IN THE NAME OF GOD
THE MOST GRACIOUS, THE MOST MERCIFUL

# STUDIES OF THE THERMAL STABILITY AND DEGRADATION MECHANISMS OF ACRYLIC ACID POLYMERS AND IONOMERS

by:

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Dedicated to:

My father

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## *SUMMARY*

This research is concerned with the preparation, characterisation and thermal degradation of acrylic acid based polymers and copolymers.

The alkali (Na and K), alkaline earth (Mg and Ca) and some transition metal salts (Zn and Co) of acrylic acid monomer and polymers together with the copolymers of styrene-acrylic acid and their sodium and potassium salts were prepared, characterised and their thermal behaviour were also studied under programmed and isothermal heating experiments using TVA,TG and DTA techniques. Degradation products were identified by spectroscopy, mass spectrometry, GC and GC-MS techniques.

A brief discussion about ionic polymers including ionomers and polyelectrolytes is presented in Chapter One. This chapter also reviews briefly the definition and classification of polymer degradation.

Chapter Two presents an introduction to the thermal analysis techniques mostly employed in this work, with emphasis on the thermal volatilisation analysis as a more sophisticated technique. The techniques which were used to identify the degradation products are briefly described.

The preparation, characterisation and polymerisation of monomers, polymers and copolymers are explained in detail in Chapter Three.

The thermal degradation of poly(acrylic acid) samples (lab-prepared and commercial sample) is the subject of Chapter Four. Programmed and isothermal heating experiments were employed to investigate the thermal behaviour of these materials. It is found that the thermal degradation of PAA commences with a dehydration reaction

occurring by intramolecular cyclisation of adjacent monomer units to give six-membered anhydride ring structures. Decarboxylation becomes important under programmed heating conditions at about 250 °C.

Under isothermal heating at 210 °C, it is found that the anhydride concentration builds up rapidly during the first 10 minutes of heating, but reaches a maximum after which there is a slow decline due to decarboxylation.

Above 300 °C, it is observed that the elimination of water and the carboxylation process seem consistent with the occurrence of both intra- and intermolecular reactions. The high production of CRF is mainly due to the decomposition of the polymer residue at high temperatures.

In Chapter Five, the thermal decomposition of alkali metal salts (Na and K) of PAA which were prepared by polymerisation and neutralisation routes, is described. Evidence is provided in this chapter which indicates that the monomer salts polymerise prior to decomposition and the thermal stability of these salts including monomers and polymers, is higher than that of PAA. These materials are stable to about 400 °C under programmed heating in vacuo.

A mechanism involving random homolysis scission of the chain followed by splitting out of side groups and intra- and intermolecular transfer reactions and metal carbonate and oxide formation has been proposed for these polymers.

In Chapter Six and Seven, the work deals with the thermal degradation of the alkaline earth metal (Mg and Ca) and transition metal (Zn and Co) salt monomers and polymers of acrylic acid. The nature of the degradation products and structural changes which occur during decomposition suggest a similar pattern of degradation for these materials. The degradation data show that the thermal stability of the alkaline earth metal salts (Mg and Ca) is higher than those of zinc and cobalt salts and that thermal stability decreases in the sequence: Ca > Mg > Zn > Co.

The thermal behaviour of these polymers is also similar to that of the monovalent metal salts of PAA, but appreciable differences exist in the relative amounts of volatile products, in which the divalent metal salts produce higher yields of liquid fraction and less cold ring fraction. The mechanism of decomposition seems consistent with that of the alkali metal salts

The thermal degradation and stability of two styrene-acrylic acid copolymer samples is considered in Chapter Eight. It is found that the thermal behaviour of these copolymers can be related to that of polystyrene and PAA. It is concluded that the mechanism of decomposition below and above 300 $^{o}$C, depends upon the composition of copolymer. The presence of acrylic acid units in the structure of copolymer causes a reduction in $T_{max}$ for the main decomposition which is lower than that of polystyrene and poly(acrylic acid). Dehydration, decarboxylation and intermolecular hydrogen transfer (fall in molecular weight) can be considered as the main processes occurring at temperature below 300 $^{o}$C.

At temperatures higher than 300 $^{o}$C, further chain scissions followed by intra- and intermolecular hydrogen transfer become predominant. Formation of the intermediate species at high temperatures followed by their decomposition to produce various products, such as hydrocarbons, carbonyl containing compounds, etc., can also be proposed.

In Chapter Nine, the thermal behaviour of the sodium and potassium salts of the styrene-acrylic acid copolymers is discussed. It is found that the thermal stability of these ionomers is dependent to the amount of sodium and potassium salts introduced and the degree of neutralisation. The major peak of decomposition ($T_{max}$) of the ionomers lies between those of polystyrene and the respective polyacrylate. The presence of the salt units in the copolymer chain markedly stabilises the ionomer relative to polystyrene and the styrene-acrylic acid copolymer.

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# CHAPTER ONE

## INTRODUCTION

### *1. HISTORY OF POLYMER SCIENCE*

*Natural polymers* have been utilized throughout the ages since in the beginning man has been dependent on *animal* and *vegetable* matter for his necessities. Natural resins and gums have been used for thousands of years.

The early history of polymers is really the conversion of natural polymers into useful materials. Examples include the vulcanization of rubber (Goodyear, 1839), Celuloid (Hyatt,1868), and viscose rayon (Cross, Bevan and Beadle,1892).

The first synthetic polymer, that is, one made from laboratory chemicals, was Bakelite (Baekeland,1907). This was made from phenol and formaldehyde.

The true nature of macromolecules was only became understood in the *1920s*, largely because of the efforts of *Staudinger*.[1] Before that time the prevailing tendency had been to formulate polymeric substances as association compounds held together by partial valences. Staudinger proposed the chain formulas for polystyrene, polyoxymethylene and rubber which he guessed might contain of the order of a hundred units. The science of high polymers arose in the 1930s and the major growth of the technology of these materials started even later.[2]

In 1929 *Carothers*[3,4] embarked on a series of investigations the object of which was to prepare polymeric molecules of definitive structures through the use of established reactions of organic chemistry, and further to investigate how the properties of these substances depend on constitution.

The science of macromolecules is divided between *biological* and *nonbiological* materials. Each is of great importance. The polymers which are used for plastics, elastomers (or rubbers), fibres and films are nonbiological synthetic polymers.

Indeed many of the organic chemicals manufactured, including monomers, are used to make polymers. The polymer industry consumes great quantities of organic materials for *solvents, stabilizers, antioxidants, plasticizers etc.*[5]

## 2. *IONIC POLYMERS*

Ionic polymers contain ions which are chemically bound within their structure . The term is not meant to apply to polymers that have been made by ionic methods, nor to those that, fortuitously, have ionic end-groups.[6] Ionic polymers-either organic or inorganic- represent a broad classification of polymers with inorganic salt groups attached to the polymer chain. Systematic work on these materials started with the work of *Brown*[7] and *Nielsen*[8] on rubbers and polyacrylates, respectively.

Water-soluble polymers containing many salt groups (ions), e.g., where every monomer repeat unit contains a pendant salt group, are called polyelectrolytes.[9] Those containing few ions are thermoplastics called ionomers.[10-15]

The ionic interactions and resultant polymer properties are dependent on the type of polymer backbone, ionic functionality (ionic content), type of ionic moiety (carboxylate, sulfonate, etc), degree of neutralisation, and type of counter ions (amine, metal, monovalent or multivalent).[9]

Synthetic ionic polymers are mostly relatively modern materials. The range of polymeric materials within the field of ionic polymers is extremely varied, extending from naturally occurring biopolymers through to ceramics and inorganic glasses.[16]

## *2.1. Ionomers*

The term of *ionomer* is usually used to describe ionic polymers which are constructed from a hydrocarbon backbone containing some pendant carboxylic acid groups which are neutralised either partially or completely to form salts.

Ionomers are generally prepared from copolymers having either acrylic or methacrylic acid as one component.13 The other component is mostly either *ethylene*[17-24] or *styrene*.[8,25,26] The concentration of the salt groups may vary but the hydrocarbon backbone is always the majority component.

As already mentioned, these materials containing salt groups have seen expansive growth in recent years. This is evident from the scientific interest manifested in the technical literature and by the appearance of several monographs devoted to the subject.[10,12,13,15,27-30]

Acrylic acid-styrene and acrylic acid salts-styrene copolymers are typical *synthetic ionomers*,the thermal behaviour of which will be discussed during this work.

## *2.2. Polyelectrolytes*

A polyelectrolyte is defined as any polymeric substance in which the monomeric units of its constituent macromolecules possess *ionisable groups.* A polyelectrolyte is always formed of a macroion in which the charged groups are related by chemical bonds, together with an equivalent number of small oppositely charged counterions which is not consistent with a simple electrolyte such as NaCl, in which the size of the oppositely charged ions are similar in magnitude.[31] When polyelectrolytes dissolve in a suitable polar solvent (generally water), spontaneously produce or can be made to produce a large number of elementary charges located along the polymer chain, these macromolecules are termed strong polyelectrolytes by analogy with low molecular weight electrolyte when the charge that appears spontaneously contains its maximum value and, in other cases, weak polyelectrolytes.

Polyelectrolytes are usually soluble in aqueous solutions due to their electrostatic nature. These materials can be classified in different ways. A polyelectrolyte may be classified electrochemically as either a polyacid, a polybase, or a polyampholyte, depending on the nature of its ionisation in aqueous solution. Polyampholytes are macromolecules having both acidic and basic groups and that are negatively charged at high pH and positively at low pH. These are neutral at isoelectric pH, where the amounts of positive and negative charges are equal. Proteins and nucleic acids, by far the most fundamentally important of the naturally occurring polyelectrolytes, are polyampholytes. The copolymer of acrylic acid and vinyl pyridine is an example of a *synthetic polyampholyte.*

Polyelectrolytes can also be classified as *linear, branched,* and *crosslinked* chains or *homo-* and *copolymers.*

It may be expected, and experiments confirm, that polyelectrolytes exhibit properties related to their macromolecular as well as to their electrolytic nature.

Qualitatively, solutions of polyelectrolytes do indeed display some behavioural similarities to both nonionic polymer solutions on one hand, and to simple electrolyte solutions on the other.

The properties of solutions containing macroions are extremely sensitive to the presence of added simple electrolytes. The addition of simple electrolytes results in a pronounced contraction of the polyion; in the presence of a large excess of simple electrolyte, the macroion is probably coiled in a manner which resembles the configuration of nonionic polymers in organic solvents.

The comparative electrochemistry of polyelectrolytes and related simple electrolytes such as poly(acrylic acid) and acetic acid indicates that the polyacid is a much weaker acid than a low molecular weight analogue. The experimental data clearly indicate that a polymeric acid binds its protons more firmly than its monomeric analogue.

Solutions containing charged macroions display large deviations from thermodynamic ideality. Even in dilute solutions of strong polyelectrolytes such as sodium poly(ethylene sulfonate), the activity coefficient of sodium ion is only about 0.25. [32]

This *nonideality* is a consequence of the large electrostatic potentials which exist in the vicinity of polyions with multiple charges; counterions become *"trapped"* in these regions of high potential and essentially lose their identity as independent mobile species.

Poly(acrylic acid), first prepared by Staudinger[33] in 1929 in the course of his extensive survey[34] of macromolecular behaviour, is a typical synthetic polyelectrolyte; it is a weak polyacid. Like propionic acid, its low molecular weight analogue, poly(acrylic acid) is soluble in several common organic solvents such as dioxane and dimethylformamide. Ionisation of the carboxylic acid groups does not occur in these solvents; the resulting solutions exhibit physicochemical properties typical of those observed for solutions of neutral polymers in general. In sharp contrast, aqueous solutions containing the polyacrylate anion [obtained by adding strong base to a solution of poly(acrylic acid)] display unique and remarkable properties characteristic of solutions containing charged macroions. The thermal behaviour of this polyacid and some of its *mono-* and *divalent* metal salts is a subject of discussion in the present work.

## *3. POLYMER DEGRADATION* [35-38]

### *3.1. Definition and Classification*

The term *polymer degradation* is used to denote changes in properties caused by chemical reactions in macromolecules. Polymer degradation, according to its various modes of initiation, can be subdivided to *thermal, mechanical, photochemical, radiation chemical, biological* and *chemical degradation.*

### *3.2. Thermal Degradation*

Thermal degradation of polymers is an important subject because it covers a broad field, ranging from the development of *thermoresistant* polymers and ablation problems to the stabilisation of *thermolabile* polymers.

It should be emphasised that scissions of chemical bonds under the influence of heat are the result of overcoming *bond dissociation energies*.The rather high thermal sensitivity of organic substances derives from the fact that molecules are composed of atoms linked together by covalent bonds. The strength of these bonds is limited. Dissociation energies of single bonds in the ground state are usually of order of 150-400 KJ mol$^{-1}$ at 25 oC.[39] The chemical structure of the repeat unit is clearly of importance in determining the thermal stability and mode of decomposition of a polymer.

A detailed understanding of how polymers break down on heating is important in the design of materials with improved properties for particular applications. The threshold temperature for breakdown determines the upper limit of temperature in fabrication and the volatile products of degradation must be known in order to guarantee the safety of workers.[40] Detailed analyses of the products of degradation of polymers are of particular interest because of well justified current concern regarding toxicity, flammability and general safety of structural materials.

There are three general types of primary thermal decomposition process which are observed in the degradation of the various addition polymers namely, *depolymerisation, elimination* and *cyclisation.*

### *3.2.1.Thermal Stability*

In relation to practical applications of polymers, *thermal stability* means the ability of a material to maintain the required mechanical properties such as *strength, toughness,* or *elasticity* at a given temperature. There are two principal factors to be considered, one *physical* and one *chemical.*

The physical requirement of a thermally stable polymer is that it has high *melting* or *softening* temperature.

The chemical factors determining thermal stability are more diverse. First, good heat resistant polymers must have bonds of ***high dissociation energy.*** Another chemical factor influencing heat resistance is the formation of *inter-* or *intramolecular bonds* on heating, resulting in a crosslinked structure.

### *3.2.2. Methods of Studying Polymer Degradation*

A variety of methods has been developed in order to investigate the thermal stability of polymers. The choice of method of the evaluation of polymer degradation depends upon the *objectives,* which may differ.

For some purposes, heating in air may be satisfactory, but for fundamental mechanistic studies, it is customary to reduce the complexity of the problem by use of an *inert atmosphere* or *vacuum.*[40]

*Thermal analysis*[41-47] is usually carried out with the aid of commercially available equipment allowing the investigation of the thermal behaviour of polymers. Probably the most important techniques are *thermogravimetry* (TG), *differential thermal analysis* (DTA), and *differential scanning calorimetry* (DSC).

Other types of experimental approach widely applied to polymer degradation studies, in which the products are normally collected, are *thermal volatilisation analysis* (TVA),[48,49,91,104] and *evolved gas analysis* (EGA).[50] The former is a much more generally applicable approach of this type which is dependent on recording the pressure which develops in a continuously evacuated system when the polymer sample degrades to volatile products. There will be more detailed discussion of these subjects within the text.

## *4 . OBJECTIVE OF THIS RESEARCH*

There is much fundamental interest in the degradation of acrylic polymers. This research probes the thermal stability and mechanism of degradation in vacuo of a number of polymers based on acrylic acid and its salts. The study complements an earlier investigation in this Department of poly(methacrylic acid) and its salts and uses a very similar experimental approach based on several thermoanalytical techniques and detailed examination of degradation products.

The effects of the different backbone structures can therefore be elucidated. The main purpose was to examine the effect of variation of the metal ion on the stability and degradation mechanism.

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# CHAPTER TWO

## EXPERIMENTAL TECHNIQUES OF POLYMER THERMAL DEGRADATION

### *1. THERMAL ANALYSIS*

### *1.1 INTRODUCTION*

Thermal analysis is defined as a group of techniques in which a physical property of a substance is measured as a function of temperature while the substance is subjected to a controlled temperature programme.

This chapter describes the various techniques employed in this research. Particular emphasis is given to TVA which is the most versatile of the techniques described and allows study of all the products of degradation.

When a polymer decomposes, there are different product fractions. The mechanisms of thermal degradation are complex and result in the formation of products with various characteristics. Products may be volatile enough to be non-condensable in a liquid nitrogen trap at -196 $^{O}$C, condensable gases and liquids which are volatile at room temperature but not at -196 $^{O}$C, tars, waxes, etc. which are volatile at degradation temperature but not at room temperature, or involatile residual materials.

The method of study of thermal degradation of a polymer depends upon the objectives of investigation. In the past twenty years the equipment for thermal analysis has been extensively developed, and many instruments are available commercially. Methods of thermal analysis provide the investigation of both physical phenomena (e.g. changes in crystallographic properties, melting, sublimation, adsorption) and chemical phenomena (e.g. dehydration, decomposition, oxidation, reduction) and they have found application in almost all the natural sciences, including chemistry, geology, mineralogy, and metallurgy. The majority of such methods follow changes in some property of the system (mass, energy, dimensions, conductivity, etc.) as a dynamic function of temperature.[46] The most important techniques are TG, DTA and TVA.

## *1. 2. THERMOGRAVIMETRY*

Thermogravimetry, TG, is used widely as a means for determining the thermal stability of polymeric materials and can provide valuable technical information. The conclusions drawn with regard to stability are only relevant within the context of loss-of-weight of the sample. There are reactions which can take place on heating a polymer and which alter drastically the physical properties of the material without an observed change in weight.[51]

In a thermogravimetric analysis, the mass of sample is recorded continuously under isothermal conditions or more commonly as the temperature is increased linearly from ambient to as high as 1500 °C. Commercially available equipment for operation to 1000 °C[52] and to 1500 °C[53] have been described. TG has also been used [54] for gas-solid interaction studies to 1600 °C. TG has been coupled with mass spectrometry in a number of systems.[55-58] Simultaneous DTA-TG equipment for operation to 1550 °C has been coupled to a quadrupole mass spectrometer.[59]

The sample may be heated under a variety of atmospheres or under vacuum. A plot of mass as a function of temperature provides both qualitative and quantitative information including the threshold temperatures and temperatures of maximum rate of weight loss for the processes occurring. The onset of degradation is characterised by the temperature at which pressure changes become detectable.

The thermogravimetric method is a dynamic one, and the system is never at equilibrium. Hence the temperatures of distinctive features on the curves are somewhat different when observed on different instruments, or on the same instrument at different rates of temperature scanning, or with different size samples, etc.

### *1.2.1 Derivative Thermogravimetry*

There is sometimes an advantage in being able to compare a TG curve with its first derivative. There are commercial thermobalances which are provided with electronic circuits to give the derivative automatically. A two-pen recorder permits a convenient direct comparison of the two curves.[47]

The major weakness of thermogravimetry as a tool for studying polymer breakdown is that it provides no information about the degradation products, which in most designs of thermobalance are also not accessible for study by other techniques.[40]

In this work, a DuPont 951 Thermobalance coupled to a DuPont 990 Thermal Analyser was employed. Degradations were performed under a dynamic nitrogen atmosphere of 50 ml per minute, with heating rate at 10 °C/min. Samples were in powder form and were of the order of 3-5 mg.

Derivative thermogravimetry (DTG) is available on the instrument used for this work and a DTG curve can be recorded simultaneously with the TG curve.

### *1.3. DIFFERENTIAL THERMAL ANALYSIS*

Melting, boiling, sublimation, change of crystalline structure, chemical reaction, etc. are transformations characterised by the temperatures at which they occur and by a change in heat content, manifested by an increase or decrease in the temperature, relative to an inert reference materials depending on whether the reaction is *exo-* or *endothermic*[46]. This is the basis of differential thermal analysis (DTA).

*Le Chatelier* was the first who used DTA to study thermal transformation in clays in 1887. Since then it has been widely used in such fields as mineralogy, soil science, metallurgy, fuel technology and the chemistry of inorganic and organic compounds.[50,60]

This technique has been recently applied to the study of a wide variety of problems involving high polymers.[61,62] Transformations can be grouped into three basic types : endothermic, exothermic and the so-called secondary order or glass transition, in which not enthalpy but the specific heat undergoes a sudden change.[63]

The furnace, heating programme and recording devices used for differential methods (DTA and DSC) are similar to those employed in thermogravimetry. Generally, the sample and reference chamber in a differential thermal analysis apparatus is designed to permit the circulation of inert or reactive gases. Some systems also have the capability for operation at high or low pressures.

In a typical apparatus, one set of thermocouple junctions is inserted into an inert material, such as aluminium oxide, which does not change in any manner through the temperature range to be studied. The other set is placed in the sample under test. With constant heating, any transition or thermally induced reaction in the sample will be recorded as a peak or dip in an otherwise straight line.

An endothermic process will cause the thermocouple junction in the sample to lag behind the junction in the inert material, and hence develop a voltage; an exothermic event will cause a voltage of opposite sign.

It is customary to plot *endotherms* downwards and *exotherms* upwards, but this convention is not universally followed.[47]

For this research, DTA analyses were performed on a DuPont 451 Thermal Analyser at a heating rate of 10 °C/min under a nitrogen flow of 80 ml min$^{-1}$.

## *1.4. DIFFERENTIAL SCANNING CALORIMETRY*

Differential scanning calorimetry (DSC) is a technique similar to DTA which involves measuring the varying energy input required to keep an inert reference and the sample at equal temperatures during a programmed heating regime.

For differential scanning calorimetry, individual heaters, located as close as possible to the sample and reference vessels, are provided. When the thermocouples indicate a temperature difference, heat is added to the cooler of the two until temperature equality is restored. The rate of heating required to keep the temperatures equal is recorded as a function of sample temperature. The ordinate of the differential thermogram can then be expressed in units of calories or millicalories per second.[64]

In general, in DSC, the sample and a reference substance are also subjected to a continuously increasing temperature; here, however, heat is added to the sample or to the reference as necessary to maintain the two at identical temperatures. The added heat, which is recorded, compensates for that lost or gained as a consequence of endothermic or exothermic reactions occurring in the sample.

DTA and DSC indicate the temperature regions of occurrence of decomposition processes, but do not distinguish these clearly from physical changes in the sample which also involve absorption or evolution of heat.

It may be said that the most sophisticated equipment available for studying degradation consists of the various instruments for pyrolysis of the polymer. Flash conditions may be used for rapid decomposition at a high temperature, followed by analysis of volatile degradation products by GC-MS and FTIR spectroscopy. This method gives considerable data on the products depending on the choice of temperatures, but there is no direct information about threshold temperatures for breakdown or number of stages, which is easily provided by TG, DTA and DSC. [40]

In the methods considered so far, the products of degradation are not collected. An experimental approach widely applied to polymer degradation studies, in which the products are also collected, is Thermal Volatilisation Analysis (TVA).

### *1.5. THERMAL VOLATILISATION ANALYSIS*

Thermal volatilisation analysis is a versatile thermoanalytical technique developed by *McNeill* and *co-workers*.[48,104,65-67]

A polymer sample, usually in the form of a powder or thin film, is heated in a continuously evacuated system. Gaseous degradation products will cause a small pressure increase as they distil from the sample to a cold trap placed some distance away. This pressure change, measured by a Pirani gauge and recorded as a function of time or temperature, gives a measure of the rate of volatilisation of product.

The system is depicted schematically in *Fig. 2.1.* A modification to the apparatus involves placing a second cold trap, B, at a temperature higher than that of the original trap, A, between the sample and pirani gauge, *Fig. 2.2.* Thus arises the possibility of differential condensation of the degradation products between the two traps. Consequently, this form of TVA is known as differential condensation TVA.

However, the form of the apparatus currently used in this laboratory is that illustrated in *Fig. 2.3*, in which a number of limbs, each with an initial cold trap and a main -196 $^{o}$C trap, are joined in parallel.

The temperature of the initial trap in each limb is different; in this laboratory temperatures of 0$^{o}$,-45$^{o}$, -75$^{o}$, -100 $^{o}$C are used.

Pirani gauges placed after each initial trap monitor the passage of volatile materials through the traps as in the basic differential condensation TVA arrangement; the addition of a Pirani gauge after the -196 $^{o}$C trap allows the detection of any non-condensable products which are lost to the pumps.

Provided care is taken to ensure that path lengths in each limb are equal, equal quantities of volatile degradation products will pass through each limb. Assuming the Pirani gauges to be matched, any difference in output from the gauges can be ascribed to differential condensation of the products.

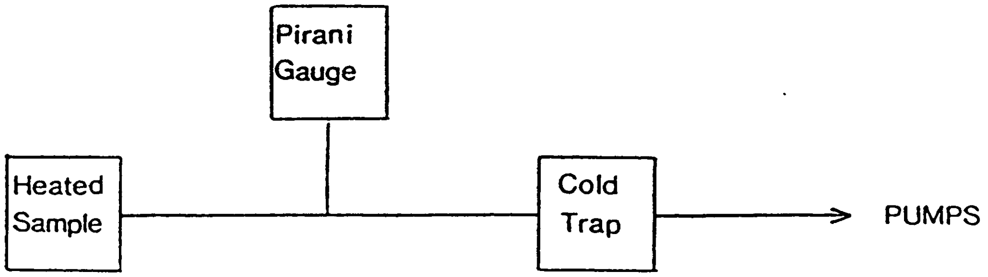


Fig. 2.1. Schematic representation of Basic TVA System.

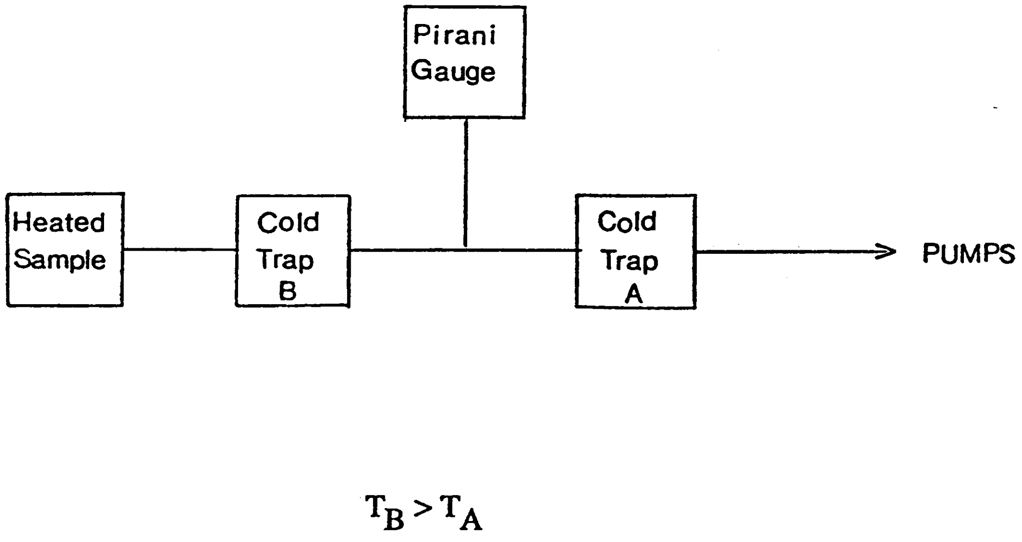


Fig. 2.2. Schematic representation of Differential Condensation TVA System.

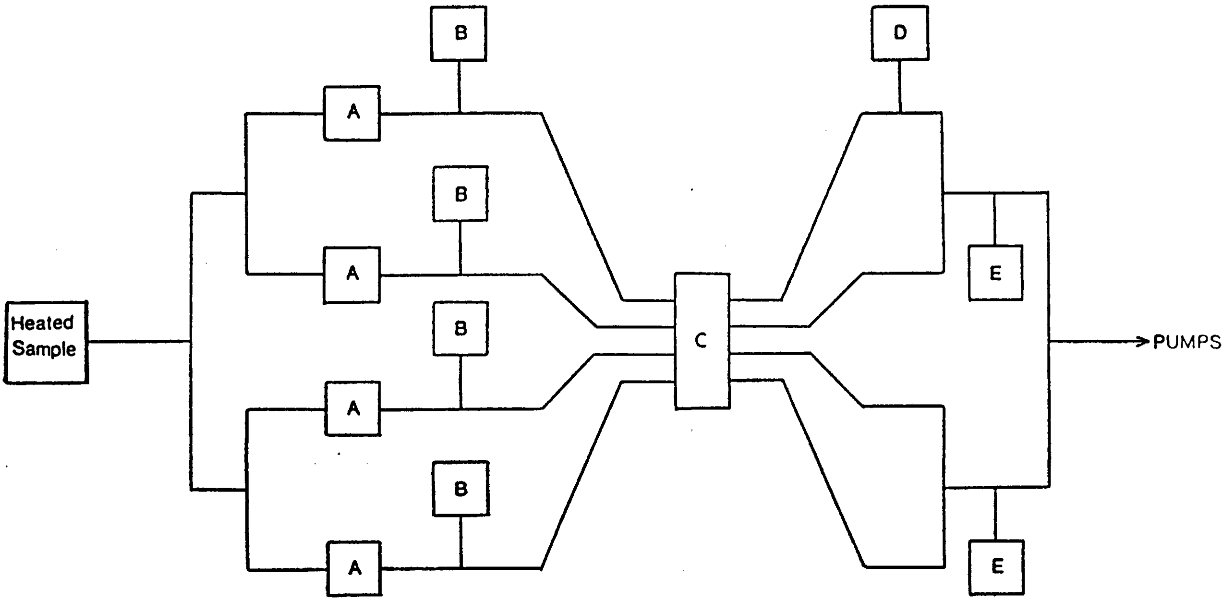


Fig. 2.3. Parallel Limb Differential Condensation TVA System

A = 0°, -45°, -75°, -100 °C traps

B, D = Pirani gauges

C = -196 °C trap

E = Sample take off points

### *1.5.1. TVA In Practice*[68]

*Fig. 2.4* shows, diagrammatically, the oven and degradation tube assembly of a typical TVA line.The oven is a Perkin Elmer F11 gas chromatography oven, modified to take the tube assembly and to work to a maximum temperature of approximately 500 $^{o}$C. The oven can be used isothermally or, by using a programming module, can provide a linear temperature increase. In this research, the oven was used almost entirely in programmed mode, using a heating rate of 10 $^{o}$C/min. Oven temperature were measured using a Type K thermocouple with 0 $^{o}$C reference and the millivolt output, along with that of the Pirani gauges, was recorded on a Leeds-Northrup Speedomax W multipoint chart recorder.

Due to a temperature differential across the tube base, sample temperatures are lower than the oven temperature, except in the case of isothermal equilibrium. Sample temperatures could be measured directly for each run but this is inconvenient and introduces the possibility of sample contamination. To overcome these difficulties, a temperature calibration curve is obtained for the degradation tube.

A second Type K thermocouple is inserted through the socket A of *Fig. 2.4* until the junction is in contact with the tube base. The system is evacuated and the oven heated in the normal fashion. Outputs from both oven and internal thermocouples are recorded to produce a chart similar to the one reproduced in *Fig. 2.5*. Using such a chart, the internal tube base temperature can be obtained for any given oven temperature. Due to the thinness of the polymer sample, the sample temperature can be taken as equal to that of the tube base. Such curves have to be obtained for each tube used and have to be repeated whenever an alternation in the position of the oven thermocouple or rewiring may alter the calibration.

The vacuum system comprises an Edwards Speedivac EO1 oil diffusion pump, backed by an Edwards Speedivac ED100 rotary pump. Using this system, pressures of $10^{-5}$ torr are obtainable. Pressures were measured using Edward G5 C2 Pirani gauge heads with Pirani 14 meter units. As TVA in the form used in this laboratory involves the comparison of the output of the five Pirani gauges attached to the vacuum lines, it is essential that the outputs are matched. The output from a Pirani gauge attached to a TVA line depends, for a constant pressure and gas composition, on the exact position of the gauge and the characteristics of the gauge itself. Thus, it is necessary to cross-calibrate the gauges. This is done as follows.[68]

First, the line is prepared as for a TVA run with all traps in place and pumped to high vacuum. The Pirani gauges are set on zero against the "sticking vacuum" of a Vacustat gauge. The line is isolated from the pumps, dry nitrogen is introduced and the line re-opened to the pumps until a Pirani output of approximately half a full scale (the maximum usually achieved during a degradation) is recorded. The outputs from the Pirani gauges to the recorder are then brought into coincidence by means of variable resistances. The line is then pumped down in steps, the coincidence of the outputs being checked at each stage. A final check is made by degrading a sample of potassium permangenate. This evolves oxygen which at the reduced pressure in use is non-condensable at -196 $^{o}$C and thus passes through all five traps, the Pirani gauges should then all register the same output.

Pirani gauge outputs are only linear over a range of 0-2 mv whilst the usual sample size (about 50 mg), on degradation gives rise to an output of 4-5 mv. Furthermore, the output is dependent on the nature of the gas as well as the absolute pressure and so that for quantitative analysis of degradation products calibration curves must be constructed.

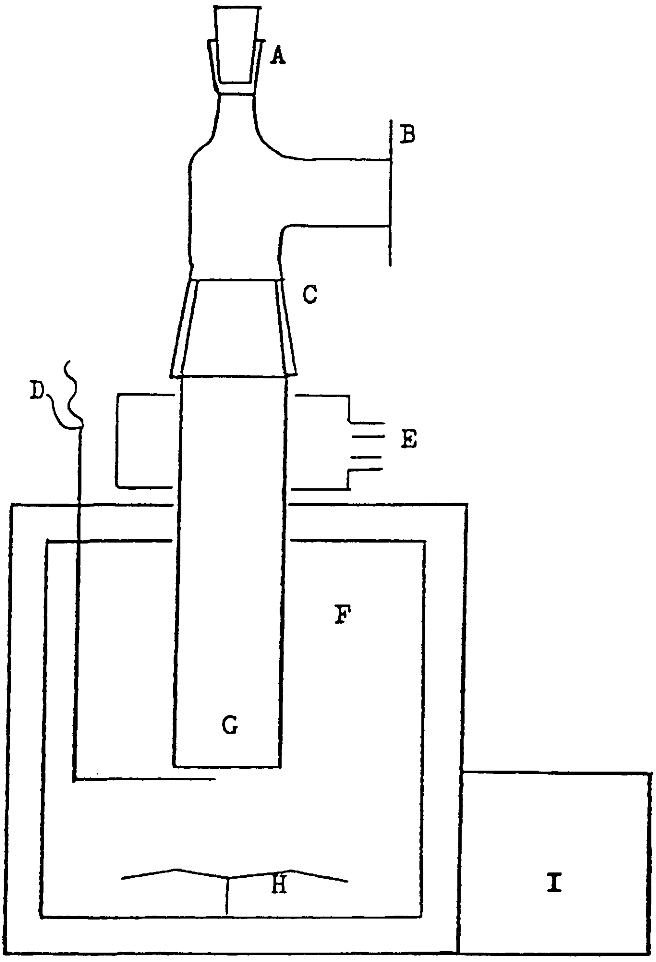


Fig. 2.4. Oven and Degradation Tube Assembly;

| | |
|---|---|
| A= B19 socket | F= Oven |
| B= Ground glass flange joint | G= Degradation tube |
| C= B40 ground glass joint | H= Fan |
| D= Type K thermocouple | I= Programming module |
| E= Water cooled jacket "cold ring" | |

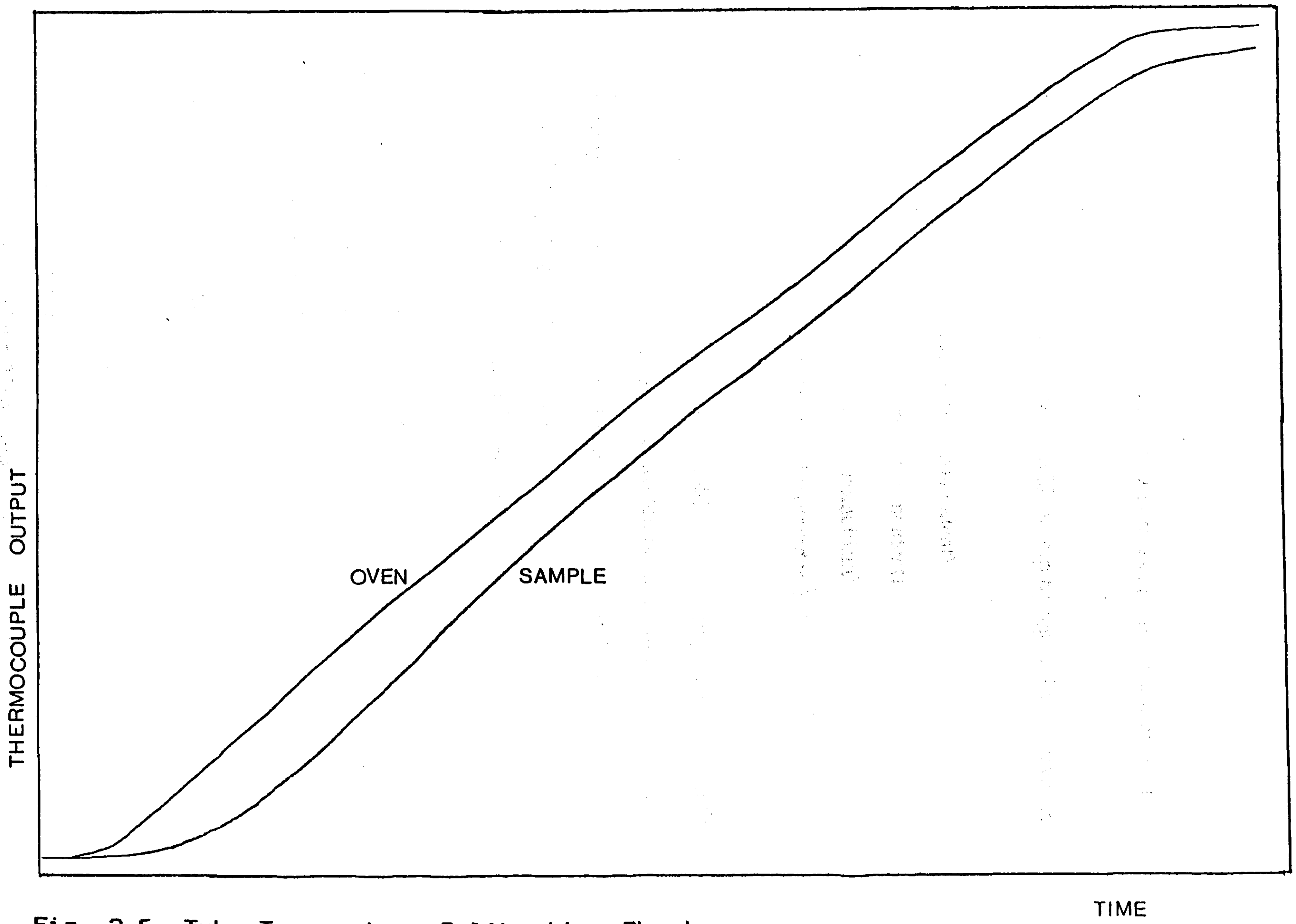


Fig. 2.5. Tube Temperature Calibration Chart

Useful qualitative results, features of the degradation process and information relevant to product composition can be obtained however, as discussed subsequently.

The following designation for the individual trap traces of TVA curves is employed in this work as standard;
______ 0°C (and colder traps if coincident)
········ -45°C (and colder traps if coincident)
--------- -75°C (and colder traps if coincident)
– – – – -100°C (and colder traps if coincident)
– · – · – -196°C.

By means of a system with various cold traps at temperatures from 0° to -196 °C preceding Pirani pressure gauges a considerable amount of information about product volatility and changes in product composition during the heating programme may be collected in a single TVA experiment, in addition to data on number of stages of breakdown and their threshold and maximum rate temperatures.[40]

When only totally volatile products and total -196 °C non-condensable products are recorded, the designation is as follows;
______ Total volatile products.
– · – · – Total -196 °C non-condensable products.

Any exception to this scheme will be noted where it occurs.

### *1.5.2. Product Analysis*

A further advantage of the TVA apparatus is that it is nondestructive of the various product fractions, which are available for further study, e.g. by spectroscopic methods. Thus the collected volatile products may be separated by controlled warming from

-196°C to ambient temperature of the trap containing the products, using the pressure gauges of the TVA system to monitor the volatilisation of each substance (subambient TVA).[91]

Degradation of a sample within the TVA apparatus gives two categories of products :

**a.** involatile residue.

**b.** volatile products.

The volatile products can be further sub-divided into three classes;

**1.** Tar/wax products which are volatile at the degradation temperature but involatile at ambient temperature. These collect at the top of the degradation tube in the region cooled by the water jacket. Consequently this type of product is referred to as the cold ring fraction (CRF). The cold ring fraction can be removed for analysis either by swabbing with a tissue soaked in a suitable solvent or by scraping with a spatula.

**2.** Products volatile at degradation and ambient temperature but condensable at -196°C, called condensables. These can be distilled from the cold trap into a suitable collection vessel (attached at point E in Fig. 2.3) for analysis by infrared spectroscopy, mass spectrometry or gas chromatography. For IR analysis, a gas cell similar to that depicted in *Fig. 2.5* is used. A mixture of condensable products is usually first fractionated by means of sub-ambient TVA.

**3.** Products non-condensable at -196 °C, called non-condensables. Those materials (hydrogen, methane, oxygen, carbon monoxide) volatile at -196 °C and thus not trapped may be studied by carrying out a degradation in a sealed system similar to the illustrated in *Fig. 2.6*.

The system is initially evacuated via stopcock A which is then closed prior to heating the sample. Condensable products are trapped in the -196 °C trap whilst the non-condensables diffuse through the system including the gas cell. At the end of the degradation, the gas cell can be removed and an IR spectrum obtained.

A more convenient method and that normally used in this laboratory, is to bleed the non-condensables as they form into a mass spectrometer fitted on-line between the main trap and pumping system. Carbon monoxide and methane are the only commonly formed -196°C non-condensables.

Involatile residues which are usually insoluble in organic solvent, may be analysed spectroscopically by first scraping some material from the base with a spatula and grinding the material to a fine powder prior to forming a KBr disc or Nujol mull. In the case of soluble residue, molecular weight measurement may be feasible.

### *1.5.3. Subambient TVA*

This technique, developed independently by *McNeill et al*[91] and *Ackermann* and *McGill*,[69-71] provides a simple method for separating the condensable products of a degradation, thus facilitating analysis. McNeill and his co-workers called the technique subambient thermal volatilisation analysis (SATVA) whereas Ackermann and McGill prefer the term differential distillation. However, the name subambient TVA will be used throughout this thesis.

The principal features of a SATVA system are shown in *Fig. 2.7.*

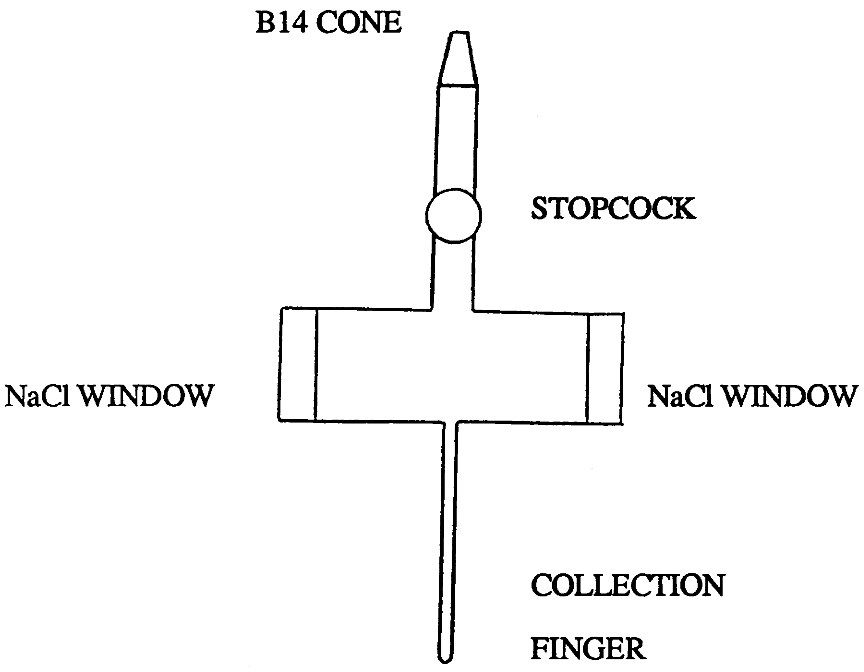
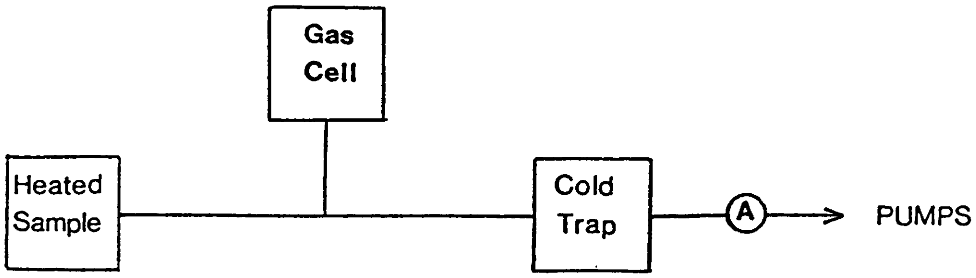


**Fig. 2.5.** Gas cell for IR and MS analyses.



A = Stopcock

**Fig. 2.6.** System for Analysis of -196 °C.

Non-condensable Degradation Products.

Degradation products from the heated sample are collected in the liquid nitrogen trap A, the entire system being continuously evacuated. The evolution of the products from the sample can be monitored on Pirani 1, as in a TVA experiment, whilst Pirani 2 may be used to monitor those non-condensable products which pass through the trap and are thus lost to the pumps, unless bled to a mass spectrometer.

Trap A, commonly called the subambient trap, is shown in detail in *Fig. 2.8*. The U-tube is surrounded by a pyrex glass vessel containing glass beads. The glass vessel is itself surrounded by a Dewar flask containing liquid nitrogen. A thermocouple measures the temperature of the U-tube.

When the collection of products has been completed, stopcock S of *Fig. 2.7* is closed and the liquid nitrogen removed from around the subambient trap, A. The trap will now begin to warm up at a rate determined by the diameter of the surrounding jacket and the size of bead used. Although not linear, the heating rate is reproducible for any given jacket. As the trap warms, each of the condensed products will vaporise in turn according to the volatility of the material concerned. The pressure changes associated with the distillation of the products from trap A to trap B are measured by Pirani 2. Both Pirani response and trap temperature are recorded as a function of time to give a trace similar to the typical example of *Fig. 2.9*.

In general, longer warm up times enhance the resolution of the peaks although complete separation of products is seldom attained. Isolation of the products giving rise to a specific SATVA peak may be achieved by omitting trap B of *Fig. 2.7* and linking SATVA trap A directly to a system such as that illustrated in *Fig. 2.10*. Initially, traps b, c, d are closed and so any product distilling from B will pass down limb 1 and be condensed in the liquid nitrogen trap, A.

When the peak corresponding to this production the SATVA trace has reached a minimum, trap b is opened and traps a and e closed (this specific order ensures that the SATVA trap is always open to the pumps preventing spurious peaks on the SATVA trace due to back pressures). Thus , the first peak product(s) are isolated in limb 1 whilst the second peak product(s) are collected in limb 2.

Similarly, further products may be collected in limb 3 and 4. Once the products have been isolated, they may be removed for analysis by distilling the material from the -196 $^{o}$C trap to an evacuated sample collection vessel, commonly a minimum volume gas cell, attached to the limb at the take-off points (marked B in Fig. 2.10).

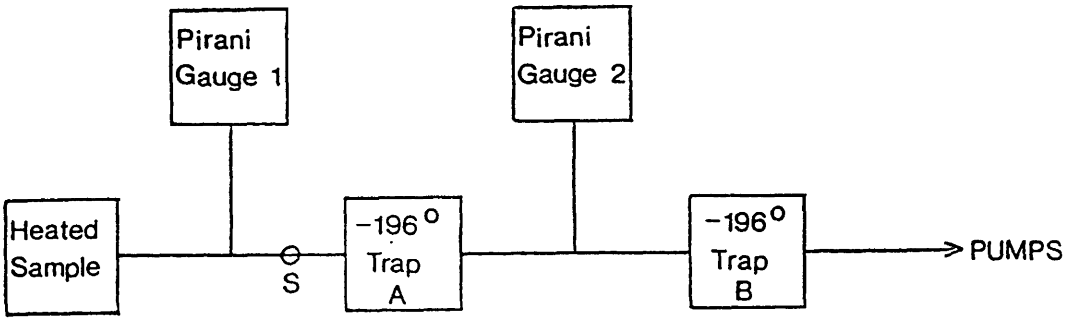
In this research, the most commonly used analytical techniques were infrared spectroscopy, mass spectrometry, GC-MS and gas chromatography.

### *1.6. TVA, TG, DTA- COMPARISON OF THE TECHNIQUES*

Generally, no single thermal analysis technique is capable of supplying all the information required for a complete understanding of thermal degradation processes. Of the methods used in this research, TVA is the most versatile.

DTA can indicate the temperature difference (thermal energy changes) between the sample and a reference material and any transition or thermally induced reaction in the sample will be recorded as a peak. To fully interpret a DTA curve, however, it is necessary to have additional information from TVA and TG.

Although TVA, unlike TG, is only semiquantitative and is unable to record the evolution of those relatively involatile products which condense on the cold ring, it has several



S = Stopcock

Fig. 2.7. Principal Features of a SATVA system

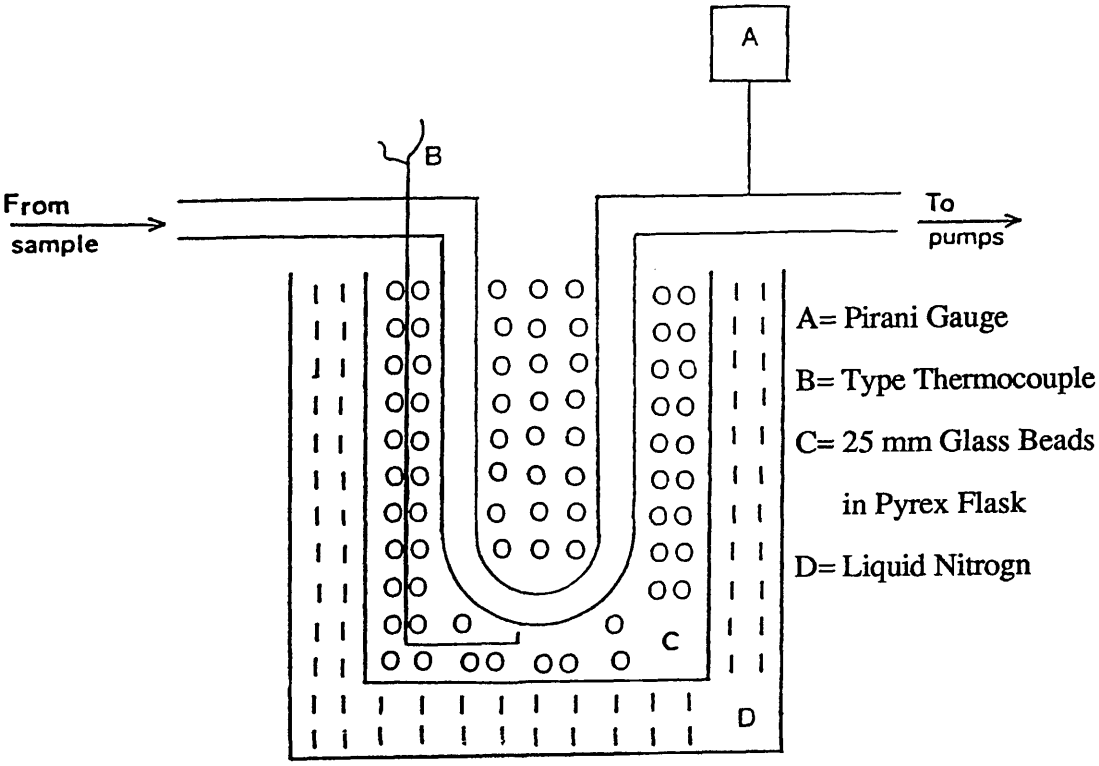


Fig. 2.8. Subambient Trap.

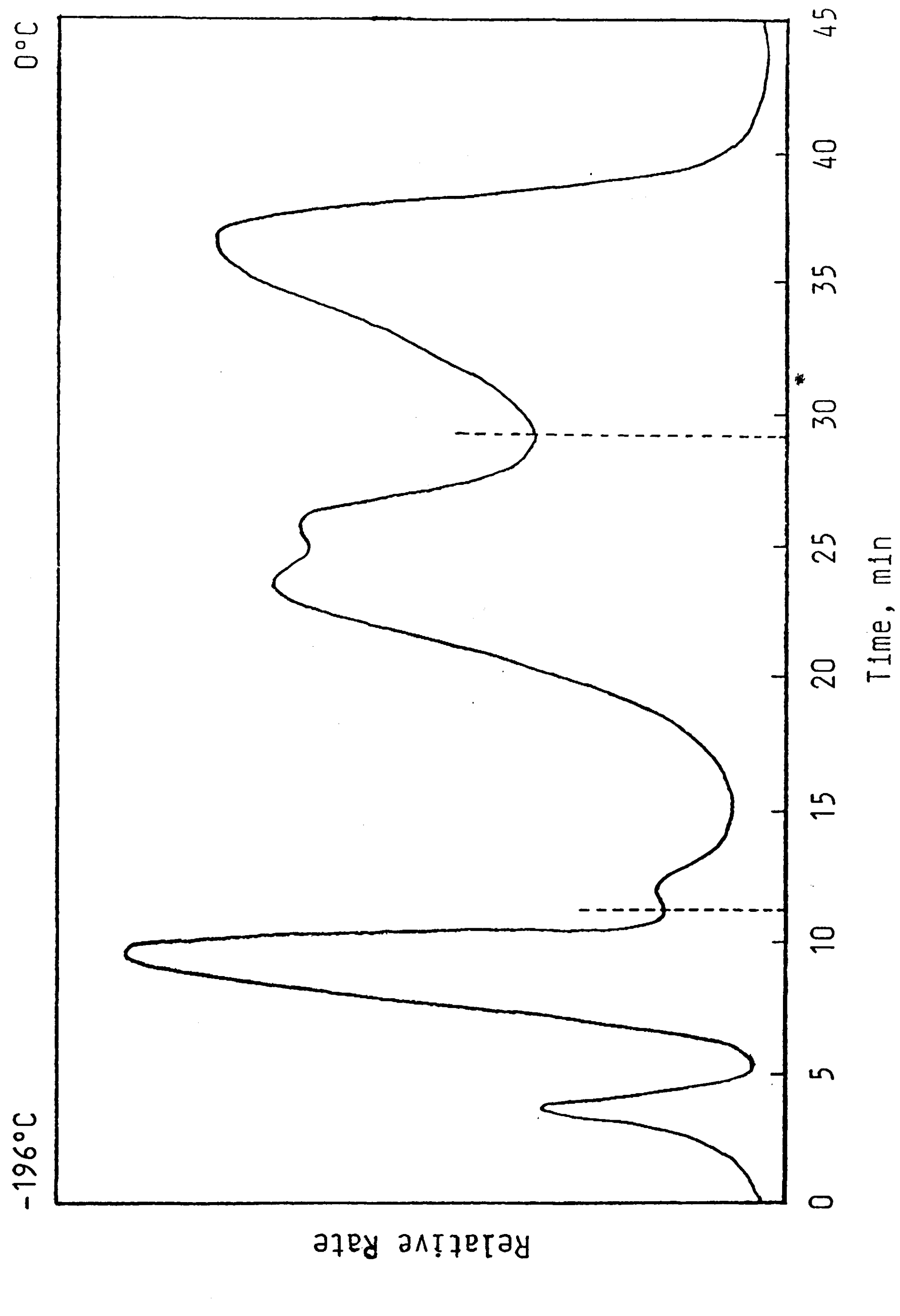
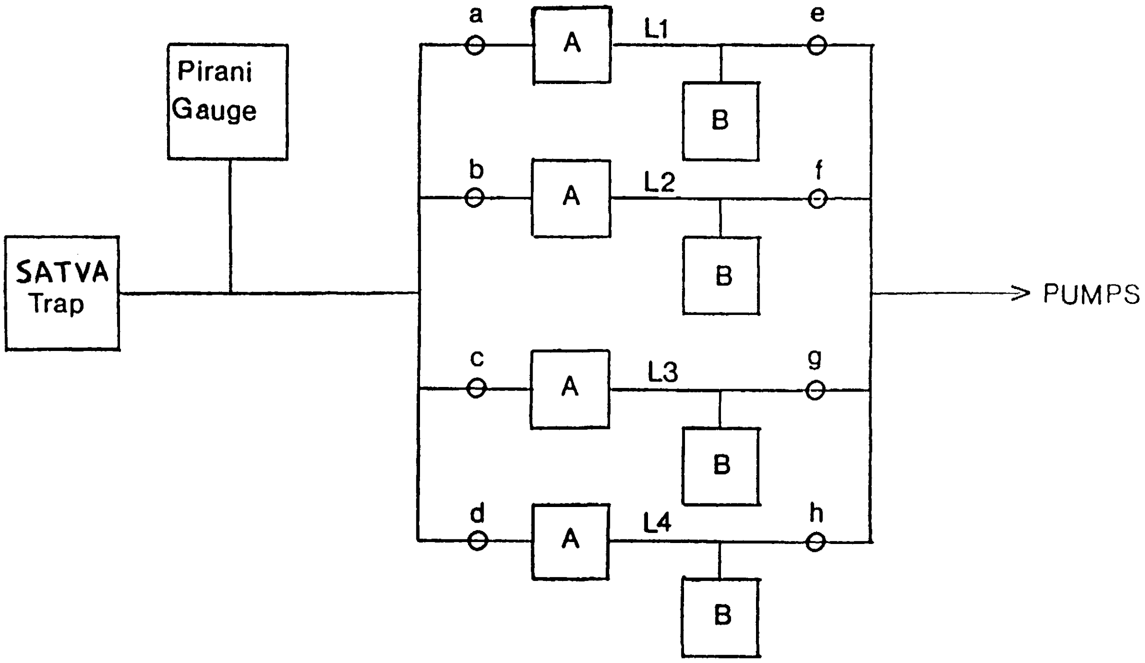


Fig. 2.9. Typical SATVA curve.



