main product of degradation obtained was short chain fragments which may be explained by a chain scission reaction at the carbonate group on the macromolecule. The primary fragmentation may be due to the characteristic loss of carbon dioxide.



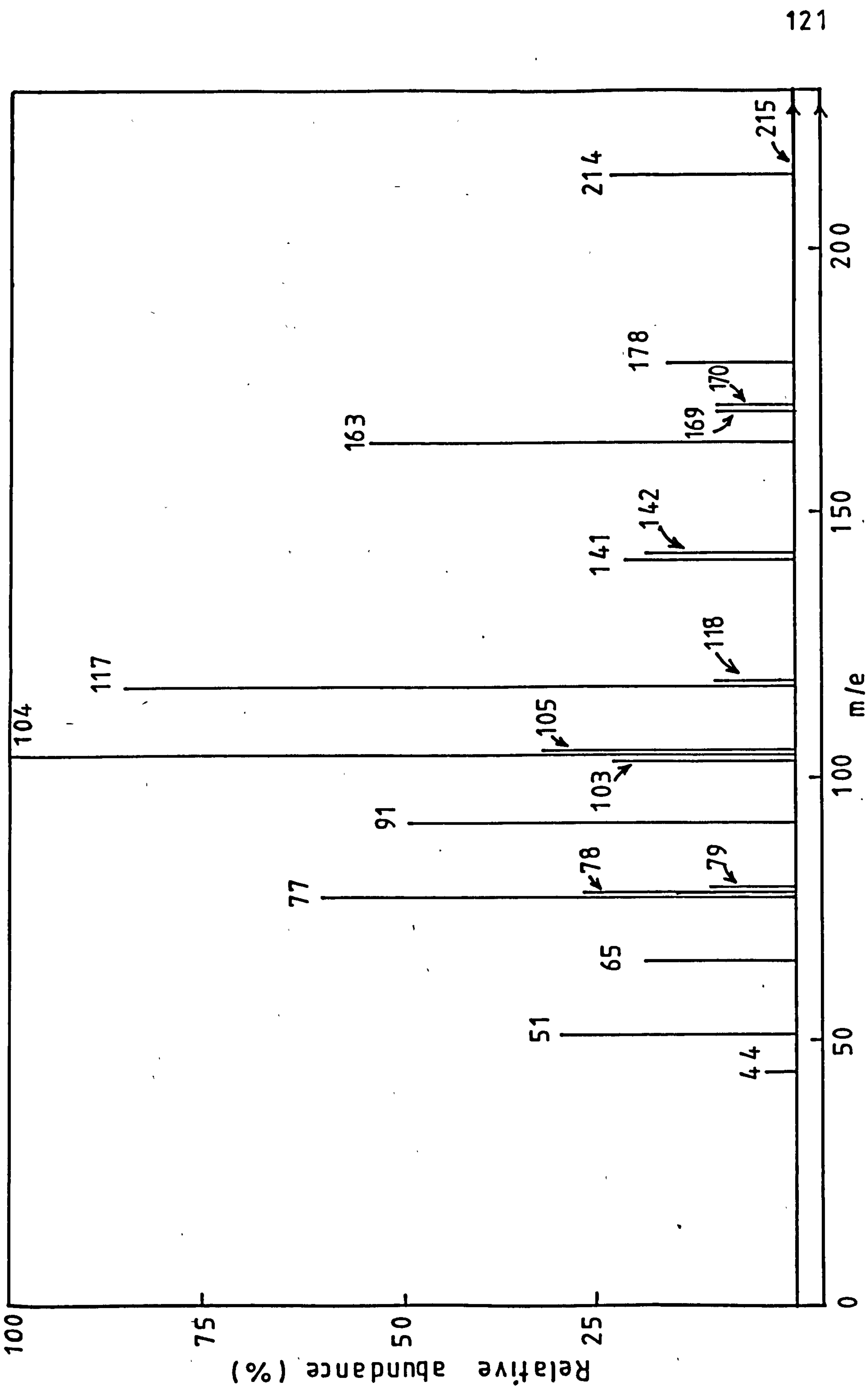
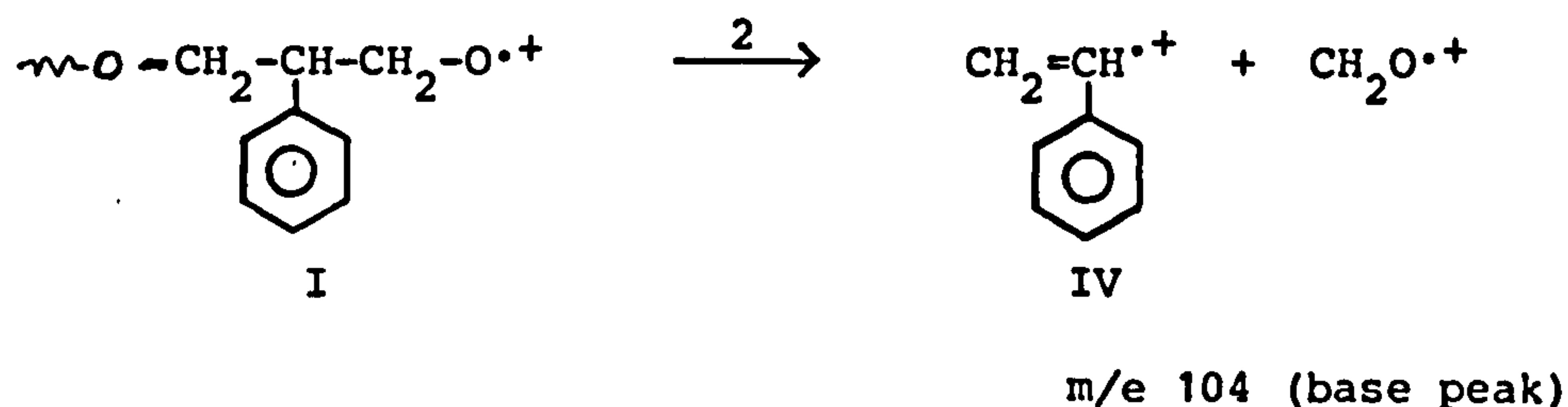


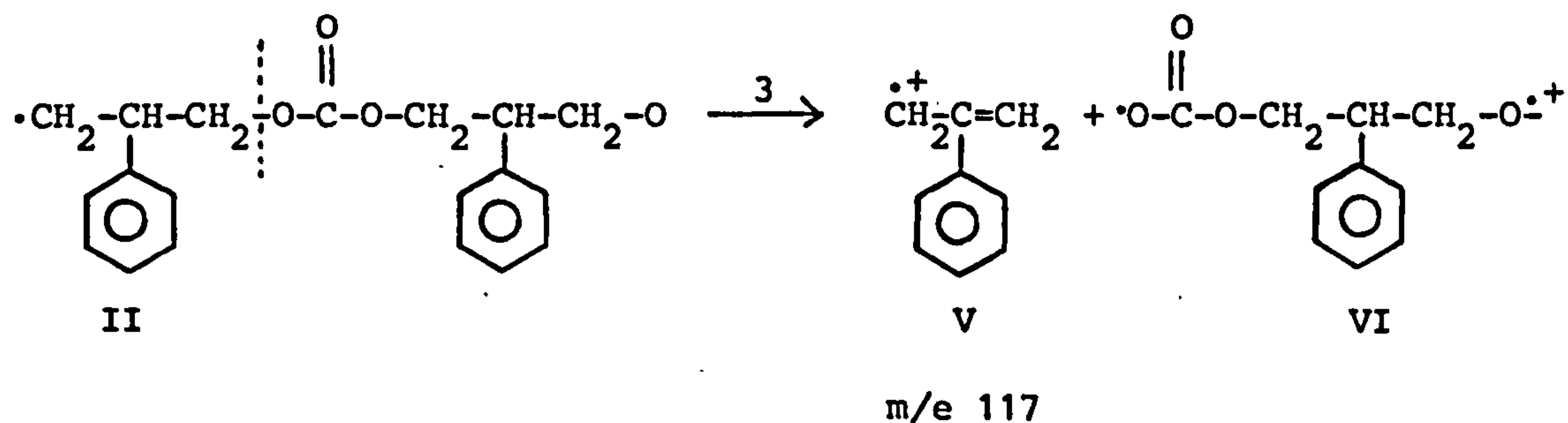
Fig. 4.22. Mass spectrum of the products of thermal degradation for poly (2-phenyl trimethylene carbonate)

The fragment ion I could undergo a further fragmentation to form fragment ions at m/e 104 and fragment m/e 30



The stability to EI of this structure IV accounts for the high relative intensity observed.

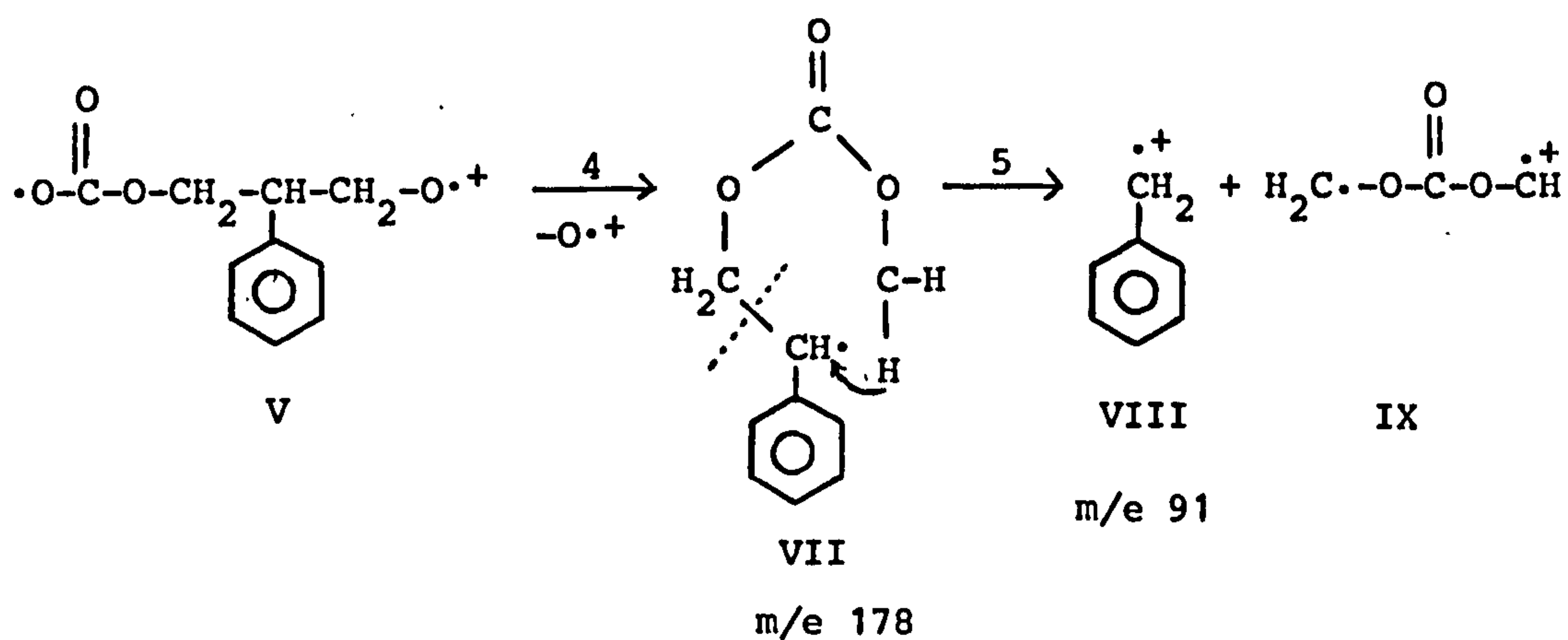
By further fragmentation of II fragment ion m/e 117 (84.98%) may be formed



The stability to EI of this structure V accounts for the high relative intensity observed.

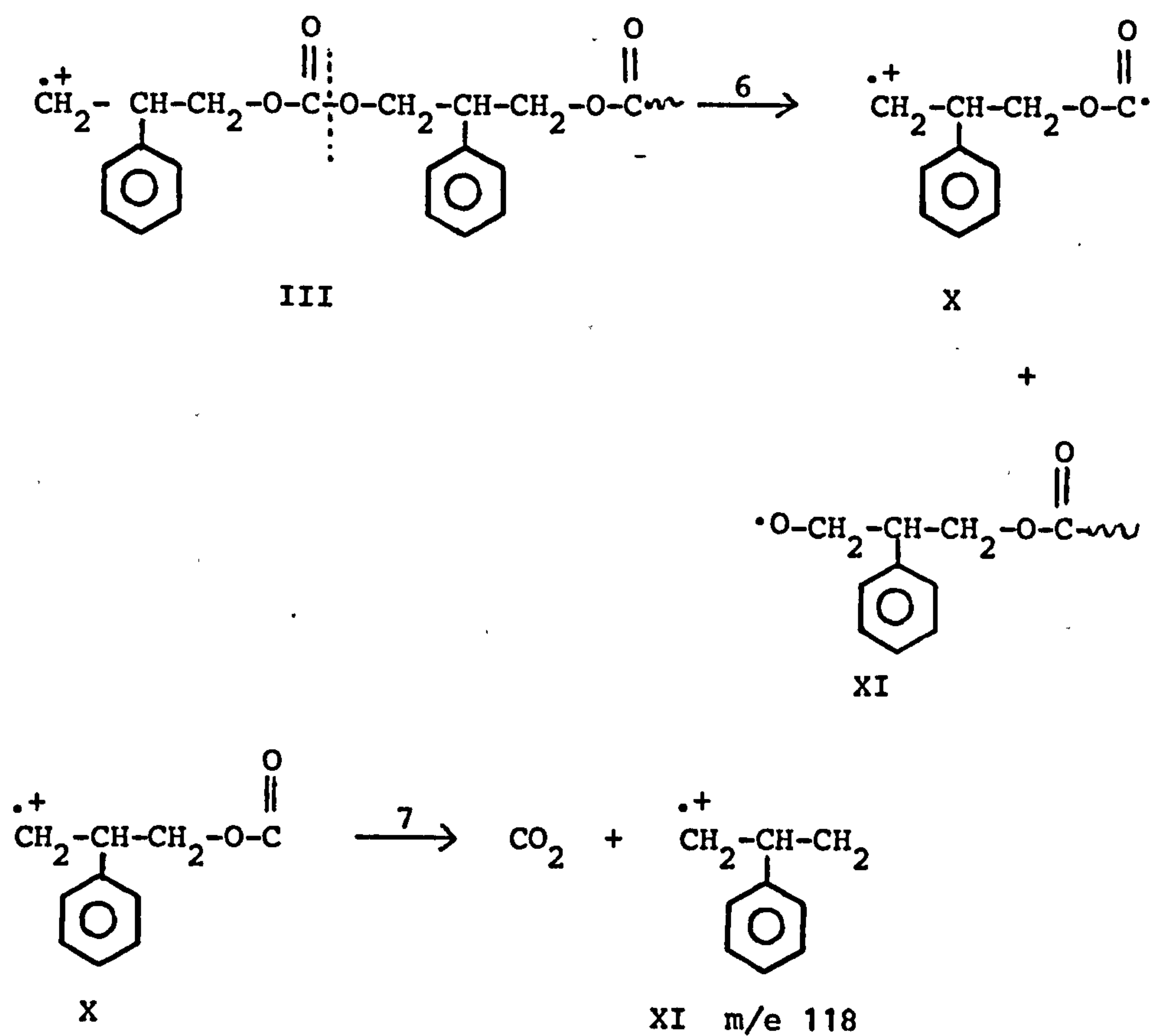
Fragment ion VI is absent in the mass spectrum maybe because of its instability to EI. It may undergo a rearrangement to give VII and by further fragmentation gives m/e 91



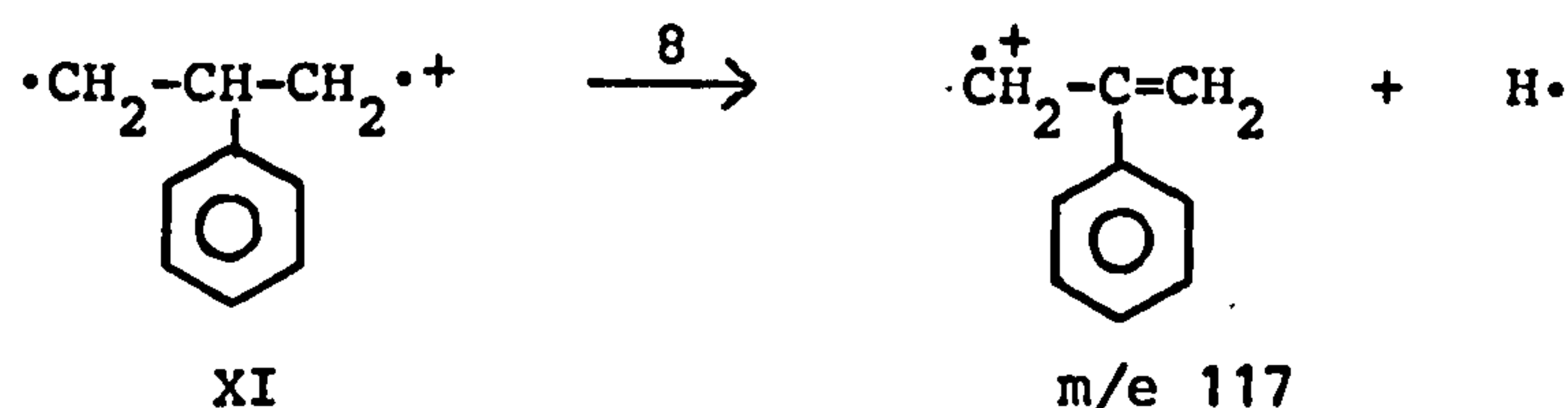


The fragment IX, highly labile, undergoes further fragmentation to give small fragments.

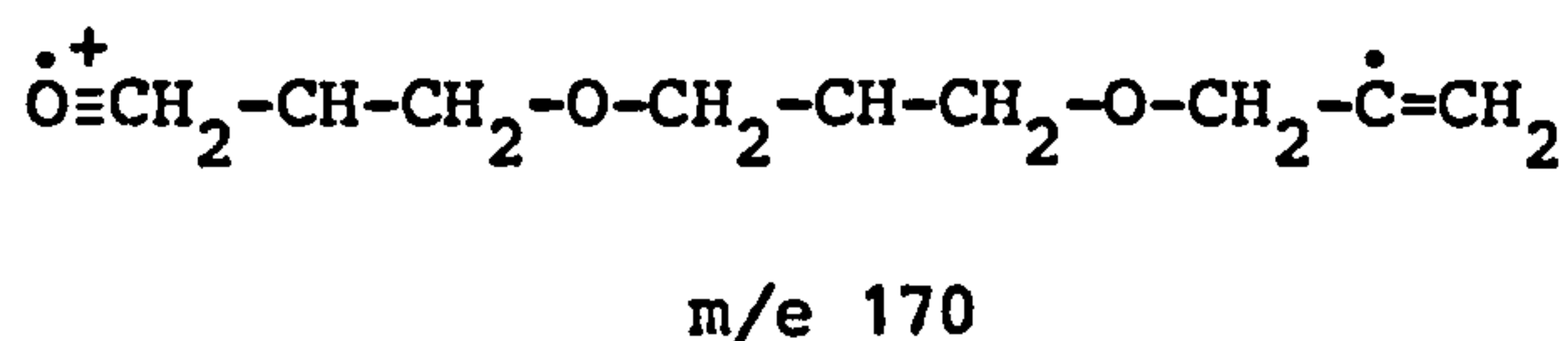
The fragment ion III could undergo fragmentation at the acyl bond of the carbonate group



The fragment ion at m/e 117 could be formed by loss of H• from fragment ion XI m/e 118



The fragments at m/e 170, 169, 163, indicate another type of fragmentation, the cleavage at the Ar-CH bond along with formation of ether bond by loss of CO<sub>2</sub> and reaction between active ends  $\sim\text{CH}_2\cdot$  and  $\cdot\text{O}-\text{CH}_2\sim$  to form aliphatic ether structures with unsaturated positions.

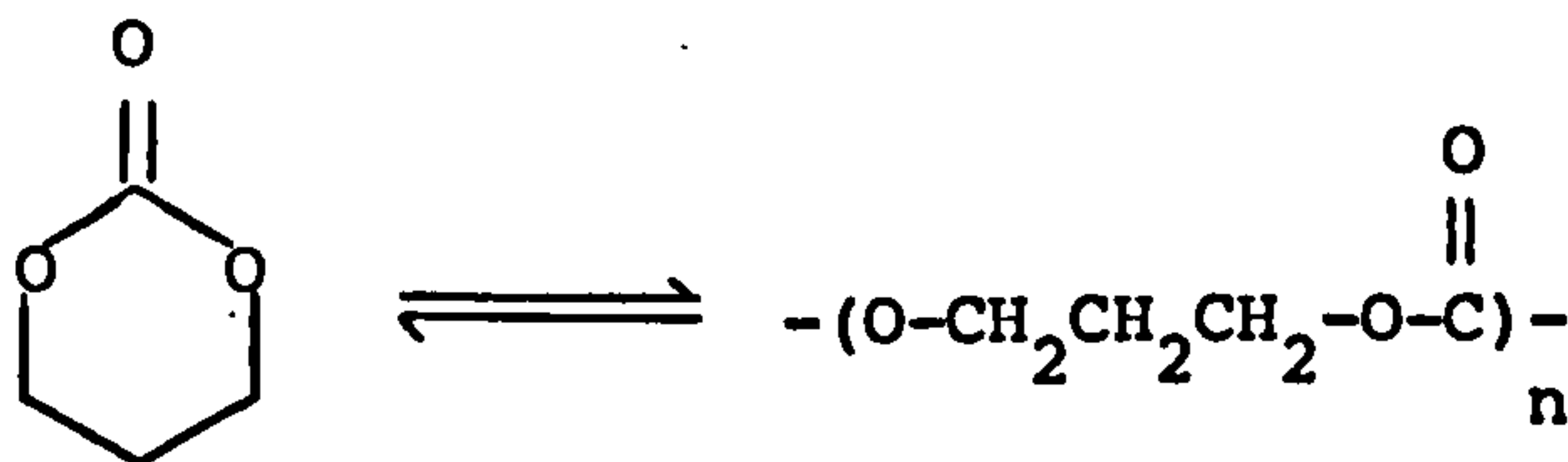


The mass spectrum of the solid product formed in TVA (CRF) exhibits peaks up to m/e 179. Other main peaks are characteristic of the fragmentation pattern of the polymer at m/e 178, 134, 105, 104 (base peak). The interesting feature in the mass spectrum is the absence of the fragment ions at 170, 169, 141, attributed to the cleavage of Ar-CH bonds which may indicate that these fragments correspond to further fragmentation of longer fragments, possibly to be formed from the polymeric structure.

#### 4.6 DISCUSSION

##### Aliphatic Polycarbonates

By comparing the analytical results in the thermal degradation of aliphatic polycarbonates, it has been found for poly(trimethylene carbonate) and poly(neopentylene carbonate) that the major product of degradation is monomer. As the temperature of degradation is increased, small amounts of oligomeric material are observed as cold ring fraction products and carbon dioxide is formed as volatile products of degradation in small amounts. These results support the conclusions of previous studies by Carothers<sup>2</sup> and Sarel *et al.*<sup>11</sup> Carothers<sup>9</sup> envisaged the reaction as being essentially a reversible polymerisation-depolymerisation conversion,



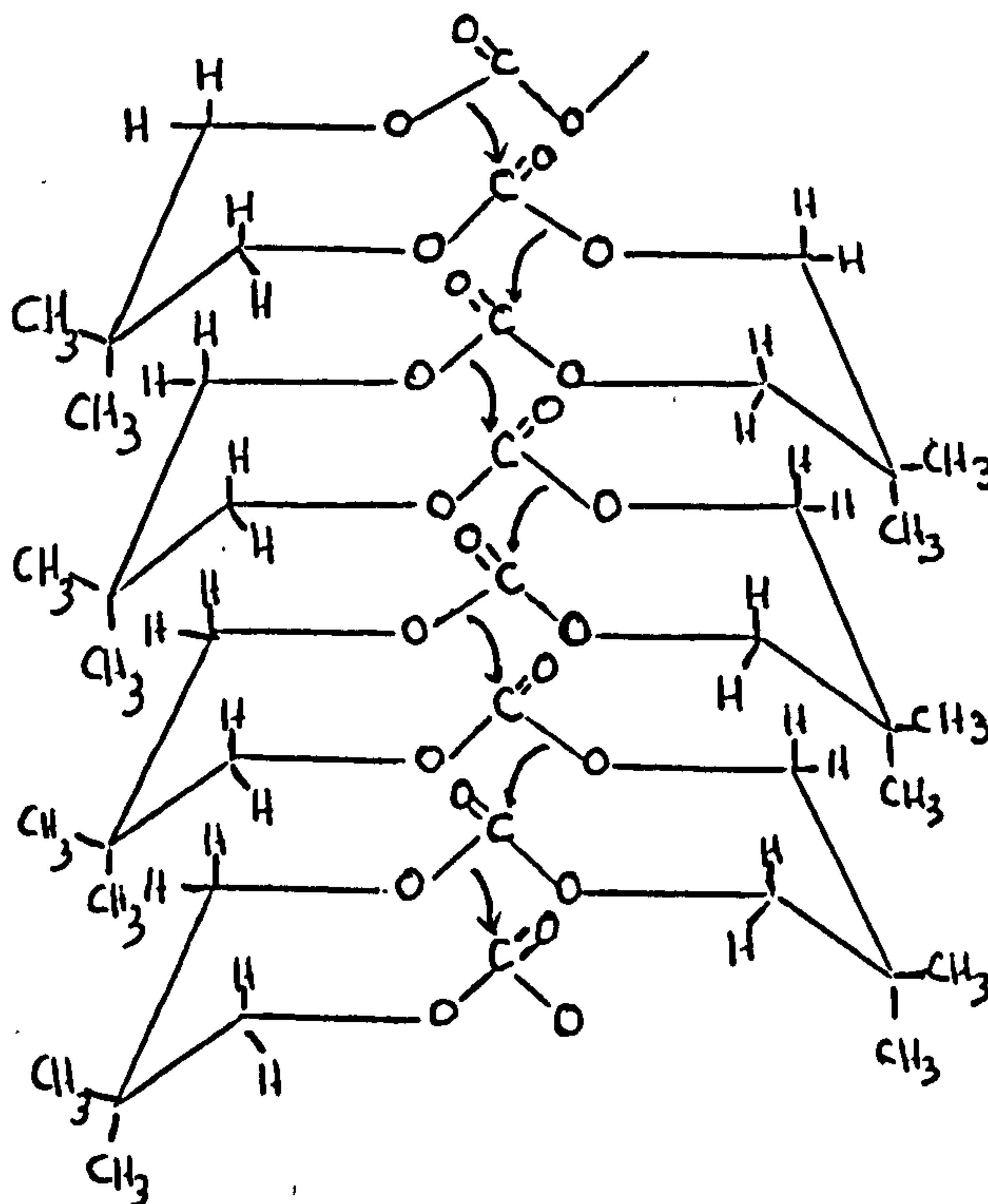
in which depolymerisation involved an ester exchange process between the segments of the polycarbonate chain, giving almost quantitative quantities of the monomer for degradations carried out under vacuum. This high monomer yield is probably due to the high probability of the close approach of atoms, 6 atoms apart in the polymer chain.

Sarel and Pohoryles<sup>12</sup> in their studies on the effect of structural differences upon the ability of six-membered cyclic carbonates to undergo reversible polymerisation-depolymerisation conversion, found that poly(neopentylene carbonate) underwent reversible polymerisation

conversion which they explain by the ester interchange mechanism.

These authors suggested that the ease of depolymerisation can probably be related to the molecular configuration adopted by the polymeric chain. They proposed a folded structure for the polymeric chain, the helical structure, based from the known effect of side chains upon the stable configuration of the main polymer chain and also from the solubility in benzene of the polymer.

This arrangement would be maintained by the dipole-dipole interactions between the non-carbonyl O-atom of a carbonate group with the carbon atom of the carbonate group along the chain, the folded six-membered ring conceivably adopts chain conformation as shown in the following schematic pattern proposed by the authors for poly(neopentylene carbonate)





The curved arrow indicates the mode of O-C-O bond interchange along the polymeric chain. X-ray and infrared spectroscopic data for the polymer before and after heat treatment indicated that the polymer can crystallise in two different solid phases, the  $\alpha$  and  $\beta$  form, the thermal transformation involves a change in the packing of crystal into shorter spacing, having a higher degree of symmetry. An  $\alpha$  form exists with interatomic spacing of 5.1 and 4.9 Å, melting at 107-109°C, and a  $\beta$  form with 5.0 and 4.8 Å spacing and higher melting point (117-119°C). Apparently the  $\beta$  form possesses physical properties approximate to those of the cyclic monomer. The polymer prepared for this study showed in the DSC an endothermic peak at 99°C, attributable to the solid-solid ( $\alpha$ - $\beta$ ) phase transition of the polymer chain. The author explained also that the drop in the yields of cyclic monomer observed for polycarbonates with bulky substituents at carbon 2, such as an ethyl group, indicates that the reversal of the polymerisation-depolymerisation process is hindered by the presence of such a bulky group.

Studies in related polyesters formed from six-membered cyclic compounds, such as lactones,<sup>65</sup> and oxalates<sup>2</sup> also showed the same properties as the six-membered cyclic carbonate on undergoing reversible polymerisation. Thus Stannet and Swarc<sup>66</sup> preferred this type of mechanism to explain the reversible polymerisation of six-membered lactones. They suggested that such an ease of interconvertibility strongly indicates that the spatial configuration of the liquid monomer units and polymer chains must be similar and that the process of ester interchange might take place by mere shifting of the bonds, with little or no movement of carbon centres. Sutton et al.<sup>65</sup> have proposed the



same mechanism as the principal route leading to the formation of monomer in the thermal degradation of poly(isopropylene carboxylate).

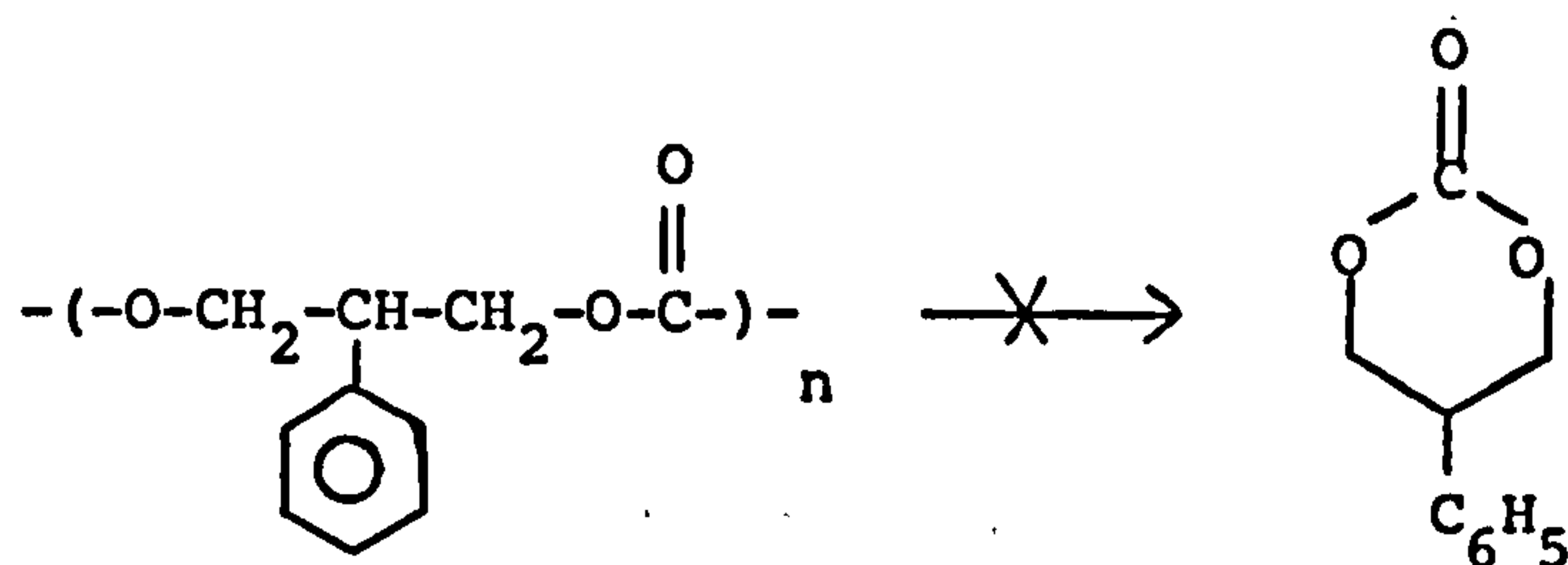
In order to explain the presence of polymer short chain fragments as cold ring fractions and the evolution of a small amount of carbon dioxide as a volatile production of degradation, when the temperature is increased, a random chain scission reaction must be present to some extent, which involves the breakdown of the carbonate group on the macromolecule backbone.

In the thermal degradation of poly(2-phenyl-trimethylene carbonate) it has been found that the major degradation product is polymer short chain fragments. On increasing the temperatures of degradation, small amounts of carbon dioxide and  $\alpha$ -methyl styrene are evolved as volatile degradation products. This observed behaviour may be related to the particular characteristics of polyesters formed from six-membered cyclic esters. It has been observed that the presence of substituents on the polymeric chain has a general depressing effect on the tendency to depolymerise reversibly.

Sarel and Pohoryles<sup>11</sup> showed in their studies on the effect of branching in 1,3-propane-diols that disubstitution at carbon atom 2, while it diminishes or even inhibits the tendency to polymerisation, has however an enhancing effect towards the formation of cyclic carbonate. On the other hand, the yields of the six-membered cyclic carbonates tend to drop markedly upon increasing the bulkiness of the alkyl substituents. They found, for example, only a 25% yield of polymer when 2,2-ethyl-isoamyl-1,3-propane diol was reacted with diethyl carbonate, whereas a similar reaction using 2-ethyl-1,3-propane diol produced 75% yield.

Poly( $\delta$ -valerolactone)<sup>67</sup> has been found to depolymerise easily to monomer at temperatures above 200°C via ester-interchange. On the other hand, poly(tetramethylglycolide)<sup>68</sup> above 200°C depolymerises quantitatively to methacrylic acid, presumably because of the pendant methyl group on the ring.

The present investigation has shown that the presence of a pendant phenyl group on the carbon 2 atom on the polymeric chain prevents the formation of the cyclic carbonate.



Monomer would not be expected because of the large quantity of energy which would be required to form a strained ring.

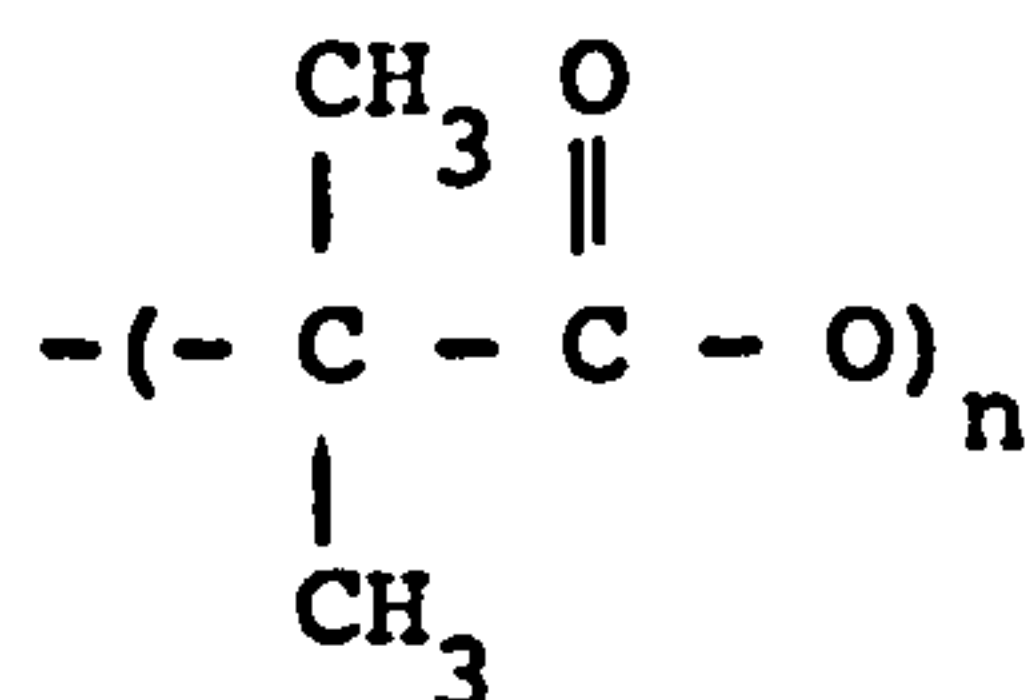
For aliphatic polycarbonates the feasible routes of ester interchange depend on the relative thermal stability of the acyl (I) and ether bonds (II) on the polymer chain.



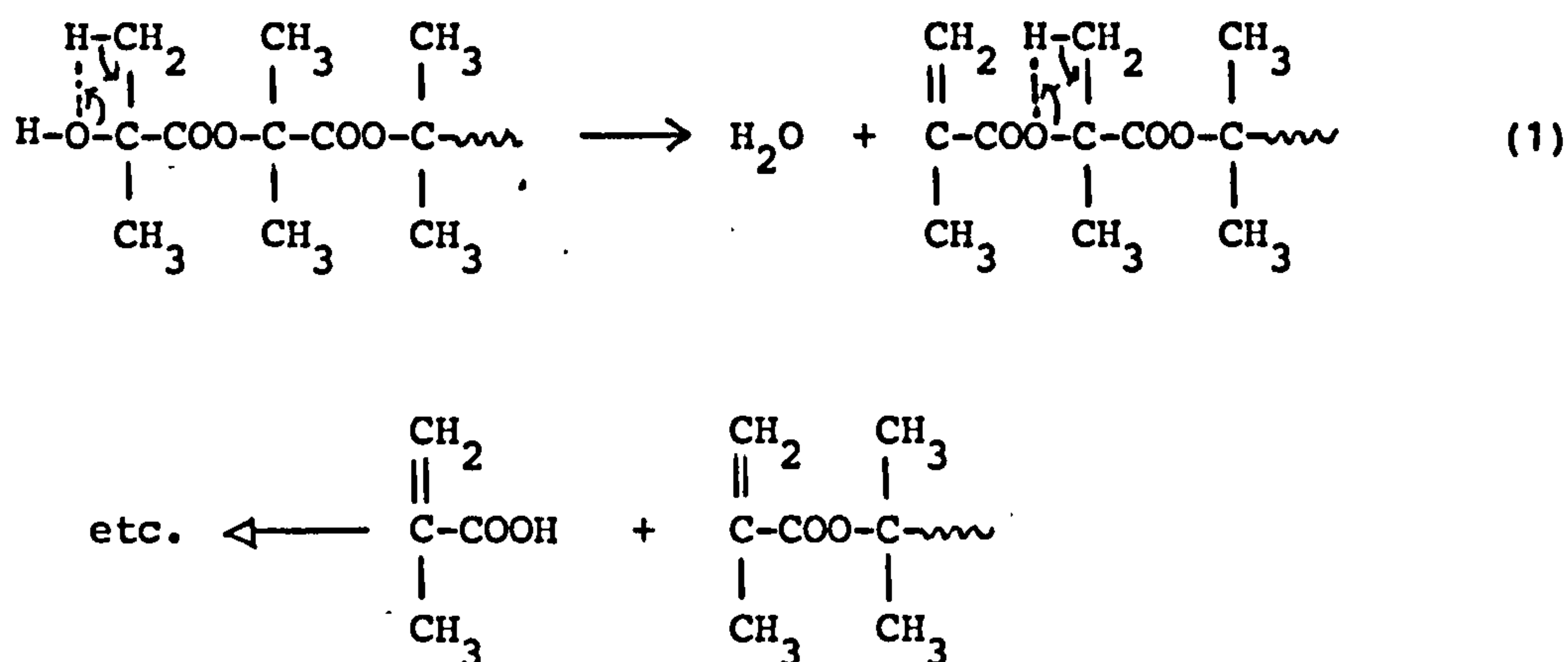
The bond dissociation energy for the  $\text{O}-\text{C}(=\text{O})$  bond lies in the range 88-99 kcal/mol, as reported<sup>15</sup> for values of bond dissociation energy calculated from the heat of formation of radicals for ester

$$\begin{array}{c} \text{O} \\ || \\ \text{R}-\text{C}-\text{O}-\text{R}' \end{array}$$
 where  $\text{R} = \text{CH}_3, \text{H}, \text{C}_6\text{H}_5$  and  $\text{R}' = \text{CH}_3, \text{C}_2\text{H}_5, n - \text{C}_3\text{H}_7, i - \text{C}_3\text{H}_7, n - \text{C}_4\text{H}_9, i - \text{C}_4\text{H}_9$ . For ether compounds,  $\text{R}-\text{O}-\text{R}'$  where  $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, i - \text{C}_3\text{H}_7$  and  $\text{R}' = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_3\text{H}_7$ ; the values are about 80 kcal/mole. From this data it is possible to conclude that the ether bond in aliphatic polycarbonate would have lower dissociation energy than the acyl bond. The effective bond dissociation energy depends, however, on the neighbouring groups in the macromolecule.

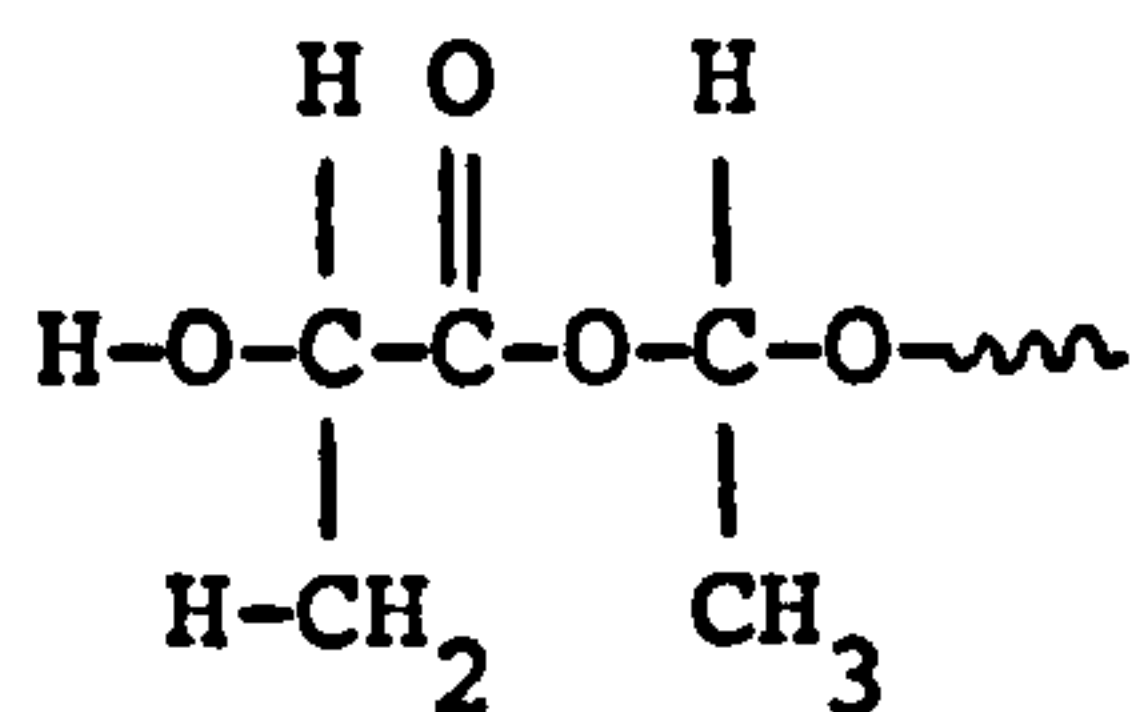
Acetylated poly(trimethylene carbonate) and poly(neopentylene carbonate) showed higher thermal stability than the original polymers. This indicates that to a certain extent initiation of the degradation process takes place at the hydroxyl end groups on the macromolecule at low temperatures. Deibig et al.<sup>68</sup> found a similar behaviour in the thermal degradation of poly(tetramethylglycolide) to give methacrylic acid



They suggested that depolymerisation to methacrylic acid was initiated at the hydroxyl chain ends by elimination of water to give allylic chain ends which activated the cleavage of the neighbouring  $\begin{array}{c} \text{O} \\ || \\ -\text{C} - \text{O} \end{array} \vdots \text{C}$  bond resulting in formation of a new allylic end group and one molecule of methacrylic acid, according to the following equations:



Adams<sup>69</sup> also has suggested that essentially the same thermal degradation mechanism can occur in polylactide, in this case

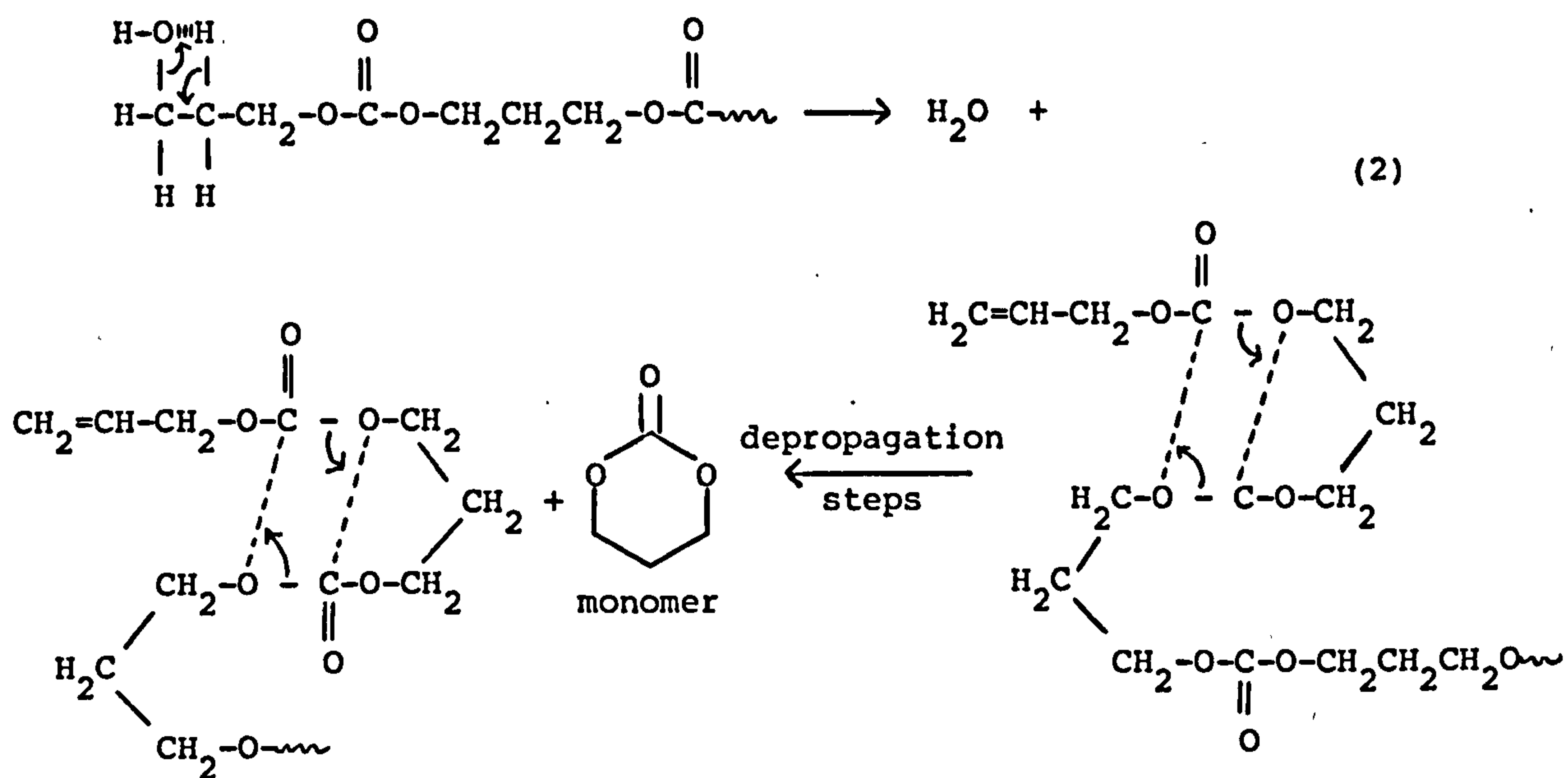


it will also be the  $\begin{array}{c} \text{O} \quad \text{H} \\ || \quad | \\ -\text{C}-\text{O}-\text{C} \\ | \\ \text{CH}_3 \end{array}$  bond which is cleaved. The one major

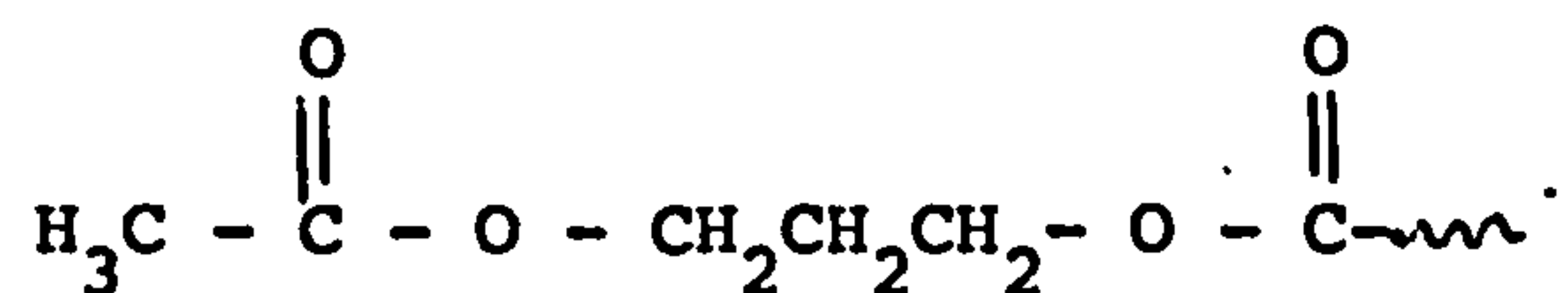
difference from the case of poly(tetramethylglycolide) is that the vinyl end group is not expelled as part of the degradation product. The same end group remains until depolymerisation is complete.

A similar process appears feasible in thermal depolymerisation of poly(trimethylene carbonate) and poly(neopentylene carbonate)





When the hydroxyl end groupson the poly(trimethylene carbonate) and poly(neopentylene carbonate) have been acetylated, e.g. poly(trimethylene carbonate),



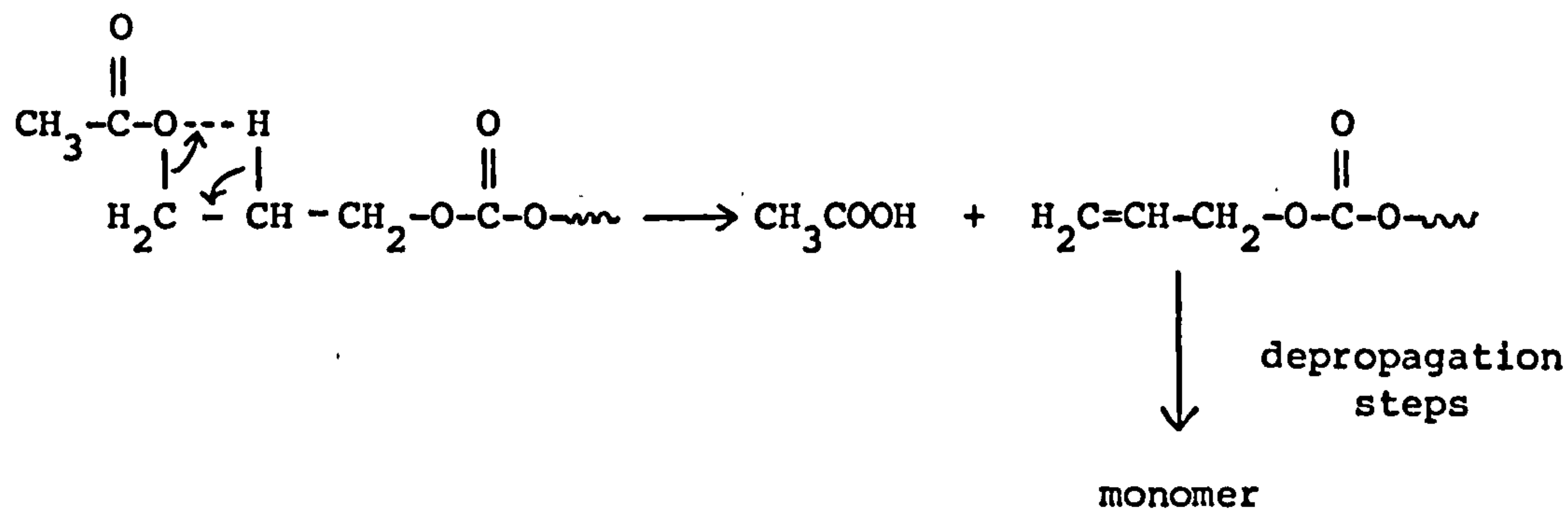
they cannot decompose via the initiation process shown above, as water cannot be eliminated with the subsequent formation of the allylic end.