L1 - L4 = Limbs 1-4

A = -196 $^{o}$C Trap

B = Take-off point

a - h = Stopcock

Fig. 2.10. System Employed for Isolation of Products via SATVA.

important advantages over TG. As well as providing valuable initial qualitative information, TVA uses considerably larger samples which facilitates further analysis of all products (-196 $^{o}$C condensable and non-condensable gases and liquids, cold ring fraction, involatile residue) particularly when coupled with SATVA.

Continually evacuating the degradation zone aids the diffusion of volatile products from the sample and limits the possibility of secondary decomposition processes.[68]

It is notoriously difficult to compare directly the temperatures of decomposition as recorded by different thermal analysis techniques due to the effects of sample sizes and forms, atmospheres and instrumental vagaries.[72]

In this project TG and DTA determinations were performed under a nitrogen atmosphere and TVA determinations under high vacuum. Consequently, some discrepancies can occur. In general, a $T_{onset}$ or $T_{max}$ temperature obtained from TG under atmospheric pressure will be higher than that obtained from TVA due to the easier evolution of volatiles in the latter, high vacuum, technique. Genuine differences in $T_{onset}$ and $T_{max}$ sometimes occur because TG measures all volatile products but TVA does not record CRF materials.

## 2. *MASS SPECTROMETRY*

The mass spectrometer is an instrument designed to ionise molecules, to resolve the ion mixture on the basis of mass-to-charge ratio (m/e), and to record the mass spectrum, showing ion intensity as a function of m/e. Generally, positive ions are produced by electron bombardment of volatile molecules, which lose one (on occasionally two) of their electrons from the collision. These ions may then degrade to fragment ions and neutral species, if sufficient energy has been impacted to them. The fragmentation pattern is characteristic of the molecular structure, with prominent peaks at m/e values corresponding to particularly stable positive ions or ions formed by elimination of stable neutral species (e.g. $H_2O$, $CH_4$, $CO_2$, CO).[73]

Most commonly, the sample is introduced as a gas from a reserviour. For liquids boiling below 150 $^{o}C$, a suitable quantity can be evaporated into the evacuated reserviour at room temperature, the sample must be introduced directly into the ionisation chamber, a procedure that requires special equipment. Gaseous samples are readily handled by expansion of a small volume into the reserviour. Nonvolatile or thermally unstable materials are often introduced directly into the ion source by means of a sample probe, which is inserted through a vacuum leak. The probe consists of a holder for a small capillary tube or cup that contains a microgram (or less) of the sample. A principal advantage of the probe is the minute quantity of sample required. The probe is equipped with a heater to volatilise the sample at the low pressure of the ion source, however, much lower temperatures are needed to produce sufficient gaseous molecules of the sample.[64]

### *2.1. GAS CHROMATOGRAPHY INLET SYSTEMS*

Sample requirements with regard to volatility and quantity (~1 μmol) are similar for both gas chromatography and mass spectrometry; thus, the effluent from a chromatographic column can serve as a sample source. Enhanced sensitivity can be realized by separating the sample components from the large excess of carrier gas (usually helium) that is always present. This separation is readily achieved by passing the effluent from the chromatographic column through a narrow tube of porous glass or Teflon which is permeable to helium atoms but not to the larger sample molecules. The latter are then bled into the ion chamber through a pinhole.[64]

In the present work, a Perkin-Elmer Sigma 3 chromatograph interfaced to a Kratos MS 30 mass spectrometer with a DS 90 data handling system was used. The column was a 15 m capillary column with *DB-5* (5% phenyl methyl silicone). Other instrumental conditions will be discussed in corresponding chapters.

In addition, a VG Micromass QX200 quadrupole mass spectrometer coupled directly to the TVA-SATVA system was occasionally used. In the VG Micromass instrument, compounds with a molecular weight less than 200 a.m.u. could be analysed; samples of the degradation products may be bled into the mass spectrometer during the degradation process. In addition condensable products may be fractionated by SATVA then samples at each peak may be admitted to the mass spectrometer.

The excellent separation qualities of gas chromatography, combined with the powerful identification properties of mass spectrometry, provides the chemist with a most useful tool for analysing complex mixtures.

### *2.2. COMPUTERISED MASS SPECTROMETRY*

In this study, a modified low resolution Kratos MS12 with a DS 55 data handling system and a high resolution Kratos DS 902S mass spectrometer with a DS 90 data system were used.

## *3. CHROMATOGRAPHY*

In this research, a Perkin-Elmer F33 instrument with flame ionisation detector and 6 ft column ( 6 ft x 0.25 in outside diameter coiled glass) of 15% FFPA (Free Fatty Acid Phase) on GCQ 80-100 mesh and a 6 ft column of Chromosorb 103 were used.

### *4. INFRARED SPECTROSCOPY*

Infrared spectra were obtained on a Philips PU 9800 FTIR, Perkin-Elmer 983 with P.E. 3600 data system and Perkin-Elmer 257 grating spectrometers. Spectra of polymers , copolymers and involatile residue of degradation products were run as KBr discs. CRF spectra were obtained by dissolution in suitable solvent and casting a film onto a salt plate (NaCl disc). Gas cells of the type shown in Fig. 2.5 were used to obtain spectra of gaseous degradation products at room temperature.

*******

# CHAPTER THREE

## PREPARATION AND CHARACTERISATION OF MONOMER & POLYMER

### *1. INTRODUCTION*

In this chapter preparation, purification and characterisation of both monomers and polymers are described. Some of the methods used for preparation and characterisation have been already suggested by *McNeill* and *Zulfiqar.*[101,102,133]

In the present study the metal salts of acrylic acid such as Na, K, Mg, Ca, Zn and Co(II) were synthesised, characterised and polymerised. The polymers will be referred to as sodium polyacrylate, etc. and abbreviated to NaPA etc., within the text.

The copolymers of styrene-acrylic acid and their sodium and potassium salts were also prepared.

### *2. PREPARATION OF THE MONOMERS*

The alkali metal salts of acrylic acid were made by neutralising the acid with the respective hydroxide in methanol and the alkaline earth metal salts were prepared by neutralisation of the acid and the corresponding oxide in aqueous solution.

### *2.1. MATERIALS*

Sodium hydroxide (BDH Chemicals Ltd), potassium hydroxide (Fisons plc), magnesium, calcium and zinc oxides (Hopkin & Williams Ltd), cobalt (II) acetate (BDH Chemicals Ltd) and acrylic acid solution (Hopkin & Williams) were used.

## *2.2. DISTILLATION OF ACRYLIC ACID*

Glacial acrylic acid is usually supplied inhibited with approximately 200 ppm of p-methoxyphenol, hydroquinone, etc. Acrylic acid was purified by distillation under reduced pressure (25 mmHg) at 60 $^{o}$C using hydroquinone (0.05 w/v%) as inhibitor.

### *2.2.1. Distillation Procedure*

Distillation was carried out in a fume cupboard, behind a safety shield, in a 250 ml round-bottomed flask fitted with a thermometer and condenser in which distillation head and receiver were connected to a water aspirator. The equipment was protected from light using aluminum foil. The pressure in the distillation head was adjusted to approximately 25 mmHg and the distillation was started by heating the stillpot cautiously. The middle fraction was collected and freshly used.

## *2.3. PREPARATION OF ALKALI METAL SALTS (Na and K)*

The metal hydroxide (AR) was dissolved in distilled methanol (AR) and the solution was maintained between 0$^{o}$ and 5 $^{o}$C in an ice bath.

Neutralisation was carried out by gradual addition of the stoichiometric amount of freshly distilled acrylic acid, using phenolphthalein as indicator. The resulting solution was filtered and the salt monomer was precipitated in anhydrous diethyl ether (AR) with constant stirring. The white solid material was separated and washed with diethyl ether and acetone (AR). Further purification was performed by two reprecipitations from distilled methanol in anhydrous diethyl ether and washing with acetone and the salt was dried under vacuum at room temperature for 24 hr before further analysis or polymerisation

## *2.4. PREPARATION OF ALKALINE EARTH METAL SALTS (Mg and Ca)*

These salts were prepared in water because of their low solubility in methanol. Magnesium oxide and calcium oxide were used as reactants for neutralisation of acrylic acid in aqueous solution. The solid metal oxide (AR grade) was added in small amounts with vigorous stirring, to an approximately 3N aqueous solution of freshly distilled acrylic acid using phenolphthalein as indicator, while the temperature was maintained at about 5 °C using an ice bath. At the phenolphthalein end point, a slight excess of acrylic acid was added and the solution was stirred continuously for two hours, then it was filtered and introduced to an excess of AR grade acetone where the monomer salt precipitated as a white solid. The monomer salt was filtered and washed with acetone. After purification by reprecipitation, it was dried in a vacuum oven at ambient temperature for 48 hr.

## *2.5. PREPARATION OF ZINC AND COBALT (II) SALTS*

The zinc salt of acrylic acid was made by gradual addition of zinc oxide to a 3N aqueous solution of the acid while the solution was kept in an ice bath with vigorous stirring. Due to high solubility of zinc acrylate in methanol in comparison with the acrylates of magnesium and calcium, the former cannot be separated from methanol solution by common non-polar precipitants, such as ether etc. Therefore, the solution was filtered to remove the unreacted zinc oxide and the salt was tried to recover by removal of the solvent. The freeze-drying method was used for further purification, with methanol as solvent. The salt was finally dried under vacuum.

Cobalt (II) acrylate was synthesised by dissolution of the appropriate amount of the sodium acrylate (already prepared) and cobalt acetate (AR grade) in methanol and the solution was stirred for 24 hr, then the cobalt acrylate was precipitated in a mixture of acetone and toluene 70 : 30 v/v. The monomer salt was filtered and washed with acetone-toluene mixture, then precipitated from dry methanol and dried under vacuum for 48 hr.

## *3. CHARACTERISATION OF MONOMERS*

Characterisation of the monomer salts was carried out by microanalysis, spectroscopy and estimation of metal contents.

### *3.1. MICROANALYSIS*

The elementary analysis of the monomers was performed using a Carla-Erba CHN Elemental Analyser. The percentages of carbon and hydrogen obtained from the analysis are listed in Table 3.1. The results of microanalysis for C and H are consistent with the theoretical values for each monomer salt.

### *3.2. METAL CONTENTS*

*Flame photometry* and *volumetry* (EDTA titrimetry) methods were employed to determine the metal content of the monomer salts. The alkali metal salts of acrylic acid were examined by flame photometry and zinc and the alkaline earth metal salt monomers were determined volumetrically.

### *3.3. DETERMINATION OF SODIUM AND POTASSIUM*

An Evan's Electroselenium Flame Photometer was used to determine sodium and potassium. In this method solutions of known and unknown concentrations of a specimen are sprayed into the flame photometer.

**Table 3.1.** Microanalysis results

| Monomer | C% | | H% | |
|---|---|---|---|---|
| | Found | Calculated | Found | Calculated |
| Na acrylate | 38.02 | 38.29 | 3.04 | 3.19 |
| K acrylate | 32.62 | 32.72 | 2.49 | 2.72 |
| Ca acrylate | 38.25 | 39.56 | 3.37 | 3.29 |
| Mg acrylate | 42.94 | 43.37 | 3.85 | 3.61 |
| Zn acrylate | 32.90 | 34.78 | 2.67 | 2.98 |
| Co acrylate | 33.85 | 35.8 | 2.96 | 2.98 |

Reagent grade sodium chloride (Formachem Ltd) and potassium chloride (Riedel-dettaen) were used to make the solutions of known concentration of sodium and potassium ions which were prepared as 10, 5, 4, 3, 2 and 1 ppm based on the metal weight. These specimens were examined in the flame photometer and galvanometer readings were taken to get calibration curves by plotting the galvanometer results against the concentration, giving a straight line in each case.

The sodium and potassium salts of acrylic acid were used as follows:
**a.** The monomer salts were first converted into their corresponding metal halides by weighing 0.05087 g of sodium acrylate and 0.07174 g of potassium acrylate sample precisely into two different crucibles (porcelain evaporating dishes) and heating at about 700 $^{o}$C to get the corresponding metal oxide. The residues (metal oxides) after ignition and dissolution in a few drops of hydrochloric acid were introduced to a 100 ml volumetric flak and the solutions were made up to the mark with deionised water.

**b.** Aqueous solutions of 0.05087 and 0.07174 grams per 100 ml deionised water of the sodium and potassium acrylate samples, respectively, were also prepared in 100 ml graduated flask to compare the flame photometric results with that of the solutions made by the route **a.**

The sodium and potassium concentrations of the unknown solution which made by both routes (**a** and **b**) were determined by flame photometry by comparing the galvanometer reading with the calibration curve. The flame photometric data are given in Table 3.2.

### *3.4. INFRARED SPECTROSCOPY*

*Fig. 3.1* shows the ir spectra of the alkali metal salt monomers which were obtained by the KBr disc technique. The characteristic bands due to C=O, C=C and C-H stretching are clearly shown in the spectra and the assignments of the peaks are summarised in *Table 3.3*.

### *3.5.DETERMINATION OF DIVALENT METAL SALTS BY VOLUMETRY*

The magnesium, calcium and zinc salts of acrylic acid were accurately weighed and heated at 725 $^{o}$C under the same conditions already used for the metal salts. The metal oxides were transferred into a 100 ml flask along with 1 ml of HCl and 0.5 ml of nitric acid to digest the residues. 5.0 g of $NH_4Cl$ (AR) and 40 ml of concentrated $NH_3$ were added to the resulting solutions of the magnesium and calcium ions and after dilution to 100 ml with deionised water, 20 ml of each solution was titrated against 0.0 1 M EDTA in the presence of a few drops of Eriochrome Black T as indicator until the colour changed from red to blue.

In the case of zinc ion, after ignition and dissolution in acid, a few drops of Xylenol orange was added as indicator and the solution was diluted with deionised water. The yellow changed to an intense red colour by addition of hexamine powder and it was then titrated with 0.01 M EDTA until the colour change to yellow occurred. The EDTA titration data are listed in Table 3.2.

The ir spectra of the divalent metal salts of acrylic acid are reproduced in ***Figs.** 3.2* and *3.3*.

**Table 3.2.** Flame photometric data for Na and K acrylate

| Monomer | Metal contents (%) | | |
|---|---|---|---|
| | Heated at 700$^{o}$C " Found " | Without heating " Found " | Calculated |
| Na acrylate | 23.57 | 23.64 | 24.46 |
| K acrylate | 34.45 | 34.06 | 35..45 |
| Mg acrylate | 14.41 | —— | 14.45 |
| Ca acrylate | 20.90 | —— | 21.97 |
| Zinc acrylate | 32.53 | —— | 31.4 |

## *4. POLYMERISATION*

The monomer salts of acrylic acid were polymerised in solution in water or methanol.

Aqueous solution polymerisation was applied for the divalent monomer salts (except zinc acrylate) under nitrogen atmosphere, but the alkali metal and zinc salts were polymerised in methanol under vacuum in sealed dilatometers.

### *4.1. NONAQUEOUS POLYMERISATION*

Polymerisation were carried out in dilatometers which had been washed with cleaning solution, distilled water, AR grade acetone and then flamed out to remove any traces of impurity.

#### *4.1.1. Purification of Solvent*

Methanol (AR) was used as solvent for polymerisation because of the considerable solubility of the alkali metal salts of acrylic acid in it .It was dried over anhydrous calcium sulphate for 48 hr then overnight with calcium hydride to remove all traces of moisture and distilled under nitrogen flow over molecular sieves. The solvent was finally degassed on a vacuum line by the usual freezing and thawing technique and distilled under vacuum into a graduated reservoir. Freezing should be carried out slowly from the bottom of the reservoir up to the top, whereas the warming up after degassing should be done instantly and thoroughly with hot water (50 $^{o}C$) otherwise the vessel would crack as a result of the high cubic coefficient of expansion of methanol.

The middle fraction of this distillate was distilled into a dilatometer containing appropriate amounts of monomer and initiator.

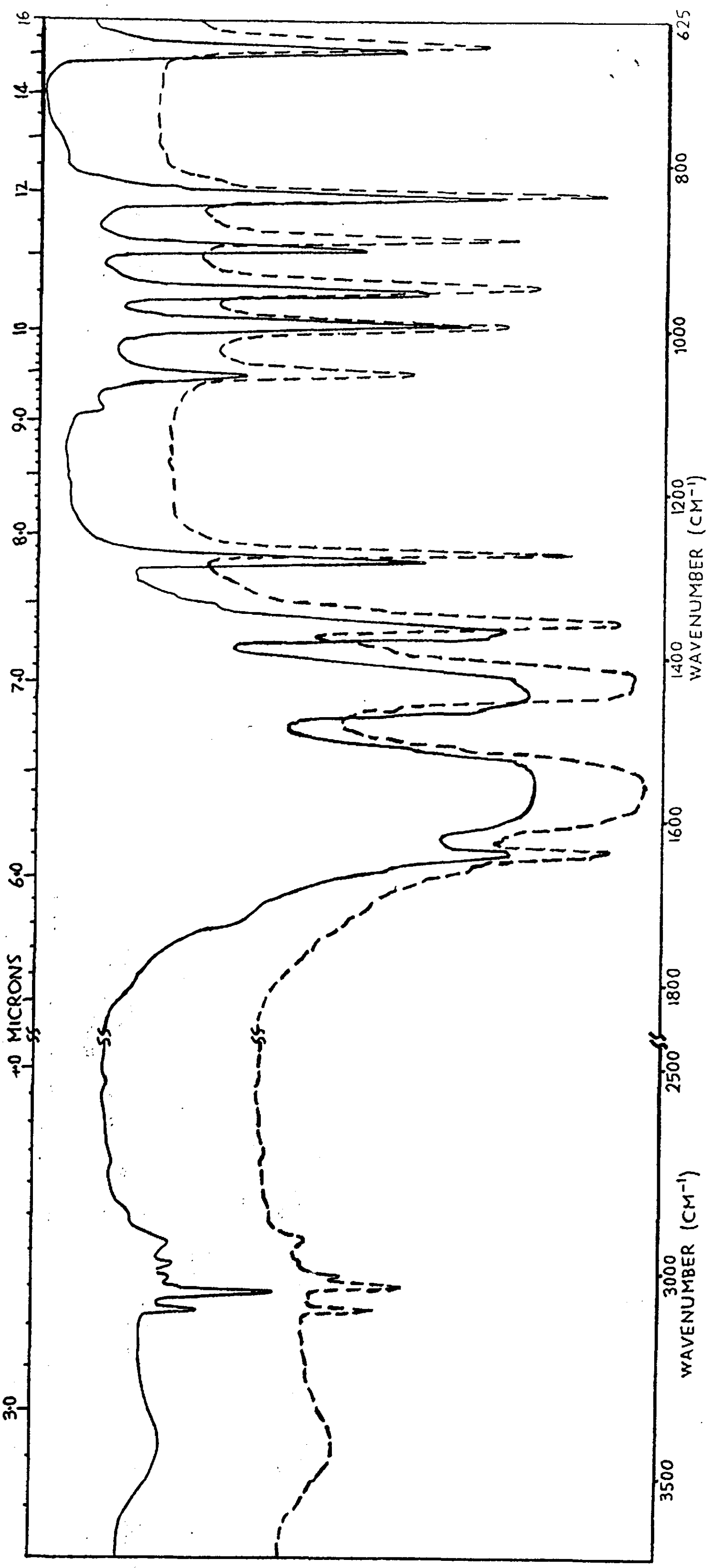


**Fig. 3.1.** Ir spectra of Na and K acrylate samples.

——— Na acrylate; ------- K acrylate

**Table 3.3.** Assignment of IR peaks of Na and K acrylate

| Frequency ($cm^{-1}$) | Mode | Group |
|---|---|---|
| 3085 (m) | C-H stretching (asymmetrical) | olefinic |
| 3043 (s) | C-H stretching (symmetrical) | olefinic |
| 3012 (w) | C-H stretching | CH |
| 2975 (w) [1285+1640] | | |
| 2915 (w) [1555+1370] | | |
| 1914 (w) [2 x 952] | | |
| 1640 (m) | C=C stretching | |
| 1570-1540 (b) | C=O stretching<br>(asymmetrical deformation) | carboxyl |
| 1440 (s) | C=O stretching<br>(symmetrical deformation) | carboxyl |
| 1430 (m) | $CH_2$ scissors | $CH_2$ |
| 1368 (s) | CH bend | CH |
| 1285 (s) | C-C stretching | |
| 1055 (m) | $CH_2$ rock | |
| 991 (s) | $CH_2$ twist | |
| 952 (s) | $CH_2$ wag | |
| 902 (m-S) | $CO_2$ deformation | carboxyl |
| 837 (s) | C-H bend | |
| 663 (m-s) | $CO_2$ rock | carboxyl |

m = medium, s = sharp (strong), b = broad

### *4.1.2. Purification of Initiator*

$\alpha,\alpha'$-Azodiisobutyronitrile (AIBN, BDH Chemicals Ltd) was used as initiator for nonaqueous polymerisation after two recrystallisations from warm methanol (AR).

### *4.1.3. Introduction of Monomer into Dilatometer*

The solid monomers were mixed thoroughly with the appropriate amount of purified initiator (usually less than 0.05 w/v %) and then introduced into the dilatometer. Any particle sticking to the surface of funnel and the stem of dilatometer was washed down with a few ml of dried and distilled methanol which was then evaporated under high vacuum. After a pressure of $10^{-5}$ torr, the solvent was transferred in the vacuum line into the dilatometer containing monomer and initiator and the dilatometer was finally sealed under vacuum.

Polymerisation was carried out at 60 $^{o}$C in a thermostated bath. The precipitated polymer was separated by filtration and washed several times with dry methanol to remove any monomer still present. The polymer was dried in a vacuum oven at 60 $^{o}$C for two days and stored in an evacuated dessicator. The polymerisation data are summarised in *Table 3.4*.

## *4.2. AQUEOUS POLYMERISATION*

### *4.2.1. Polymerisation of Acrylic Acid*

Polymerisation of freshly distilled acrylic acid was carried out in the presence of 0.1 w/v% AIBN initiator.[135] The product was purified by dissolution in distiled water and isolated from the aqueous solution by freeze-drying, followed by subsequent evacuation at about 40 $^{o}$C for 80 hr.

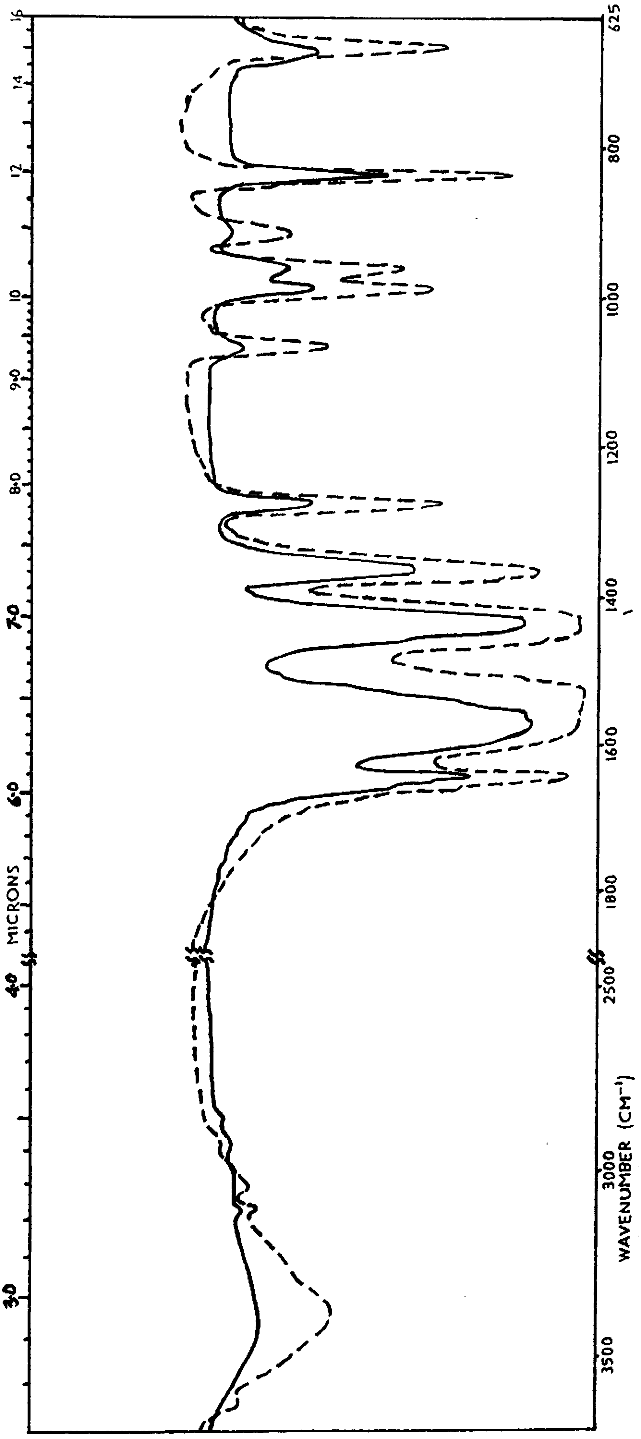


**Fig. 3.2.** Ir spectra of Mg and Ca acrylate samples

——— Mg acrylate; ------- Ca acrylate

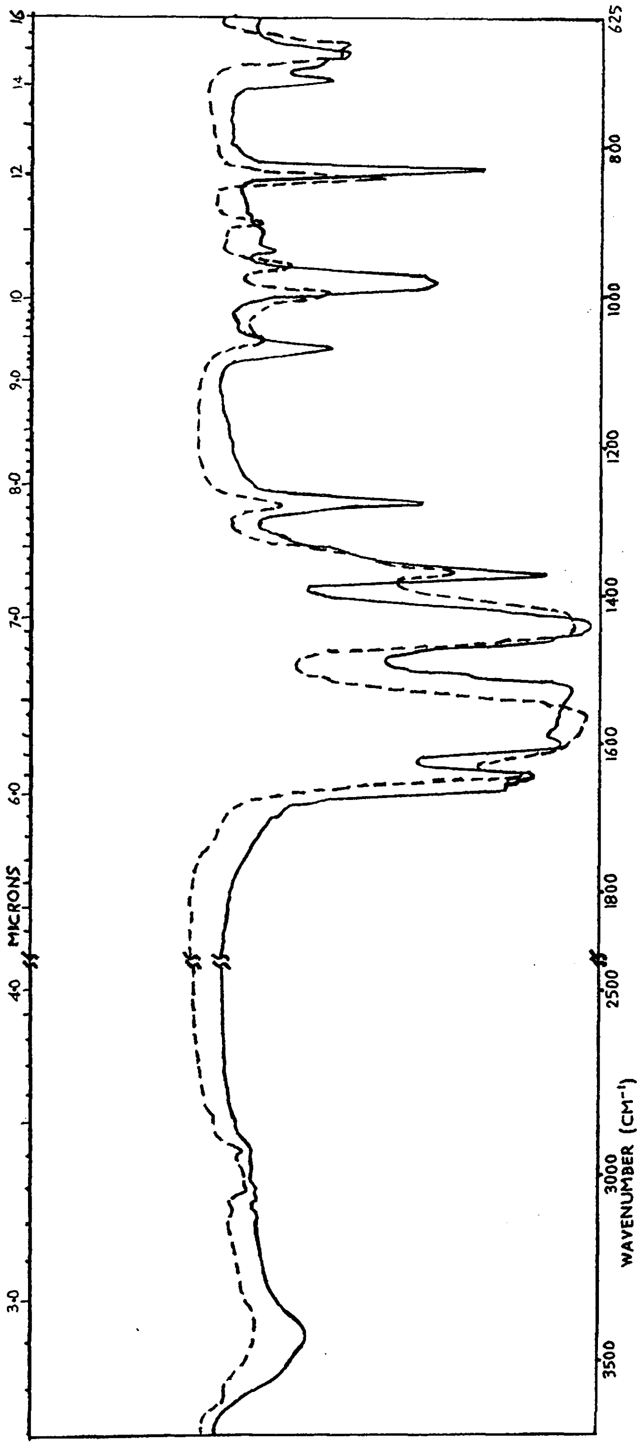


**Fig. 3.3.** Ir spectra of Zn and Co (II) acrylate samples

——— Zn acrylate; ------ Co (II) acrylate

### *4.2.2. Polymerisation of the Alkaline Earth Metal Salts*

Appropriate amounts of the alkaline earth metal salt of acrylic acid and deionised water were introduced into a 250 ml round-bottomed three neck flask, equipped with a thermometer, nitrogen inlet and a condenser. The mixture was continuously stirred under a stream of oxygen free nitrogen for two hr to dissolve the monomer salt and remove dissolved oxygen. After the addition of ammonium persulphate (0.1 w/v%). the solution was maintained in a 60 $^{o}$C thermostated bath.

The flask was removed after a considerable time of polymerisation.The contents, which were sticky, were isolated and washed several times with deionised water. They were dried under vacuum at 70 $^{o}$C for at least 50 hr. The homopolymers are insoluble in water and were purified by successive washing with distilled water to remove monomer.

*Table 3.5* shows the monomer and initiator concentrations, temperature and time which were employed during polymerisation of the divalent metal salts of acrylic acid.

## *5. PREPARATION OF THE POLYMERS VIA NEUTRALISATION*

Samples of sodium, potassium, magnesium. calcium, zinc and cobalt (II) polyacrylate were also made by neutralisation of poly(acrylic acid) with the respective hydroxide or oxide.

### *5.1.POLYMERS OF THE ALKALI METAL SALTS*

Sodium and potassium polyacrylate samples were prepared by neutralisation of the respective hydroxide solution in methanol with a solution of PAA in the same medium and in the same way as for the preparation of the monomers.

### *5.2. POLYMERS OF THE ALKALINE EARTH METAL SALTS*

Samples of magnesium and calcium polyacrylate were also made by neutralisation of the acid, in the same way as in the preparation of the corresponding monomers, except that the temperature was maintained at 40 °C.

### *5.3. POLYMERS OF THE ZINC AND COBALT (II) SALTS*

#### *5.3.1. Zinc Polyacrylate*

Zinc polyacrylate was synthesised by neutralisation of an aqueous solution of poly(acrylic acid) with zinc oxide in the presence of phenolphthalein as indicator.

#### *5.3.2. Cobalt (II) Polyacrylate*

Cobalt polyacrylate was made by gradual addition of an aqueous solution of PAA to the appropriate volume of a solution of cobalt (II) acetate $[(CH_3COO)_2Co \cdot 4H_2O]$ over four hours. The dark red solid polymer was isolated, washed several times with distilled water then dried under vacuum at 70 °C for 60 hr.

Each of the polymers made by neutralisation was filtered washed and dried in a vacuum oven at 60 °C for at least 48 hr.

In the subsequent data and discussion, the polymers made directly by polymerisation of the monomers will be denoted MePA (Me=metal) and those prepared from PAA by neutralisation will be distinguished as MePA*.

## *6. POLYMER CHARACTERISATION*

The polymers were characterised in the same way as in the case of the monomers.

**Table 3.4.** Nonaqueous polymerisation data

| Polymer | Monomer (w/v%) | Initiator (w/v%) | Time (hr) |
|---|---|---|---|
| NaPA | 8 | 0.02 | 4 |
| KPA | 6 | 0.01 | 3 |
| ZnPA | 7.1 | 0.05 | 3.5 |

**Table 3.5.** Aqueous polymerisation data for magnesium and calcium acrylate samples.

| Polymer | Monomer (g) | Solvent ($H_2O$) ml | Initiator [$(NH_4)_2S_2O_8$] (w/v%) | Time (hr) | Yield (%) |
|---|---|---|---|---|---|
| MgPA | 7.48 | 80 | 0.07 | 1.5 | 28.8 |
| CaPA | 8.45 | 80 | 0.1 | 3 | 44 |

*Table 3.6.* shows the analytical data obtained for those polymers made by polymerisation of the monomers.

## *7. PREPARATION OF ST/AA COPOLYMERS & THEIR Na AND K SALTS*

Two styrene-acrylic acid copolymers (40 and 45 mole % AA) were prepared and the copolymer with 40 mole % acrylic acid was used to prepared the alkali metal salts.

### *7.1. MATERIALS*

Styrene (Prolabo), acrylic acid (Hopkin & Williams Ltd), AIBN (BDH Chemicals Ltd), sodium hydroxide (BDH Chemicals Ltd) and potassium hydroxide (Fisons plc) were used as starting materials.

### *7.2. PURIFICATION OF MATERIALS*

Acrylic acid monomer and AIBN (initiator) were purified as already described in sections 2.2 and 4.1, respectively.

#### *7.2.1. Purification of Styrene Monomer*

Styrene monomer was washed twice with equal amounts of a 10% solution of sodium hydroxide in a separating funnel to remove inhibitor, then washed several times with distilled water to remove any traces of sodium hydroxide. The resulting styrene monomer was dried over anhydrous calcium sulphate for 5 hr then overnight with calcium hydride and molecular sieves successively in a refrigerator. Finally, the monomer was distilled under vacuum and degassed immediately prior to use.

**Table 3.6.** Analytical data of polymers made by polymerisation route.

| Polymer | C(%) | | H(%) | | Metal content (%) | |
|---|---|---|---|---|---|---|
| | Calc.* | Found | Calc.* | Found | Calc.* | Found |
| NaPA | 38.29 | 37.40 | 3.19 | 3.45 | 24.46 | 23.89 |
| KPA | 32.72 | 31.70 | 2.72 | 3.05 | 35.45 | 34.90 |
| MgPA | 43.37 | 42.98 | 3.61 | 3.85 | 14.45 | 15.23 |
| CaPA | 39.56 | 38.72 | 3.29 | 3.59 | 21.97 | 20.95 |
| ZnPA | 34.78 | 35.54 | 2.89 | 3.08 | 31.40 | 31.93 |
| CoPA | 35.82 | 35. 46 | 2.98 | 3.16 | 29.35 | 28.78 |

* Calculated.

## *7.3. PREPARATION OF STYRENE-ACRYLIC ACID COPOLYMER*

The copolymers were made by solution polymerisation in methanol. In a three-necked flask equipped with mechanical stirrer, condenser, thermometer and nitrogen inlet, dry methanol was introduced while the temperature was maintained between $0^{o}$ and 5 $^{o}$C under a gentle stream of oxygen-free nitrogen gas. Styrene and acrylic acid monomers were added gradually and the solution was left for 30 min under nitrogen flow to remove any dissolved oxygen. After addition of AIBN as initiator, polymerisation was carried out under a blanket of nitrogen at 60 $^{o}$C in a thermostated bath for at least 1.5 hr. The resulting solution was removed and the copolymer was precipitated in distilled water. The white solid was filtered, washed several times with distilled water and dried under vacuum at 50 $^{o}$C for 48 hr. The copolymerisation data are summarised in *Table 3.7.*

## *7.4. CALCULATION OF MOLE % ACRYLIC ACID*

### *7.4.1. Mole% Acrylic Acid in Monomer Feed*

In a solution of two components A and B, the mole fractions $X_A$ and $X_B$ are expressed as

$$X_A = \frac{n_A}{n_A + n_B} \qquad X_B = \frac{n_B}{n_A + n_B}$$

where $n_A$ and $n_B$ are the numbers of moles A and B in some given quantity of solution. The mole fractions, then, are such that $X_A + X_B = 1$

The mole fractions of acrylic acid in the monomer feed were calculated from the weights of styrene and acrylic acid used.

### *7.4.2. Mole% Acrylic Acid in Copolymer*

Copolymer compositions were calculated from the monomer feed concentrations using the copolymer equation[2]

$$F_1 = (r_1 f_1^2 + f_1 f_2) / (r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2)$$

where $F_1$ is the mole fraction of acrylic acid in the copolymer, $f_1$ and $f_2$ the mole fractions in the monomer feed of acrylic acid and styrene, respectively, and $r_1$ and $r_2$ the respective reactivity ratios for AA and styrene.

Values for $r_1$ and $r_2$ were those reported by *Chaplin et al*[173] and recalculated by *Greenley*[136]; $r_1$=0.136, $r_2$=0.253. The copolymer composition data are given in *Table 3.8*.

## *7.5. CHARACTERISATION OF THE COPOLYMER*

*Erdi* and *Morawetz*[137] studied the solution behaviour and rheology of neutralised styrene-methacrylic acid copolymers. They investigated the copolymer composition by titration of carboxylic acid groups.

Some investigators[138-140] have studied the composition of styrene-methacrylic acid copolymers using infrared and ultraviolet spectroscopy and *Kozluk et al*[141] have recently used proton magnetic resonance ($H^1$ NMR).

The styrene-acrylic acid copolymer samples were characterised using FTIR technique. *Fig. 3.4* shows the respective spectra obtained for the copolymers.

The characteristic bands of both styrene and acrylic acid are present in the 3200-625

$cm^{-1}$ spectral region. The bands at 3085-3026 $cm^{-1}$ are due to C-H stretching of aromatic group and the bands at 2925 and 2857 $cm^{-1}$ to C-H stretching of $CH_2$ and CH. The bands at 1740 and ~1705 $cm^{-1}$ are characteristic of the nonbonded and hydrogen-bonded carbonyl group in the acrylic acid segments of copolymer. The peaks at 1601, 1583 and 1493 $cm^{-1}$ are assigned as the ring stretching modes of the aromatic groups of styrene. The band at 1450 $cm^{-1}$ is related to the bending mode of methyl groups. Bands at 758 and 698 cm-1 are due to the out-of-plane C-H bending mode of the monosubstituted benzene. These data are consistent with those obtained by *Urban et al*[142], who studied the structure of styrene-acrylic acid copolymer using Fourier Transform Infrared Spectroscopy.

## *8. PREPARATION OF Na AND K SALTS OF ST/AA COPOLYMER*

The sodium and potassium salts of styrene-acrylic acid copolymer were obtained by neutralisation of the respective copolymer containing 40 mole % acrylic acid with the corresponding hydroxide.

### *8.1. NEUTRALISATION*

Appropriate amount of the styrene-acrylic acid copolymer was dissolved in acetone (solutions of 5-10 %) and then titrated with a standard solution of the respective hydroxide in methanol (about 0.5 N) with phenolphthalein as indicator. At the end point, pink solutions were obtained and were stirred for 3 hr (under nitrogen) to ensure that no retarded neutralisation reaction takes place. Blank titration of acetone was performed. The neutralisation solution was precipitated into 5 volumes of rapidly stirred acetone and the white solid copolymer was isolated and dried under vacuum at 40 $^{o}C$ for 72 hr.

Table 3.7. Copolymerisation data for ST/AA copolymer

| ST/AA copolymer | ST* | | AA** | | Methanol (ml) | Initiator (g) | Time (hr) | Conversion (%) |
|---|---|---|---|---|---|---|---|---|
| | (ml) | (g) | (ml) | (g) | | | | |
| 1 | 150 | 136.4 | 40 | 38.0 | 150 | 0.5 | 1.5 | 5.5 |
| 2 | 43 | 39.0 | 17.1 | 17.8 | 100 | 0.5 | 1.5 | 6 |

* Styrene monomer.

** Acrylic acid monomer.

**Table 3.8.** Composition data for ST/AA copolymer samples

| | Copolymer 1 | Copolymer 2 |
|---|---|---|
| Mole% AA in monomer feed | 30 | 40 |
| Mole% AA in copolymer | 40 | 45 |
| Conversion (%) | 5.5 | 6 |

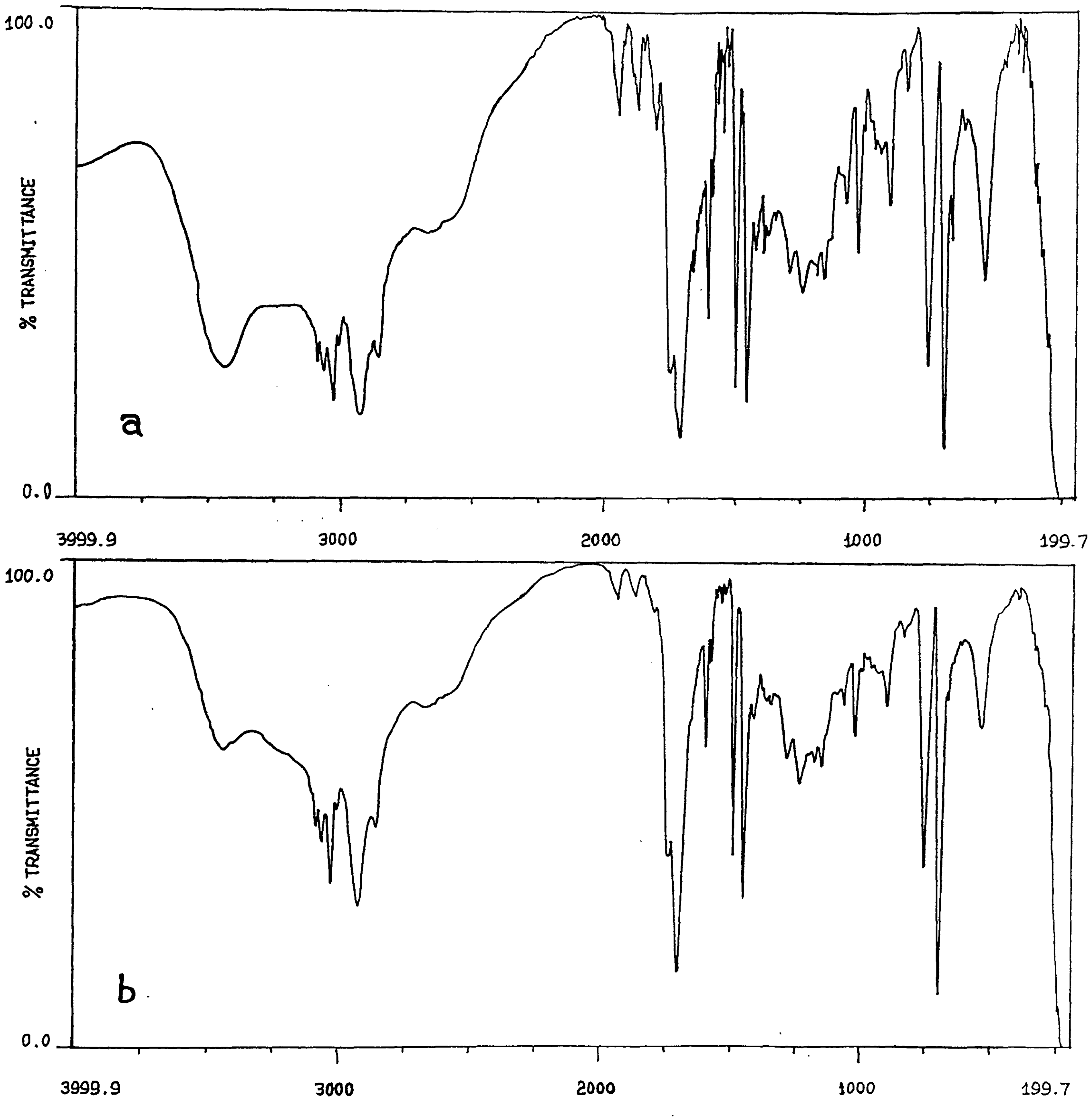


**Fig. 3.4.** FTIR spectra of the styrene-acrylic acid copolymers

a. ST/AA copolymer 1

b. ST/AA copolymer 2

## *8.2. CHARACTERISATION OF Na AND K SALTS OF ST/AA COPOLYMER*

The copolymers were characterised by FTIR spectroscopy. *Fig. 3.5* shows the FTIR spectra of the sodium and potassium acrylate-styrene copolymer samples.

The main bands of interest are those arising at about 1610-1500 and 1430-1300 $cm^{-1}$ due to conversion of carboxyl groups to carboxylate ions. There is significant indication of carboxylate formation, as shown in Fig . 3.5. The disappearance of bands at 1760 and 1700 $cm^{-1}$ due to nonbonded and hydrogen-bonded carbonyl groups is consistent with the formation of the salts. Since FTIR spectra show the absorptions due to carboxyl groups have decreased but not completely disappeared, this indicates that some unreacted acrylic acid units are present in the copolymers.

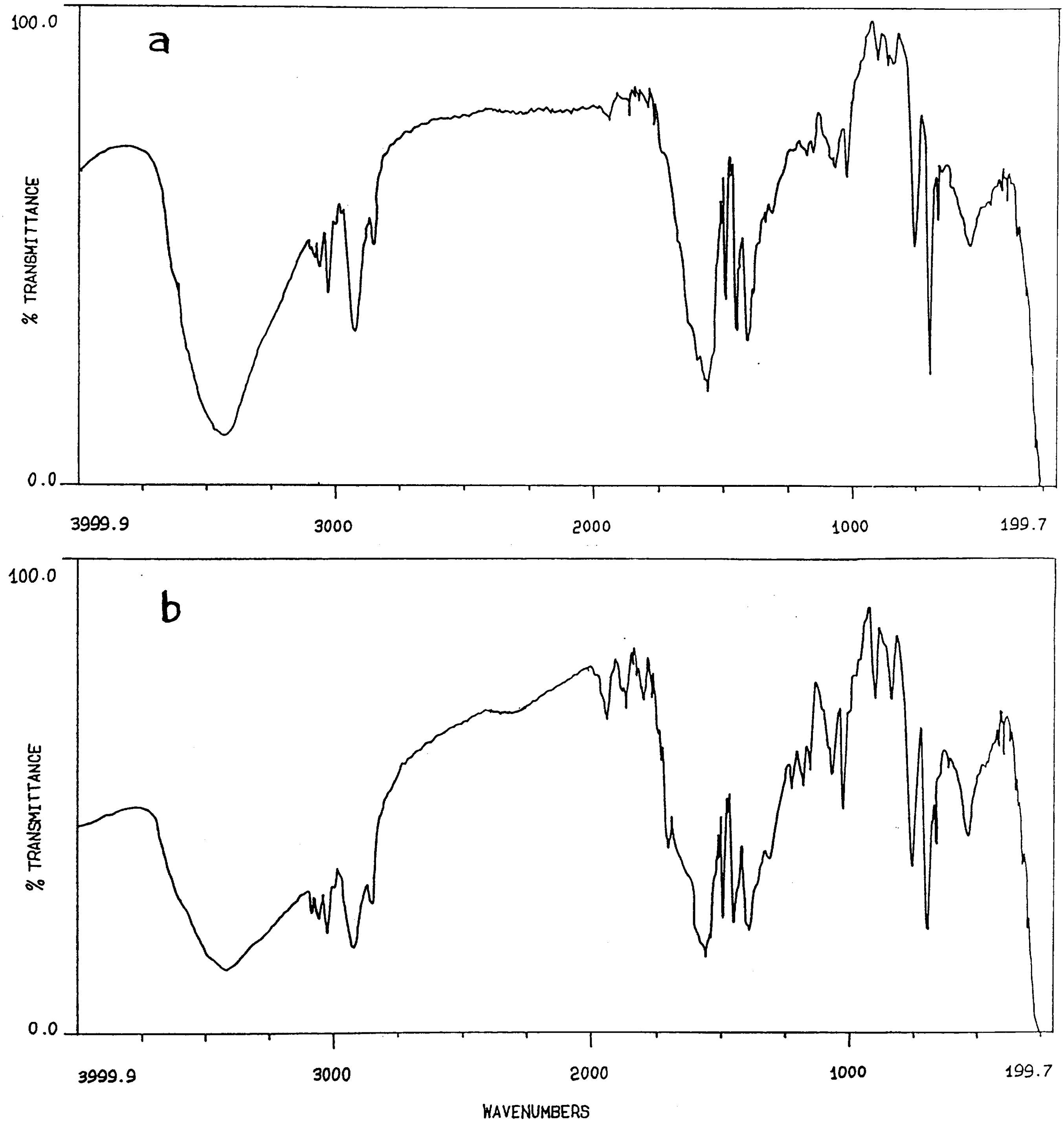


**Fig. 3.5.** FTIR spectra of the styrene-acrylic acid copolymers

**a.** ST/NaA copolymer

**b.** ST/KA copolymer

# CHAPTER FOUR

## THERMAL DEGRADATION OF POLY(ACRYLIC ACID)

### *1. INTRODUCTION*

### *1.1. GENERAL ASPECTS OF ACRYLIC ACID*

Acrylic acid is moderately strong carboxylic acid with dissociation constant of 5.5 x $10^{-5}$. The *two-stage oxidation* of propylene is the most economical process for the manufacture of this material. This acid is commercially available in better than 98% purity containing 10-200 ppm inhibitor.

*Phenolthiazine, hydroquinone*(HQ), or *hydroquinone monomethylether*(MEHQ) are commonly used inhibitors[74] which the effectiveness of the phenolic components (HQ,MEHQ) depends on the presence of oxygen. In general, the monomer should not be stored for longer than one year due to polymerisibility.

The acid is corrosive to many metals and should be stored in stainless steel, glass and aluminum vessels. It has relatively high freezing points, 13-14 $^{o}$C; because of this and the potentially violent polymerisation, the acid requires special handling conditions to avoid freezing and thawing.

### *1.2. POLYMERISATION*

Linear polymers of acrylic acid can be prepared using the general *free-radical* initiation systems used for other vinyl monomers.

Polymerisation in aqueous solution at less than 20-30% concentration is readily controlled. Polymerisation of highly concentrated pure acrylic acid can be very unsafe; the high heat of polymerisation can rise to values at which the polymer decomposes to generate gaseous products at a rapid rate; a hazard of explosion exists if the material is in a closed or poorly vented vessel.[75]

Acrylic acid monomer can polymerise in aqueous solution and nonaqueous media. In aqueous solution, it is preferable to use redox initiators such as ***persulfate bisulfite*** system at temperatures in the 50-70 $^{o}$C region.

Acrylic acid can be polymerised in nonaqueous solvents, such as benzene, which dissolve the monomer, but not the polymer. Initiators such as ***azobisisobutyronitrile*** (AIBN) are suitable .

### *1.2.1. COPOLYMERISATION*

Acrylic acid is readily copolymerised with many other monomers due to the combination of its highly reactive double bonds and its miscibility with both water-soluble and oil- soluble monomers.

### *1.2.2. SOLUBILITY*

The solid polymeric acid is very hygroscopic and it absorbs water rapidly on exposure to moisture. The polymer is insoluble in its monomer, but is very soluble in dilute bases. Poly(acrylic acid) is ***soluble*** to the extent of at least 1-2 pph W/V in water, dioxane, dimethylformamide, ethanol, methanol and isopropyl alcohol. Acetone, diethyl ether, benzene, and aliphatic hydrocarbons are nonsolvents for polymer.[76]

### *1.2.3. CHEMICAL PROPERTIES*

#### *1.2.3.1. Acid Strength*

Acrylic acid polymer is a weaker acid than the corresponding monomers. Hence, it is a good buffer in the pH range of 4 - 6.4.

#### *1.2.3.2. Cation Binding*

Alkali metal and other salts of acrylic acid are not readily converted to the free acid by ordinary dialysis.[77]

Cations behave as if bound to the polymer; this is due to the strong electrostatic forces surrounding regions of a cation bearing many ionised carbonyl groups. As a result, the cations spent much their time close to (bound to) the polymeric anion.

This ion binding increases with extent of *ionisation,* with decreased size (ie, increased charge density) of the cation, and with increased acid strength of the ionisable groups on the polymer chain.[78]

*Multivalent* cations are bound more firmly and extensively than are *univalent* ions.[79]

### *1.3. USES*

Acrylic acid polymer and copolymers are used in field as varied as mining, textile and paper manufactures, cosmetics, adhesives, oil well drilling, agricultural soil modification, water clarification and dental cements.

## *1.4. PREVIOUS WORK ON THERMAL DEGRADATION OF PAA*

The main features of the thermal degradation of poly(acrylic acid), PAA, have been known for many years, but certain aspects of the degradation products and mechanism at higher temperatures (above 300 $^{o}$C) still remain the subject of discussion.

*Otsu and Quach*[80] examined the differences in the thermal degradation of ***head-to-head*** and ***head-to-tail*** poly(acrylic acid) by using thermogravimetry. They showed that h-h poly(acrylic acid) degrades at lower temperatures and in a different manner from h-t PAA, the degradation of which becomes discernable at 150 $^{o}$C and proceeds in two steps.

*Eisenberg et al*[81], who studied the degradation kinetics and glass transition temperature of poly(acrylic acid) have shown that anhydride formation in PAA is a first order reaction, as also is decarboxylation, the latter being much slower than the former.

The thermal characterisation of PAA has been studied by *Maurer et al*[82], who reported that atactic and syndiotactic PAA appear to differ significantly with regard to glass transition temperature and thermal stability. They have shown that maximum water evolution (due to anhydride formation) and carbon dioxide evolution (due to anhydride decomposition) occur at about 170$^{o}$ and 230 $^{o}$C, respectively, in PAA (atactic) vs. ~200$^{o}$ and ~260 $^{o}$C,respectively, in PAA (syndiotactic). They assumed that these differences may be a direct consequence of tacticity or possibly an indirect effect due to enhanced hydrogen bonding in the syndiotactic polymer.

*Roux et al*[83], who studied the pyrolysis of PAA and poly(methacrylic acid), PMAA, in the range 160-240 °C in a non-oxidation atmosphere, suggested that the kinetics of evolution of light products indicate a competition between dehydration and decarboxylation reactions. They believed *water, carbon dioxide* and *monomer* (PMAA only) were the products of pyrolysis of PAA and PMAA in that temperature range. No formation of *carbon monoxide* or acrylic acid *monomer* was observed.

*Grant* and *Grassie*[84] showed that six-membered glutaric anhydride type rings result from intramolecular reaction of adjacent carboxyl groups in the decomposition of h-t PMAA at about 200 °C. This dehydration reaction was found to be accompanied by a small amount of depolymerisation to monomer.

Some investigations were extended to higher temperatures (above 250 °C) in order to obtain further information on the degradation process. For example, *McGaugh* and *Kottle*[85] investigated the thermal degradation of PAA in air. They reported that on the range 25-150 °C, the major reaction is the formation of anhydride groups, then at 150-275 °C unsaturation begins to appear, as well as structures indicated from the infrared absorption to be ester or cyclic ketone. They also noted that above 350 °C, the unsaturation becomes very evident. The same workers[86] have also examined the thermal degradation of acrylic acid-ethylene copolymers, using TG and TVA. They reported that the degradation mechanism of the acrylic acid portions of the copolymer consisted of dehydration of the acid groups forming anhydride, followed by decarboxylation of the anhydride leading to unsaturation.

*Nicholson et al*[87-89] have recently studied the thermal behaviour of partially neutralised PAA at 250 °C. They showed that different chemical processes, namely dehydration and decarboxylation, occur at this temperature depending on the nature of the counterion.

## *1.5. AIM OF THIS WORK*

In the present work, the thermal behaviour of poly(acrylic acid) has been investigated using the TVA and TG techniques to provide a basis for a series of studies of the degradation of PAA salts using the same experimental approach.

The degradation studies were also carried out by using two approaches. Programmed heating was carried out at 10 $^{o}$C/min to temperatures from 170-500 $^{o}$C and the polymer was also heated isothermally at 210 $^{o}$C for different times, under TVA conditions.

Quantitative measurements of the main product fractions have been made. The gaseous, volatile liquid and cold ring fraction (CRF) products from the TVA degradation have been analysed by IR, MS (mass spectrometry) and GC-MS techniques.

# *2. THERMAL DEGRADATION*

Thermal behaviour of two poly(acrylic acid) samples have been investigated; ie, laboratory prepared PAA as described in Chapter Three and a commercial sample (Aldrich), in powder form, with Mw 250,000, Tg 106 $^{o}$C which was used without further purification, for comparison with the laboratory one.

### *2.1. PROGRAMMED HEATING EXPERIMENT*

#### *2.1.1. Thermal Volatilisation Analysis*

The polymers were examined as 70 mg powder samples in a TVA system under vacuum as described in Chapter Two. Programmed heating was at a rate of 10°C/min. The TVA curves for both polymers are shown in *Fig. 4.1.*

It is clear from these curves that in each case decomposition begins at about 175 °C, but appreciable rates of breakdown are observed only above 200 °C. Both polymers show a *three stage decomposition* and from inspection of the separation of the traces, it is evident that product composition is different at each stage, the product volatility becoming greater as the degradation temperature rises. In particular, *non-condensable gases* are only formed only above about 300 °C, in which temperature region the presence of materials covering a wide range of volatilities is indicated.

In degradation below 300 °C, the volatile material produced consists almost entirely of substances condensable at -196 °C (liquid nitrogen trap). This stage of decomposition is mainly due to dehydration and decarboxylation processes.

There is no major difference in behaviour between the commercial and laboratory samples on the basis of the TVA data. The TVA results for both polymers are nearly the same, not only in respect of presence of the degradation peaks below 300 °C, but also in the character of the degradation products, as revealed by their volatility in the TVA system.

Gravimetric data were obtained under TVA conditions in experiments in which the polymer sample was placed in a thin glass, flat-bottomed sample tube, 25 mm base diameter, weighed before and after the experiment, placed inside the TVA tube and in contact with its flat base. Data are shown in *Table 4.1.* Quantitative measurement of carbon dioxide evolution was carried out by a calibration method previously described.[90]

### *2.1.2. Subambient Thermal Volatilisation Analysis (SATVA)*

Condensable volatile degradation products from polymer samples degraded to 500 °C using the TVA technique, collected in a liquid nitrogen trap in the vacuum system, were separated by the SATVA method[91], by allowing the trap to warm up from -196 °C to ambient temperature in a controlled manner, with continuous removal of volatile products monitored by following the pressure change using a Pirani gauge. A SATVA trace for the products from the laboratory PAA sample is shown in *Fig. 4.2.* Products corresponding to each SATVA peak were collected separately for identification.

### *2.1.3. Product Analysis*

The -196 °C condensable products of degradation separation into fractions by the SATVA technique were collected in gas cells and cold fingers. The degradation products were identified by infrared spectroscopy, mass spectrometry and GC-MS techniques.

The use of several techniques was required since interpretation of the spectra is difficult as each fraction contains a mixture of products. In this investigation, minor products from degradation of PAA to 500 °C, present as a liquid associated with the last fractions of the SATVA separation, were examined by GC-MS. The degradation products are listed in *Table 4.2.*

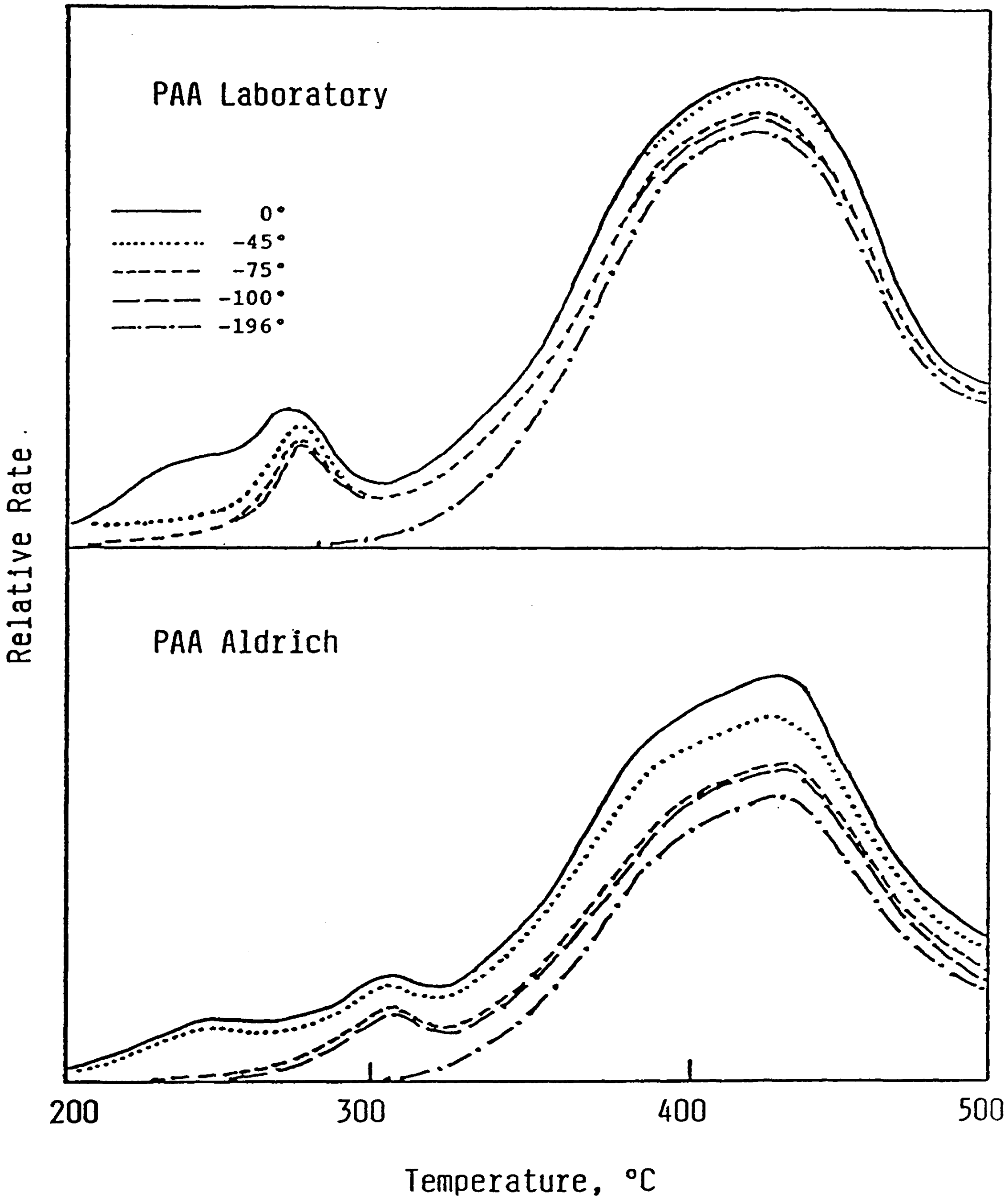


**Fig.4.1.** TVA curves for laboratory and commercial PAA samples, heating rate 10 °C/min.

**Table 4.1.** TVA data for commercial and laboratory PAA samples, degraded under programmed heating conditions to 500 °C.

| polymer | $T_{onset}$ °C | $T_{max}$ °C | Wt % residue | Wt % CRF | Wt % volatile fraction $CO_2$ | $H_2O$ | other | Ratio of volatile/ CRF products |
|---|---|---|---|---|---|---|---|---|
| PAA (Aldrich) | 190 | 435 | 12.5 | 28.9 | 26.5 | 29.2 | 2.9 | 2.0 |
| PAA (laboratory) | 190 | 435 | 9.2 | 38.2 | 25.7 | 24.5 | 2.4 | 1.4 |

Cold ring fraction (*light brown waxy*) products, which collected on the cooled upper part of the TVA tube or on an inserted cold finger,were removed using a volatile solvent. These were examined by mass spectrometry; products identified are listed in *Table 4.3*.

The CRF quantities which amount to approximately 30% of the sample weights and their proportions from the volatile products are clearly indicative of the importance of backbone scission, in addition to dehydration and decarboxylation, during the thermal degradation of the polymers.

The cold ring fractions were light brown waxy materials with rather similar ir spectra,*Fig. 4-2a*, showing peaks at;

| | |
|---|---|
| 3020 $cm^{-1}$ (shoulder) | olefinic C-H stretching |
| 2920, 2880 $cm^{-1}$ | C-H stretching for CH, $CH_2$ |
| 1690-1740 $cm^{-1}$ (broad) | C=O stretching for carbonyl |
| 1640 $cm^{-1}$ (shoulder) | C=C stretching |
| 1440 $cm^{-1}$ (s) | C-O stretching |
| 1380 $cm^{-1}$ (w) | C-H bend |
| 1380-1440 $cm^{-1}$ | OCO stretching |
| 1270 $cm^{-1}$ | O-H bend |
| 1240 $cm^{-1}$ | C-C stretching |
| 1150-1250 $cm^{-1}$ | C-O stretching |
| 820 $cm^{-1}$ | |

these bands are consistent with the ir spectrum of acrylic acid monomer. Since the monomer is unlikely to appear in CRF, and weak bands at 1640 and 3020 $cm^{-1}$ indicate the presence of carbon- carbon double bond, these materials are *short chain fragments* (oligomer), which are sufficiently volatile to escape from the hot zone and appear as CRF. The presence of anhydride type structures in CRF was also

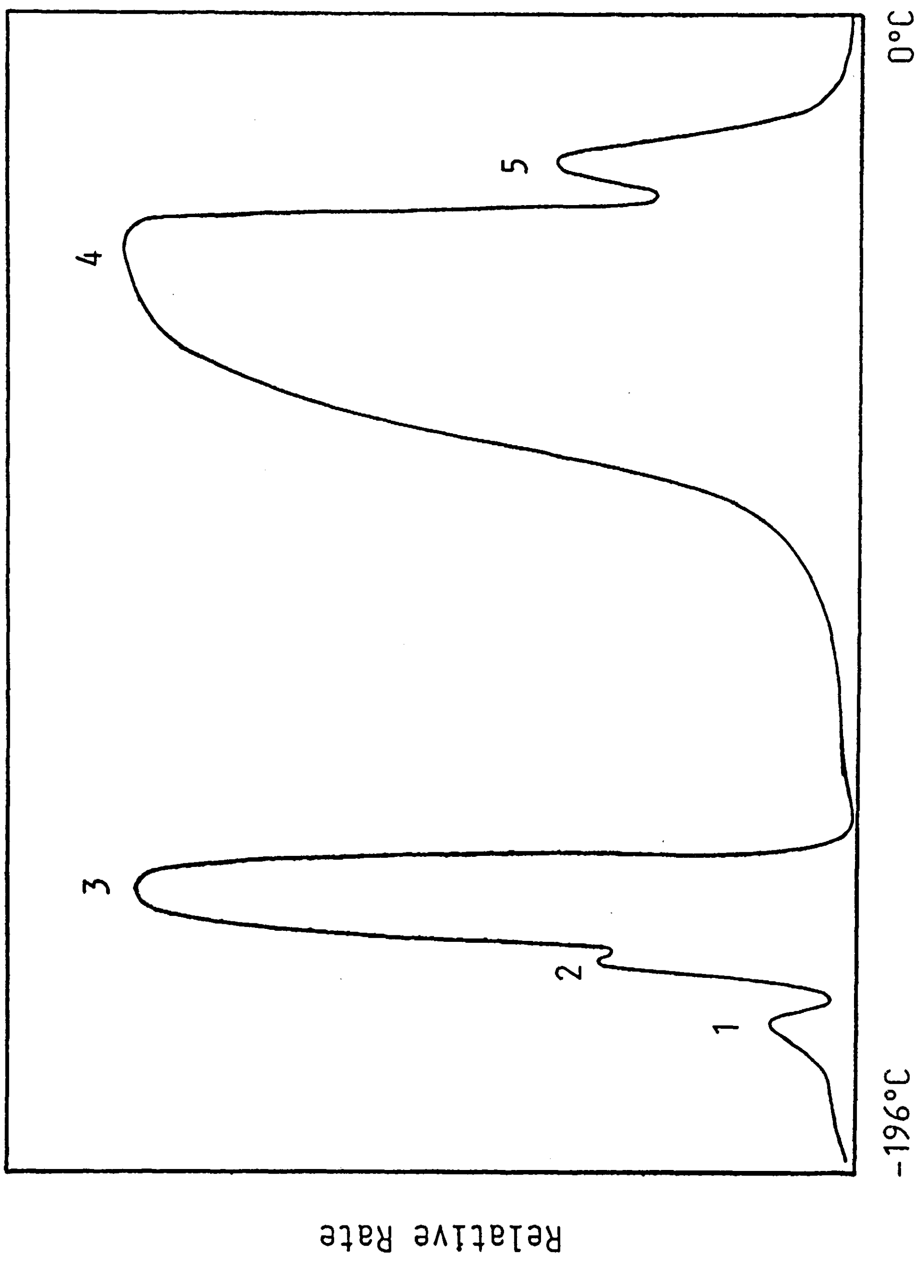


**Fig. 4.2.** Subambient TVA for warm-up from -196 °C to room temperature of condensable volatile products of degradation to 500°C under TVA conditions of laboratory PAA sample. See Table 4.2 for corresponding product assignments: peaks 1 to 3 comprise the gases and volatile liquids and peaks 4 and 5 the less volatile liquid fraction.

**Table 4.2.** Products of PAA degradation to 500 °C in the TVA system under vacuum using programmed heating.

| polymer | Gases and volatile liquids | | | other liquids | | Cold Ring Fraction | Residue |
|---|---|---|---|---|---|---|---|
| | non-condensable* at -196 °C | condensable at -196 °C | | major | minor* | | |
| | | major | minor* | | | | |
| PAA (laboratory) | $CH_4$<br>CO | $CO_2$ | Acetone<br>Ketene<br>Ethylene<br>Propylene<br>Butene-1<br>Methyl vinyl ketone<br>Benzene | $H_2O$ | Acrylic acid<br>Toluene<br>Xylene | Short chain fragments such as dimer, trimer, etc., including anhydride rings | Black char |
| PAA (Aldrich) | $CH_4$<br>CO | $CO_2$ | Acetone<br>Ketene<br>Ethylene<br>Propylene<br>Butene-1<br>Benzene<br>Toluene<br>Methyl vinyl ketone | $H_2O$ | Acrylic acid | Short chain fragments such as dimer, trimer, etc., including anhydride rings | Black char |

* Weight per cent of these products amounted to 3% of sample weight.

**Table 4.3.** Products identified in the cold ring fraction from degradation of laboratory PAA under TVA conditions to temperature shown.

| Product* | m/e | Temperature of CRF fraction | |
|---|---|---|---|
| | | 375°C | 400 or 500°C |
| Unsaturated and saturated anhydride dimer | 126, 128 | present | present |
| Unsaturated and saturated acid dimer | 144, 146 | " | " |
| Unsaturated and saturated acid/ anhydride trimer | 198, 200 | " | " |
| Unsaturated acid trimer | 216 | " | " |
| Unsaturated and saturated anhydride tetramer | 252, 254 | " | " |
| Unsaturated and saturated tetramer with acid/anhydride/acid sequence | 270, 272 | " | " |
| Unsaturated acid tetramer and pentamer | 288, 360 | " | " |
| Unsaturated anhydride hexamer | 378 | " | " |
| Unsaturated hexamer with acid/ anhydride/acid/anhydride sequence | 396 | " | " |
| Unsaturated acid hexamer and heptamer | 432, 504 | absent | " |
| Unsaturated anhydride octamer | 504 | absent | " |

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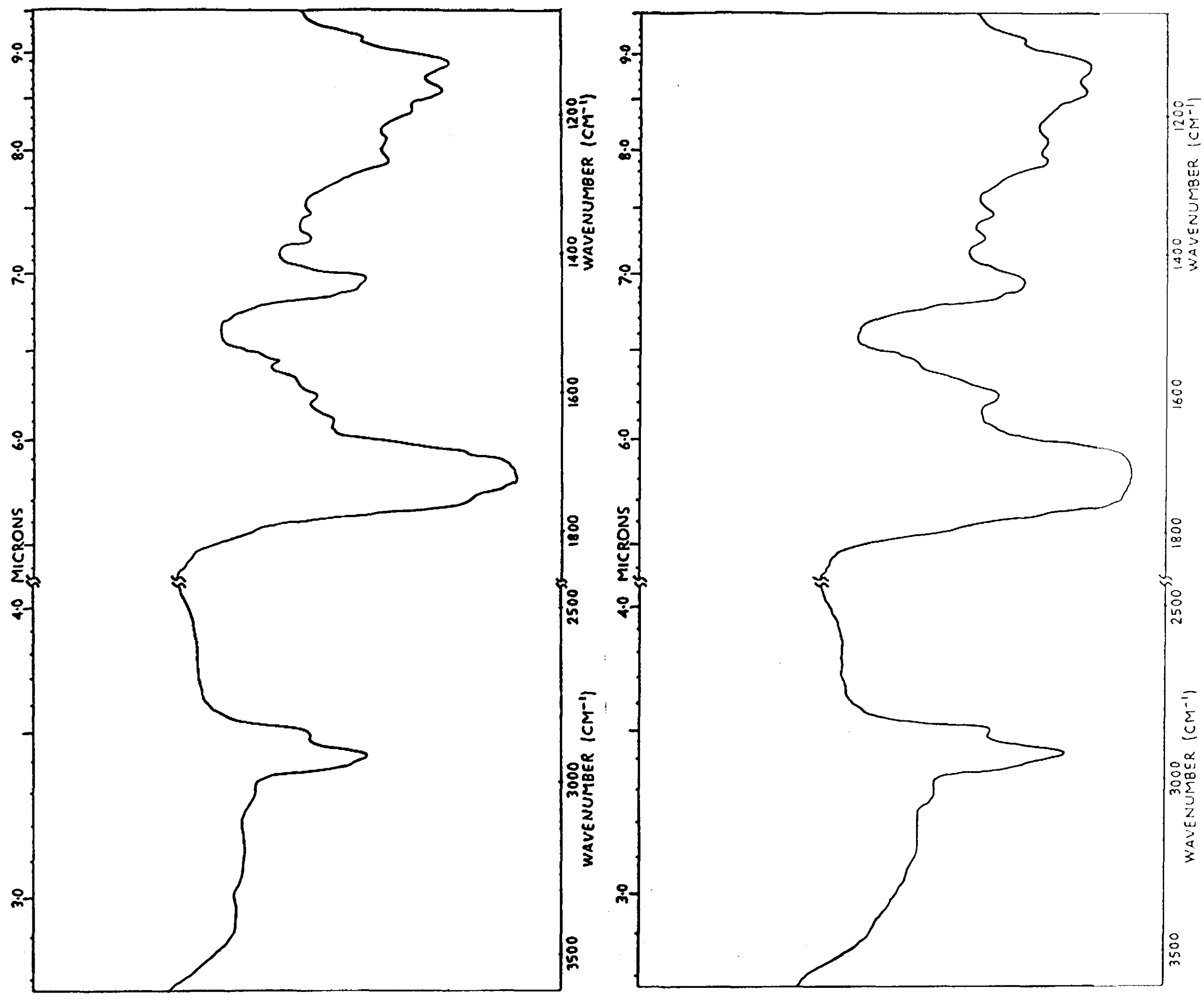
* For corresponding chemical structures, see mechanism section of text.



a

b

Fig. 4.2a. IR spectra of CRF of PAA samples.

a. Laboratory-made PAA sample.

b. Commercial PAA sample.

demonstrated by using preparative TLC (thin layer chromatography) and mass spectrometric techniques.

### *2.1.4. Partial Degradation under TVA Conditions*

The polymers were partially degraded in order to permit quantitative determination of carbon dioxide and water at different stages of decomposition. Programmed heating at 10 $^{o}$C/min was used and samples were heated to temperatures corresponding to the end of each stages of reaction as shown in the TVA curves for heating to 500 $^{o}$C, illustrated in Fig.4.1.

Corresponding data are shown in *Table 4.4*. It appears likely that evolution of carbon dioxide increases gradually due to the decarboxylation process, as the degradation temperature increases.

## *2.2. THERMOGRAVIMETRY*

The TG and DTG curves obtained under dynamic nitrogen at 10 $^{o}$C/min heating rate, shown in *Fig.4.3*, indicate two stages of breakdown, starting at about 200$^{o}$ and 330 $^{o}$C, respectively. An initial weight loss below 100 $^{o}$C in the case of the commercial sample is due to release of water absorbed by the polymer.

The first stage of breakdown (to 330 $^{o}$C) accounts for about 35% and 33% weight loss, respectively, in the commercial and laboratory PAA samples; the corresponding overall weight losses (to 500 $^{o}$C) are 85% and 86%. The TVA and TG results are in reasonable agreement.

### *2.3. CHANGES in IR SPECTRA during DEGRADATION of PAA*

For this part of the investigation, polymer *films* were made by dissolving 5 mg of PAA in AR methanol, casting a thin film on a Teflon sheet and drying in a vacuum oven at 40 °C for 24 hr.

**Table 4.4.** Quantitative data for major volatile degradation products at different extents of degradation in the TVA system under programmed heating(10°/min)

| Stage of Degradation | PAA (Aldrich) | | | PAA(Laboratory) | | |
|---|---|---|---|---|---|---|
| | T,°C | Wt% $CO_2$ | Wt% $H_2O$ | T,°C | Wt% $CO_2$ | Wt% $H_2O$ |
| 1st | 275 | 5.5 | 12.8 | 285 | 12.9 | 14.0 |
| 2nd | 320 | 8.5 | 3.8 | 470 | 14.7 | 16.6 |
| 3rd | 470 | 12.5 | 12.6 | — | — | — |
| Total Wt.% | | 26.5 | 29.2 | | 27.6 | 30.6 |

The polymer was *partially* degraded under vacuum at 10 °C/min heating rate to 170°, 200°, 210°, 230°, 260°, 290°, 350°, 380° and 440 °C, respectively. A 5 mg film was heated progressively to each of the above temperatures and the ir spectrum was recorded at each stage.

The main bands of interest are those arising at about 1805,1760 and 1040 $cm^{-1}$ due to conversion of some of the carbonyl groups to anhydride rings[83,85] ,as shown in *Fig.4.4.*

There is no significant indication of anhydride formation at 170 °C, but this structure increases gradually from 200° to 290 °C.

*Anhydropoly(acrylic acid)* is the main product obtained from heating at 260 °C. Above this temperature, the increase in carbon dioxide evolution already noted means that the anhydride structures formed are beginning to decompose. At temperatures above 290 °C, the IR absorptions due to anhydride decrease.

In the same temperature region, ketone and hydrocarbon minor products can be detected and the film, which is still white at 290 °C, becomes yellow at 350 °C and brown at 440 °C.

## *2.4. ISOTHERMAL EXPERIMENTS*

A 5 mg film of the polymer was degraded *isothermally* at 210 °C under vacuum in the TVA system for different periods. The ir spectrum was recorded in each case; the results are shown in *Fig.4.5.*

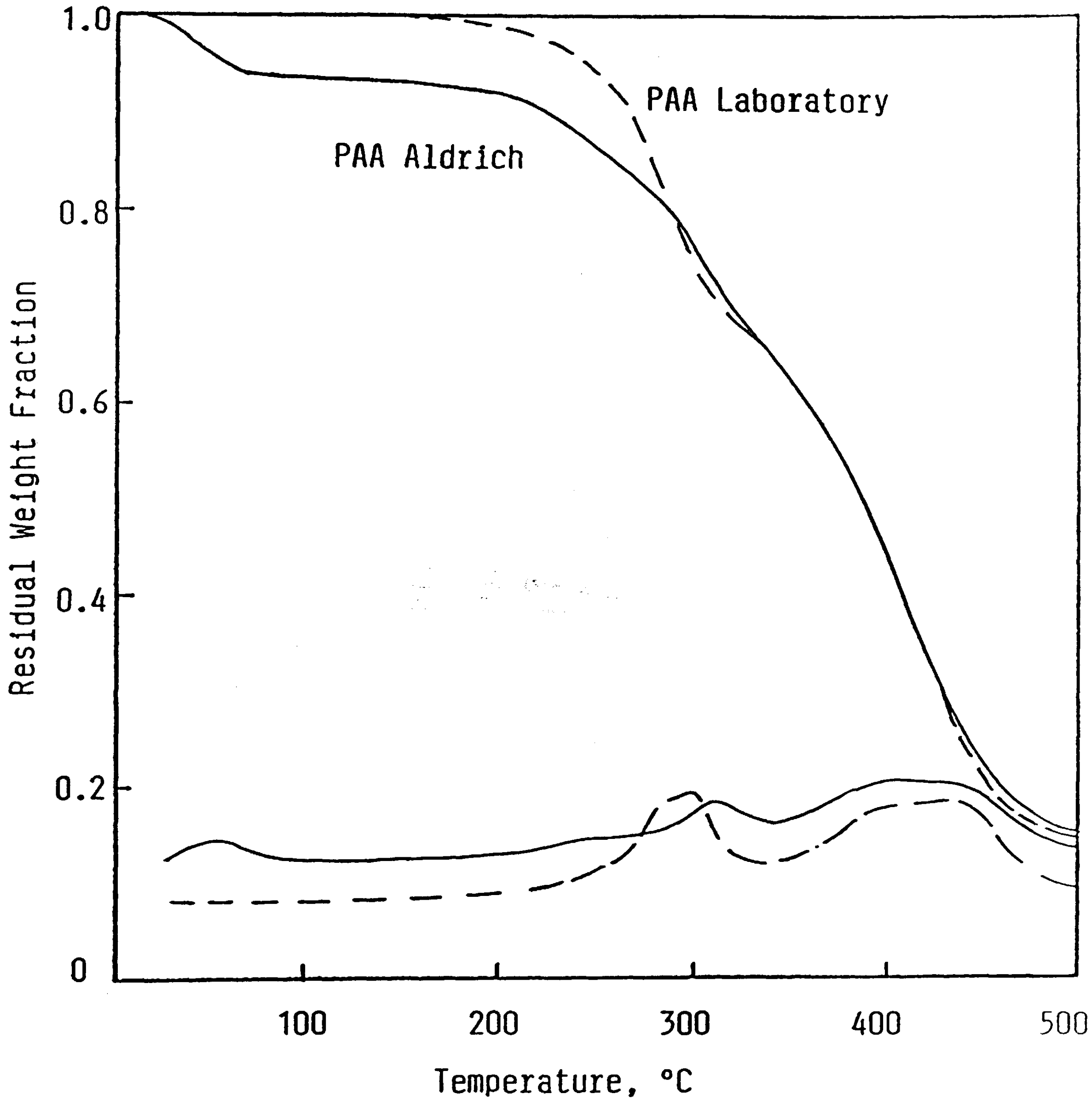


Fig. 4.3. TG and DTG curves for laboratory (-----) and commercial (——) PAA samples. Dynamic nitrogen atmosphere, heating rate 10°C/min.

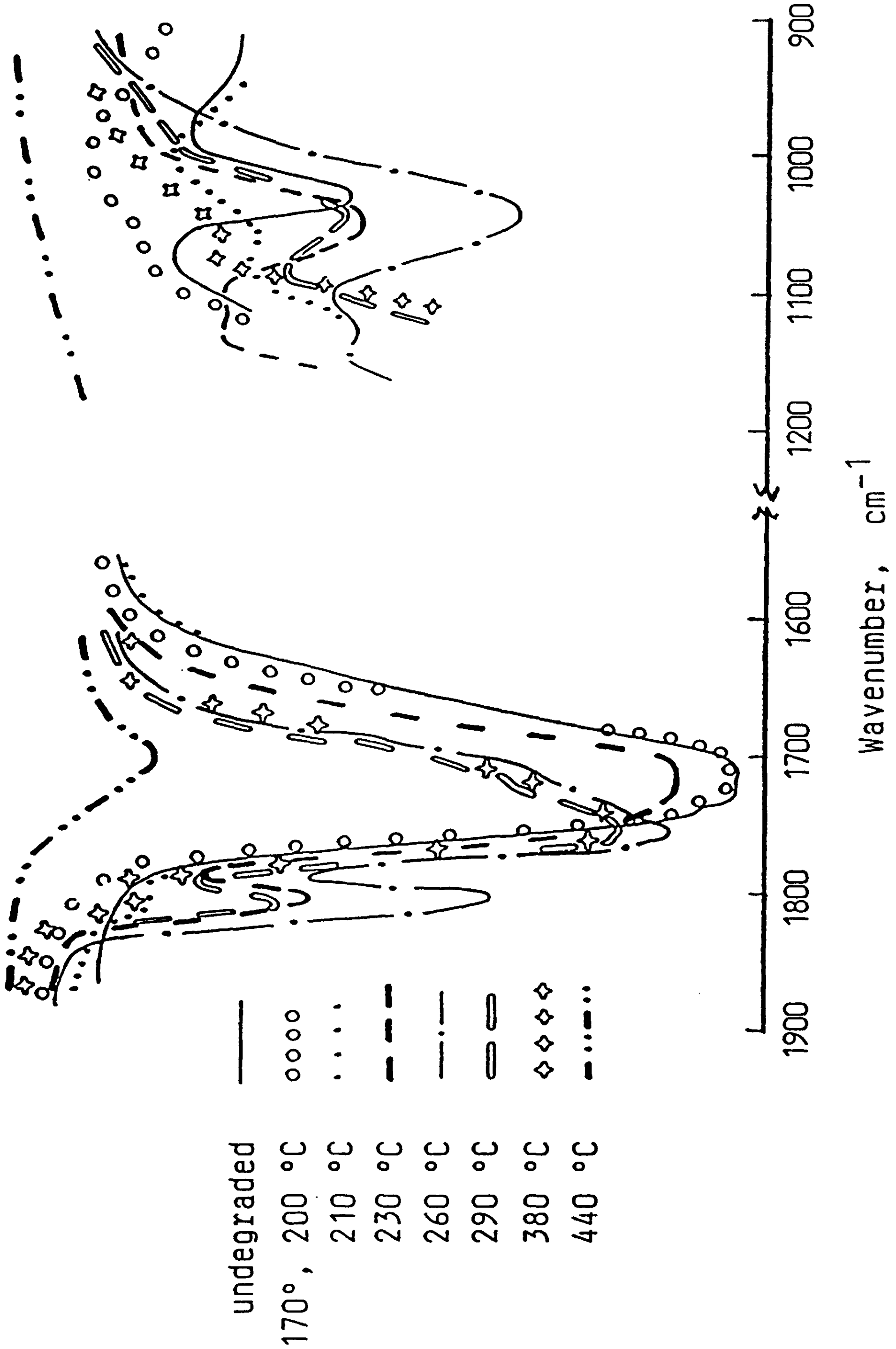


**Fig.4.4.** Infrared spectra of undegraded commercial PAA and films degraded to various temperatures in the TVA system under programmed heating.

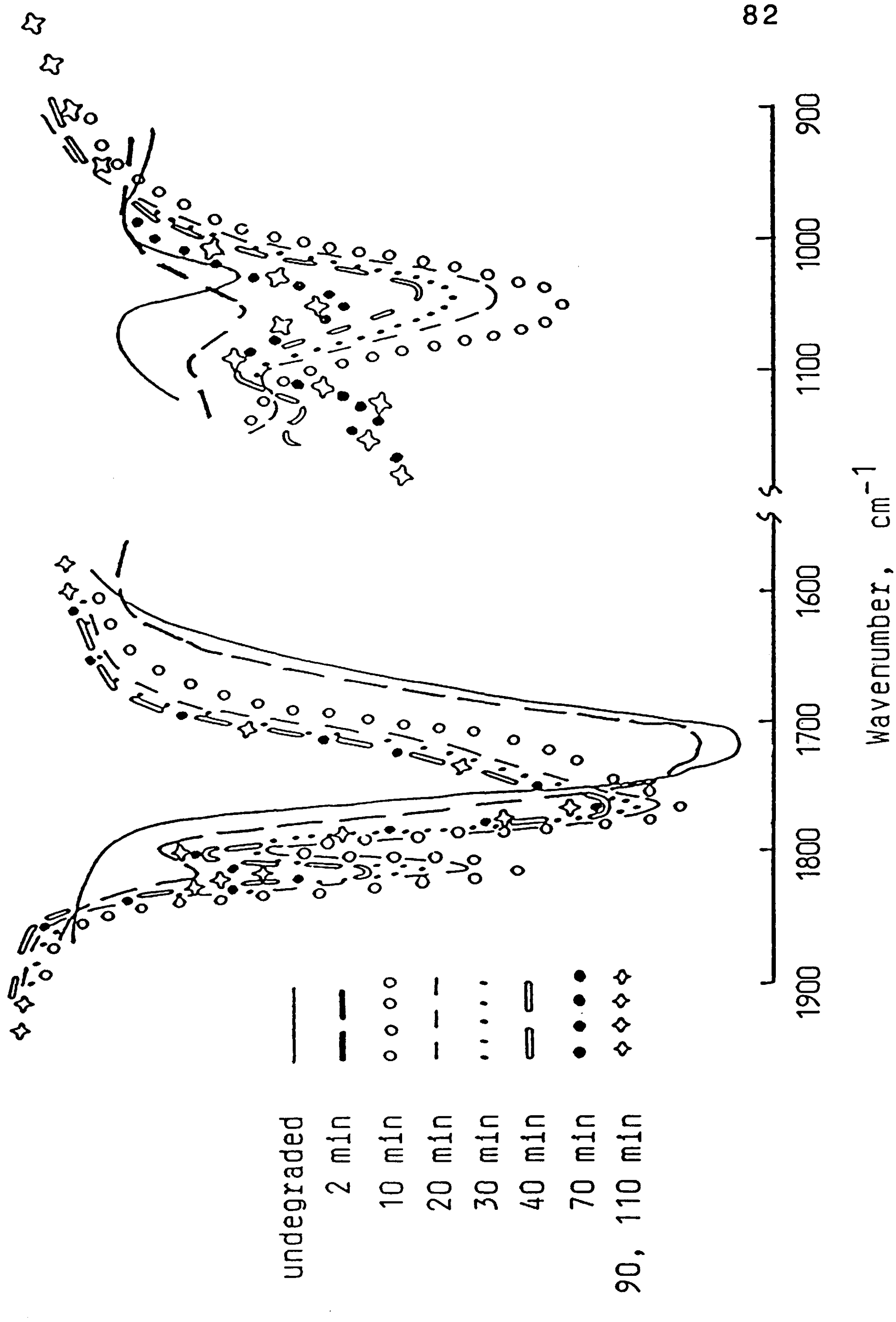


**Fig.4.5.** Infrared spectra of undegraded commercial PAA and films degraded for various periods at 210$^{0}$C in the TVA system.

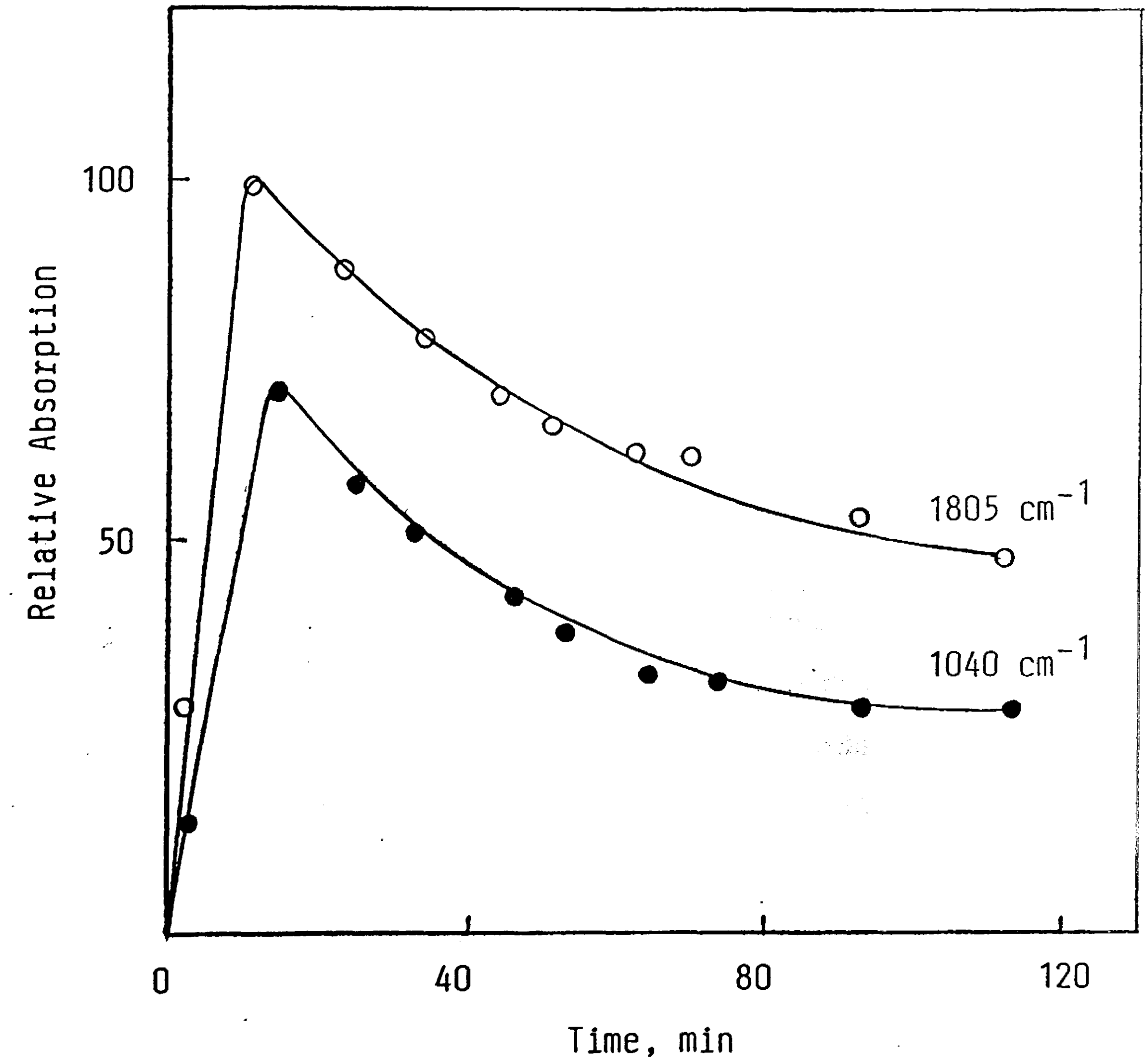


**Fig.4.6.** Variation of anhydride absorption intensities at 1805 and 1040 $cm^{-1}$ in commercial PAA film with time of heating at 210 °C.

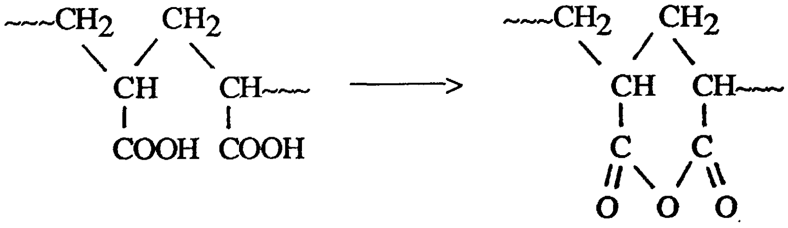
The most notable feature is again the appearance of strong anhydride absorptions. It is evident that the anhydride concentration reaches a maximum after 10 min heating at this temperature. The rapid rise and subsequent slow decline in anhydride concentration as a function of time, at 210 °C, as shown by intensities of absorption at 1805 and 1040 $cm^{-1}$, respectively, are illustrated in *Fig.4.6*.

## *3. MECHANISM OF DEGRADATION*

Three main processes may be discerned in the decomposition of poly(acrylic acid), namely *dehydration*, *decarboxylation* and *chain scission*.

### *3.1. DEHYDRATION*

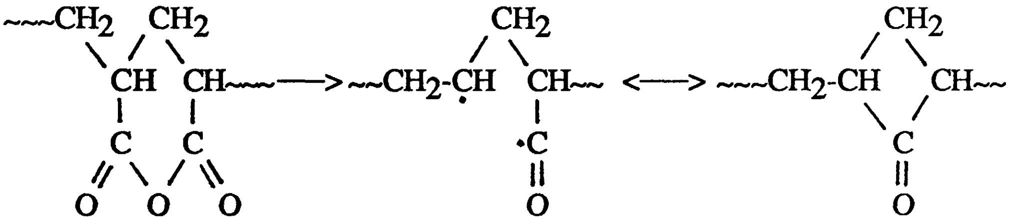
This could occur by *intra-* or *intermolecular* reaction of carboxyl groups. The nature of the reaction has been discussed.[81,83,84,89] It appears that the reaction temperature is of major importance, temperatures above 200 °C being required for intermolecular reaction to occur, probably between *COOH* groups left *isolated* after random intramolecular dehydration involving adjacent monomer units occurring at lower temperatures. The intramolecular reaction leads to the formation of six-membered glutaric anhydride type rings:



In this study, the TVA data indicate that water evolution commences at about 170 °C and reaches maximum rate around 250 °C, under programmed heating conditions.

### 3.2. DECARBOXYLATION

Decarboxylation is evident at temperatures above 200 °C and has been found to become increasingly important above 250 °C. Carbon dioxide evolution due to anhydride decomposition can be envisaged as occurring as follows :

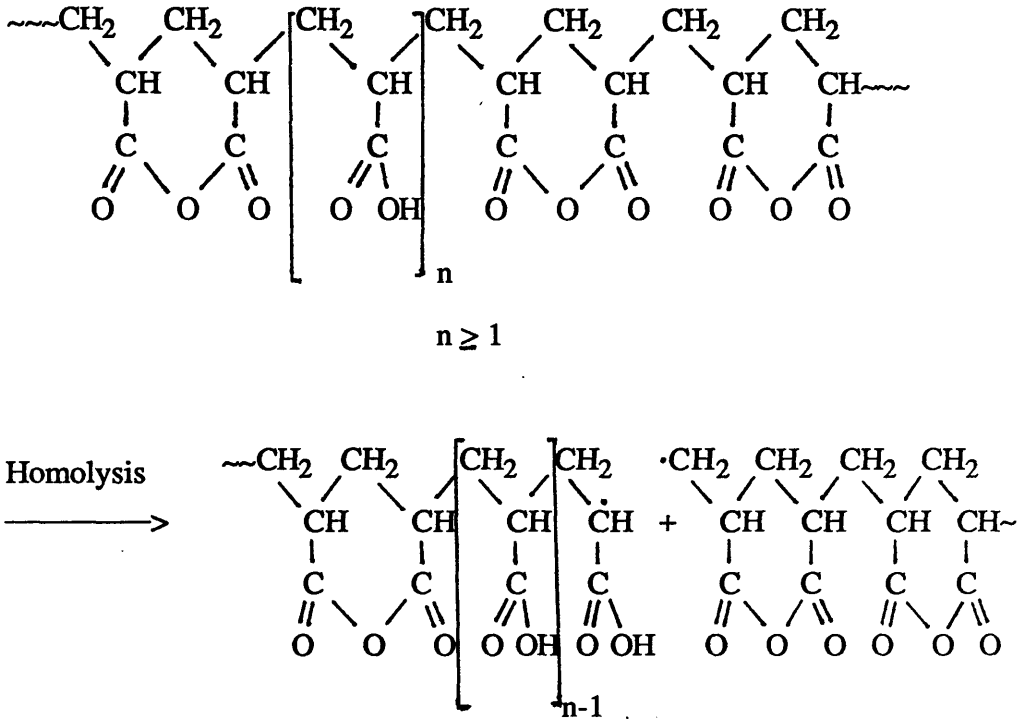


(I)

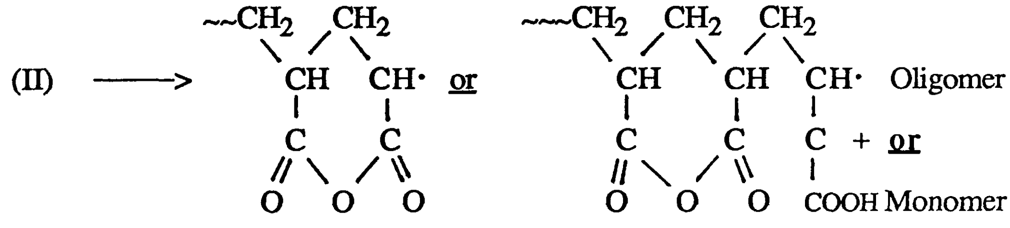
At high temperatures, the postulated intermediate species (I) can be regarded as the source of minor products of degradation amounting to about 3% of the sample weight, such as carbon monoxide, ketene, ketones and saturated compounds, in reactions in which it undergoes fragmentation.

### 3.3. CHAIN SCISSION

The formation of significant amounts of cold ring fraction, consisting of *dimer, trimer, etc.*, at high temperatures is possibly due to release of fragments with short sequences of acrylic acid units, previously isolated between anhydride rings. Chain scission may occur at points adjacent to the anhydride rings, followed by further reaction of the macroradicals so formed :

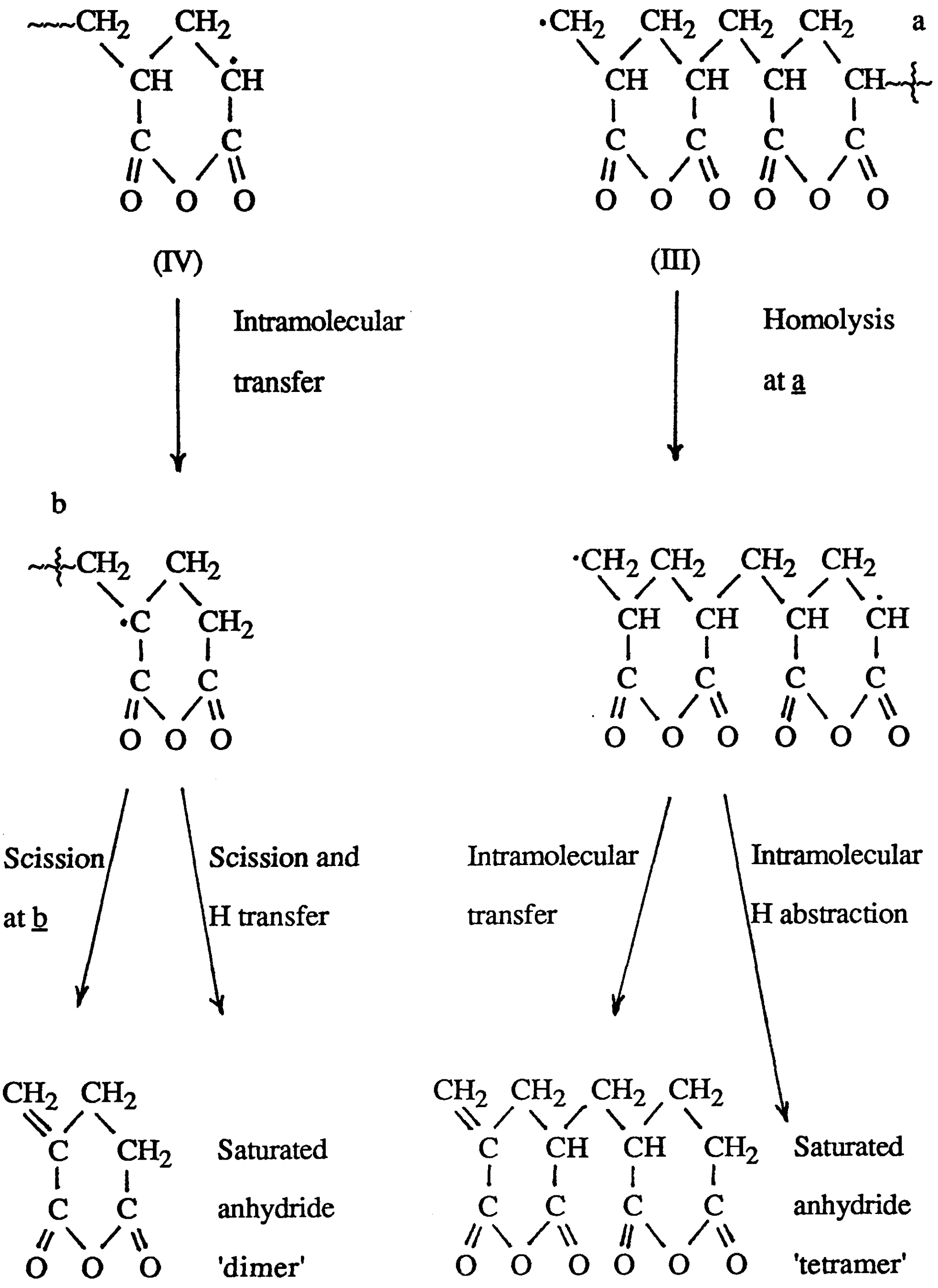


(II) (III)



(IV) (V)

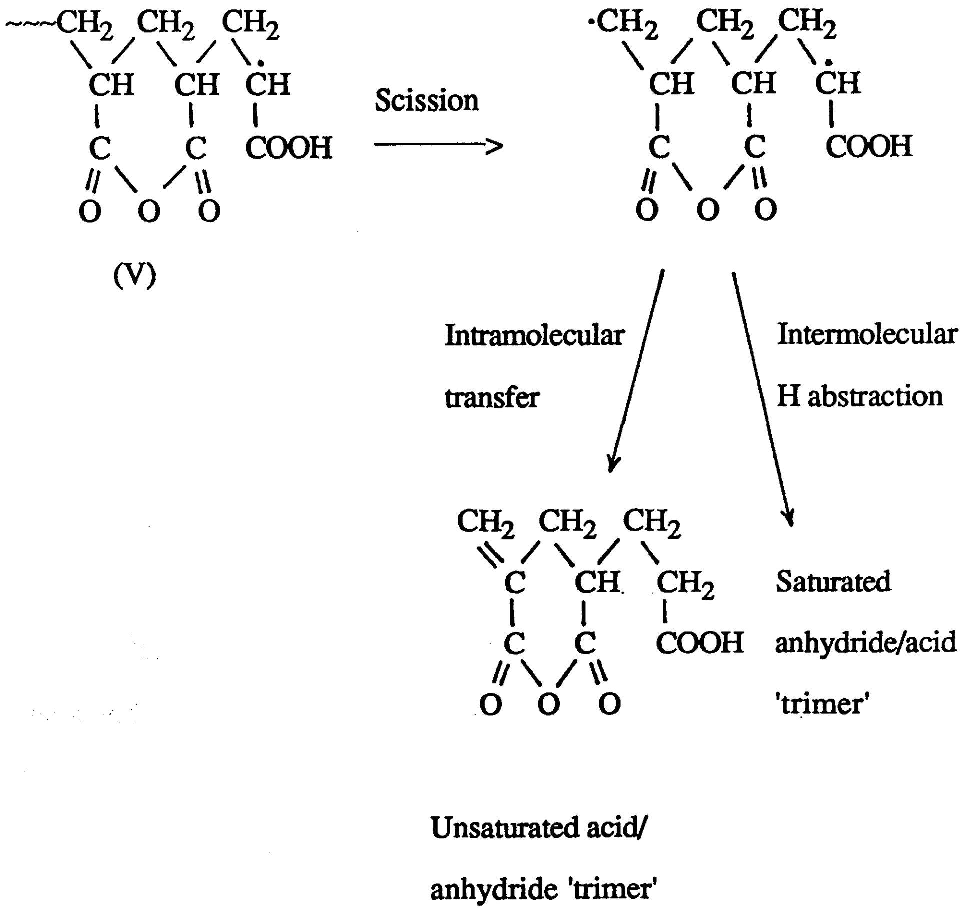
The other fragments of the CRF shown in Table 4.3 may form in reactions in which macroradicals (III), (IV) and (V) undergo homolysis and hydrogen transfer. In case of radicals (III) and (IV), the CRF products are purely anhydrides :



Unsaturated
anhydride
'dimer'

Unsaturated
anhydride
'tetramer'

Similar reactions of radical (V), however, lead to the CRF products containing both anhydride rings and carboxylic acid structures :



## *4. CONCLUSIONS*

The thermal degradation of poly(acrylic acid) commences with a dehydration reaction occurring by intramolecular cyclisation of adjacent monomer units to give six-membered anhydride ring structures. Decarboxylation to give carbon dioxide as a product becomes important under programmed heating conditions at about 250 °C and both water and carbon dioxide continue to be evolved in heating up to 500 °C. A number of other volatile products, including monomer, are formed, but only in trace amounts.

Under isothermal heating at 210 °C, it is found that the anhydride concentration builds up rapidly during the first 10 minutes of heating, but reaches a maximum after which there is a slow decline due to decarboxylation.