Dudina et al.<sup>70</sup> studied the thermal degradation of poly(oxymethylene). They showed that the activation energies of degradation for a hydroxyl chain ended polymer and an acetylated chain ended polymer were 26 and 32 kcal/mol, respectively. The difference in activation energies (6 kcal/mol) was attributed to the higher strength of the  $\text{CH}_3-\text{C}(=\text{O})-\text{O}-\text{C}$  bond compared to that of the polymer  $\text{H}-\text{O}-\text{C}$ . The same

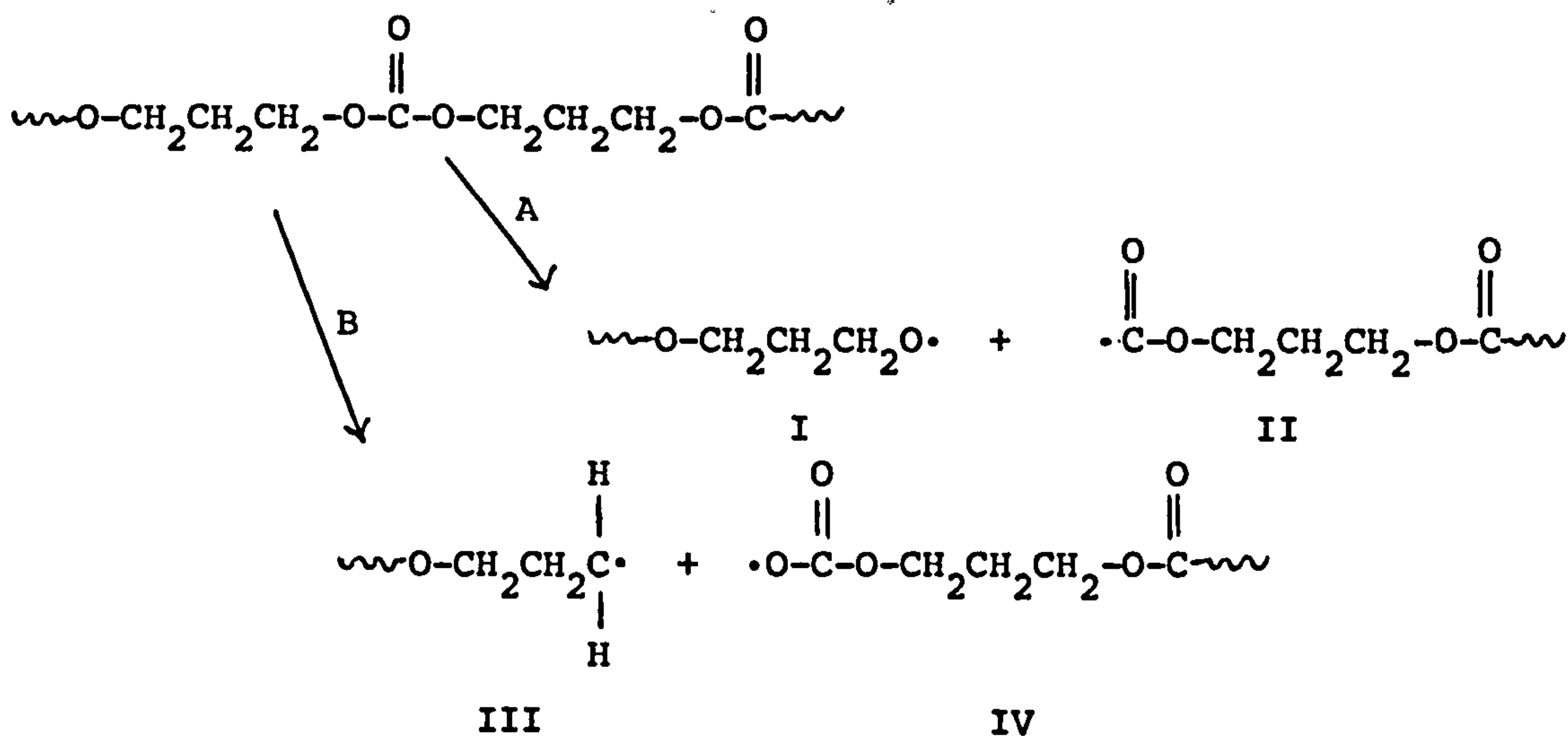


explanation can be applied for acetylated polycarbonate. The initiation step of the decomposition of acetylated chain ends may involve the

cleavage of the  $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{CH}_2-$  end to acetic acid and an allylic end group

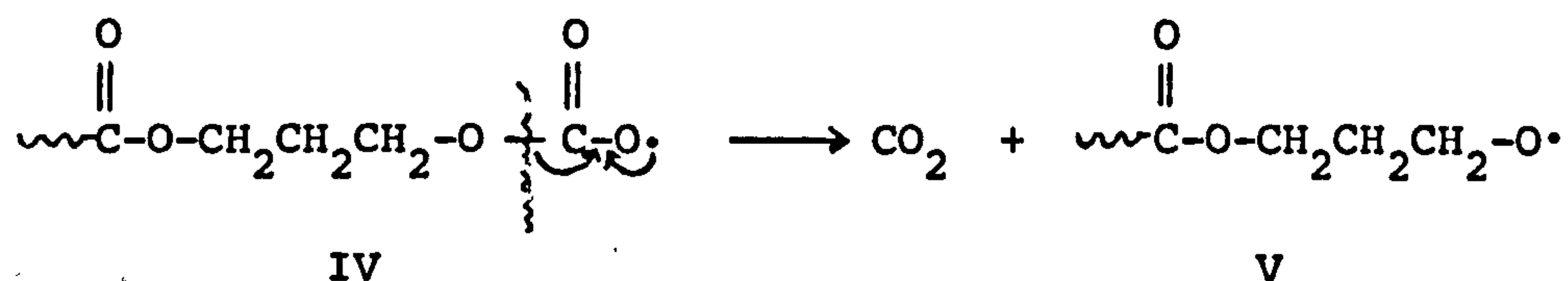


The oligomeric fragments and the carbon dioxide, the remaining degradation products, are most likely to be formed via homolytic scission of the polymer chain. The carbonate group on the polymer chain can be broken at two sites on the polymer backbone,

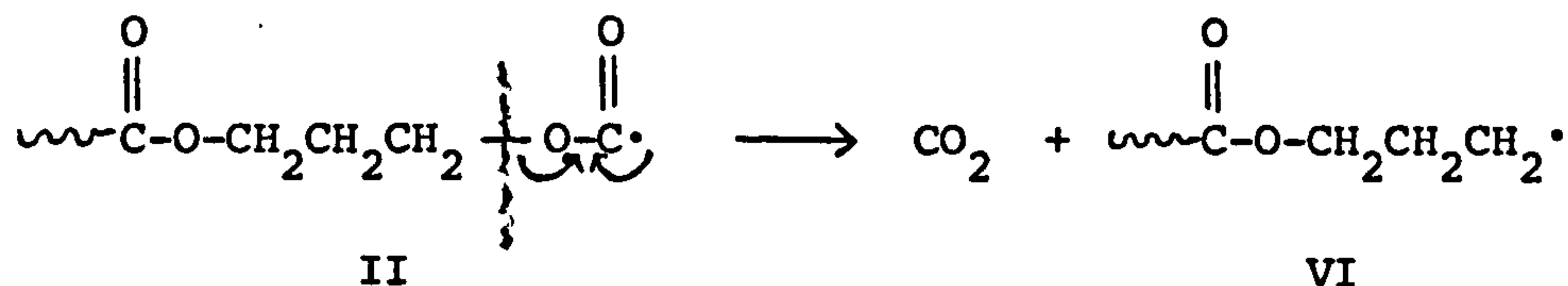


The route A involves the cleavage of an acyl bond, with higher dissociation energy, to form an oxycarbonyl radical end (II).

Pathway B involves cleavage of an ether bond which is expected to have lower dissociation energy. Therefore, it may take place preferentially at the degradation temperatures. Formation of carbon dioxide could result by decomposition of the radical IV



Route A at higher temperatures of degradation may also lead to  $\text{CO}_2$  by further decomposition of radical II



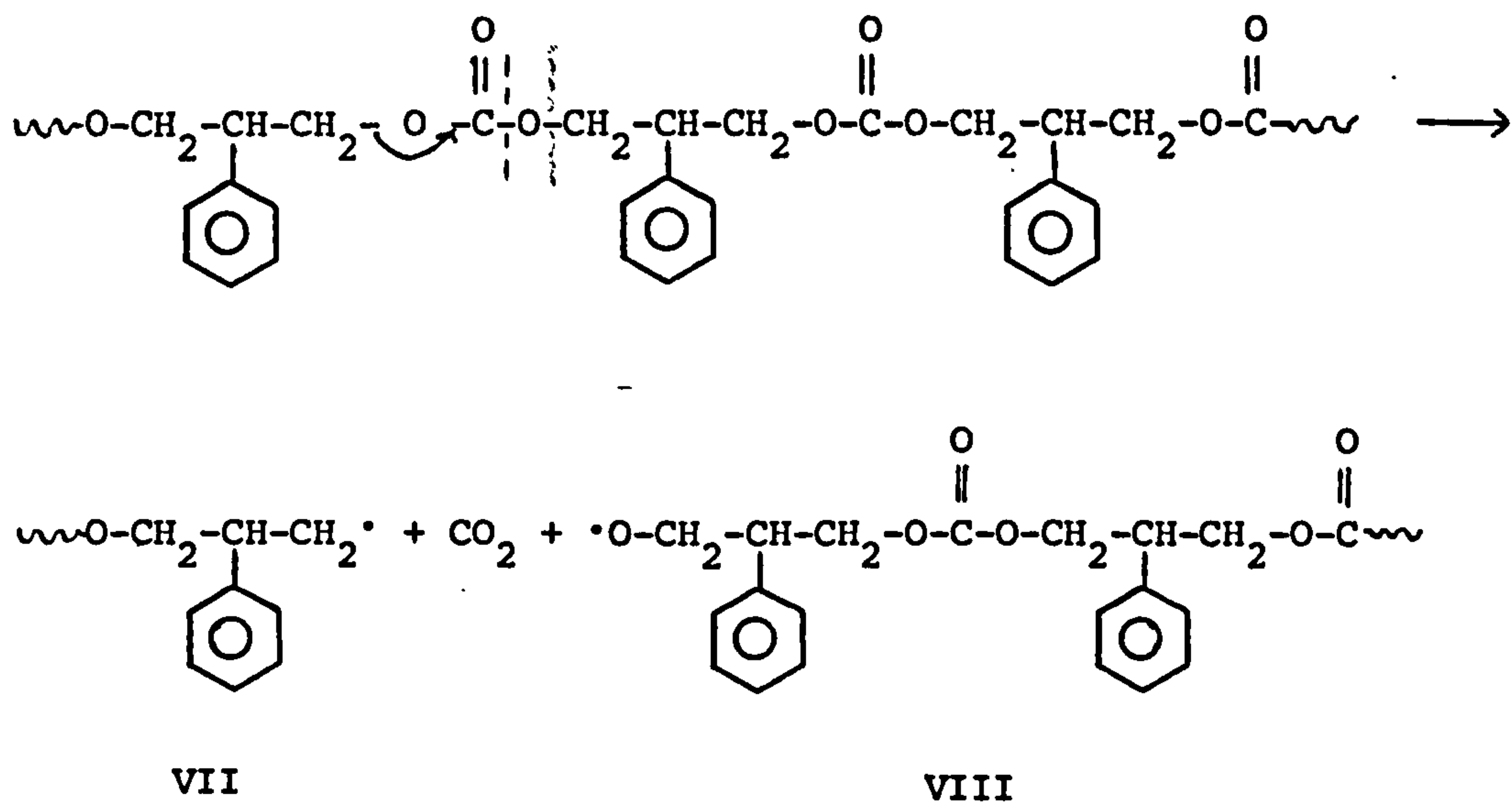
The labile chain ends with  $\text{CH}_2\cdot$  can lead to termination by recombination reactions to form lower molecular weight chain fragments which can volatilise from the reaction medium.

The presence of a pendant phenyl group on the carbon atom 2 hinders the depolymerisation to a six-membered cyclic structure. As has already been discussed, the ease of depolymerisation can be related to the spatial configuration adopted by the polymeric chain. In poly(2-phenyl trimethylene carbonate) the helical structure will be impeded by the bulkiness of the phenyl group, which may be axially bonded and provide a steric approach control between the O-atom of a carbonate group and the carbon atom of another  $\text{O}-\overset{\text{O}}{\parallel}\text{C}-\text{O}$  group along the macromolecule.

In this case the polymerisation-depolymerisation equilibrium will be displaced towards the formation of oligomeric structures because the steric repulsion makes cyclisation thermodynamically unlikely.

At the lower temperatures the degradation may take place at the carbonate group via a homolytic scission with the formation of small amounts of  $\text{CO}_2$  and short chain fragments which may volatilise from the medium of the reaction when the volatilisation threshold is lower than the temperature of degradation.

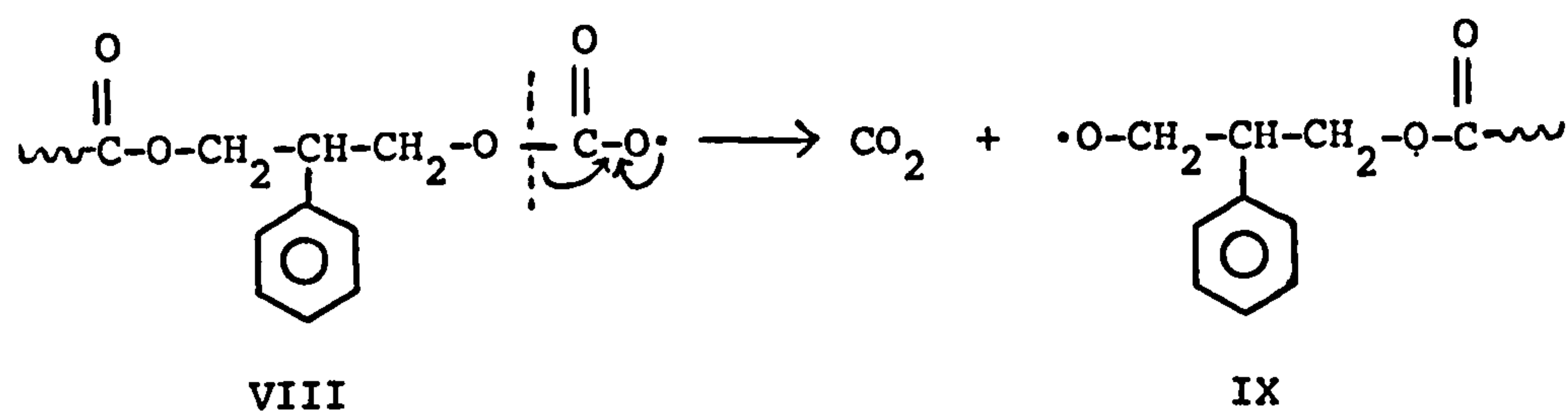
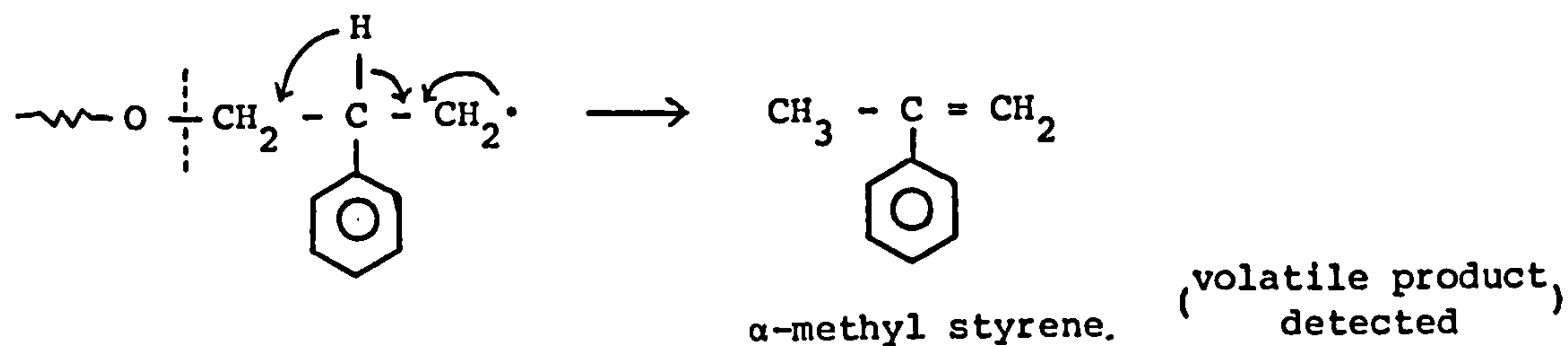
At the higher temperatures the amount of carbon dioxide



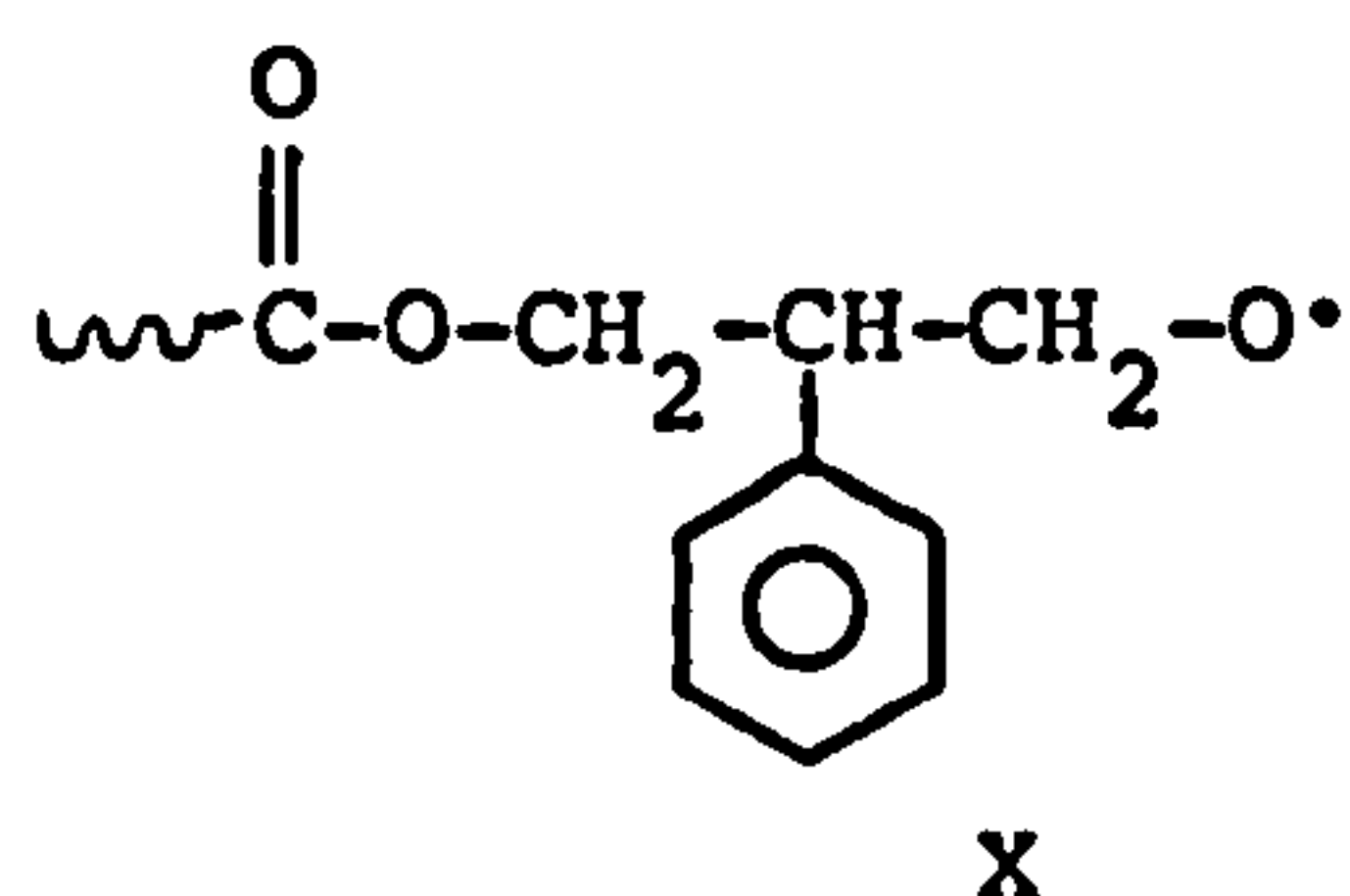
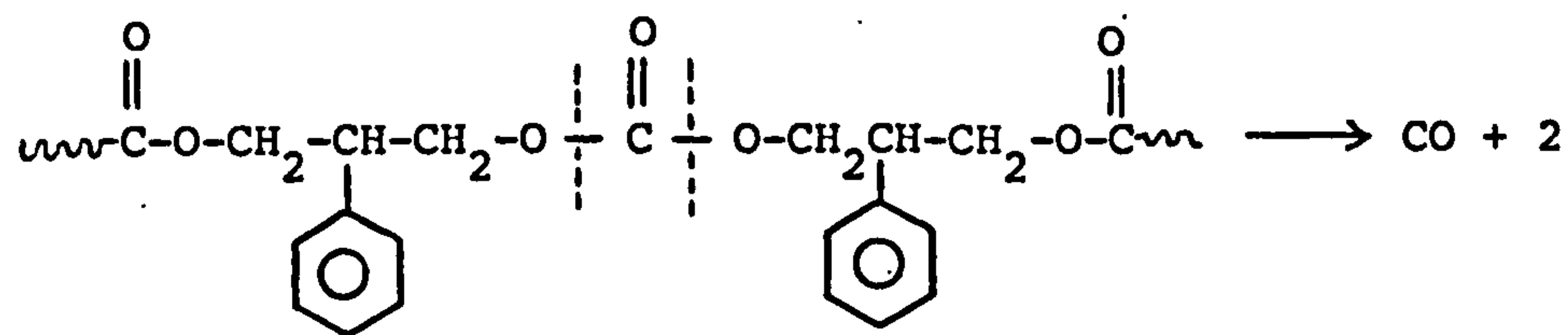
increases and when the temperature of the reaction reaches about  $300^\circ\text{C}$  the second volatile product of degradation,  $\alpha$ -methyl styrene is observed. This indicates that another process is operative at the higher temperatures.

Thus polymer fragments VII and VIII may undergo further homolytic scission to produce the volatile products observed.

Polymer fragment VII with  $\text{CH}_2^\bullet$  end groups could produce  $\alpha$ -methyl styrene



At higher temperatures  $\sim 400^\circ\text{C}$  a small amount of carbon monoxide was detected. This product could be produced by homolytic scission at the carbonate group on the macromolecule backbone





## 4.7 PROGRAMMED DEGRADATIONS FOR ALIPHATIC-AROMATIC POLYCARBONATES

### 4.7.1 Poly(p-xylylene carbonate)

#### 4.7.1.1 Thermogravimetry (TG)

Two different samples, A and B (see p.61) of poly(p-xylylene carbonate) were analysed. The TG curves for both samples were obtained in vacuum and nitrogen atmosphere (fig. 4.23 and 4.24).

The TG curves for sample A show a two-step decomposition process in vacuum with rate maxima at 257° and 287°C, the greater part of the weight loss occurring at the first stage. There is a shift of the base line from the start of the heating in vacuum with little change in the rate of volatilisation at this stage. This may be due to desorption of solvent trapped in the polymer. This behaviour is not observed in nitrogen. The onset of major weight loss in vacuum occurs at a lower temperature (162°C) than in nitrogen atmosphere (175°C). This effect has been previously explained. For nitrogen atmosphere, the decomposition process occurs in three stages, with most of the weight loss associated with the second stage, rate maximum at 330°C. In the third stage, the rate of volatilisation remains fairly constant between 340° and 500°C. This behaviour may be due to the gradual molecular weight drop of the residue with the slow distillation of chains as they become short enough to vaporise.

The TG curves for sample B show a one-step decomposition process with rapid weight loss in both environments. There is a continuous shift of the base line from the beginning of the heating.



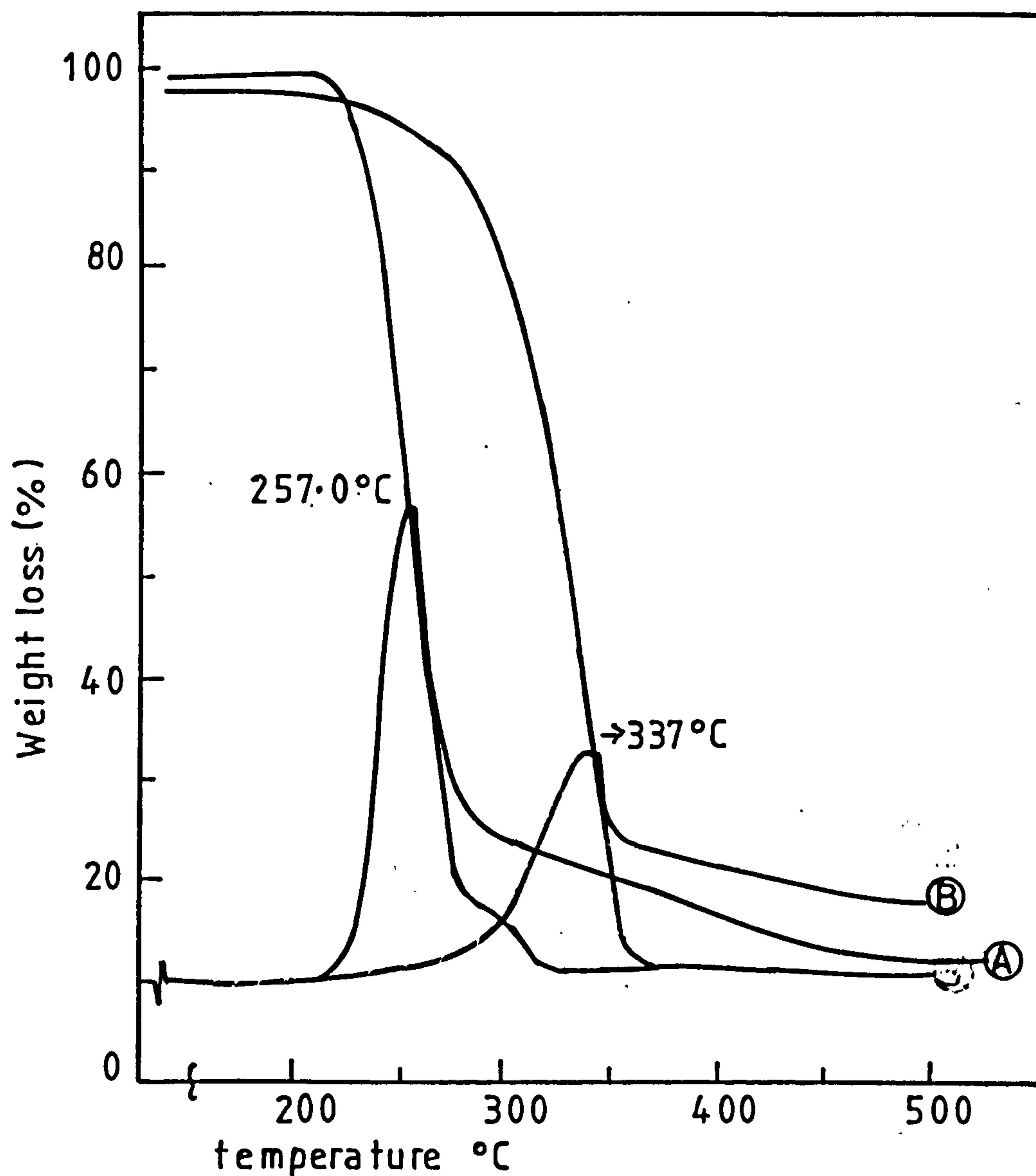


Fig. 4.23. TG curves for poly (p - xylylene carbonate) to 500°C under vacuum at 10°C/min curves (A) sample A (B) sample B

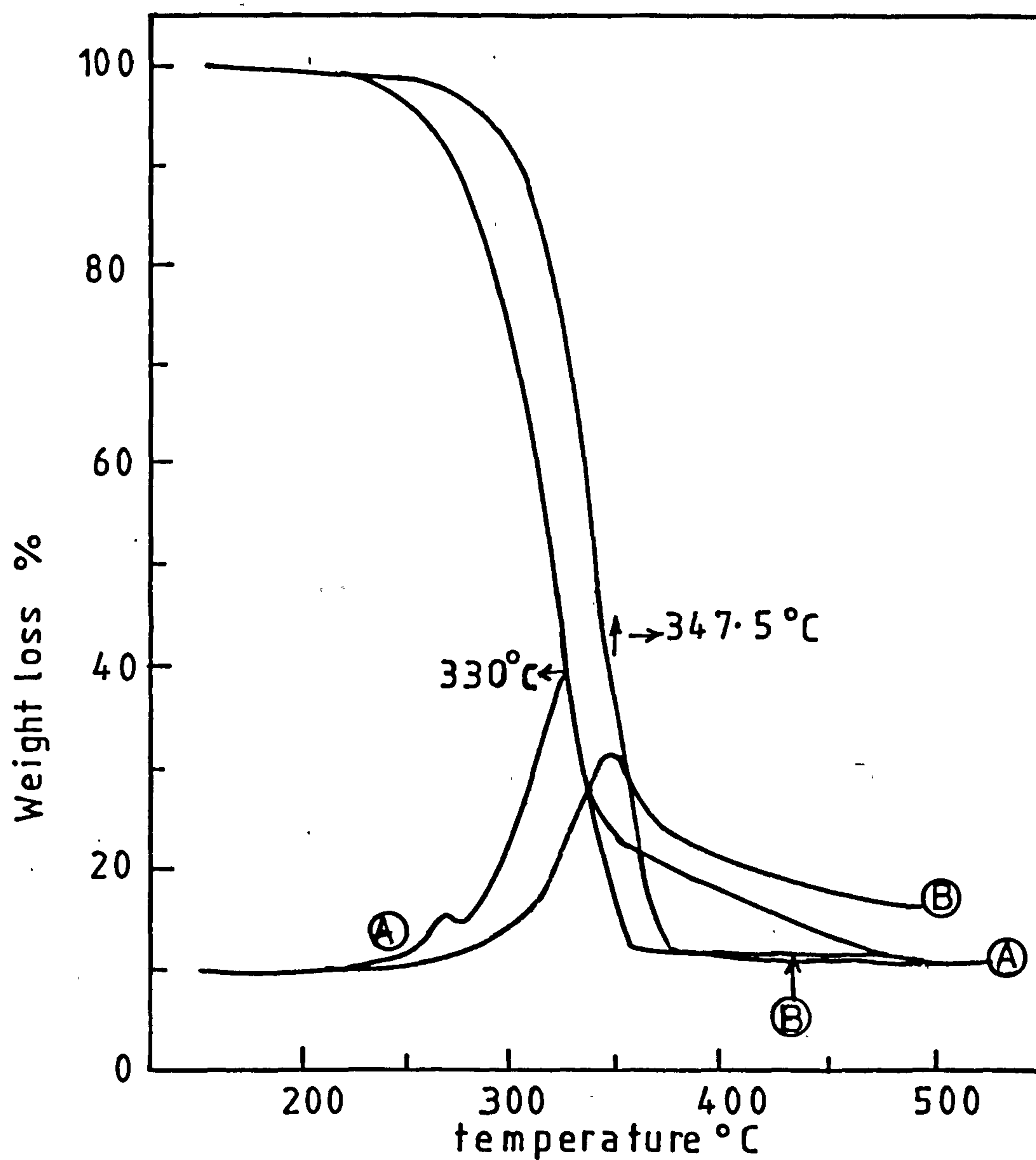


Fig.4.24 TG curves for poly(p-xylylene carbonate) in  $N_2$  atmosphere, heated to  $500^\circ\text{C}$ ,  $10^\circ\text{C}/\text{min}$  curve (A) sample A (B) sample B

However, the rate of volatilisation remains constant, which suggests the slow evolution of solvent trapped within the polymer; this behaviour is not so pronounced in nitrogen atmosphere. The onset of weight loss in vacuum occurs at a lower temperature ( $\sim 215^{\circ}\text{C}$ ) than in nitrogen atmosphere ( $\sim 250^{\circ}\text{C}$ ). This may be due to the fact that in vacuum the volatilisation process is more efficient. The temperature of the rate maximum is very nearly identical, being  $337^{\circ}\text{C}$  in vacuum and  $347^{\circ}\text{C}$  in nitrogen atmosphere. The ultimate residue left after the degradation process is 17.5% in vacuum and 16.5% in  $\text{N}_2$ .

#### 4.7.1.2 Differential Scanning Calorimetry (DSC)

DSC curves for both samples, A and B, are indicated in figs. 4.25 and 4.26, respectively.

The curve for sample A (fig. 4.25) indicates a process which is endothermic at low temperature and followed by an exothermic process at higher temperature. Three distinct minima can be seen at  $212^{\circ}$ ,  $253^{\circ}$  and  $322^{\circ}\text{C}$ , followed by a continuous upward (exothermic) shift of the base line up to  $500^{\circ}\text{C}$ . For this material, it has been found by TVA that on degradation at a temperature as low as  $200^{\circ}\text{C}$ , a crystalline product was formed and the residue left was not melted. The endothermic peaks at  $212^{\circ}\text{C}$  and  $253^{\circ}\text{C}$  can be associated with the breakdown and melting process, respectively. The endothermic peak at the higher temperature and the exothermic process are associated with decomposition process of the polymer.

The DSC curve for sample B, indicated in fig. 4.26, shows an endotherm with minimum at  $212^{\circ}\text{C}$  which may be attributed to the

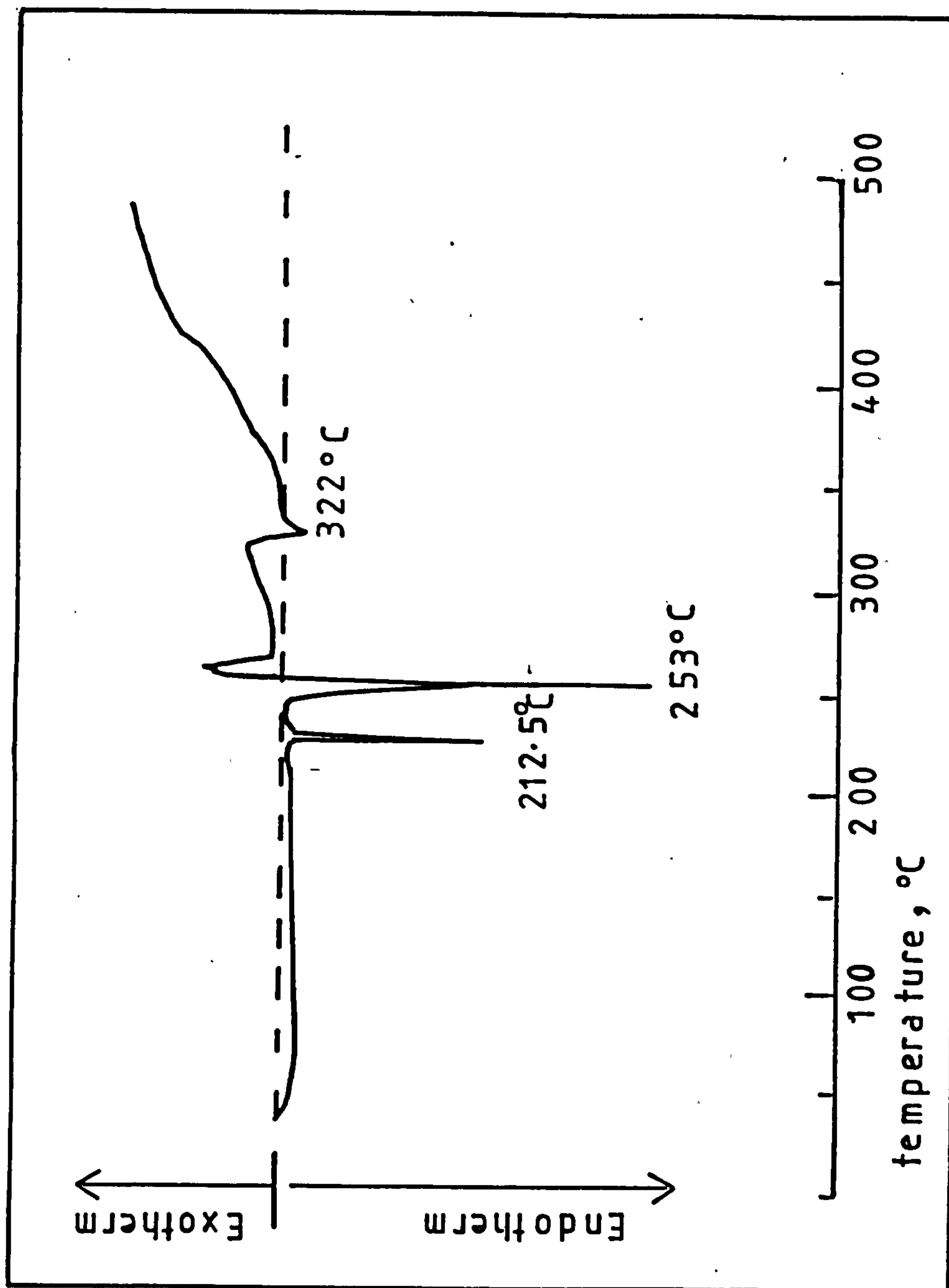


Fig.4.25 DSC curve for poly (p-xylylene carbonate) sample A under  $N_2$  heating rate  $10^\circ C/min$

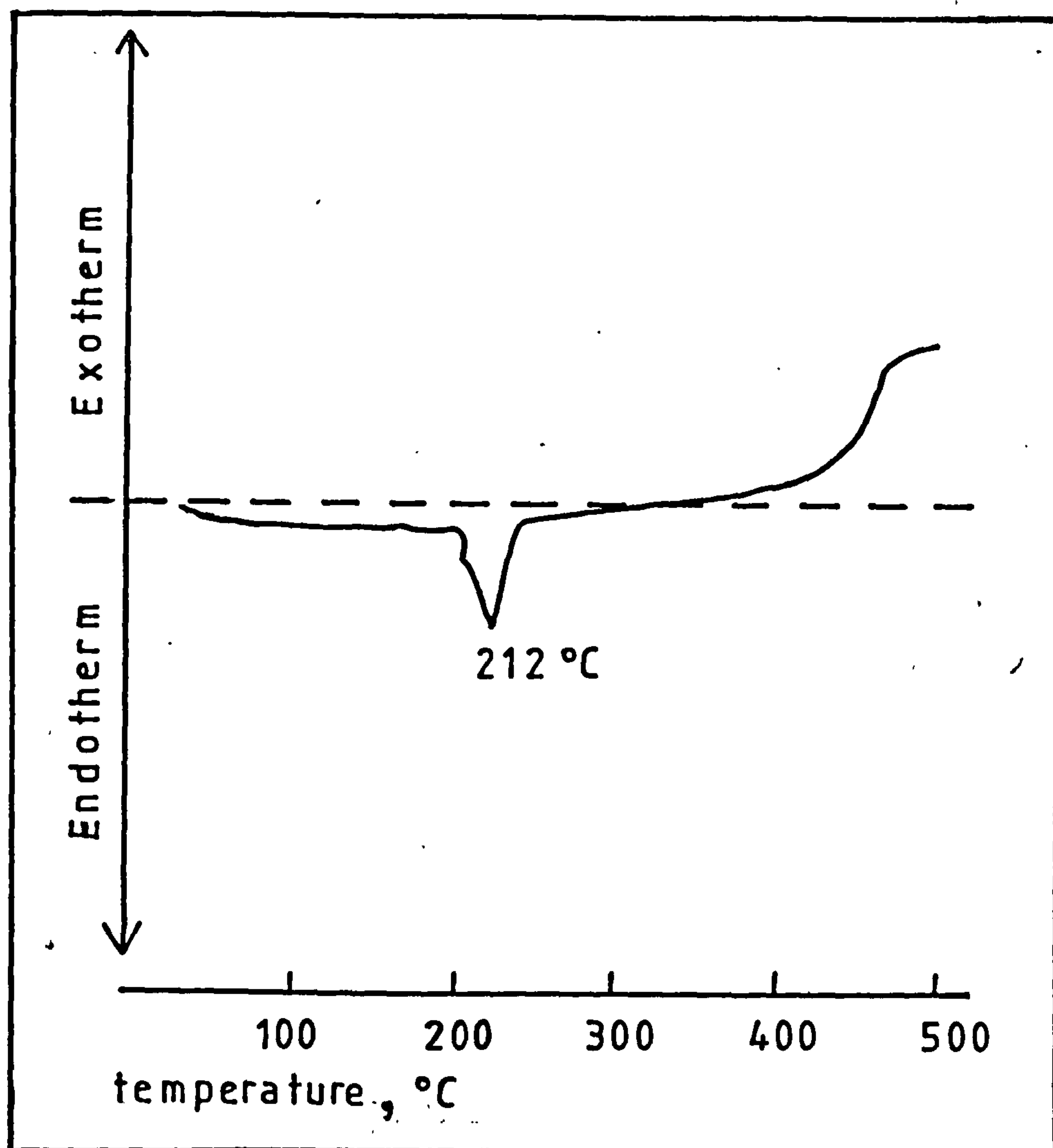


Fig 4.26 DSC curve for poly(p-xylylene carbonate) sample B under N<sub>2</sub> atm. heated to 500 °C at 10 °C/min.



decomposition process of the polymer. Above that temperature, a continuous upward shift (exothermic) of the base line is observed up to 500°C. This behaviour may be due to the decomposition process occurring in the degrading material.

#### 4.7.1.3 Thermal Volatilisation Analysis (TVA) for Sample A

The TVA curve for sample A heated to 500°C is presented in fig. 4.27. The evolution of volatile products occurs in three stages with maxima at 278°, 322° and 438°C. The first two volatilisation processes overlap in temperature range. The non-coincidence of the traces indicates that all the processes produce materials of a wide range of volatility. The large separation in the traces at -100°C and -196°C, is indicative of the presence of highly volatile material only condensable at -196°C, for instance, CO<sub>2</sub>.

The differences in temperature between the rate maximum of weight loss in TG and the first stage of volatilisation in TVA are due to the production at low temperature of material of low volatility which is collected as cold ring fraction.

#### 4.7.1.4 Subambient Thermal Volatilisation Analysis (SATVA) for Sample A products

The SATVA curve for the volatile degradation products formed on heating to 500°C is shown in fig. 4.28. All the substances were analysed by means of infrared and mass spectrometry. The first sharp peak (-146°C) corresponds to carbon dioxide; the second peak at -63°C is assigned to a mixture of water and p-tolualdehyde and the third peak (~-5°C) to the presence of p-tolualdehyde, respectively.

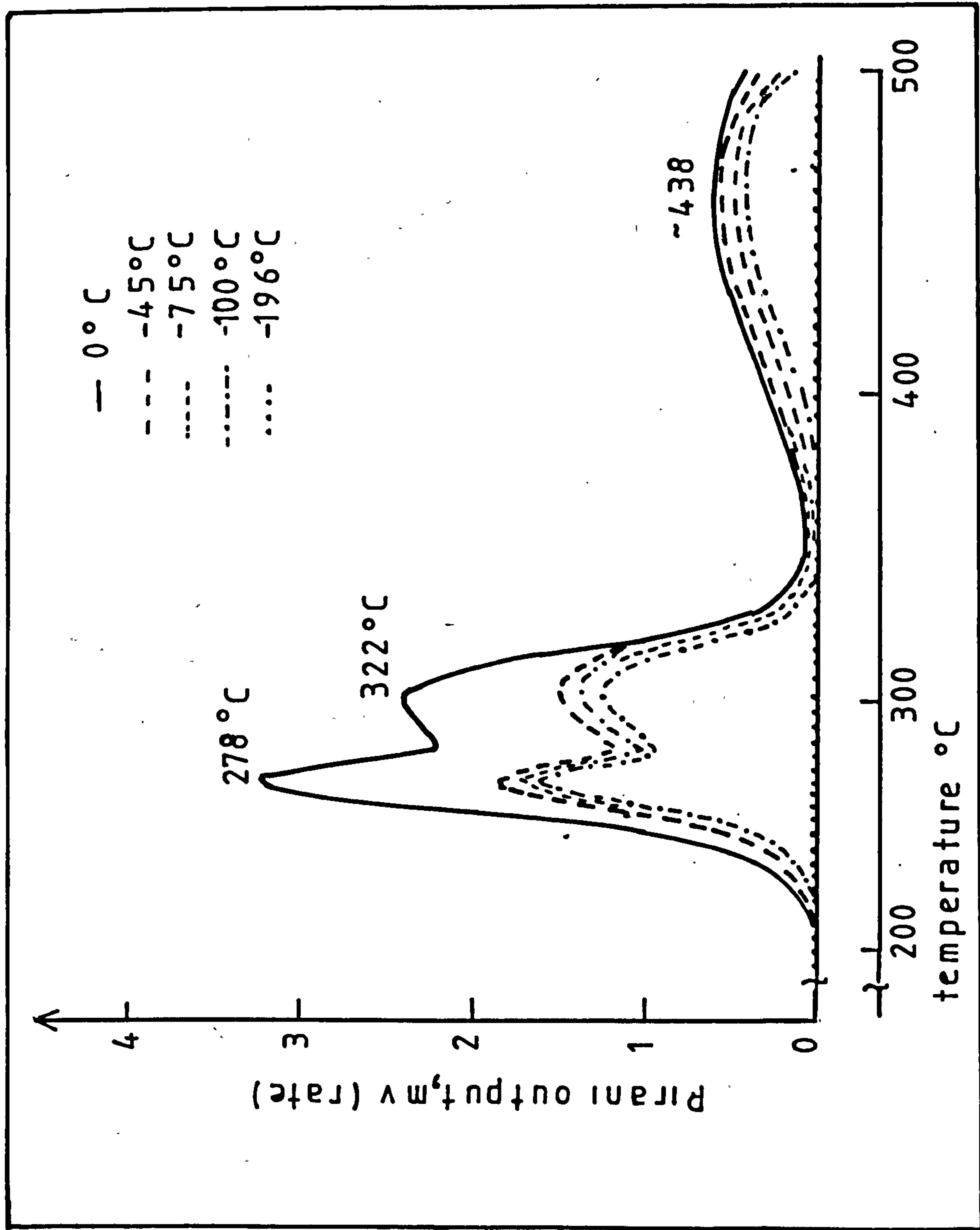


Fig.4.27. TVA curve for poly (p-xylylene carbonate) sample A heated to 500°C at 10°C / min.

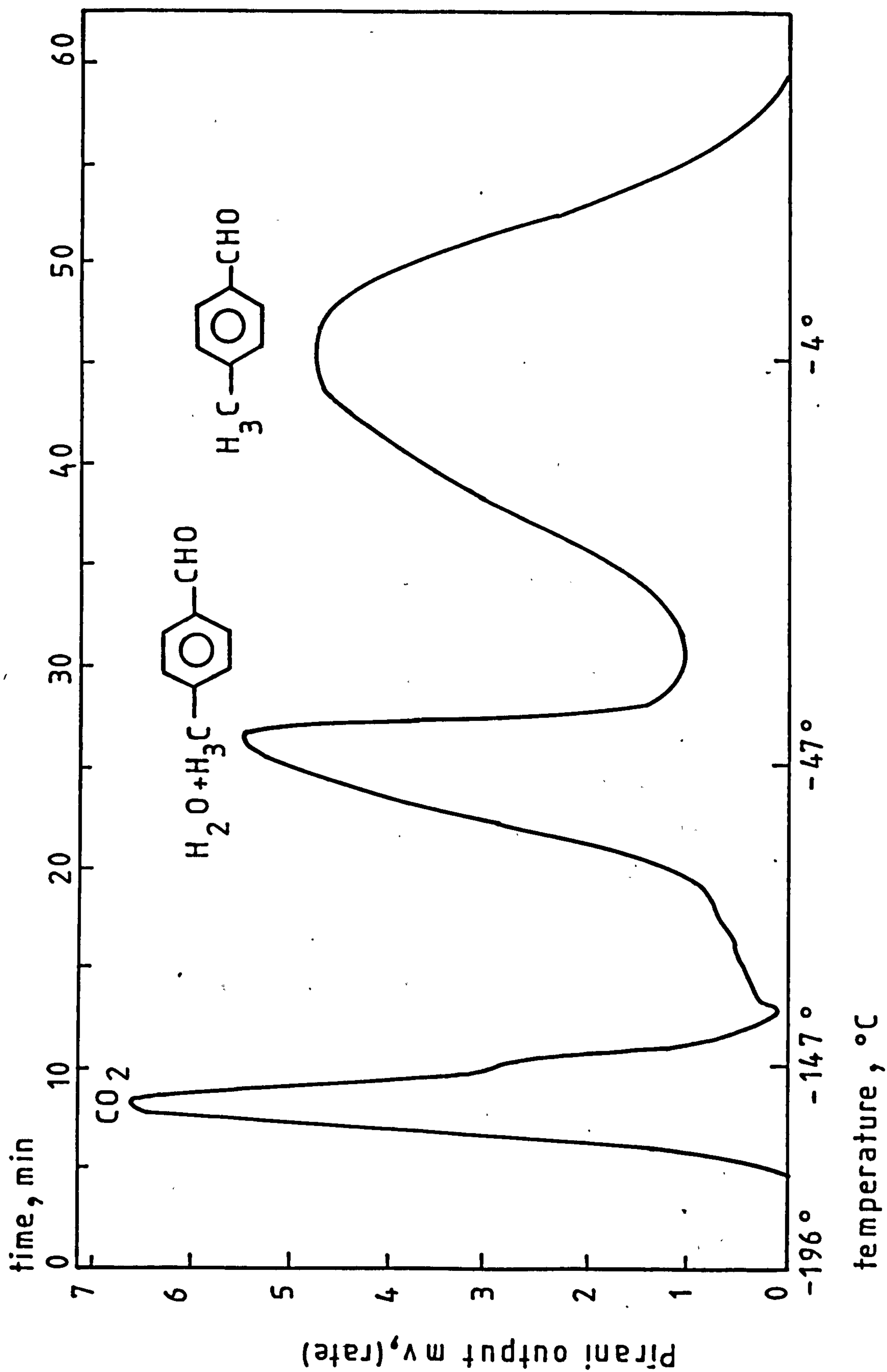


Fig. 4.28 SATVA curve for products of degradation of poly (p-xylene carbonate) sample A under vacuum at 10°C/min.

#### 4.7.1.5 Characterisation of Cold Ring Fractions

Degradation of poly(p-xylylene carbonate) sample A by heating to 500°C gives a band of yellow-greenish coloured waxy material as CRF. This material was collected and analysed by infrared, nmr and GC-mass spectrometry.

The infrared spectrum of the total material (KBr disc), shown in fig. 4.29, indicates several bands which may be attributed to the presence of the volatile degradation product p-tolualdehyde (indicated with \* in the spectrum). The other bands may be attributed to the presence of polymer short chain fragments. The evidence for these polymer short chain fragments was obtained when they were precipitated by adding diethyl ether and subsequently separated and the solvent evaporated. The resulting crystalline solid (needles) was partially soluble in chloroform and benzene. Evaporation of the yellow ethereal solution which remains left a yellow resin-like material as residue.