Above 300 °C, the elimination of water and the decarboxylation process seem consistent with the occurrence of both intra- and intermolecular reactions. The latter processes may involve acrylic acid units left in the chains between anhydride ring structures.

Above 350 °C, the polymer residue decomposes mainly to cold ring fraction products, volatile at degradation temperature under vacuum but not at room temperature. These consist of short chain fragments derived from two or more original repeat units; these may contain only anhydride rings or both ring and carboxylic acid structures. Small amounts of other volatile products, including carbon monoxide are also formed at these higher temperatures.

*******

# CHAPTER FIVE

## THERMAL BEHAVIOUR OF Na AND K POLYACRYLATE

### *1. INTRODUCTION*

Acrylic and methacrylic acid and their salts are the most important constituents of ionic polymers. Various salts of these acids have been polymerised in *solid state, aqueous* and *nonaqueous media.*[92-102] Most of the research on acrylic and methacrylic polymers has been directed towards the esters and comparatively less attention has been given to the salts of these materials. In recent years metal-containing polymers have been suggested as semiconductors and thermal and chemical resistant materials.[95]

Some polyelectrolytes such as the metallic salts of polymeric acids have elastic moduli several times greater than those of the common thermoplastic materials, a high softening temperature, good thermal stability, and a very low coefficient of thermal expansion.[103] These materials remain rigid up to very high temperature, above 400 $^{o}$C.

Many of the properties of solid polymers depend primarily upon weak intermolecular forces rather than upon the strong covalent forces along the polymer chain. Ionic bonds are among the strongest known and might be expected to impart many desirable properties to polymers.

The thermal decomposition of the simple carboxylic acid salts leads mainly to the respective ketones and inorganic solids.[104-106]

The degradation behaviour and the mechanism of degradation of the salts of poly(acrylic acid) have been the subject of a number of reports.[93,94,96,107] Thermal decomposition of acrylic acid salt polymers is considered to occur mainly via a *free radical mechanism*[108-110], in which assumed by rearrangement of an *intermediate radical* produced a variety of ketones.

The degradation behaviour of the alkali metal salts of poly(methacrylic acid), investigated in this laboratory,[102] is also consistent with mechanisms based on radical intermediates. *Nicholson et al*[88,89] have recently studied the thermal behaviour of films of the partially neutralised PAA at 250 °C. They showed that different chemical processes occur at this temperature depending on the nature of the counterion, as described in the previous chapter (section 1.4).

*Hetper et al*[93], who studied the thermal behaviour of Na, Mg and Ca polyacrylates, reported that the main decomposition reactions of the sodium salt polymer take place in the temperature range 420-470 °C. They suggested that the thermal decomposition of the metal polyacrylates proceeds via *side-chain* and *main chain scission* of the polymer, without depolymerisation. They showed that the solid residue after decomposition was the metal carbonate or oxide, while the volatile products consisted of $H_2$, CO, $CO_2$, saturated and unsaturated hydrocarbons (aliphatic and aromatic) and aliphatic ketones.

In this chapter, the thermal behaviour and mechanism of degradation of sodium and potassium acrylate and polyacrylate , investigated using TVA, TG and DTA techniques, are considered.

## 2. *THERMAL STABILITY OF ACRYLATE METAL SALTS*

It was considered useful to have a prior knowledge of thermal behaviour of these salts for comparison with their respective homopolymers. Sodium and potassium acrylate , prepared by the method which already described (Chapter Three, section 2.3), were investigated using the same experimental approach.

### *2.1. TG AND DTA RESULTS*

The TG results for the monomer salts confirm high thermal stability. A small weight loss, amounting to 4% of original sample weight, was observed up to 400 °C. Above this temperature the sharp release of volatile materials begins. The corresponding DTA curves (Fig. 5.1) show the occurrence of *two processes*, namely thermal polymerisation (exotherm) and main decomposition (endotherm).

Thermogravimetric results and analysis of the products of thermal degradation indicated a similarity with the degradation pattern of the corresponding homopolymers. The TG and DTG curves for the monomer salts are shown in *Fig. 5.2.*

### *2.2. THERMAL VOLATILISATION ANALYSIS*

The TVA curves obtained for the two monomer salts are reproduced in *Fig.5.3*. In all cases the samples (70 mg) were degraded in the powder form up to 500 °C at a rate of 10 °/min under TVA conditions. All TVA traces consist of single broad peak having $T_{max}$ (the temperature at which the rate of volatilisation is a maximum) about *450 °C.* The separation of traces in the higher temperature region of reaction is indicative of variety of products, from liquid of moderate volatility to non-condensable gases.

TVA data for the two monomer metal salts are shown in *Table 5.1.*

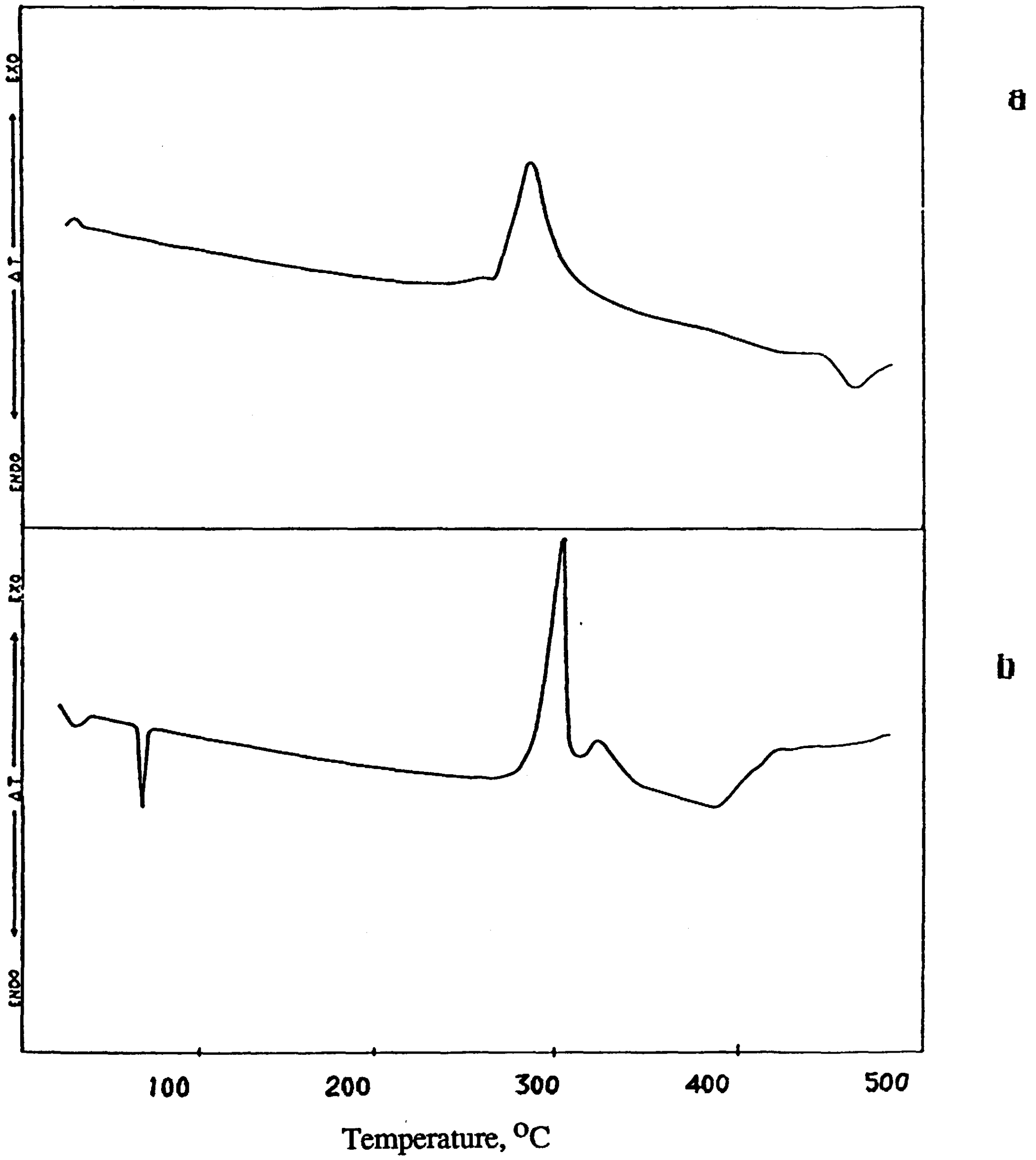


**Fig. 5.1.** DTA curves (dynamic nitrogen atmosphere, heating rate10°C/min) for sodium and potassium acrylate samples. a. NaA ; b. KA

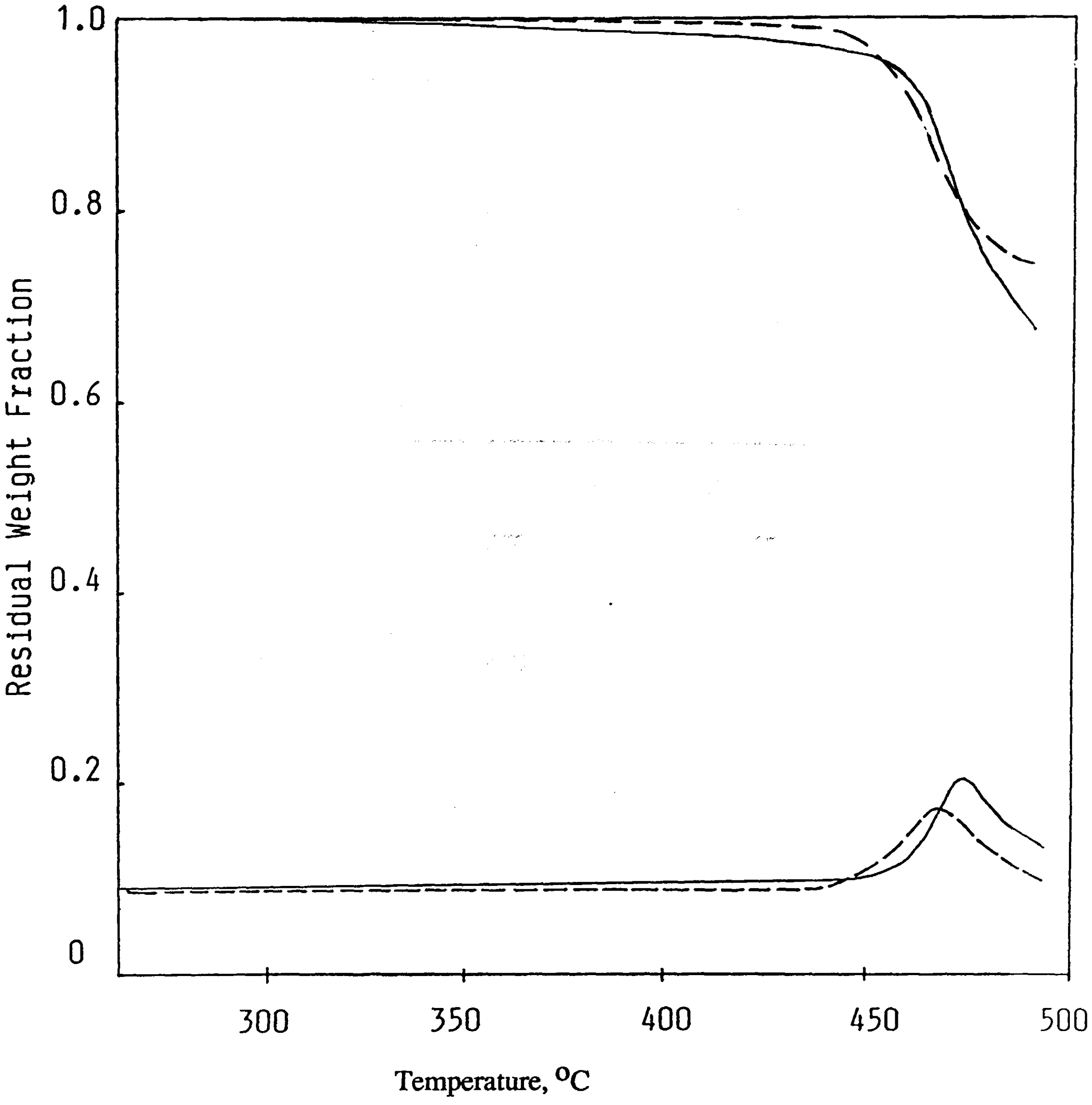


**Fig. 5.2.** TG and DTG curves (dynamic nitrogen atmosphere, heating rate 10°C/min) for sodium and potassium acrylate samples.

——— NaA ; ---- KA

**Table 5.1.** TVA data for degradation of sodium and potassium acrylate samples.

| Monomer | Threshold degradation temperature °C | $T_{max}$ °C | Wt% residue at ~ 500 °C observed |
|---|---|---|---|
| Na acrylate | ~ 370 | ~ 450 | 65 |
| K acrylate | ~ 370 | ~ 450 | 73 |

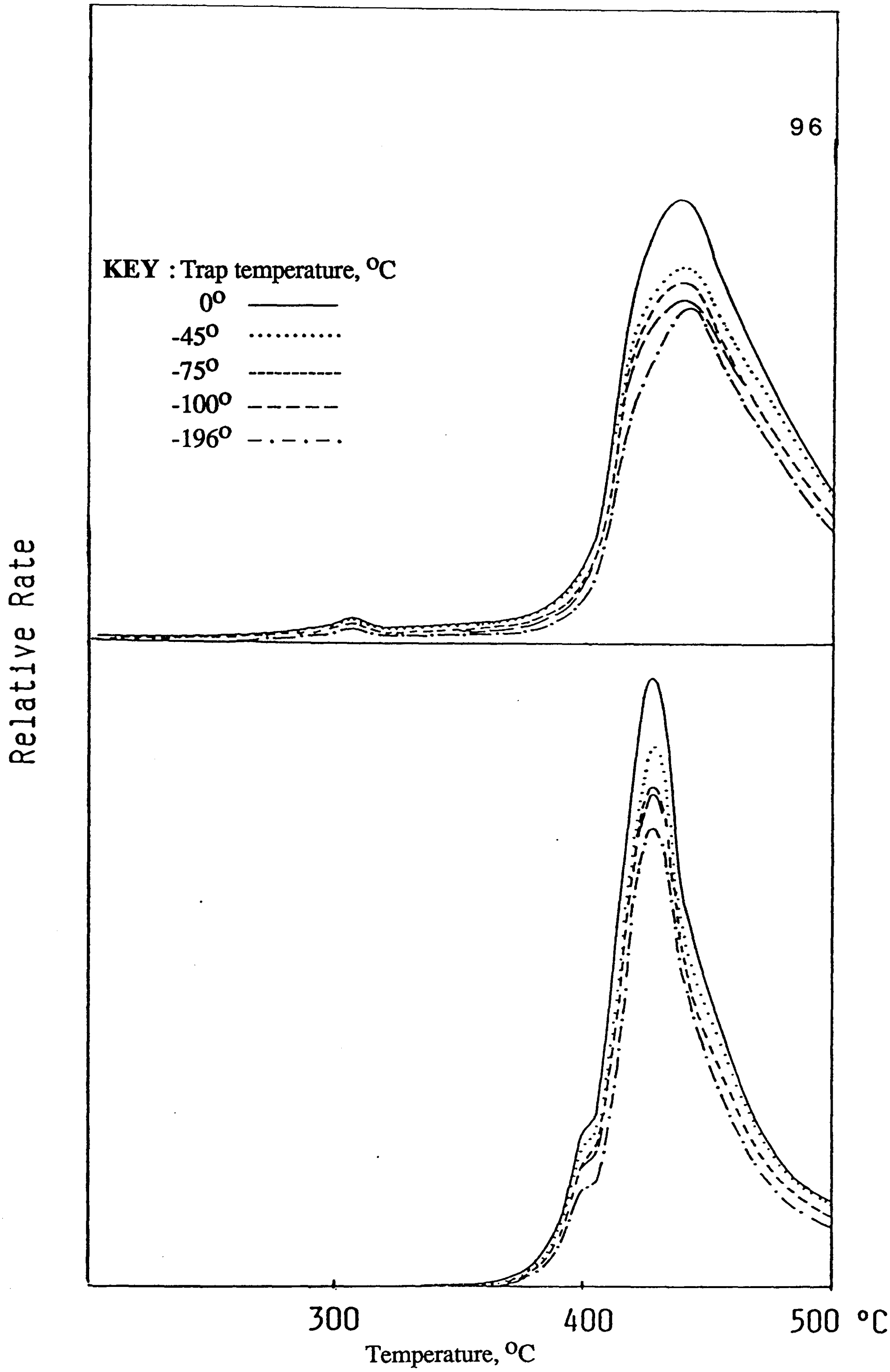


**Fig. 5.3.** TVA curves (vacuum, heating rate 10°C/min) for sodium acrylate (above) and potassium acrylate (below).

## *2.3. PRODUCT ANALYSIS*

The *various* degradation products, namely ***residue, cold ring fraction, liquid fraction*** and ***gaseous products*** including non-condensable gases were examined after degradation of 75 mg samples of the monomer metal salts to 500 $^{o}$C under TVA conditions. The product analysis was carried out spectroscopically.

The non-condensable products were identified using mass spectrometry as *carbon monoxide* and *methane.*

Condensable volatile degradation products collected in a liquid nitrogen trap in the vacuum system, were separated by the SATVA method. The SATVA trace for warm up from -196 $^{o}$C to 0$^{o}$C of condensable volatile product fraction to 500 $^{o}$C under TVA conditions of sodium acrylate is shown in *Fig. 5.4.*

Products were collected in four fractions as indicated and examined by i.r. spectroscopy. The first fraction peak was due to ethene. The second fraction contained carbon dioxide and ketene. The third fraction consisted primarily of acetone. The corresponding ir spectra are illustrated in *Figs. 5.5a* and *5.5b,* respectively.

The cold ring fractions from the degradation of these monomer salts were yellow solids, which gave similar infrared spectra. The bands at *1540-1570* and *1430-1450* cm$^{-1}$ due to asymmetric and symmetric stretching modes of the carboxylate group can be readily identified in the ir spectrum of the CRF.

Other bands at *1368, 1295, 1050* and *660* cm$^{-1}$ in this fraction all also belong to the polymer repeat structure. But the absence of a band at *1640* cm$^{-1}$ due to carbon-carbon double bond suggests the absence of monomer in the CRF. The ir spectrum of the CRF is shown in *Fig.* 5.6.

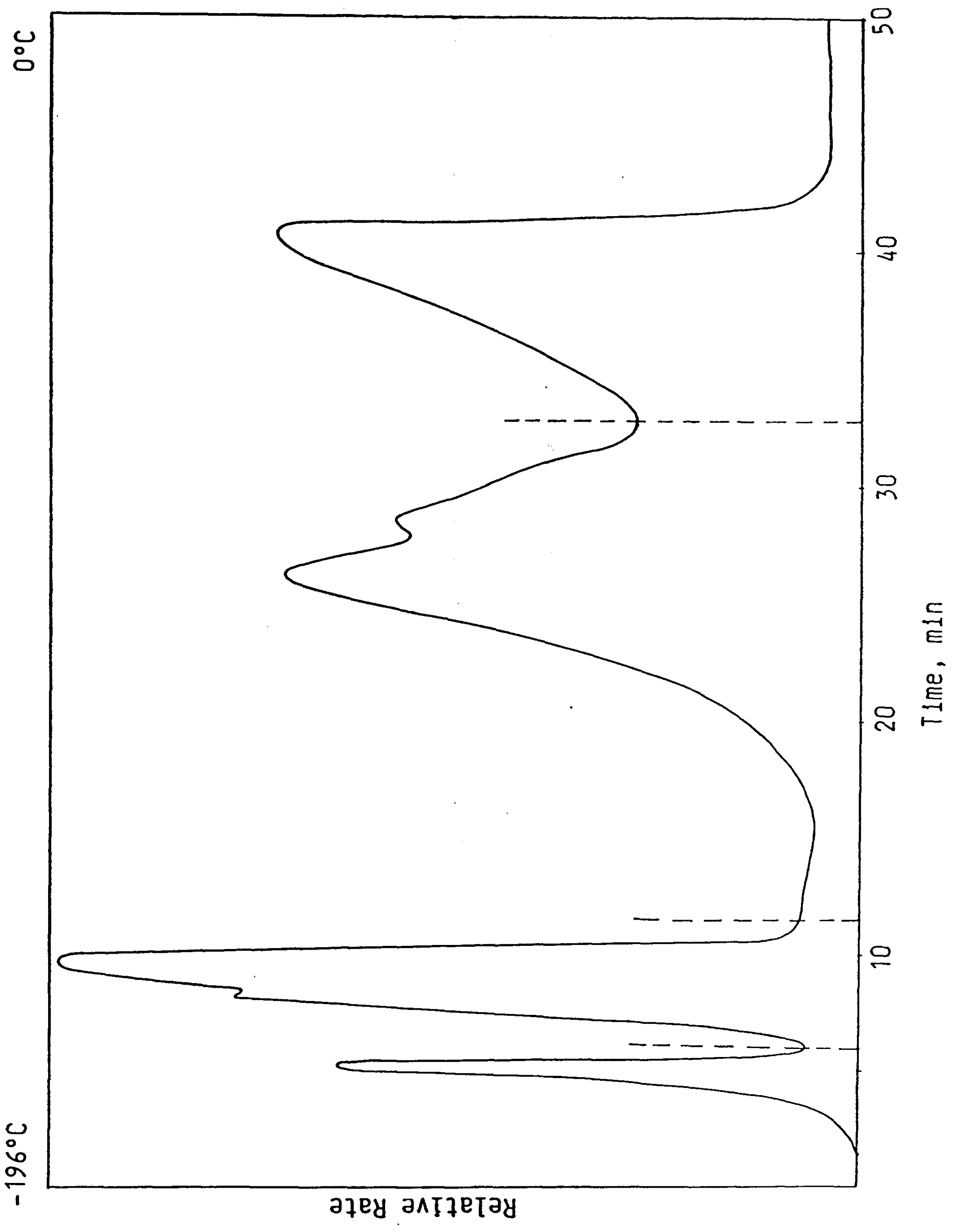
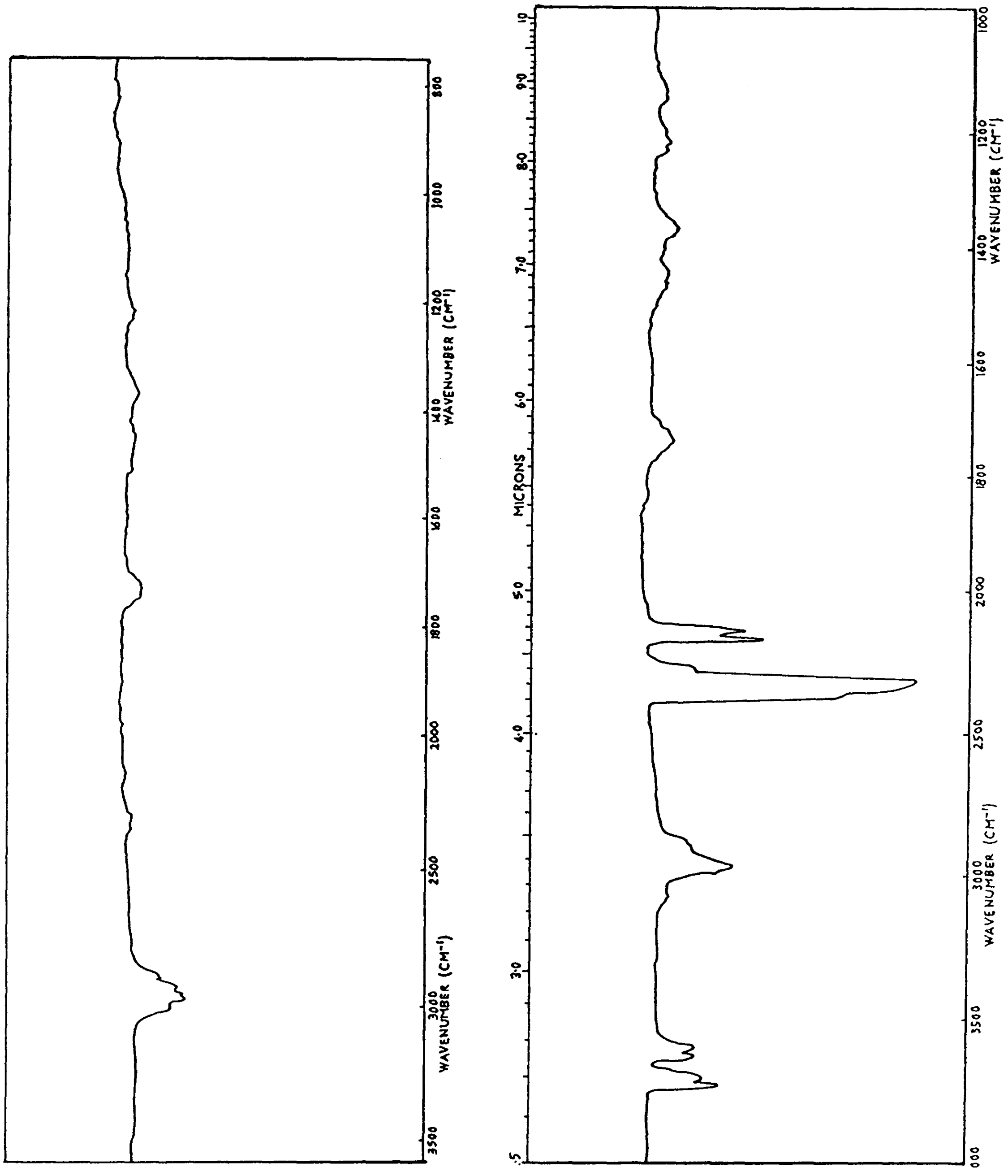


**Fig. 5.4.** SATVA curve of the condensable product fraction from degradation to 500°C under TVA conditions of sodium acrylate



First fraction

Second fraction

**Fig. 5.5a.** IR spectra of the first and second fraction peaks on SATVA trace.

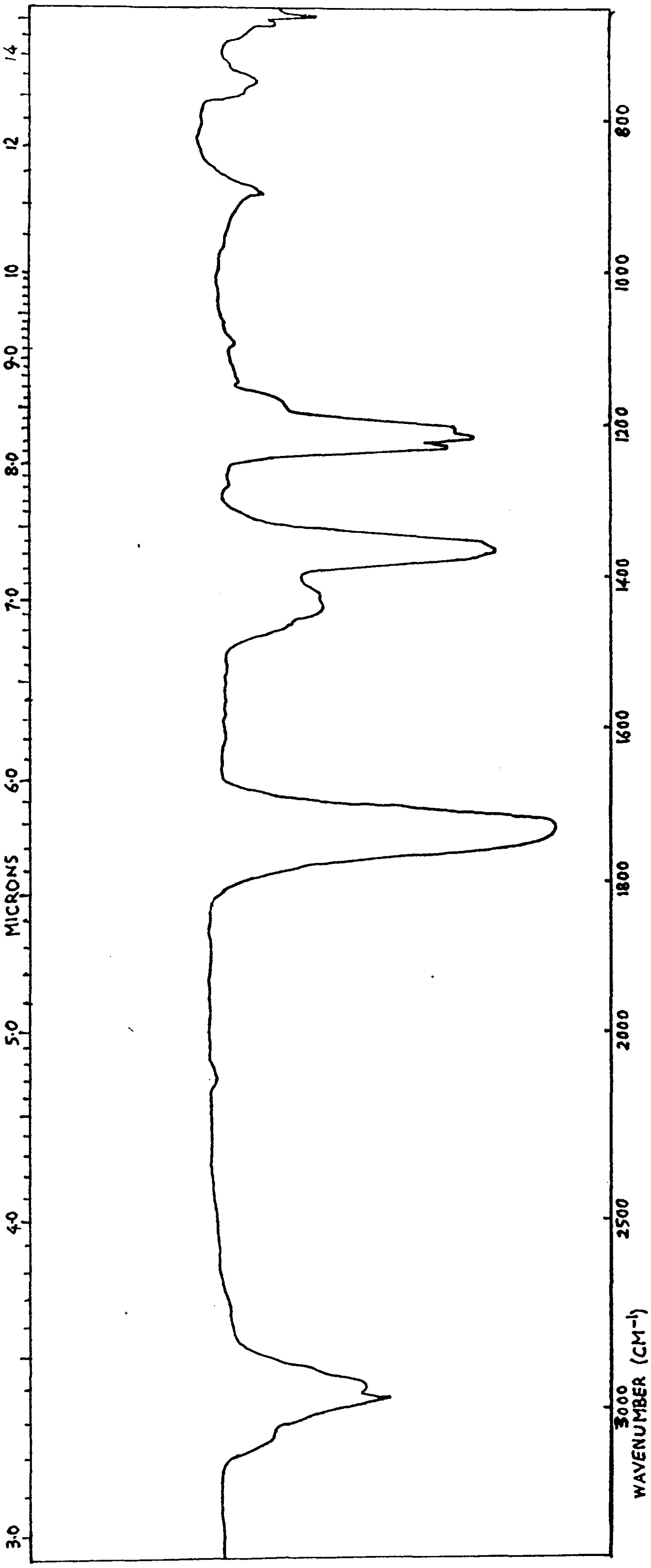
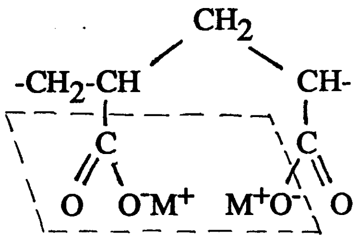


**Fig. 5.5b.** IR spectrum of the third fraction peaks on SATVA trace. of sodium acrylate.

The above mentioned bands suggest that short chain fragments are present resulting from thermal polymerisation in the hot zone followed by decomposition of the polymer initially produced.

The involatile black material (residue) showed *metal carbonate* as a major product. Although no *metal oxide* was identified by ir spectroscopy, the presence of carbon and metal oxide in the residue are expected. The ir spectrum of the involatile fraction of degradation of sodium acrylate is illustrated in *Fig. 5.6.*

As the monomer salts seem to polymerise in the solid state on heating, metal carbonate formation may occur by *elimination* from adjacent salt groups as shown below :

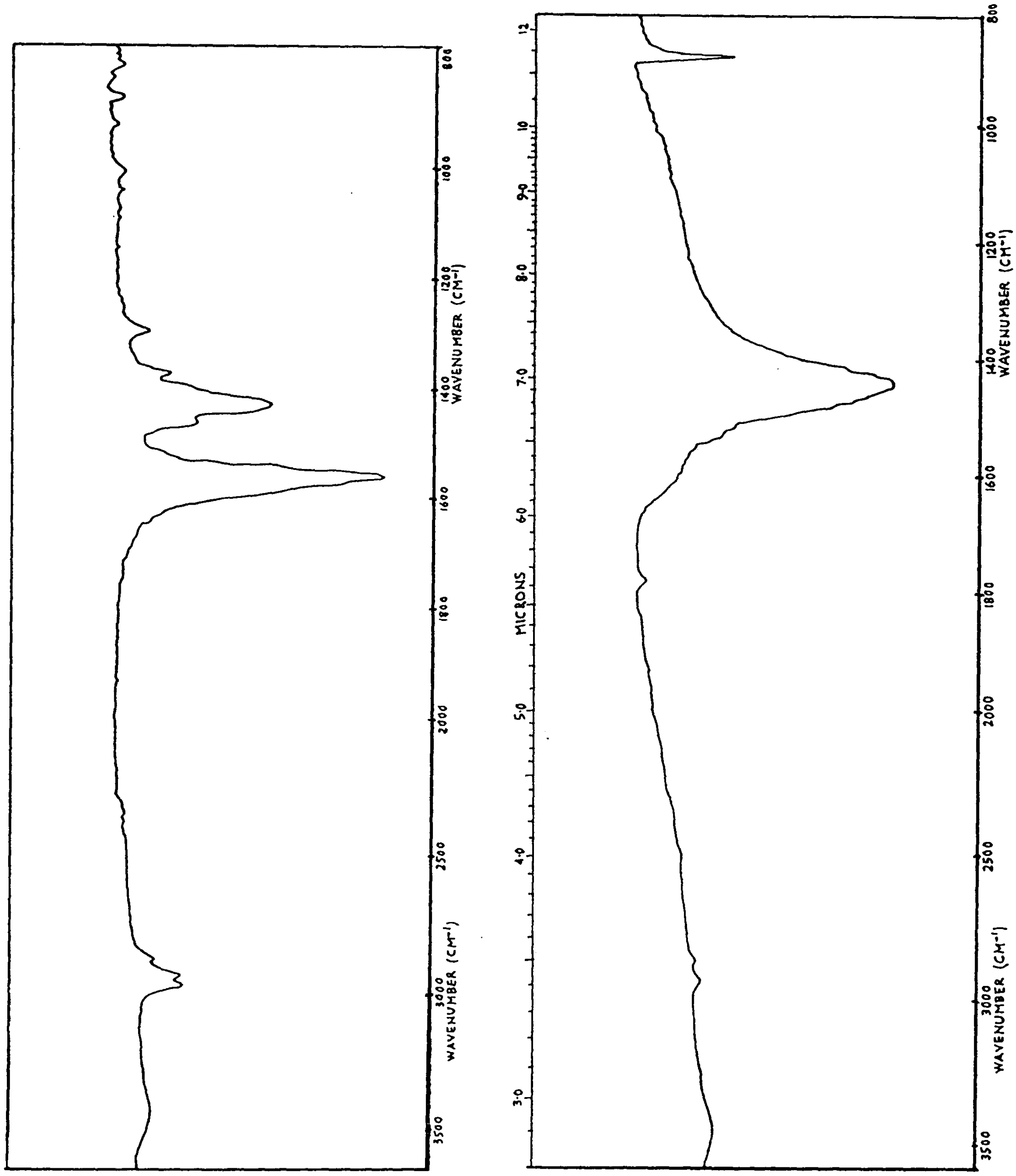


### 3. THERMAL BEHAVIOUR OF HOMOPOLYMERS

The thermal degradation of sodium and potassium polyacrylate has been investigated following the same experimental approach as used in studies of the corresponding monomer salts.

### 3.1. THERMAL VOLATILISATION ANALYSIS

The homopolymers were examined as 70 mg powder samples in a TVA system in which



CRF Residue

**Fig. 5.6·** IR spectra of the CRF and the involatile fraction of degradation of sodium acrylate.

differential condensation of products at trap temperatures of $0^{o}$,-$45^{o}$, -$75^{o}$, -$100^{o}$ and -196 $^{o}$C were used. The TVA curves for the polymers are shown in *Figs. 5.7*and *5.8*. All four traces are very similar, in which the threshold temperature ($T_{onset}$) for decomposition is about 260 $^{o}$C. It is clear from the TVA traces that volatile materials including a non-condensable fraction at -196 $^{o}$C appear at a temperature around 300 $^{o}$C and the maximum rate of volatilisation ($T_{max}$) occurs at about 450 $^{o}$C for the polymers made by polymerisation.

TVA results for those polymers which were prepared by neutralisation indicate that non-condensable products are evolved at about 360 $^{o}$C and $T_{max}$ ca. $440^{o}$ and 470 $^{o}$C for sodium and potassium polyacrylate, respectively.

*Gravimetric* data under TVA conditions were obtained by placing the polymer sample in a thin glass flat-bottomed sample tube, weighed before and after the experiment, in contact with the base of TVA tube.

The TVA curves for sodium polyacrylate show two peaks below 420 $^{o}$C which are smaller in size than that due to the main degradation process.

From partial degradation of these polymers it was established that the small amount of the volatile material produced below *420 $^{o}$C* consists of carbon dioxide.

Quantitative measurement of carbon dioxide evolution was carried out by a method described previously in Chapter Four section 2.1.1.

TVA data for the polymers are summarised in *Table 5.2*.

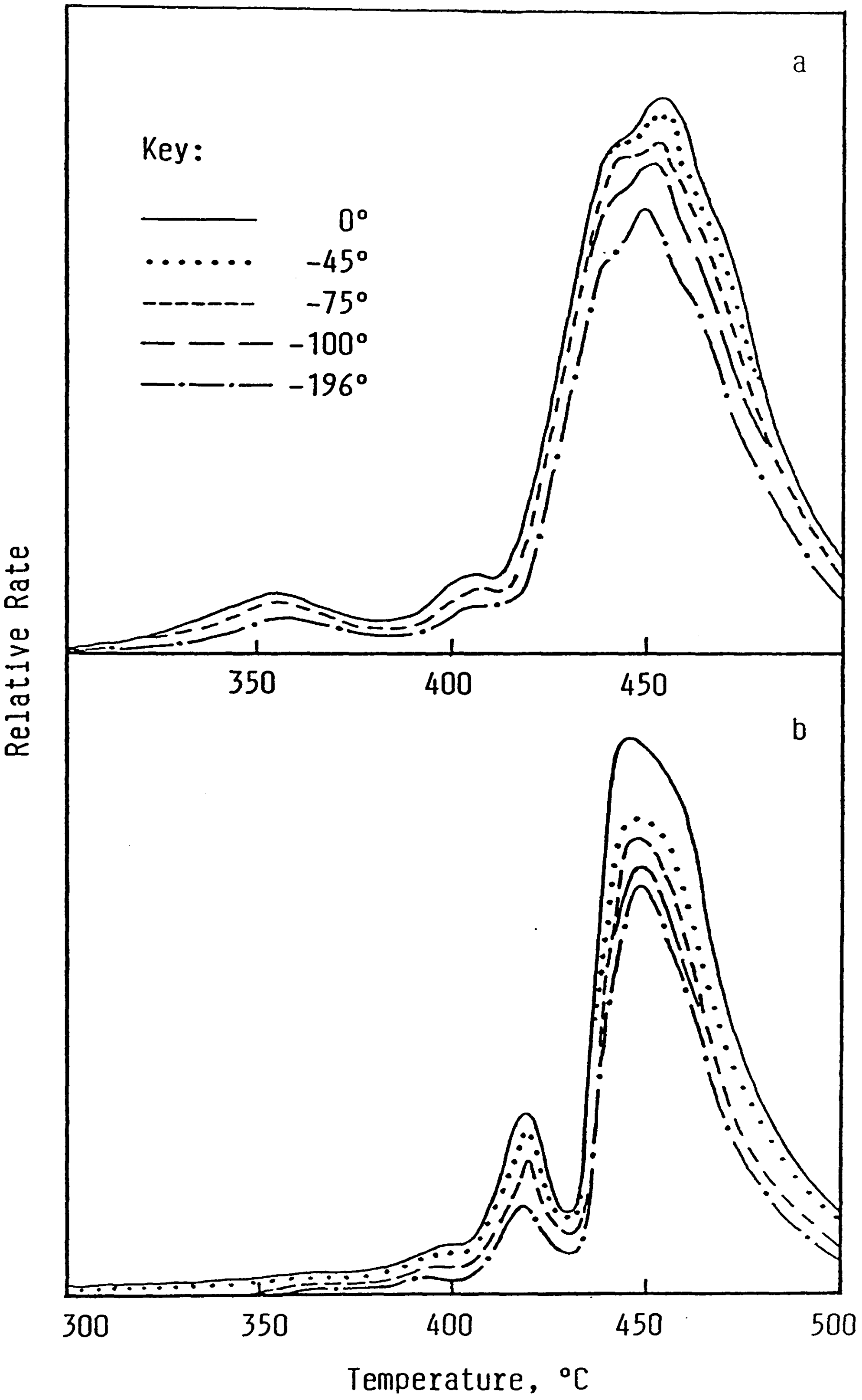


**Fig. 5.7.** TVA curves (vacuum, heating rate 10$^{O}$C/min) for sodium polacrylate samples:

**a.** NaPA prepared by polymerisation ;

**b.** NaPA made by neutralisation .

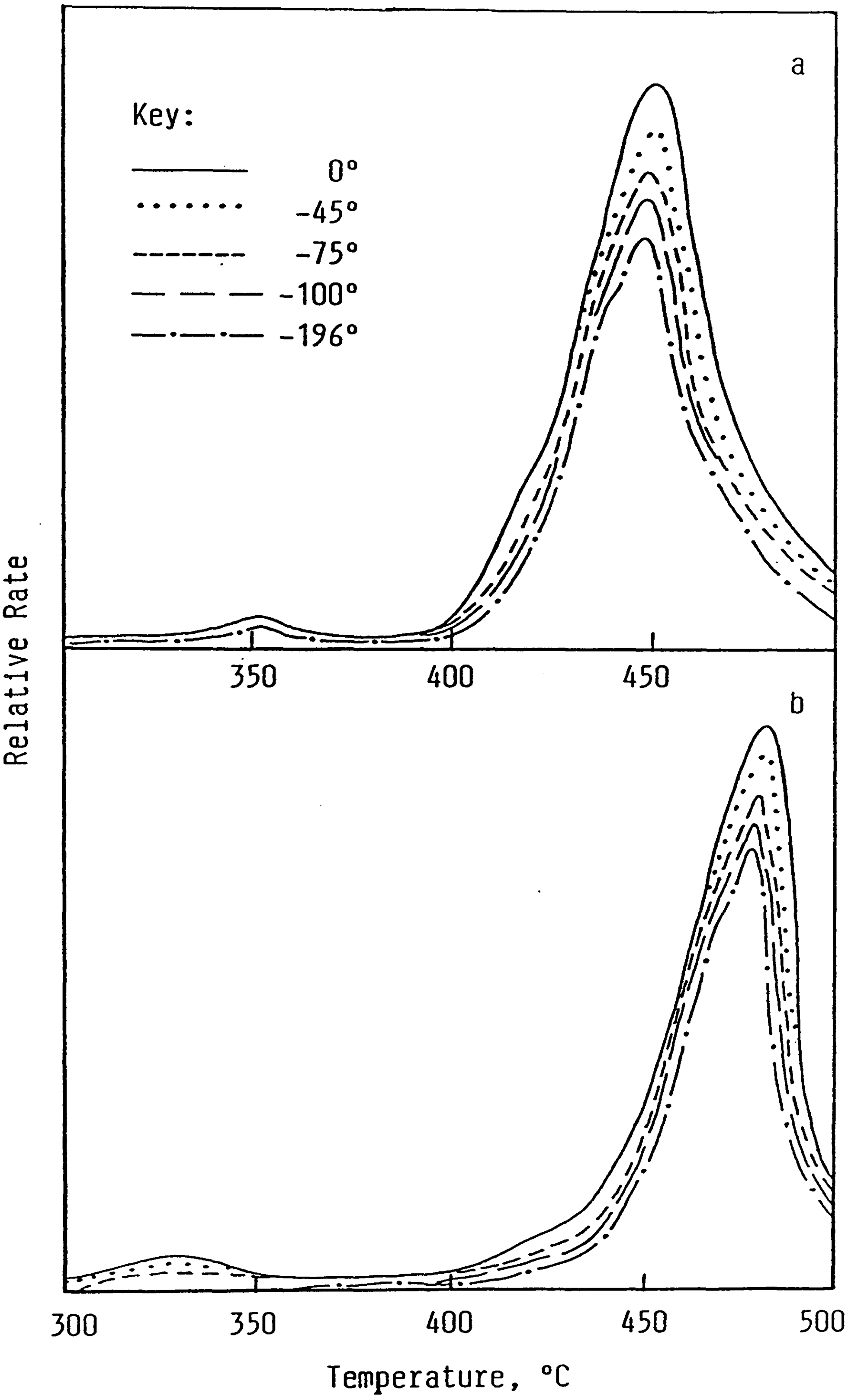


**Fig. 5.8.** TVA curves (vacuum, heating rate 10$^{o}$C/min) for potassium polyacrylate samples :

**a.** KPA made by polymerisation ;

**b.** KPA prepared by neutralisation .

### *3.1.1. Product Analysis*

The degradation products were examined by IR, MS, and GC-MS techniques.

#### *3.1.1.1. Residue*

The ***involatile*** fraction (residue) for each of the four polymers was shown by ir spectroscopy to consist mainly of the metal carbonate. Although no metal oxide was identified by infrared spectroscopic analysis, the presence of this material in the residue is to be expected in view of the nature of the other degradation products. The formation of crack carbon often takes place when thermal decomposition is performed in a ***non-oxidising*** atmosphere[111-113] and sometimes even in air.[107]

The percentage of residue from the original sample if degraded under vacuum is different from that if the same sample is degraded under nitrogen. For example, the percentages of residue for NaPA and KPA are 49 and 56 under vacuum (TVA), but 60 and 64, if degraded under nitrogen (TG).

The differences are attributed to the short chain fragments which escape from the hot zone to the upper part of the TVA tube under high vacuum conditions, while these fragments fail to do so under nitrogen at atmospheric pressure.

#### *3.1.1.2. Cold Ring Fraction*

The cold ring fraction materials from the four polymers, which were yellow solids, gave similar infrared spectra showing bands at *1508-1575* and *1430-1450* $cm^{-1}$ due to the asymmetric and symmetric stretching modes of the carboxylate ion, respectively. The corresponding spectra are shown in *Fig. 5.9.*

**Table 5.2.** TVA data for degradation of sodium and potassium polyacrylate samples made by both routes.

| Polymer | $T_{onset}$ °C | Initial temp. for non-condensable gases, °C | $T_{max}$ °C | Wt% residue at ~500 °C | Wt% CRF at ~500 °C | Wt% of condensable volatile products at~500 °C ($CO_2$ included) | Wt% $CO_2$ |
|---|---|---|---|---|---|---|---|
| NaPA | 260 | 300 | 445 | 48.7 | 5.5 | 45.8 | 13 |
| NaPA* | 250 | 350 | 440 | 48.7 | 7.8 | 43.5 | 12.5 |
| KPA | 270 | ~300 | 445 | 51.5 | 5.8 | 42.7 | 12.8 |
| KPA* | 255 | ~370 | 470 | 56.6 | 3.9 | 39.5 | 11.5 |

* Polymers synthesised by neutralisation of PAA with the respective hydroxide in methanol.

The mass spectrometric analyses were consistent with the presence of the short chain fragments such as *dimer, trimer, etc.* and traces of *monomer* salts. Some of the products of the cold ring fraction of sodium polyacrylate (made by polymerisation) detected by mass spectrometry are listed, in respect of importance, in *Table 5.3.*

### *3.1.2. Subambient Thermal Volatilisation Analysis (SATVA)*

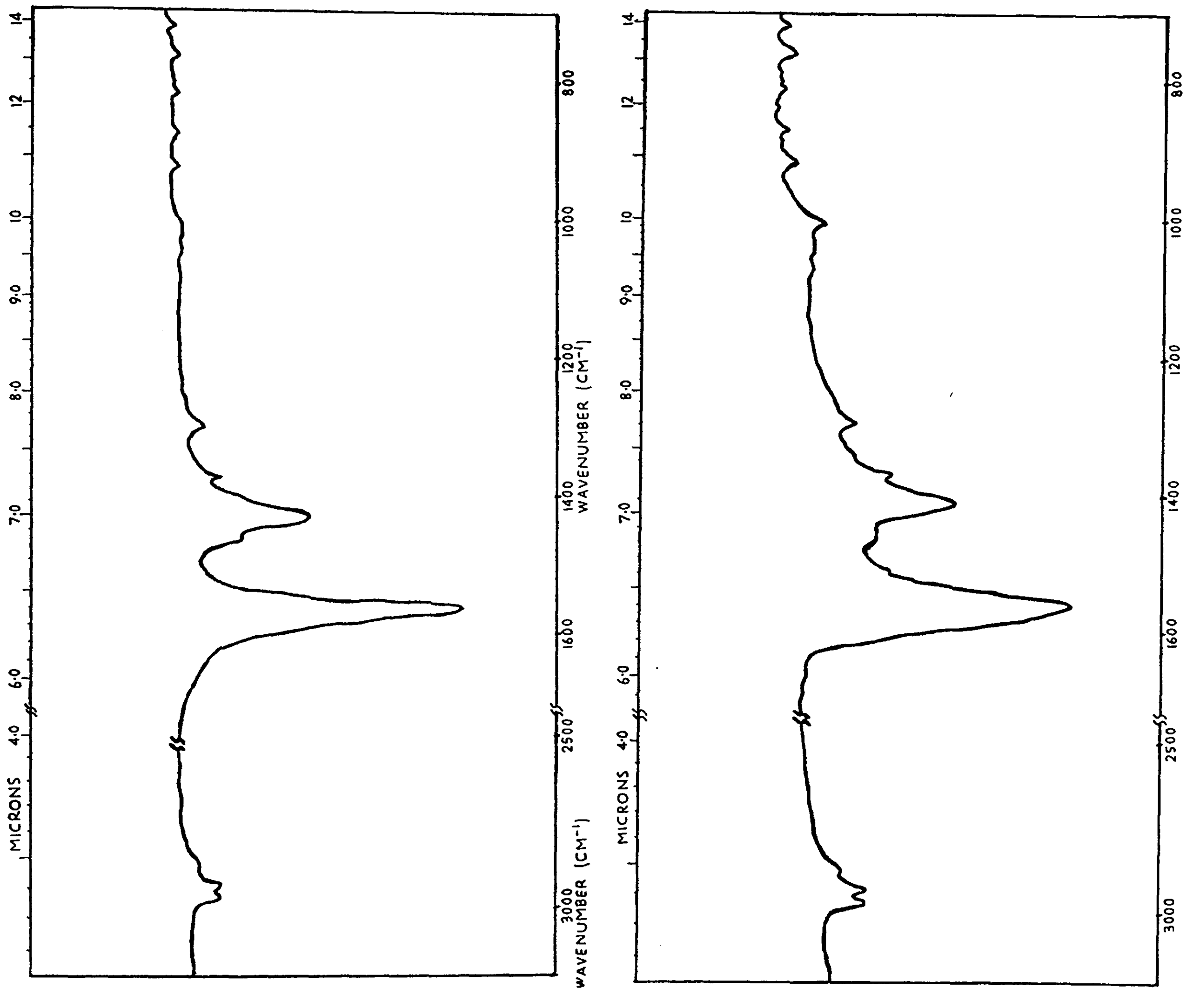
Condensable volatile degradation products from polymer sample degraded to 500 °C using the TVA technique, collected in a liquid nitrogen trap in the vacuum system, were separated by the SATVA method. SATVA traces for warm up from -196 °C to 0 °C of the condensable volatile product fraction to 500 °C under TVA conditions of the polymers obtained by polymerisation are shown in *Figs.5.10*and *5.11* Products were collected in three fractions as indicated, the first two collected in gas cells and the third as liquid in a cold finger.

#### *3.1.2.1. Condensables As Gaseous Products*

The condensable gaseous products were examined by ir spectroscopy and mass spectrometry. These products were clearly found to consist of *carbon dioxide* and *acetone* as major products together with small amounts of ketene, ethylene, propene, 1-butene, benzene, toluene, 1,3-cyclopentadiene, acrolein (only NaPA), acetaldehyde (only NaPA) and cyclopentene (only KPA).

#### *3.1.2.2. Condensables As Liquid Fraction*

The third fractions were very complex and were subjected to GC-MS (See also Tables 5.4, 5.5 and Figs. 5.12, 5.13.). Product analysis of the less volatile condensable liquid



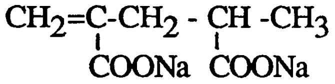
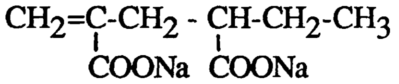
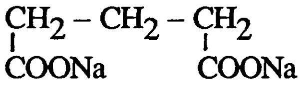
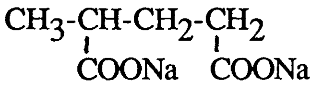
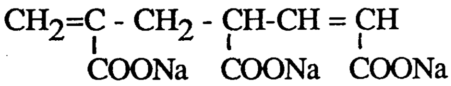
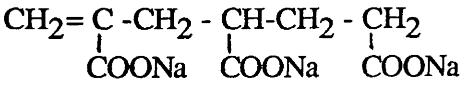
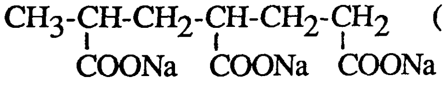
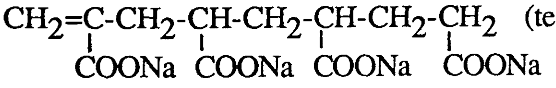
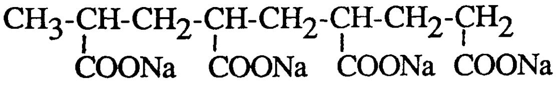
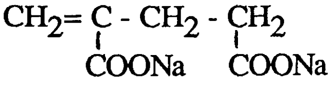
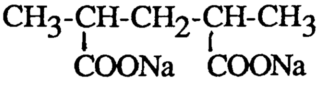
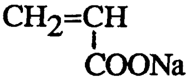
a

b

Fig. 5.9. Infrared spectra of CRF of sodium and potassium polyacrylates.