The infrared spectrum of the crystalline solid (KBr disc) consists of bands which are mainly characteristic of the polymer; only minor differences are observed (fig. 4.30). In the region 3100-3000  $\text{cm}^{-1}$  three bands at 3070, 3045 and 3020 are clearly distinguishable. These bands are attributable to the C-H stretching vibration of the aromatic ring. The absorptions at 2970 and 2885  $\text{cm}^{-1}$  are characteristic of the C-H stretching vibration of the  $-\text{CH}_2-$  groups in poly(p-xylylene carbonate). A weak band at 2830  $\text{cm}^{-1}$  is attributable to the CH stretching vibration of  $-\text{CH}_2-$  group in the oligomer. In the region 1100-700  $\text{cm}^{-1}$  new bands are present at 1070 and 995  $\text{cm}^{-1}$  which are attributable to a different spatial conformation of the

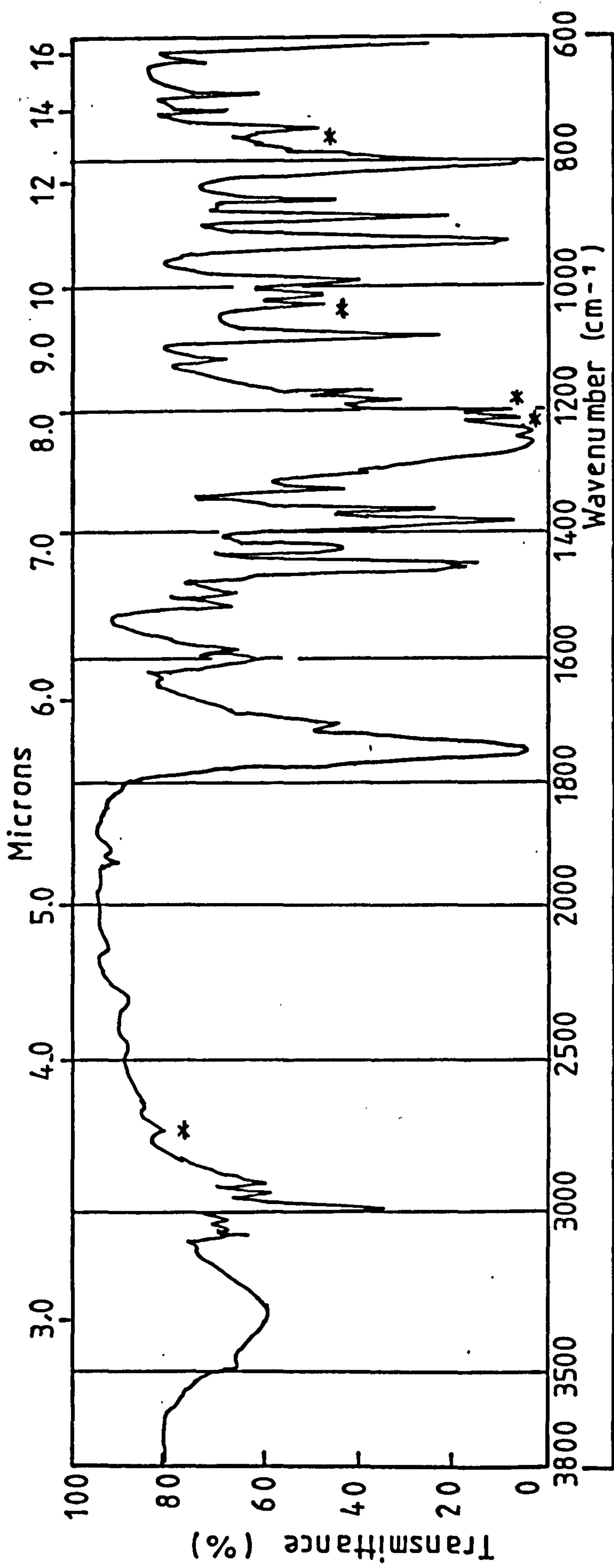


Fig. 4 29 Infrared spectrum of total fraction CR F for poly (p - xylylene carbonate ) heated to 500°C (KBr disc.)



oligomeric chains in comparison with the polymer. Microanalysis of the product gave C = 68.87%, H = 4.87% and O = 29.30%. These are in good agreement with the theoretical values for the molecular formula  $(C_9H_8O_3)_n$ .

The nmr spectrum of the soluble material in  $DCCl_3$  (fig. 4.31) shows a singlet at 7.14  $\delta$  (ppm). The first peak arises from the coupling of protons on the aromatic ring, a singlet indicates that all protons are chemically equivalent (this may be expected from a p-xylylene structure). The chemical shifts at 5.34  $\delta$  (ppm) and 4.98  $\delta$  (ppm) (shifted toward lower field in relation to normal ester  $R-CO-O-\underline{CH_2}-R'$ ,  $\delta$  ppm = 3.7-4.1) could be explained in terms of the deshielding effect of two adjacent carbonate groups present in a regular fashion on the chain fragment.

The infrared spectrum of the yellow resin-like material indicates a complex pattern of absorption bands probably arising from a mixture of different materials.

A GC-MS investigation of the total cold ring material for sample A gave three different peaks. The first peak, retention time 19.7 min, with a molecular ion at  $m/e$  120, corresponds to p-tolualdehyde. The second peak, retention time 22.1 min, with a molecular ion at  $m/e$  136, corresponds to p-methyl benzoic acid, which could arise from the oxidation of the first compound. The third peak, at retention time 25.8 min, gave intense peaks in the mass spectrum at  $m/e$  266, 253, 295, 164, which may be due to the fragmentation of an oligomer.

The presence of the volatile product p-tolualdehyde, was already indicated in the mass spectrum.

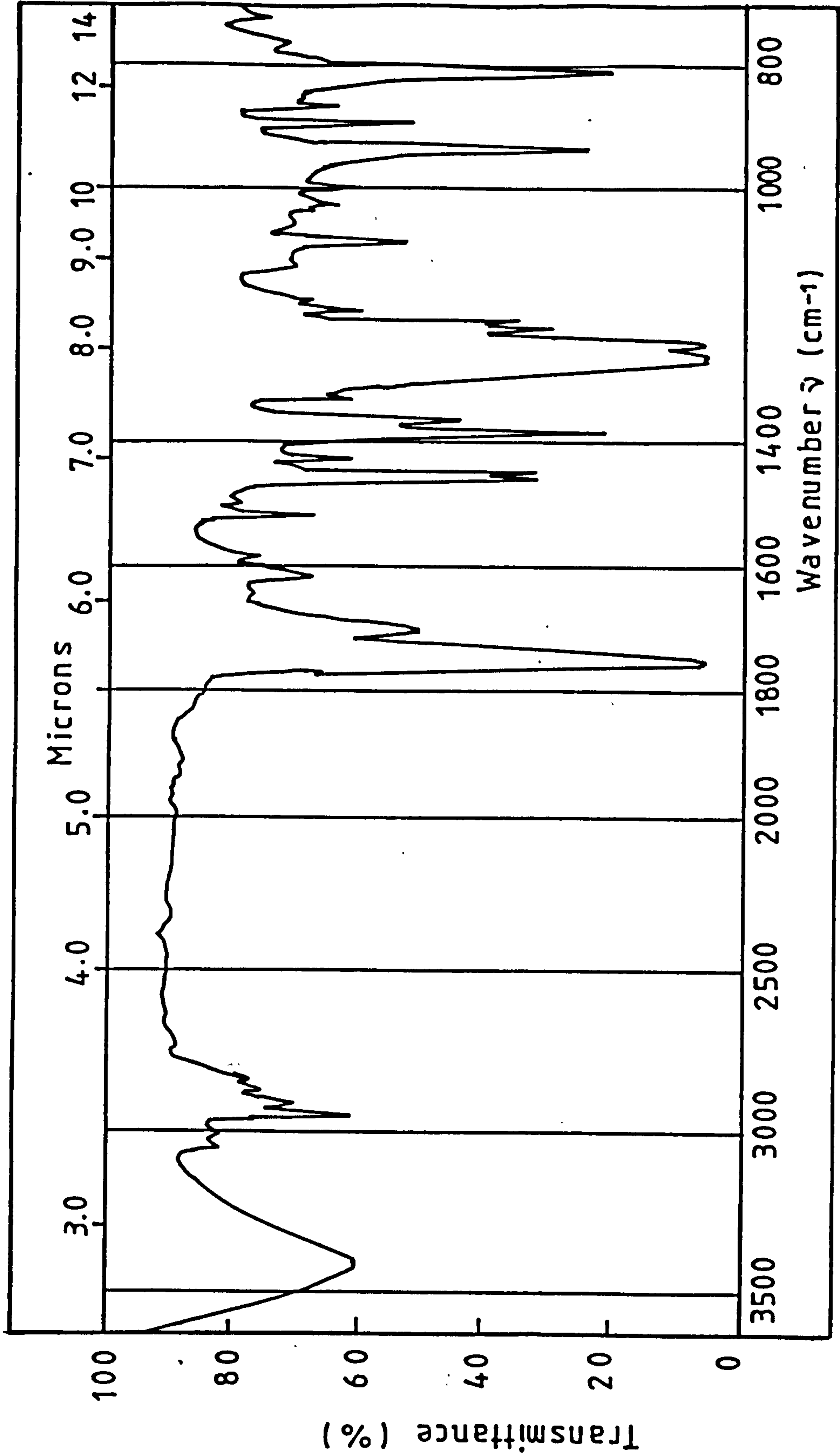


Fig. 4.30 Infrared spectrum for CRF of poly(p-xylylene carbonate) sample A in TVA heated to 500°C (KBr disc.)

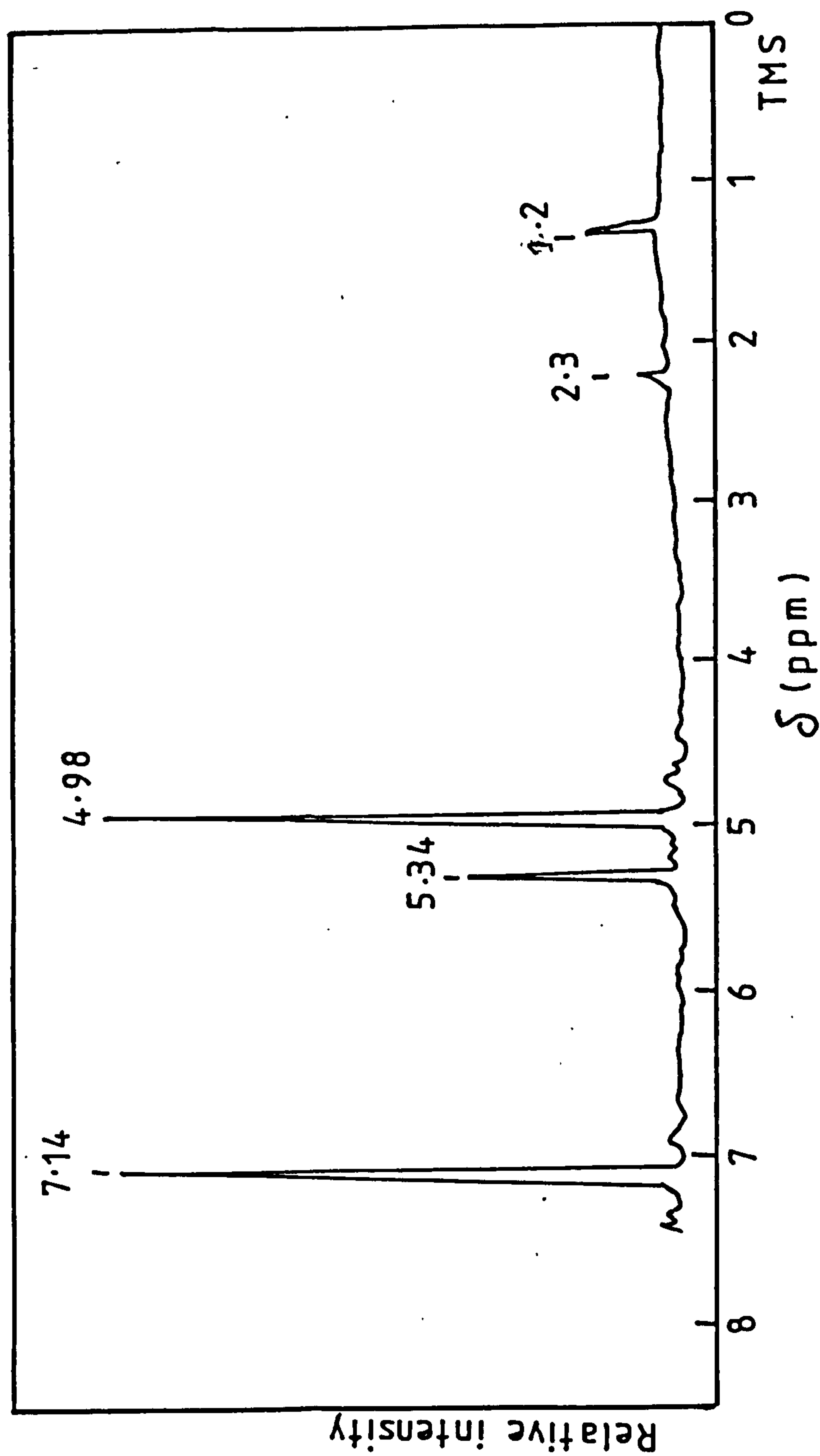


Fig. 4.31. nmr spectrum of degradation product (RF) crystalline solid for poly(p-xylylene carbonate) sample A heated to 500°C

#### 4.7.1.6 Thermal Volatilisation Analysis (TVA) for Sample B

The TVA curve for poly(p-xylylene carbonate), sample B, is shown in fig. 4.32.

From the 0°C TVA curve, it is observed that the evolution of volatile material takes place in one stage with rate maximum of volatilisation at ~400°C.

The process of degradation produces substances of a wide range of volatility which is indicated by the lack of coincidence of the traces. The large separation of the -100°C and -196°C traces suggests the presence of a substance, for example CO<sub>2</sub>, which is volatile at -100°C but condensed at -196°C. Non-condensable gases are also produced in small amounts as indicated by the -196°C trace, e.g., carbon monoxide.

The difference in temperature between the maximum rate of volatilisation in TVA (400°C) and TG (337°C) indicates that in the degradation process, products which are volatile at degradation temperature and involatile at ambient temperature, are formed at 337°C. This was confirmed by performing isothermal TVA experiments. When samples were heated at 250° and 265°C, no volatile products were collected in the -196°C trap. However, a solid material was collected on the cold ring for all degradation temperatures. This proved that the weight loss observed in TG at temperatures as low as 337°C is due to the production of cold ring fraction at low temperatures during the degradation process.

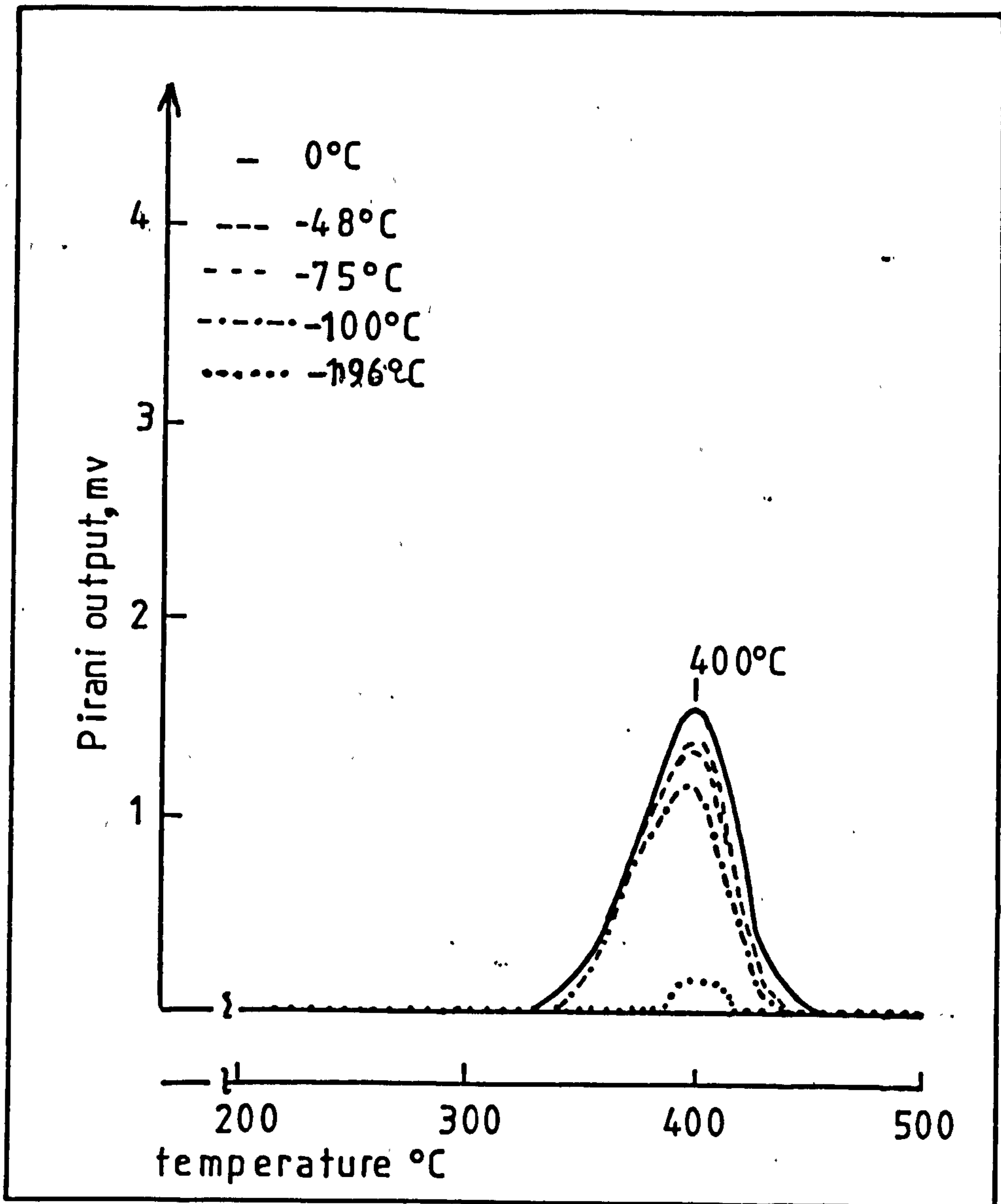


Fig. 4.32 TVA curve for poly(p-xylylene carbonate) sample B heated to 500°C at 10°C/min



#### 4.7.1.7 Subambient Thermal Volatilisation Analysis (SATVA) for Sample B Products

The SATVA curve for the volatile degradation products for sample B is shown in fig. 4.33. The material corresponding to each peak was analysed and assigned by means of infrared, mass and nmr spectrometry, where applicable.

The peaks at  $-146^{\circ}$ ,  $-47^{\circ}$  and  $-6^{\circ}\text{C}$  correspond to carbon dioxide, a mixture of water and p-tolualdehyde and p-tolualdehyde, respectively.

#### 4.7.1.8 Characterisation of Cold Ring Fraction

The cold ring fraction obtained by heating in TVA sample B gives a band of yellow-greenish coloured waxy material. The material was analysed by infrared spectroscopy.

The infrared spectrum (fig. 4.34) consists of bands which are characteristic of the polymer. The only difference is a better resolution of the bands. In general this spectrum is comparable to the infrared spectrum already shown for sample A.

The TVA results suggest that in the degradation of poly(p-xylylene carbonate) the main degradation product is short chain fragments (CRF) which probably form by main chain scission at the carbonate groups. The evolution of a small amount of volatile degradation products, e.g., carbon dioxide and p-tolualdehyde, indicates that secondary reactions occur.

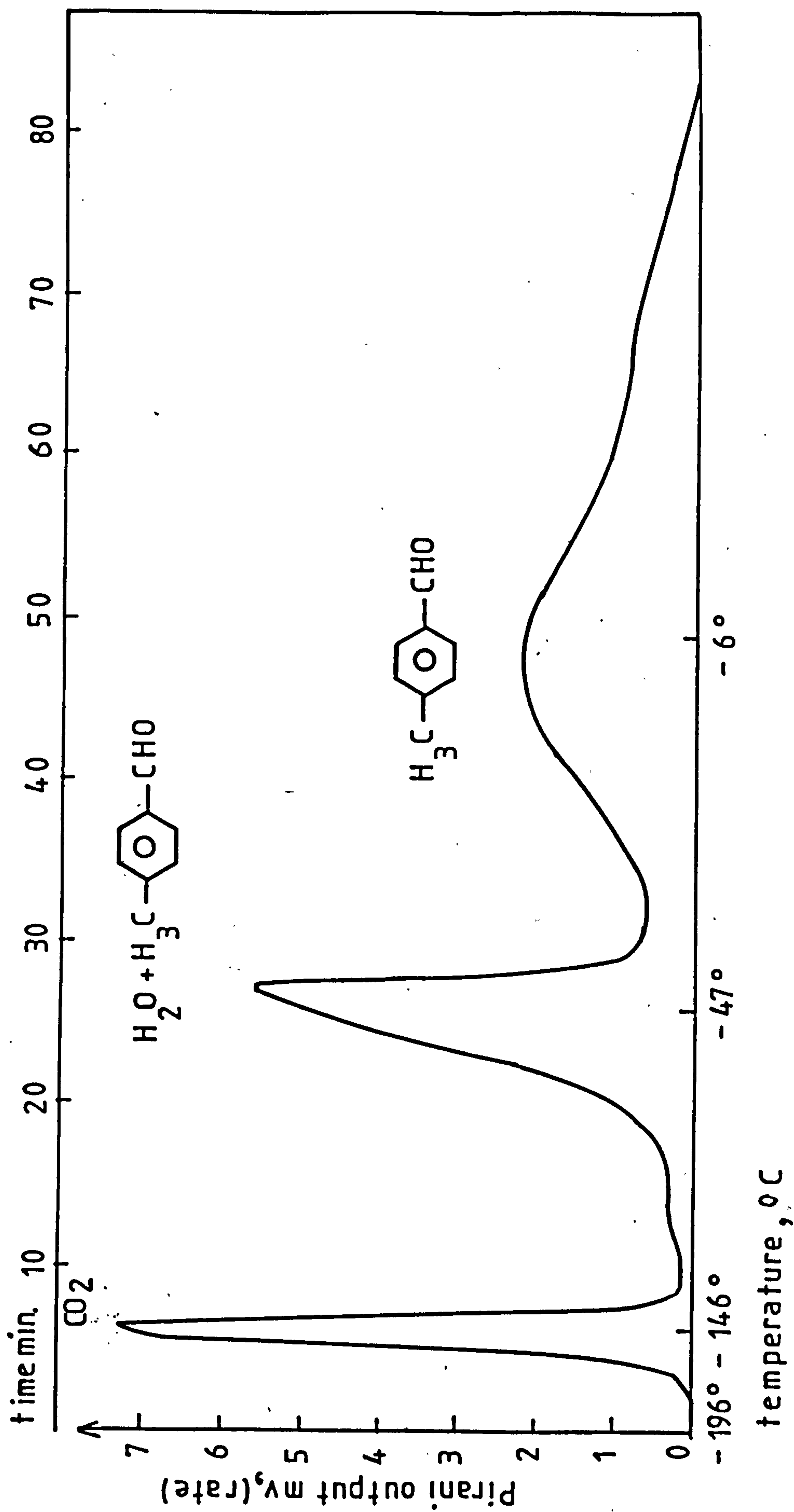


Fig.4.33 SATVA curve of products of degradation of poly(p-xylylene carbonate) sample B to 500°C under vacuum at 10°C/min.

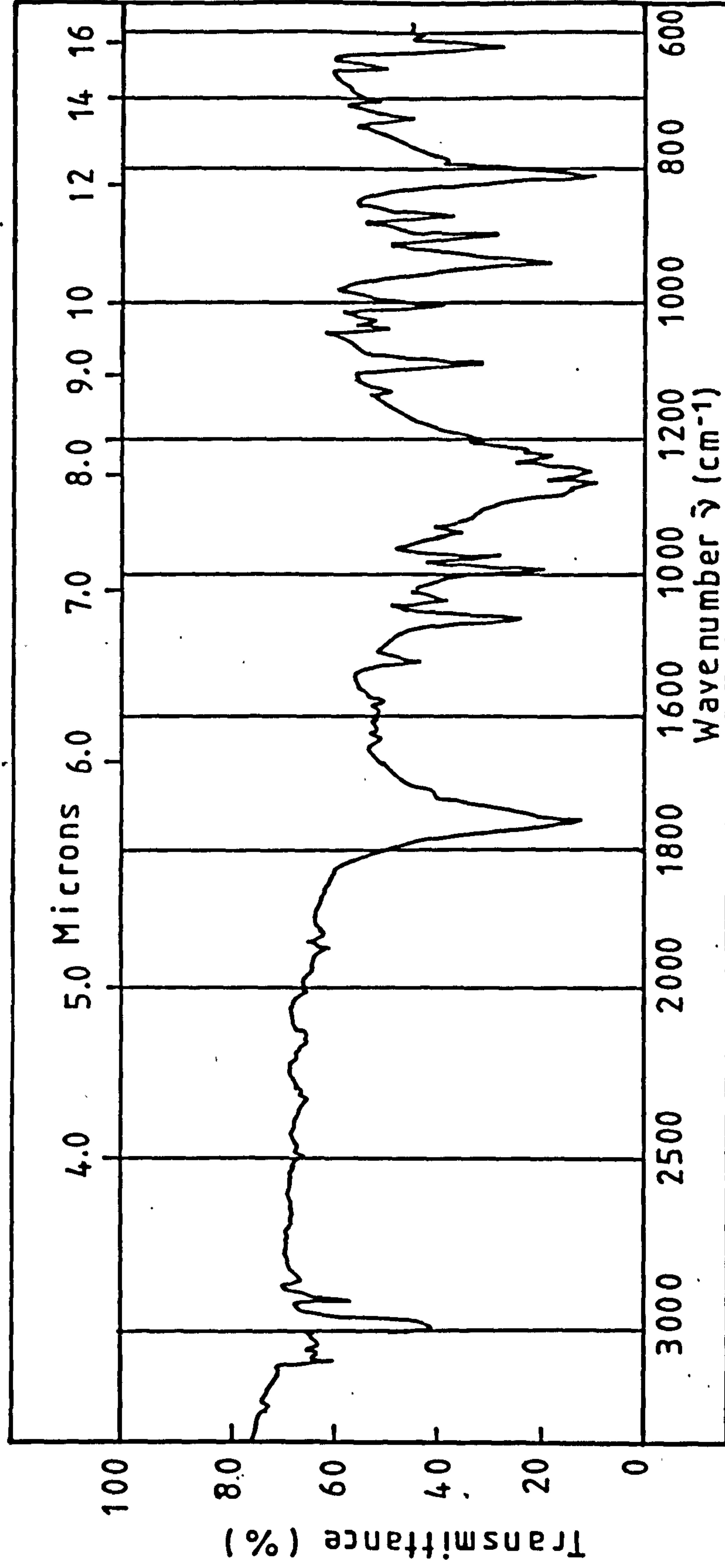


Fig.4.34. Infrared spectrum for CRF (crystalline solid) for poly (p - xylene carbonate) sample B in TVA heated to 500°C

#### 4.8 ISOTHERMAL DEGRADATIONS FOR ALIPHATIC-AROMATIC POLYCARBONATES

##### 4.8.1. Production of Condensable Gases

The SATVA curves for the products of degradation when poly(p-xylylene carbonate) samples A and B (see p. 61) were degraded under vacuum for one hour at various temperatures, were recorded. The purpose was to observe any change in the nature of the degradation products evolved as the temperature was increased.

Sample A gives the same volatile products for all temperatures of degradation.

Sample B gives no volatile materials after the degradation at 250°C, but at 270°C carbon dioxide is formed and p-tolualdehyde appears as a product when the temperature of degradation reaches 290°C.

Water is not present in the products of degradation at 250°C, but appears at 260°C and subsequent higher temperatures of degradation. Qualitatively, it was observed that the amount of each substance, including water, increased with temperature. If water is present as an impurity in the polymer, the amount should be constant for all temperatures of degradation. These observations suggest that some water is produced as a degradation product.

These results suggest structural differences between samples A and B.

##### 4.8.2 Characterisation of Cold Ring Fractions

The cold ring fractions formed after heating samples of poly(p-xylylene carbonate) sample A at 200°, 250° and 275°C under



vacuum for one hour, were collected and analysed by infrared and nmr spectrometry.

At 200°C, a white crystalline solid was observed. At higher temperatures, the CRF became progressively more yellow-coloured.

The infrared spectra of these products consists of bands which are mainly characteristic of the polymer, but in the region 3500-2800  $\text{cm}^{-1}$ , small differences are evident (fig. 4.35).

The bands in the region 3360-3220  $\text{cm}^{-1}$  can be attributed to the stretching vibration of OH groups ( $\text{H}_2\text{O}$  absorbed). In the region 2965-2880  $\text{cm}^{-1}$ , bands occur at 2960, 2918 and 2882. Those at 2960 and 2882  $\text{cm}^{-1}$  are characteristic of the polymer. The band at 2918 could be attributed to the stretching for  $-\text{CH}_3$  groups.

The nmr spectrum of this fraction, along with the spectrum of the fraction at 275°C, is shown in fig. 4.36.

Peaks of different intensity occur in the region 7.41-7.14  $\delta$  (ppm). The singlet at 7.14  $\delta$  (ppm), clearly the most intense, corresponds with the same peak present in the nmr spectrum of the crystalline solid obtained under programmed degradation conditions. These peaks arise from the coupling of hydrogen atoms on aromatic groups.

The intense singlet with chemical shift at 4.98  $\delta$  (ppm) is in the region of absorption for a methylene group adjacent to a carbonate group.

For sample B, the infrared spectrum for the cold ring fraction obtained after heating at 275° is shown in fig. 4.37. This spectrum consists of bands which are mainly characteristic of the polymer. In the region 3480-3380  $\text{cm}^{-1}$  a broad band may be attributed to  $-\text{OH}$  groups or



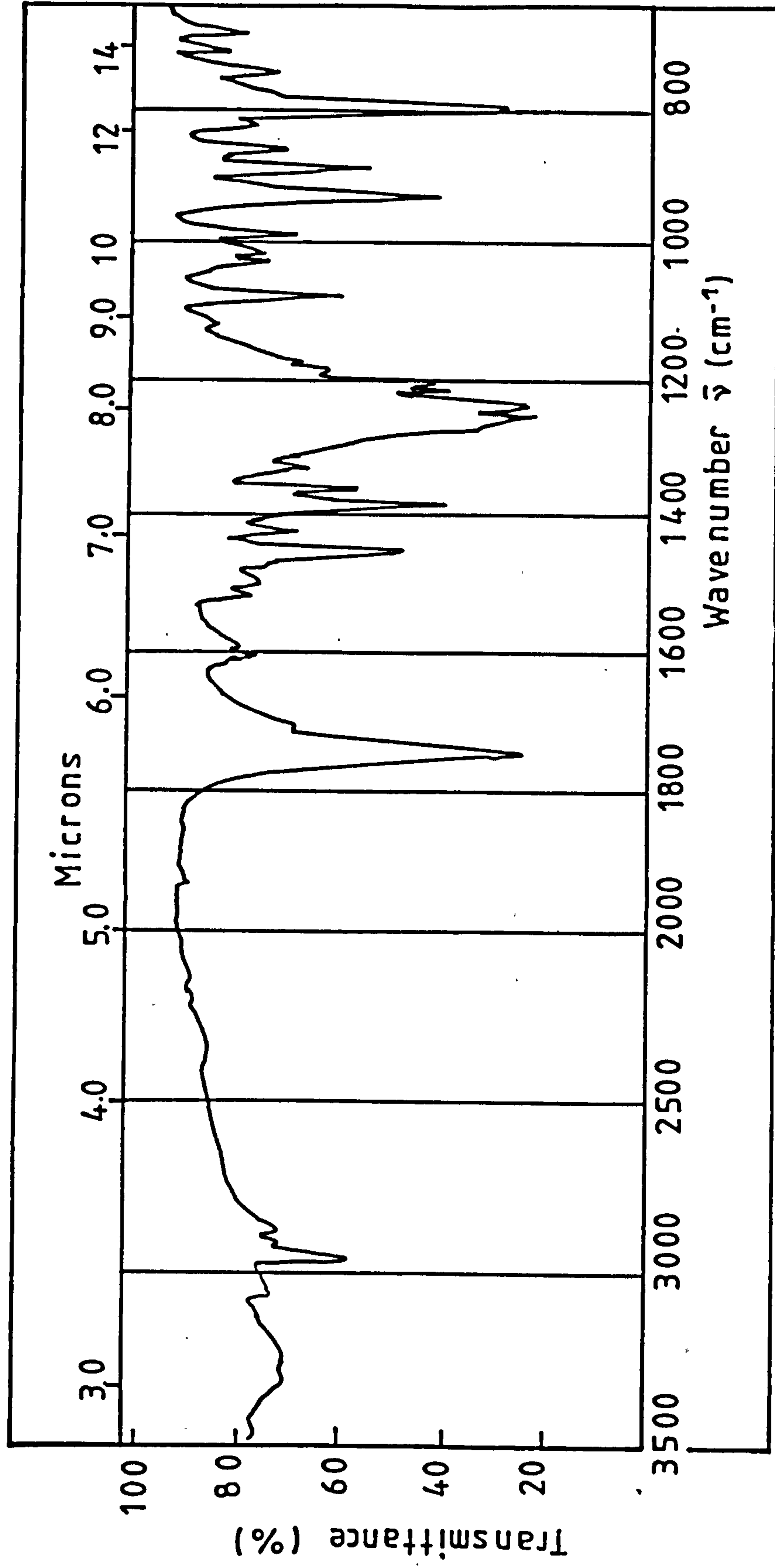


Fig.4.35. Infrared spectrum for C R F of poly(p- xylylene carbonate )  
sample A in TVA heated to 200°C (KBr disc)

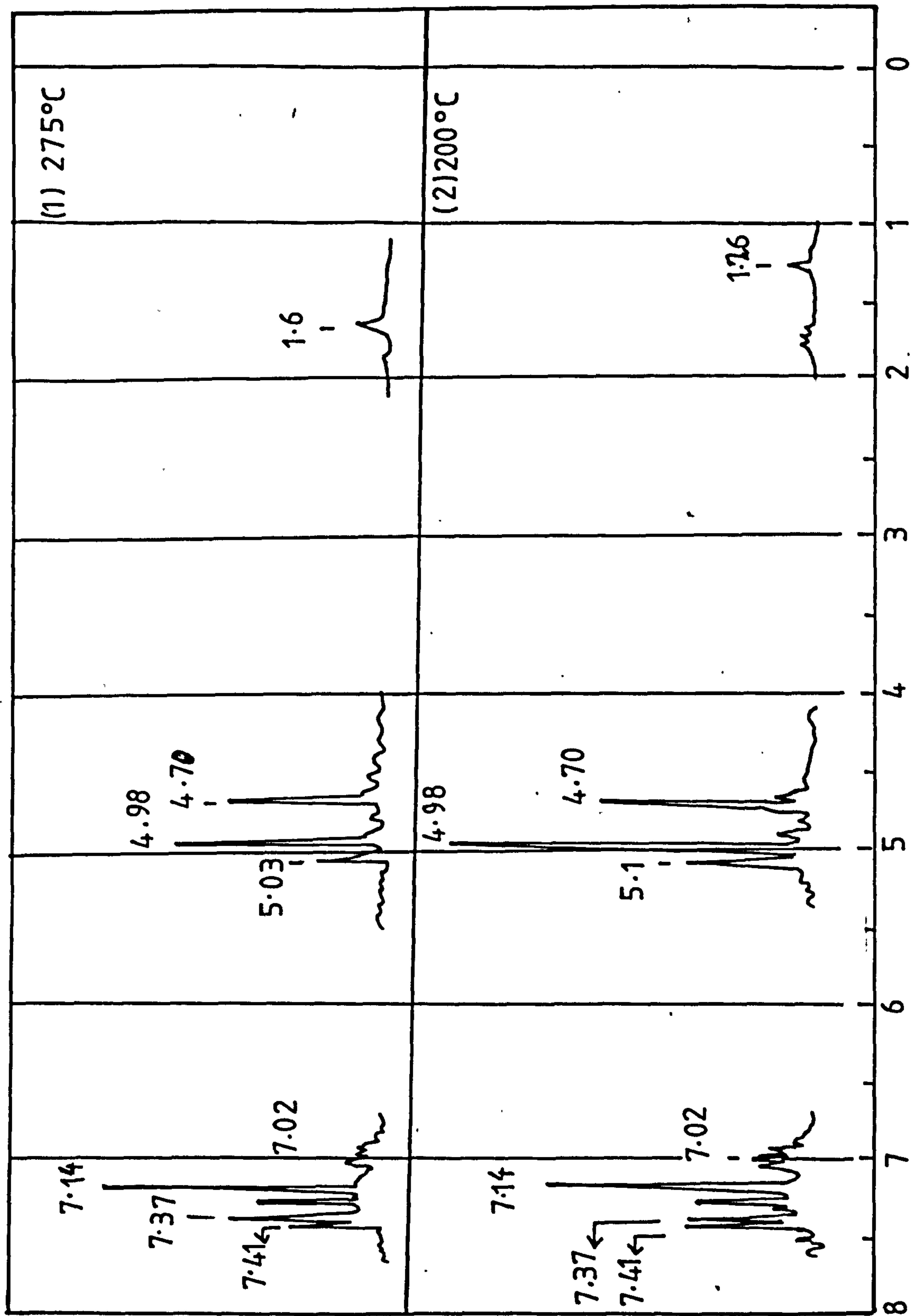


Fig. 4.36. nmr spectrum for degradation product (total CRF) of poly (p-xylylene carbonate) sample A, heated at 275° and 200°C, respectively

water absorbed. Four bands are observed at 2963, 2923, 2880 and 2850  $\text{cm}^{-1}$ . Those at 2960 and 2880 are characteristic of the polymer. The bands at 2920 and 2850 are attributed to the presence of methyl groups.

The nmr spectrum of this CRF, fig. 4.38 shows a multiplet at 7.40-7.14  $\delta$  (ppm) which can be attributed to the resonance of protons on aromatic rings. An ill-defined multiplet centred on 5.18  $\delta$  (ppm) and a highly intense singlet at 4.97  $\delta$  (ppm) can be attributed to the resonance of protons on methylene groups linked to carbonate groups. Two distinct singlets at 2.30  $\delta$  (ppm) and 1.20  $\delta$  (ppm) suggest the presence of a methyl group of an aromatic ring and an isolated methyl group, respectively.

The peaks at 7.14 and 4.97  $\delta$  (ppm) are in the same position as the peak for the crystalline CRF obtained from sample A under heating. The presence of polymer short chain fragments is verified by the appearance of peaks at 7.38 and 5.18  $\delta$  (ppm). These peaks have identical chemical shifts to the values reported by Soga et al.,<sup>44</sup> for a similar polymer.

It may therefore be concluded that the cold ring fractions obtained under isothermal heating for both polymers A and B are of similar nature and consist of polymer short chain fragments. The presence of OH and a methyl group is indicated for sample B.

The difference in texture and colour from a white crystalline solid to a yellow waxy-like solid may suggest that the relative proportions of different molecular weight polymer short chain fragments change with temperature.

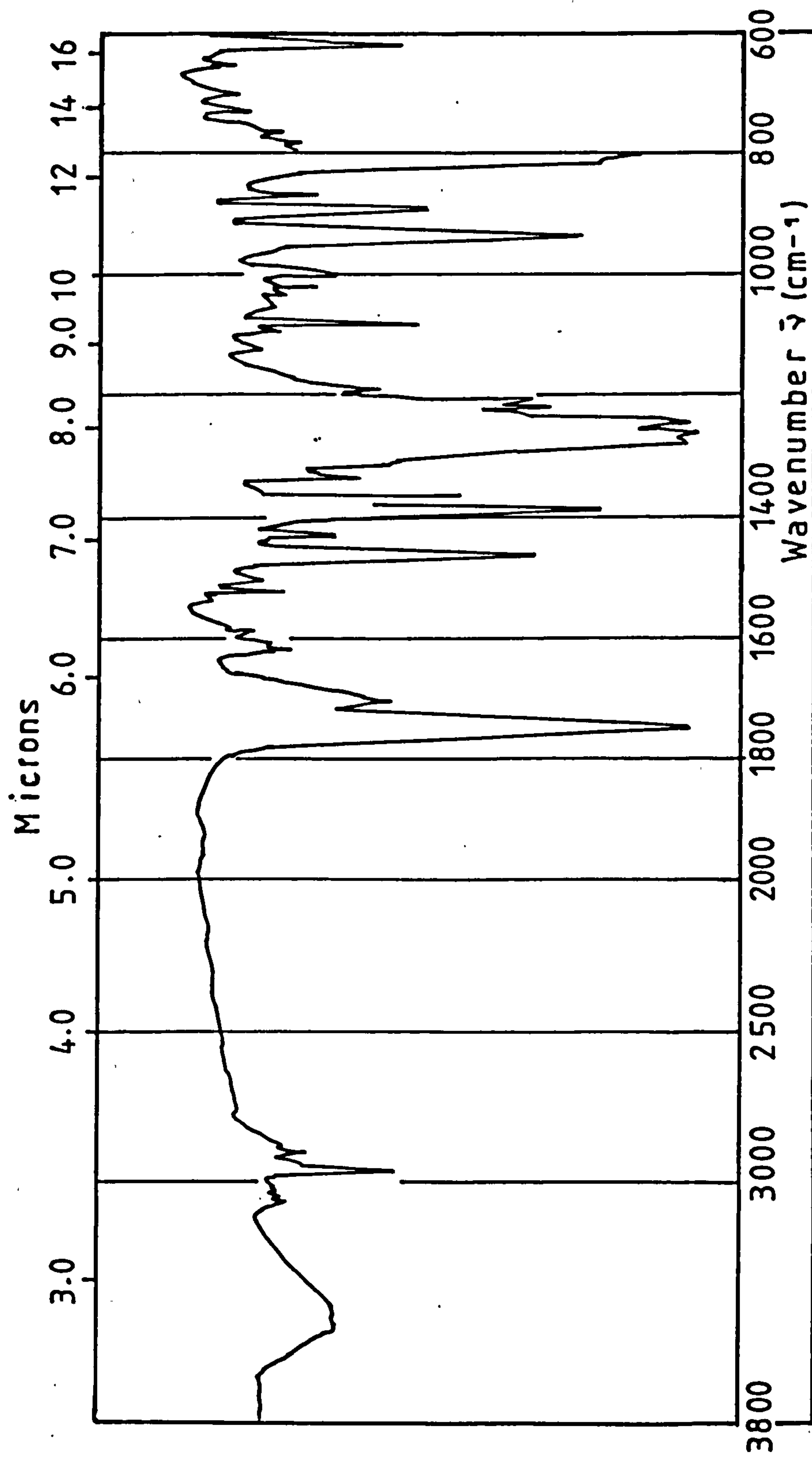


Fig. 4.37 Infrared spectrum for products of degradation total CRF of poly (p-xylylene carbonate) heated to 275°C for one hour

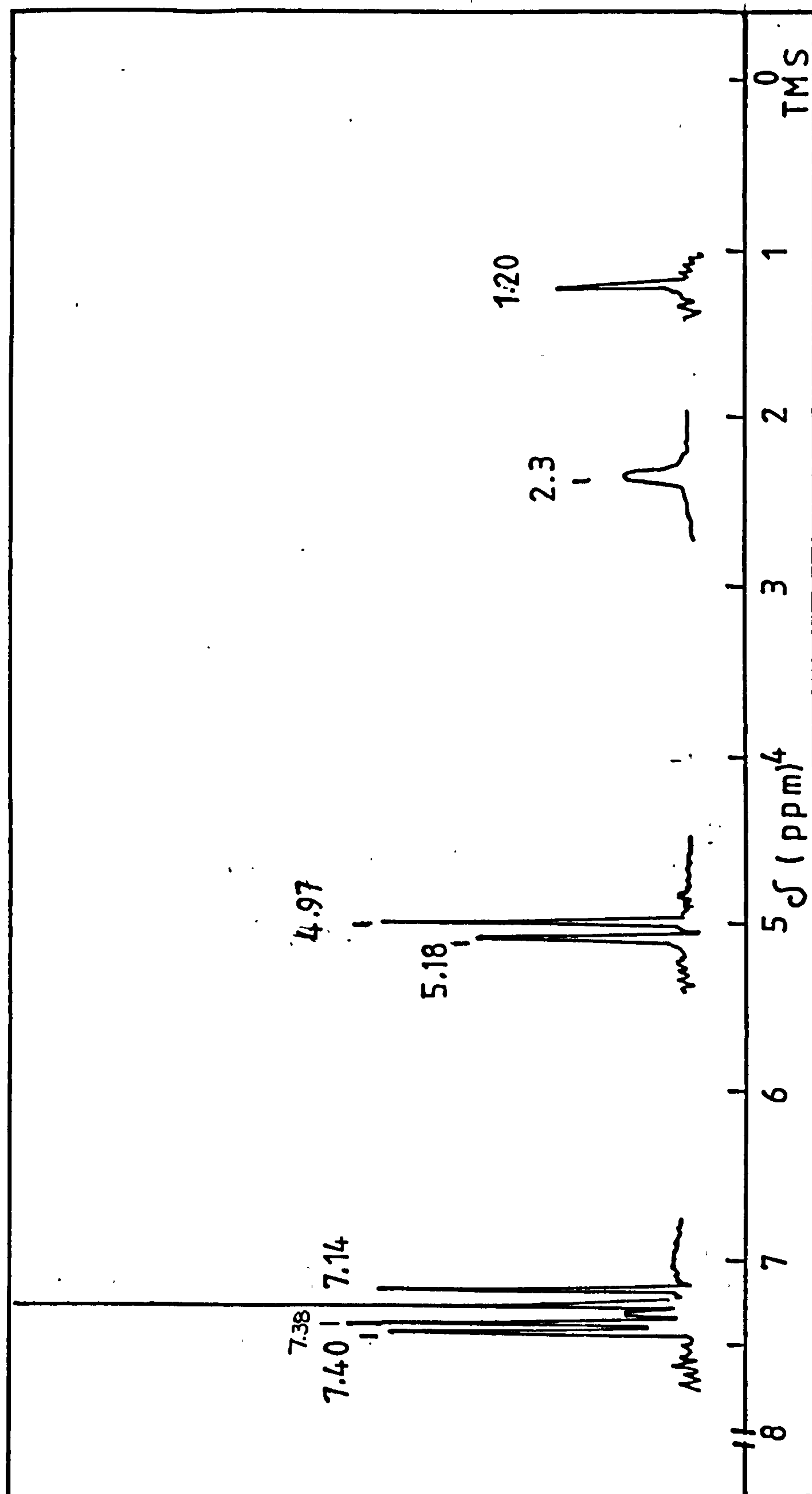


Fig. 4.38. nmr spectrum for products of degradation (cold ring) for poly (p-xylene carbonate) sample B heated to 275°C.



#### 4.8.3 Spectral Changes for Polymer Residue

In order to observe any structural change within the polymer as it was degraded a sample of poly(p-xylylene carbonate) sample A, was heated for one hour at 275°C. An infrared spectrum (KBr disc) of the remaining residue was recorded (fig. 4.39). The resulting spectrum showed poorer resolution of the bands and the appearance of a strong band in the region 3500-3400  $\text{cm}^{-1}$ . The bands in the region 3080-3020  $\text{cm}^{-1}$  are extensively overlapped and at higher frequency than the corresponding bands in the polymer. The bands corresponding to C-H stretching vibrations at 2920 and 2860  $\text{cm}^{-1}$  are extensively overlapped. In the region 1100-1000 some bands are also highly overlapped.

Therefore, structural changes take place on heating and this suggests that along with the main chain scission, with the subsequent volatilisation of short chain fragments, secondary reactions are likely to occur in the reacting macromolecules in the residual polymer.

#### 4.9 RATES OF THERMAL DEGRADATION FOR POLY(p-XYLYLENE CARBONATE)

In order to obtain a better insight into the degradation process for poly(p-xylylene carbonate) the rates of thermal degradation for samples A and B for various temperatures were obtained.

Isothermal TG experiments under vacuum were performed for both sample A and sample B.

Samples of polymer A were heated at 200°, 210° and 220°C, respectively. In the case of polymer B, samples were heated at 240°, 250°, 260° and 270°C respectively. Using these curves, graphs of the

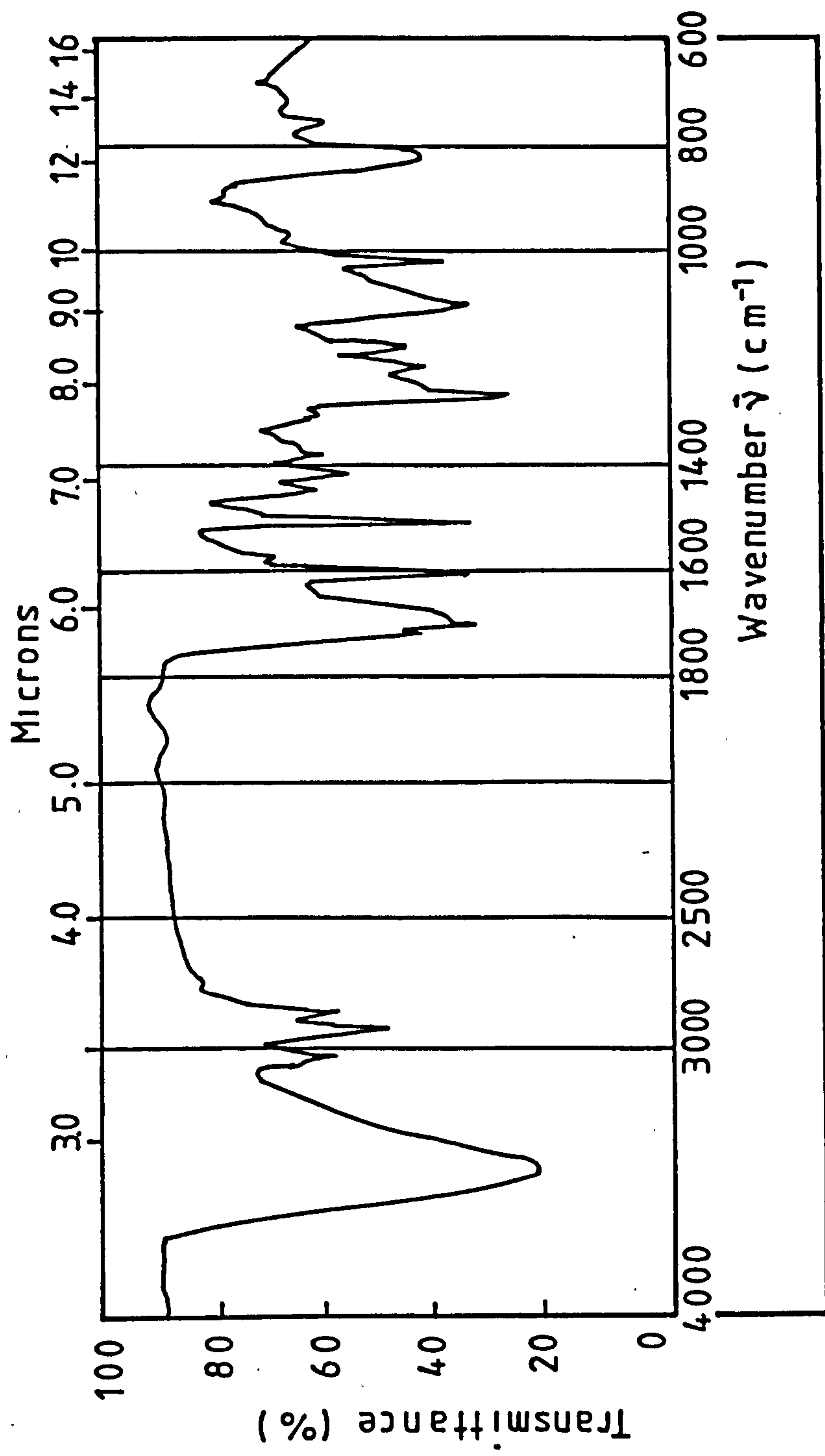


Fig.4.39 Infrared spectrum of residue from poly (p-xylylene carbonate) heated at 275°C for 1hour (KBr disc)

percentage of residue and extent of degradation versus time were made for each temperature (figs. 4.40 and 4.41). By means of these plots the curves for degradation for each polymer versus percentage of volatilisation were derived (figs. 4.42 and 4.43).

The curves clearly show that the rates of degradation increase with temperature. At the lower temperatures, the initial low rates may indicate that the polymers initially degrade at the chain ends. As has already been observed by TVA, the main product of the degradation consists of short chain fragments which are likely to be formed by homolytic cleavage at the carbonate group on the macromolecule backbone. The presence of the p-xylylene group in the backbone of the polymer may hinder the cyclization because of the lower torsional flexibility of the skeletal bonds from an open chain fragment by an ester interchange process.

The considerable increase in rate with temperature and the appearance of volatile degradation products, e.g. carbon dioxide, water and p-tolualdehyde during the degradation process, gives an indication of random fragmentation of the polymer chains involving the carbonate groups, with the production of carbon dioxide. Formation of p-tolualdehyde may be by secondary reaction of the reacting macromolecule.

The presence of non-condensable gaseous products, e.g. carbon monoxide for polymer B, also indicates that free radical reactions which involve the carbonate group, may occur.

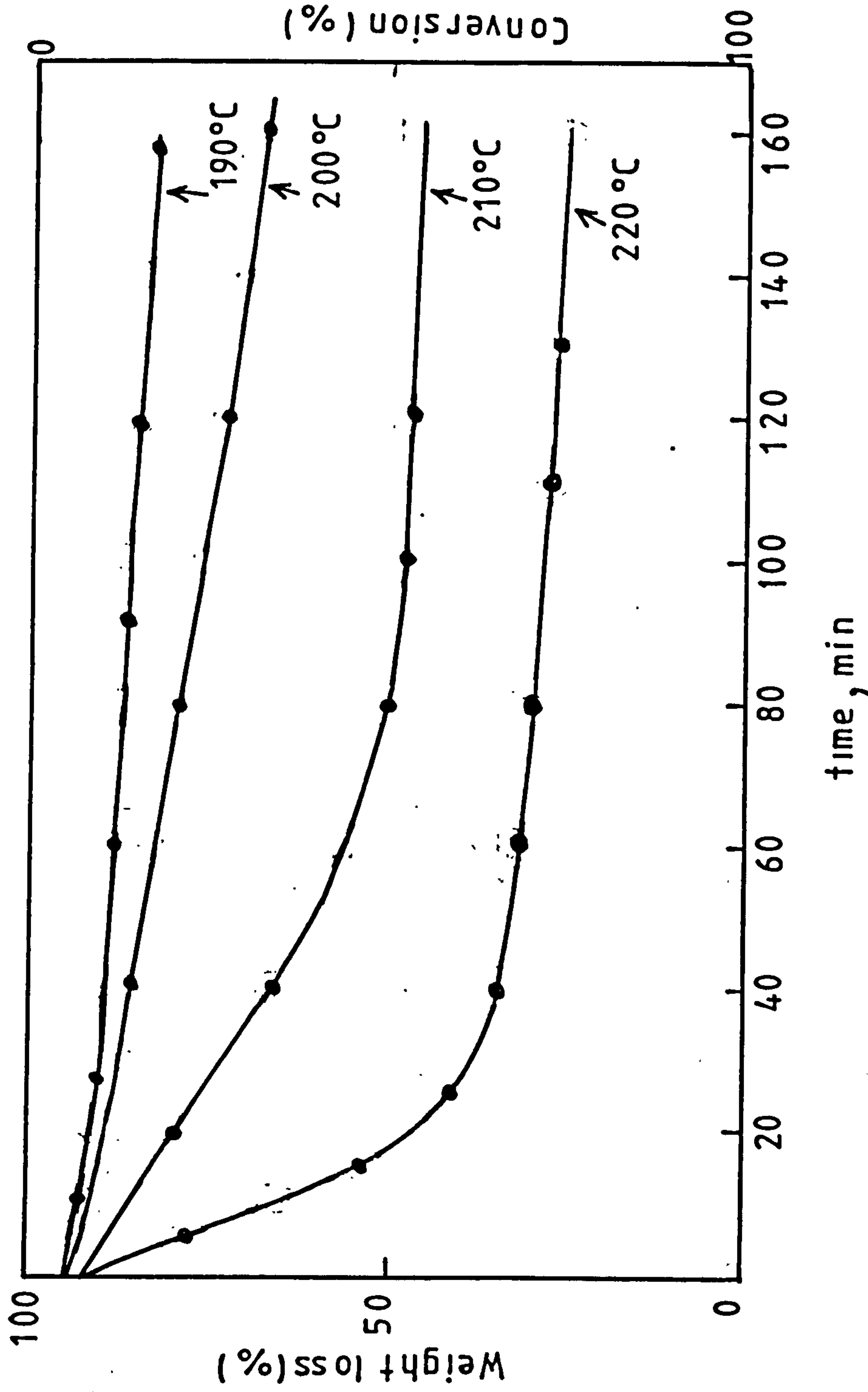


Fig. 4.40 Percentage of weight loss and conversion by TG for poly(p-xylylene carbonate) sample A under vacuum 220°C, 210°C, 200°C, and 190°C respectively.

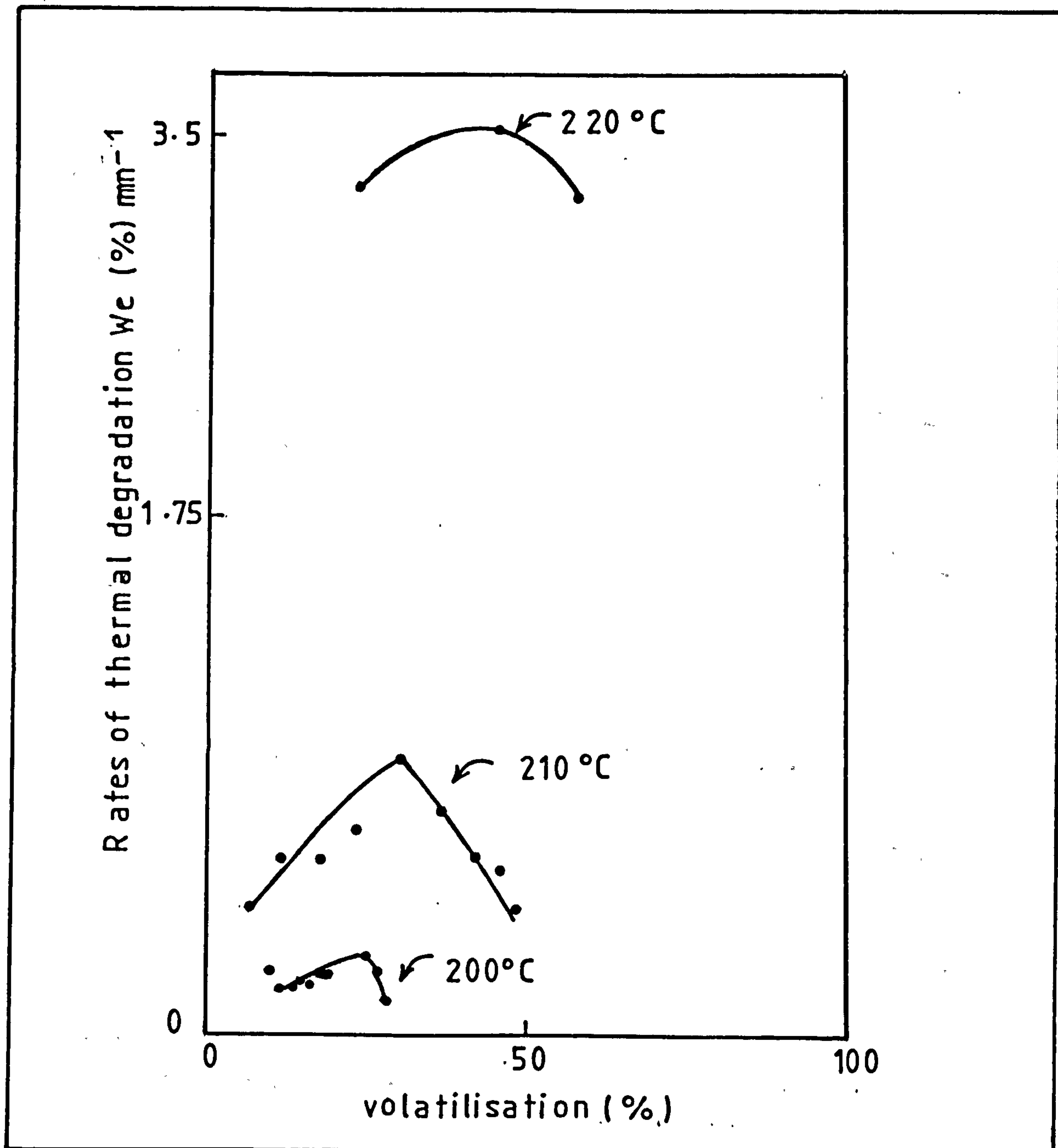


Fig. 4.41 Rates of thermal degradation for poly (p-xylylene carbonate) sample A by TG at 200°, 210° and 220°C respectively, under vacuum vs volatilisation



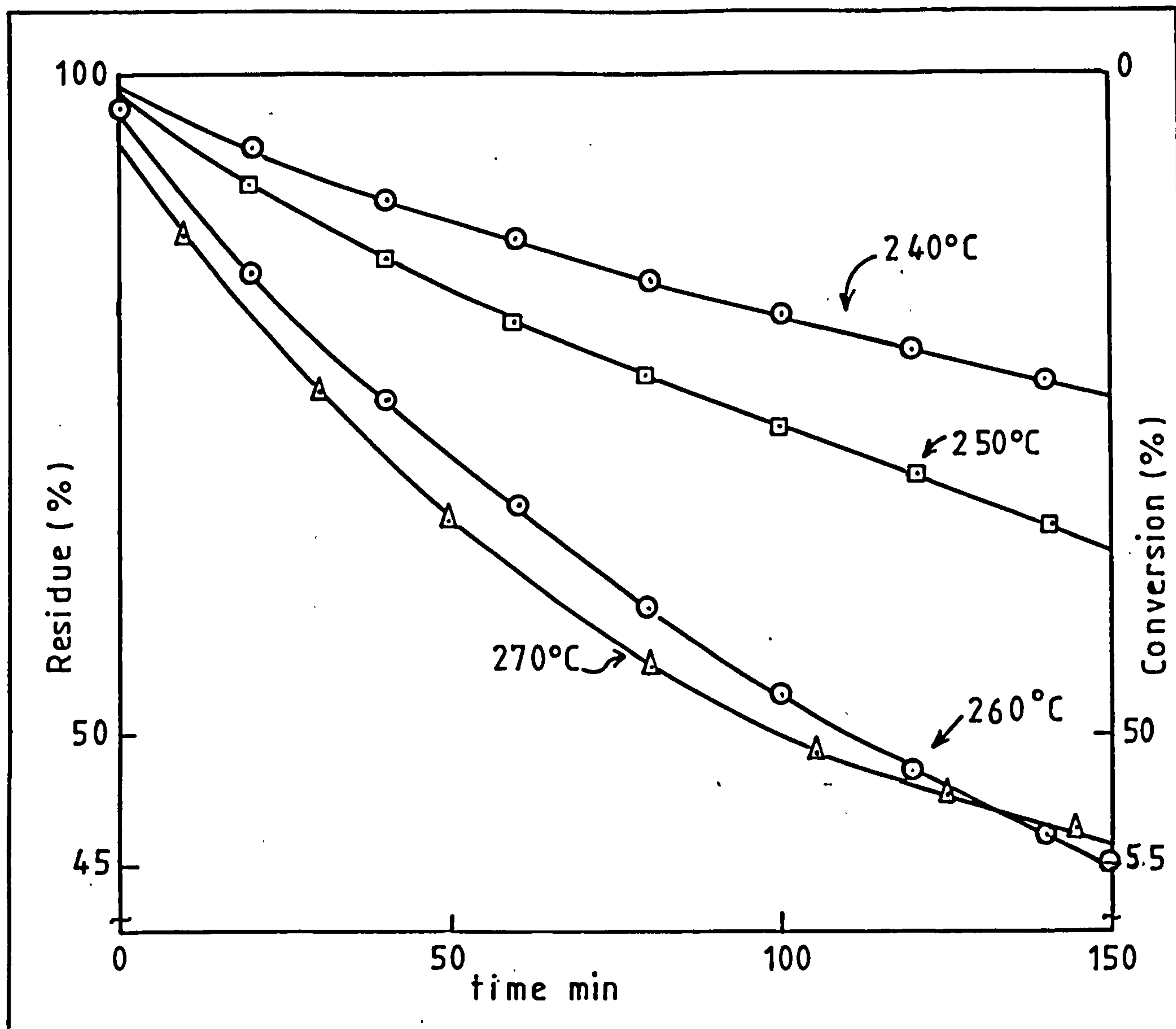


Fig. 4.42. Percentages of residue and conversion for poly(p-xylylene carbonate) sample B by TV heated at 270°, 260°, 250° and 240°C respectively

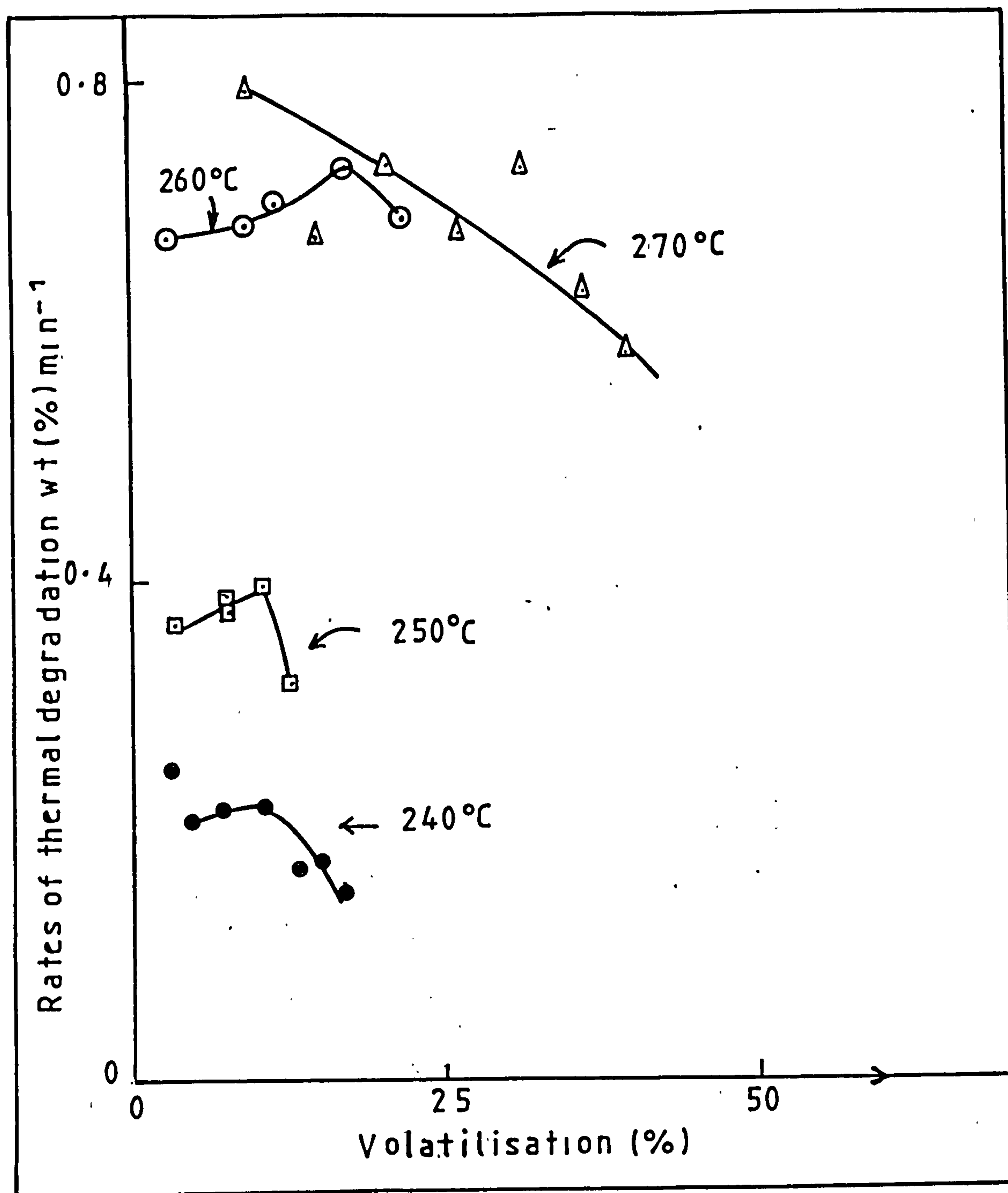


Fig.4.43 Rates of thermal degradation for poly (p-xylylene carbonate) sample B by TG at 240°, 250°, 260°, 270°C respectively vs volatilisation (%).

#### 4.10 HYDROXYL END-GROUPS DETERMINATION

Experiments aimed at establishing hydroxyl end-groups for poly(p-xylylene carbonate) sample A, the least thermally-stable polymer, gave negative results. Thus when a sample of the powdered polymer was treated with acetic anhydride, as already explained in Chapter 2, the starting material was recovered unchanged. The temperature of maximum rate of volatilisation for the materials assessed by TG in N<sub>2</sub> atmosphere was the same as the original polymer (287°C). The negative results may be due to the insolubility of the polymer. Due to the negative results, sample B was not subjected to the same experiment.

#### 4.11 THE MASS SPECTRUM OF DEGRADED POLY(p-XYLYLENE CARBONATE) AND ITS COLD RING FRACTION

The fragmentation pattern by electron impact for poly(p-xylylene carbonate) sample A is shown in fig. 4.44. The spectrum exhibits peaks up to m/e 361. Other major peaks are at m/e 266, 165, 121, 120, 119, 105, 104, 103, 102, 92. The mass spectral data suggest the formation of oligomeric fragments which could be formed by a chain scission process. The spectrum also indicates the formation of prominent fragment ions at m/e 121 and 120, which may be related to the volatile product p-tolualdehyde (MW = 120g/mol), one of the volatile products formed in the TVA degradation. The stability of this structure accounts for the high relative abundance of the molecular ion, at the lower range several fragment ions, at m/e 119, 92, 91, 65, 63, could be related to the further thermal fragmentation of the structure (according to the reported mass spectrum of p-tolualdehyde).

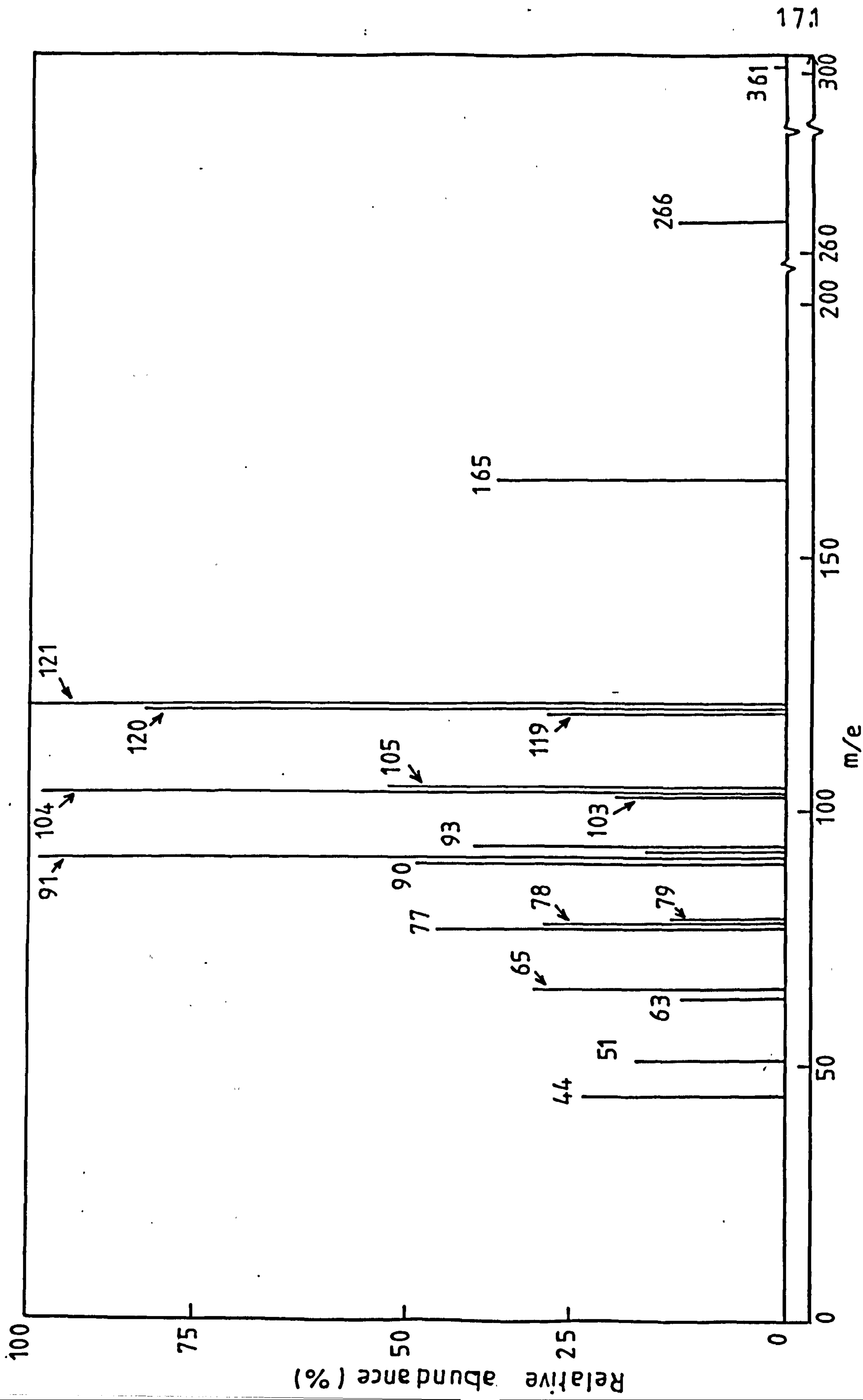
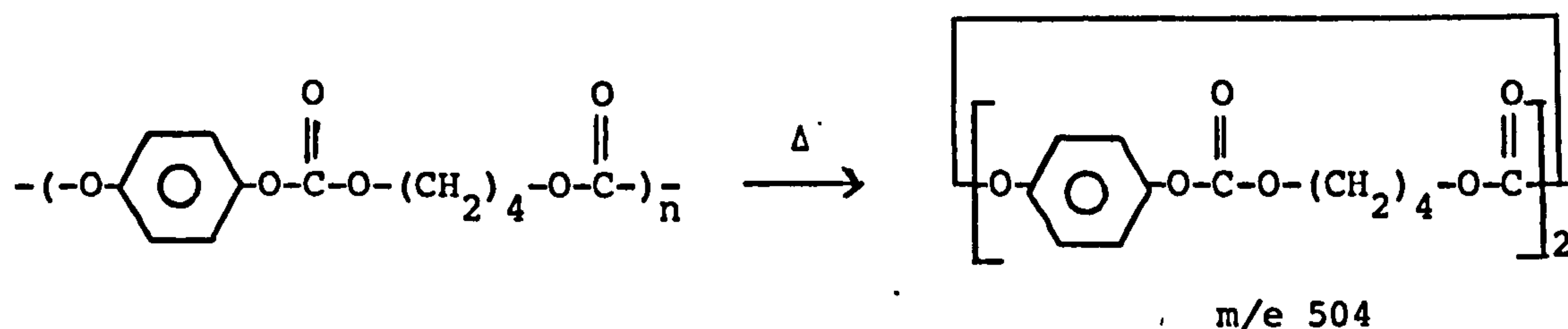


Fig. 4.44 Mass spectrum of the products of the thermal degradation for poly (p-xylylene carbonate) sample A

There appears to be no evidence of cyclic oligomers formed by an ester interchange process. However, this process could not be ruled out. Foti et al.<sup>71</sup> reported that a poly(n-butyl-p-resorcinol carbonate) underwent a thermal decomposition by direct pyrolysis in the mass spectrometer by an ester interchange process with formation of six different cyclic oligomers. The molecular ions of these oligomers were not very intense, probably because of the instability of these partially aliphatic structures to electron impact. The cyclic dimer appeared to be the most stable.



In view of this an intramolecular ester interchange process could be envisaged for poly(p-xylylene carbonate) with the cyclic oligomers being highly unstable to EI.

The main peaks in the mass spectrum of the CRF (crystalline solid) obtained when poly(p-xylylene carbonate) sample A was heated to 500°C in TVA degradation gives peaks up to 328. This fragment ion could be attributed to the presence of the cyclic dimer (MW 328g/mol). Other major peaks are at m/e 266, 165, 121, 120, 119. All these peaks are also related with major peaks observed in the mass spectrum of the polymer. From the evidence obtained by mass spectrometry it can be concluded that the crystalline solid (CRF) may consist of short chain fragments which degrade in the mass spectrometer giving the characteristic fragmentation as the polymeric system.



#### 4.12 DISCUSSION

##### Aliphatic-Aromatic Polycarbonates

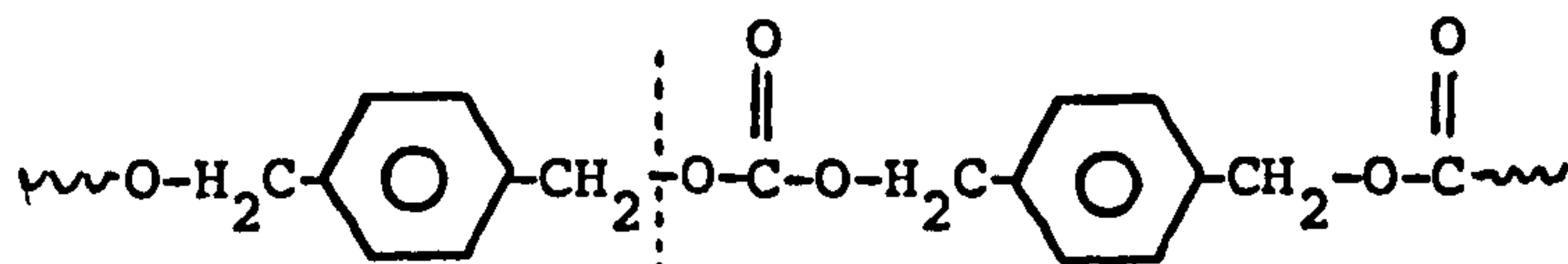
From TVA degradations it has been determined that the main products of degradation of poly(p-xylylene carbonate) samples A and B are solid degradation products (CRF) which consist of a mixture of short chain fragments. Minor amounts of volatile products, carbon dioxide, p-tolualdehyde, water and carbon monoxide were also identified. Measurements of the relative proportions of some of the products will be discussed in a later chapter.

From these results the following types of reactions may be considered to represent the probable mechanism of degradation:-

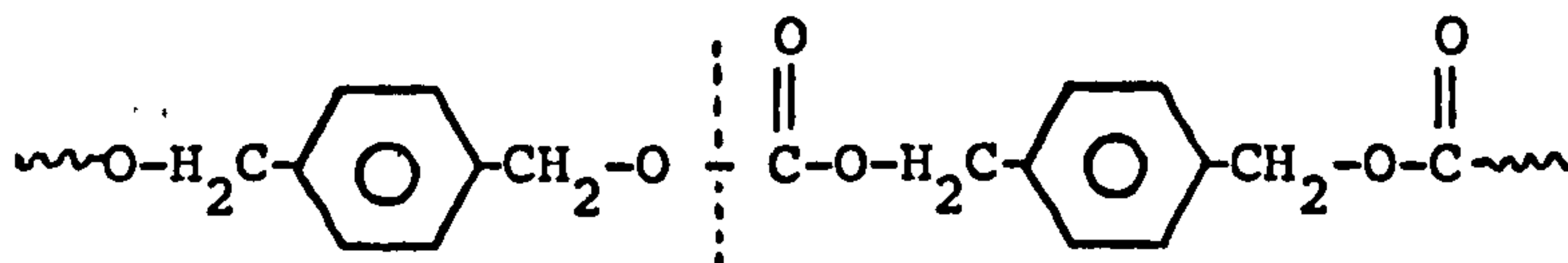
- a) At the lower temperatures, main chain scission reactions may take place, most probably at the carbonate groups with evolution of carbon dioxide, causing the formation of short chain fragments which volatilise from the reaction medium when the length is lower than the volatilisation threshold at the degradation temperatures.
- b) At higher temperatures, random chain scission and thermal elimination at the carbonate groups may explain the formation of higher amounts of carbon dioxide and p-tolualdehyde. The TVA curve showed that radical reaction resulting from homolytic scission of the carbonate group, causing decarbonylation, is of little importance below 400°C.
- c) Depolymerisation via an ester interchange reaction initiated at the chain ends, causing the formation of cyclic oligomers.

The presence of polymer short chain fragments as CRF may be explained through a random chain scission at the carbonate groups with evolution of small amounts of carbon dioxide and formation of oligomeric structures.

The scission at the carbonate group may occur at two possible sites.

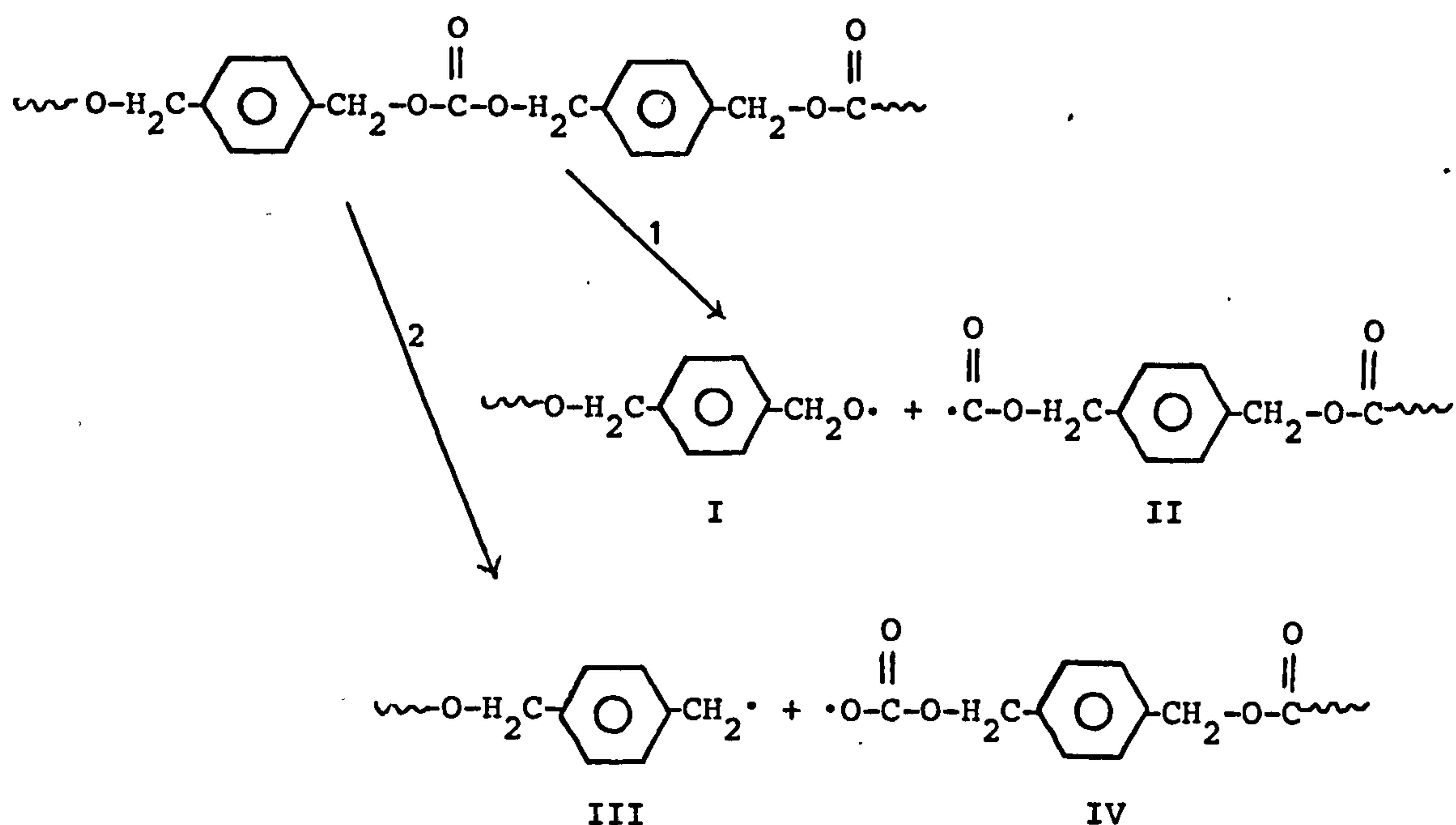


Cleavage of an ether bond



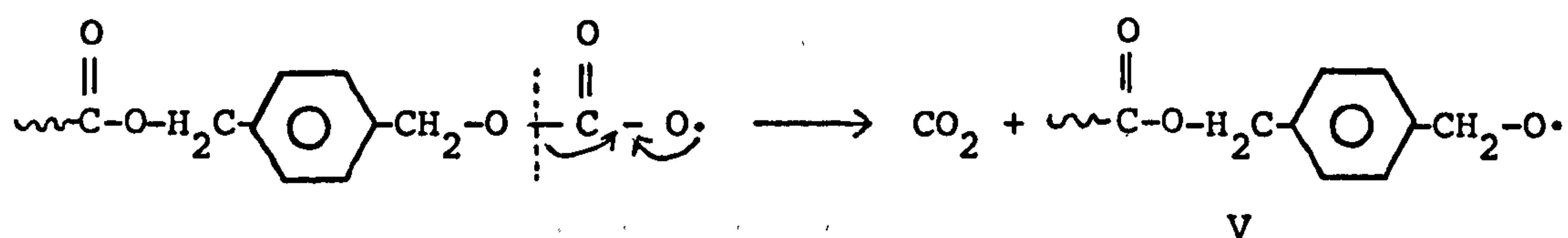
Cleavage of an ester bond

The bond dissociation energy of the acyl bond is higher in general terms than that of the ether bond, as already seen for aliphatic polycarbonates, although the actual energy depends on the electronic environment in the macromolecule. Thus the bond cleavage would be through two possible different pathways, to give

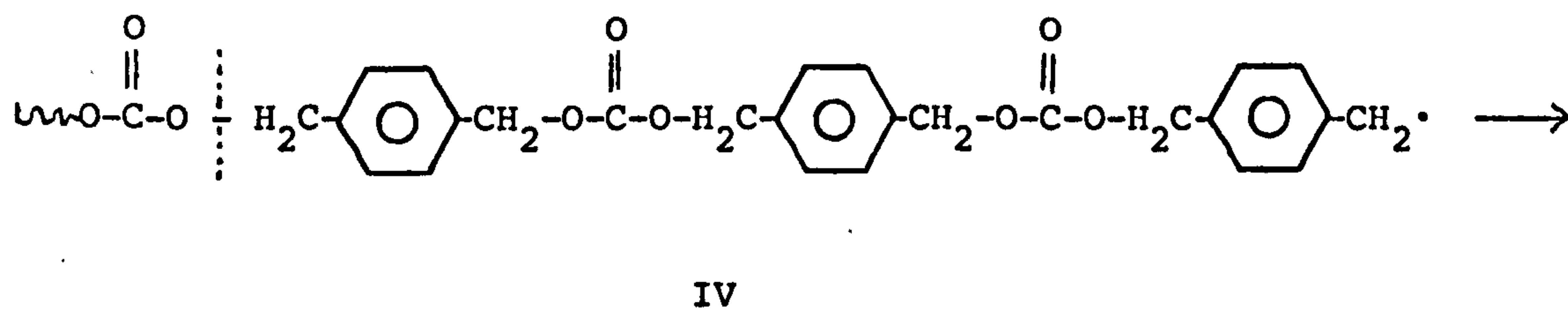


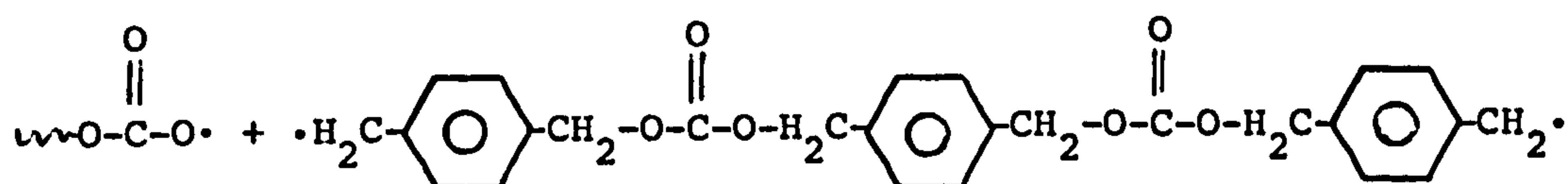
The pathway 1 would involve much more energy because the ester bond is cleaved. The pathway 2, which involves an ether cleavage, would require less energy. Thus the latter would be the preferred route of breakdown.

The labile fragment IV formed by route 2 can undergo decarboxylation by homolytic scission of the acyl bond



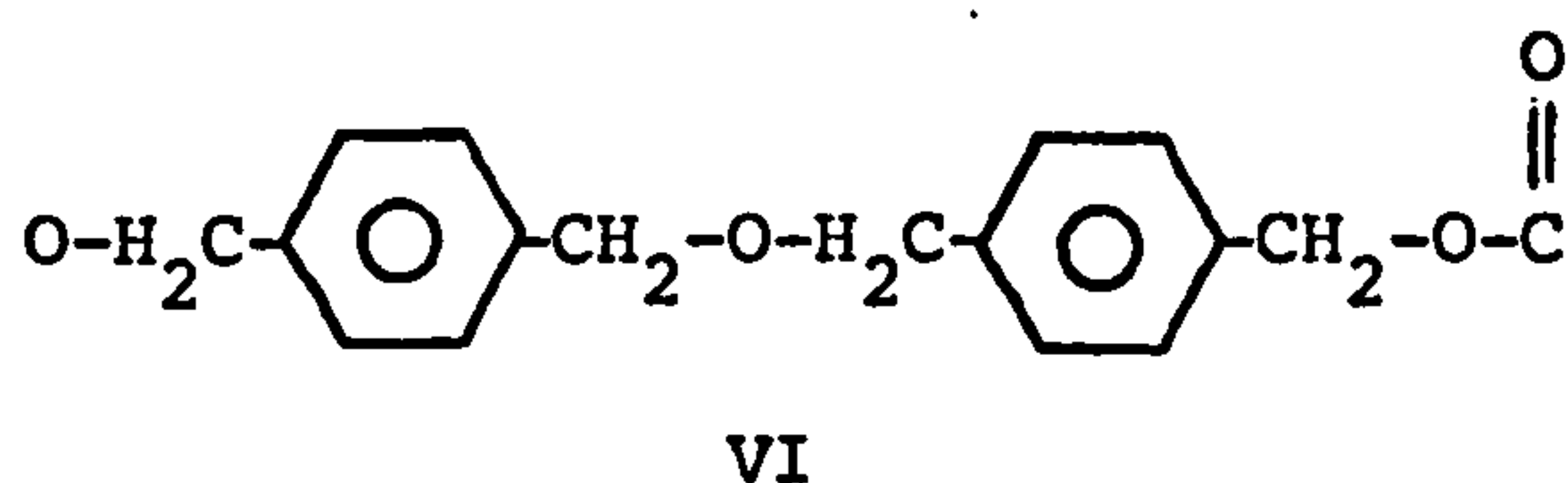
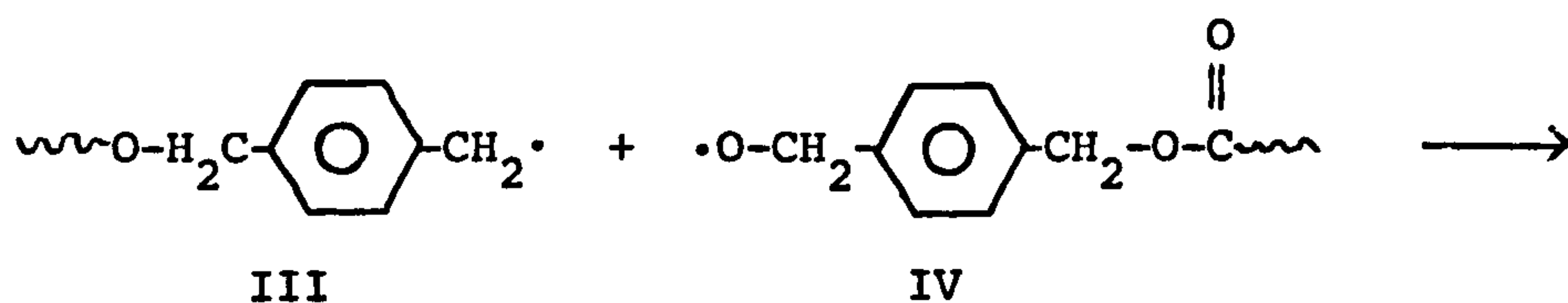
Fragments IV and V could have a further fragmentation to form short chain fragments





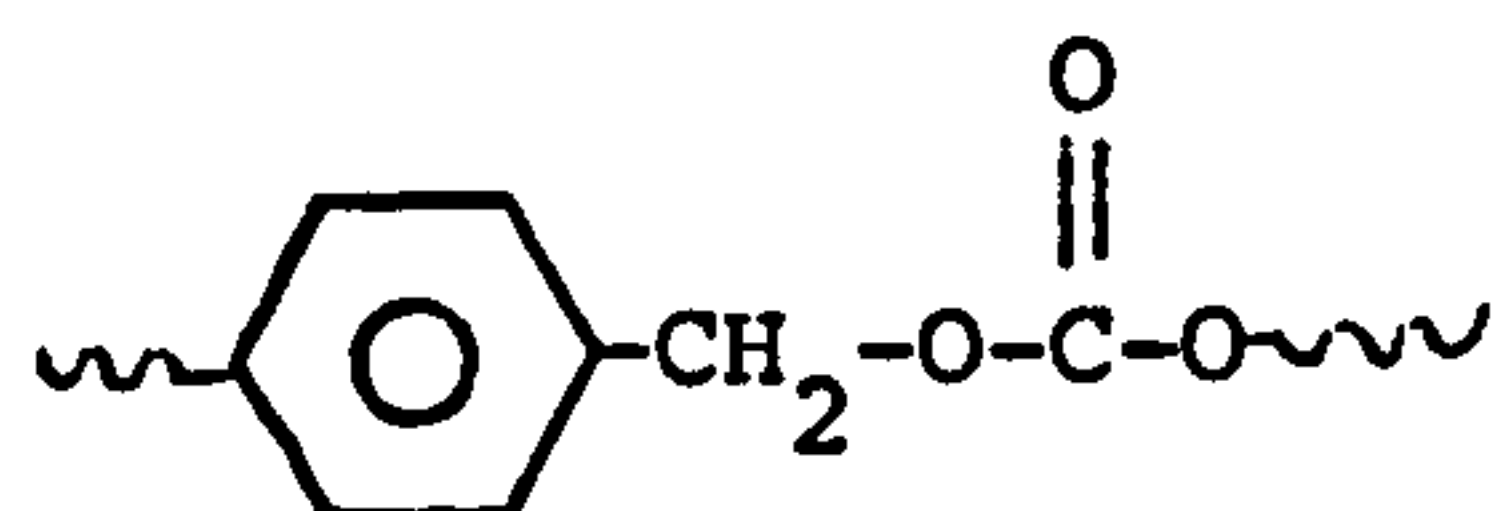
Short chain fragments

Fragments IV and V could react with fragment III by recombination to form an ether-p-xylylene structure which could also undergo further



fragmentation at the newly formed ether group on the macromolecule and volatilise or remain in the reaction medium.

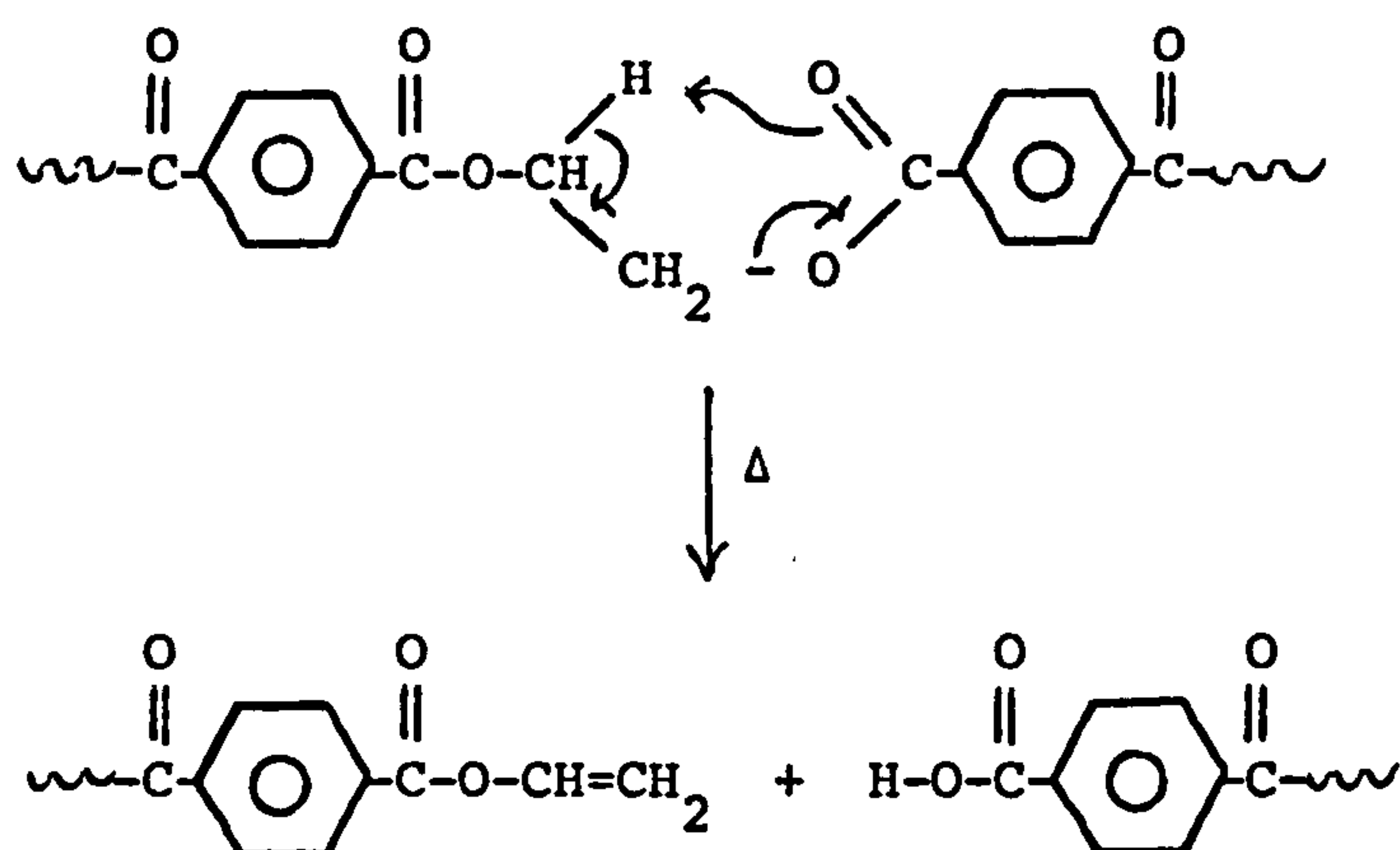
It is known that the thermal decomposition of the model compound benzyl ethyl carbonate yielded  $\text{CO}_2$ , dibenzyl ether, benzaldehyde and toluene.<sup>14</sup> Thus polycarbonates containing the



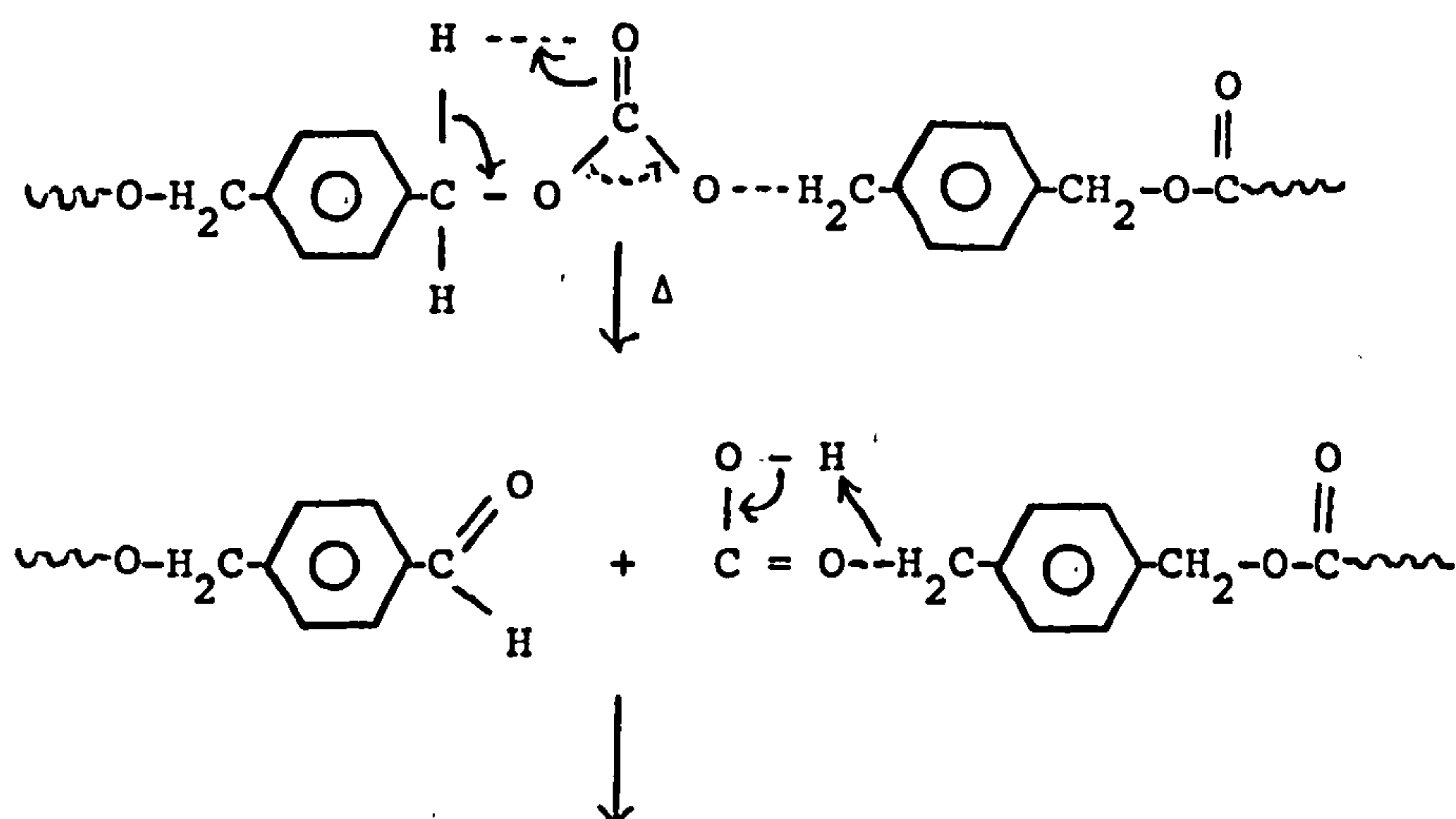
groups would thermally decompose to  $\text{CO}_2$ , polybenzyl ether, aromatic compounds and probably crosslinking due to secondary reaction arising by the reaction of aldehyde group during the degradation process.