**a.** Na acrylate, **b.** K acrylate.

**Table 5.3.** Products identified in the cold ring fraction from degradation of sodium polyacrylate* under TVA conditions.

| Product | m/e |
|---|---|
|  $\mathrm{CH_2{=}\underset{COONa}{C}{-}CH_2{-}\underset{COONa}{CH}{-}CH_3}$ | 202 |
|  $\mathrm{CH_2{=}\underset{COONa}{C}{-}CH_2{-}\underset{COONa}{CH}{-}CH_2{-}CH_3}$ | 216 |
|  $\mathrm{\underset{COONa}{CH_2}{-}CH_2{-}\underset{COONa}{CH_2}}$ | 176 |
|  $\mathrm{CH_3{-}\underset{COONa}{CH}{-}CH_2{-}\underset{COONa}{CH_2}}$ (saturated dimer) | 190 |
|  $\mathrm{CH_2{=}\underset{COONa}{C}{-}CH_2{-}\underset{COONa}{CH}{-}CH{=}\underset{COONa}{CH}}$ | 280 |
|  $\mathrm{CH_2{=}\underset{COONa}{C}{-}CH_2{-}\underset{COONa}{CH}{-}CH_2{-}\underset{COONa}{CH_2}}$ (trimer) | 282 |
|  $\mathrm{CH_3{-}\underset{COONa}{CH}{-}CH_2{-}\underset{COONa}{CH}{-}CH_2{-}\underset{COONa}{CH_2}}$ (saturated trimer) | 284 |
|  $\mathrm{CH_2{=}\underset{COONa}{C}{-}CH_2{-}\underset{COONa}{CH}{-}CH_2{-}\underset{COONa}{CH}{-}CH_2{-}\underset{COONa}{CH_2}}$ (tetramer) | 376 |
|  $\mathrm{CH_3{-}\underset{COONa}{CH}{-}CH_2{-}\underset{COONa}{CH}{-}CH_2{-}\underset{COONa}{CH}{-}CH_2{-}\underset{COONa}{CH_2}}$ (saturated tetramer) | 378 |
|  $\mathrm{CH_2{=}\underset{COONa}{C}{-}CH_2{-}\underset{COONa}{CH_2}}$ (dimer) | 188 |
|  $\mathrm{CH_3{-}\underset{COONa}{CH}{-}CH_2{-}\underset{COONa}{CH}{-}CH_3}$ | 204 |
|  $\mathrm{CH_2{=}\underset{COONa}{CH}}$ | 94 |

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* Prepared by polymerisation

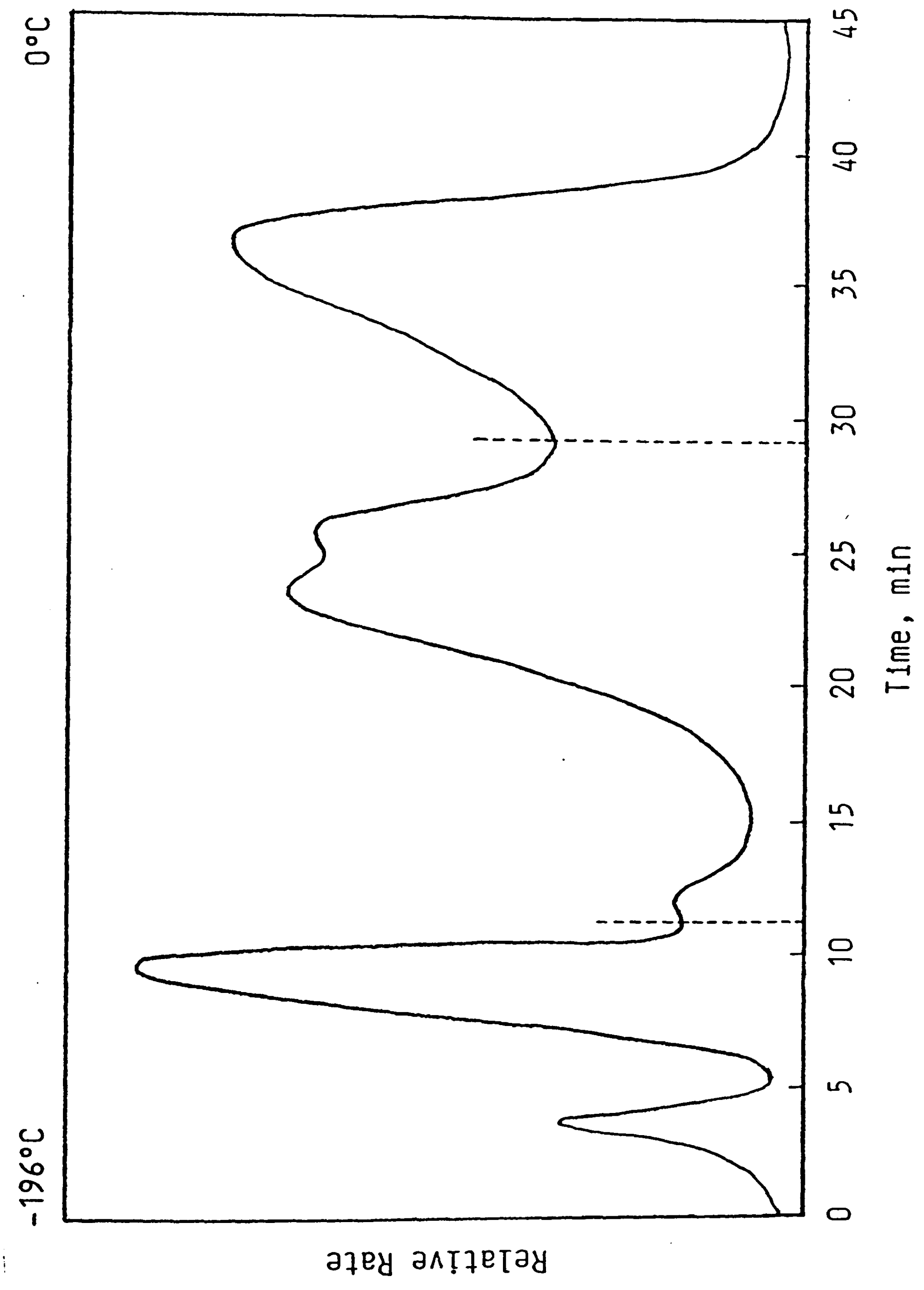


**Fig. 5.10.** SATVA curve of condensable volatile product fraction from degradation to 500 °C under TVA conditions of sodium polyacrylate.

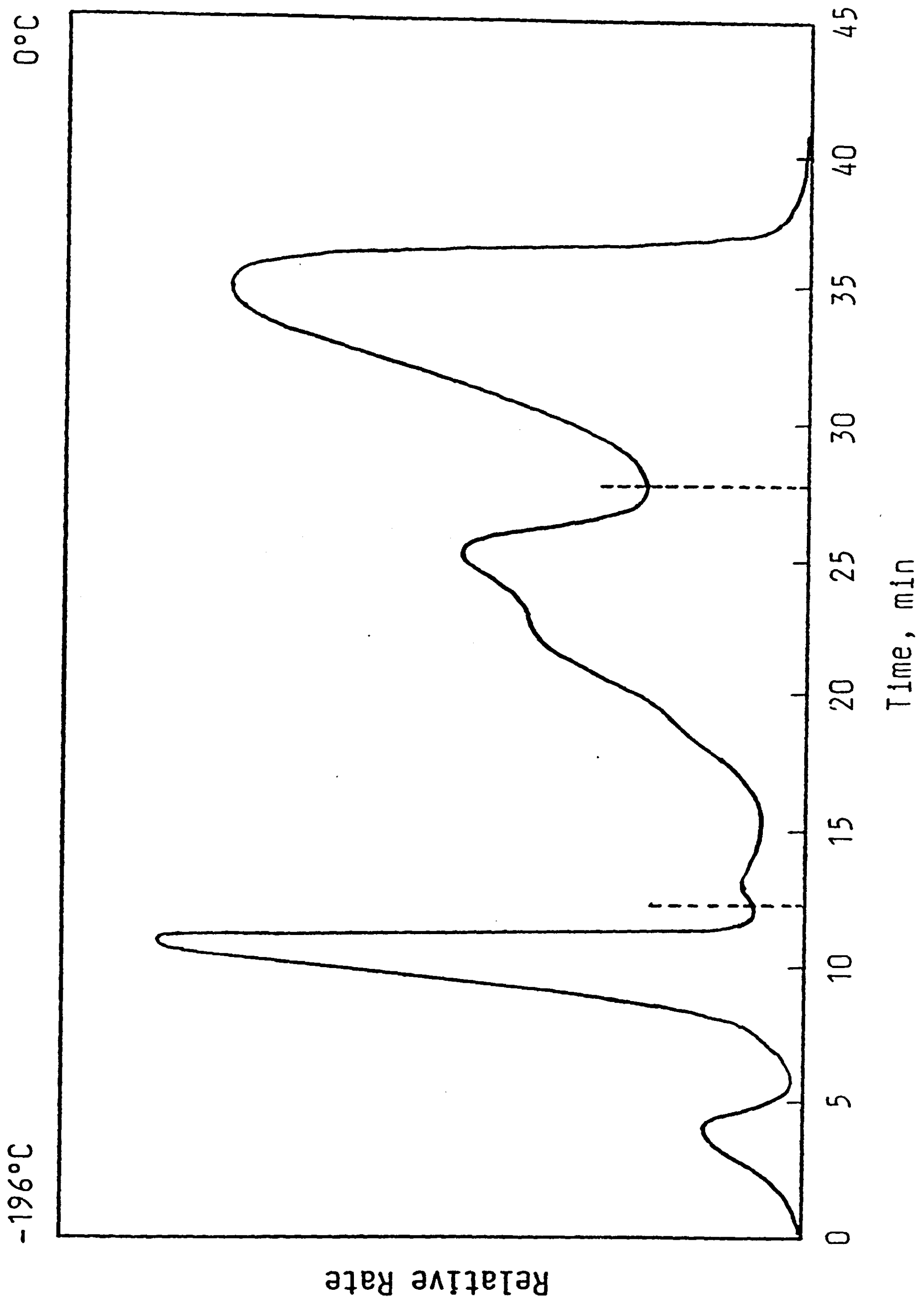


**Fig. 5.11.** SATVA curve of condensable product fraction from degradation to 500°C under TVA conditions of potassium polyacrylate.

fraction separated by SATVA was carried out using IR, MS, GC and GC-MS techniques. Instrumental conditions during the GC-MS analysis for liquid fraction of the polymers were as follows;

Injector temperature 250 °C, voltage 70 ev, column temperature initially 50 °C for 5 min then programmed at 2-5 °C/min to 200 °C, helium gas flow rate 10 ml/min. The corresponding chromatograms obtained in GC-MS analyses of the liquid fractions obtained in SATVA separation of condensable volatile products of the polymer synthesised by polymerisation are illustrated in *Figs. 5.12* and *5.13.*

All the materials detected in the degradation products from sodium and potassium polyacrylate samples prepared by polymerisation are listed in *Tables 5.4* and *5.5,* respectively.

### *3.1.2.3. Non-condensable Gases*

***Methane*** and ***carbon monoxide*** were identified by mass spectrometry as non-condensable gaseous products.

## *3.2. THERMOGRAVIMETRY (TG)*

TG and DTG curves of the polymers degraded under nitrogen are reproduced in *Figs. 5.14* and *5.15*. The TG curves for the four polymers have been presented on two diagrams to facilitate comparison. It is clear that the polymer prepared by polymerisation, are more stable.

The first stage of breakdown in NaPA and KPA, made by neutralisation, occurs at about 400° and 300 °C, respectively, and it accounts for 10% weight loss. The main decomposition appears at temperature around 450 °C with 40 and 36% weight loss, respectively.

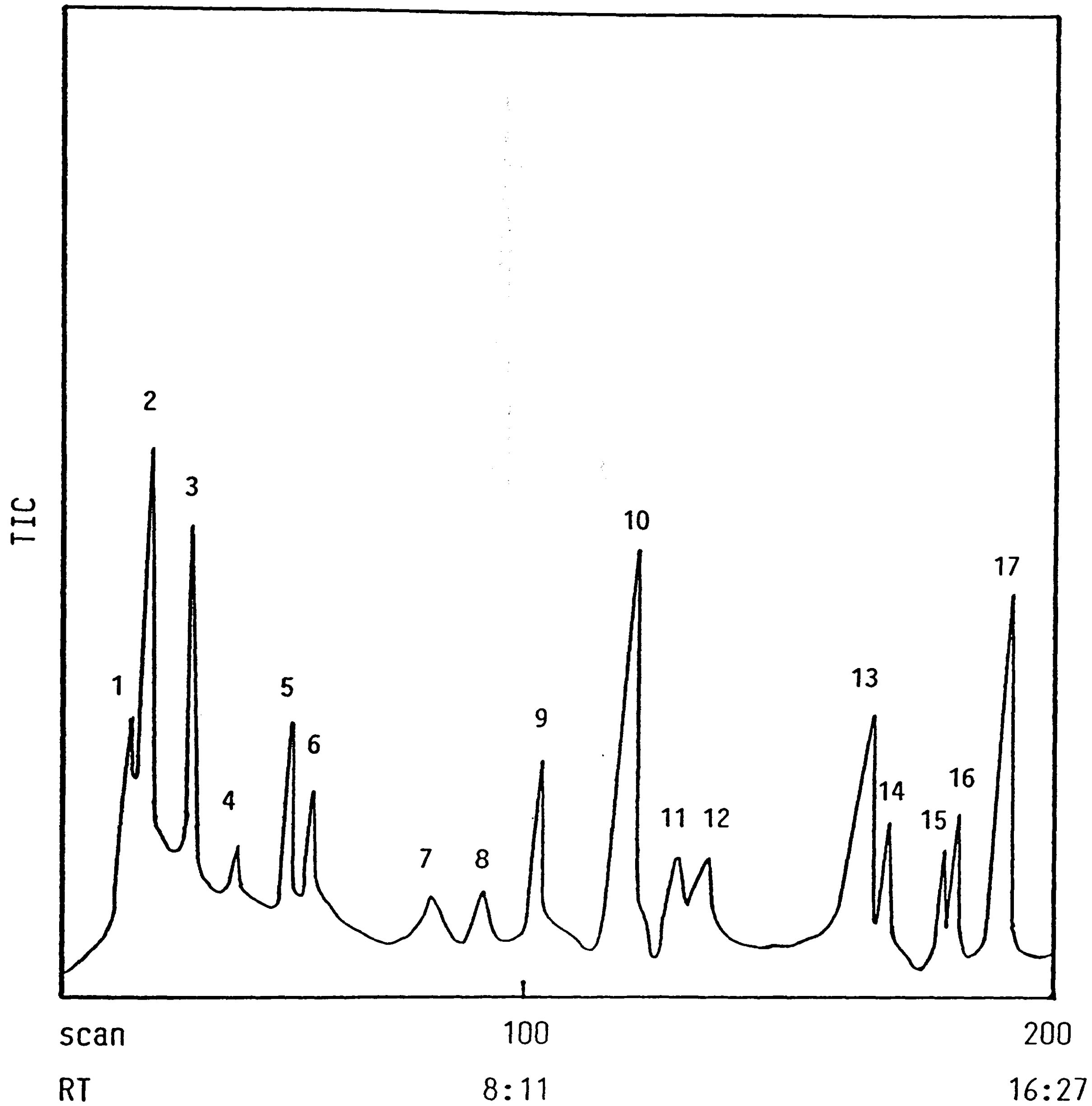


**Fig.5.12.** GC-MS chromatogram of the less volatile liquid fraction of sodium polyacrylate,prepared by polymerisation.

Assignments: **1** acetone, **2** methyl ethyl ketone, **3** THF (impurity), **4** methyl isopropyl ketone, **5** methyl n-propyl ketone, **6** diethyl ketone, **7** methyl propenyl ketone, **8** 3-hexanone, **9** toluene, **10** 2-hexanone,**11** and **12** unknown **13** 2-methyl-cyclopentanone + mesityl oxide, **14** and **15** unknown, **16** and **17** xylenes.

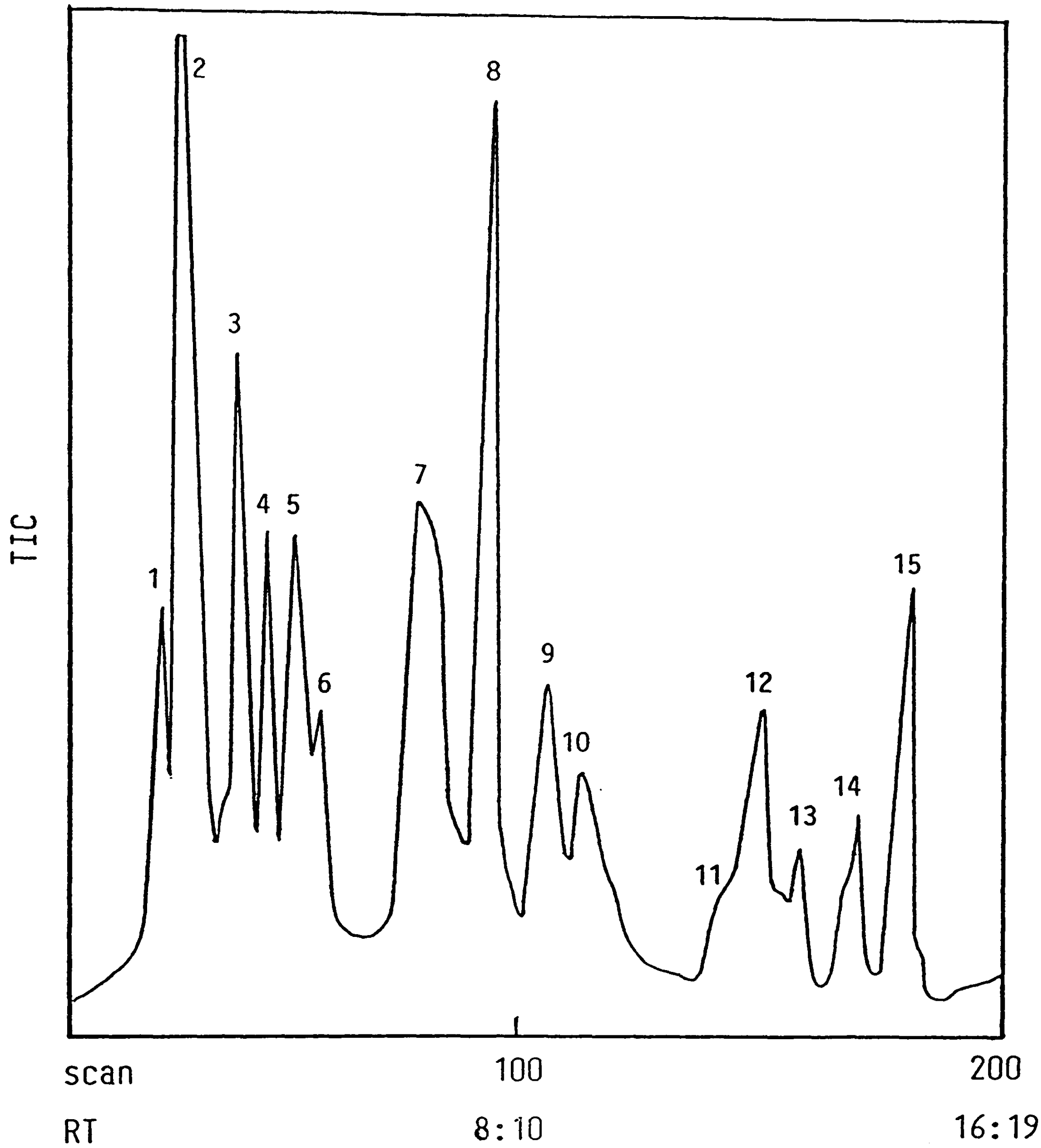


**Fig. 5.13.** GC-MS chromatogram of the less volatile liquid fraction of potassium polyacrylate, made by polymerisation. Assignments: **1** acetone, **2** methyl ethyl ketone, **3** unknown, **4** 1,4-cyclohexadiene, **5** 1-methyl-cyclopentene, **6** methyl n-propyl ketone, **7** 1-methyl-1,3-cyclohexadiene, **8** toluene, **9** 2-hexanone, **10** mesityl oxide, **11** unknown, **12** mesityl oxide, **13** unknown, **14** and **15** xylenes.

**Table 5.4.** Products of degradation of sodium polyacrylate to 500 $^{o}$C at 10 $^{o}$C/min under TVA conditions

| Non-condensable products at -196 $^{o}$C | condensable volatile products at -196 $^{o}$C | | | | CRF (yellow solid) | Residue (black) |
|---|---|---|---|---|---|---|
| | Gases | Liquid Fraction | | | | |
| IR | IR, MS | IR, MS | GLC | GC-MS | IR, MS | IR |
| CO<br>$CH_4$ | $CO_2$<br>Acetone<br>Ethylene<br>Propene<br>1-Butene<br>Ketene<br>Benzene<br>Toluene<br>Acrolein<br>Propanal<br>Acetaldehyde | Benzene<br>Toluene<br>Diethyl ketone<br>Methanol* | Acetone<br>Propanal<br>Methyl ethyl ketone<br>Diethyl ketone<br>Cyclopentanone<br>Benzene<br>Toluene<br>Xylene | Acetone<br>Benzene<br>Methyl ethyl ketone<br>Methyl isopropyl ketone.<br>Diethyl ketone<br>Methyl propenyl ketone<br>3-Hexanone<br>2-Hexanone<br>2-Methyl cyclopentanone<br>Mesityl oxide<br>Toluene<br>Xylene | Short chain fragments including dimer, trimer and traces of monomer | Sodium carbonate as a major product |

* Impurity (solvent)

**Table 5.5.** Products of degradation of potassium polyacrylate to 500 °C at 10 °C/min under TVA conditions.

| Non-condensable products at -196 °C | Condensable volatile products at -196 °C | | | | CRF (yellow solid) | Residue (black) |
|---|---|---|---|---|---|---|
| | Gases | Liquid Fraction | | | | |
| IR | IR, MS | IR, MS | GLC | GC-MS | IR, MS | IR |
| CO<br>$CH_4$ | $CO_2$<br>Acetone<br>Ethylene<br>Propene<br>1-Butene<br>Ketene<br>Cyclopentene<br>1,3-Cyclopentadiene | Acetone<br>Methyl ethyl ketone<br>Benzene<br>Toluene<br>Methanol* | Acetone<br>Propanal<br>Butanal<br>Methyl ethyl ketone<br>Diethyl ketone<br>Cyclopentanone<br>Benzene<br>Toluene<br>Xylene<br>Methanol* | Acetone<br>Benzene<br>Methyl propyl ketone<br>2-Hexanone<br>Mesityl oxide<br>1,4-Cyclohexadiene<br>1-Methyl cyclopentene<br>1-Methyl 1,3-cyclohexadiene<br>Toluene<br>Xylene | Short chain fragments such as dimer, trimer and traces of monomer | Potassium carbonate as a principal product |

* Impurity (solvent)

### *3.3. DIFFERENTIAL THERMAL ANALYSIS* (DTA)

The DTA curves of the polymers were recorded in the range 25- 485 °C under nitrogen atmosphere, shown in *Figs. 5.16* and *5.17.*

The DTA results of the homopolymers do not give any indication of the *exothermic* effect which were attributed to thermal polymerisation of the corresponding monomer salts. According to the DTA curves, the main step of decomposition of the investigated polymer salts is observed at high temperature between 400° and 480 °C.

The endothermic effect is probably caused by polymer chain scission and the exothermic one may be explained by metal oxide formation during the partial decomposition of the residue (metal carbonate).

The DTA, TG and DTG data of four polymers are summarised in *Table 5.6*.

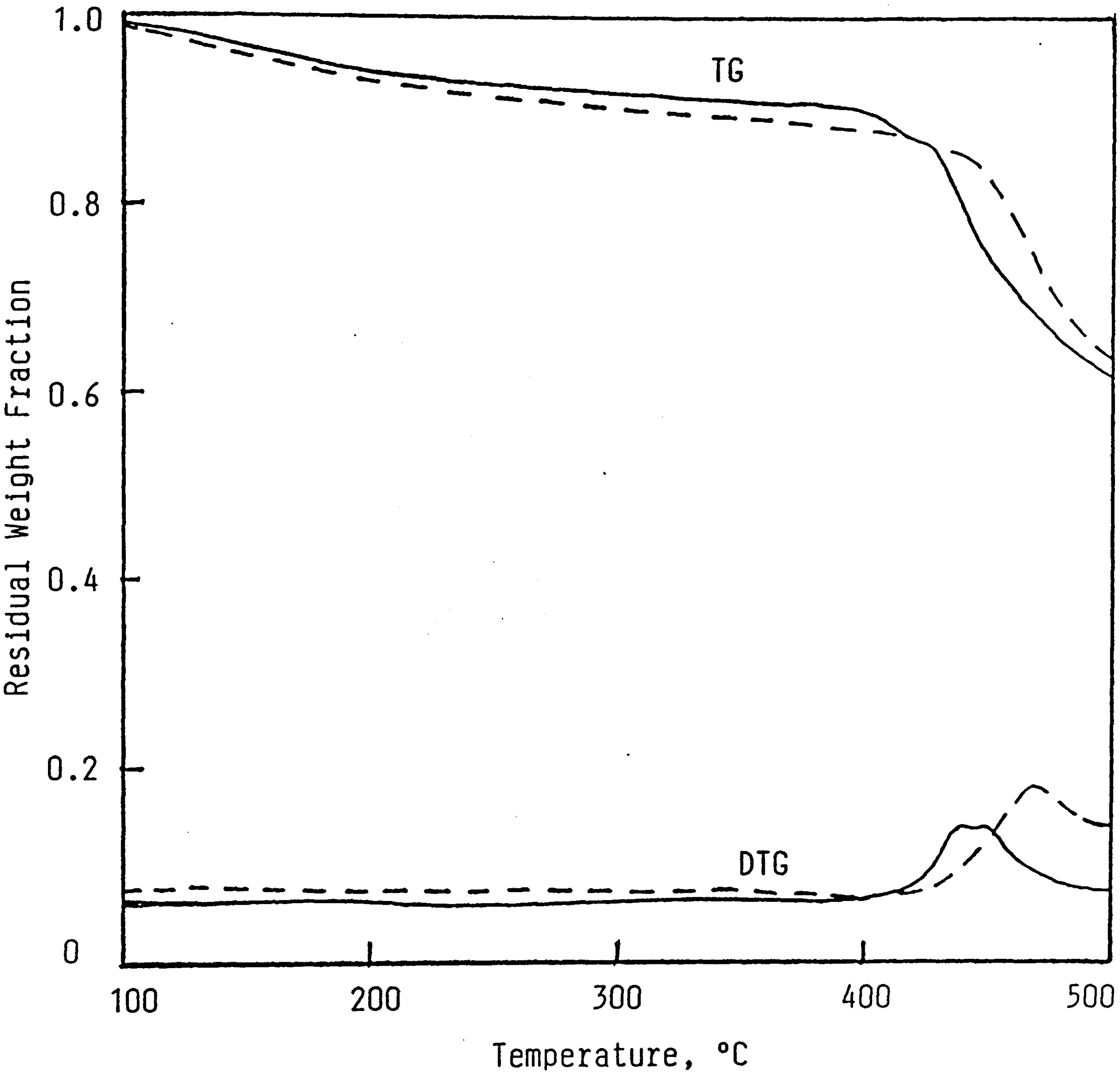


Fig. 5.14. TG and DTG curves (dynamic nitrogen atmosphere, heating rate 10°C/min) for sodium polyacrylate samples prepared by both routes.

——— NaPA made by neutralisation.

------- NaPA made by polymerisation.

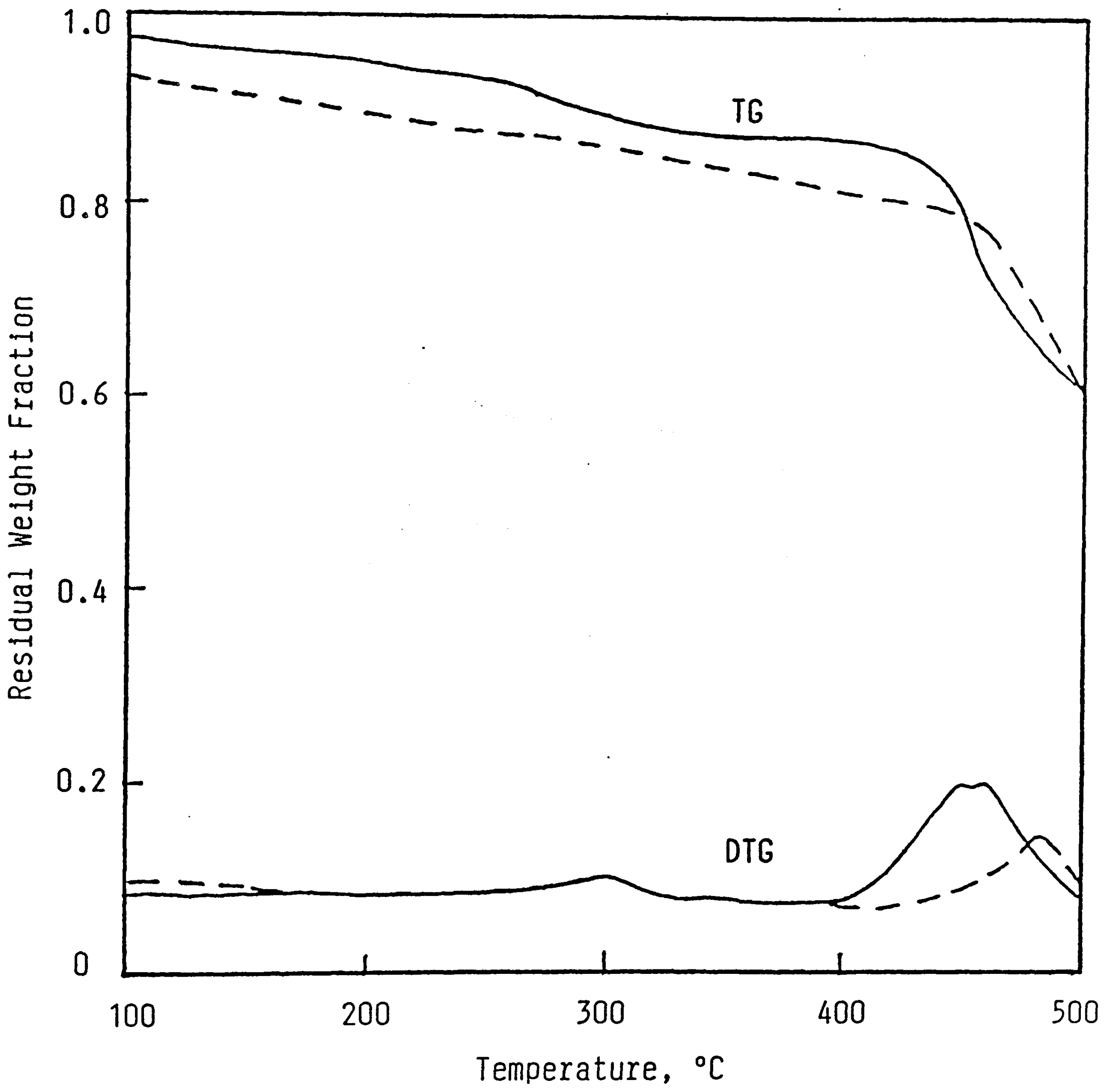


**Fig. 5.15.** TG and DTG curves (dynamic nitrogen atmosphere, heating rate 10$^{o}$C/min) for potassium polyacrylate samples prepared by both routes.

—— KPA made by nutralisation.

------ KPA made by polymerisation.

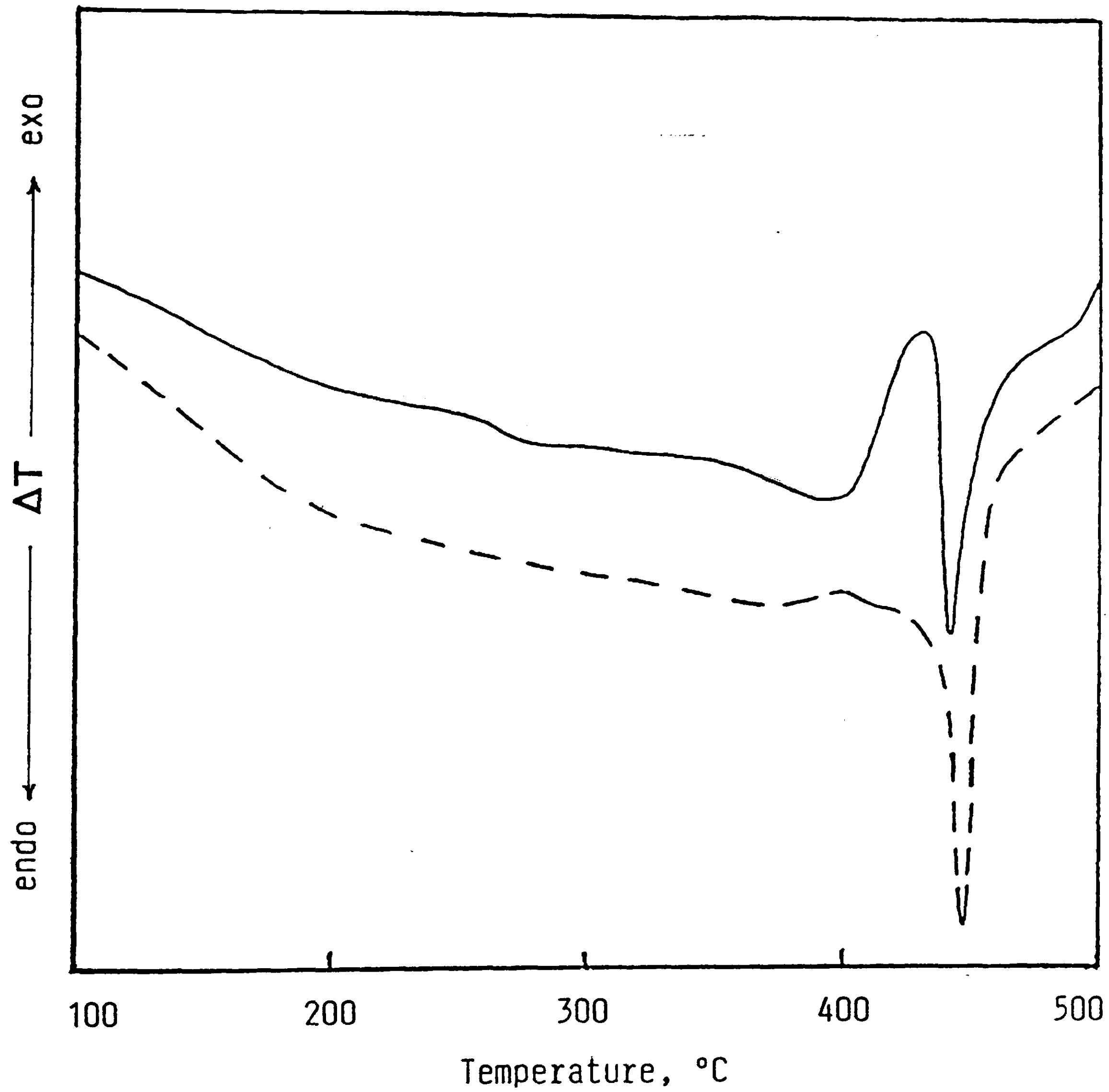


Fig. 5.16. DTA curves (dynamic nitrogen atmosphere, heating rate 10°C/min) for sodium polyacrylate samples prepared by both routes.

——— NaPA made by neutralisation.

------- NaPA prepared by polymerisation.

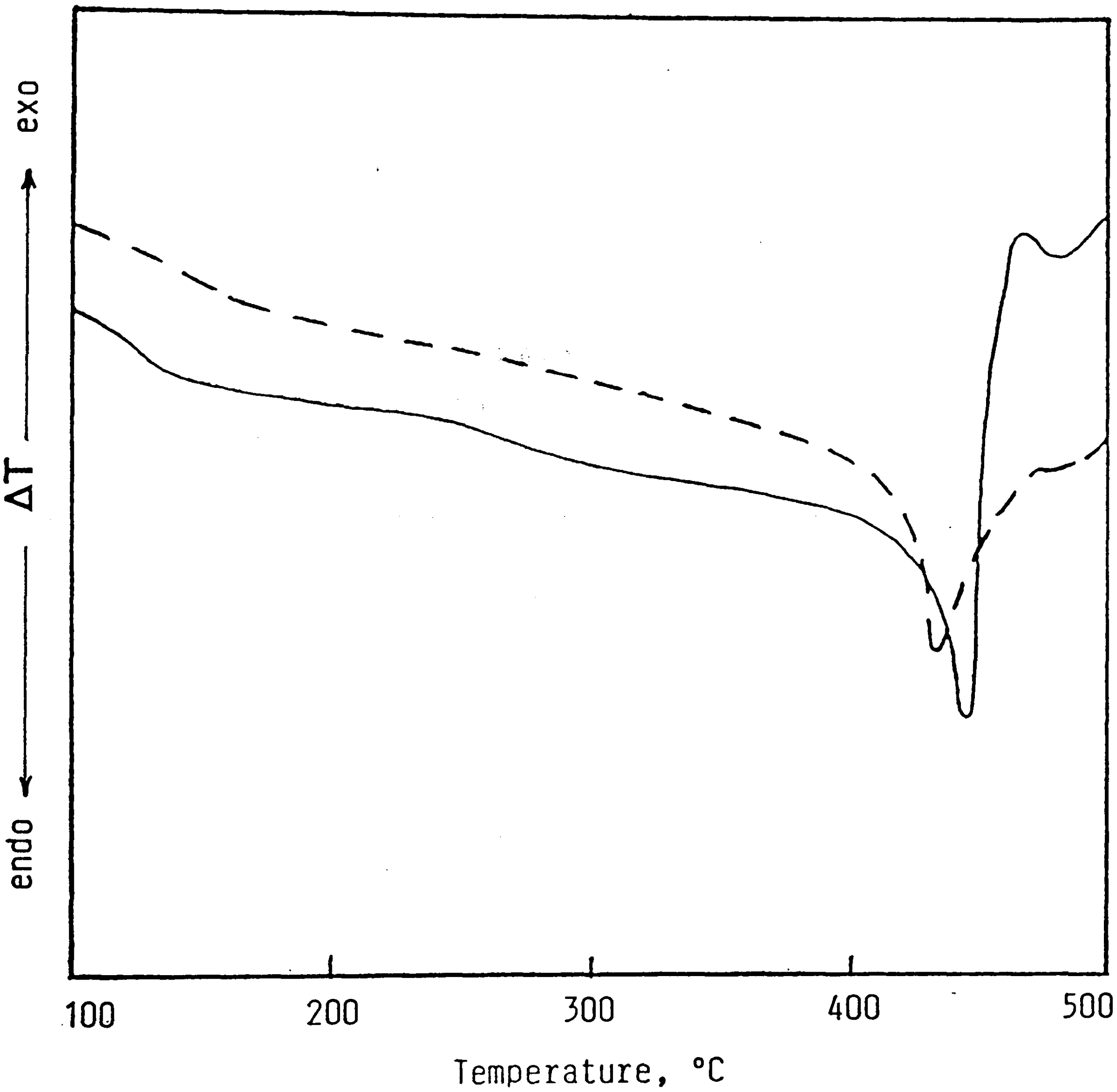


**Fig. 5.17.** DTA curves (dynamic nitrogen atmosphere, heating rate $10^{\circ}$C/min) for potassium polyacrylate samples prepared by both routes.

——— KPA made by neutralisation.

------- KPA prepared by polymerisation.

**Table 5.6.** DTA, TG and DTG data for sodium and potassium. polyacrylate samples made by both routes.

| | DTG | | | TG | DTA | | |
|---|---|---|---|---|---|---|---|
| Polymer | Peak temp., °C | Temp. range, °C | Wt% loss for stage | Total Wt% loss in the range | Peak temp., °C 25-500 °C | Temp. range, °C | Thermal effect |
| | – | 25-430 | 17 | | | | |
| NaPA | | | | 36 | 440 | 430-450 | endo |
| | 470 | 430-490 | 19 | | | | |
| | – | 25-380 | 10 | | | | |
| NaPA* | 400 | 380-420 | 6 | 40 | 450 | 430-455 | endo |
| | 440 | 420-490 | 26 | | | | |
| | – | 25-430 | 18 | | | | |
| KPA | | | | 40 | 440 | 430-450 | endo |
| | 470 | 430-490 | 22 | | | | |
| | – | 25-280 | 6 | | | | |
| KPA* | 290 | 280-320 | 4 | 40 | 450 | 435-455 | endo |
| | 450 | 400-490 | 30 | | | | |

* Polymers synthesised from PAA and respective hydroxides.

## *4. MECHANISM OF DEGRADATION*

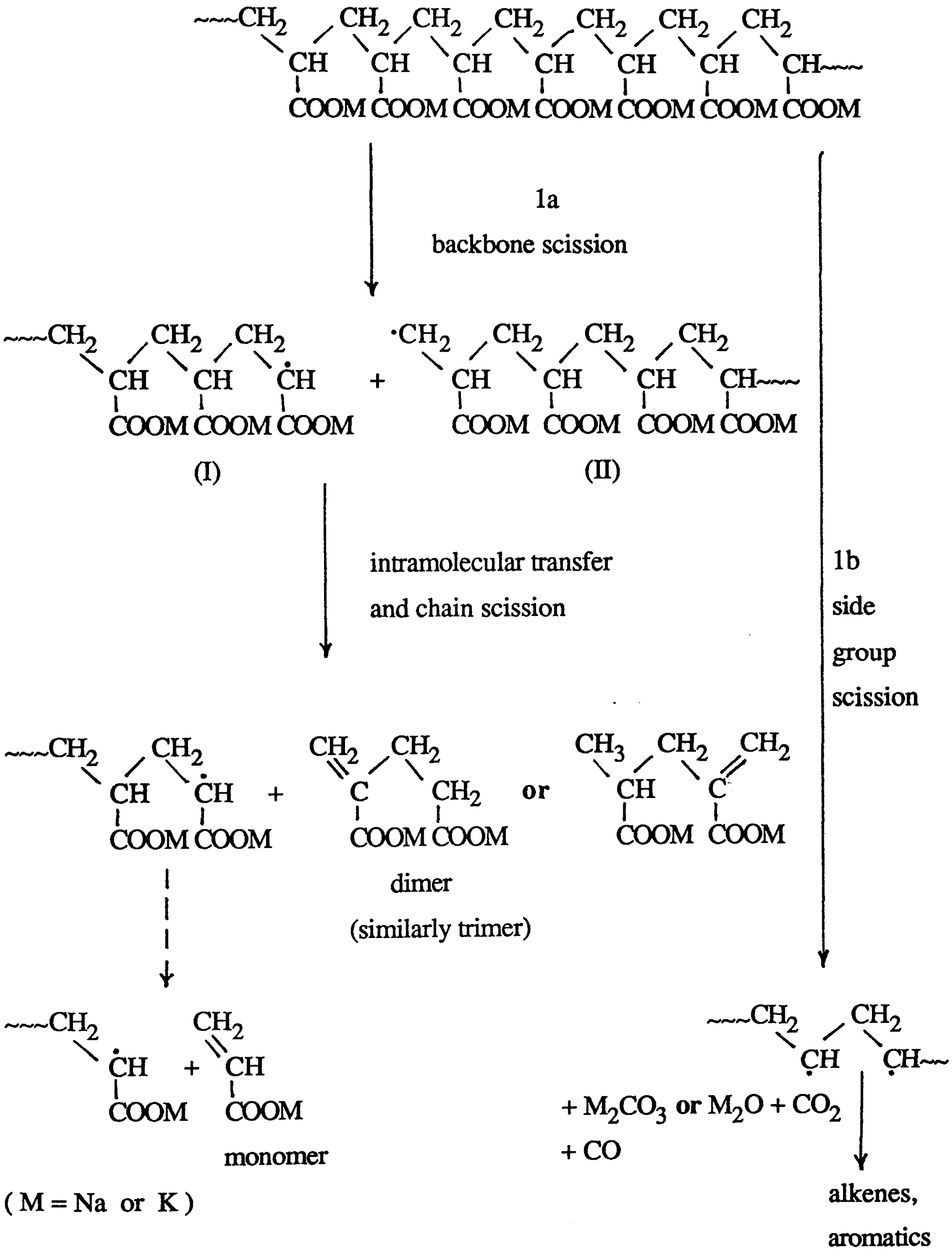
As already mentioned the pyrolysis of some of the salts of aliphatic carboxylic acids is a well known route for the formation of ketones; the reaction has been proposed to occur via *radical intermediates.*[108-110]

There have been several studies of the thermal degradation behaviour of salts of poly(acrylic acid),[93,94,96,107,114,115] but most of these have focused attention on the alkaline earth salts. One study has examined some transition metal polyacrylates.[94] Hetper and coworkers[93] studied the thermal behaviour of Na, Ca and Mg polyacrylate and reported the temperature range of decomposition for NaPA as 420-470 °C. They suggested that the thermal decomposition of metal acrylates proceeds via *side chain* and *main chain scission* without *depolymerisation*. Volatile products reported were $H_2$, CO, $CO_2$, saturated and unsaturated hydrocarbons and aliphatic ketones.

The degradation behaviour of the alkali metal salts of poly(methacrylic acid) has been studied in detail by *McNeill* and *Zulfiqar*[101] using a similar approach to the present investigation. It was found that there were two main routes in the decomposition, the predominent reaction involving *chain scission* and *depolymerisation* to produce monomer or the corresponding isobutyrate, plus side group reactions leading to metal carbonate and a variety of carbonyl-containing organic molecules. Under TVA conditions, the monomer and isobutyrate appear as CRF, which amounted to about 35-38% of the products when NaPMA and KPMA were degraded to 500 °C at 10°/min. These polymers also gave about 7% carbon dioxide and 7-10% liquid volatile products. The degradation behaviour of polymethacrylate salts in general and of copolymers of methacrylate salts with methyl methacrylate, has been reviewed by *McNeill.*[116]

It is well established from many studies in the case of the esters that polyacrylates and polymethacrylates differ in degradation behaviour mainly as a result of the *tertiary hydrogen atoms* in the backbone of the former, which tend to participate in transfer processes leading to chain fragments such as *dimer, trimer,* etc. In the case of polyacrylates, side group decomposition is also much more evident than in most of the polymethacrylates, since *depolymerisation* has been found to occur to a minimal extent.[40] The tendency of polyacrylates to undergo reactions involving transfer of the tertiary hydrogens is also evident in the degradation behaviour of poly(acrylic acid), which was discussed in detail in Chapter Four. Both poly(acrylic acid) and poly(methacrylic acid),[84] however, differ greatly in their degradation behaviour from that of their salts because of the ease of intramolecular dehydration in the case of the acid polymers.

The degradation behaviour of NaPA and KPA is explicable in terms of main chain and side group scission reactions, accompanied to a limited extent by intramolecular transfer of the macroradicals. It differs from that of the corresponding polymethacrylate salts, as might be expected, in leading to very little of the salt monomer as a product. The main features of the degradation are summerised in *Scheme 1*.

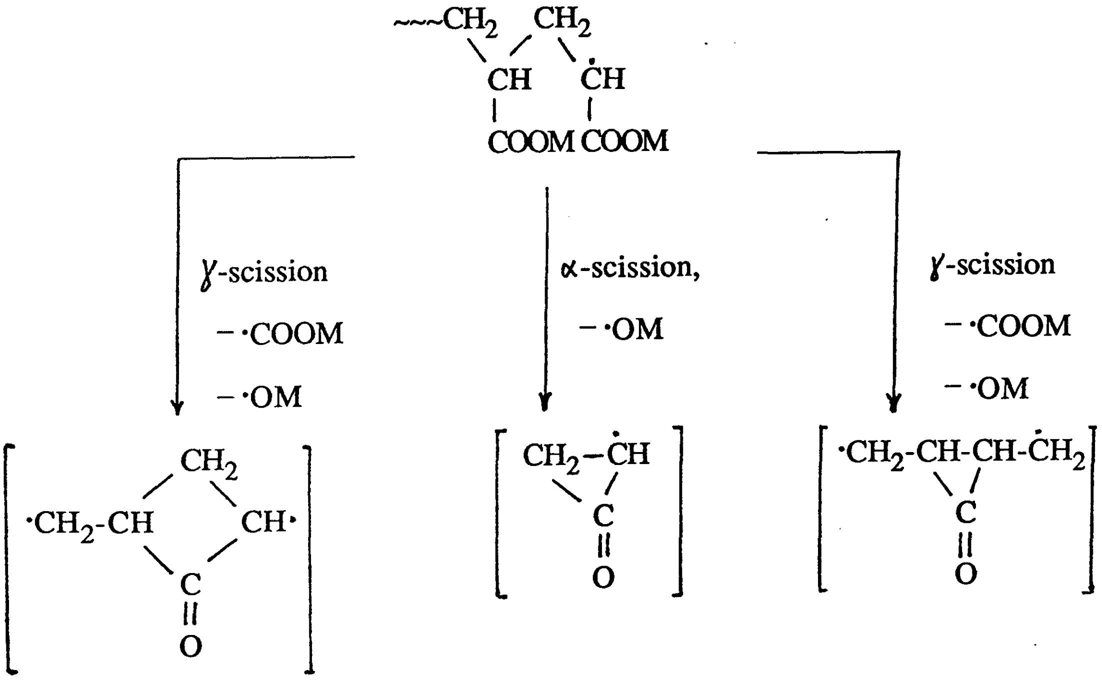

1a
backbone scission
(I)
(II)
intramolecular transfer
and chain scission
1b
side
group
scission
dimer
(similarly trimer)
or
monomer
( M = Na or K )
+ $M_2CO_3$ or $M_2O$ + $CO_2$
+ CO
alkenes,
aromatics

Scheme 1

Main chain scission (reaction 1a) leads to two terminal macroradicals, (I) and (II), which can then react by intramolecular transfer to give dimer, trimer, etc. or to a very small extent by depolymerisation to give monomer. Further reactions of macroradical (I) are discussed below.

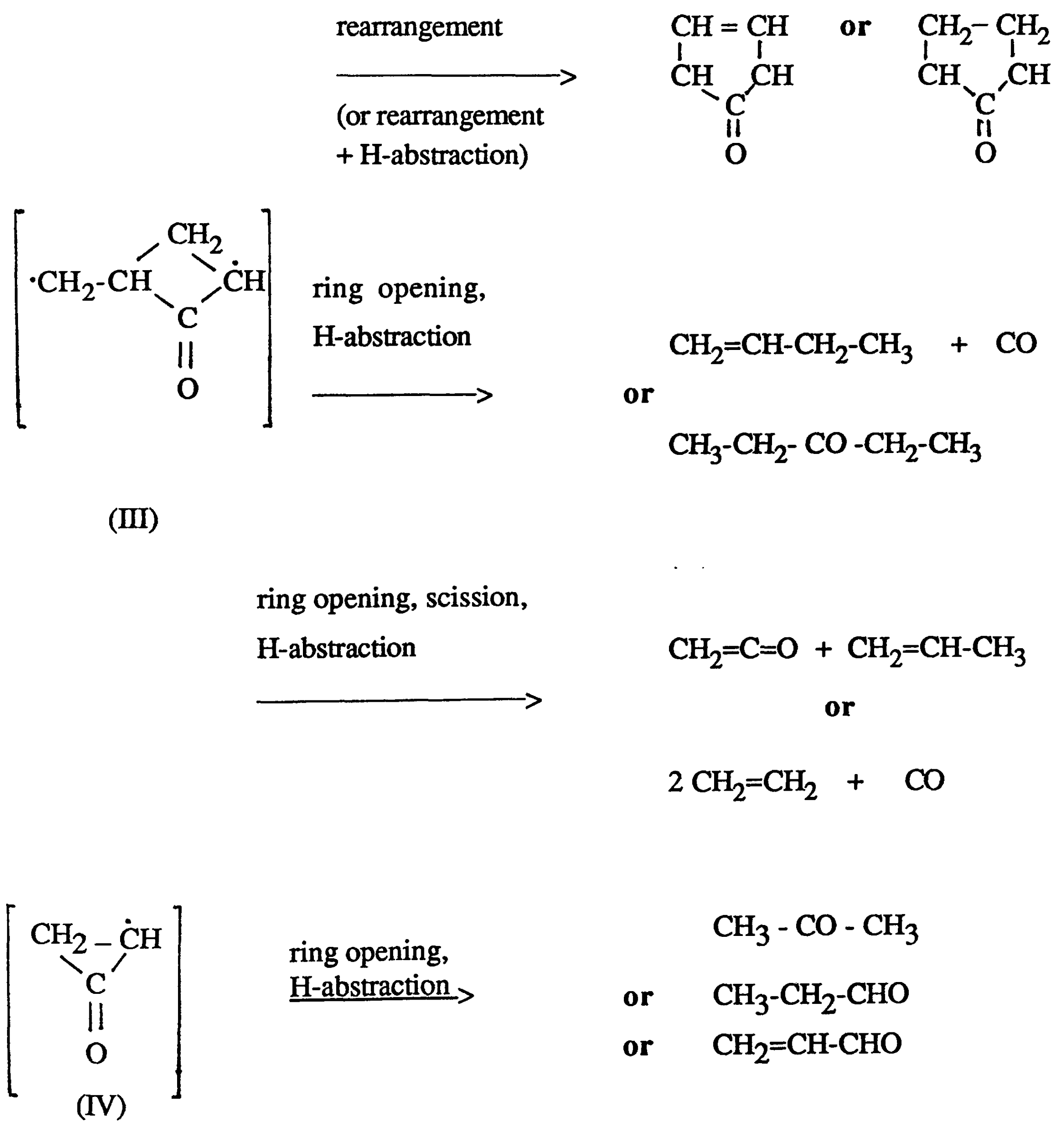
Side group scission (reaction 1b) leads to the formation of metal carbonate, metal oxide, carbon dioxide and carbon monoxide, while secondary reactions of the backbone following several such scissions can explain the formation of alkenes and aromatics.

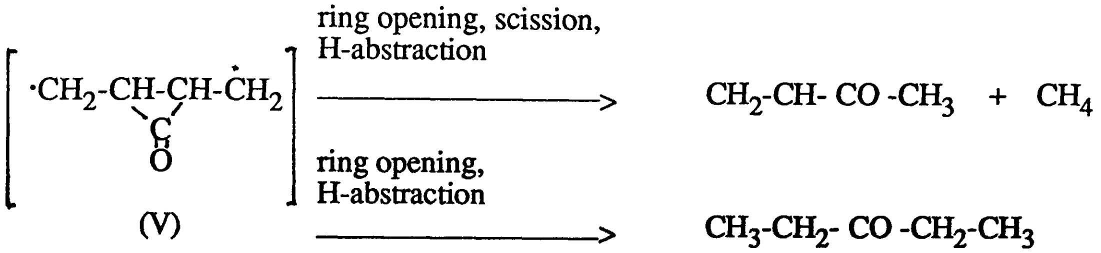
Side group scissions from the terminal macroradical (I) as shown in *scheme 2*, followed by backbone scissions, lead to the transient formation of the species shown as structures (III), (IV) and (V).



Scheme 2

Further reactions of these intermediates, as shown in *scheme 3*, can explain the formation of the great variety of degradation products, such as cyclic and acyclic ketones, aldehydes, certain alkenes, ketene and methane.





Scheme 3

The degradation behaviour of NaPA and KPA therefore parallels that of the corresponding polymethacrylates in some respects. The differences in behaviour are precisely as would be expected from what is already known about the decomposition of acrylate and methacrylate polymers. Thus, the acrylates differ from the methacrylates in giving very little monomer salt, but as a result of intramolecular transfer some short chain fragments are produced. The relatively involatile monomer salt appears in the polymethacrylate salt degradations in the cold ring fraction of products. This fraction, limited to dimer, trimer, etc. in the case of the polyacrylate salt degradations, forms a small proportion of the products in the latter case. In the absence of depolymerisation, side group reactions have greater importance. In both of these classes of alkali metal salt polymer, however, the ultimate solid residue is predominantly the metal carbonate.

## *5. CONCLUSIONS*

The polymers of the sodium and potassium salts of acrylic acid have been prepared by free radical polymerisation of the respective monomers in methanol solution. Both polymer salts were also made by neutralisation of the appropriate metal hydroxide solutions in methanol by addition of a poly(acrylic acid) solution in the same medium. The alkali metal acrylate salts are soluble in water and methanol and may be polymerised in the latter medium to avoid from any effects which might result from hydrolysis. These polymers are soluble in water and insoluble in methanol.

Their degradations were studied under programmed heating condition, by TVA, TG and DTA. These materials are stable to about 400 $^{o}$C under programmed heating at 10 $^{o}$C/min in vacuo.

There are similarities in the degradation behaviour of sodium and potassium polyacrylate. A reaction mechanism for the decomposition of these materials has to account for carbon dioxide, acetone, metal carbonate and short chain fragments as major products and for a variety of volatile products such as ketones (cyclic and acyclic), aldehydes, hydrocarbons, ketene, carbon monoxide and aromatics as minor products.

A mechanism involving random homolytic scission of the chain followed by splitting out of side groups and intra- and intermolecular transfer reactions, and metal carbonate or oxide formation has been proposed and discussed for these materials.

The presence of cycloolefins and aromatics among the volatile decomposition products testifies to side group scission and cyclising of fragments of the naked main chain.