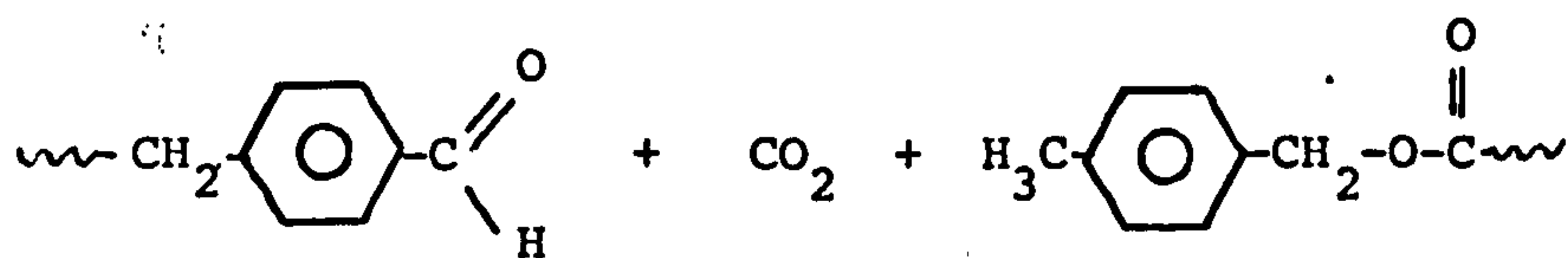
At the higher temperatures  $\text{CO}_2$  and p-tolualdehyde are evolved at the same temperatures of degradation for sample B. Thus another mechanism may operate which gives, simultaneously, these products. Luderwald<sup>72</sup> has proposed that in the direct pyrolysis in a mass spectrometer a polyester such as poly(ethylene terephthalate) may be thermally degraded by a thermal cis-elimination which must simultaneously yield a carboxyl group with a thermally formed vinyl ester group.



A similar mechanism may be envisaged for poly(p-xylylene carbonate). This proposed mechanism may be represented as:







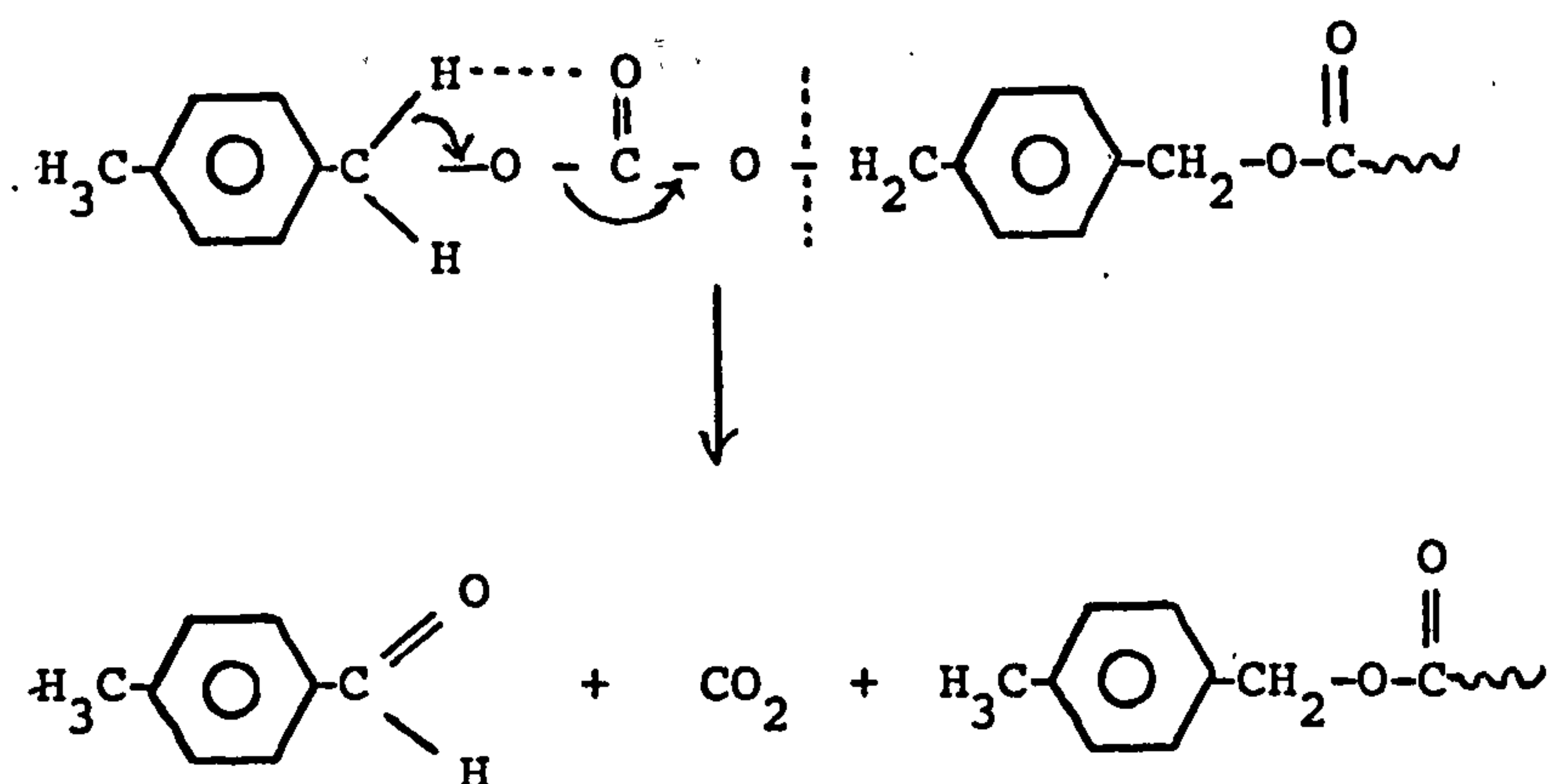
benzyl aldehyde fragments

VII

p-methyl benzyl end  
group fragments

VIII

Fragments VII and VIII could undergo further fragmentation to form the volatile product p-tolualdehyde.

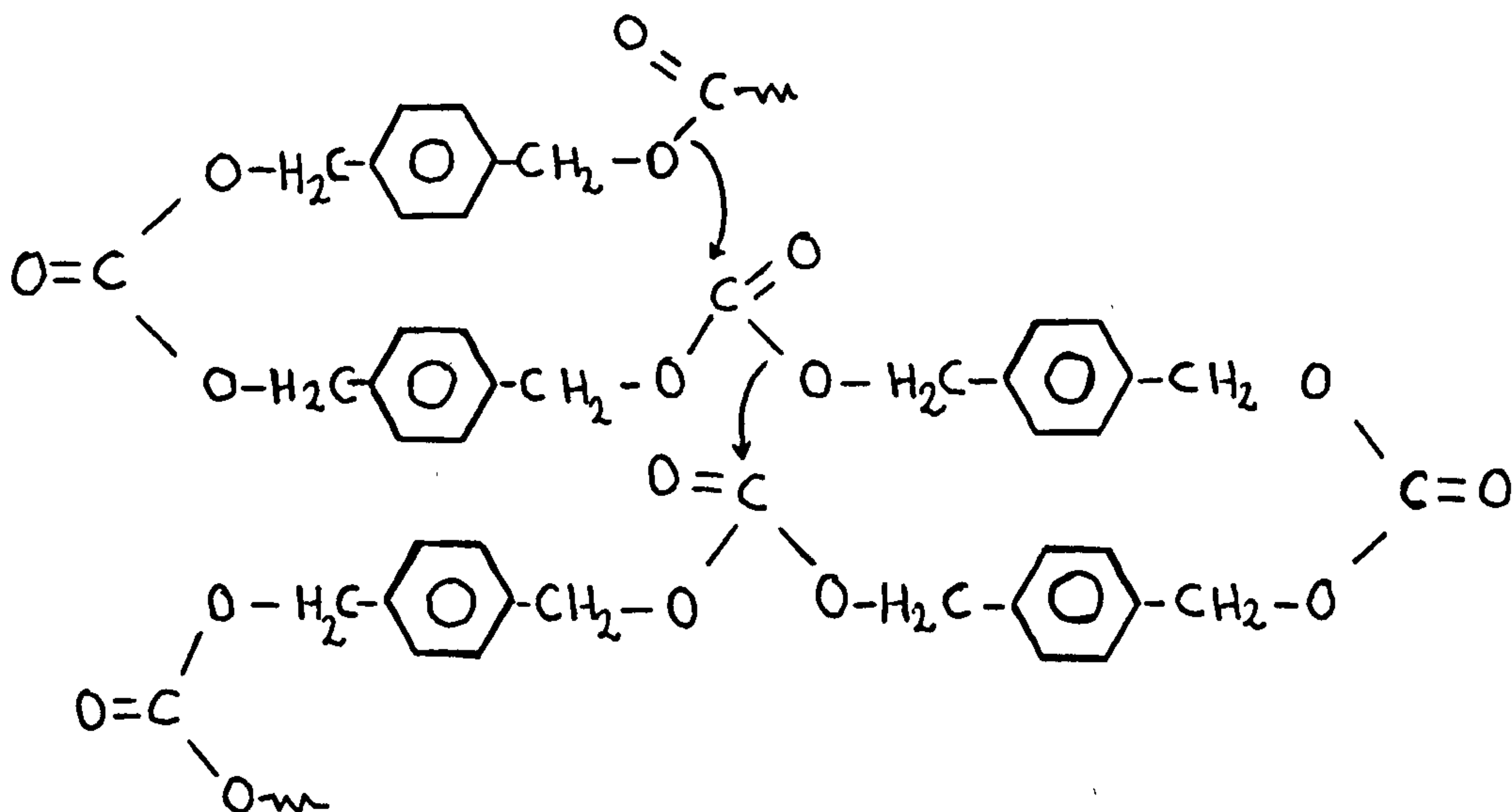


p-tolualdehyde

The occurrence of secondary reactions in TVA experiments is less likely because the amount of polymer degraded is small (~50 mg) and the large base area of the degradation tube, in addition to the vacuum ( $10^{-4}$  mm Hg) reduces the possibility of diffusion-controlled reactions and secondary thermal degradation reactions occurring because the pyrolysis products are immediately removed. However, a small proportion of reacting macromolecules with aldehyde end groups could participate in intermolecular reaction with the formation of crosslinks, producing products of lower volatility which may remain in the medium and cause

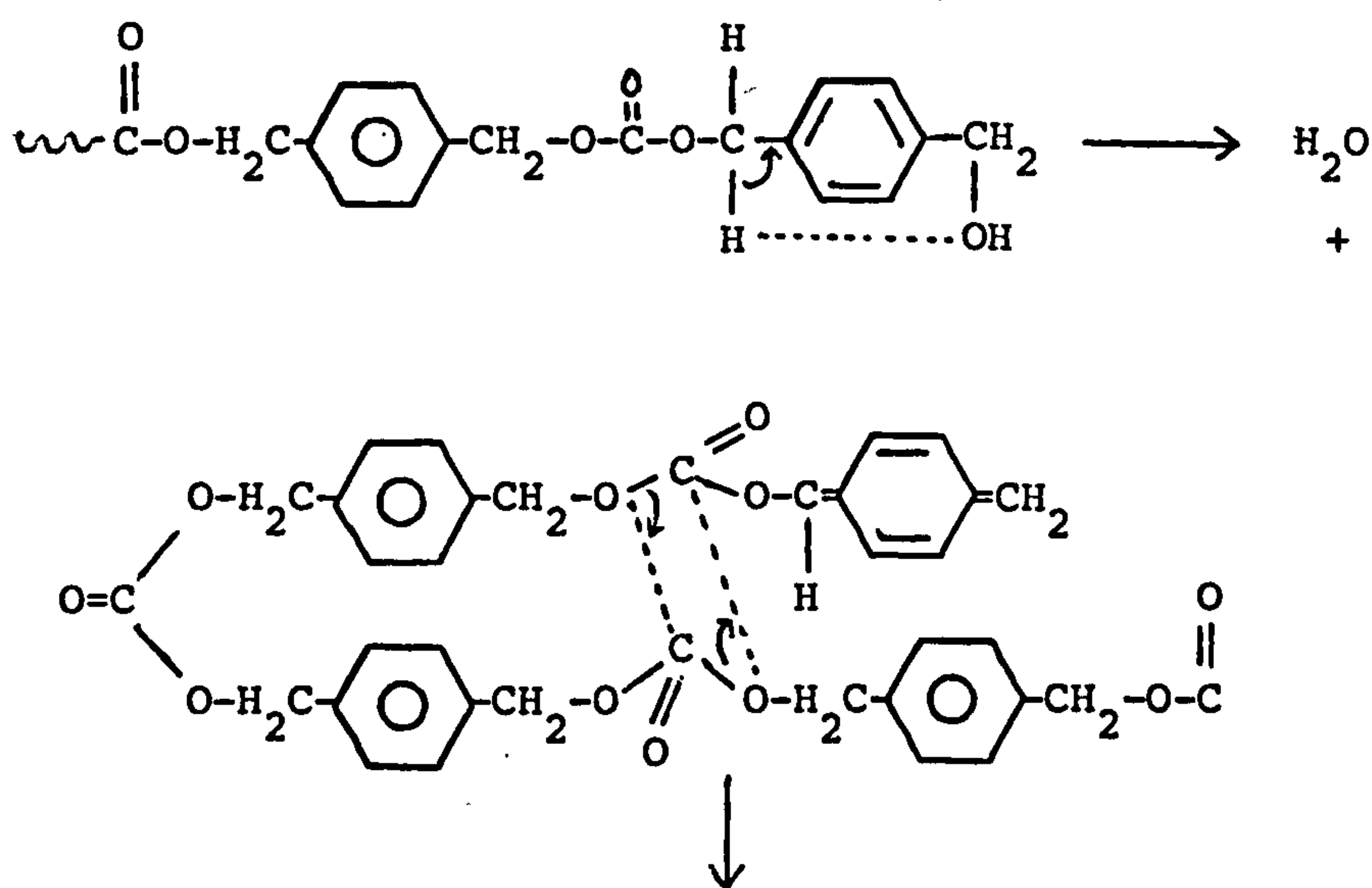
formation of residue. The small amount of residue obtained was a hard carbonaceous material.

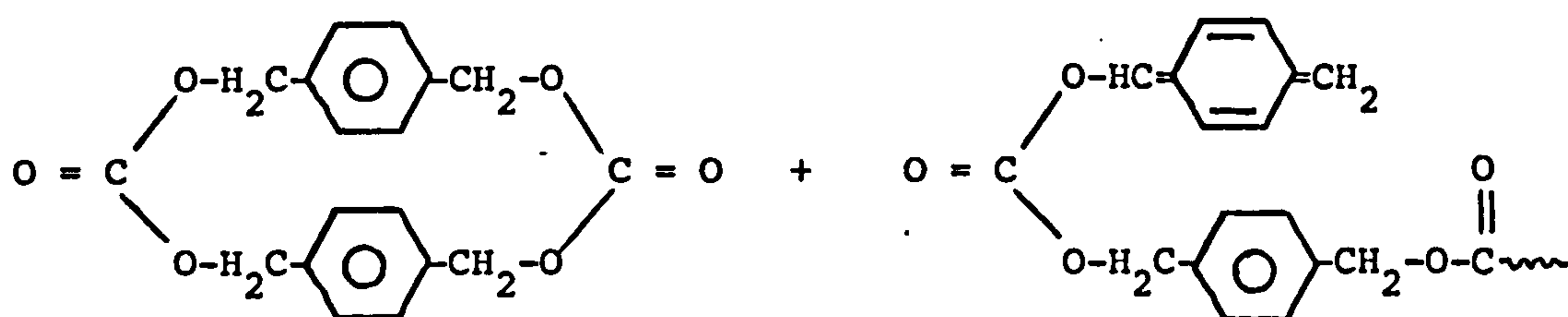
From the mass spectrometry results obtained for the polymer and the solid product (CRF) and by comparison of the results of other workers<sup>71</sup> using structurally related polycarbonates, it may be envisaged that the degradation of poly(p-xylylene carbonate) occurs by an intramolecular ester interchange process within different segments of the polymeric chain, in a concerted fashion, between an oxygen atom of a carbonate group with the carbon at the CO of another carbonate group along the macromolecule. However, due to the restriction of the rotational freedom of the chains imposed by the p-xylylene group, the formation of a cyclic structure is only possible between two or more structural units in order to produce unstrained rings. As a convenient hypothesis, a folded structure for the polymeric chain, represented as follows, is assumed:



The poor thermal stability of poly(p-xylylene carbonate) in the presence of basic compounds such as NaOMe, which catalyse ester interchange reactions supports the idea of an ester interchange mechanism.

The low rates of degradation at low conversions may indicate that the degradation could be initiated at the hydroxyl end group at the chain ends. However, the attempt to test this by acetylation of the hydroxyl end groups gave negative results, as has already been explained, possibly because the insolubility of the polymer prevents the acetylation reaction. Hence, the proposed mechanism of initiation of the degradation at the chain ends is only based on the assumption that it is likely that the polymer would have hydroxyl end groups. A possible initiation mechanism would be through a dehydration process involving the elimination of water by reaction of the hydroxyl end group and a hydrogen in the p-xylylene group. The resulting highly reactive p-xylylene structure would activate the adjacent carbonate group, represented as follows:





dimer 328g/mol

The process of depolymerisation to give cyclic oligomers may thus involve a concerted reaction between the oxygen atom of the activated carbonate group and the next but one carbonyl group along the macromolecule. In this mechanism, the p-xylylene end is not expelled but is retained until the depolymerisation is complete.

#### 4.13 PROGRAMMED DEGRADATIONS FOR AROMATIC POLYCARBONATES: BISPHENOL A POLYCARBONATE (LABORATORY AND COMMERCIAL SAMPLES)

##### 4.13.1 Thermogravimetry (TG)

In figs. 4.45 and 4.46 are shown the TG curves obtained in nitrogen atmosphere and vacuum at a heating rate of 10°C per minute. The derivative TG curve for nitrogen atmosphere is also shown in the same figures.

The volatilisation process for both environments occurs in one stage, with a rate maximum of volatilisation at about 462°C. The gradual initial weight loss, which is more pronounced in vacuum, is attributed to desorption of solvent. For the commercial sample, similar behaviour is observed with a rate maximum of volatilisation at 462°C. The residues, after degradation, are 26% (N<sub>2</sub>) and 23% (Vac) for laboratory and 24.3% (N<sub>2</sub>) and 22.5% (Vac) for commercial sample respectively.



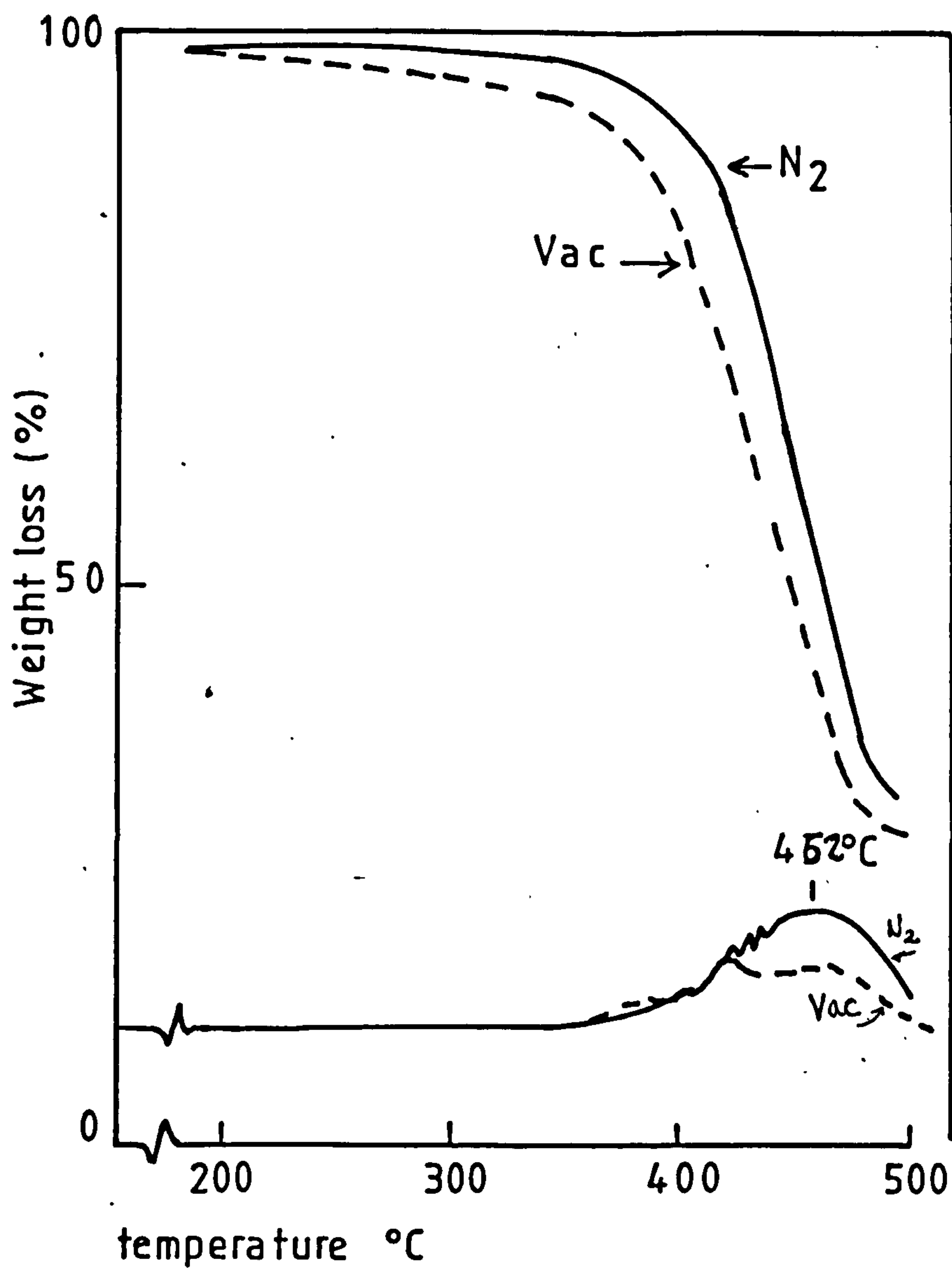


Fig. 4.45. TG curves for bisphenol A polycarbonate for N<sub>2</sub> atm and vacuum heated to 500°C at 10°C/min.



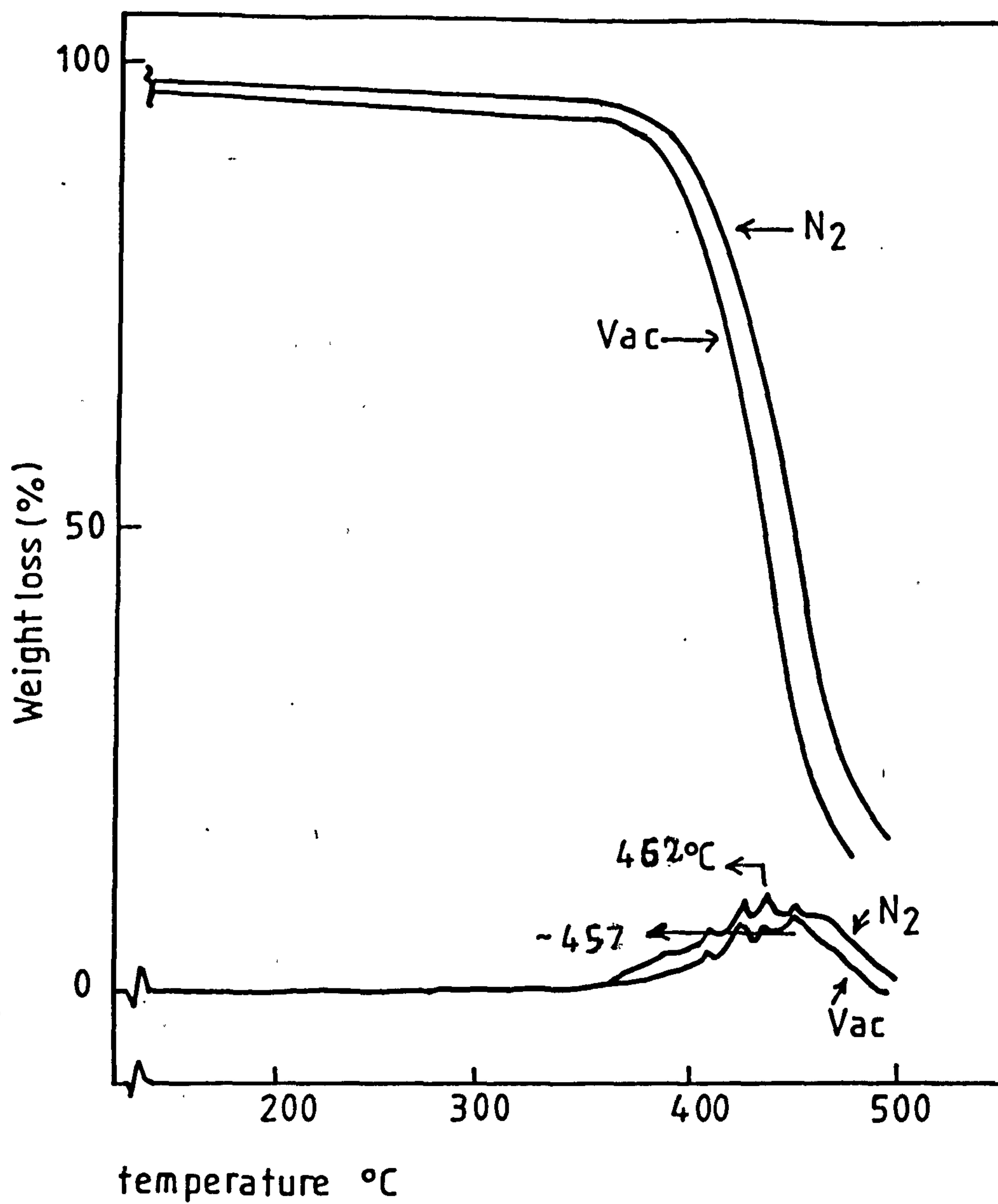


Fig.4.46. TG curves for bisphenol A polycarbonate (commercial sample) heated to 500°C at a heating 10°C/min

#### 4.13.2 Differential Scanning Calorimetry

The DSC curve obtained for nitrogen atmosphere at a heating rate of 10°C per minute is indicated in fig. 4.47. The small endothermic peak with minimum at about 250°C is attributable to the melting of the polymer. The second endotherm with minimum at about 450°C indicates a greater energy change. This may be attributed to the breakdown of the polymer. Between these endotherms an upward shift (exothermic) of the base line is observed.

The same behaviour is observed in the DSC curve for the commercial sample.

#### 4.13.3 Thermal Volatilisation Analysis

In fig. 4.48 are shown the TVA curves for the two polymer samples heated to 500°C at a rate of 10°C per minute.

From the 0°C TVA curve it is observed that the evolution of volatile material takes place in one stage, supporting the evidence already obtained from TG.

The lack of coincidence of the traces indicates that in the process of degradation substances of different volatility are produced. Non-condensable gases are also formed, as indicated by the -196°C trace. The non-condensable gases were directly analysed by mass spectrometry via an on line Micromass QX 200 spectrometer attached to the TVA apparatus.

The mass spectrum shows peaks at  $m/e$  28, assigned to carbon monoxide and at  $m/e$  16, attributed to methane.

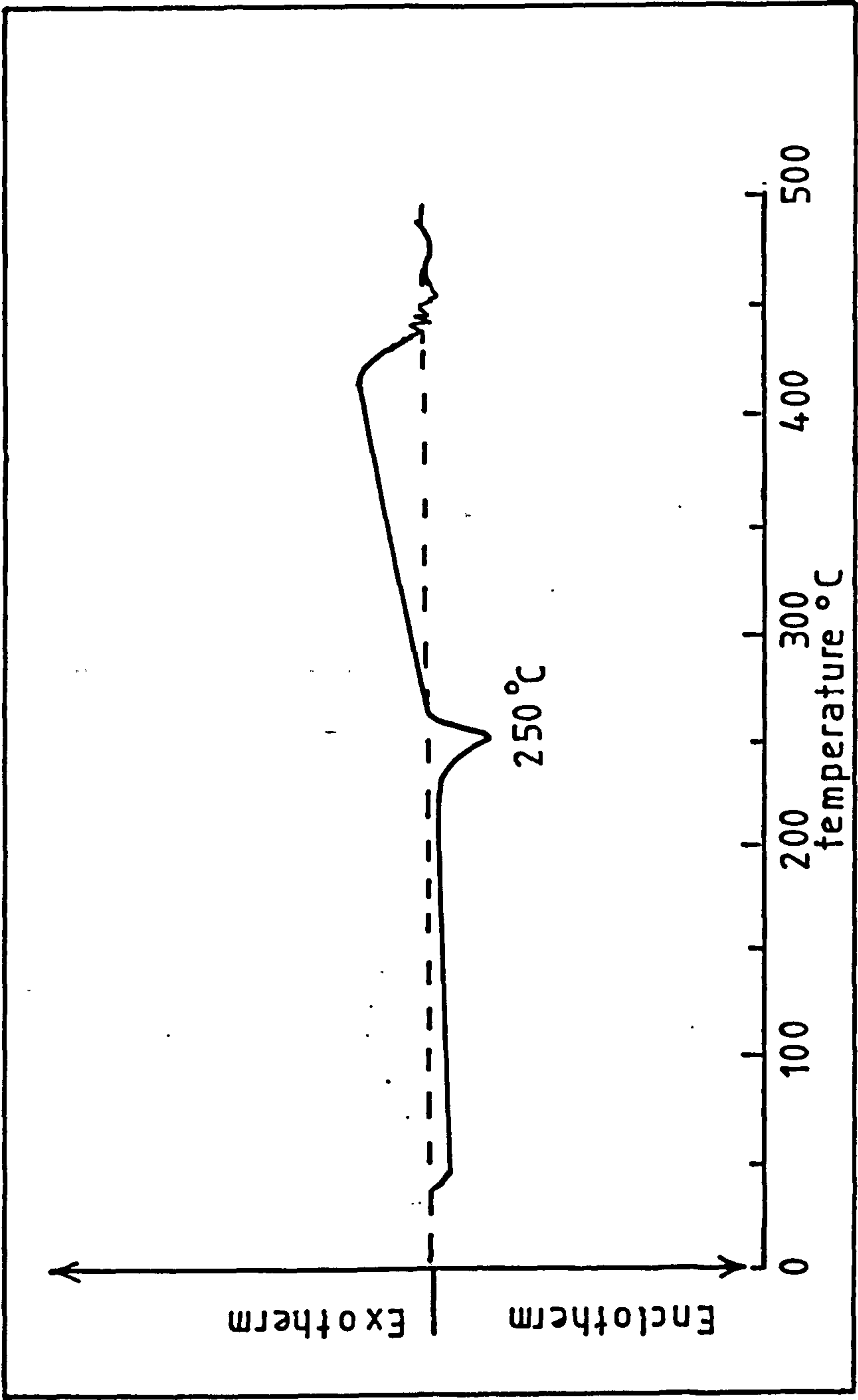


Fig.4.47. DSC curve for bisphenol A polycarbonate (laboratory sample) heating rate 10°C/ min.

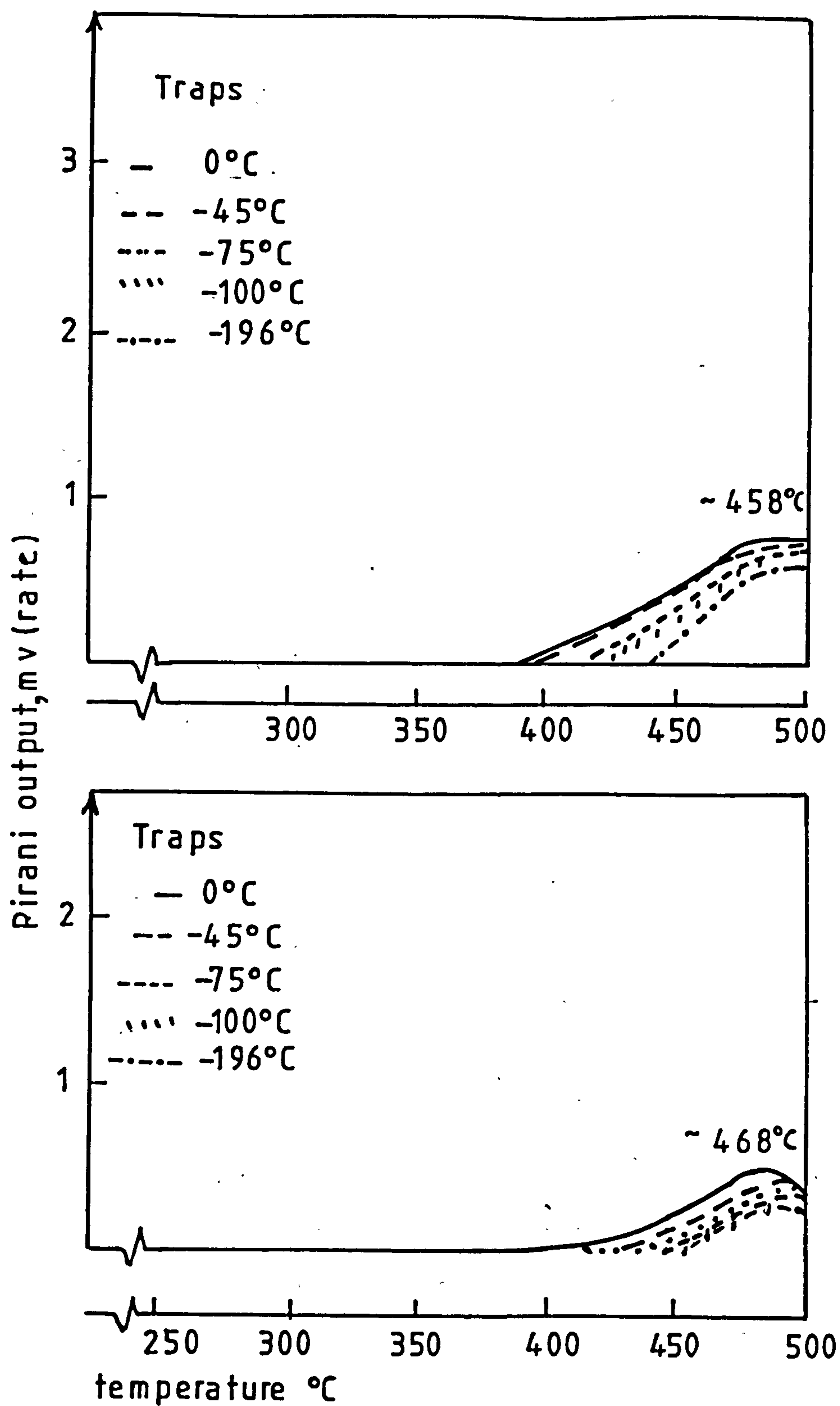


Fig.4.48. TVA curves for bisphenol A polycarbonate heated to 500°C at a heating 10°C/min  
 (1) laboratory sample  
 (2) commercial sample.

#### 4.13.4 Subambient Thermal Volatilisation Analysis (SATVA)

The condensable volatile products evolved in the degradation process of the two samples of bisphenol A polycarbonate were fractionated by SATVA and analysed spectroscopically. The SATVA curves obtained are shown in fig. 4.49.

The laboratory sample shows a SATVA curve with four peaks at  $-144^{\circ}$ ,  $-66^{\circ}$ ,  $-35^{\circ}$  and about  $-3^{\circ}\text{C}$ . The products were analysed by mass and GC-mass spectrometry when required. The first peak is due to carbon dioxide. The products corresponding to the second and third peaks gave a mass spectra with peaks at  $m/e$  94 (phenol),  $m/e$  108 (4-methyl-phenol) and  $m/e$  18 (water). The products giving the fourth SATVA peak were analysed by GC-mass spectrometry giving two GC peaks. The first peak with retention time 10 minutes gave a mass spectrum corresponding to phenol and the second with retention time 9.8 minutes, gave a mass spectrum showing a molecular ion at  $m/e$  136 due to 1-hydroxy-4-isopropyl benzene (p-cumenol).

The SATVA curve for bisphenol A polycarbonate (commercial sample) after purification by continuous extraction with diethyl ether and methanol is shown in the same figure 4.49. It consists of four peaks at  $-149^{\circ}$ ,  $-66^{\circ}$ ,  $-34^{\circ}$  and at about  $0^{\circ}\text{C}$ . The first peak is due to carbon dioxide. Products giving the remaining peaks were collected and analysed by GC-mass spectrometry. The second peak products gave two GC peaks with retention times at 1.0 and 6.9 minutes and corresponding  $m/e$  values of 94 and 108, attributed to phenol and 1-hydroxy-4-methyl-benzene respectively. The third peak products also included some phenol and 1-hydroxy-4-methyl-benzene, together with 1-hydroxy-4-



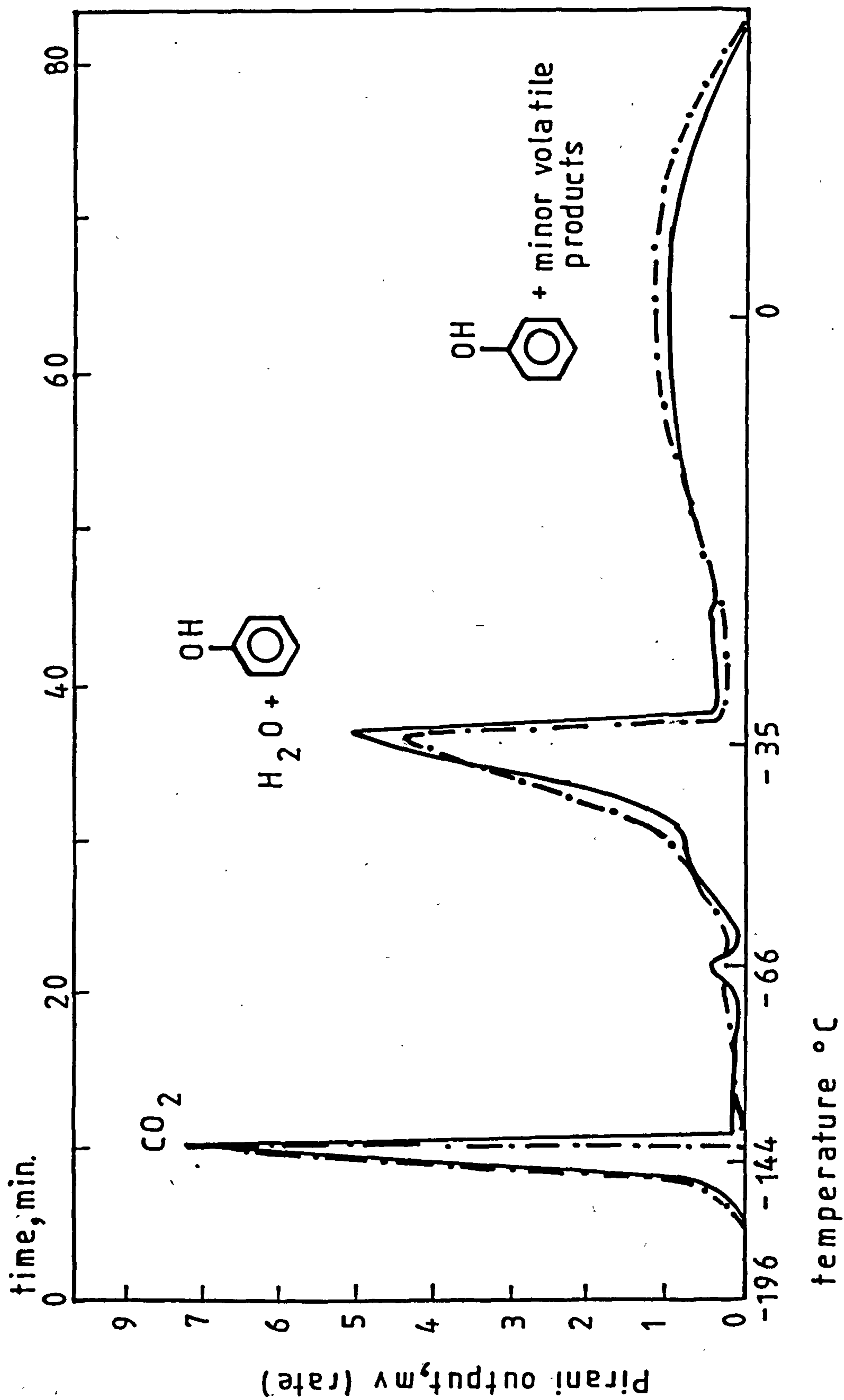


Fig. 4.49 SATVA curves for products of degradation of bisphenol A polycarbonate to 500°C, heating at 10°C/min, under vacuum

(—) commercial sample.  
 (-·-) laboratory sample.

isopropyl-benzene ( $m/e$  136). All these volatile products are produced in small amount. Some water was also present but is not considered a genuine product of degradation, since the polymers tend to absorb some water.

Therefore, in the degradation of bisphenol A polycarbonate (both laboratory and commercial samples) the volatile products are: carbon monoxide, methane, carbon dioxide, phenol, 1-hydroxy-4-methylbenzene and 1-hydroxy-4-isopropylbenzene.

#### 4.13.5 Characterisation of Cold Ring Fractions

The cold ring fraction formed when bisphenol A polycarbonate was heated to 500°C at a rate of 10°C per minute was collected and analysed by infrared spectroscopy and GC-mass spectrometry.

The white film deposited on the walls of the degradation tube, after bisphenol A polycarbonate (laboratory sample) was heated was collected by washing with dichloromethane and the solvent was allowed to evaporate. Two different substances were separated - a colourless crystalline solid and a yellow resin-like material. The former was soluble in chloroform and partially soluble in benzene and insoluble in diethyl ether and water. The latter was soluble in diethyl ether, benzene and chloroform.

The infrared spectrum (fig. 4.50) of the crystalline CRF shows bands which are characteristic of the polymer, except for the better resolution of the band and the appearance of some bands. In the region 3100-3000  $\text{cm}^{-1}$  two distinct bands are observed at 3040 and 3020  $\text{cm}^{-1}$  which are attributed to the C-H stretching vibration of the aromatic

ring. The bands at 2970-2880 and a shoulder at 2940  $\text{cm}^{-1}$  are more intense and better resolved. The second band is at higher intensity, 10  $\text{cm}^{-1}$ , than in the polymer. These bands are attributed to the C-H stretching of the  $\text{CH}_3$  group and the formation of a  $-\text{CH}_2-$  group. The spectrum also shows a change-in-band intensity in the range of the aliphatic C-H bond for  $\text{CH}_3$  groups frequency at 1410, 1365  $\text{cm}^{-1}$  and the appearance of two new bands at 1010-1000  $\text{cm}^{-1}$  and 758-740  $\text{cm}^{-1}$ .

The examination by thin layer chromatography of both fractions showed the presence of several compounds. The crystalline compound was shown to form three different substances, and a small amount of bisphenol A was detected. The resin-like material showed a greater amount of bisphenol A (by comparison with a pure sample) and other various substances attributed to polymer short chain fragments.

The GC-MS investigation of the crystalline CRF gave various peaks. The two major GC-MS peaks with retention times 5.1 and 21.8 minutes, respectively, were analysed. The first peak may be attributed to 1-hydroxy-4-isopropyl benzene ( $m/e$  136). The second peak product gives a mass spectrum with  $m/e$  408. This may be due to oligomers.

The microanalysis of the crystalline solid (after purification, three times, by precipitation with diethyl ether) gave C = 75.92%, H = 4.90%. These values are slightly different from the corresponding experimental values for the original polymer (C = 75.2%, H = 5.51%). The differences are attributed to the presence of short chain fragments which probably have a structure close to that of the original polymer.

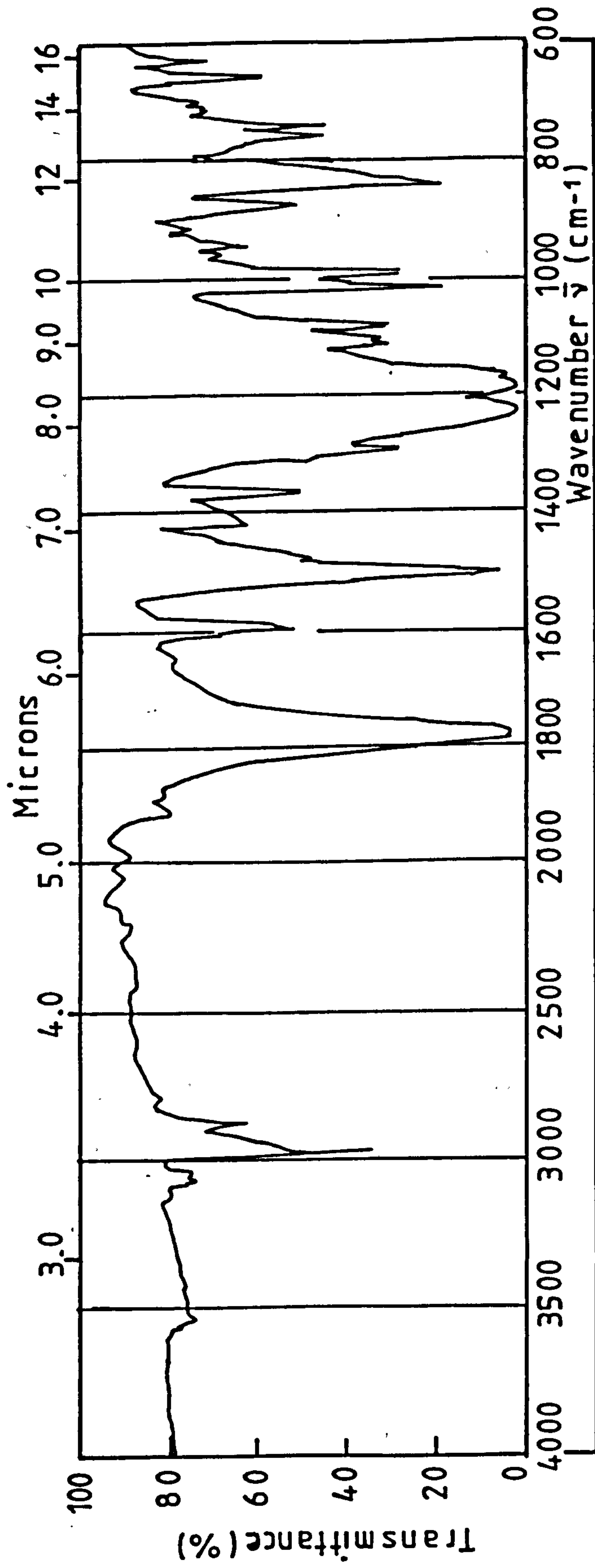


Fig. 4.50 Infrared spectrum for the products of degradation CRF (crystalline solid) of bisphenol A polycarbonate (laboratory sample) heated to 500°C at 10°C/min.



The yellow resin-like material separated from the crystalline solid, as already explained, was analysed by GC-mass spectrometry.

Five major GC peaks were obtained at retention times 9.8, 12, 15.6, 16.2 and 17 minutes, respectively. The first peak is attributed to the presence of 1-hydroxy-4-isopropyl-benzene ( $m/e$  136) (the retention times are not comparable with the previous MS data). The products at the other GC peaks observed at longer retention times, give an MS signal at  $m/e$  254 which is attributed to an oligomer. It is interesting to note that all GC peaks, although they have different retention times, give similar MS fragmentation patterns with common peaks at  $m/e$  228, 212, 199, 169, 165, 122, 119, 66 and 44, indicative of the presence of oligomeric material.

The cold ring fraction obtained in the TVA of bisphenol A polycarbonate (commercial sample) was analysed by GC-mass spectrometry. Three major GC peaks were obtained at retention times 9.8, 13 and 17.8 minutes with largest ion at  $m/e$  241, 395 and 442, respectively.

Therefore, it may be concluded that for both polymers the cold ring fraction consists of a mixture of different chain fragments, which may be formed by main chain scission reaction and volatilise from the reaction medium when the volatilisation threshold is lower than the degradation temperature.



#### 4.14 ISOTHERMAL DEGRADATIONS FOR AROMATIC POLYCARBONATES

Samples of bisphenol A polycarbonate were degraded for one hour at 207°, 220°, 300°, 357° and 400°C, respectively, under vacuum. A SATVA curve was recorded and the products were analysed by mass spectrometry. At all temperatures of degradation a peak at about -60°C was observed due to the presence of water. At 300°C, small amounts of phenol and 4-methyl phenol as volatile products were detected. A thin film of CRF was also deposited on the inner walls of the degradation tube. At 375°C carbon dioxide is produced along with the previously mentioned volatile products. At 400°C all the degradation products are produced in greater amounts.

#### 4.15 RATES OF THERMAL DEGRADATION OF BISPHENOL A POLYCARBONATE

Isothermal TG curves for both samples were obtained at various temperatures under vacuum. Using these curves graphs of percentage of residue (residue %) versus time were made, which are shown in fig. 4.51 and 4.52. These plots were used to derive the rate of thermal degradation as a function of percentage of volatilisation (figs. 4.53 and 4.54). In the case of the curves for bisphenol A polycarbonate (laboratory sample), it can be observed that initially the polymer degrades rapidly then, after about 50% volatilisation, the rates begin to decrease. The initial high rates obtained may be explained on the grounds that some different reaction, or combination of reactions, prevail in the initial stages of the thermal degradation, for example hydrolysis. The drop in the rates above 50% of volatilisation may be explained if crosslinking develops in the residue during the heating and principally the reason can be due to sample depletion.

For bisphenol A polycarbonate (commercial sample), at the lower temperatures, the polymer degrades slowly then, after about 20% volatilisation, there is a pronounced increase of the rate of degradation. For higher temperatures, this period of slow rate is shorter. The drop in the rates above 30% of volatilisation is also observed.

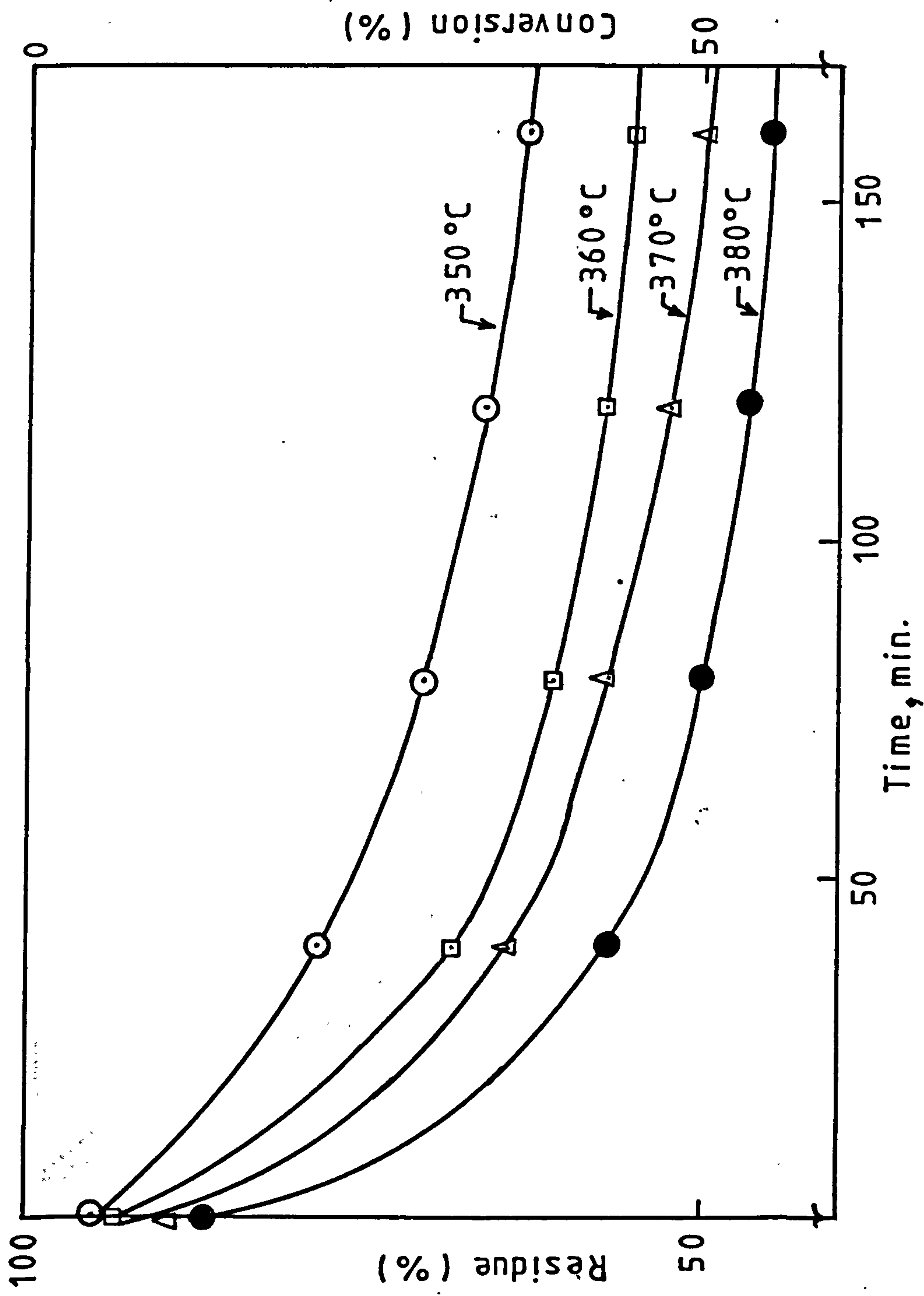


Fig. 4.51. Percentages of residue and conversion for bisphenol A polycarbonate (laboratory sample), by TG heated at 380°, 370°, 360° and 350°C respectively

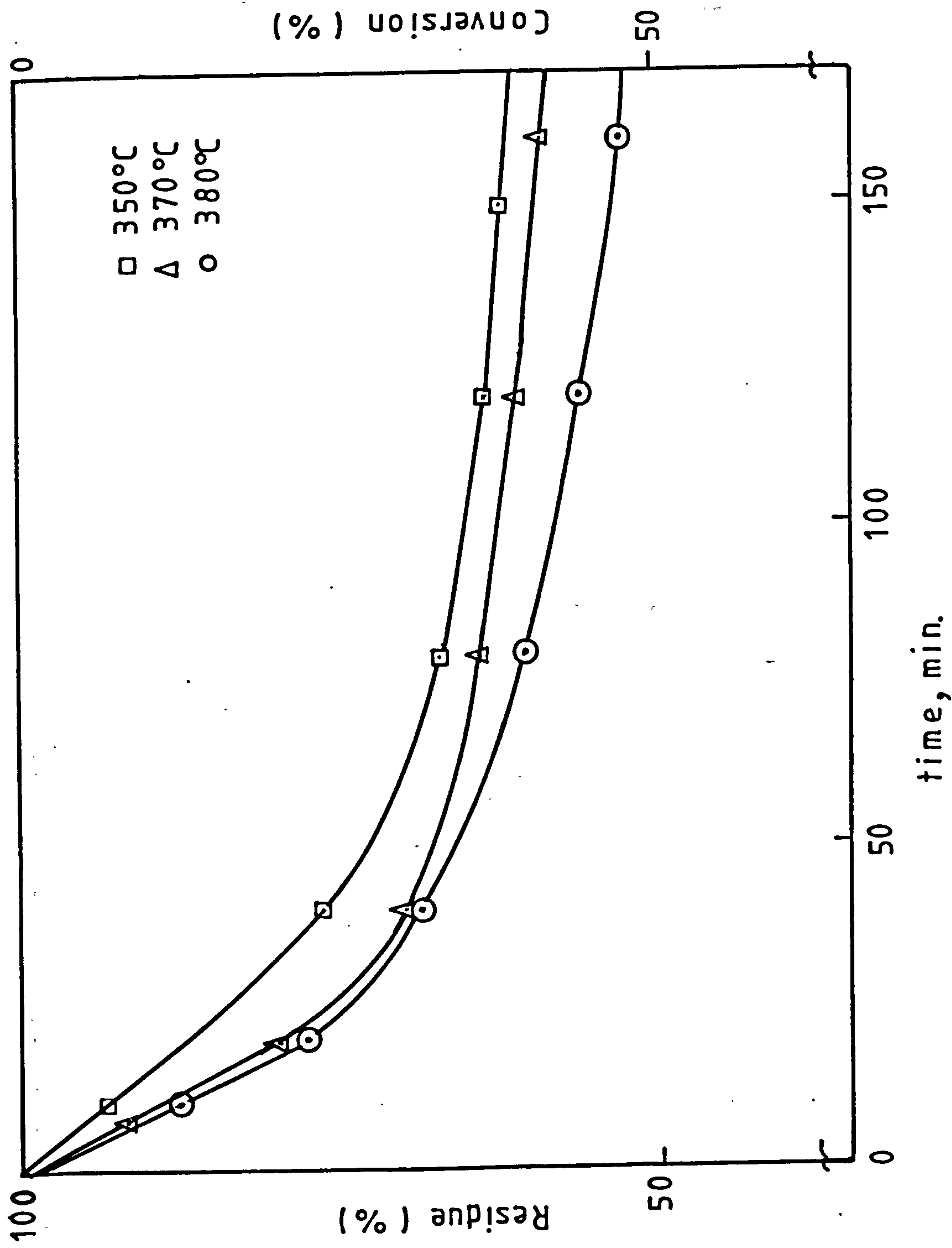


Fig. 4.52. Percentages of residue and conversion for bisphenol A polycarbonate (commercial sample), by TG heated at 350°, 370° and 380°C respectively.

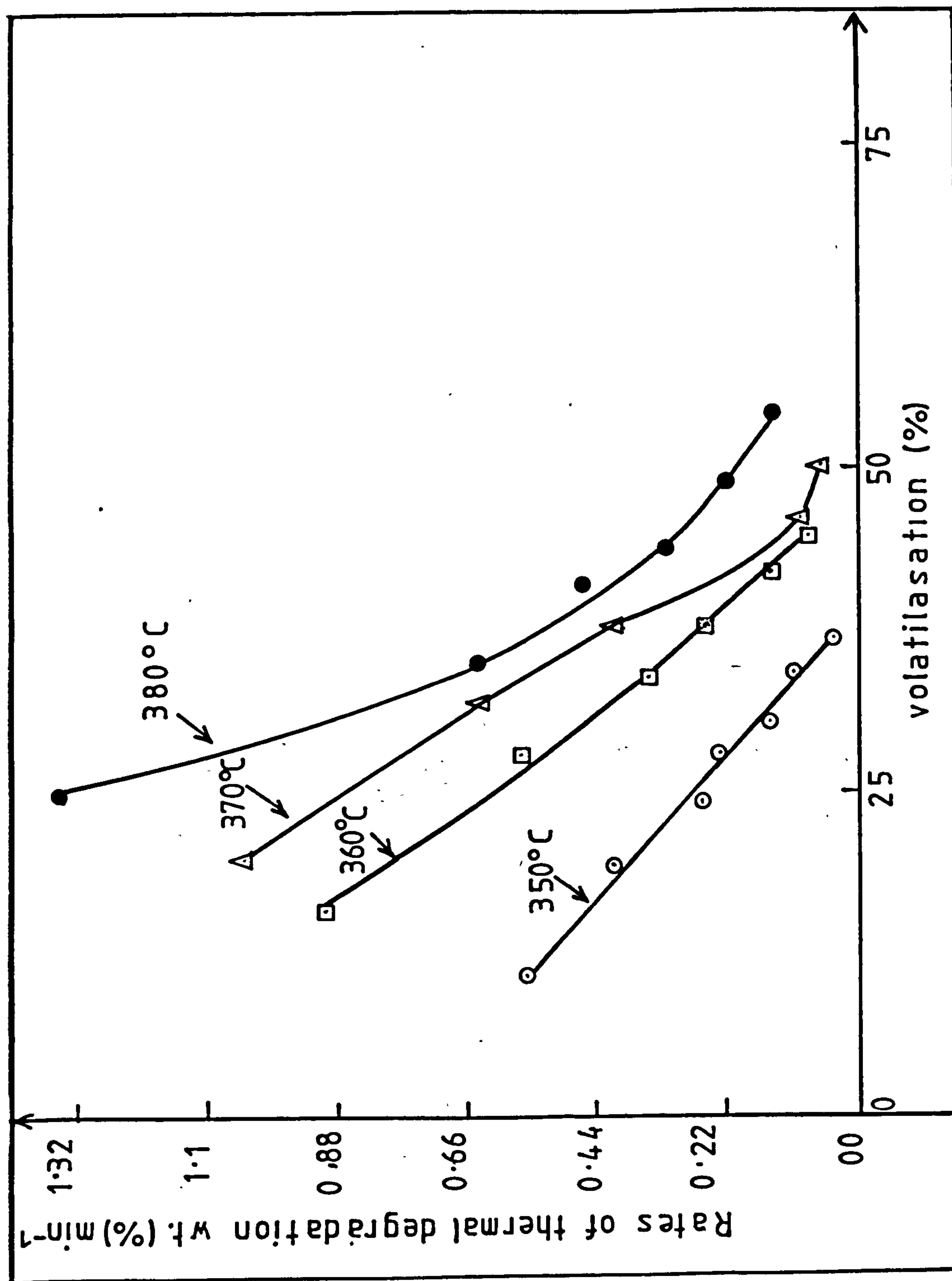


Fig. 4 53. Rates of thermal degradation of bisphenol A polycarbonate (laboratory sample), by TG at 350°, 360°, 370° and 380°C respectively.



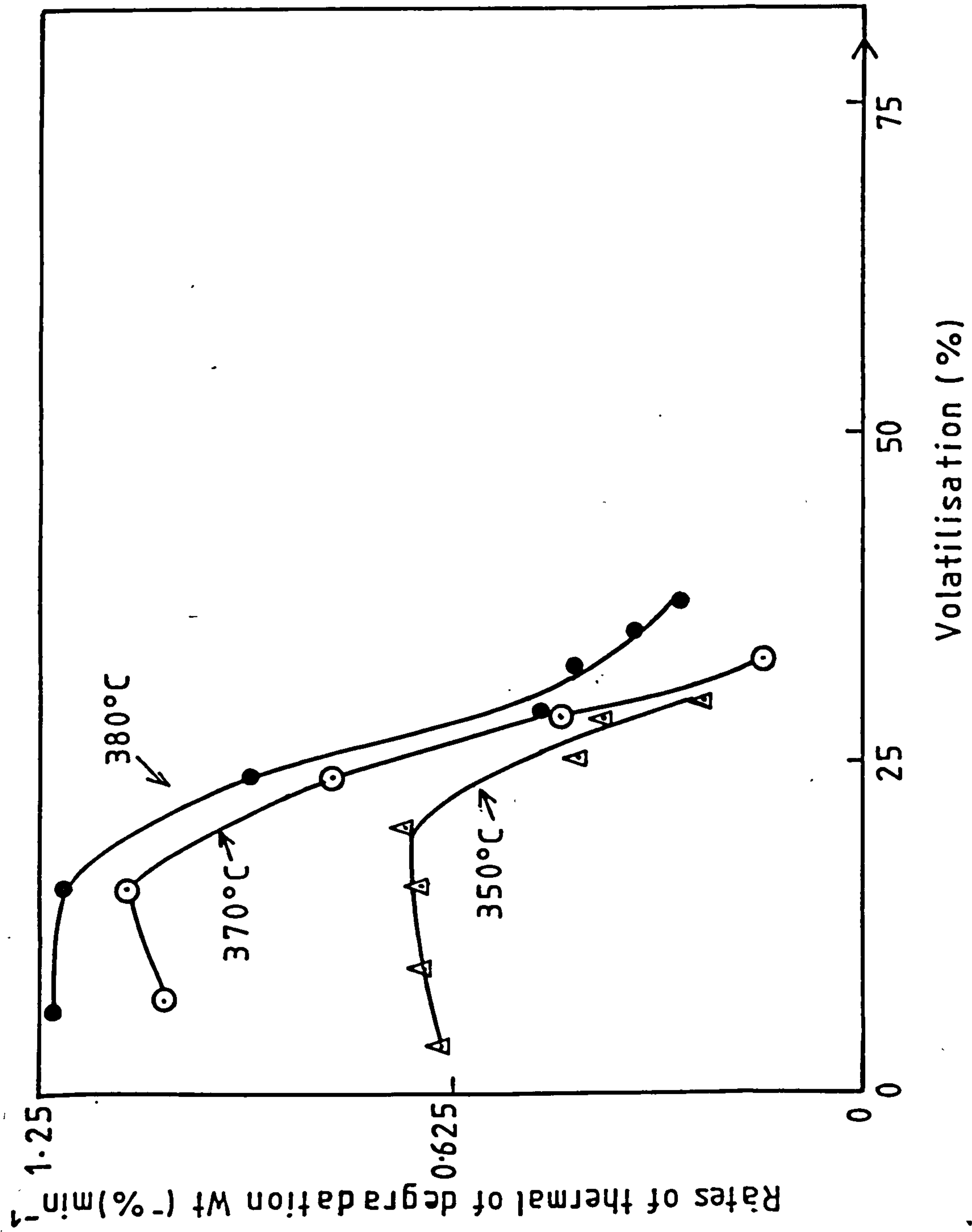


Fig. 4.54 Rates of thermal degradation for bisphenol A polycarbonate (commercial sample) by TG at 350°, 370° and 380°C, respectively

4.16      THERMAL DEGRADATION OF BISPHENOL A POLYCARBONATE IN THE  
PRESENCE OF 1,4-DIAMINO ANTHRAQUINONE (DAA)

Samples of bisphenol A polycarbonate (laboratory sample) were mixed with the free radical inhibitor DAA in the proportions 4:1 and 1:1 (polymer:DAA) and dissolved in dichloromethane. Films were cast on a stainless steel plate.

The resultant films were degraded to 500°C at a heating rate of 10°C/min. TVA curves were recorded and the volatile products were fractionated by SATVA. The polymers were also isothermally degraded by TG at 370°C. From the curves obtained, plots of percentage of residue and extent of degradation versus time, were determined. The plots obtained, together with those for the original polymer, degraded at the same temperature, are shown in fig. 4.55. Using these graphs, the rate of thermal degradation of bisphenol A polycarbonate alone and mixed with DAA, were derived. These curves are shown in fig. 4.56.

The TVA curve obtained showed the same characteristics as the curve for pure polymer. The only striking difference was the decrease in the amount of volatile products, in comparison with the same amount of pure polymer (~17 mg). These features of the thermal degradation under programmed heating are in agreement with the behaviour observed in isothermal heating.

From the diagrams, it can be seen that the inhibitor has a marked effect on the volatilisation of bisphenol A polycarbonate, but does not suppress it completely. This indicates that radicals participate in the degradation process. It is also clearly seen that

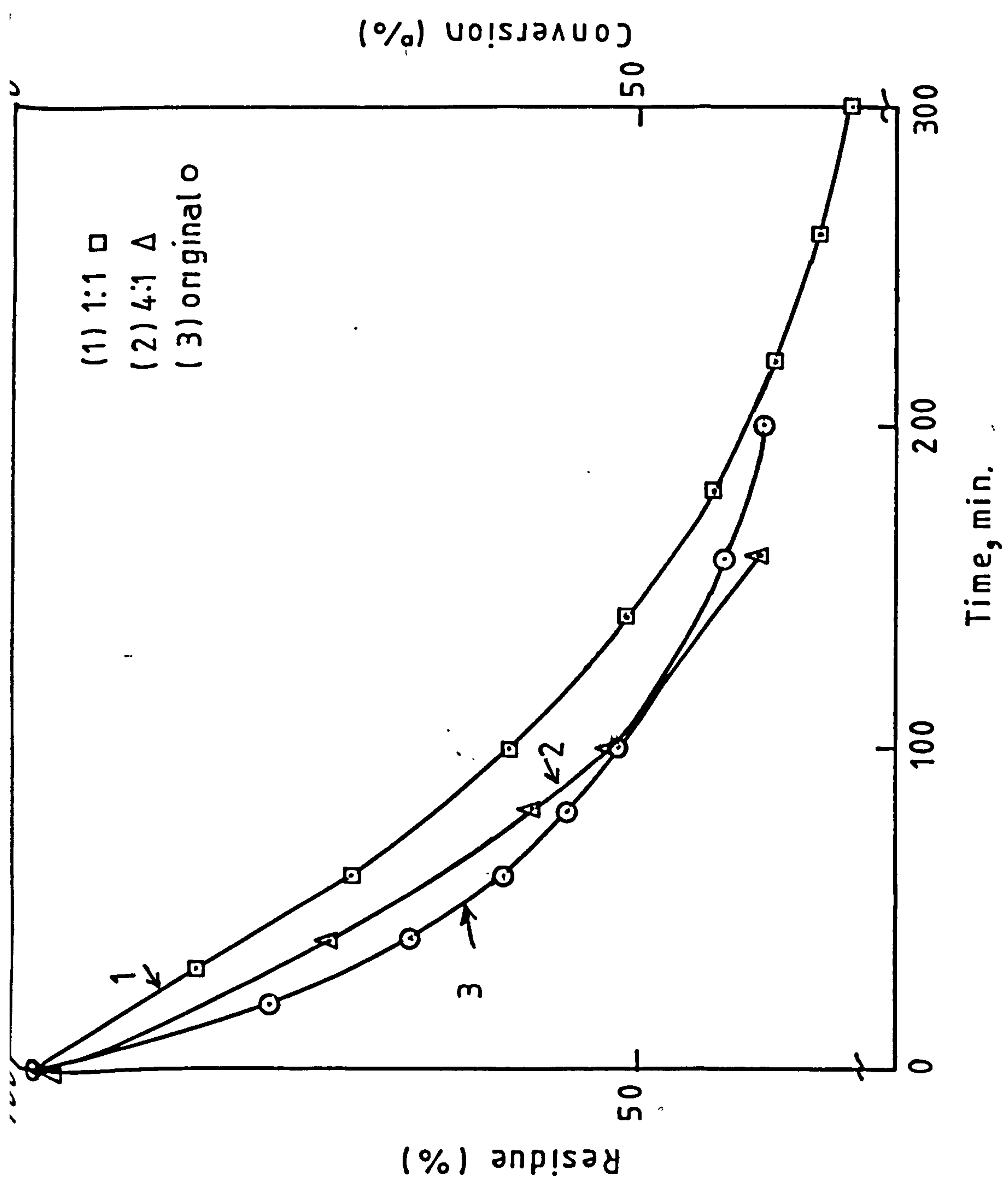


Fig. 4.55. Percentage of residue and conversion for bisphenol A polycarbonate (laboratory sample) mixed with DAA.

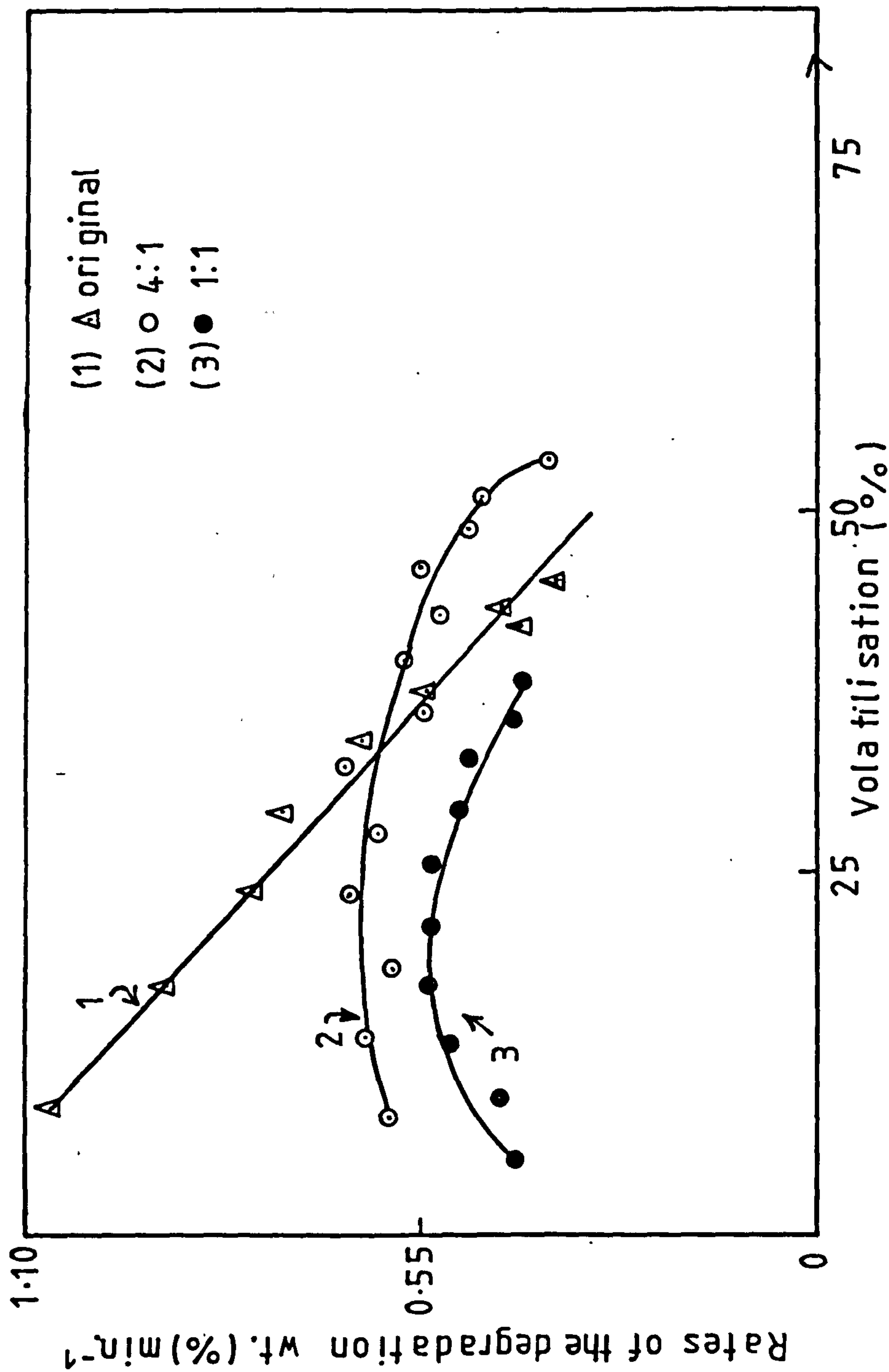


Fig. 4.56 Rates of thermal degradation for bisphenol A polycarbonate (laboratory sample) mixed with DAA curve (1) original (2) 4:1 (3) 1:1

for the 4:1 mixture the depressing effect is lower than the effect observed for the 1:1 mixture, as was expected.

Therefore, DAA inhibits a proportion of the random chain scission character of the thermal degradation of bisphenol A polycarbonate.

#### 4.17 THE MASS SPECTRA OF DEGRADED BISPHENOL A POLYCARBONATE AND ITS COLD RING FRACTION

The mass spectra of bisphenol A polycarbonate and its cold ring fraction formed in the TVA apparatus were obtained as already explained. The mass spectrum of bisphenol A polycarbonate is shown in fig. 4.57.

A thorough study of the direct pyrolysis in the MS of bisphenol A polycarbonate has already been reported by Wiley<sup>73</sup> and Foti et al.<sup>71</sup> Peaks indicate the formation of a cyclic dimer (such a dimer has never been isolated), cyclic trimer and tetramer were observed and these assignments were made by comparison with the spectra of authentic samples.<sup>73</sup> Foti et al.<sup>71</sup> reported the formation of cyclic dimer (m/e 508) and cyclic trimer (m/e 762) by intramolecular ester exchange in the fragmentation of bisphenol A polycarbonate.

The mass spectra of the bisphenol A polycarbonates (laboratory and commercial samples) analysed in this study also gave peaks at m/e 747 and m/e 508, respectively, generated from the cyclic trimer (m/e 762) by loss of 15 mass units and the dimer (m/e 508). The methyl radical elimination is at the isopropylidene group,<sup>71,73</sup> which also



accounts for the presence of the peaks at  $m/e$  449 and 405 in the dimer. In the lower mass range of the spectrum of bisphenol A polycarbonate there is a peak at  $m/e$  228, assigned to bisphenol A (4,4'-isopropylidene diphenol). Other ions correlated well with this structure and are found at  $m/e$  213, 197, 134 and 94. This fragmentation pattern suggests that intramolecular ester interchange reactions (giving cyclic oligomers) predominate in the primary thermal fragmentation process of aromatic polycarbonates. This pattern of fragmentation is also related to the fragmentation patterns of the model compounds bisphenol A and diphenyl carbonate, reported by other authors.<sup>64,74</sup>

After bisphenol A polycarbonate was heated to 500°C under vacuum in the TVA system, the different products of the degradation were collected and analysed.

The cold ring fraction deposited on the inner wall of the degradation tube was collected by washing with dichloromethane. After evaporation of the solvent two different fractions were obtained: a white crystalline solid and a yellow resin-like material.

The crystalline CRF was degraded in the MS12 spectrometer. The mass spectrum shows peaks which correlated well with the fragmentation pattern for the polymer. A peak at  $m/e$  508 indicates the presence of the cyclic dimer.<sup>71,73</sup> Other peaks found in the spectrum at  $m/e$  493, 464, 449 and 405 (base peak) correspond with the fragmentation pattern of the cyclic dimer. The series of peaks at  $m/e$  228, 213, 197, 134 and 94 indicate the presence of bisphenol A.

In Table 4.2 are detailed the oligomers formed by the direct pyrolysis-mass spectrometry of bisphenol A polycarbonate (laboratory and

TABLE 4.2

Oligomers formed by direct pyrolysis-mass spectrometry of  
 bisphenol A polycarbonate (laboratory and commercial samples)  
 and the cold ring fraction (CRF) obtained by TVA

Bisphenol A polycarbonate			CRF
Wiley m/e	commercial s. m/e	laboratory m/e	formed in the TVA m/e
762	-	-	-
747	747	-	-
-	-	-	510
509	509	509	509
508	508	508	508
493	-	493	493
-	-	-	464
449	449	-	449
423	-	-	-
-	-	-	421
-	-	-	420
-	407	407	407
-	406	406	406
405	405	405	405
-	-	-	378
-	-	-	377
357	-	-	357
329	-	-	329
315	-	-	-
-	-	-	314
-	-	-	312
-	-	-	253
228	228	228	228
213	213	213	213

commercial samples) and the cold ring fraction produced in the TVA in this study. The oligomers formed by direct pyrolysis-mass spectrometry of a bisphenol A polycarbonate, as reported by Wiley,<sup>74</sup> are also indicated.

It is interesting to establish correlations between the fragmentation processes observed with the polymer degraded by direct pyrolysis-mass spectrometry and thermal degradation in the TVA system. During this work, it has been observed that isothermal degradation at 300°C gives a small amount of cold ring fraction, phenol and 4-methyl phenol as volatile products. When the temperature of degradation is 357°C, carbon dioxide and 4-isopropyl phenol are also formed. Most of these products are directly related to abundant fragments,  $C_9H_{11}O$ ,  $C_8H_7O$  and  $C_7H_7O$ , which all appear in the spectra.

These findings suggest that the thermal decomposition of the bisphenol A polycarbonate and the solid degradation product CRF, obtained in TVA experiments, occurs in the mass spectrometer via the same mechanism, most probably an interchange reaction. This supports the view that the short chain fragments (CRF) may have a structure close to that of the original polymer.

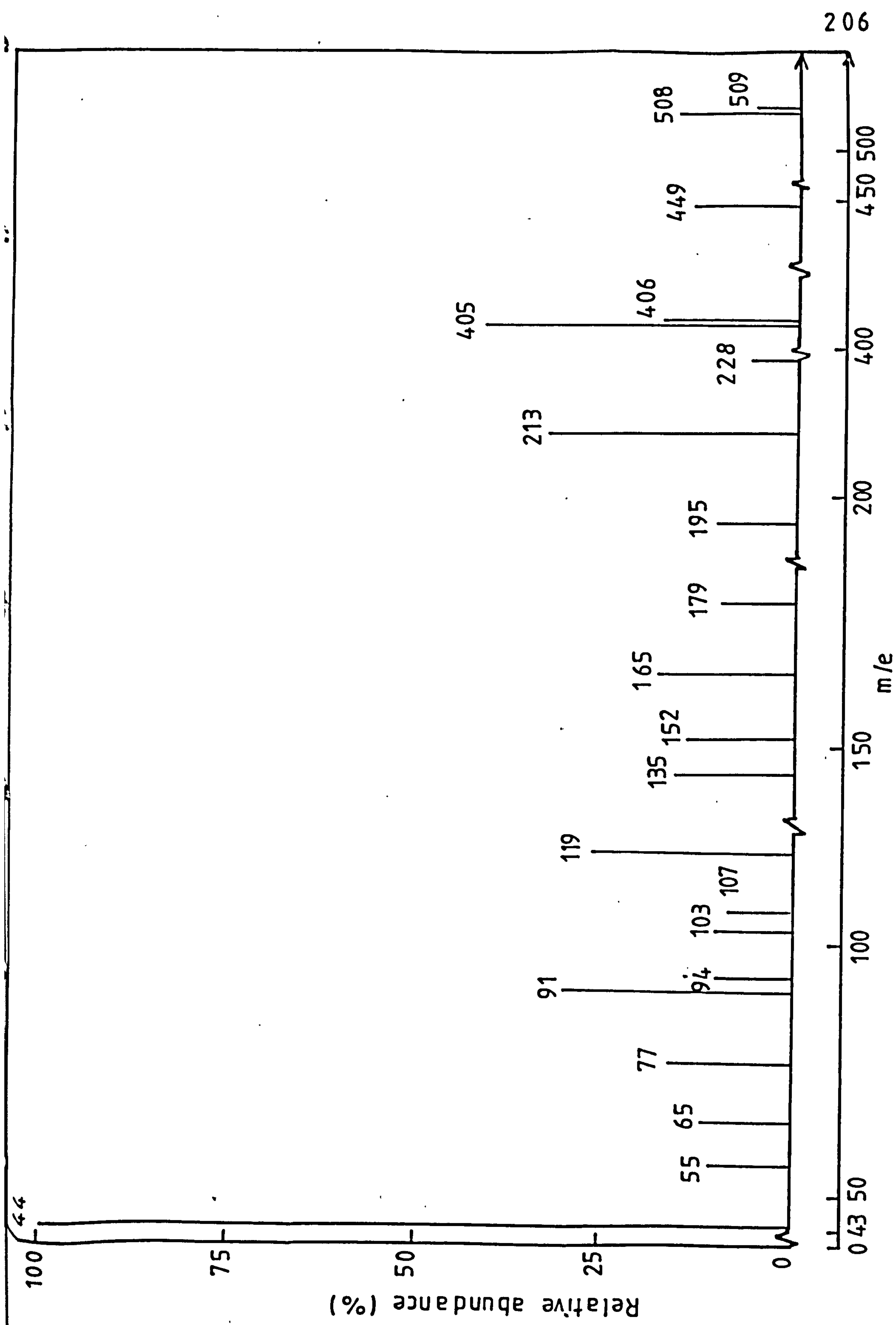


Fig. 4.57. Mass spectrum (70 eV) of the products of the thermal degradation for bisphenol A polycarbonate (laboratory sample)



#### 4.18 DISCUSSION

##### Aromatic Polycarbonates

The principal features of the thermal degradation of bisphenol A polycarbonate by TVA are as follows: the main products of the degradation are oligomeric products (CRF) and residue. The evolution of small amounts of carbon dioxide, carbon monoxide, methane, phenol, 1-hydroxy-4-methyl benzene and 1-hydroxy-4-isopropyl benzene is also observed. These results are in agreement with earlier findings by other workers.

Davis and Golden<sup>17-21</sup> have reported several studies of the thermal decomposition of bisphenol A polycarbonate. The earlier work was mainly concerned with the microstructural changes produced in the polymer. They claimed that the polymer underwent random chain scission when heated in a sealed evacuated vessel at various temperatures. On the other hand, when studies were carried out in a continuously evacuated system the polymer was found to crosslink rapidly to form an insoluble gel.<sup>18,21</sup> The large discrepancy between the two results is explained by Davis and Golden as being due to the competition between hydrolysis and condensation. Lee<sup>22</sup> also investigated the thermal degradation of bisphenol A polycarbonate. He claimed that the most active group on the macromolecule is the carbonate group which showed sensitivity towards hydrolysis and alcoholysis. Yacubovich et al.<sup>23</sup> claimed that depolymerisation is enhanced by the presence of acidic and basic impurities which may well be formed in sufficient amounts during the degradation reaction.



Davis and Golden also determined that the main volatile products collected during bisphenol A polycarbonate degradation were carbon dioxide, phenol and bisphenol A, but smaller amounts of other compounds, including carbon monoxide, methane, 2-(p-hydroxy phenyl)-2-phenyl propane and diphenyl carbonate have also been observed. They also found that the rate of gas evolution in an evacuated system at 360°C was  $2 \times 10^{-5}$  millimoles of gas per gram of polymer per second and the composition was 95% CO<sub>2</sub>, 3% CO and 2% CH<sub>4</sub>.<sup>20</sup> At higher temperatures the rate increased and the content of CO and CH<sub>4</sub> also appeared to increase. The fact that carbon dioxide is the major volatile product supports the view that the carbonate linkage is the most reactive group in the polymer. Lee<sup>22</sup> also detected 1-hydroxy-4-ethyl benzene, 1-hydroxy-4-isopropenyl-benzene, 1-hydroxy-4-isopropyl-benzene and cresol. The rapid evolution of phenol and, to a limited extent, of diphenyl carbonate at the onset of degradation, involves reaction at the end groups (either phenyl or hydroxyl).<sup>19</sup>

Bartosiewicz and Booth<sup>75</sup> found that on heating thin films (~ 1 μm) at 200°C under continuous evacuation for different periods of time the  $\bar{M}_w$  and  $\bar{M}_n$  of the polymer increased. Eventually a gel was formed. They argued that this result is consistent with the Davis and Golden mechanism of thermal degradation of bisphenol A polycarbonate i.e., the principal reactions are condensation and branching. Chain scission, due to hydrolysis of the carbonate linkage, is absent under these conditions.

The thermal degradation of bisphenol A polycarbonate has also been studied by simulation of processing conditions. Kovarskaya<sup>16</sup>

found that scission reactions occurred during processing of the polycarbonate, which may lead to deterioration of the mechanical Properties of the finished product. This behaviour is found because processing conditions correspond to thermal exposure without removal of volatiles. The effect of moisture was also discussed, since even small amounts of water in the bisphenol A polycarbonate melt will cause degradation by hydrolysis of the carbonate linkage accompanied by a release of  $\text{CO}_2$ . The solid bisphenol A polycarbonate must be thoroughly dried to a moisture content below 0.01% before melting. The absence of atmospheric oxygen is also a requirement, since oxygen causes discolouration and perhaps promotes crosslinking reactions. Abbas<sup>24</sup> studied the changes in molecular weight occurring during degradation of bisphenol A polycarbonate carried out in a capillary rheometer, which again corresponds to a thermal degradation without efficient removal of volatile degradation products. He claimed that under these conditions polycarbonate did not degrade by a random scission mechanism.

Bisphenol A polycarbonate<sup>71</sup> has also been degraded by direct pyrolysis in a mass spectrometer with electron impact as ionisation mode at different sample inlet probe temperatures in the range 220°-410°C. These studies have suggested that the primary degradation process of the polymer is an ester interchange producing cyclic structures, i.e., dimer, trimer and tetramer. Furthermore, this mode of fragmentation enhances the dimethylation process of the isopropylidene structures in the polymer.

In the present study, bisphenol A polycarbonate was degraded by the thermal volatilisation analysis technique with fractionation of

the volatile products by SATVA; complementary thermal analysis techniques also used were TG and DSC.

TVA technique enables the degradation of the polymer to be carried out under continuous evacuation ( $10^{-4}$  mm Hg) and programmed or isothermal heating. It is also possible to collect the different product fractions of the degradation in a single experiment. The TVA curve obtained indicates that the rate of volatilisation for both non-condensable and condensable products increases with temperature. This result agrees with the earlier findings of Davis and Golden for a similar polymer under vacuum conditions.<sup>20</sup>

The non-condensable products of the degradation, i.e., CO and CH<sub>4</sub>, were identified by mass spectrometry via an on line VG Micromass mass spectrometer attached to the TVA system.

The condensable products were fractionated by SATVA and analysed by infrared spectroscopy and mass spectrometry. The products obtained were CO<sub>2</sub>, phenol and 1-hydroxy-4-methyl-benzene.

The solid degradation product (CRF) was analysed by infrared spectroscopy and GC-MS spectrometry and found to consist of short chain fragments, bisphenol A and 1-hydroxy-4-isopropyl-benzene.

The residue after degradation consisted of a hard, carbonaceous material.

The relative proportions of some of the products of degradation are discussed in a later chapter.

From the analysis of the results it can be observed that these are consistent with the Davis and Golden mechanism of thermal degradation of bisphenol A polycarbonate under vacuum conditions, i.e., the primary

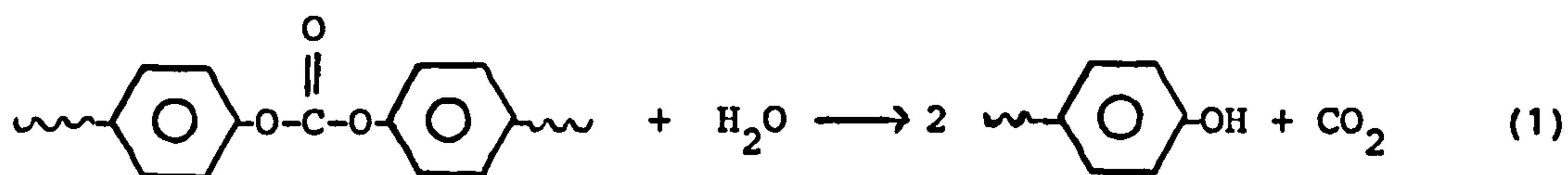


degradation step is a main chain scission reaction due to hydrolysis or phenolysis of the carbonate group with the production of short chain fragments, bisphenol A and phenol. Branching reactions and eventual gelation occur due to the continuous removal of the volatile products formed during degradation.

The fact that in the present investigation carbon dioxide is the main volatile product formed again indicates that the carbonate group is the most reactive group in the macromolecule.

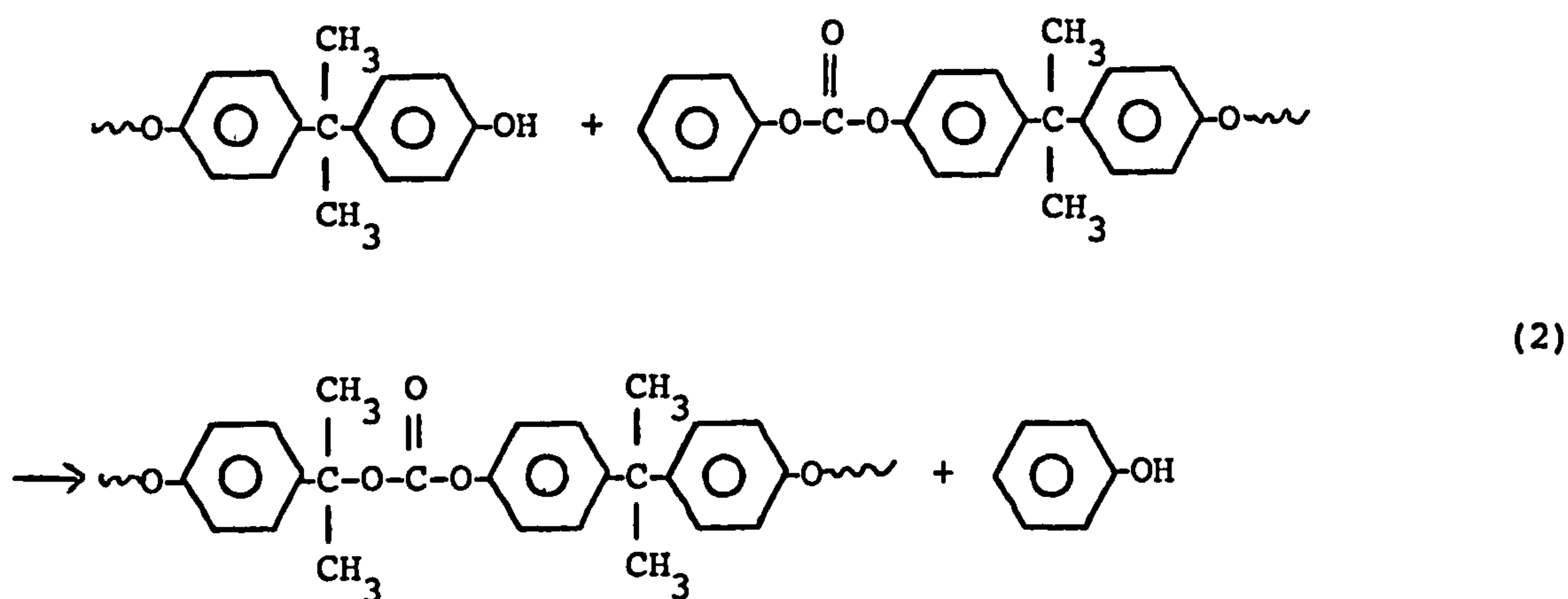
Water was also observed as a condensable product. Although the polymer was kept at ambient temperature under vacuum, some water remained because the polymer tends to absorb it strongly. It has been observed<sup>20</sup> that traces of moisture remain even after drying at 353°C at  $10^{-5}$  mm Hg for 5.3 hours. It is most likely that residual water in the polymer is responsible for the primary degradation by hydrolysis at the carbonate groups.

The Davis and Golden mechanism involves the following processes. The initial stage is a random chain scission by a hydrolytic process at the carbonate group which produces hydroxyl end groups and carbon dioxide.

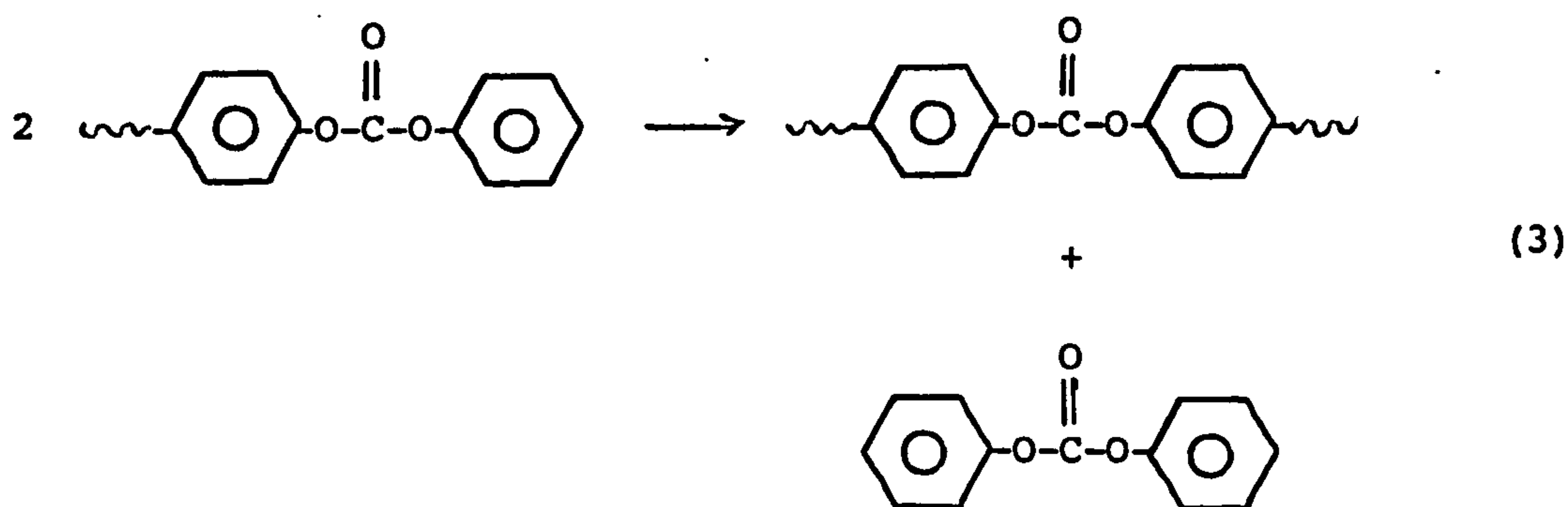


The short chain fragments formed may volatilise from the reaction when the length is lower than the volatilisation limit at the degradation temperature or remain in the medium.

Polymer molecules with hydroxyl end groups may react with phenyl end groups producing phenol in small amounts. Phenol was observed as a volatile condensable product when the polymer was heated at 300°C



Polymer molecules containing phenyl-carbonate end groups  
evolve diphenyl carbonate quantitatively



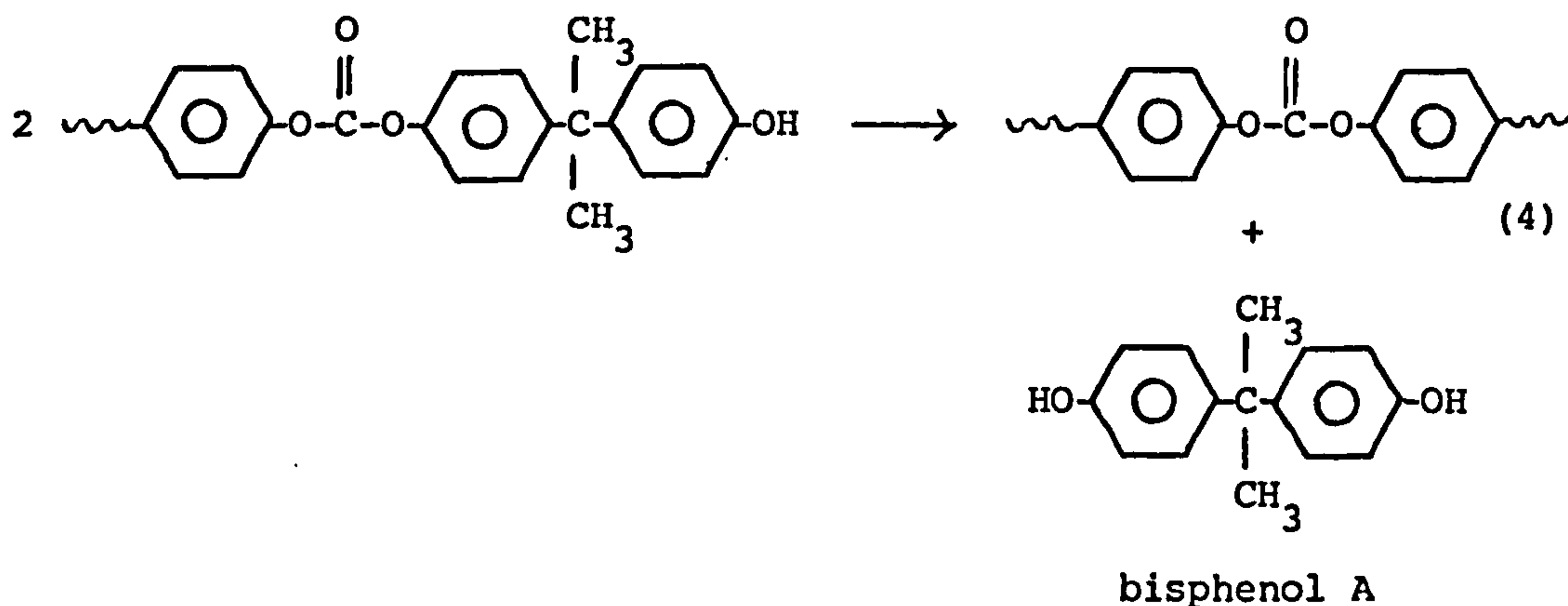
In this study, however, diphenyl carbonate was not observed as degradation product.

In a continuously evacuated system, as in TVA, there is an efficient removal of the products of degradation. Therefore, the



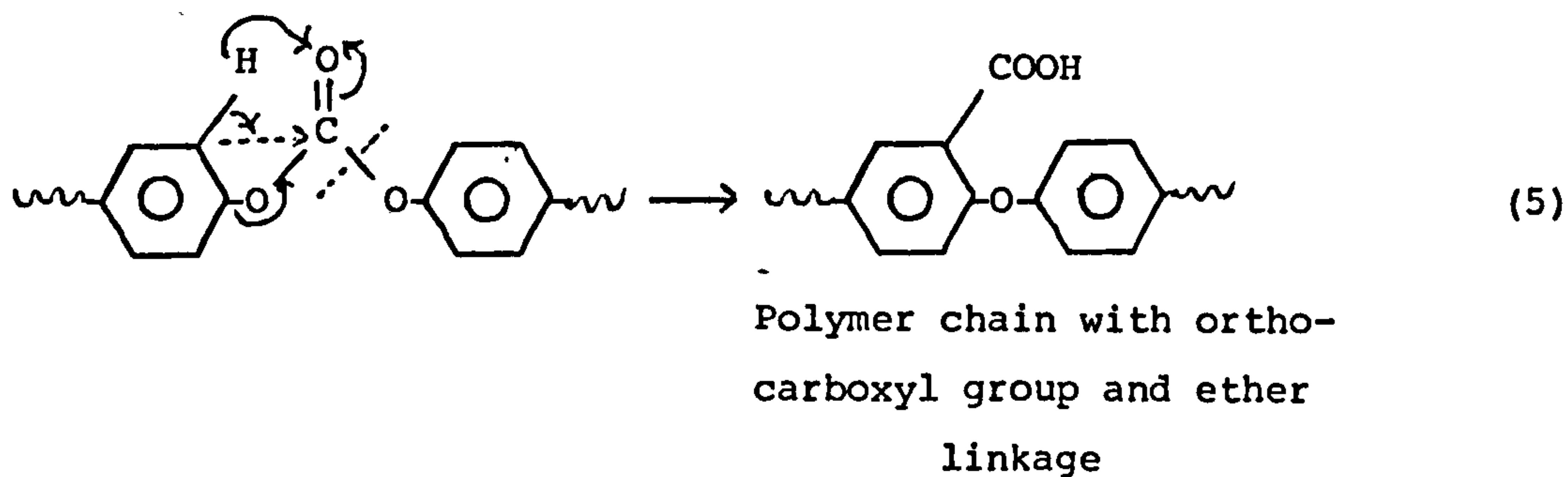
overall effect of these three reactions is further condensation.

Davis and Golden<sup>19</sup> proposed that the condensation reactions occur principally by elimination of bisphenol A; this product was collected as cold ring fraction in the TVA experiment

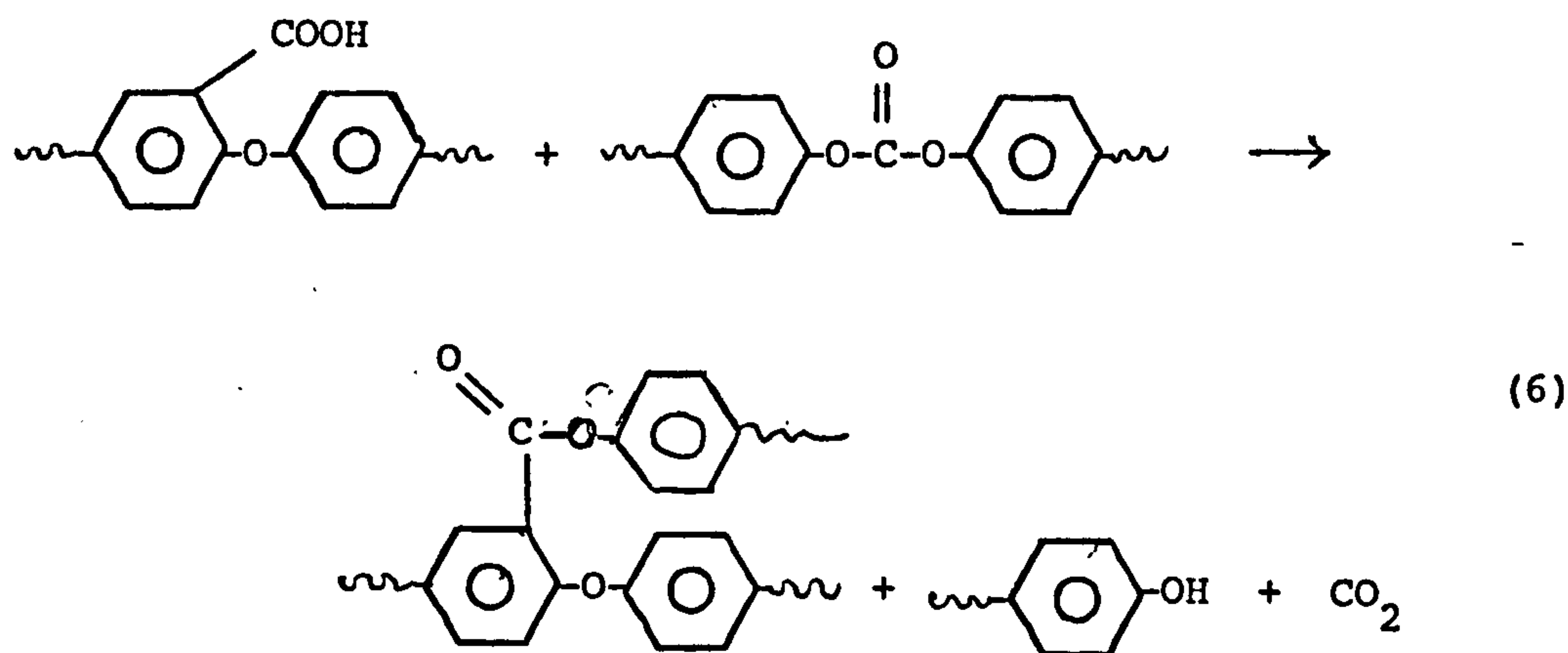


The processes which lead to branching and eventually gelation have been explained by the elucidation of the mode of degradation of the carbonate group in the thermal degradation of the model compound diphenyl carbonate.<sup>74</sup> Thermal degradation at temperatures below 500°C leads to a rearrangement of the carbonate group to form 2-phenoxybenzoic acid which undergoes a further series of reactions to form diphenyl ether, xanthone, phenol and phenyl-2-phenoxybenzoate, together with carbon dioxide and carbon monoxide. If a similar mechanism is applicable to the thermal breakdown of the polymer system, the following reactions will account for the volatile products, carbon dioxide and bisphenol A, as well as explaining branching and gelation in the degrading polymer residue.