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# CHAPTER SIX

## THERMAL DEGRADATION OF MAGNESIUM AND CALCIUM POLYACRYLATE

### *1. INTRODUCTION*

*Furukawa* and his coworkers were the first to investigate the dry distillation of the alkaline earth metal (Ca and Ba) salts of poly(acrylic acid) and poly(methacrylic acid). Initially, they reported only one cyclic ketone.[117] In subsequent papers[114,115,118-120], however, they reported the formation of twelve and fifteen different ketones, respectively, in the degradation of calcium polymethacrylate (CaPMA) and polyacrylate (CaPA), in the range 350-500 °C. They reported that CaPA and CaPMA gave similar behaviour on thermal degradation, which might be assumed to occur through a radical decomposition mechanism. They, however, considered that the multiplicity of products is the result of the decomposition of the higher ketones to smaller ones.

*Hetper et al*[93] studied the thermal behaviour of sodium, calcium and magnesium polyacrylate. They found that the main decomposition of Ca and Mg polyacrylate takes place in the temperature range 450-490 °C. They reported that in the solid residues after decomposition of the Ca salt, carbonate was present, whereas magnesium polyacrylate decomposes to magnesium oxide at these high temperatures. They suggested that the thermal degradation of the metal polyacrylates proceeds via side-chain splitting and main chain scission of the polymer, without depolymerisation.

*Ardagh* and coworkers,[108] who studied the pyrolysis of calcium acetate, suggested that the high temperature reaction proceeds by a chain mechanism, initiated by the formation of free radicals.

*Bell and Reed,*[110] who studied the pyrolysis of barium acetate and formate mixtures, using isotopic tracer techniques, showed the formation of ketone and aldehyde to be by a free radical mechanism. *O,Neill* and *Reed*[121] have shown that pyrolysis of sodium isobutyrate, a compound which decomposes about 400 °C, yields a substantial quantity of acyclic ketones.

Some investigators[122,123] reported that in the degradation of acid salts, the yield of acetone varies markedly according to the metal present, even when such changes are restricted to alkali and alkaline earth metals.

*McNeill* and *Zulfiqar,*[102] who studied the thermal behaviour of the alkaline earth metal salts of poly(methacrylic acid), proposed that the mechanism of degradation is based on radical intermediates. They noted that depolymerisation, which was found to be important in degradation of the alkali metal polymethacrylates, cannot occur to the same extent in the corresponding alkaline earth metal salts polymers because, except in the case of magnesium salt, the monomers are involatile and cannot distil out of the reaction zone before decomposition. They suggested that the alternative process, involving formation of ketones and metal carbonate or oxide, therefore predominates.

*Nicholson* and his coworkers[87] have examined the influence of two cations, magnesium and calcium, on the thermal behaviour of poly(acrylic acid). They found that the partially neutralised products based on these ions, unlike the corresponding materials with Li, Na and K ions, did not undergo thermal decarboxylation at 250 °C.

In the present study, the thermal behaviour and mechanism of degradation of calcium and magnesium polyacrylate were investigated. It was found that the results are consistent with a free radical mechanism, in agreement with the conclusions of various investigators.[102,110,121]

## 2. *THERMAL STABILITY AND DEGRADATION OF MONOMER SALTS*

Dry distillation of calcium acrylate has been studied by ***Furukawa*** et al[120], who reported fifteen ketones.

The thermal behaviour and stability of magnesium and calcium acrylate were studied using TVA, TG and DTG as described in the previous chapter.

### 2.1. *DIFFERENTIAL THERMAL ANALYSIS*

DTA curves for the monomer salts are shown in ***Fig. 6.1***. The DTA curves were recorded in the range 25-485 °C in nitrogen atmosphere. It was found that the monomers polymerise in the solid state before degradation and the exothermic peaks in the DTA curves confirm that the thermal polymerisation takes place at about 240 °C. The absence of the endotherm in the DTA curve of calcium acrylate up to 485 °C, due to the main decomposition step, indicates that this salt is more stable than the magnesium salt.

### 2.2. *THERMOGRAVIMETRY*

TG was carried out under nitrogen and the corresponding curves are shown in *Fig. 6.2*. The TG curves show two decomposition processes above 400 °C.

An initial weight loss below 120 °C is due to the release of water. Above 120 °C, the samples are still losing weight but only slowly. The main step of decomposition is observed at high temperature around 470 °C with 27 and 45% weight loss for calcium and magnesium acrylate, respectively.

The percentages of residue from the original sample at 500 °C for Mg and Ca acrylate indicate 61 and 33% weight loss, respectively. The difference is attributed to the decomposition of magnesium carbonate (unstable close to 500 °C) to magnesium oxide.

The TG data, shown in *Table 6.1*, confirm the high thermal stability of the monomer salts. The main decomposition process is observed at about 460 °C and no considerable weight loss is shown below this temperature.

**Table 6.1.** TG data for magnesium and calcium acrylate.

| Monomer | Wt. loss% at 120 °C | Wt. loss% at 425 °C | Wt. loss% at 500 °C | Residue % at 500 °C |
|---|---|---|---|---|
| Mg acrylate | 15 | 21 | 61 | 39 |
| Ca acrylate | 6 | 12 | 33 | 67 |

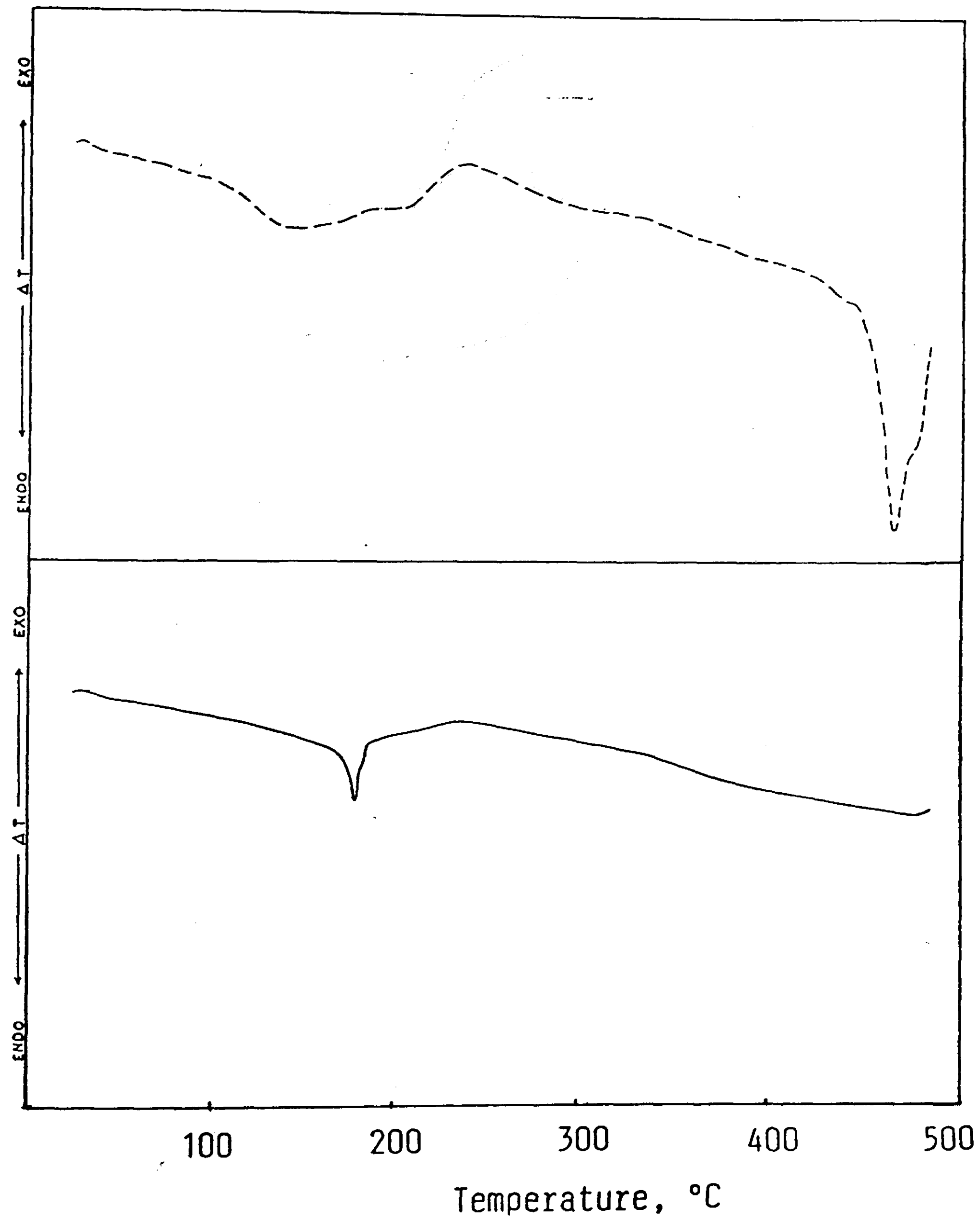


**Fig. 6.1.** DTA curves (dynamic nitrogen atmosphere, heating rate 10°C/min) for magnesium and calcium acrylate samples. ------ Mg acrylate; —— Ca acrylate.

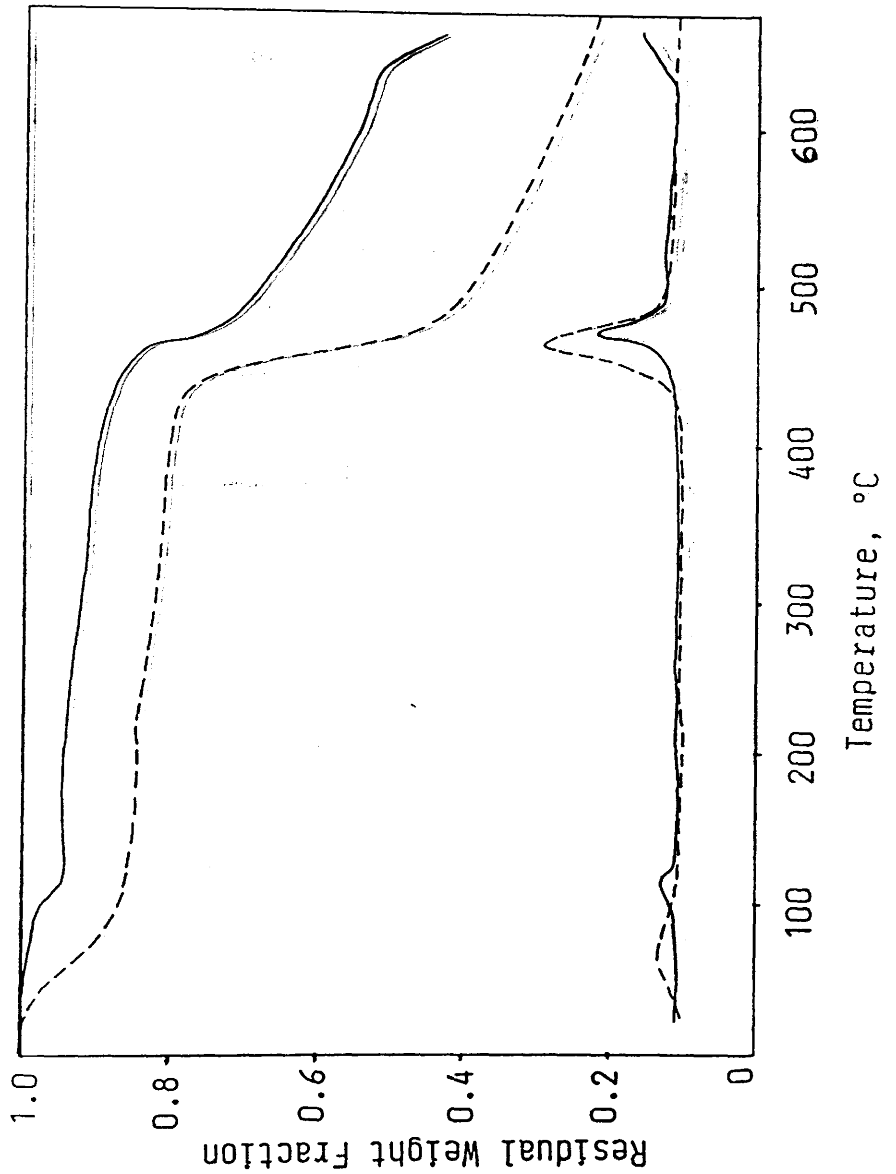


**Fig. 6.2.** TG and DTG curves (dynamic nitrogen atmosphere, heating rate $10^{o}$C/min) for magnesium and calcium acrylate samples;

------- Mg acrylate; ——— Ca acrylate.

## *2.3. THERMAL VOLATILISATION ANALYSIS*

It is clear from the TVA curves for both monomer salts (Fig. 6.3) that no volatile degradation product is evolved at temperature below 420 °C. The sharp release of volatile products, including non-condensable gases, begins above this temperature. Magnesium acrylate shows two poorly resolved stages of decomposition between 420° and 500° with $T_{max}$ around 455° and 480 °C. The TVA curve for calcium acrylate consists of a single peak having a $T_{max}$ at about 485 °C.

The separation of traces in TVA curve is indicative of a variety of products. TVA data for both monomer salts, given in *Table 6.2* are consistent with the TG and DTA data.

**Table 6.2.** TVA data for degradation of magnesium and calcium acrylate samples.

| Monomer | $T_{onset}$ °C | $T_{max_1}$ °C | $T_{max_2}$ °C | Wt% $CO_2$ |
|---|---|---|---|---|
| Mg acrylate | 360 | 455 | 480 | 17.5 |
| Ca acrylate | 390 | — | 485 | 11.5 |

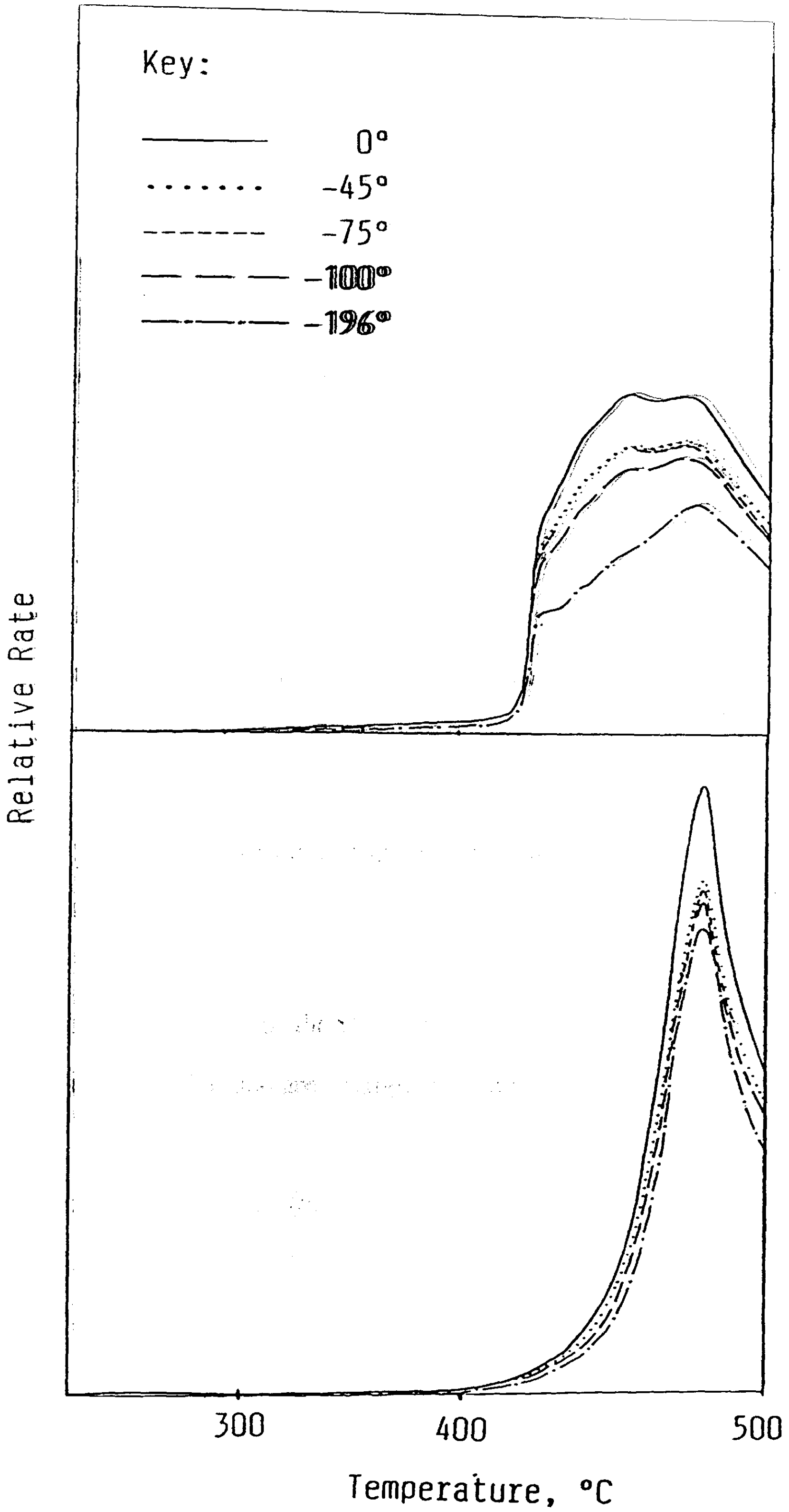


**Fig.6.3.** TVA curves(vacuum, heating rate 10°C/min) for magnesium acrylate (above) and calcium acrylate (below).

### *2.3.1. Product Analysis*

The degradation products obtained from the monomer salts were examined spectroscopically. This method does not allow identification of all the products, particularly the liquid and cold ring fractions.

After the monomer salts were heated to 500 $^{o}$C in the TVA system, the condensable volatile products collected in liquid nitrogen trap in the vacuum system were separated by the SATVA technique. The SATVA curve for warm up from -196 $^{o}$C to 0 $^{o}$C of these products in the case of magnesium acrylate is illustrated in *Fig. 6.4*. The corresponding ir spectra are reproduced in *Figs. 5a, 5b,* and *6.*

Carbon dioxide , acetone, ketene, propene and 1-butene are present as condensable gaseous products.

It is found that the ir spectra of the cold ring fractions of the magnesium and calcium acrylate samples are similar and are negligible in amount.

Metal carbonate and metal oxide (only from Mg acrylate) were identified in the residue.

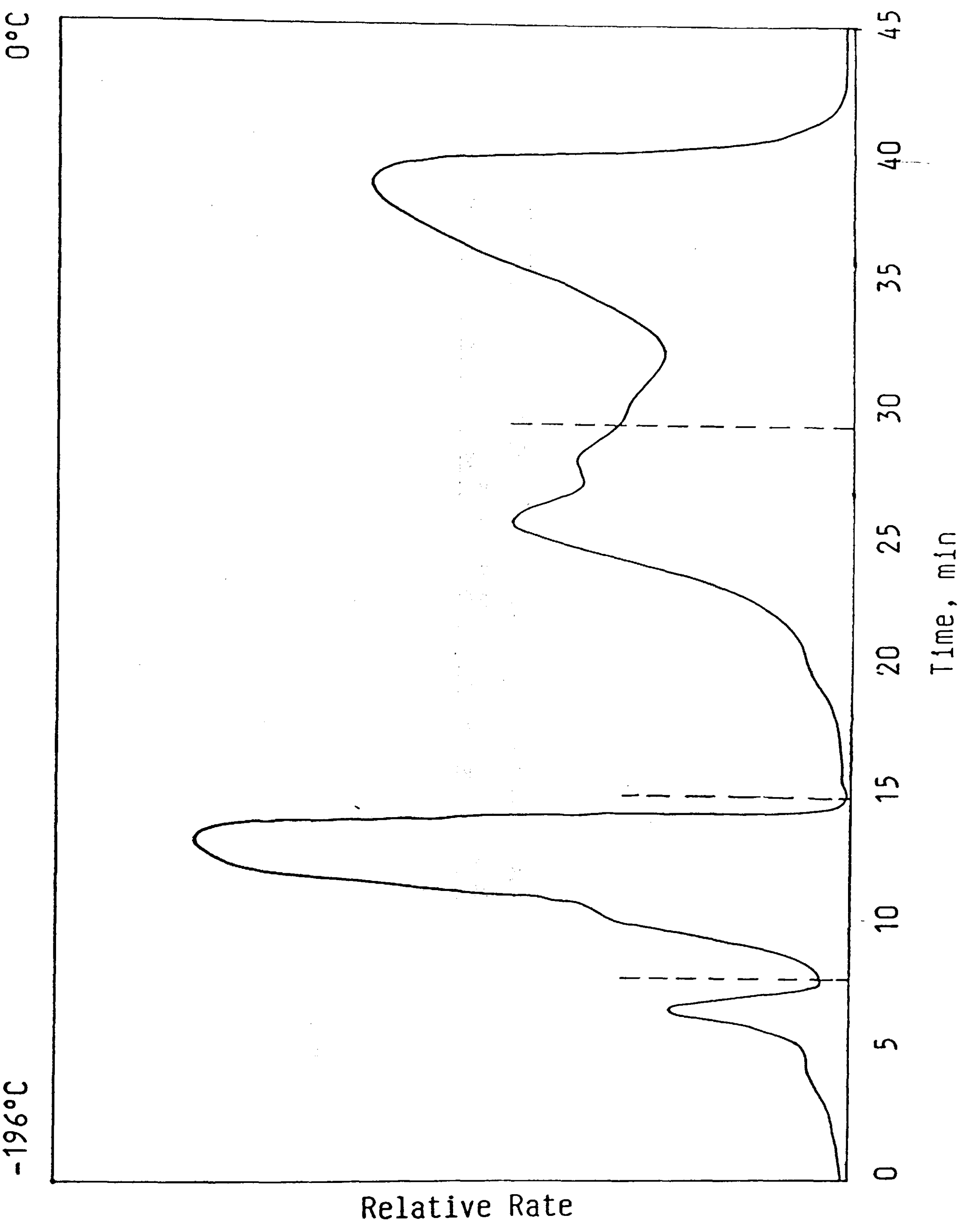
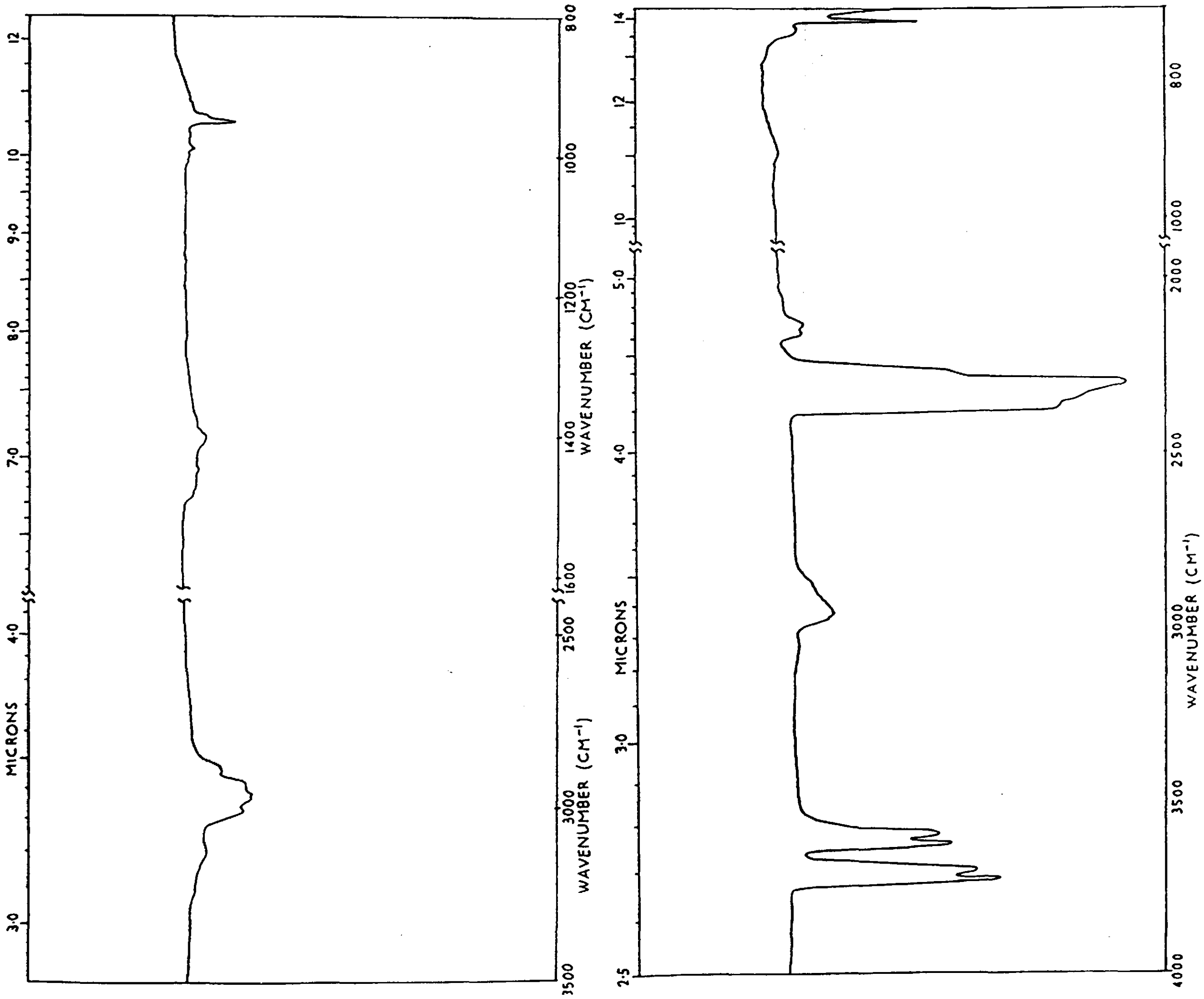


**Fig. 6.4.** SATVA curve of condensable product fraction from degradation of magnesium acrylate to 500 °C in the TVA system at 10°/min.



First

fraction

Second

fraction

**Fig. 6.5a.** Ir spectra of the first and second fraction peaks on SATVA trace, shown in Fig. 6.4.

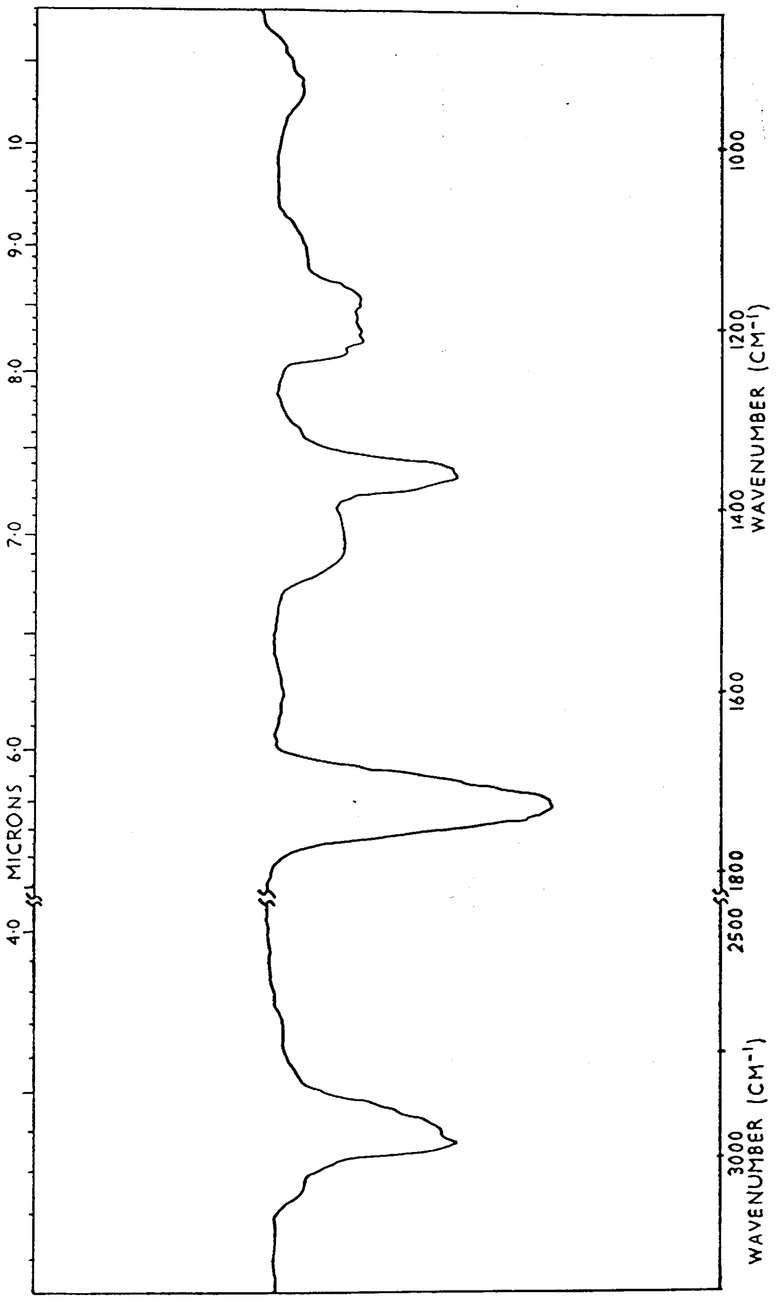
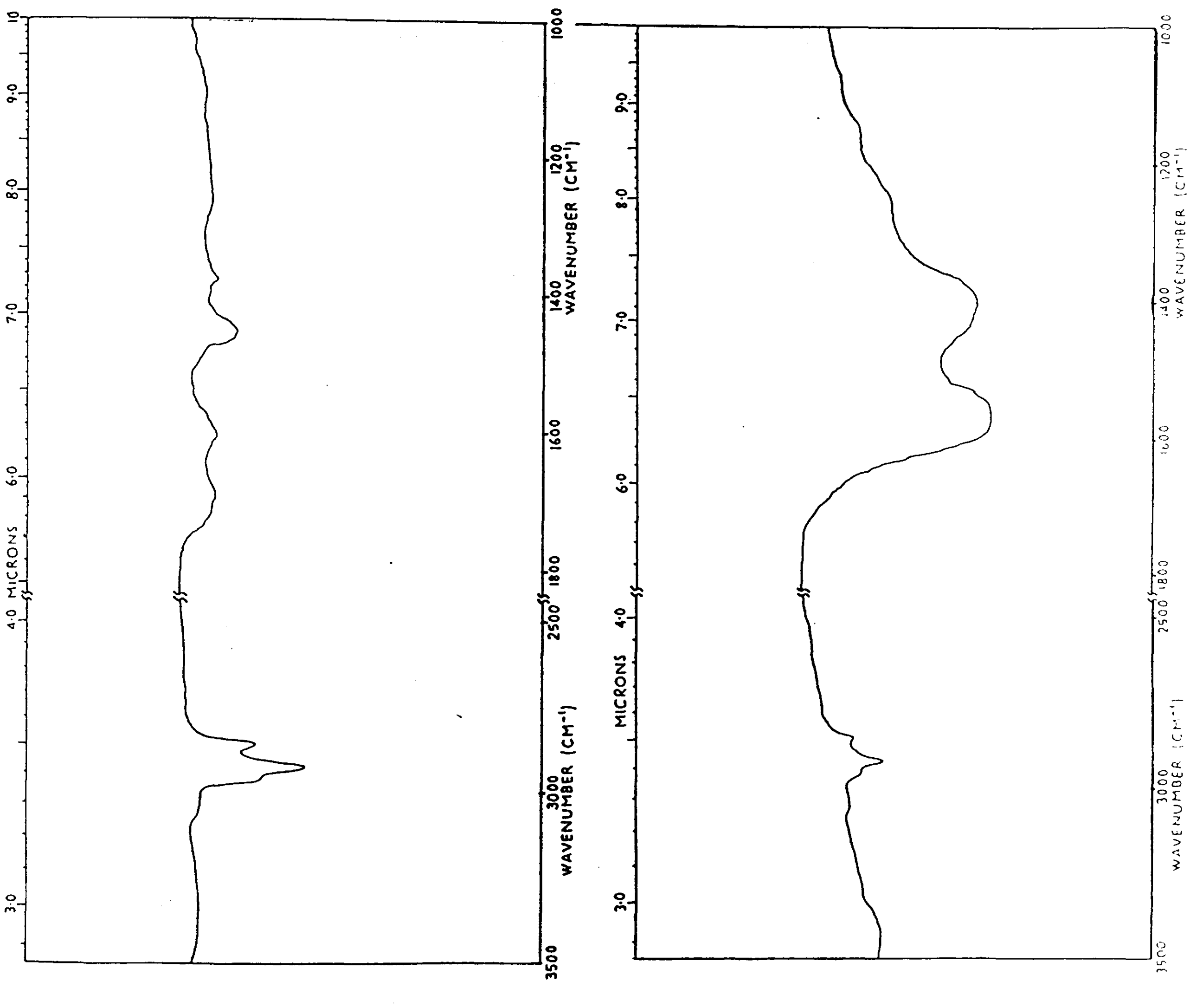


**Fig. 6.5b.** Ir spectrum of the third fraction peaks on SATVA trace, shown in Fig. 6.4.



CRF

Residue

Fig. 6.6. Ir spectra of the CRF and the involatile fraction from degradation of magnesium acrylate to 500 °C in the TVA system.

## *3. THERMAL BEHAVIOUR OF Mg AND Ca ACRYLATE HOMOPOLYMERS*

The thermal behaviour of these homopolymers shows some similarities to that of the alkali metal salts of PAA, previously described in Chapter Five, but appreciable differences exist in the relative amounts of volatile products and the variety of acyclic ketones.

In this chapter, the homopolymers made directly by polymerisation of the monomers will be denoted MgPA and CaPA and those made from PAA by neutralisation will distinguished as CaPA* and MgPA*.

### *3.1. THERMOGRAVIMETRY*

The TG and DTG curves obtained in the degradation of the four polymers are reproduced in *Figs. 6.7* and *6.8*. The TG curves for calcium polyacrylate, shown in *Fig. 6.8,* indicate a gradual weight loss up to the point above 450 $^{o}$C at which rapid breakdown occurs,beginning at a temperature around 175 $^{o}$C in which it accounts for 10 and 20% weight loss for CaPA and CaPA*, respectively. The rate of weight loss increases until a plateau appears at ca. 490$^{o}$, corresponding to a 38% weight loss for CaPA and CaPA* at 470 $^{o}$C. MgPA and MgPA* show 8 and 21% weight loss at 350$^{o}$C, respectively.

The polymers made by neutralisation ( and especially MgPA* ) show much earlier onset of weight loss, which is probably due to release of water or partial degradation as dehydration and decarboxylation of some unreacted acid units in the chains.[82,84,124] The main decomposition leaving metal carbonate and metal oxide (only the magnesium salt) is observed above 450 $^{o}$C. Total weight losses near 500 $^{o}$C for MgPA and MgPA* are 59 and 69%, respectively.

### *3.2. DIFFERENTIAL THERMAL ANALYSIS*

The thermal stability of the polymers was also examined by the DTA technique to 500° and 1000 °C under dynamic nitrogen and argon, for magnesium and calcium polyacrylate, respectively. The DTA curves are shown in *Fig. 6.9.* The DTA curves of the polymers do not exhibit the exothermic effect assigned to thermal polymerisation of the respective monomer salts. The DTA curve in the case of magnesium polyacrylate, shows the gradual partial degradation which is apparent in the TG traces, as an endothermic drift, followed by a sharp endotherm in the same temperature region as the TG rate maximum at about 470 °C. The exotherm showing at about 520 °C for calcium polyacrylate possibly corresponds to the structural changes such as the transition of $CaCO_3$ (aragonite) to $CaCO_3$ (calcite). The endothermic effect at ca. 870 °C is due to the calcium carbonate decomposition. Characteristic features of the thermal behaviour of the polymers established by TG, DTG and DTA are listed in *Table 6.3.*

### *3.3. THERMAL VOLATILISATION ANALYSIS*

All the polymers were examined as 75 mg powder samples in a TVA apparatus. The corresponding TVA traces are reproduced in *Figs.6.10* and *6.11.*

It is clear from the TVA traces that volatile products including a non-condensable fraction appear at a temperature around 290 °C for CaPA$^*$ and MgPA$^*$ and at about 420 °C for CaPA and MgPA. This difference, which was also apparent in the alkali metal salt polymers made by both routes, probably arises from the instability of acrylic acid units left unreacted in the structure of the polymers prepared by neutralisation. The TVA curves of CaPA and MgPA show a single peak due to the main decomposition between 460 and 500 °C showing $T_{max}$ at about 480 °C, consistent with the TG data. TVA traces for the polymers synthesised by neutralisation indicate the initial partial

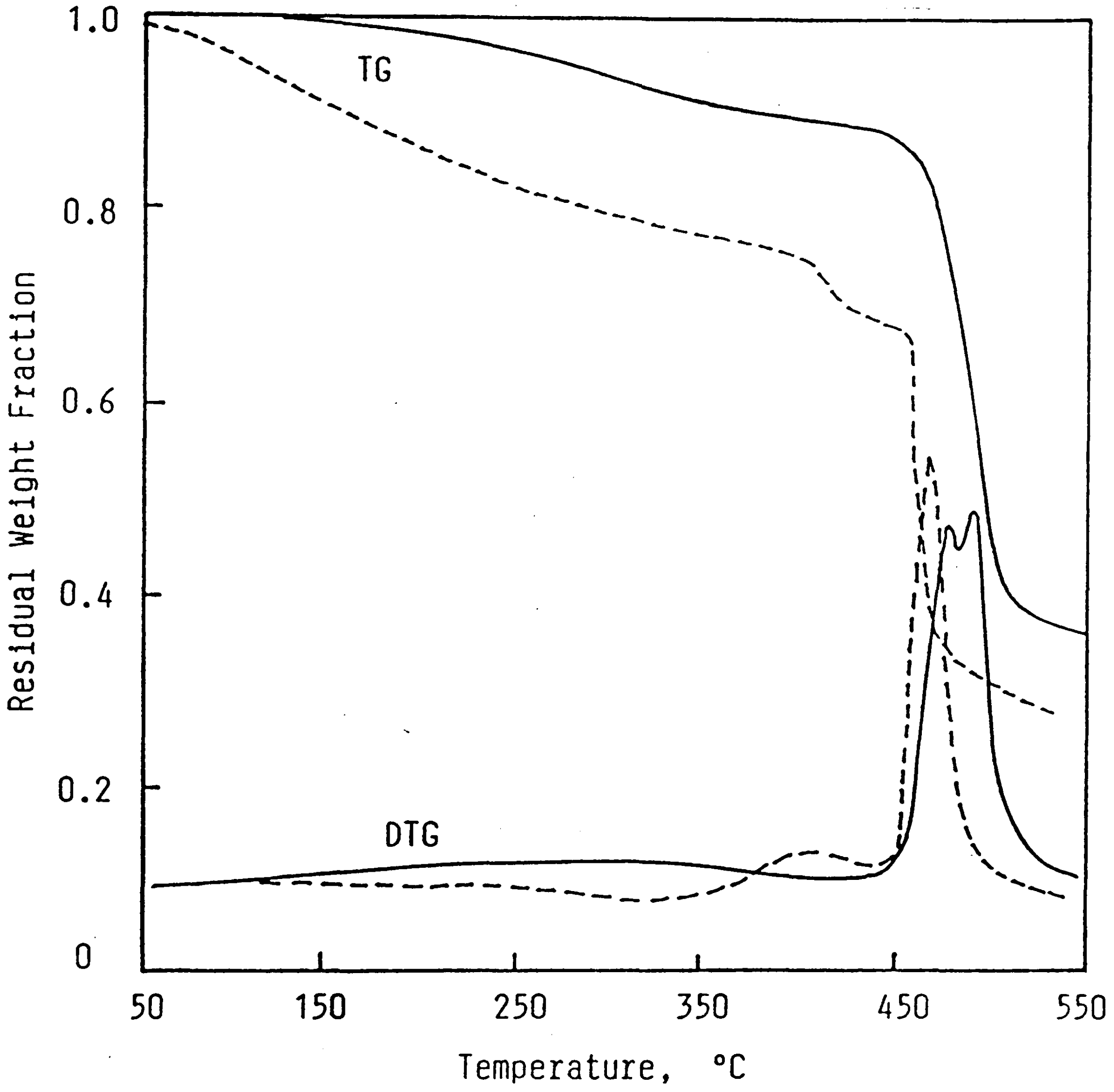


**Fig. 6.7.** TG and DTG curves (dynamic nitrogen atmosphere, heating rate 10°C/min) for magnesium polyacrylate samples.

—— MgPA, ----- MgPA*

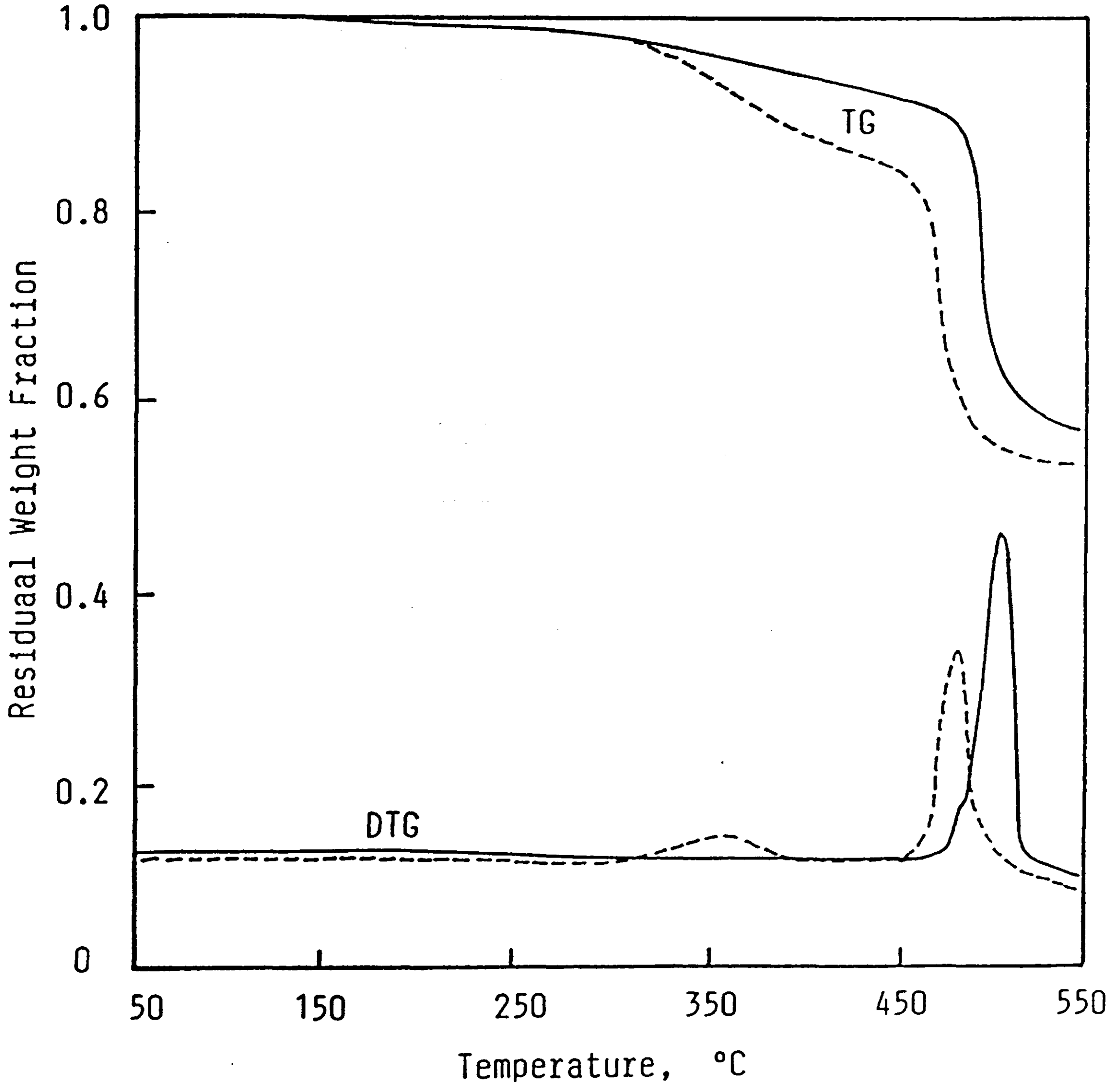


**Fig. 6.8.** TG and DTG curves (dynamic nitrogen atmosphere, heating rate 10°C/min) for calcium polyacrylate samples.

—— CaPA, ----- CaPA*

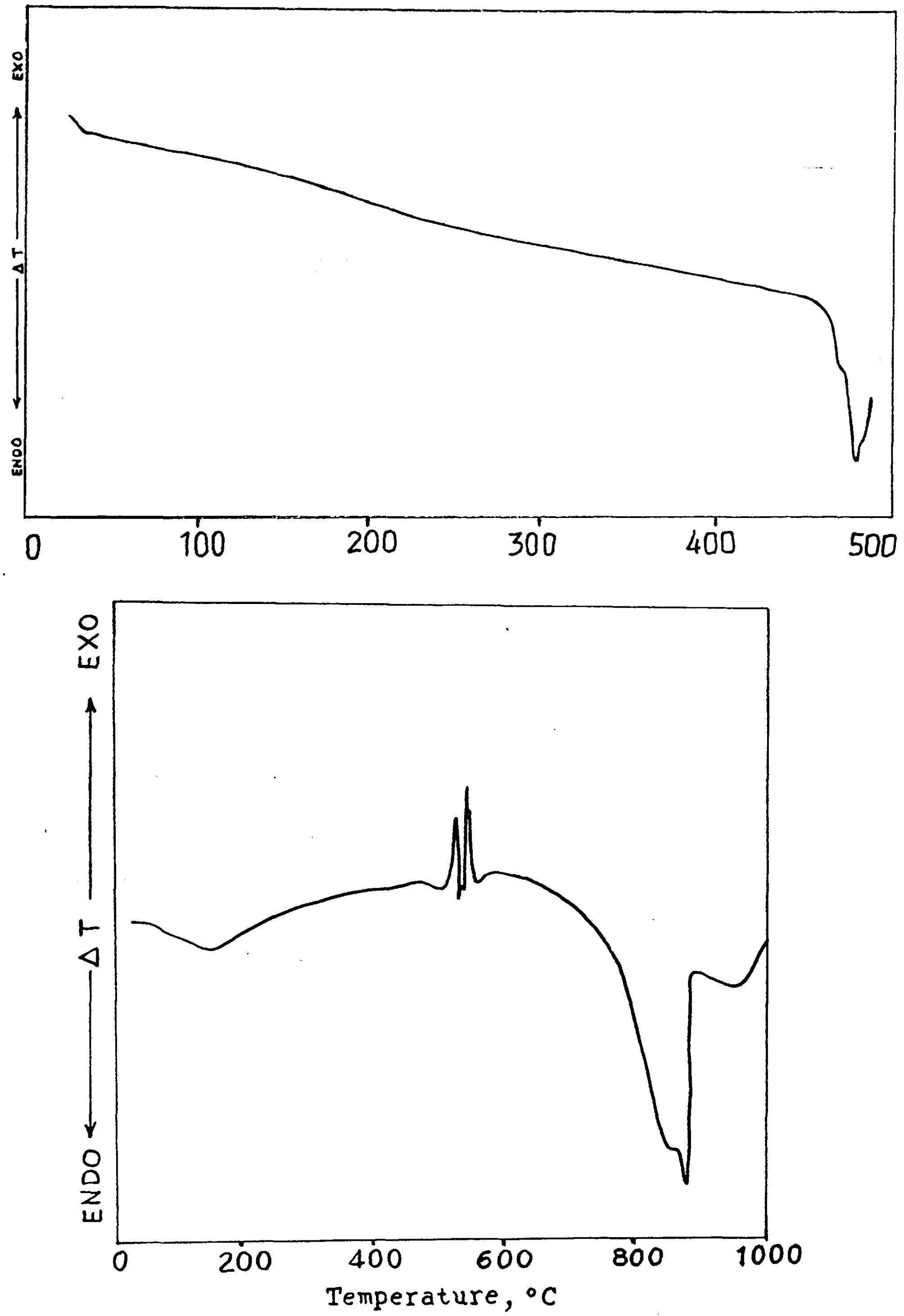


**Fig. 6.9.** DTA curves (dynamic nitrogen atmosphere, heating rate 10°C/min) for magnesium polyacrylate (above) and calcium polyacrylate (below).

degradation in the appearance of a smaller peak at lower temperature than the main decomposition peak.

The separation of the TVA traces is clearly indicative of a wide range of products.

Quantitative measurements of the main product fractions were carried out as described previously in Chapter Four. The high yield of carbon dioxide produced in the degradation of magnesium polyacrylate results from the instability of magnesium carbonate at 500 °C under vacuum.

Calcium and magnesium polyacrylate samples prepared by neutralisation show higher carbon dioxide yields than the CaPA and MgPA due to the decarboxylation of some unreacted carboxylic groups in the chain.

The TVA data for the polymers are summarised in *Table 6.4*.

### *3.3.1. Product Analysis*

The degradation products of the polymers to 500 °C under normal TVA conditions were investigated by the same techniques already described in Chapter Five. These were examined as four main fractions, consisting of the involatile residue, the cold ring fraction, the condensable volatile fraction and the non-condensable gases.

SATVA traces for the polymers made by polymerisation are reproduced in *Figs. 6.12* and *6.13*.

**Table 6.3.** DTG, TG and DTA data for magnesium and calcium polyacrylate samples made by both routes.

| Polymer | DTG | | TG | | DTA | |
|---|---|---|---|---|---|---|
| | Peak temp., °C | Temp. range, °C | Wt loss% for stage | Total Wt loss% in the range 25 - 500 °C | Peak temp., °C | Temp. range, °C |
| | — | 160-450 | 12.5 | | 470 | 450-475 |
| MgPA | 475 | 450-480 | 27.5 | 63.5 | 478 | 475-485 |
| | 485 | 480-520 | 23.5 | | | |
| | — | 25-375 | 22.5 | | 38 | 30-50 |
| MgPA* | 420 | 375-445 | 8.5 | 69 | 400 | 375-425 |
| | 465 | 445-500 | 38 | | 470 | 460-485 |
| | — | 160-470 | 10 | | 35 | 25-40 |
| CaPA | 475 | 470-485 | 5 | 45 | 520 | 510-540 |
| | 495 | 485-520 | 30 | | 870 | 800-880 |
| | — | 170-300 | 4.5 | | 45 | 30-50 |
| CaPA* | 360 | 300-425 | 12 | 47.5 | 520 | 500-530 |
| | 470 | 425-520 | 31 | | 865 | 800-880 |

* Polymers made by neutralisation.

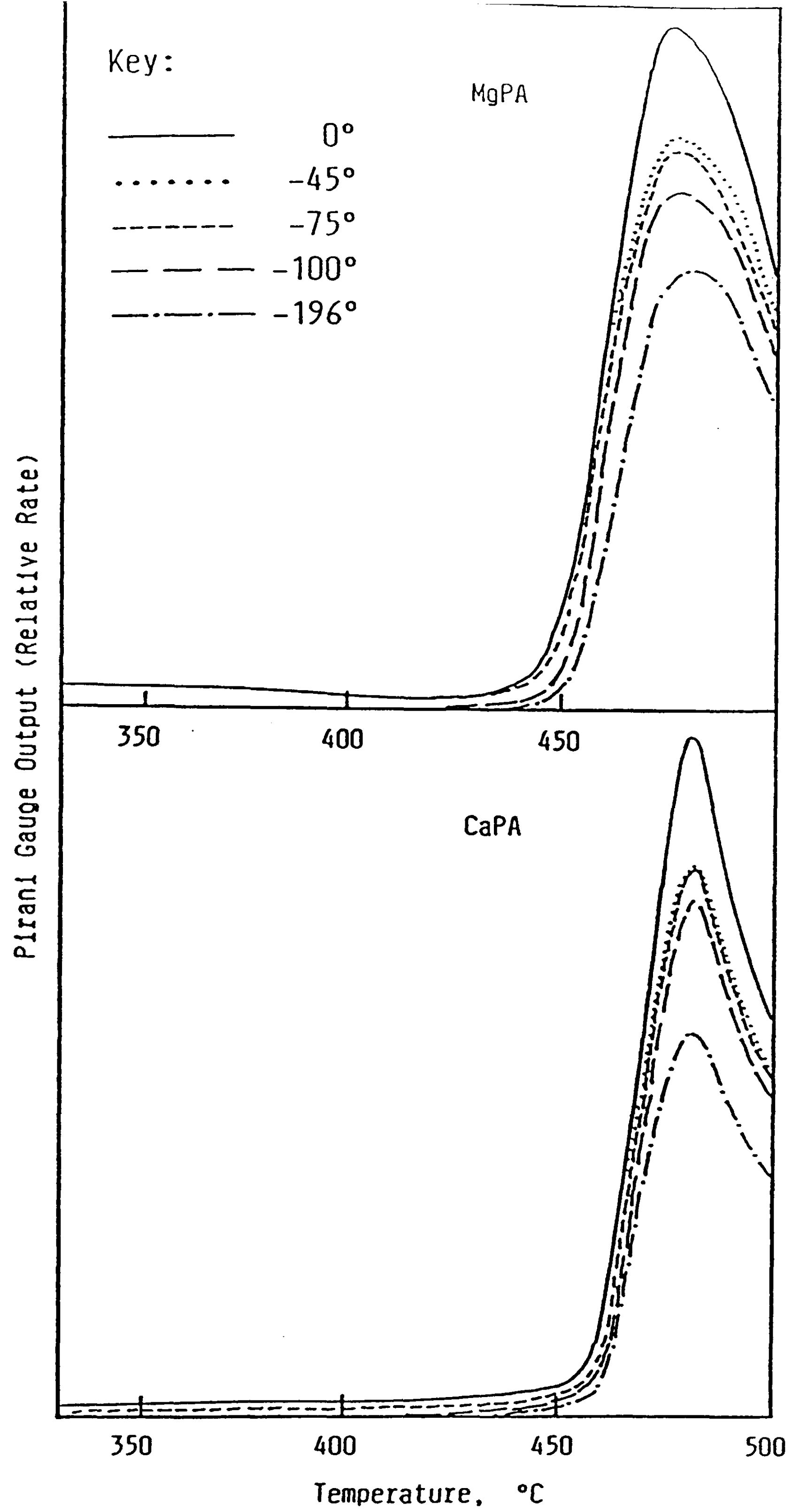


**Fig. 6.10.** TVA curves (vacuum, heating rate 10°C/min) for magnesium and calcium polyacrylate samples prepared by polymerisation. Magnesium polyacrylate (above); Calcium polyacrylate (below)

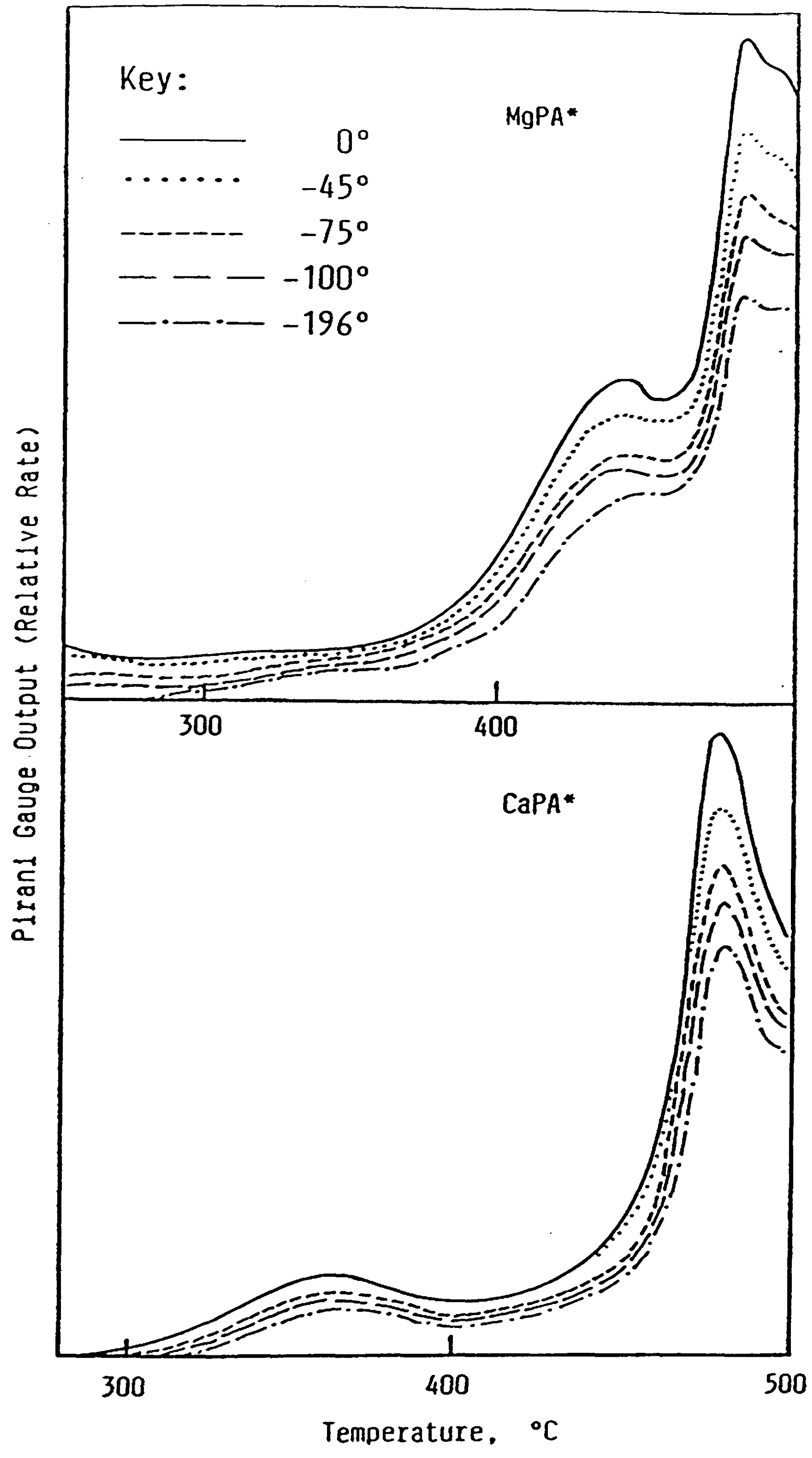


**Fig. 6.11.** TVA curves (vacuum, heating rate 10°C/min) for magnesium and calcium polyacrylate samples made by neutralisation. Magnesium polyacrylate (above); Calcium polyacrylate (below).