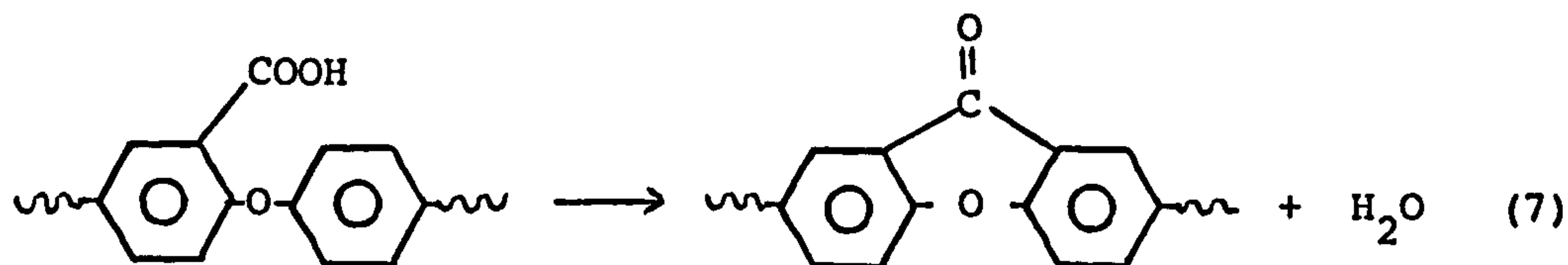
Branching originates by the rearrangement of the carbonate linkage to produce an ether bond linking two aromatic rings and an ortho-carboxyl group



Subsequent reaction with another carbonate linkage leads to a trifunctional branch point



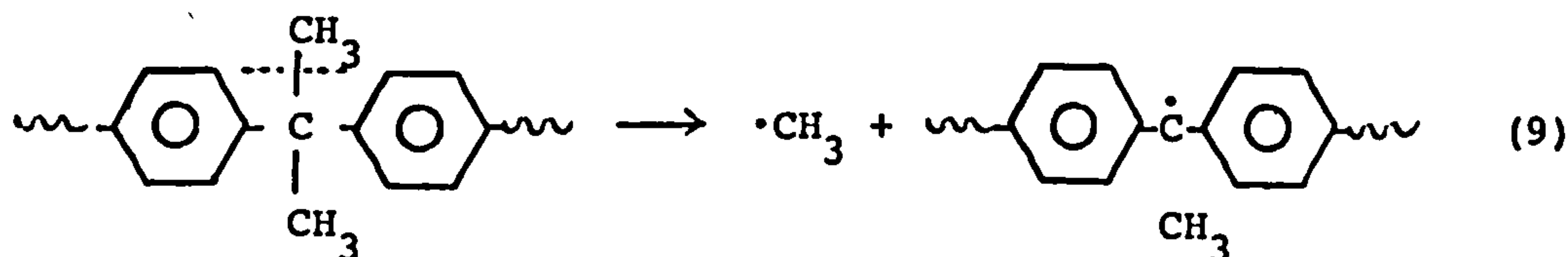
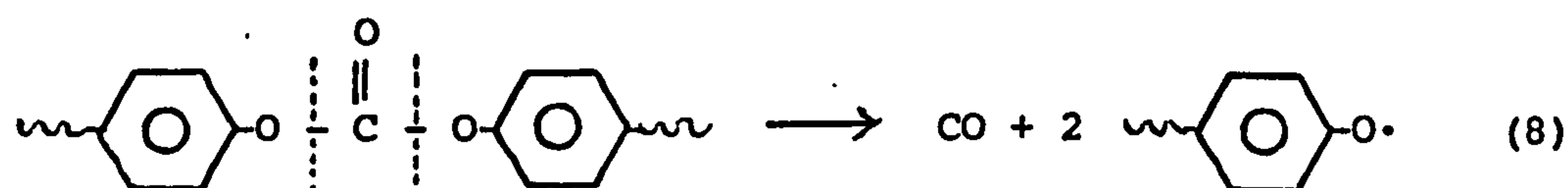
An alternative reaction for the o-carboxyl group is the elimination of water to form an xanthone.



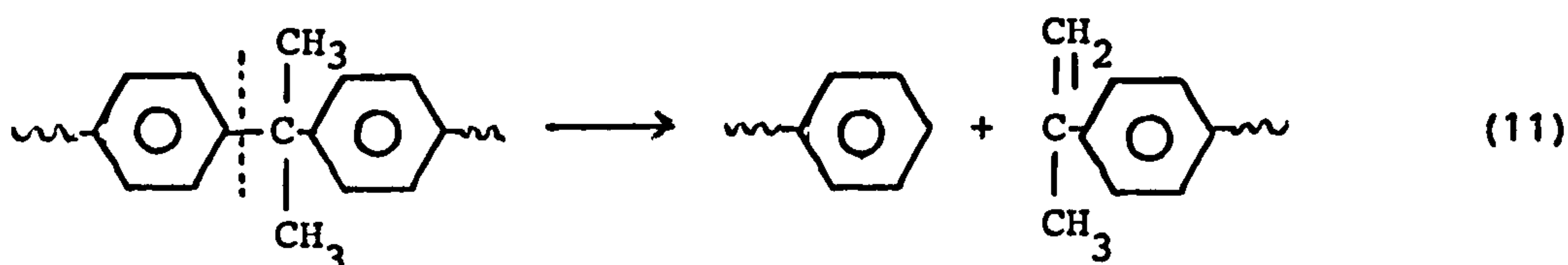
In a sealed system water subsequently reacts by equation (1), but it volatilises out in a continuously evacuated system.

When the polymer is heated in vacuum, branching will occur via reactions (5) and (6), whether or not volatiles are removed from the system. However, gelation will only result if the scission process reaction (1) is suppressed by removal of free hydroxyl groups (water). When the volatiles are left in the system, scission reactions will predominate. The residue left after degradation was a hard material that carbonised when heated at 400°C or higher temperatures. This indicates that the residue consists of highly involatile material.

Non-condensable gases, i.e., carbon monoxide and methane, are also observed when the temperature reaches about 400°C. These products are most likely to form by homolytic scission at the carbonate group and the isopropylidene groups reactions (8), (9) and (10)

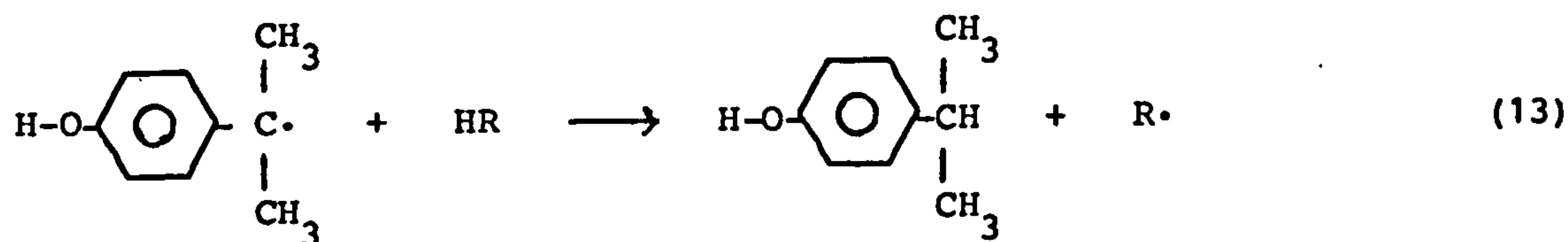
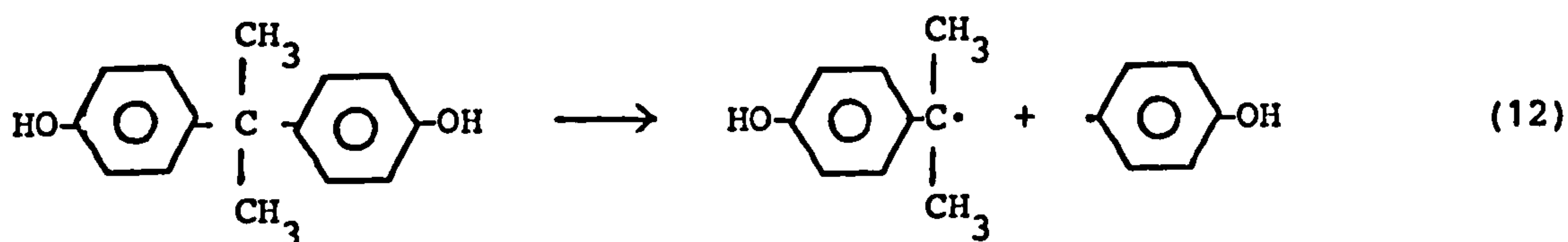


Main chain scission at the isopropylidene group, followed by disproportionation of the radicals, is also possible, resulting in the formation of phenyl and isopropylidene end groups. This reaction may account for the increase of short chain fragments as the degradation temperature increases

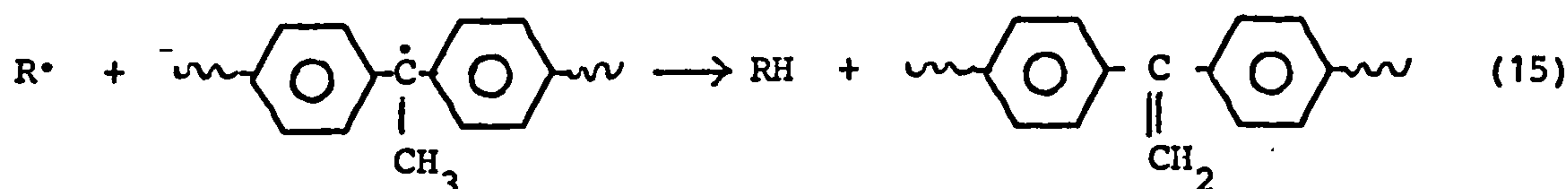
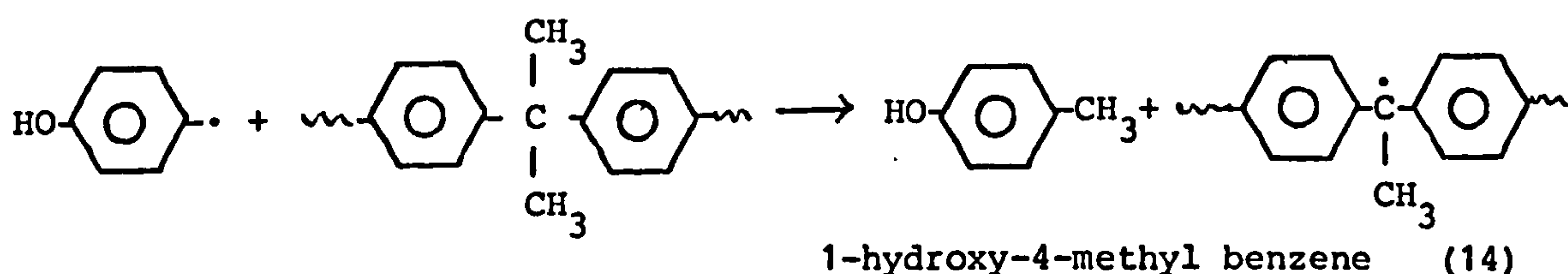


The formation of traces of 1-hydroxy-4-methyl-benzene and 1-hydroxy-4-isopropyl-benzene was also observed. The source of these products is less evident. In TVA experiments, the amount of products degraded is small (~ 50 mg), the large base area of the degradation tube and the continuous evacuation reduce the possibility of diffusion-controlled reactions and secondary thermal degradation reactions, because the products of degradation are immediately removed. However, because of the high melt viscosity of bisphenol A polycarbonate, there is a possibility that some volatile product such as bisphenol A does not volatilise out and undergoes further decomposition. Hence an alternative source for these products may be the decomposition of bisphenol A, and radicals involved in the decomposition may possibly react with the polymer as follows:





1-hydroxy-4-isopropyl-benzene

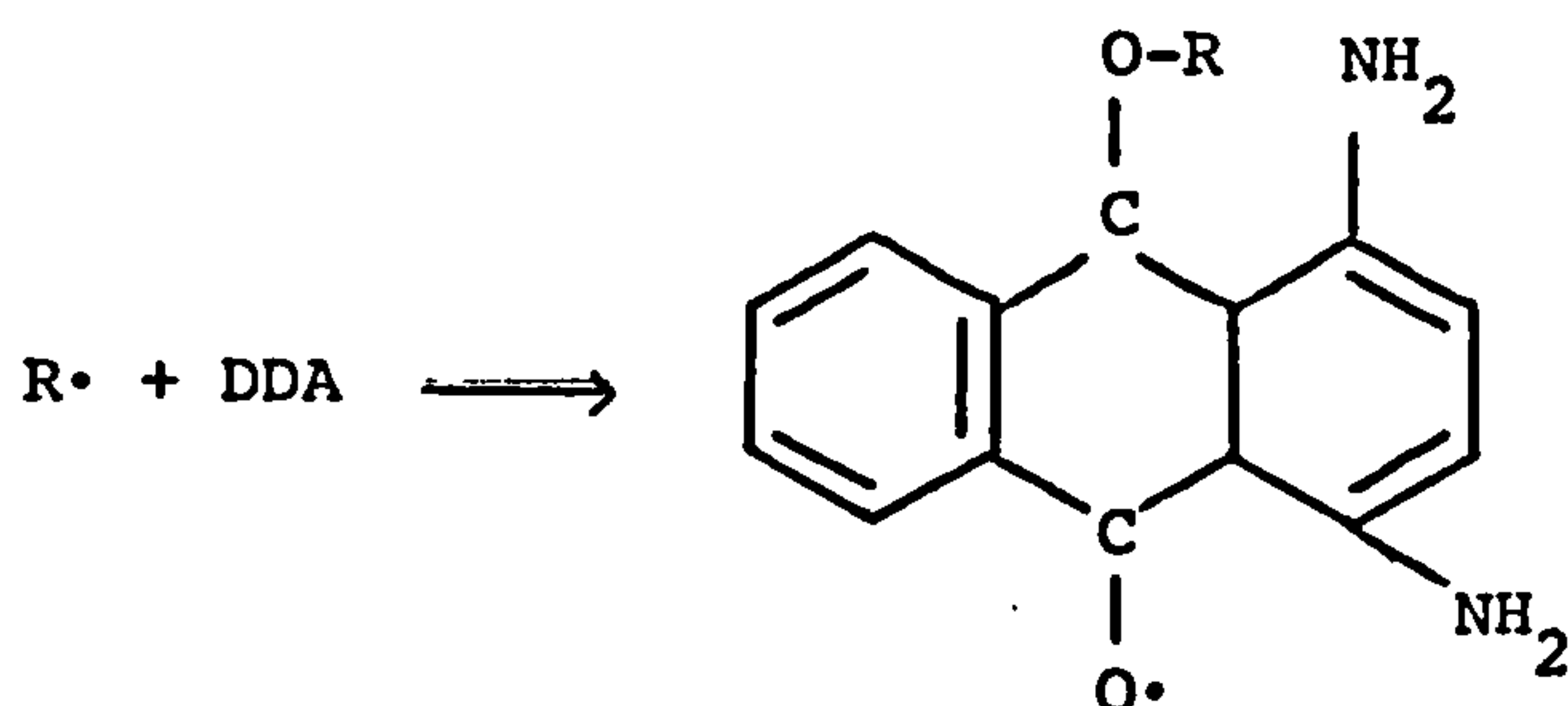


In this study, the degradation of bisphenol A polycarbonate has also been carried out in the presence of a free radical inhibitor, DAA, in two different proportions, 1:1 and 4:1 (polymer:DAA). From the analysis of the results, it was observed that the volatilisation was markedly suppressed.

Reactions such as high temperature thermal degradation usually proceed randomly: the active intermediates, e.g. radicals, attack the reactive bonds without discrimination, but in the presence of small amounts of inhibitors these reactions are susceptible to inhibition or retardation. Inhibitors may react with already formed free radicals,



but they cannot prevent the initiation of degradation by thermal chain scission. Substances such as 1,4-diamino-anthraquinone are believed to react with the polymer radicals produced on initiation to form stable radicals. This probably occurs by means of addition at the carbonyl group.



The newly formed radical can be further stabilised by reaction with another polymer radical or by disproportionation.

Grassie and Melville<sup>76</sup> studied the effect of DAA on the degradation of PMMA. They used DAA because it is chemically stable up to 240°C and involatile at pressures as low as  $10^{-6}$  mm Hg, and was suitable for use under the conditions of the thermal degradation. Poly(methyl methacrylate) depolymerises quantitatively to monomer under the effect of heat by initiation at the unsaturated chain ends in polymers polymerised via a radical route. When such a polymer was degraded in the presence of traces of DAA, the depolymerisation was almost totally suppressed. They were able to establish in this way the radical nature of the reaction.

In the thermal degradation of bisphenol A polycarbonate in the presence of DAA a drastic decrease of the amount of volatile products was observed by TVA and a retardation of the rate of degradation

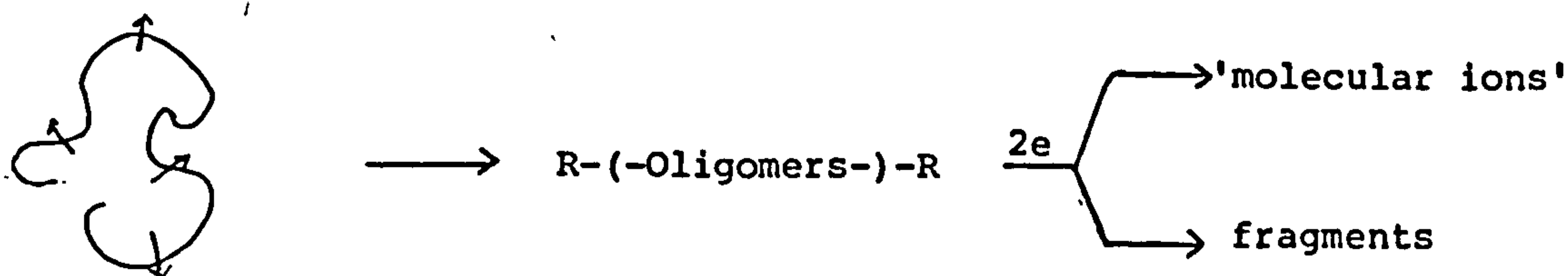
was also determined by means of isothermal TG.

These results suggest that free radicals are intermediates in the production of volatile degradation products.

Bisphenol A polycarbonate and the solid product of degradation (CRF) obtained by TVA, which consists of short chain fragments, was degraded in the mass spectrometer (70 eV). The fragmentation pattern resembled that found by other authors<sup>71</sup> using a similar polymer.

Foti et al.<sup>71</sup> degraded bisphenol A polycarbonate in the mass spectrometer at low energy (16 eV) and using a sample temperature of 290°C. The results suggested that in the primary fragmentation process an ester interchange reaction predominates, causing the formation of cyclic oligomers. Wiley<sup>73</sup> also studied the thermal degradation of bisphenol A polycarbonate in the mass spectrometer. The results suggested that cyclic oligomers were also formed. These results were compared with the fragmentation patterns of model compounds.

Luderwald<sup>72</sup> studied the fragmentation pattern of polyesters in the mass spectrometer. He suggested that using low pyrolysis temperatures results in a more selective pyrolysis mechanism, which increases the possibility of detecting characteristic structural elements in the pyrolysis products. The low degradation rates obtained at these temperatures increase the probability that the pyrolysis products are fragments which still contain the basic polymer structure, one, two or several units in length. He proposed the following general equation:



The subsequent electron-impact ionisation yields positive ions of the pyrolysis products (molecular ions) as well as their fragment ions. Hence, according to this model, the direct pyrolysis of bisphenol A polycarbonate in the mass spectrometer (70 eV) should lead to a mixture of products several repeat units in length, together with fragments.

The fragmentation pattern of bisphenol A in the mass spectrometer showed a base peak at  $m/e$  508 which it has been suggested corresponds to the cyclic dimer.<sup>73</sup> The peak at  $m/e$  762 is attributed to the cyclic trimer. The fragments observed may result from loss of carbon dioxide ( $m/e$  44) starting from the molecular ions. This elimination produces the fragment ion at  $m/e$  418 in the cyclic trimer and the fragment ions at  $m/e$  464 and 420 in the cyclic dimer, as proposed by Wiley.<sup>73</sup> Other fragmentations detected involved the loss of 15 mass units ( $\dot{\text{C}}\text{H}_3$ ) from the molecular ion and from the fragments. The methyl radical elimination is from the methyl groups of the isopropylidene structure; this is also characteristic of the fragmentation of the model compound bisphenol A.



## CHAPTER FIVE

### QUANTITATIVE DETERMINATION OF DEGRADATION PRODUCTS

The discussion in earlier chapters has been based on qualitative data regarding products. In this chapter quantitative measurements are presented.

#### 5.1 GENERAL PROCEDURE FOR QUANTITATIVE DEGRADATION OF POLYMERS IN TVA SYSTEM

Degradations were performed in the TVA system following the procedure outlined below.

Samples of polymers were degraded in a thin glass bottle placed within the TVA tube, to enable the resulting residue of degradation to be determined. Samples were heated, both under programmed heating to 500°C at a heating rate of 10°C per minute, and isothermally for various periods of time. The cold ring fractions (CRF) were collected on a cold finger inserted into the degradation tube, as has already been described in Chapter 2 (fig. 2.2). The upper CRF, which consisted of solids, condensed further up on the cold finger and the lower CRF were collected separately by washing with a suitable solvent, then placed in glass bottles and, after the solvent had been removed by evaporation, the resulting residue was weighed.

The condensable volatile products of degradation were collected in the SATVA cold trap, and fractionated, as has already been explained

in Chapter 2.

The quantities of solid products are presented in percentage by weight of the original polymer degraded. The quantities in moles and grams of condensable volatile products of degradation evolved are calculated per 100 repeat structural units of original polymer degraded. The experimental results obtained for degradations performed heating isothermally are summarised in Tables

## 5.2 ALIPHATIC POLYCARBONATES

### 5.2.1 Programmed Degradation for Poly(trimethylene carbonate)

#### 5.2.1.1 Analysis of Solid Products

Through all the experiments, samples of poly(trimethylene carbonate) prepared at 150°C  $\bar{M}_n$  3690 were used.

The upper CRF, which consisted mainly of monomer, and the lower CRF, consisting of a mixture of monomer and a small amount of polymer chain fragments, as determined by TVA (p. 76) amounted to 73% and 21% of the original polymer weight, respectively.

#### 5.2.1.2 Analysis of Carbon Dioxide

Small samples (< 10 mg) of poly(trimethylene carbonate) were degraded ( $\bar{M}_n$  3690).

The experimental results show that the average quantity of carbon dioxide (the significant condensable volatile product of degradation) obtained per 100 repeat structural units of original polymer degraded is 2.6 moles.



## 5.2.2 Isothermal Degradations for Poly(trimethylene carbonate)

### 5.2.2.1 Analysis of Solid Products

Fifty milligram samples of poly(trimethylene carbonate) were degraded. The same polymer sample ( $\bar{M}_n$  3690) was used.

Table 5.1 shows details of the percentage yields of cold ring fractions and residue heated at different temperatures for one hour.

From the experimental results it can be observed that the monomer production rises sharply within a short temperature interval. At the higher temperature a small amount of polymer short chain fragments (less volatile product) is also formed. This indicates that chain scission occurs to some extent, along with the depolymerisation reaction.

The maximum yield of upper CRF (monomer) and the total solid fraction occurs at 214°C. At higher temperatures some secondary reactions occurring during the degradation process involve the formation of a greater amount of the volatile produce of degradation, carbon dioxide. At temperatures up to 180°C degradation is very slow.

Fig. 5.1 shows the percentage yield of cold ring fraction and residue left from poly(trimethylene carbonate) heated to 180°C and 190°C for different periods of time in the TVA system.

From the examination of fig. 5.1, it can be seen that degradation at 180°C is negligible in the first 90 minutes of heating, after which degradation occurs giving upper CRF and residue as main products of degradation. On the other hand, significant degradation of the polymer occurs at 190°C when it is heated for one hour. A considerable amount of total CRF (monomer) is produced after heating

TABLE 5.1

Percentages by weight of cold ring fractions and  
residue from poly(trimethylene carbonate) heated  
at different temperatures for one hour

temperature °C	upper CRF %	lower CRF %	total CRF %	residue %	TSF %
175	-	-	-	98.2	98.9
185	4.9	-	4.9	94.0	98.9
190	11.9	2.4	14.3	80.5	94.8
214	61.0	34.2	95.2	3.2	98.4
243	43.7	48.9	92.6	5.2	97.8

TSF - Total solid fraction (total percentage of cold ring fraction  
+ residue collected expressed in percentage of the original  
weight of polymer.

The difference to 100% of the total mass, corresponds to  
impurities such as water or solvent evolved in the heating  
process.

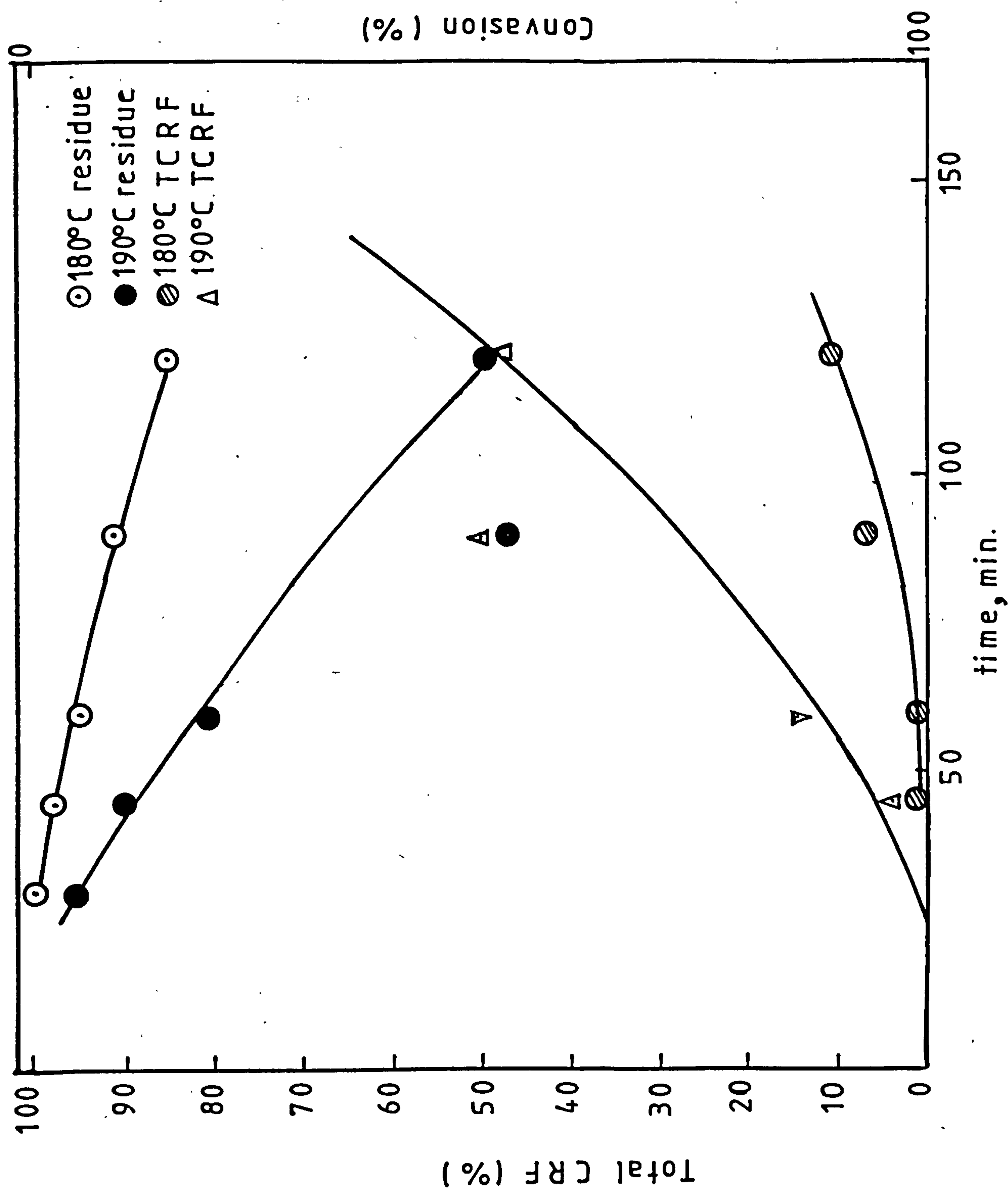


Fig. 5.1 Percentages yield of total CRF and residue left from poly(trimethylene carbonate) heated in the TVA system for different periods of time.

for a period of 90 min. (50.2%). One can be led to the conclusion that the initial retardation of reaction may be due to impurities such as water clinging to the carbonyl groups of the macromolecule.

The percentages by weight of total solid fraction obtained by TVA at 190°C compared with that obtained by isothermal TG in vacuum at the same temperature (see p.97) are of the same order: 14.3% by TVA and 20% by TG.

The considerable increase in rate with temperature, as has already been seen in Chapter four, and the appearance of carbon dioxide as a minor volatile product can lead to the conclusion that for higher temperatures than 195°C, the carbonate groups on the macromolecule are capable of undergoing reaction with the production of carbon dioxide. The splitting of a carbonate group gives very labile radicals which may lead to the formation of polymer chain fragments. The evidence that this process may be operative at high temperatures is given by the fact that the amount of lower CRF (less volatile fragments) increases with temperature.

#### 5.2.2.2 Analysis of Carbon Dioxide

The amount of carbon dioxide produced after heating poly(trimethylene carbonate) at 190°, 200°, 214° and 243°C, respectively, for one hour, was determined. In Table 5.2 are detailed the quantities of gas produced in moles and weight percentages based on the original weights of polymer degraded.

From the results it can be seen that carbon dioxide begins to be formed at 200°C; the amount produced at all temperatures is relatively small.



TABLE 5.2

Percentage of carbon dioxide after heating  
poly(trimethylene carbonate) at different  
temperatures for one hour

temperature °C	CO <sub>2</sub> mole %	CO <sub>2</sub> weight %	TSF % initial weight
190	-	-	94.8
200	0.14	0.06	98.3
214	0.38	0.16	98.4
243	0.94	0.41	97.1

- mole % CO<sub>2</sub> : moles of CO<sub>2</sub> produced per 100 structural units  
in the original polymer

weight % CO<sub>2</sub>: weight of carbon dioxide produced as percentage  
of polymer

TSF : total solid fraction.



### 5.2.3 Programmed Degradations for Poly(neopentylene carbonate)

#### 5.2.3.1 Analysis of Solid Products

Samples of poly(neopentylene carbonate) were degraded according to the general procedure already described. Through all the experiments, samples prepared at 150°C  $\bar{M}_n$  4332, were used.

The upper CRF formed mainly of monomer, and the lower CRF consisting of a mixture of monomer and polymer short chain fragments as found by TVA (see p83) were determined. The experimental results give upper CRF 73% and lower CRF 21% of the original weight of polymer, respectively.

These results are in agreement with the previous report that monomer is the main product of degradation,<sup>11</sup> but also provide supporting quantitative data.

The relatively high amount of monomer produced (75%) shows the ease of depolymerisation owing to the high probability of close approach of atoms in the helical structure.<sup>11</sup>

#### 5.2.3.2 Analysis of Carbon Dioxide

Small samples (<1 mg) of poly(neopentylene carbonate) were degraded ( $\bar{M}_n$  4332). The yield of carbon dioxide evolved after degradation was determined, as already described.

The average yield of carbon dioxide was 7.6 moles per 100 structural units of the original polymer degraded.

This result indicates that additional chain scission at the carbonate group occurs to some extent, along with the depolymerisation

reaction. These results are in agreement with the fact that low molecular weight dialkyl carbonates thermally decompose, giving off carbon dioxide.

#### 5.2.4 Isothermal Degradations for Poly(neopentylene carbonate)

##### 5.2.4.1 Analysis of Solid Products

Fifty milligram samples of poly(neopentylene carbonate) were heated under vacuum at various temperatures for one hour.

In Table 5.3 are detailed the percentages by weight of CRF and residue based on the initial weight of polymer.

From the analysis of the results, it can be seen that the amount of monomer produced increases with temperature, reaches a maximum at 290°C then decreases at 300°C. Polymer short chain fragments are formed in small amounts at 300°C. This indicates that at this temperature secondary reactions occur to some extent simultaneously with the depolymerisation reaction. Degradation is negligible at temperatures up to 255°C.

In Table 5.4 are shown the percentages by weight of the cold ring fractions and residue after the degradation of poly(neopentylene carbonate) in TVA experiments at 190°, 210° and 220°, respectively, for different periods of time. From the results, it can be seen that degradation only becomes significant after 4 hours of heating at each temperature. This behaviour may be explained on the grounds that water absorbed by the polymer may act by initially retarding the process of degradation.

TABLE 5.3

Percentages by weight of the different cold ring fractions  
and residue of poly(neopentylene carbonate) heated at  
various temperatures for one hour

temperature °C	upper CRF %	lower CRF %	total CRF %	residue %	TSF %
255	-	-	-	98.6	98.6
275	74.3	-	74.3	18.1	92.4
290	78.2	-	78.2	6.6	84.8
300	65.8	11.4	77.2	18.1	81.7

TSF - Total solid fraction based on percentage of original polymer.

The difference from 100% of the total mass corresponds to  
impurities such as water or solvent trapped within the  
polymer.

TABLE 5.4

Percentage yields of cold ring material and residue from  
poly(neopentylene carbonate) by TVA heating under vacuum  
at 190°, 210° and 220°C for different periods of time

temperature time h	190°C			210°C		220°C	
	<u>3.0</u>	<u>3.5</u>	<u>4.0</u>	<u>3.0</u>	<u>4.0</u>	<u>1.0</u>	<u>4.0</u>
upper CRF %	-	-	12.0	5.3	23.6	-	69.6
lower CRF %	-	-	-	-	-	-	-
total CRF %	-	-	12.0	5.3	23.6	-	69.6
residue %	97.1	96.7	86.0	93.7	65.3	99.8	19.6
total solid fraction %	97.1	96.7	98.0	99.0	88.9	99.8	89.2



#### 5.2.4.2 Analysis of Carbon Dioxide

Carbon dioxide produced when poly(neopentylene carbonate) was heated at 300°, 308°, 330° and 350°C, respectively, for one hour was determined quantitatively.

The results obtained are detailed in Table 5.5. Examination of these shows that poly(neopentylene carbonate) begins to produce carbon dioxide at ~ 308°C. The amount produced progressively increases with temperature, suggesting that some secondary reaction occurring at higher temperatures during the degradation process involves the formation of carbon dioxide.

#### 5.2.5 Programmed Degradation for Poly(2-phenyl-trimethylene) carbonate

##### 5.2.5.1 Analysis of Solid Products

Poly(2-phenyl-trimethylene carbonate) degraded ( $\bar{M}_n$  3500) under the conditions which have already been described gives polymer short chain fragments as cold ring fraction (see p.89).

The quantitative analysis showed that the average percentage yield of CRF was 85% of the original weight of polymer.

This result agrees well with the behaviour already described that a bulky substituent in the carbon atom 2 of the diol moiety hinders the ring formation, diminishing the amount of cyclic monomer obtained.

#### 5.2.6 Isothermal Degradations for Poly(2-phenyl-trimethylene carbonate)

##### 5.2.6.1 Analysis of Solid Products

Thirty milligram samples of poly(2-phenyl-trimethylene carbonate) were heated at various temperatures for one hour. The



TABLE 5.5

Percentages of carbon dioxide after heating  
poly(neopentylene carbonate) at different  
temperatures for one hour

temperature °C	CO <sub>2</sub> mole %	CO <sub>2</sub> weight %	TSF initial weight %
275	-	-	92.40
300	0.10	0.03	81.70
308	0.18	0.06	80.30
330	4.20	1.40	77.00
350	11.20	3.80	75.80

mole % CO<sub>2</sub> : moles CO<sub>2</sub> produced per 100 structural units in the  
initial polymer

weight % CO<sub>2</sub> : weight of CO<sub>2</sub> produced per 100 grams of initial  
polymer

TSF : Total solid fraction (residue + upper and lower CRF)

experimental results obtained are shown in Table 5.6.

The analysis of the results shows that degradation occurs to a significant extent only above 200°C. The percentage of CRF increases with temperature. On increasing the temperature of degradation from 275°C to 305°C, however, the amount of cold ring fraction decreases slightly. Within this range of temperature the second significant volatile product of degradation,  $\alpha$ -methyl styrene, begins to be evolved, which indicates that another degradation process is also involved at this higher temperature.

#### 5.2.6.2 Analysis of Carbon Dioxide

Small samples of poly(2-phenyl-trimethylene carbonate) were degraded at different temperatures for one hour.

The experimental results are shown in Table 5.7. From these it can be seen that carbon dioxide begins to be formed at about ~ 254°C, the amount progressively increases at higher temperatures.

### 5.3 ALIPHATIC-AROMATIC POLYCARBONATES

#### 5.3.1 Programmed Degradation for Poly(p-xylylene carbonate)

##### 5.3.1.1 Analysis of Solid Products

Two different samples A and B (see p.61) of poly(p-xylylene carbonate) were degraded. The CRF consisting of polymer short chain fragments were collected and determined.

The percentages by weight for both samples A and B amounted to 46.5% and 56.2%, respectively. The corresponding residues were

TABLE 5.6

Percentages by weight of cold ring fraction and residue  
of poly(2-phenyl-trimethylene carbonate) heated at  
various temperatures for one hour

Temperature °C	CRF %	Residue %	TSF %
200	-	92.1	92.1
225	4.6	89.4	94.0
254	28.2	60.9	88.9
275	90.5	6.0	96.6
305	83.5	1.0	84.5

CRF % : Cold ring fraction (consisting of polymer short chain fragments)

TSF : Total solid fraction. The amount corresponding to cold ring + residue. The difference from 100% of the total mass corresponds to impurities such as water or solvent trapped within the polymer.

TABLE 5.7

Moles and weight percentages of carbon dioxide evolved after heating poly(2-phenyl-trimethylene carbonate) at various temperatures for one hour

Temperature °C	moles %	weight %	TSF %
200	-	-	92.1
225	0.94	0.23	94.0
254	4.98	1.23	88.9
275	10.2	2.52	96.6
305	15.3	3.78	84.5

mole % CO<sub>2</sub> : moles of CO<sub>2</sub> produced per 100 structural units in the original polymer

weight % CO<sub>2</sub> : weight of carbon dioxide produced as percentage of original weight of polymer

TSF : total solid fraction.

4.5% and 14.2% by weight of the original weight of the polymer.

#### 5.3.1.2 Analysis of Condensable Products

Small samples of poly(p-xylylene carbonate) sample A were degraded. The number of moles of condensable products formed in each case was determined, as has already been explained in Chapter two.

The average quantities of carbon dioxide and p-tolualdehyde obtained were 56.7 and 49.2 moles per 100 repeat structural units of the original degraded polymer, respectively.

The same amounts expressed as percentage by weight corresponded for carbon dioxide and p-tolualdehyde to 15.2% and 13.2% of the original degraded polymer, respectively.

#### 5.3.2 Isothermal Degradations for Poly(p-xylylene carbonate)

##### 5.3.2.1 Analysis of Solid Products

Samples A and B of poly(p-xylylene carbonate) were heated at various temperatures for one hour. In Table 5.8 are shown the average Percentages by weight of CRF and corresponding residues for both polymer samples.

From the analysis of the results it can be seen that for sample A at 260°C the CRF is the major solid product of degradation and beyond the CRF decreased. The residue is negligible at this temperature and beyond there is a little increase. At 220°C the degradation is slow.

For sample B there is a progressive increase of CRF up to 345°C and beyond the CRF decreased. The residue decreases steadily with temperatures up to 370°C. However, at the higher temperature of



395°C there is a slight increase. From the qualitative evidence obtained in isothermal heating of this sample, the decrease of CRF for the higher temperatures must be associated with the production of greater amounts of the volatile degradation products, e.g. CO<sub>2</sub> and p-tolualdehyde. This can lead to the conclusion that at these higher temperatures, along with the scission reaction, another degradation process is also involved.

In the literature there is no reference to the probable degradation products of this particular polymer. However the volatile products formed agree well with the suggested degradation products in the pyrolysis of the model compound benzyl ethyl carbonate.<sup>14</sup>

For these polymers the volatile degradation products were not quantitatively measured at isothermal degradation.

## 5.4 AROMATIC POLYCARBONATES

### 5.4.1 Programmed Degradation for Bisphenol A Polycarbonate

#### 5.4.1.1 Analysis of Solid Products

Two different polymers (laboratory and commercial samples) were degraded. The amounts of cold ring fraction, consisting of polymer chain fragments, and corresponding residue, were determined.

The results of the degradation showed that the average percentage by weight of CRF for both laboratory and commercial sample (25 to 50 mg) amounted to 27.3% and 25.6% of the initial polymer weight, respectively. The corresponding residues obtained were 35.2% and 35.7%.

TABLE 5.8

Percentages by weight of cold ring fractions and residues  
for poly(p-xylylene carbonate) samples A and B heated at  
various temperatures for one hour

Samples	A				B			
Temperature °C	220	260	300	395	270	295	345	385
CRF %	7.9	98.4	41.8	44.9	21.4	34.7	65.3	52.4
Residue %	89.3	1.0	17.4	9.3	75.8	48.6	17.2	16.4
TSF %	97.2	99.4	59.2	61.7	97.2	83.3	82.5	61.3

CRF % = Percentage of cold ring fraction (consisting of short chain fragments)

TSF % = Percentage of total solid fraction.

The percentages by weight of residue obtained are slightly higher than those obtained by TG (23% and 22.5%) for laboratory and commercial samples, respectively. It was observed that when higher amounts of polymer were degraded (~ 100 mg) the amount of residue left increased to about 65%.

#### 5.4.1.2 Analysis of Carbon Dioxide

The condensable volatile products formed after degradation of bisphenol A polycarbonate in significant amounts were carbon dioxide and phenol. However, due to the fact that phenol could not be satisfactorily separated from water and other minor products by SATVA, it was impossible in practice to measure the amount of phenol evolved. For this reason only the quantitative analysis for carbon dioxide is given.

The experimental results show that the average quantity of carbon dioxide moles obtained per 100 repeat structural units of original polymer (laboratory and commercial samples) degraded determined by SATVA are 39.1 and 38.3 moles, respectively.

#### 5.4.2 Isothermal Degradations for Bisphenol A Polycarbonate (Laboratory and Commercial Samples)

##### 5.4.2.1 Analysis of Solid Products

Isothermal degradation at various temperatures for both samples were carried out.

The experimental results obtained are presented in Table 5.9

From the examination of the results, it is observed that the CRF production rises on increase of temperature. At higher temperatures

some secondary reactions occur to some extent during the degradation process which involves the formation of various volatile products.

At temperatures up to 300°C degradation is very slow.

TABLE 5.9

Percentages by weight of cold ring fraction and residue obtained after heating bisphenol A polycarbonate (laboratory and commercial samples) at various temperatures for one hour

Samples	Laboratory						Commercial					
Temperature °C	300	325	360	370	380	390	300	325	360	407	434	455
CRF %	2.1	6.0	10.0	13.2	15.1	15.9	3.2	5.4	9.6	9.0	12.9	14.7
Residue %	94.5	89.8	85.0	80.5	77.7	76.6	94.9	92.4	88.5	86.2	82.9	79.6
TSF %	96.6	95.8	95.0	93.7	92.8	92.5	98.1	97.8	98.1	96.2	95.8	94.3



## CHAPTER SIX

### GENERAL CONCLUSIONS

Several distinct processes may be discerned in the thermal decomposition of the three classes of polycarbonates analysed in this study.

- (a) Aliphatic polycarbonates depolymerise by an intramolecular exchange, starting at the end groups between the acyl link of one carbonate group with the carbon of the carbonyl group of a neighbouring carbonate group with the formation of the cyclic monomer.

The polymerisation-depolymerisation equilibrium is affected by stereochemical factors, i.e., position and bulkiness of substituents.

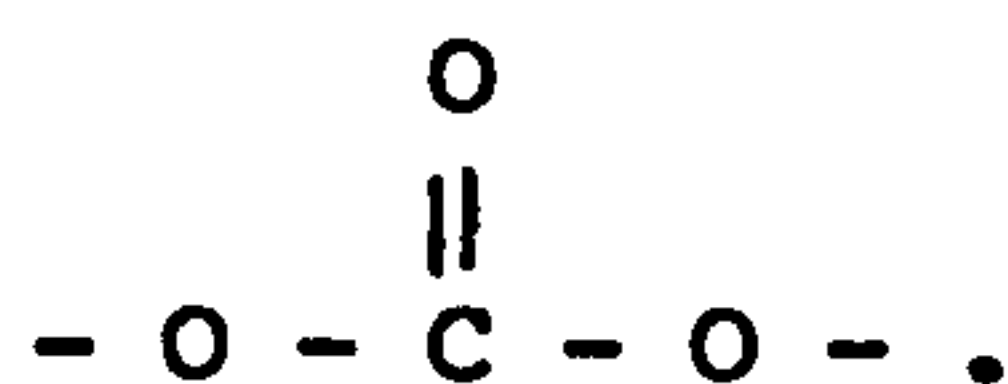
Random scission in competition with depolymerisation at the higher degradation temperatures results in the formation of short chain fragments and carbon dioxide.

- (b) Aliphatic-aromatic polycarbonates have comparable thermal stability to the aliphatic polycarbonates, stable to  $\sim 200^{\circ}\text{C}$ . A polymer polymerised at higher temperature was found to be more stable; this may be due to the presence of p-xylylene ether structures in the polymer. A complete analysis of the products of degradation of poly(p-xylylene carbonate) sample B provided evidence in support of a two stage decomposition reaction. The lower temperature stage was found to proceed by a random chain scission at the

carbonate groups. The higher temperature process was shown to produce carbon dioxide and p-tolualdehyde. A possible mechanism via a thermal elimination for this process has been postulated.

- (c) Aromatic polycarbonates were shown to have higher thermal stability. A complete degradation product analysis for bisphenol A polycarbonate provided evidence in support of a two-stage decomposition reaction. The lower temperature process corresponds to a main chain scission reaction due to hydrolysis or phenolysis at the carbonate group. Branching reactions occur due to the thermal rearrangement of the carbonate group and eventual gelation occurs due to the removal of the volatile products formed during degradation. These results are consistent with the mechanism of thermal degradation of bisphenol A polycarbonate, first postulated by Davis and Golden.

The study confirms the view that in the three different classes of polycarbonates, the most reactive group towards thermal degradation in the macromolecule is the carbonate group,



### SUGGESTIONS FOR FURTHER WORK

The work outlined in this thesis could be extended in three main areas:

- (1) The analytical procedure which was applied to the homopolymer could be applied to the study of blends of bisphenol A polycarbonate:PMMA to determine whether its thermal breakdown is affected by the presence of free radicals formed in the thermal degradation of PMMA.
- (2) TVA could be applied to study the thermal breakdown to poly(ester carbonate) copolymers based on bisphenol A, terephthalic acid and phosgene.
- (3) TVA could be applied to study the thermal degradation of bisphenol A polycarbonate previously heated in an oxygen atmosphere. The products of degradation could be collected for analysis. The volatile products formed could be fractionated by SATVA and analysed to obtain a complete picture of the mechanism operative in its thermal breakdown.

## APPENDIX A

ACTIVATION ENERGY FOR BISPHENOL A POLYCARBONATE DEGRADATION

In order to obtain an energy of activation which could be compared with those values quoted by Davis and Golden<sup>11</sup> for a similar polycarbonate, isothermal TG curves for bisphenol A polycarbonate laboratory and commercial samples were obtained at 360°, 370°, 380° and 390°C, respectively, in a N<sub>2</sub> atmosphere. Using these curves, plots of percentage of volatilisation ( $W_L/W_O$  %) versus time were made and are shown in figs. A.1 and A.2, where  $W_L$  is the weight of polymer lost after time L and  $W_O$  is the original weight of the polymer. Initially all the curves are linear then deviate from linearity after about 50% volatilisation. The Wilhelmy equation<sup>65</sup> was applied to the isothermal curves and expressed graphically in the form of  $W_t/W_O$  versus time, see figs. A.3-A.9 where  $W_O$  and  $W_t$  are the linear regions of the TG curves. The rates of degradation determined for each temperature are shown in table 1.

The Arrhenius plots of  $\log K$  versus  $1/T \cdot K$  are shown in figs. A.11-A.12. Activation energies of  $27.7 \pm 4$  kcal/mol (laboratory sample) and  $25.5 \pm 0.5$  kcal/mol (commercial sample), respectively, were calculated from the slopes of these plots.

Activation energies previously reported are collected in table 2. From thermogravimetric measurements Lee<sup>22</sup> obtained an activation energy of 33 kcal/mol. The degradation rate was determined



as the time to 7% weight loss. By measuring the rate of gas evolution, Kovarskaya<sup>24</sup> determined an activation energy of 36.5 kcal/mol.

Davis and Golden<sup>11</sup> based their calculation on the rate of total gas evolution in the interval 300°C to 389°C. They obtained an activation energy of 28 kcal/mol, which is closer to our result. An activation energy for the degradation process by thermogravimetry in a N<sub>2</sub> atmosphere has not previously been reported.