Products were collected in four fractions as indicated and assignments were made by IR and MS are as follows :

**a**. Magnesium polyacrylate;

Peak 1: ethene

Peak 2 (a, b) : carbon dioxide (major), ketene, propene, 1-butene.

Peak 3 (a, b) : acetone (major), ketene, methyl ethyl ketone, methyl vinyl ketone,
acrolein, ethanal, propanal, benzene, toluene.

Peak 4: toluene, benzene, xylene, mesitylene, diethyl ketone, methyl n-propyl ketone,
cyclopentanone ., di-n-propyl ketone, ethyl vinyl ketone.

**b**. Calcium polyacrylate;

Peak 1 (a, b) : ethene.

Peak 2 (a, b, c) : carbon dioxide (major), ketene, propene, 1-butene.

Peak 3 (a, b, c, d) : acetone (major), acrolein, methyl ethyl ketone, methyl vinyl ketone,
ethanal, benzene, toluene, ketene.

Peak 4: toluene, benzene, xylene, mesitylene, diethyl ketone, methyl n-propyl ketone,
cyclopentanone, di-n-propyl ketone, ethyl vinyl ketone.

### *3.3.1.1. Residue*

The black residues for the polymers were examined by infrared spectroscopy. The metal carbonate and metal oxide (only from the magnesium salt) were the principal solid materials in the involatile residues. The spectra of the residues , particularly in the case of calcium polyacrylate, imply the presence of a small amount of undegraded polymer.

**Table 6.4.** TVA data for degradation of magnesium and calcium polyacrylate samples made by both routes.

| Polymer | $T_{onset}$ °C | $T_{max}$ °C | Wt % residue at 500 °C | Wt % CRF at 500 °C | Wt % condensables and non-condensables at 500 °C ( incl. $CO_2$ ) | Wt % $CO_2$ |
|---|---|---|---|---|---|---|
| MgPA | 160 | 490 | 48.8 | 1.4 | 49.8 | 16.3 |
| MgPA* | 135 | 435,470 | 37.5 | 1.2 | 61.3 | 19.7 |
| CaPA | 185 | 490 | 56.8 | 0.8 | 42.4 | 11.7 |
| CaPA* | 140 | 375,490 | 50 | 0.5 | 49.5 | 14.5 |

* Polymer prepared by neutralisation.

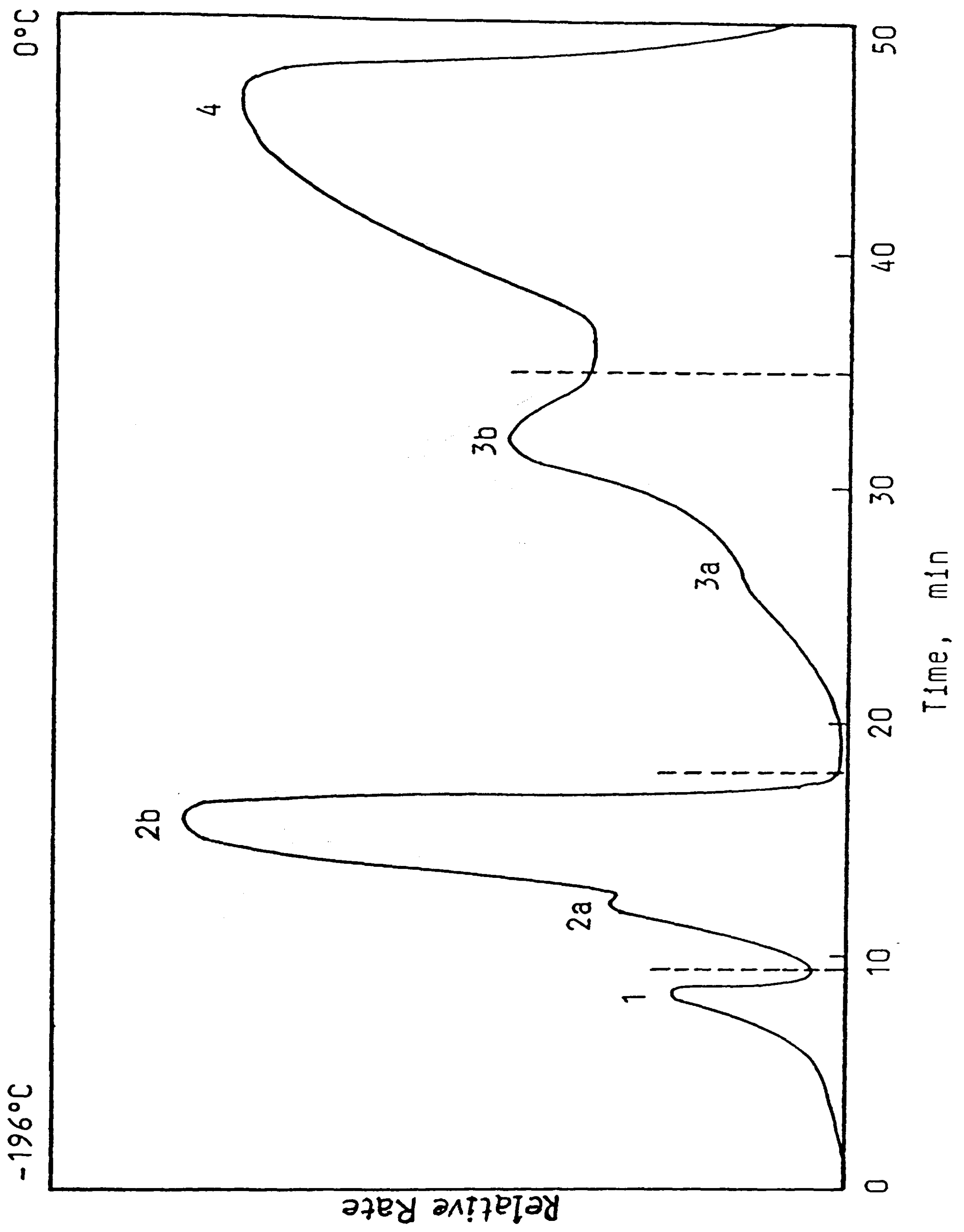


**Fig. 6.12.** SATVA curve for warm up from -196 °C to 0 °C of condensable volatile product fraction from degradation to 500 °C under TVA conditions of magnesium polyacrylate. Products were collected in four fractions as indicated.

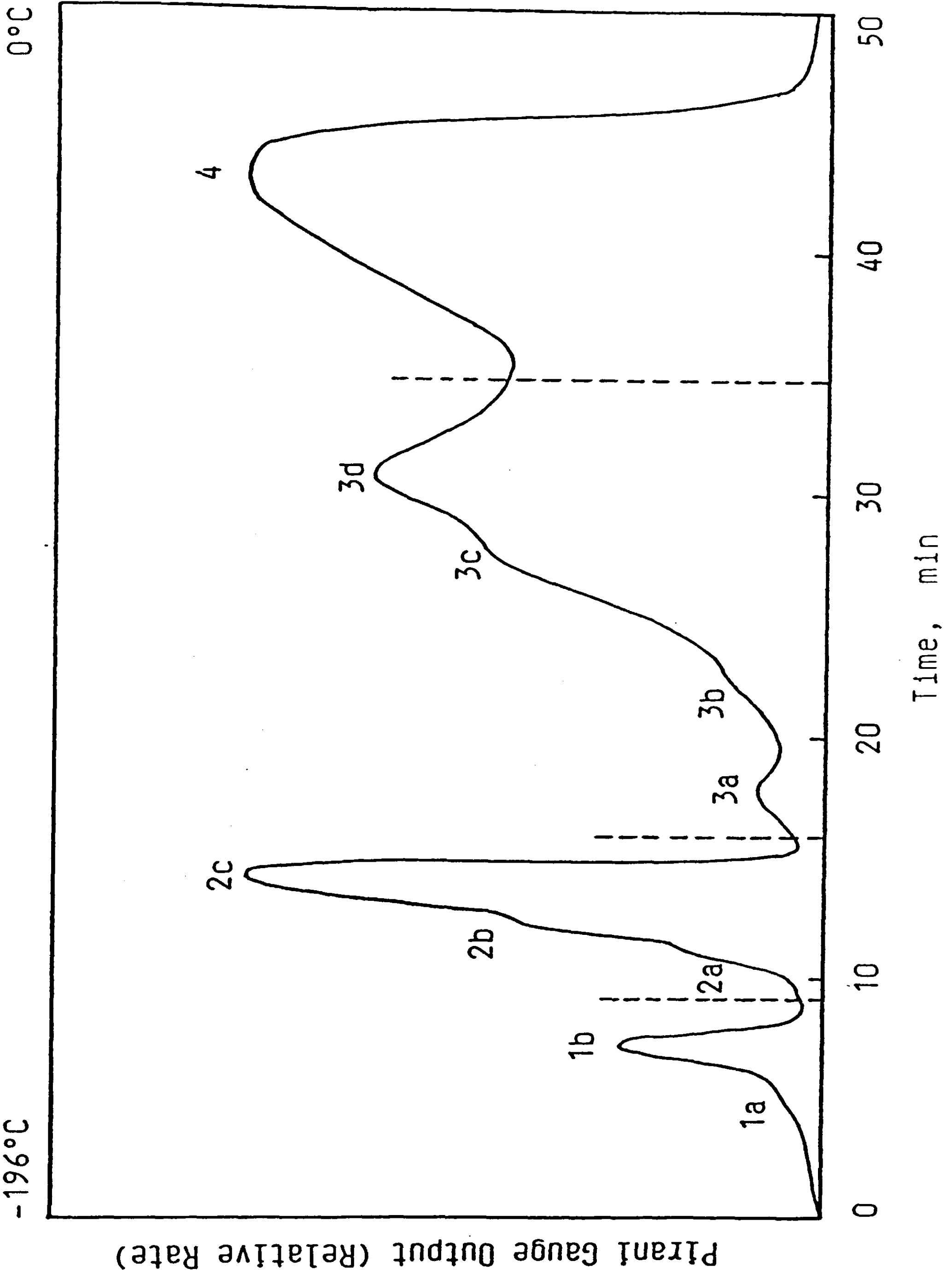


**Fig.6.13.** SATVA curve for warm up from -196 °C to 0 °C of condensable volatile product fraction from degradation to 500 °C under TVA conditions of calcium polyacrylate.

Products were collected in three fractions as indicated

### *3.3.1.2. Cold Ring Fraction*

The cold ring fraction materials from the degradation of these polymers were yellow solids, amounting to less than 1.5 % of the original sample weight, and the corresponding infrared spectra were obtained using the KBr disc technique. The spectra were all similar.

Mass spectrometric analyses of the cold ring fractions were consistent with the the presence of various fragments containing carbonyl and carboxyl groups including traces of the monomer salts. Some of the fragments of CRF of MgPA including products identified are listed in *Table 6.5*.

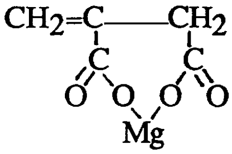
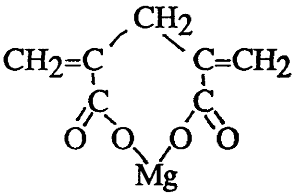
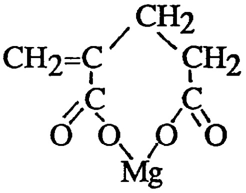
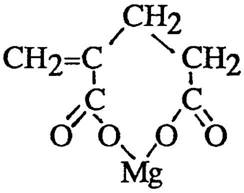
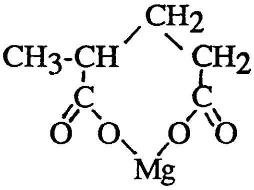
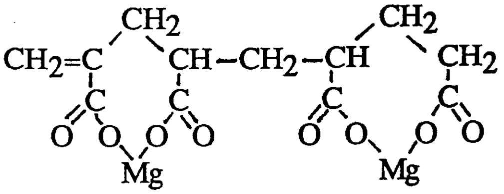
### *3.3.1.3. Volatile Gaseous Products*

Infrared spectroscopic analysis of the non-condensable volatile materials established methane and carbon monoxide.

The condensable gaseous products were identified by infrared spectroscopy and mass spectrometry and the corresponding products are given in *Tables 6.6* and *6.7.*

Carbon dioxide and acetone were identified as major volatile products from the degradation of calcium and magnesium polyacrylate. Carbon dioxide evolution from CaPA and MgPA seems to be a straightforward result of the decomposition of respective metal carbonate. It is clearly evident that magnesium carbonate decomposes completely to magnesium oxide and carbon dioxide at about 500 $^{o}$C, whereas only a fraction of calcium carbonate decomposes at this temperature because the thermal stability of the carbonates increases with the size of the ion.

Table 6.5. Products identified in the cold ring fraction from degradation of magnesium polyacrylate* under TVA conditions.

| Products | m/e |
|---|---|
|  | 152 |
|  | 178 |
|  | 166 |
|  | 180 |
|  | 168 |
|  | 332 |

* Magnesium acrylate sample prepared by polymerisation.

### *3.3.1.4. Liquid Fraction*

Qualitative analysis of the volatile products collected as a liquid fraction in the SATVA separation was carried out by using a similar experimental approach previously described in Chapter Five. A 6 ft column of chromosorb 103 was used isothermally at 160 $^{o}$C for GC purposes, apart from programmed heating for which a different column was used. The chromatograms for the GC-MS investigations of these fractions from the degradation of MgPA and CaPA, reproduced in *Figs. 6.14* and *6.15*.

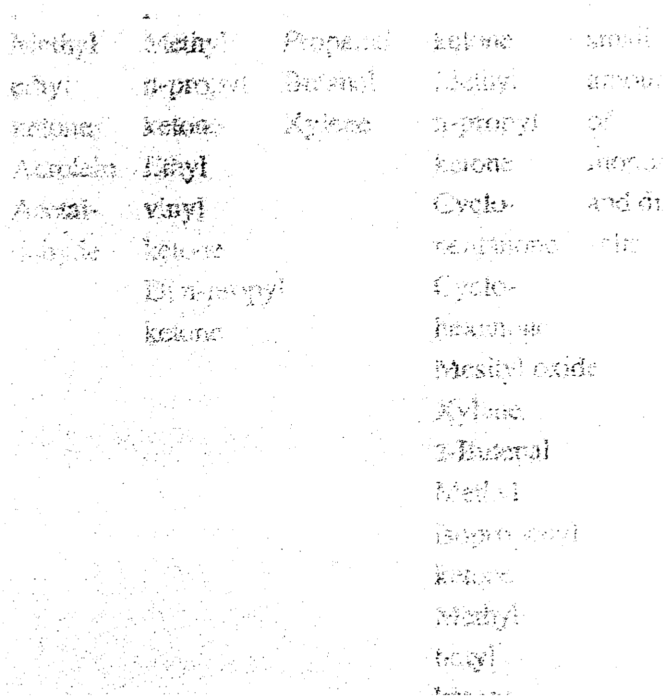


**Table 6.6.** Products of degradation of magnesium polyacrylate to 500 °C at 10 °C/min under TVA conditions.

| Non-condensable products at -196 °C | Condensable volatile products at -196 °C | | | | CRF (yellow solid) | Residue (black) |
|---|---|---|---|---|---|---|
| | Gases | Liquid Fraction | | | | |
| IR | IR, MS | IR, MS | GC | GC-MS | IR, MS | IR |
| CO<br>$CH_4$ | $CO_2$*<br>Acetone*<br>Ethene<br>Propene<br>1-Butene<br>Ketene<br>Benzene<br>Cyclopentene<br>Methyl ethyl ketone<br>Acrolein<br>Acetaldehyde | Benzene<br>Toluene<br>Diethyl ketone<br>Methyl ethyl ketone<br>Cyclopentanone<br>Methyl n-propyl ketone<br>Ethyl vinyl ketone<br>Di n-propyl ketone | Benzene<br>Toluene<br>Methyl ethyl ketone<br>Diethyl ketone<br>Cyclopentanone<br>Propanal<br>Butanal<br>Xylene | Acetone<br>Toluene<br>Methyl ethyl ketone<br>Ethyl isopropyl ketone<br>Diethyl ketone<br>Methyl n-propyl ketone<br>Cyclopentanone<br>Cyclohexanone<br>Mesityl oxide<br>Xylene<br>2-Butenal<br>Methyl isopropenyl ketone<br>Methyl butyl ketone | Short chain fragments containing carbonyl and carboxylic groups including small amounts of monomer and dimer salts | Magnesium oxide as a major product |

* Major products.

**Table 6.7.** Products of degradation of calcium polyacrylate to 500 °C at 10 °C/min under TVA conditions.

| Non-condensable products at -196 °C | Condensable volatile products at -196 °C | | | | CRF (yellow solid) | Residue (black) |
|---|---|---|---|---|---|---|
| | Gases | Liquid Fraction | | | | |
| IR | IR, MS | IR, MS | GC | GC-MS | IR, MS | IR |
| CO<br>$CH_4$ | $CO_2$*<br>Acetone*<br>Ethene<br>Propene<br>1-Butene<br>Benzene<br>Toluene<br>Ketene<br>Acrolein<br>Butanal<br>Propanal<br>Methyl ethyl ketone | Benzene<br>Toluene<br>Xylene<br>Mesitylene<br>Mesityl oxide<br>Cyclopentanone<br>Methyl ethyl ketone<br>Diethyl ketone<br>Ethyl vinyl ketone<br>Methyl butyl ketone<br>Ethyl n-propyl ketone | Acetone<br>Butanal<br>Propanal<br>Methyl ethyl ketone<br>Diethyl ketone<br>Cyclopentanone<br>Benzene<br>Toluene<br>Xylene | Acetone<br>Methyl ethyl ketone<br>Diethyl ketone<br>Methyl propenyl ketone<br>Ethyl n-propyl ketone<br>3-Methyl cyclopentanone<br>Cyclohexa-2-enone<br>2-Methyl cyclohexanone<br>1-Methyl cyclohexa-1-en-3 one<br>Toluene<br>Xylene | Fragments derived from the monomer repeat unit, including traces of monomer salt | Mainly calcium carbonate |

* Major degradation products.

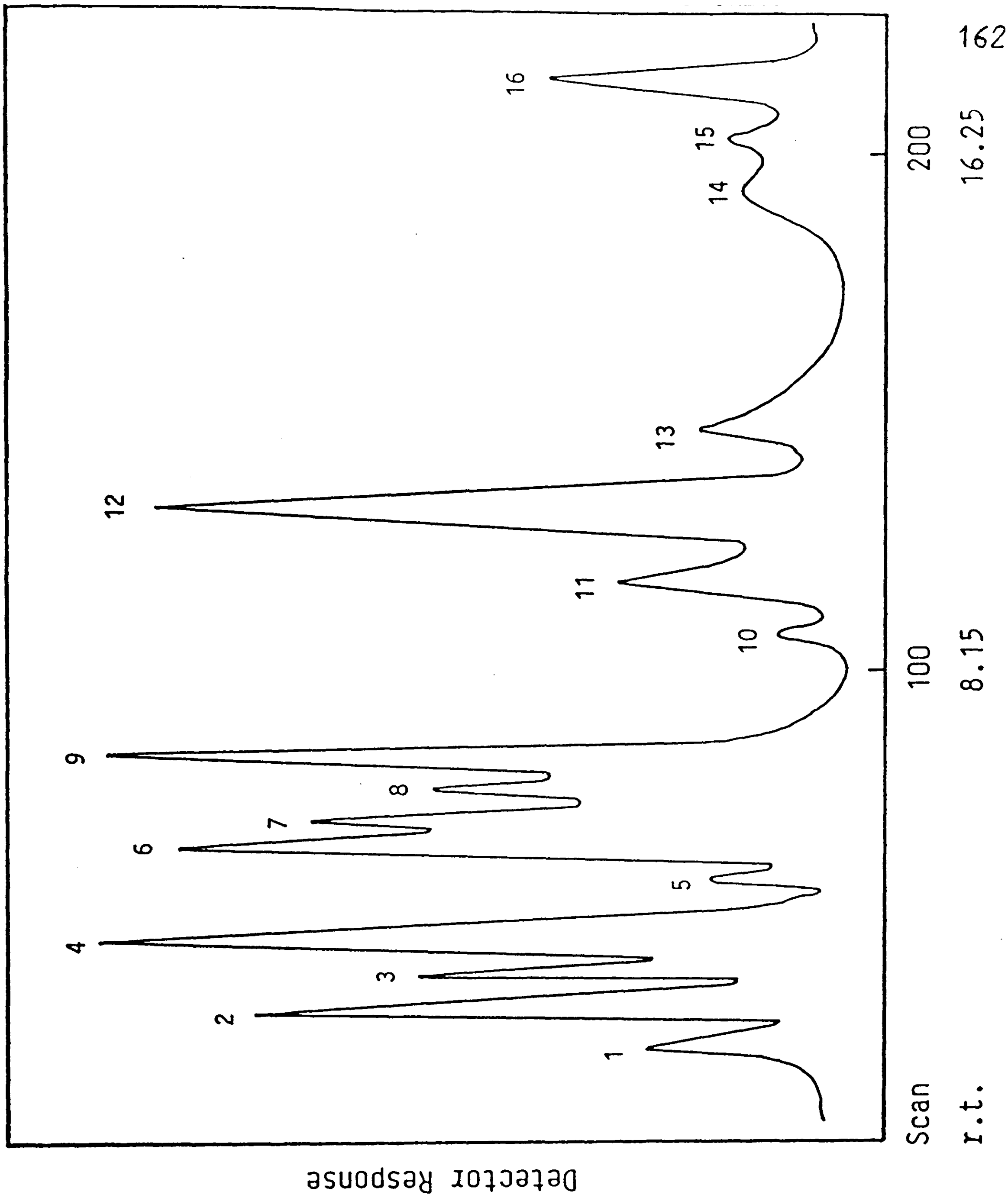


**Fig. 6.14.** GC-MS chromatogram of the less volatile liquid fraction of magnesium polyacrylate, prepared by polymerisation. Assignments: **1** unknown, **2** acetone, **3** methyl ethyl ketone, **4** 2-butenal, **5** unknown, **6** methyl n-propyl ketone, **7** 3-methyl-3-butene-2-one, **8** cyclopentanone, **9** diethyl ketone, **10** mesityl oxide, **11** methyl isopropyl ketone, **12** toluene, **13** methyl n-butyl ketone, **14** cyclohexanone, **15** xylene, **16** xylene.

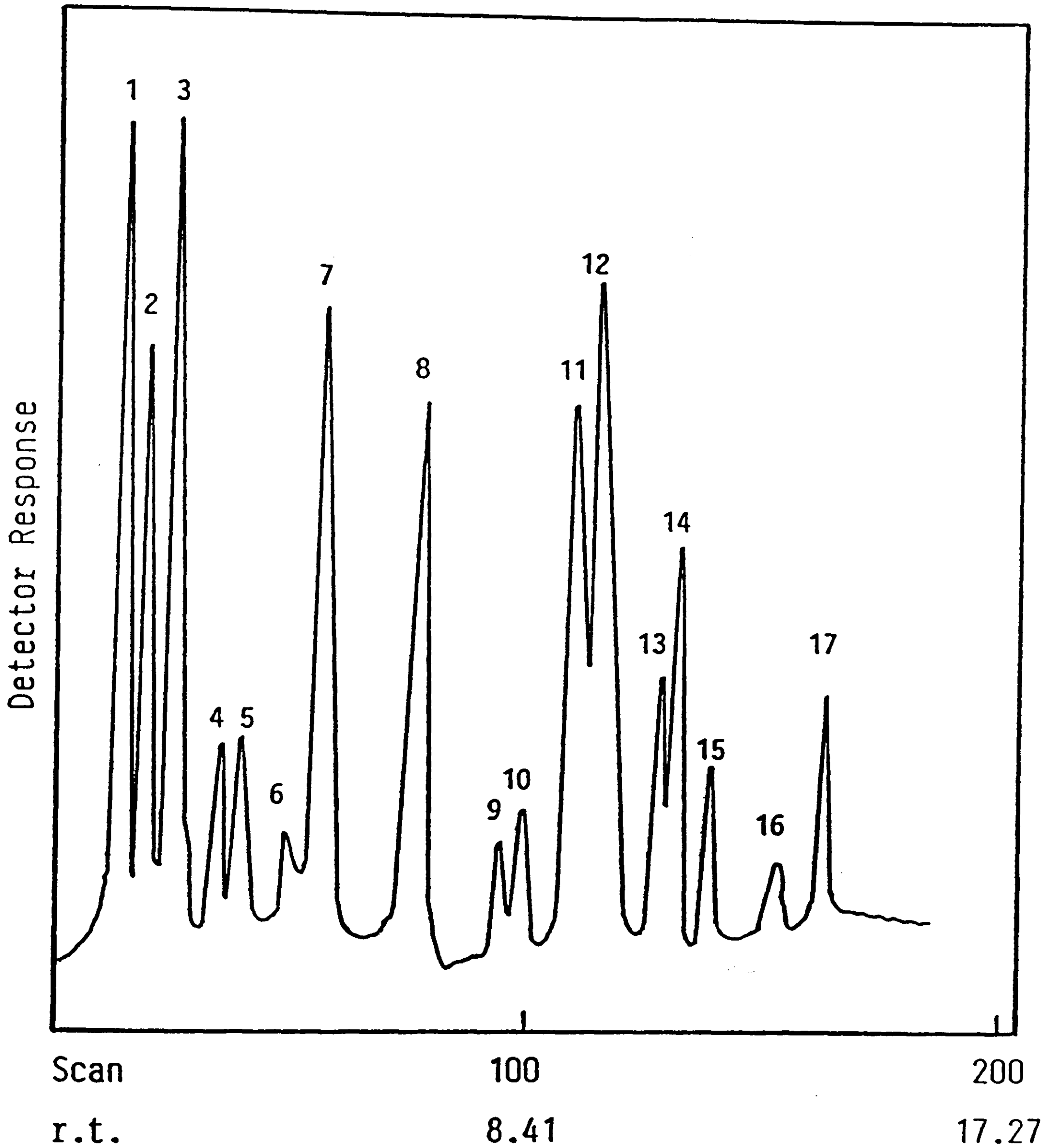


**Fig. 6.15.** GC-MS chromatogram of the less volatile liquid fraction of calcium polyacrylate, made by polymerisation. Assignments: **1** acetone, **2** methyl ethyl ketone, **3** diethyl ketone, **4** methyl propenyl ketone, **5** methyl n-butyl ketone, **6** toluene, **7** cyclopentanone, **8** 3-methylcyclopentanone, **9** xylene, **10** xylene, **11** cyclohexanone, **12** unknown, **13** cyclohexa-2-eneone, **14** unknown, **15** 2-methylcyclohexanone, **16** unknown, **17** 1-methylcyclohexa-1-ene-3-one.

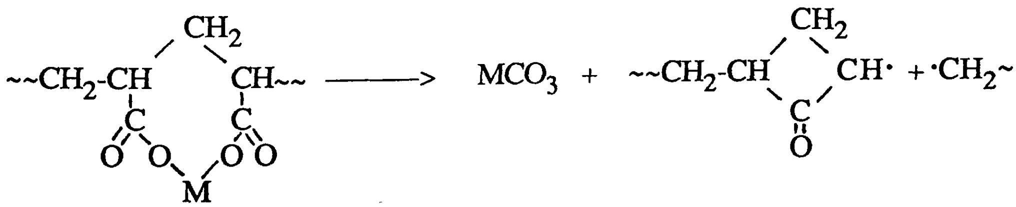
## *4. MECHANISM OF DEGRADATION*

*Furukawa et al* [115] reported that CaPA and CaPMA show similar degradation behaviour which they proposed occurred through a radical mechanism. These workers attributed the multiplicity of ketonic products to decomposition of higher ketones to form smaller ketones. Other investigators[102,108,110] have also explained the mechanism of degradation of carboxylic acid salts, including the alkaline earth metal salts of PAA, in terms of radical intermediates.

A comparison of the results of this investigation with those of the alkali metal polyacrylates already described in previous chapter, reveals striking similarities in the degradation products. The effect of the different metals is evident mainly in the relative amounts of the various materials formed. Acetone and carbon dioxide are the most important products. It is particularly striking that the yields of CRF products from MgPA and CaPA are very low, of the order of 1% of the sample weight.

The following course of degradation may occur;

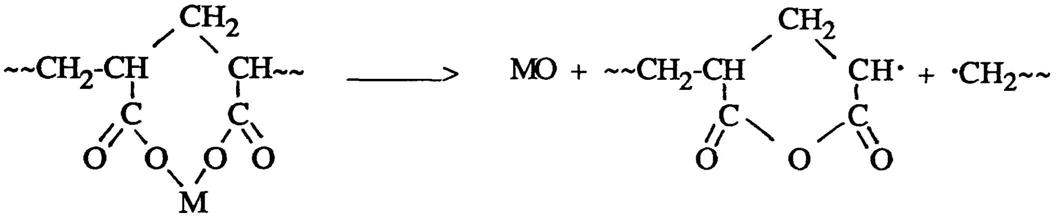
**a.** Intramolecular formation of metal carbonate which can result in the polymer chain containing eight-membered cyclic rings followed by backbone scission which leads to terminal macroradical, (I);

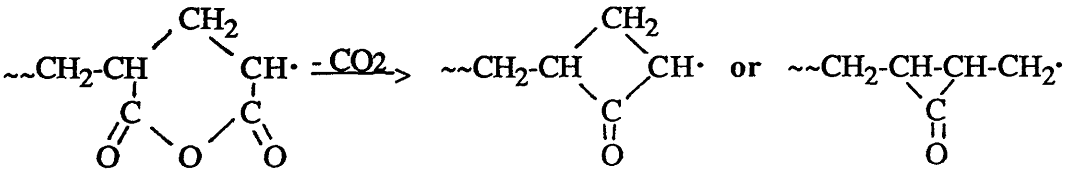


(I)

( M= Mg or Ca )

**b.** Intra- or intermolecular formation of metal oxide, which causes anhydride formation, followed by main chain scission and anhydride decomposition, leads to the transient formation of the species shown as structures (I) and (II);





(I) (II)

Further reactions of the two intermediate terminal ring structures , (I) and (II), can lead to the formation of various volatile products such as cyclic and acyclic ketones, ketene etc., similar to those presented in the mechanisms for NaPA and KPA degradation, following initial scission at or near the terminal ring structure.

## *5. CONCLUSIONS*

The results of investigation on the thermal degradation and stability of calcium and magnesium salts of acrylic acid and poly(acrylic acid) may be summarised below :
Calcium and magnesium acrylate and polyacrylate were found to be thermally stable to about *400 $^oC$.*

The thermal stability of the polymers prepared by polymerisation is higher than that of those made by neutralisation, however, there is no major difference in degradation route between them on the basis of the TVA data.

More carbon dioxide is evolved in the degradation of magnesium polyacrylate, due to instability of its residue at high temperature, than in the case of the calcium salt.

Carbon dioxide percentage for the polymers obtained from neutralisation is more than for the polymers synthesised by polymerisation, because of the presence of unreacted acrylic acid units in the chain of the former.

The thermal behaviour of these polymers is similar to that of the monovalent metal salts of poly(acrylic acid), but appreciable differences exist in the relative amounts of volatile products in which the divalent metal salts produce higher yields of liquid fraction and less cold ring fraction.

The divalent metal salts ( Ca and Mg ) of PAA are comparatively more stable than the monovalent salts. As described in Chapter 4 (section 1.2.3.2), multivalent cations are bound more firmly and extensively than are univalent ions.[79] This ion binding increases with extent of ionisation and with decreased size ( ie, increased charge density ) of the cation.

# CHAPTER SEVEN

## THERMAL DEGRADATION OF ZINC AND COBALT(II) SALTS OF POLY(ACRYLIC ACID)

### *1. INTRODUCTION*

The very rapid and steady progress in the field of applications of synthetic polyelectrolytes has naturally stimulated further interest in the problems of synthesis and in the thermal stability of this type of polymer.

Amongst the earlier work in this field may be mentioned *Hagendorn's*[125], who studied the production of films, fibres and formed articles from the metal salts of polymeric carboxylic acids. Recently there has been a revival of interest in this type of material, which now forms the bases of dental filling compositions.

Water-soluble PAA salts find use as polyelectrolytes. This type of structure is also present in zinc polycarboxylate dental cements, of which the simplest commercial examples depend upon reaction between zinc oxide and PAA. Zinc polycarboxylate cement, the first ionic polymer cement, was developed by *Smith*[126] because of the defects of existing dental luting agents, in particular the inability to form true adhension bonds to enamel and dentine. It is the product of the hardening reaction that occurs when finely powdered zinc oxide is mixed with aqueous solutions of poly (acrylic acid). The dental zinc polycarboxylate cements are rapidly hardening cements and will set within a few minutes at oral temperatures. Smith has shown that strength is developed rapidly and quotes an example where 75% of the 24 hr strength was attained within 15 min of preparation. The most important properties that zinc polyacrylate cement has lie in its adhesive properties and its blandness towards living tissues.

More relevant to the field of ionic polymer dental cements is the evidence that zinc forms a complex[127] involving two carboxylate ions. Ion binding gives rise to phase changes, gelation and precipitation of salts of polyelectrolytes. The ionic polymer dental cements are based on this phenomenon. *Wall* and *Drennan*[128] were amongst the first to study this topic, and considered that the gelation of poly(acrylic acid) by divalent cations was to be attributed principally to ion association with the consequent formation of salt bridges. However, they recognized that there were factors other than simple coulombic attraction.

*Gronowski et al*[94] studied the thermal stability, kinetics and activation energy of the main decomposition of Zn, Ni, Co and Cu polyacrylate. They also showed that thermal stability of zinc acrylate and polyacrylate is more than cobalt, nickel and copper acrylate and polyacrylate. They suggested that zinc acrylate can more easily be polymerised than the others and that the main decomposition of the monomer salts was preceded by thermal polymerisation. They indicated that the thermal degradation of these salts is nearly the same. It was found that the activation energies of decomposition for zinc, cobalt and nickel polymers are higher than those of the corresponding monomer salts, while the reaction order does not change. They also agreed with the literature[111,129,130] which shows that zinc acrylate decomposes to zinc oxide in nitrogen and the other acrylates ( Co, Ni, Cu ) to the respective metals.

Thermal stability of zinc, cobalt, nickel and copper salts of poly(acrylic acid) is also similar to the thermal stability sequence for the oxalates[131,132] and formates[132] of the same metal salts.

Thermal behaviour of some transition metal salts of poly(acrylic acid), namely Fe(III), Cr(III), Ni(II), Co(II) and Mn(II) was studied by *Skupinska* and his coworkers[95], who reported that the divalent metal cations are more stable than trivalent ones, because the latter, bonded by three carboxylic groups, probably form more rigid structures, causing greater tensions in the polymer chain, which would result in a decrease in polymer resistance. They considered, however, that the low thermal stability of these salts compared with pure poly(acrylic acid)[84] is due to the catalytic effect of the transition metal cations in the polymers.

It has been reported in other studies[94,133] that the solid residue of degradation of the divalent transition metal acrylates is the respective metal oxide together with some carbon.

The thermal degradation of zinc polymethacrylate has been studied in this laboratory by *McNeill* and his coworkers[133] who found that on heating carbon dioxide, dimethyl ketene, isobutene, butene, ethene, aldehydes, cyclic and acyclic ketones, monomer and isobutyrate were formed as volatile degradation products. They reported that the breakdown of zinc polmethacrylate shows many similarities to the behaviour of the alkaline earth metal salts of poly(methacrylic acid).

The stability of zinc carbonate at a temperature of *450 °C* was investigated by *Zulfiqar*[134] and it was found to decompose completely to zinc oxide under vacuum. He has suggested that the divalent metal polymethacrylates gave no monomers or isobutyrate as cold ring fraction because of low volatility except for zinc polymethacrylate.

In the case of the divalent metal salts, there could be the formation of the intramolecular structure involving pairs of carboxyl groups associated with the metal ions.

The polymers examined in the present study are zinc and cobalt(II) polyacrylate; their thermal degradation and stability and also that of the respective monomer salts have been investigated and compared with the behaviour of the alkaline earth metal salts previously described.

## 2. *STUDY OF THERMAL DEGRADATION OF MONOMER SALTS*

Thermal degradation of zinc acrylate and cobalt acrylate was investigated by thermogravimetry, differential thermal analysis and thermal volatilisation analysis. In all cases using programmed heating to 500 °C at 10 °C per minute was used. TG and DTA were under nitrogen atmosphere , whereas the TVA experiments were made under vacuum. The volatile products in the TVA experiments were separated by subambient TVA and identified.

The main decomposition process of the zinc monomer salt is observed at about *460 °C* there is little volatilisation below *390 °C*. The TG, DTA and TVA data confirm a high thermal stability for this monomer. This is rather similar to the thermal stability of magnesium and calcium acrylate and differs from the behaviour of the cobalt monomer salt. The main decomposition of cobalt acrylate is observed around *390 °C.*

### *2.1. DIFFERENTIAL THERMAL ANALYSIS*

The DTA curves for 10 mg powder samples of zinc and cobalt acrylate samples, respectively, which were recorded in the range 25-485 °C in nitrogen atmosphere are illustrated in *Fig. 7.1.* It is found that the monomer salts polymerise in the solid state before decomposition. Exothermic peaks show that the thermal polymerisation of the monomers takes place at about 240 °C. The endothermic effects at about 470° and 390 °C correspond to the main step of decomposition of the Zn and Co(II) monomer salt, respectively.

The endothermic effect at about 210 °C, in the case of cobalt acrylate , is possibly due to dehydration of the monomer salt.

### *2.2. THERMOGRAVIMETRY*

The TG curves were obtained using a heating rate of 10°/min in a dynamic nitrogen atmosphere and are reproduced in *Fig. 7.2.*

The TG curve of zinc acrylate shows an initial weight loss below 280 °C in the range 125-275 °C and it accounts for 11.5 % weight loss. The main degradation of this monomer salt is observed at 460 °C in the range of temperature of 375-500 °C amounting 35.5 % weight loss.

In temperature range of 125-270 °C, the TG curve reveals 10 % weight loss for cobalt acrylate which seems to be consistent with 3/2 moles of $H_2O$ per mole of each monomer salt. Above 200 °C,the monomer salt decomposes in a multi-step manner which is different from zinc acrylate. The decomposition extends over a wide range of temperature, with successive small weight losses amounting to 44 % up to 500 °C. The total weight losses of Zn and Co acrylate samples at 500 °C are 46.5 and 49 %, respectively.

The main features of the TG, DTG and DTA data of the monomer salts are summarised in *Table 7.1.*

### *2.3. THERMAL VOLATILISATION ANALYSIS*

The TVA curves obtained for both monomer salts are reproduced in *Fig. 7.3* and indicate that there is discrepancy in thermal degradation of these monomers.

### *2.3.1. Zinc Acrylate*

The TVA traces of zinc acrylate consist of a single broad peak having a $T_{max}$ around 450$^{o}$C. It is clear from the TVA curve that no significant volatile material is given off at temperatures below 370 $^{o}$C. After this temperature, a more extensive release of volatile fraction begins and gives a peak with $T_{max}$ at about 450 $^{o}$C. Below 260 $^{o}$C, in the range 110-260 $^{o}$C the slow release of volatile material may be accounted for the evolution of water due to dehydration process.

The separation of traces in the main step of degradation is indicative of a variety of products. TVA data for zinc acrylate are in good agreement with the TG, DTG and DTA results.

### *2.3.2. Cobalt Acrylate*

The TVA traces for cobalt acrylate indicate three stages of decomposition which extend over a wide range of temperature between 280$^{o}$ and 500 $^{o}$C showing $T_{max}$ values around 340, 370 and 390 $^{o}$C.

It is clear from the TVA traces that volatile material including a non-condensable fraction appears at a temperature around 290 $^{o}$C ($T_{onset}$) and that the maximum rate of volatilisation occurs at about 390 $^{o}$C ($T_{max}$). All five traces are well separated during the first and second step of degradation, which indicate the presence of a variety of products.

The TVA data for cobalt acrylate are also consistent with the DTA and TG results. The main features of the TVA data for both monomer salts are shown in *Table 7.2*.

Quantitative measurements of degradation products were carried out using the same experimental approach already described in previous chapters.

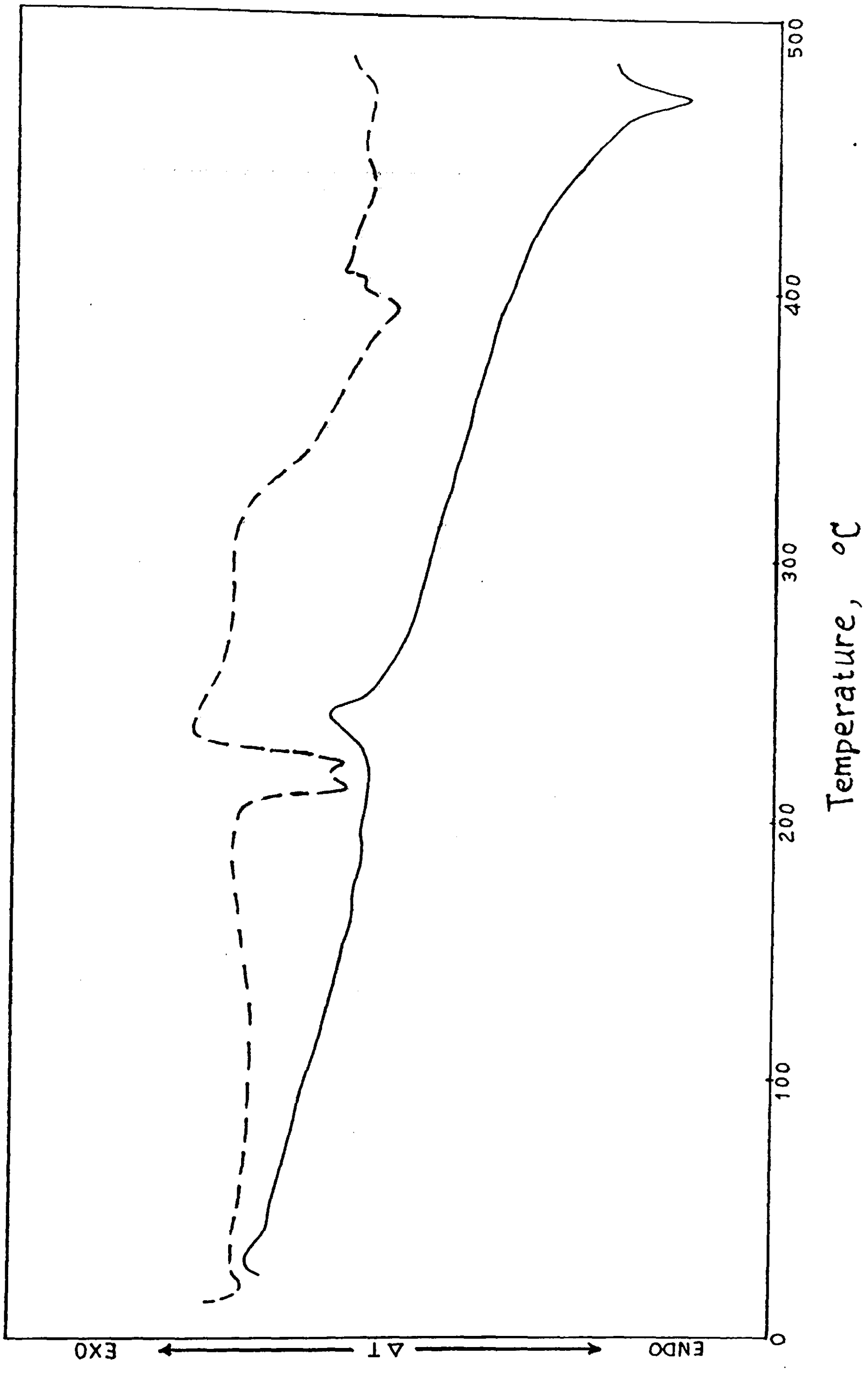


**Fig. 7.1.** DTA curves (dynamic nitrogen, heating rate 10°C/min) for zinc and cobalt acrylate samples.

——— Zn acrylate; --------- Co acrylate.

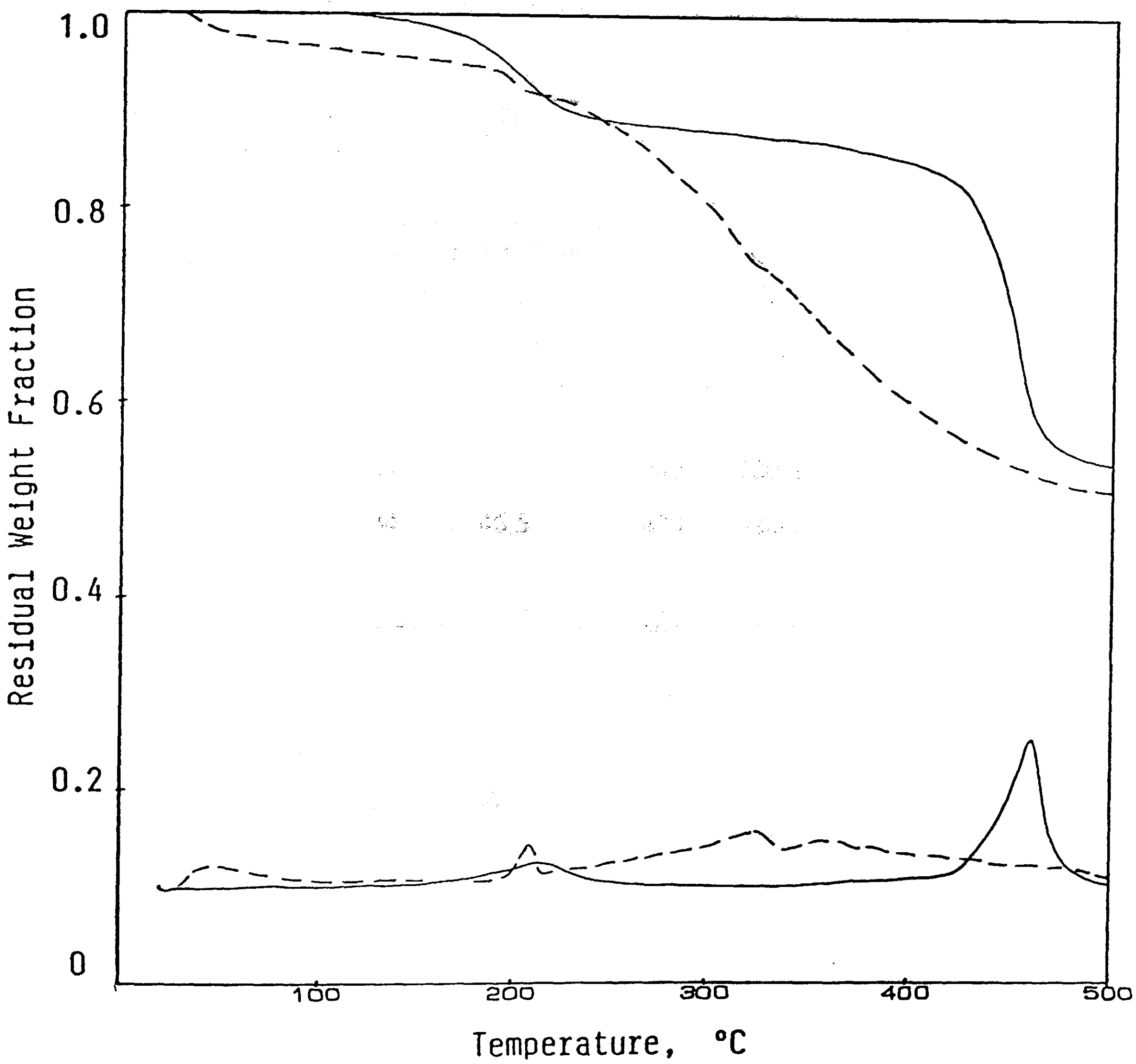


**Fig. 7.2.** TG and DTG curves (dynamic nitrogen, heating rate 10°C/min) for zinc and cobalt acrylate samples.

———— Zn acrylate; --------- Co acrylate.

**Table. 7.1.** TG, DTG and DTA data for zinc and cobalt acrylate samples.

| Monomer | DTG | | TG | | DTA | | |
|---|---|---|---|---|---|---|---|
| | Peak temp. °C | Temp. range °C | Wt % loss for stage | Total Wt % loss in the range 25-525 °C | Peak temp. °C | Temp. range °C | Thermal effect |
| Zinc acrylate | 210 | 125-275 | 11 | | 240 | 220-250 | exo* |
| | 460 | 375-500 | 34 | 46.5 | 470 | 420-480 | endo** |
| Cobalt acrylate | 50 | 25-75 | 3.5 | | 205 | 195-210 | endo |
| | 205 | 125-275 | 10.5 | | 220 | 215-230 | endo |
| | 325 | 274-330 | 14 | | 235 | 230-250 | exo* |
| | 360 | 330-500 | 21 | 49 | 390 | 375-400 | endo** |

* Due to thermal polymerisation.

** Due to the main decomposition.

### *2.4. Product Analysis*

Volatile condensable gases and liquid products obtained from degradation of 75 mg samples of the monomer salts to 500 °C were collected and fractionated by SATVA and analysed using ir spectroscopy and mass spectrometry. The corresponding SATVA curves and ir spectra are illustrated in *Figs. 7.4* to *7.8.*

The residue and cold ring fraction were also identified spectroscopically. The respective ir spectra are reproduced in *Figs. 7.9* and *7.10.*

#### *2.4.1. Identification of Products of Degradation by IR and MS*

#### 2.4.1.1. Zinc acrylate

#### *2.4.1.1a. Residue*

Zinc oxide was established as a major product together with carbon.

The formation of zinc metal during the degradation is explained by reduction of the oxide in the presence of carbon.[143,144] The oxide is reduced with the formation of carbon monoxide :

$$ZnO \; + \; C \longrightarrow Zn \; + \; CO$$

#### *2.4.1.1b. Cold Ring Fraction*

Zinc acrylate and zinc metal were found as the principal products and traces of short chain fragments. The cold ring fraction consists of the zinc metal (light blue), monomer salt (white) and a small amount of short chain fragments including ketonic and carboxylic groups (brown). The zinc metal was found as a deposit on the head connection of the TVA tube (above the cold jacket).