TABLE 1

Rates of thermal degradation ( $\text{sec}^{-1}$ )

Temp/sample	laboratory	commercial
360°C	$7.5 \times 10^{-3}$	$2.8 \times 10^{-3}$
370°C	$8.4 \times 10^{-3}$	$3.1 \times 10^{-3}$
380°C	$1.4 \times 10^{-2}$	$2.7 \times 10^{-3}$
390°C	$2.0 \times 10^{-2}$	$3.8 \times 10^{-3}$

TABLE 2

Activation energies for the thermal degradation  
of bisphenol A polycarbonate

Method of detection	Atmosphere	Temperature range (°C)	$\Delta E$ kcal/mol	Ref number
CO <sub>2</sub> evolution	sealed vacuum	-	21	24
Thermogravimetry	sealed vacuum	-	25	24
Viscometry	sealed vacuum	360-420	23.8	24
Viscometry	sealed vacuum	305-400	31.5	24
Thermogravimetry	air	465-515	33	22
Gas evolution	varying concentration of oxygen	260-300-	36.5	24
Gas evolution	continuous vacuum	300-389	28	11
Gel permeation chromatography	air (close rheometer)	300-330	26.7	24
Thermogravimetry	N <sub>2</sub>	360-390	27.2±4 25.5±0.5	This work

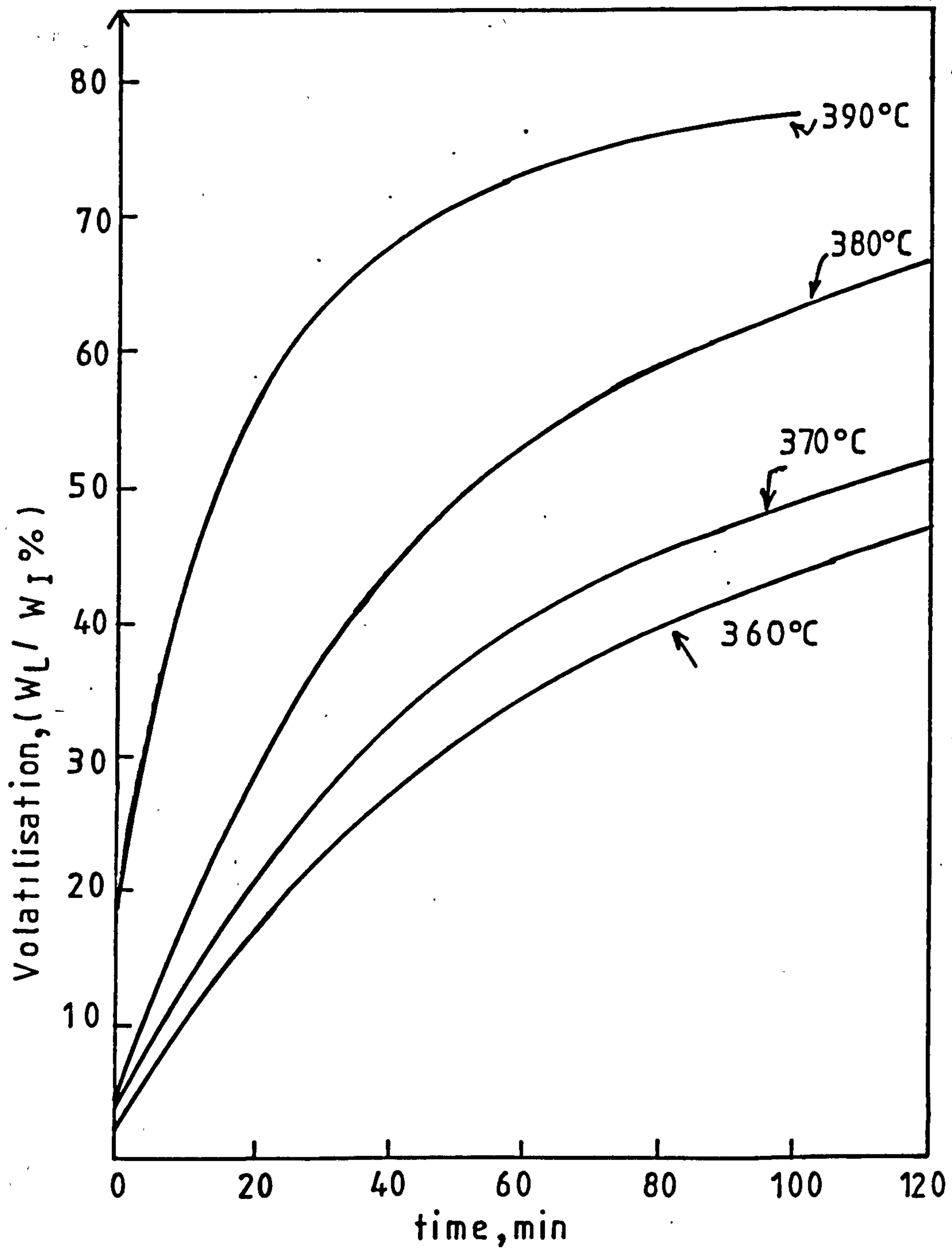


Fig. A.1. Percentages of volatilisation vs time for bisphenol A polycarbonate (laboratory sample) at various temperatures.

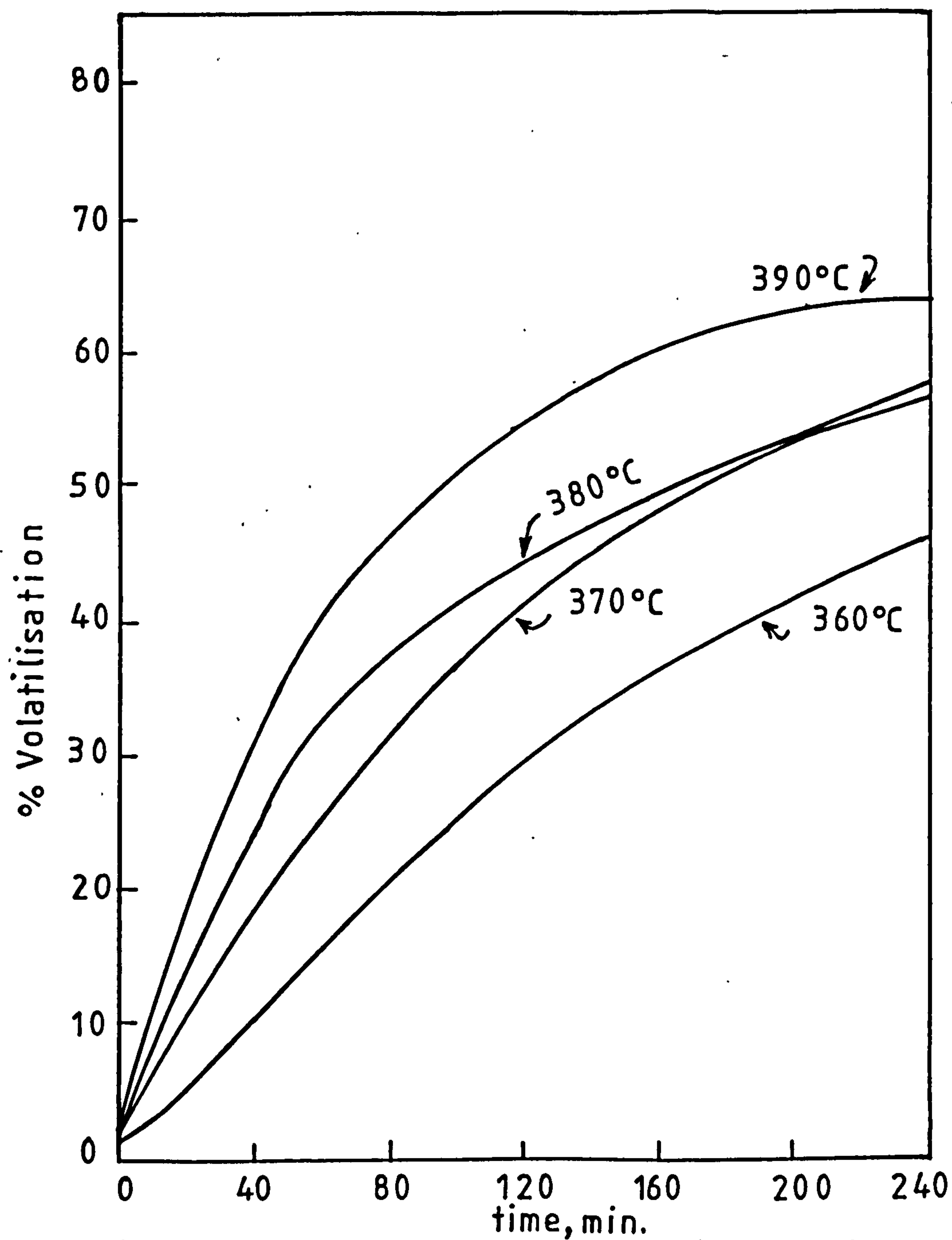


Fig. A.2 Percentages of volatilisation vs time for bisphenol A polycarbonate (commercial sample) at various temperatures.

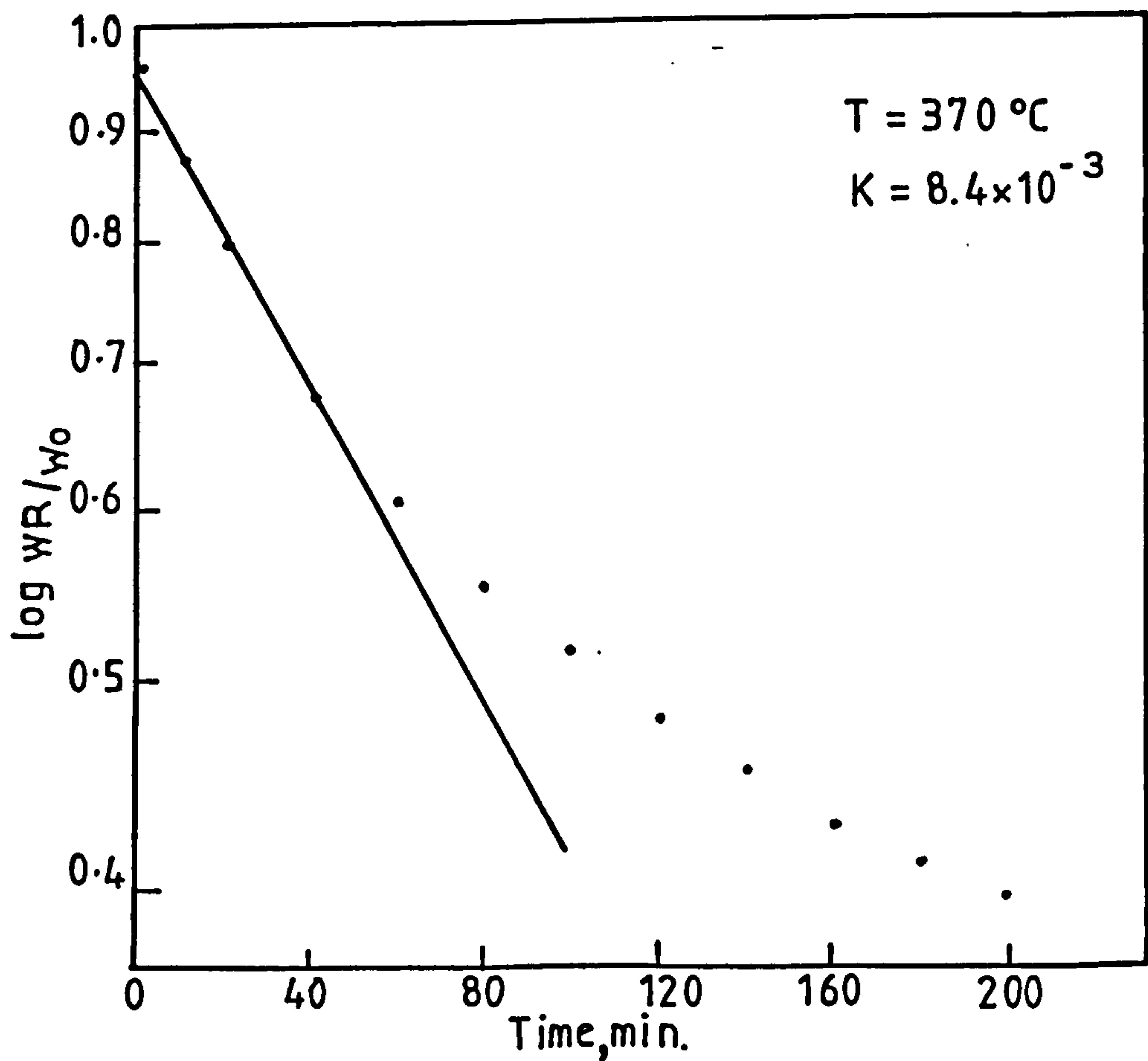
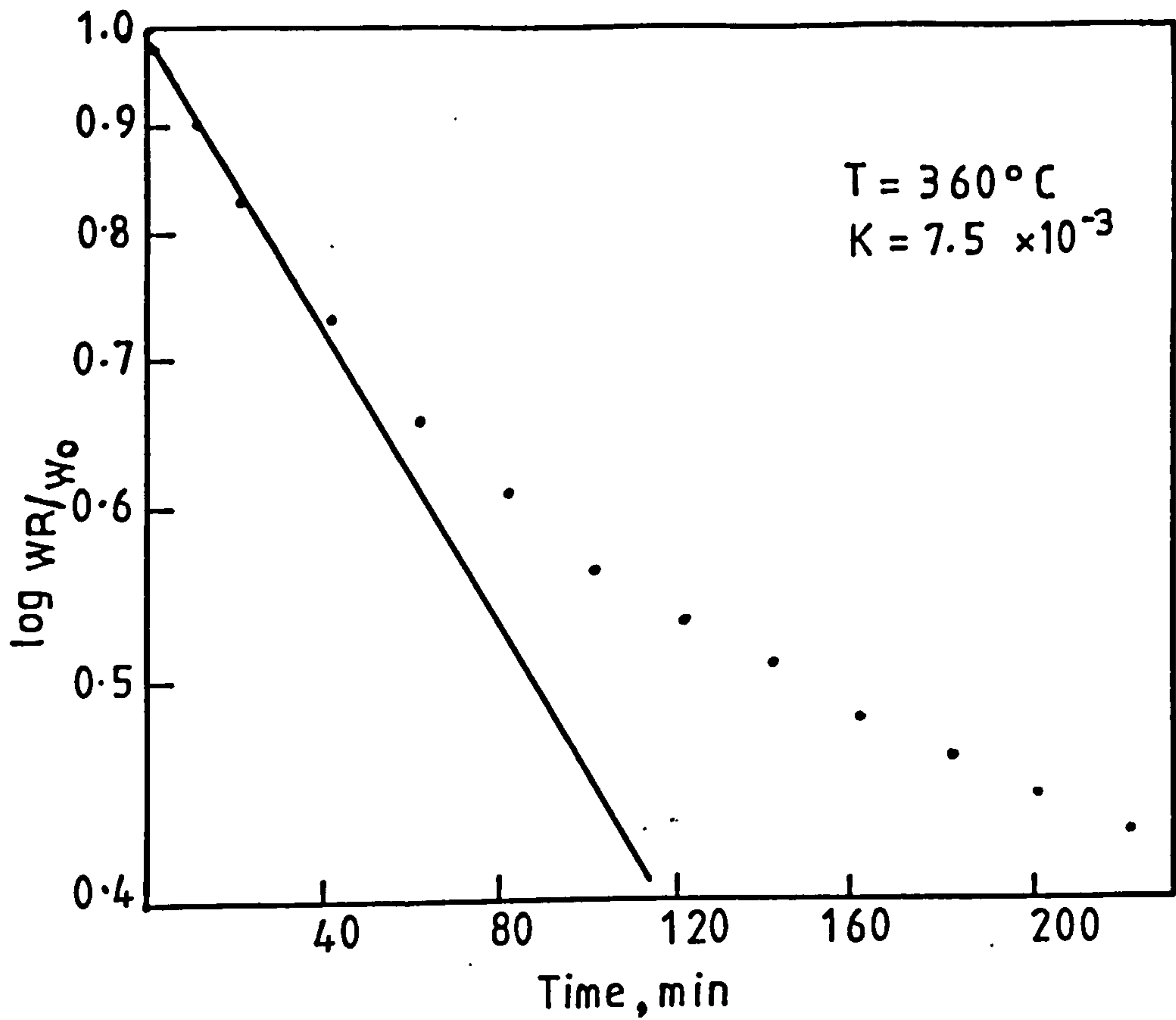


Fig. A3-A4  $\log WR/w_0$  vs time for bisphenol A polycarbonate (laboratory sample)



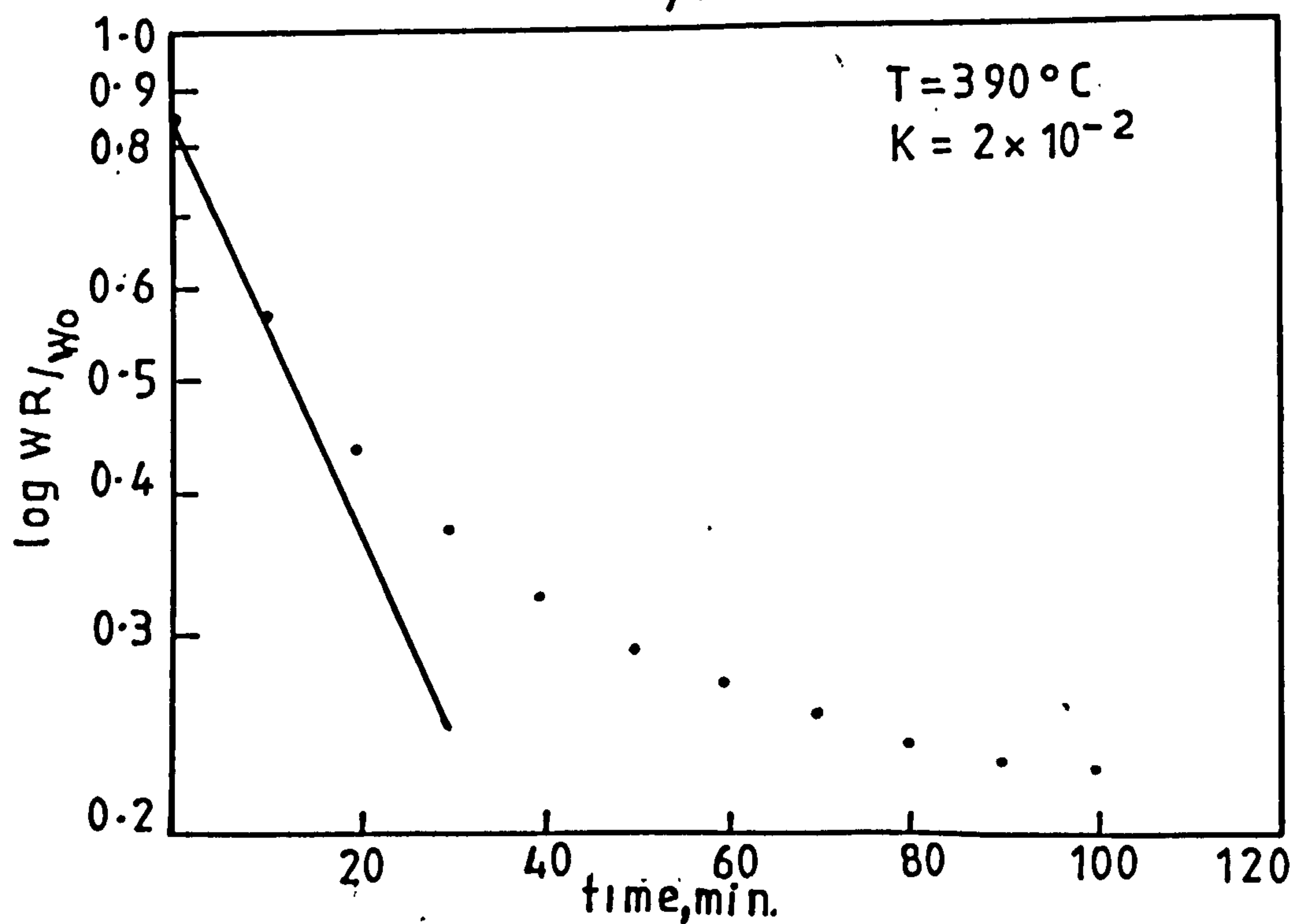
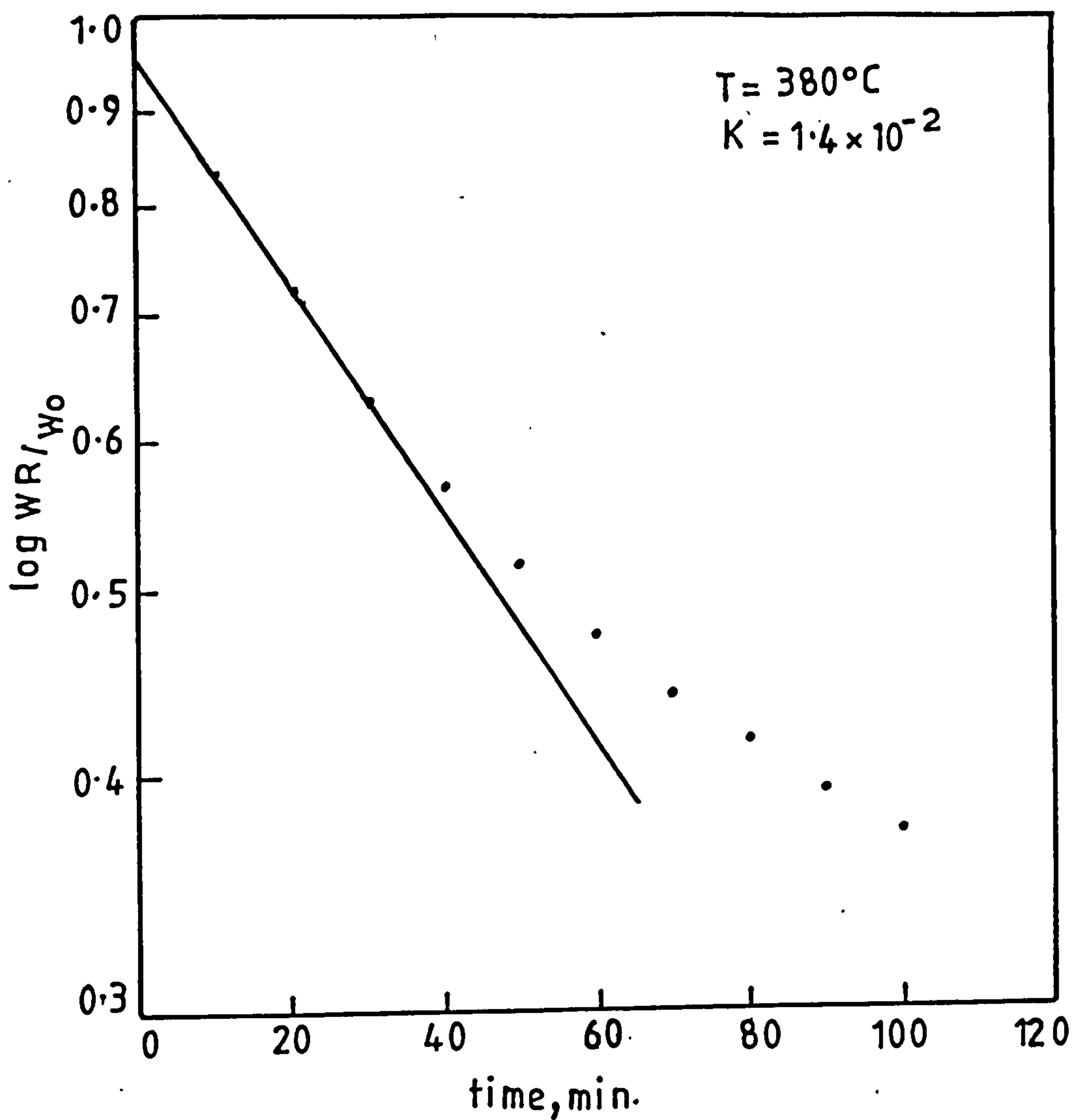


Fig. A5-A6.  $\log WR/w_0$  vs time for bisphenol A polycarbonate (laboratory sample)

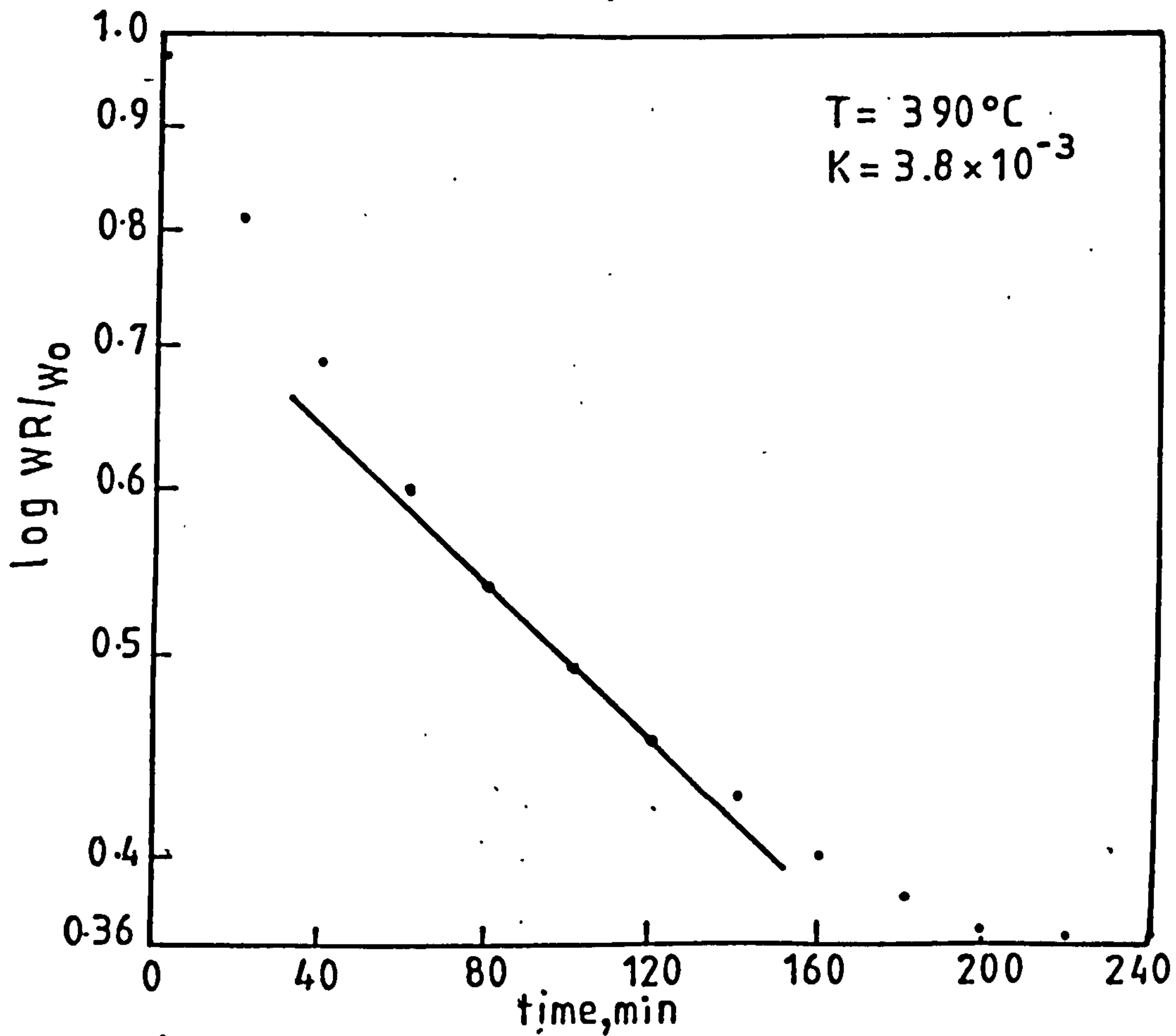
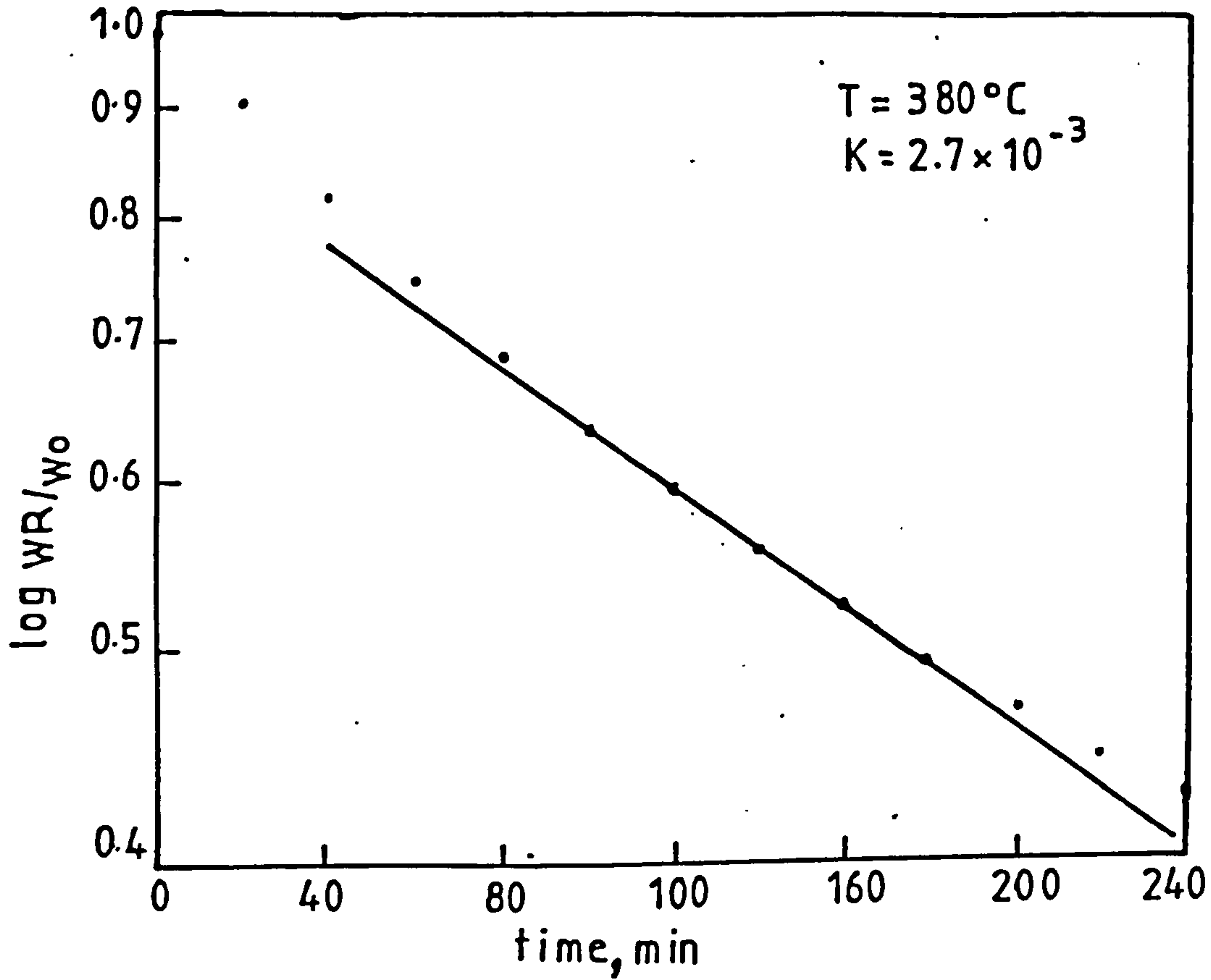


Fig. A7 - A8  $\log WR/w_0$  vs time for bisphenol A polycarbonate (commercial sample)

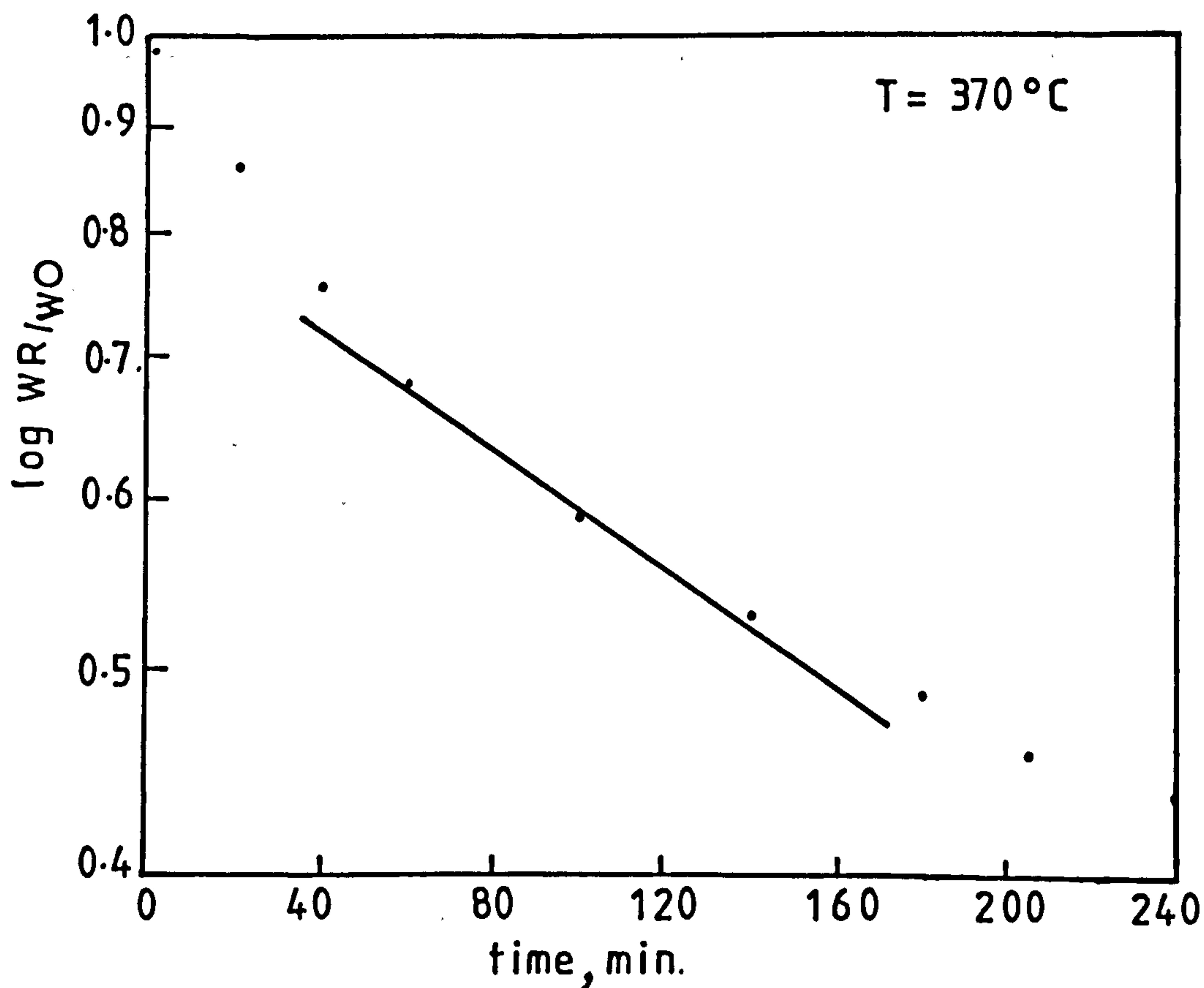
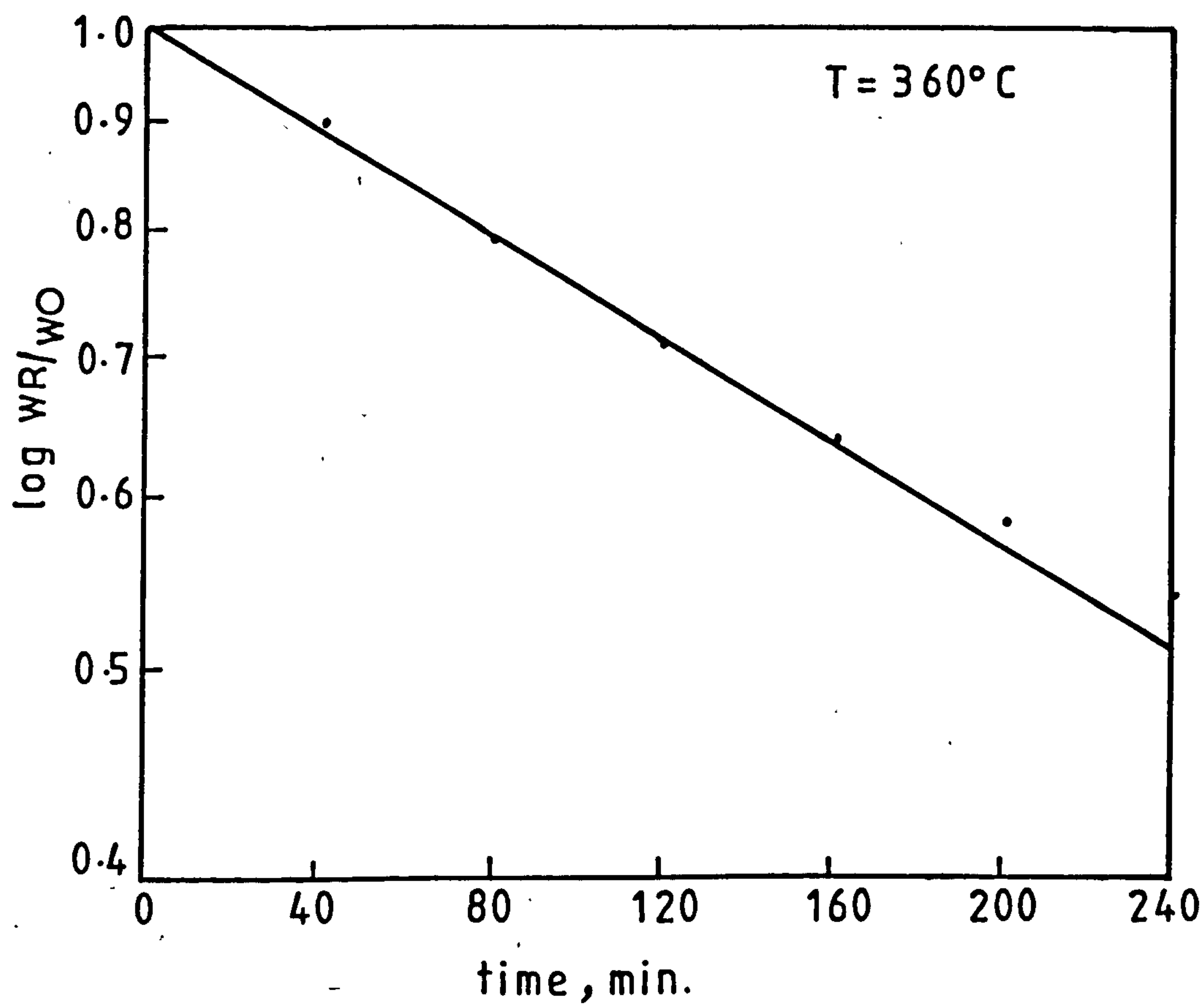


Fig. A7 and A8  $\log WR/wo$  vs time for  
Bisphenol A polycarbonate

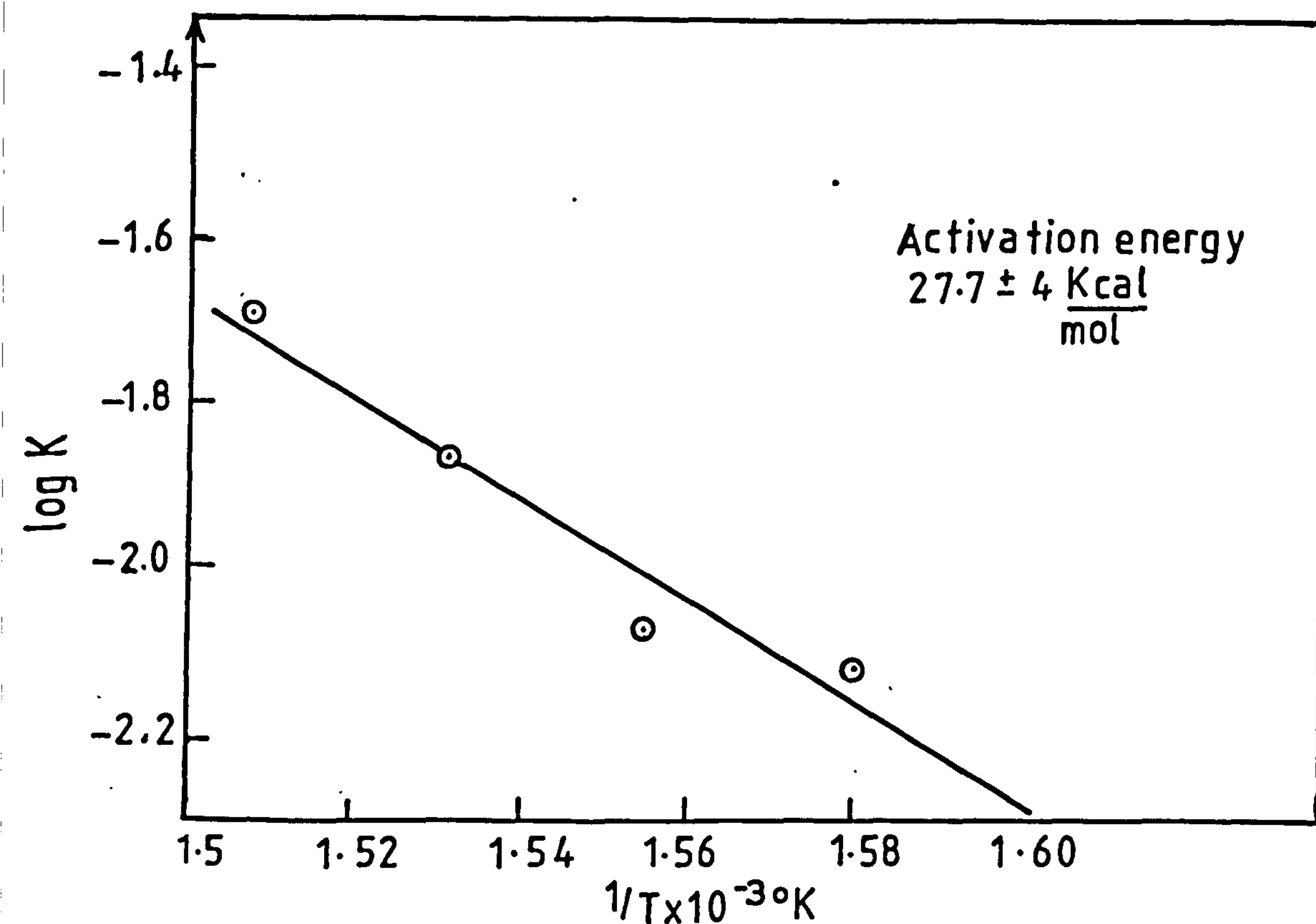


Fig. A.9 Activation energy for bisphenol A polycarbonate (laboratory sample)

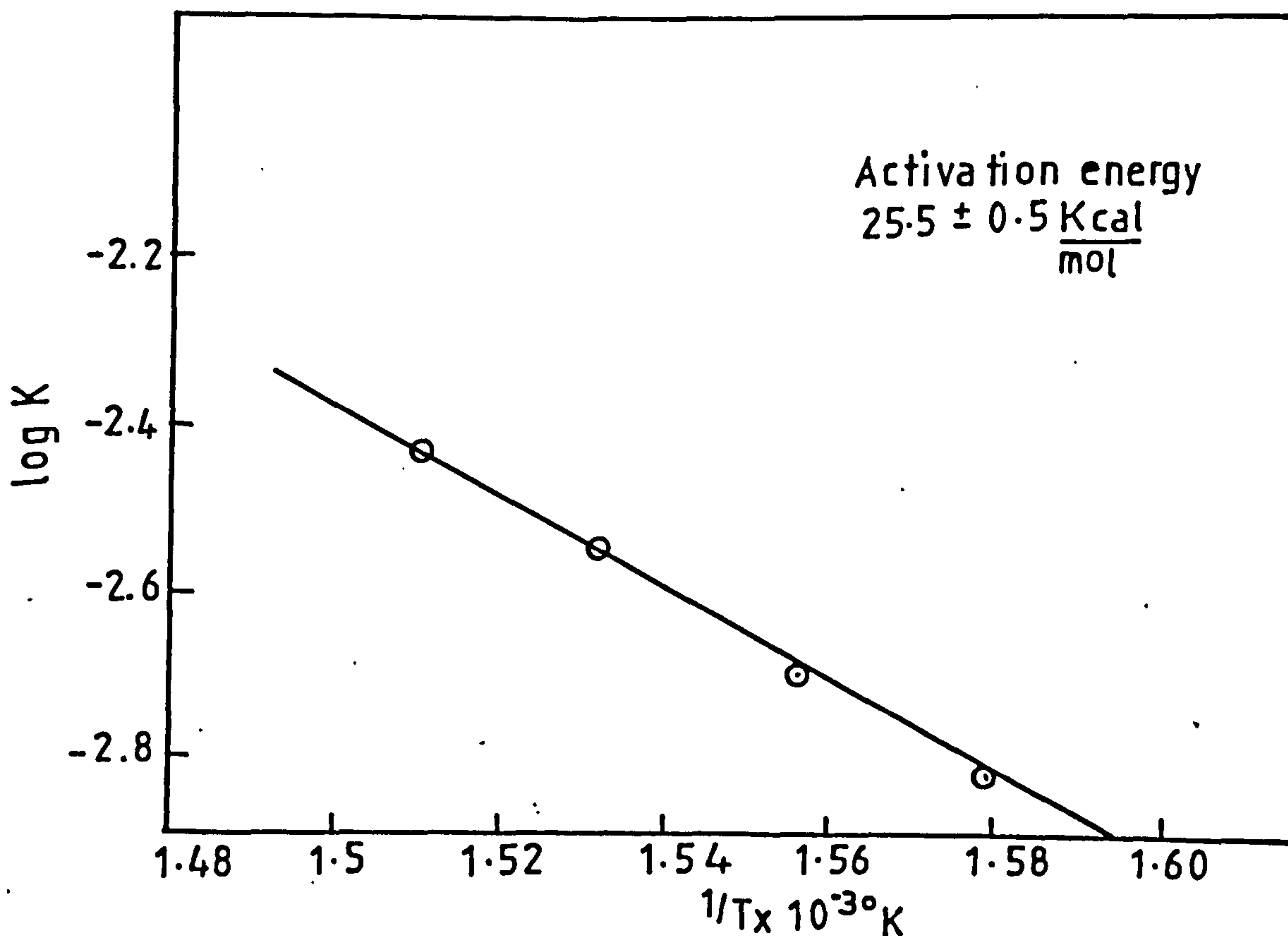


Fig. A.10 Activation energy for bisphenol A polycarbonate (commercial sample)

## REFERENCES

1. H. Staundinger, Ber., 53, 1073 (1920).
2. H.F. Mark and G.S. Whitby, The Collected Papers of Wallace Hume Carothers. Interscience Publishers INC. (1965).
3. H.H.G. Jellinek (Ed.). Degradation of Vinyl Polymers. Academic Press, New York (1955).
4. N. Grassie, Chemistry of High Polymer Degradation Processes. Interscience, New York (1956).
5. S.L. Madorsky, Thermal Degradation of Organic Polymers, Interscience, New York (1964).
6. K. Tibor, Polymer Degradation, Van Nostrand Reinhold Company INC., New York (1983).
7. G. Scott, Developments in Polymer Stabilisation, Applied Science Publishers, London; 6, 295 (1983).
8. N. Grassie, Chemical Reactions of Polymers, (E.M. Fettes, Ed.). Interscience, New York (1964).
9. W.H. Carothers and F.J. Van Natta, J. Am. Chem. Soc., 52, 314 (1930); J.H. Hill and W.H. Carothers, J. Am. Chem. Soc., 55, 5031 (1933).
10. B.H. Hall, Jr., A.K. Schneider, J. Am. Chem. Soc., 80, 6409-6412 (1958).
11. H. Sarel and L. Pohoryles, J. Am. Chem. Soc., 80, 4596 (1958).
12. L.A. Pohoryles and S. Sarel, Compt. Rend., 245, 2321 (1957).
13. S. Sarel, I. Levin and L. Pohoryles, J. Org. Chem., 3079 (1960).
14. H. Schnell, 'Chemistry and Physics of Polycarbonates'. Wiley Interscience, New York, 27 (1964).



15. C.D. Hurd, The Pyrolysis of Carbon Compounds. Chemical Catalogue Co., New York (1929).
16. B.M. Kovarskaya, Soviet Plastics, 10, 12 (1962).
17. A. Davis and J.H. Golden, Makromol. Chem., 78, 16 (1964).
18. A. Davis and J.H. Golden, Nature, 206, 397 (1965).
19. A. Davis and J.H. Golden, J. Makromol. Sci. - Revs. Makromol. Chem., C3 1, 49-68 (1969).
20. A. Davis and J.H. Golden, J. Gas. Chromatog., 1967 (Feb.), 81.
21. A. Davis and J.H. Golden, Makromol. Chem., 110, 180 (1967).
22. L.H. Lee, J. Polym. Sci., 2, 2859 (1964).
23. A. Yakubovich, G.Ya. Gordon, L.I. Maslennikova, E.M. Grobman, K.I. Tret'yakova and N.I. Kokoreva, J. Polym. Sci., 55, 251 (1961).
24. K. Abbås, Polym., 21, 936 (1980).
25. H.F. Mark and N. Bikales, Encyclopedia of Polymer Science and Technology, 5, 11. John Wiley and Sons, Inc. (1969).
26. E.S. Sherman, A. Ram, and S. Kenig, Polym. Eng. Sci., 22(8), 457 (1982).
27. I.C. McNeill, Developments in Polymer Degradation. (Grassie N. Ed.), 1, Applied Science Publishers, London, 43 (1977).
28. I.C. McNeill and D. Neill, Thermal Analysis; Schwenker R.F. and Garn P.D. (Eds.). Academic Press, London, 1, 353 (1969).
29. I.C. McNeill, Thermal Analysis; Schwenker R.F. and Garn P.D. (Eds.). Academic Press, London, 1, 417 (1969).
30. I.C. McNeill, J. Polym. Sci., A4, 2479 (1966).
31. I.C. McNeill, Europ. Polym. J., 1, 3, 409 (1967).

32. I.C. McNeill, *Europ. Polym. J.* 1, 6, 373 (1970).
33. I.C. McNeill and A. Jamieson, *Europ. Polym. J.*, 10, 217 (1974).
34. I.C. McNeill, T. Straiton and P. Anderson, *J. Polym. Sci., Polym. Chem. Ed.* 18, 2085 (1980).
35. L. Ackerman and W.J. McGill, *J. South Afr. Chem. Inst.*, 26, (3), 82 (1973).
36. I.C. McNeill, L. Ackerman, S.N. Gupta, M. Zulfiqar and S. Zulfiqar, *J. Polym. Sci. Part A1* (1976).
37. S. Sarel, L.A. Pohoryles, and R. Ben-Shosham, *J. Org. Chem.*, 24, 1873 (1959).
38. H. Krzikalla and K. Merkel (to Badische-Anilin-und Sodafabrik A.G.) *Ger. Pat.* 857, 948 (1952).
39. W.R. Peterson (to E.I. Dupont de Nemours & Co.), *U.S. Pat.* 2,210, 817 (1952).
40. H.F. Piepenbrink in E. Müller, Ed., VIII/III, 245, George-Thieme-Verlag, Stuttgart (1952).
41. D.D. Reinolds and J. Van den Berghe (to Eastman Kodak Co.) *U.S. Pat.* 2, 788,971 (1957).
42. D.D. Reinolds and J. Van den Berghe (to Eastman Kodak Co.) *U.S. Pat.* 2, 789,968 (1957).
43. J.R. Caldwell (to Eastman Kodak Co.), *U.S. Pat.* 2, 799,666 (1957).
44. K. Soga, S. Hosoda and S. Ikeda, *J. Polym. Sci. Chem. Ed.*, 17, 517 (1979).
45. A. Einhorn, *Ann.*, 300, 135 (1898).
46. C.A. Bischoff and V. Hedenstroëm, *Ber.*, 35, 3431 (1902).

47. H. Schnell, *Angew. Chem.*, 68, 633 (1956).
48. T.P. Losev, O.V. Smirnova and Y.V. Smurova, *J. Polym. Sci. U.S.S.R.*, 55, 663 (1963).
49. Farbenfabriken Bayer, A.G. *Neth. App.* 6, 602, 868 (1967).
50. F. Hostettler, and E.F. Cox, *U.S. Pat.* 3, 305, 605 (1967).
51. R. Poisson, G. Sturtz, *Polym. Bull.*, 1, 12, 883 (1979).
52. *Ibid*, 897 (1979).
53. M.R. MacLavey *et al.*, *J. Polym. Sci., Polym. Chem. Ed.*, 18, 2501 (1980).
54. O.V. Smirnova, D.F. Kutepov, V.P. Bolmosova, A.A. Atruschkevich, *tr-Mosk-Khim-technol-Inst. im. D.I. Mendecleva*, 110, 50 (1980).
55. W.F. Christopher and D.W. Fox 'Polycarbonates', Reinhold (Ed.), New York (1962).
56. H. Adkins *et al.*, *J. Am. Chem. Soc.*, 70, 3121 (1948).
57. S. Searles *et al.*, *J. Am. Chem. Soc.*, 24, 1839 (1959).
58. P.A. Marshall *et al.*, *Aust. J. Chem.*, 30, 141 (1977).
59. Hiromichi Ohta *et al.*, *J. Org. Chem.*, 47, 2400 (1982).
60. J. Katzhendler, L.A. Poles and S. Sarel, *J. Chem. Soc. B*, 1847 (1971).
61. J.M.G. Cowie, *Polymer Chemistry and Physics of Modern Materials*. K. Stead (Ed.), Intertext Books, Chapter 2 (1973).
62. J.V. Braun, *Ann.*, 472, 1 (1929).
63. F.W. Billmeyer, *Textbook of Polymer Science*, 2nd Ed., Wiley, Interscience, New York (1973).
64. P. Brown and C. Djerassi, *J. Am. Chem. Soc.*, 88(11), 2469 (1966).