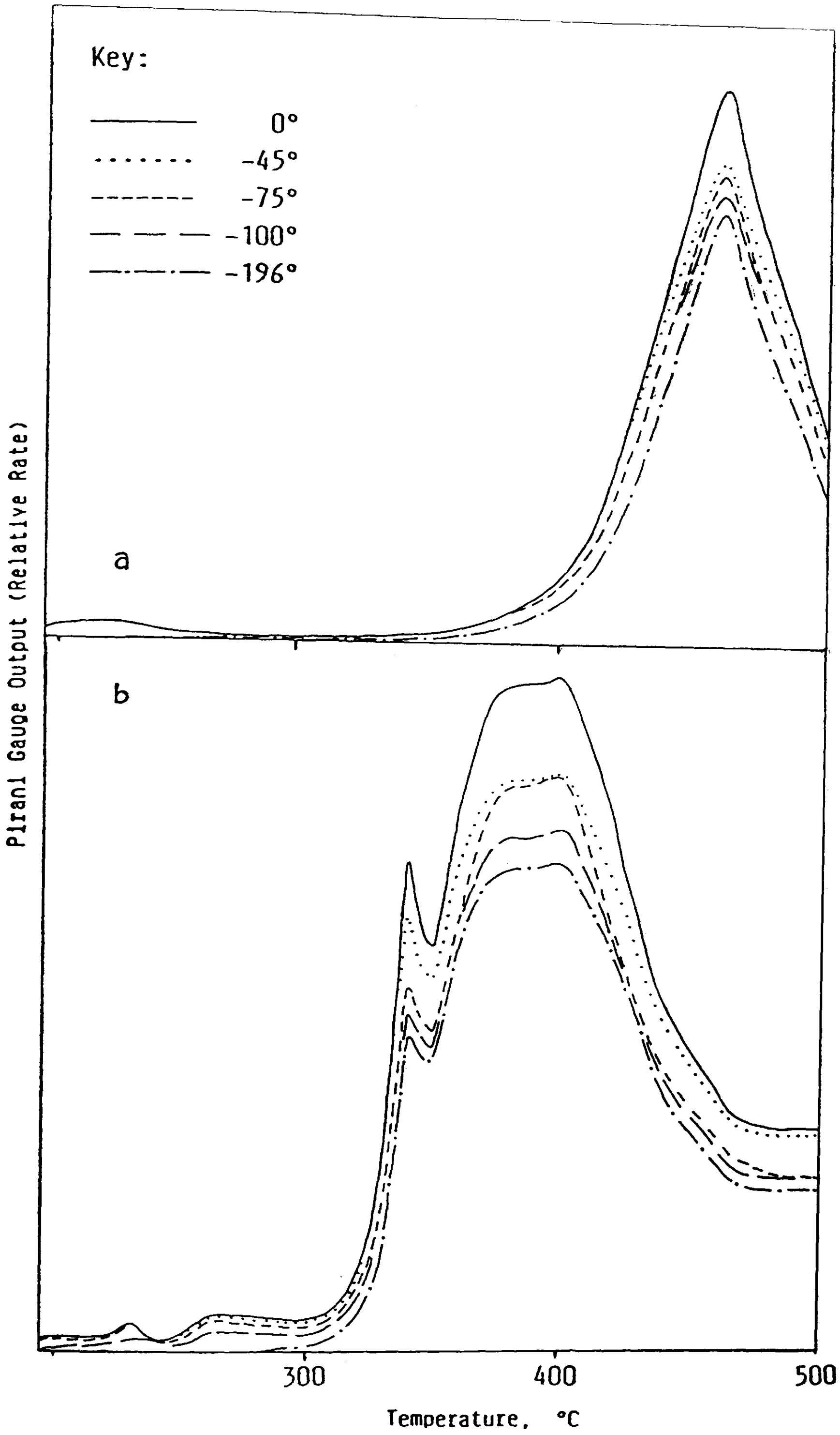


**Fig. 7.3.** TVA curves (vacuum, heating rate 10$^{0}$C/min) for zinc and cobalt acrylate samples.

a. Zn acrylate; **b**. Co acrylate.

**Table. 7.2.** TVA data for degradation of zinc and cobalt acrylate samples.

| Monomer | $T_{onset}$ for non-condensable $^{o}C$ | $T_{max}$ $^{o}C$ | Wt % residue at 500 $^{o}C$ | Wt % CRF at o 500 $^{o}C$ | Wt % condensables and non-condensables ( incl. $CO_2$ ) | Wt% $CO_2$ |
|---|---|---|---|---|---|---|
| Zinc acrylate | 340 | 455 | ~30 | 12.5 | 57.5 | 16 |
| Cobalt acrylate | 290 | 340, 390 | ~55 | 1.3 | 43.7 | 15.5 |

### *2.4.1.1c. Condensables Detected as Gaseous and Liquid Products*

Carbon dioxide (major), ethene, ketene, 1-butene, acrolein, methyl ethyl ketone, cyclopentene, cyclopentanone, 1,3-cyclopentadiene, methyl vinyl ketone, acetone (trace), benzene and toluene were identified.

### *2.4.1.1d. Less Volatile Liquid Fraction*

Acrylic acid and water were established as the major products together with small amounts of mesitylene, xylene and benzene.

#### *2.4.1.1e. Non-condensables*

Carbon monoxide and methane were identified as non-condensables.

### *2.4.1.2. Cobalt Acrylate*

#### *2.4.1.2a. Residue*

Cobalt carbonate was present as a major product together with cobalt oxide.

#### *2.4.1.2b. Cold Ring Fraction*

The ir spectrum of the CRF is nearly the same as the ir spectrum of the respective homopolymer. The strong bands at about 1560 and 1430 $cm^{-1}$ are consistent with the presence of short chain fragments containing carboxyl ion in the cold ring fraction. Short chain fragment formation may occur via thermal polymerisation of the monomer salt in the hot zone before escape to the cooled part of the TVA tube.

#### *2.4.1.2c. Condensables Detected as Gaseous Products*

Carbon dioxide and acetone were found as major products together with ethene, ketene, acetaldehyde, acrolein, propanal as minor and traces of benzene and toluene.

#### *2.4.1.2d. Less Volatile Liquid Fraction*

Water, acrylic acid, methyl ethyl ketone and acetic acid (impurity) were found as liquid fraction.

The acetic acid impurity may be due to unreacted cobalt acetate which has been used as a starting material.

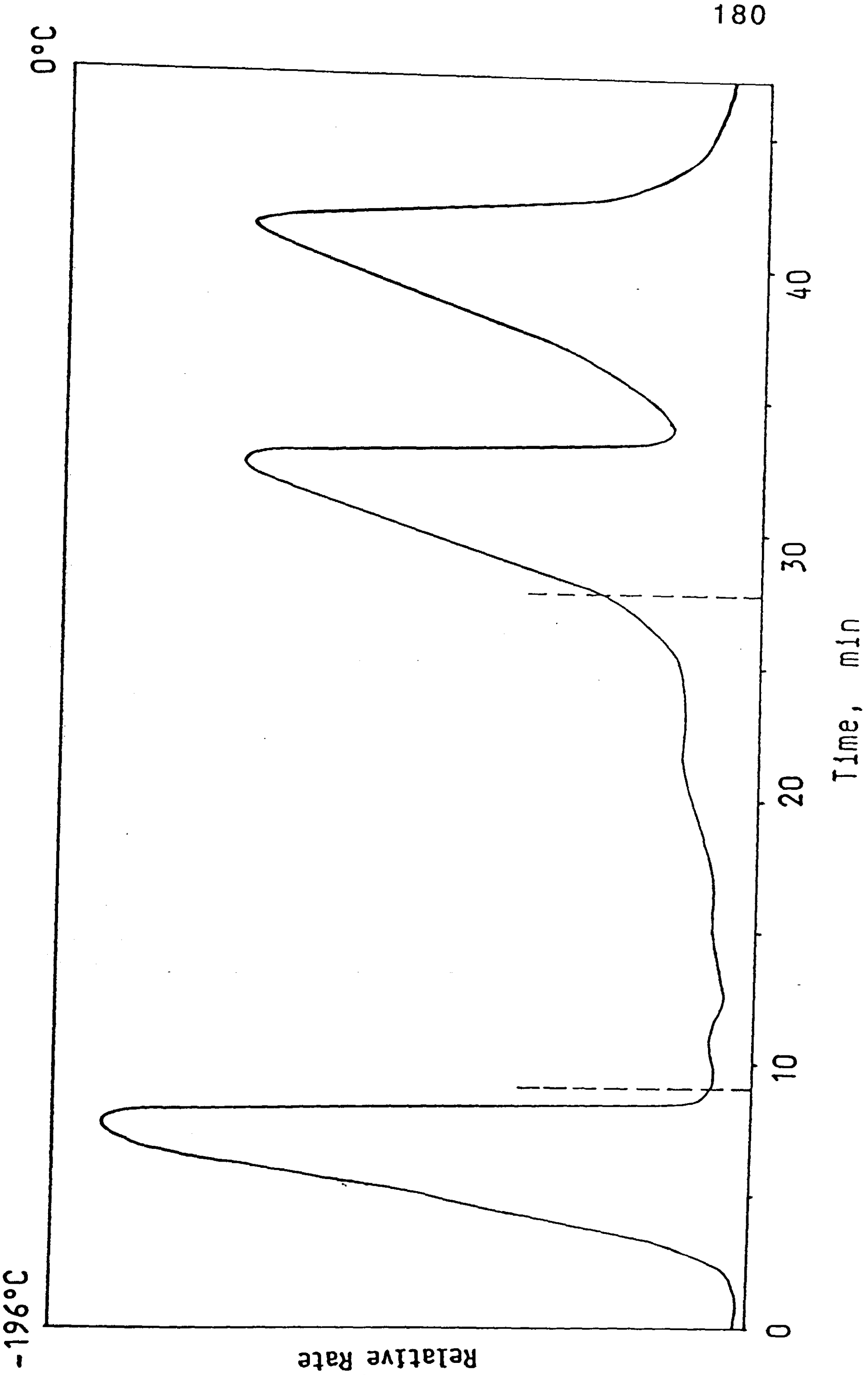


**Fig. 7.4.** SATVA curve of the condensable product fraction from degradation of zinc acrylate to 500 °C under TVA conditions.

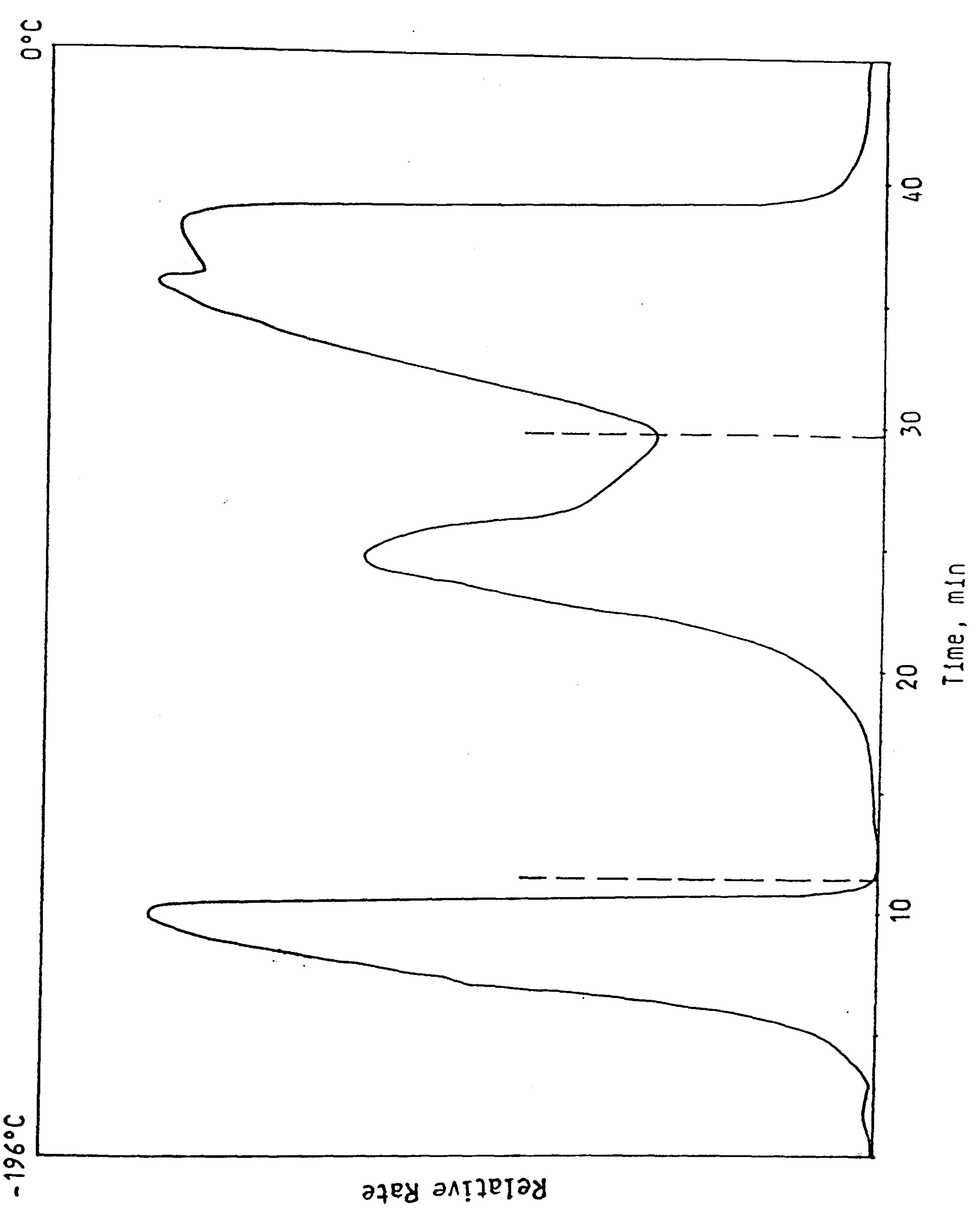


Fig. 7.5. SATVA curve of the condensable product fraction from degradation to 500 °C under TVA conditions of cobalt acrylate.

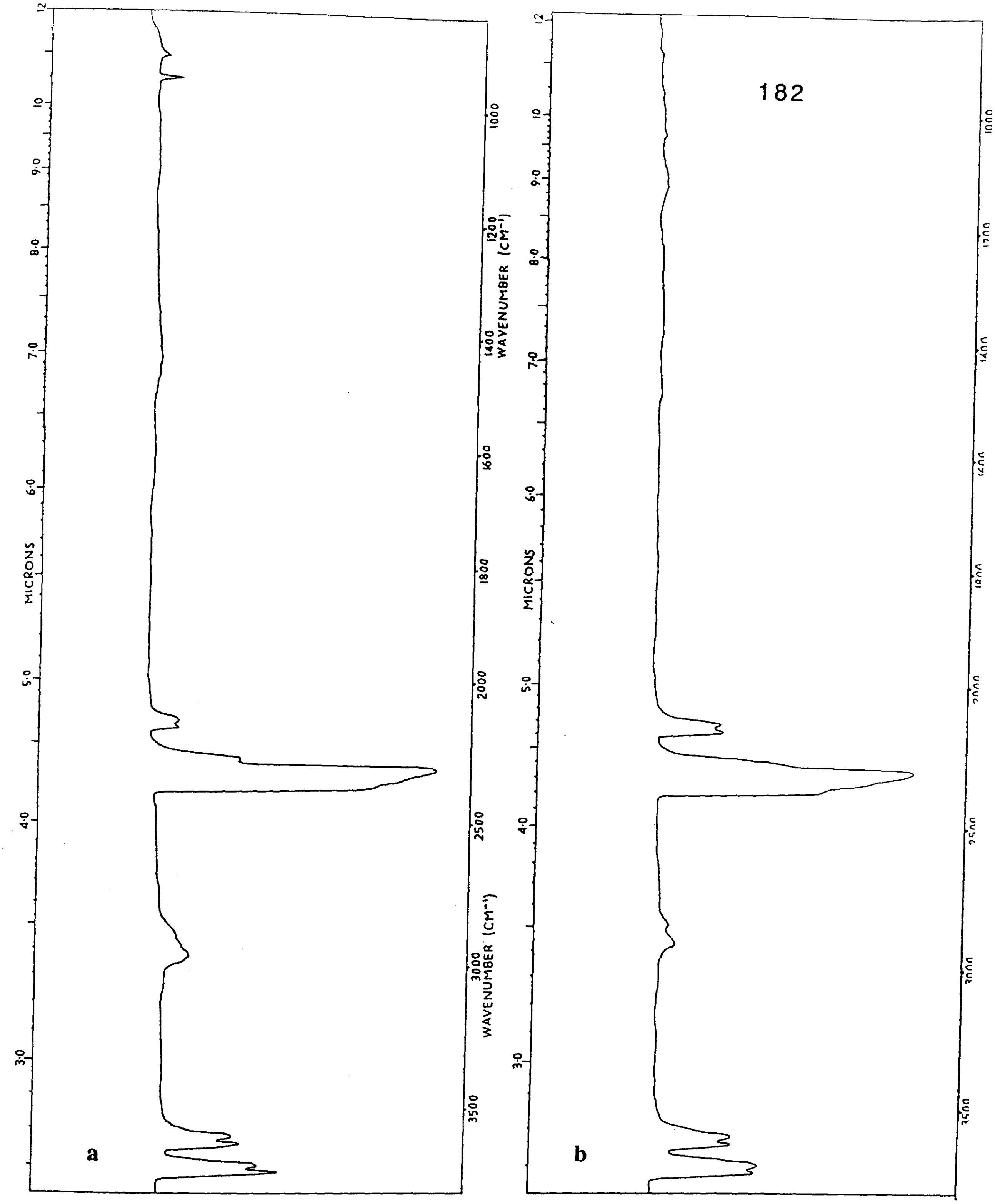


**Fig. 7.6.** Ir spectra of first fraction of degradation products to 500 °C for zinc and cobalt acrylate samples.

**a.** Zn acrylate; **b.** Co acrylate

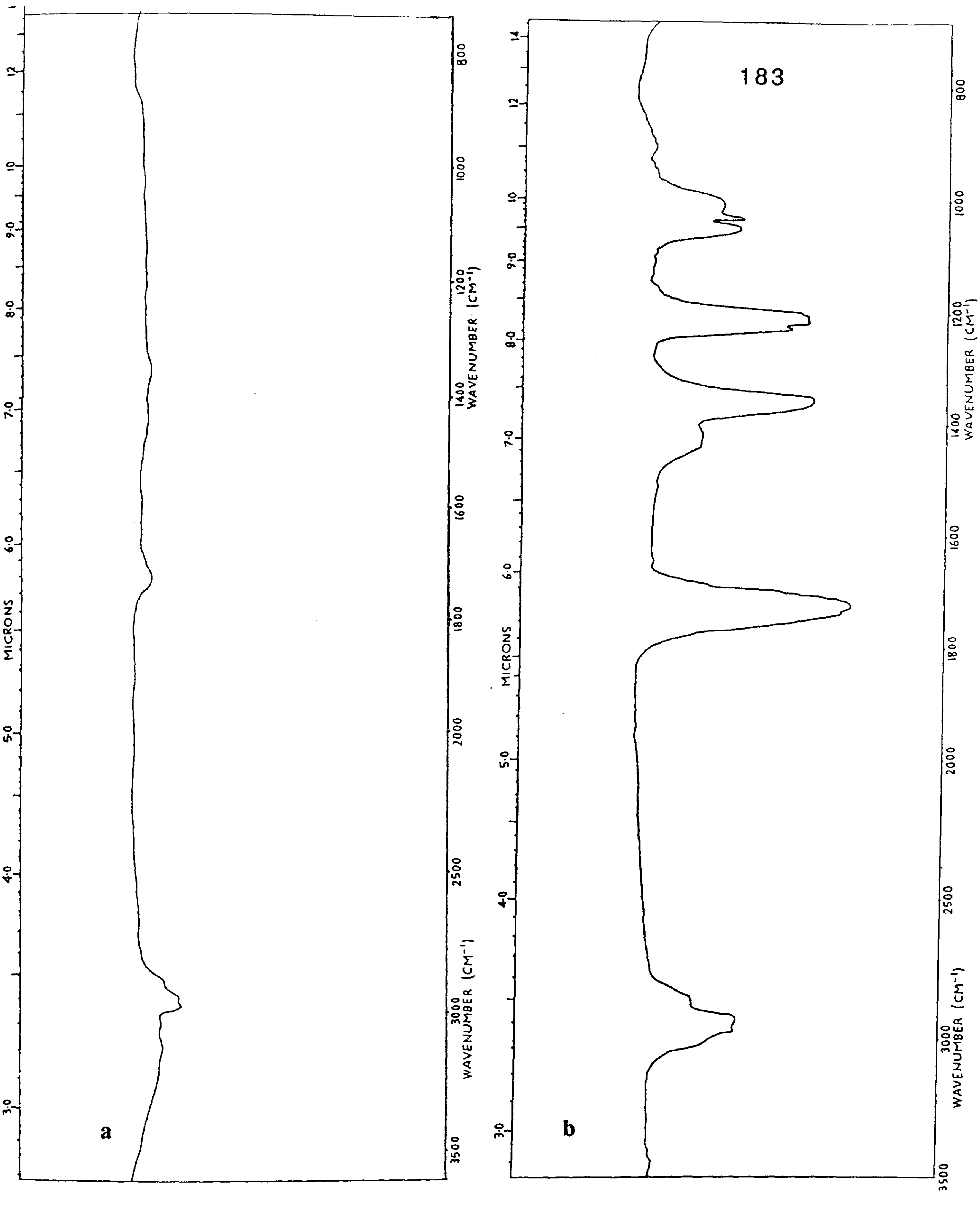


**Fig. 7.7.** Ir spectra of second fraction of degradation products to 500 °C for zinc and cobalt acrylate samples.

**a.** Zn acrylate; **b.** Co acrylate

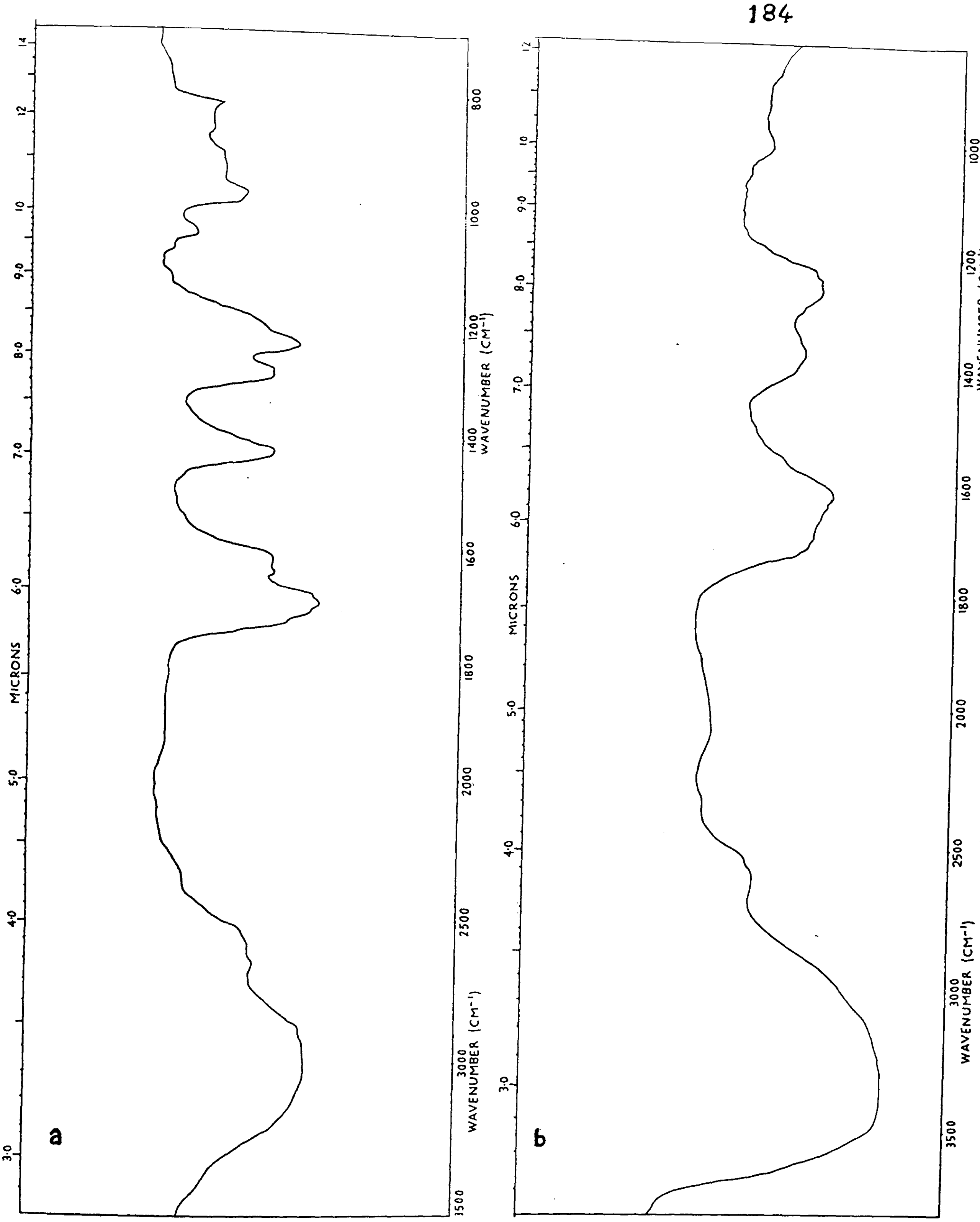


**Fig. 7.8.** Ir spectra of third fraction of volatile condensable products of zinc and cobalt acrylate samples.

**a.** Zn acrylate, **b.** Co acrylate.

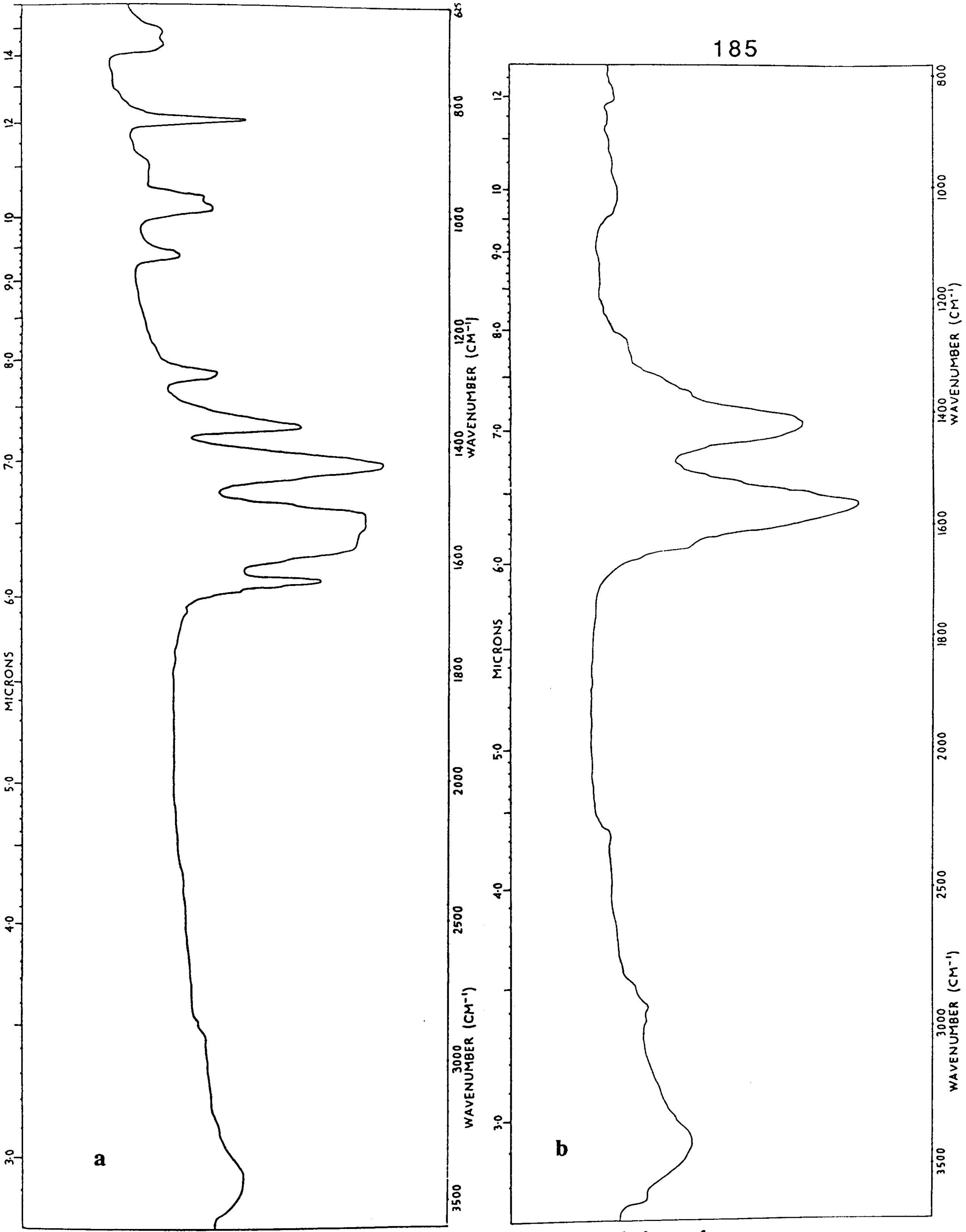
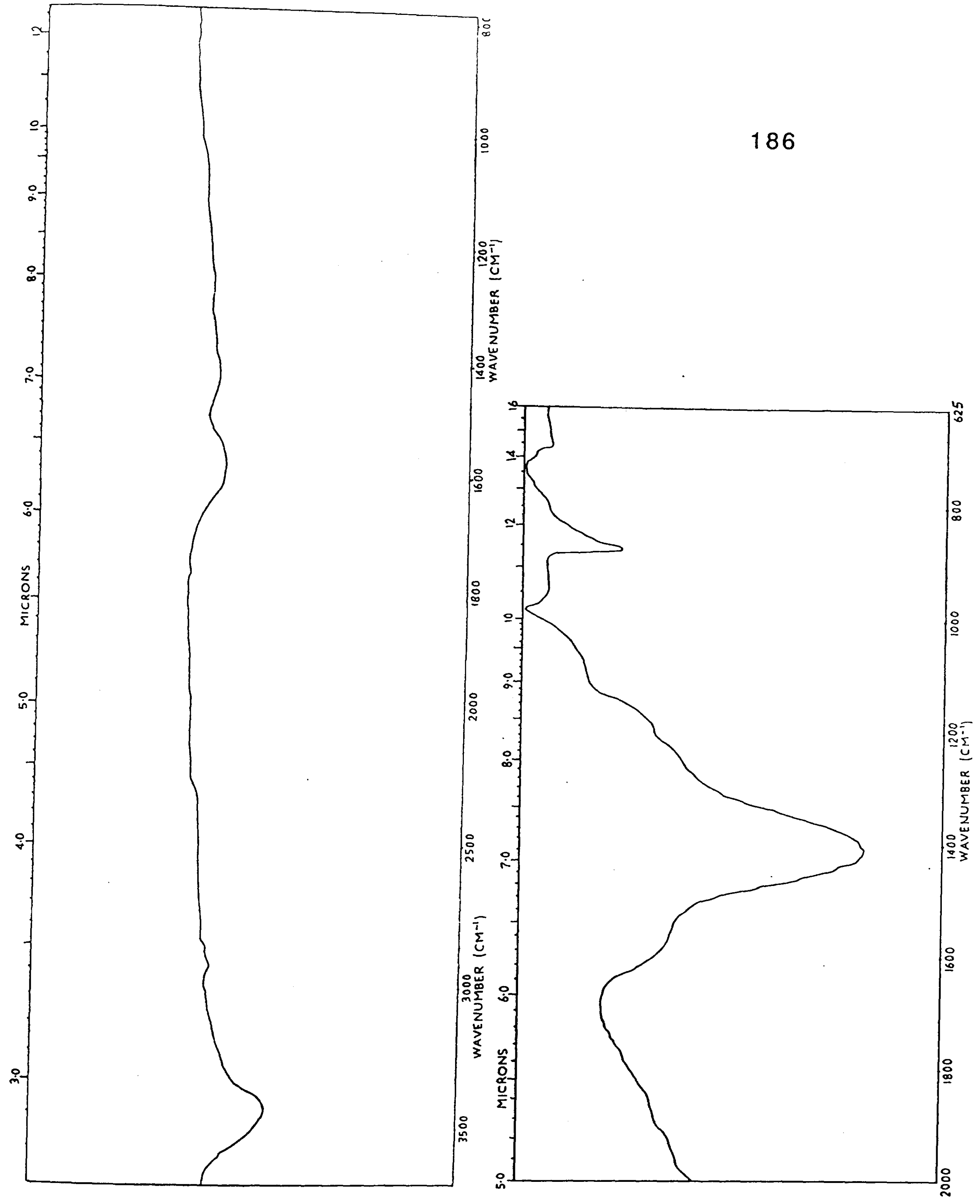


**Fig. 7.9.** Ir spectra of cold ring fractions of zinc and cobalt acrylate

a. Zn acrylate; b. Co acrylate.



a

b

**Fig. 7.10.** Ir spectra of residues of zinc and cobalt acrylate.

**a.** Zn acrylate; **b.** Co acrylate.

### *2.4.1.2e. Non-condensables*

Methane and carbon monoxide were presented.

## *3. THERMAL DEGRADATION OF ZINC & COBALT(II) POLYACRYLATE*

The degradation of ZnPA and CoPA were studied using TG, DTA and TVA as described previously in the earlier chapter.

In the subsequent data and discussion, the polymers made directly by polymerisation of the monomers will be denoted ZnPA and CoPA and those prepared from PAA by neutralisation will be distinguished as ZnPA$^*$ and CoPA$^*$.

### *3.1. DIFFERENTIAL THERMAL ANALYSIS*

None of the DTA curves of the polymer samples show the exothermic effect due to thermal polymerisation as was observed in the cases of the respective monomer salts.

The DTA curves obtained in the degradation of the four polymers are reproduced in *Figs.7.11* and *7.12*. The DTA curves for the cobalt polyacrylate sample show the gradual partial degradation which is apparent in the TG traces.

All the DTA curves show an endothermic effect at temperatures between 425-485 $^{o}$C corresponding to the main step of decomposition. In this range of temperature, two successive stages of degradation of the polymers are observed corresponding to metal carbonate formation followed by decomposition to metal oxide.

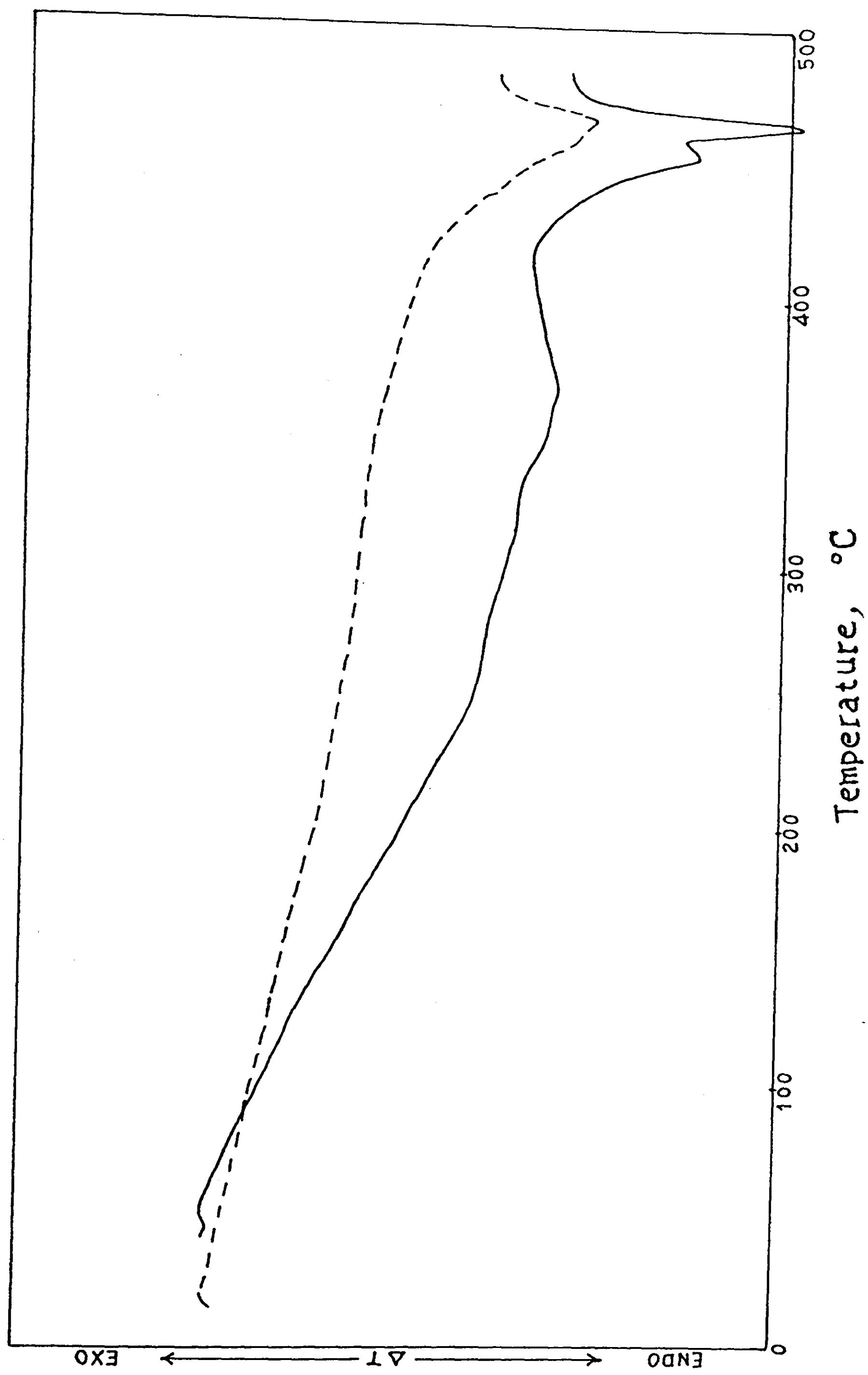


**Fig. 7.11.** DTA curves (dynamic nitrogen, heating rate 10°C/min) for Zn polyacrylate samples.

——— ZnPA; ------ ZnPA*

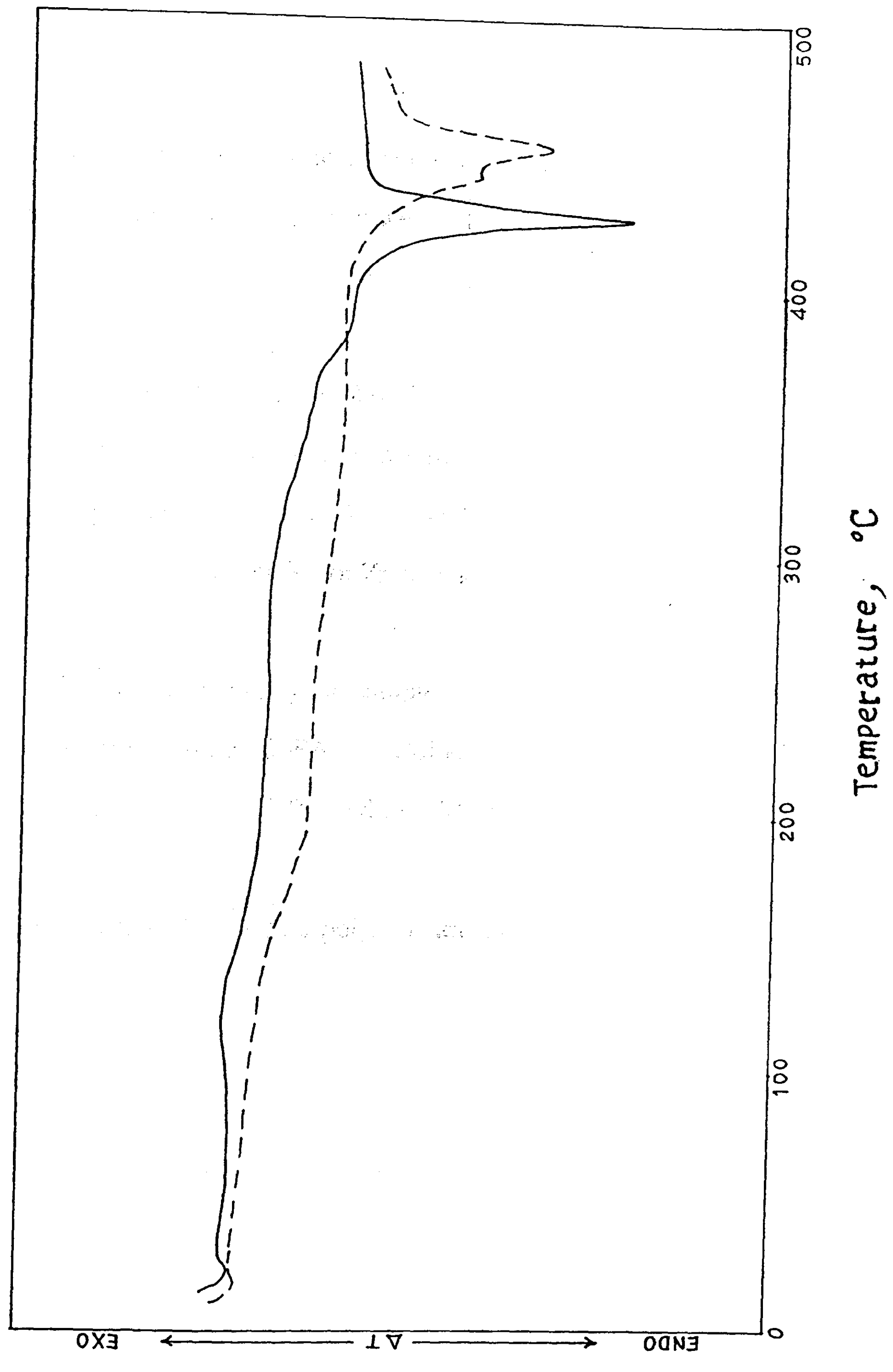


**Fig. 7.12.** DTA curves (dynamic nitrogen, heating rate 10°C/min) for Co polyacrylate samples.

——— CoPA; ------ CoPA*

### *3.2. THERMOGRAVIMETRY*

The TG and DTG curves for the polymers are illustrated in *Figs. 7.13* and *7.14*. All four samples show the characteristic of a gradual weight loss from approximately 150 °C up to the point above 400 °C at which rapid breakdown occurs.

The curves for the zinc polyacrylate samples show an initial weight loss below *425 °C*, amounting to about 6.5 and 8.5 % weight loss for ZnPA and ZnPA*, respectively. At 500°C, the total weight loss was 27 and 45 %, respectively. The rate maximum for the main decomposition occurs near 460 °C for ZnPA and ZnPA*.

The TG curves for the cobalt polyacrylate samples indicate $T_{max}$ about 425 and 475 °C due to the main decomposition of CoPA and CoPA*, respectively. At 500 °C the total weight loss was 58.5 and 64 % for CoPA and CoPA*, respectively.

The DTA, TG and DTG data for the four polymers are listed in *Table 7.3*.

### *3.3.THERMAL VOLATILISATION ANALYSIS*

The TVA curves for the polymers are reproduced in *Figs. 7.15* and *7.16*. The TVA traces of ZnPA and ZnPA* show a single broad peak due to the main decomposition, between 430 and 500 °C, having $T_{max}$ at about 480 °C. It is clear from these that volatile products, including a fraction which is non-condensable at -196 °C, begin to be evolved from the polymers made by polymerisation and neutralisation at around 350 and 360 °C, respectively.

The TVA curves for cobalt polyacrylate show two peaks ( a peak and a shoulder) below 400 °C which are smaller in size than that due to the main decomposition process between

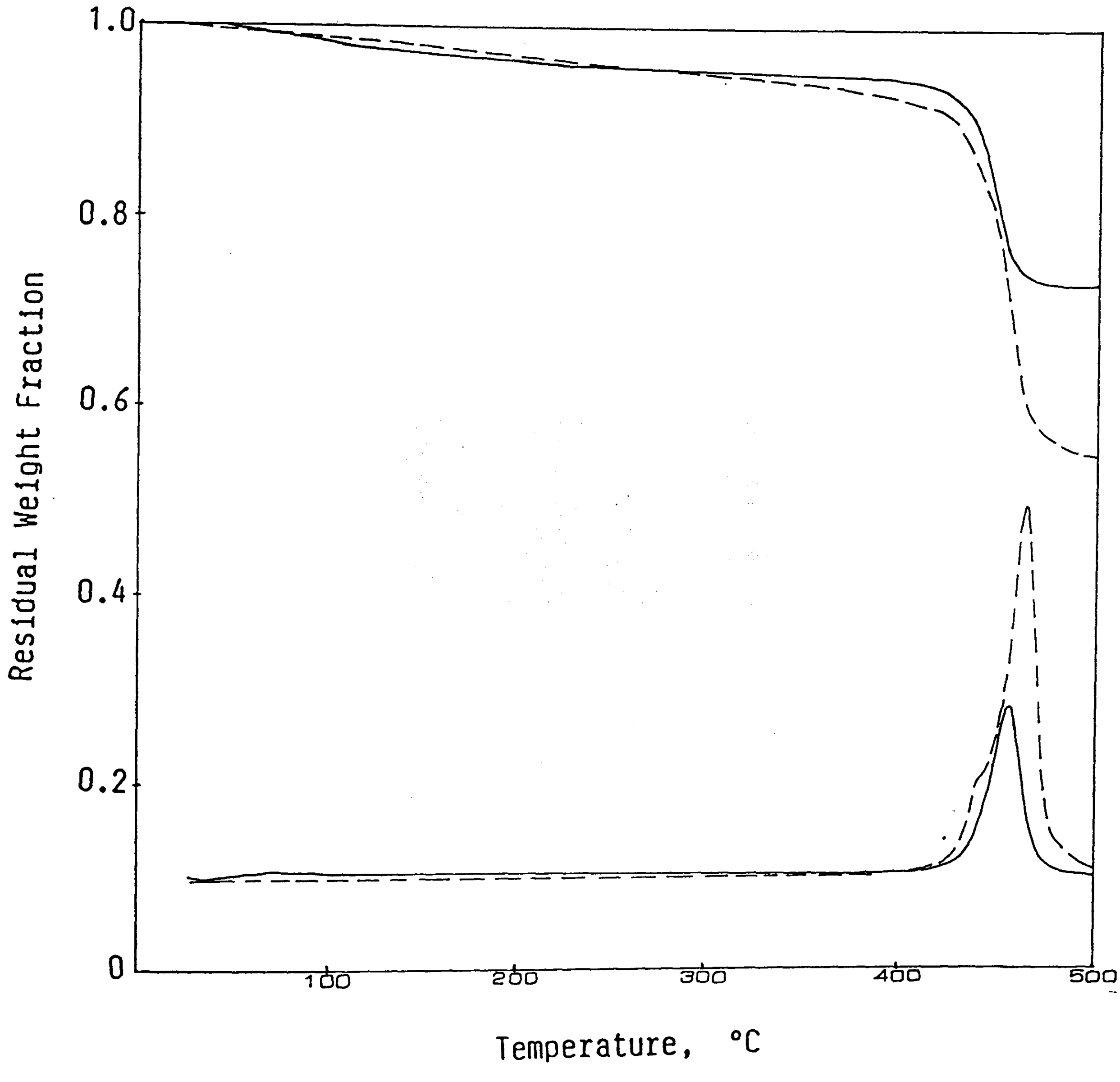


**Fig. 7.13.** DTG and TG curves (dynamic nitrogen, heating rate $10^oC/min$) for zinc polyacrylate samples.

——— ZnPA; -------- ZnPA*

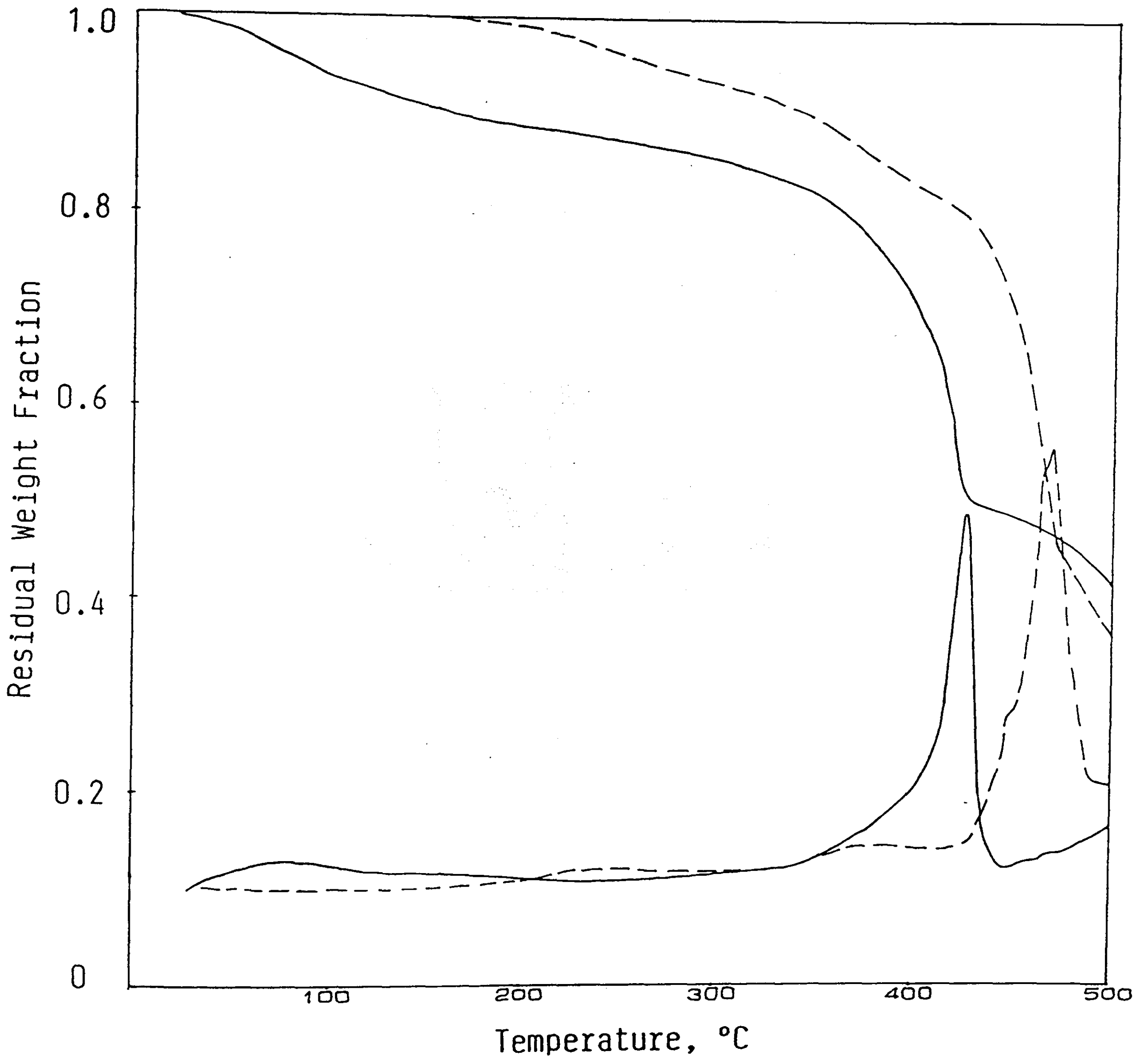


**Fig. 7.14.** DTG and TG curves (dynamic nitrogen, heating rate $10^{\circ}C/min$) for cobalt polyacrylate samples.

——— CoPA; -------- CoPA*

**Table 7.3.** DTG, TG and DTA data for zinc and cobalt polyacrylate samples made by both routes.

| polymer | DTG | | | TG | DTA | | |
|---|---|---|---|---|---|---|---|
| | Peak temp. °C | Temp. range, °C | Wt. loss (%) for stage | Total wt. loss (%) up to 500 °C | Peak temp. °C | Temp. range °C | Thermal effect |
| | — | 50-425 | 9 | | | | |
| ZnPA* | 440 | 425-450 | 7 | 45 | 455[a] | 425-460 | endo[b] |
| | 465 | 450-500 | 29 | | 465 | 460-475 | endo[b] |
| | — | 50-425 | 7 | | 455[a] | 425-460 | endo[b] |
| ZnPA | 455 | 425-500 | 20.5 | 27.5 | 465 | 465-475 | endo[b] |
| | 250 | 175-300 | 6.5 | | | | |
| | 385 | 300-425 | 13.5 | 64 | 385[a] | 350-400 | endo[b] |
| CoPA* | 470 | 425-500 | 44.0 | | 427 | 400-450 | endo[b] |
| | 75 | 50-150 | 9.0 | | | | |
| | — | 150-375 | 13.0 | 58.5 | | | |
| CoPA | 425 | 375-450 | 29.5 | | 440[a] | 425-450 | endo[b] |

* Polymers made by neutralisation.

a. Shoulder

b. Due to the main decomposition.

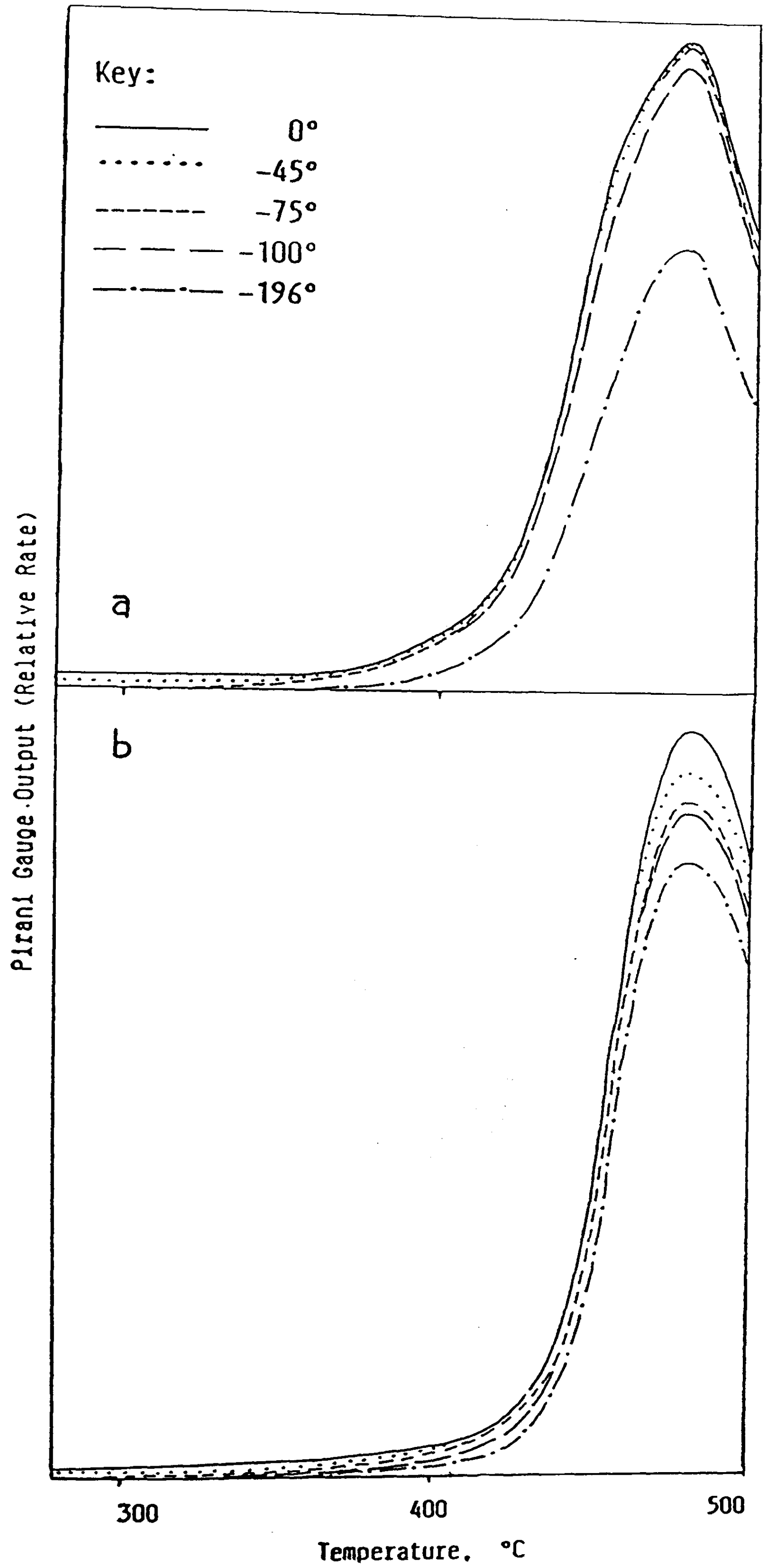


**Fig. 7.15.** TVA curves (vacuum, heating rate 10°C/min) for zinc polyacrylate samples.

**a.** ZnPA*; **b.** ZnPA

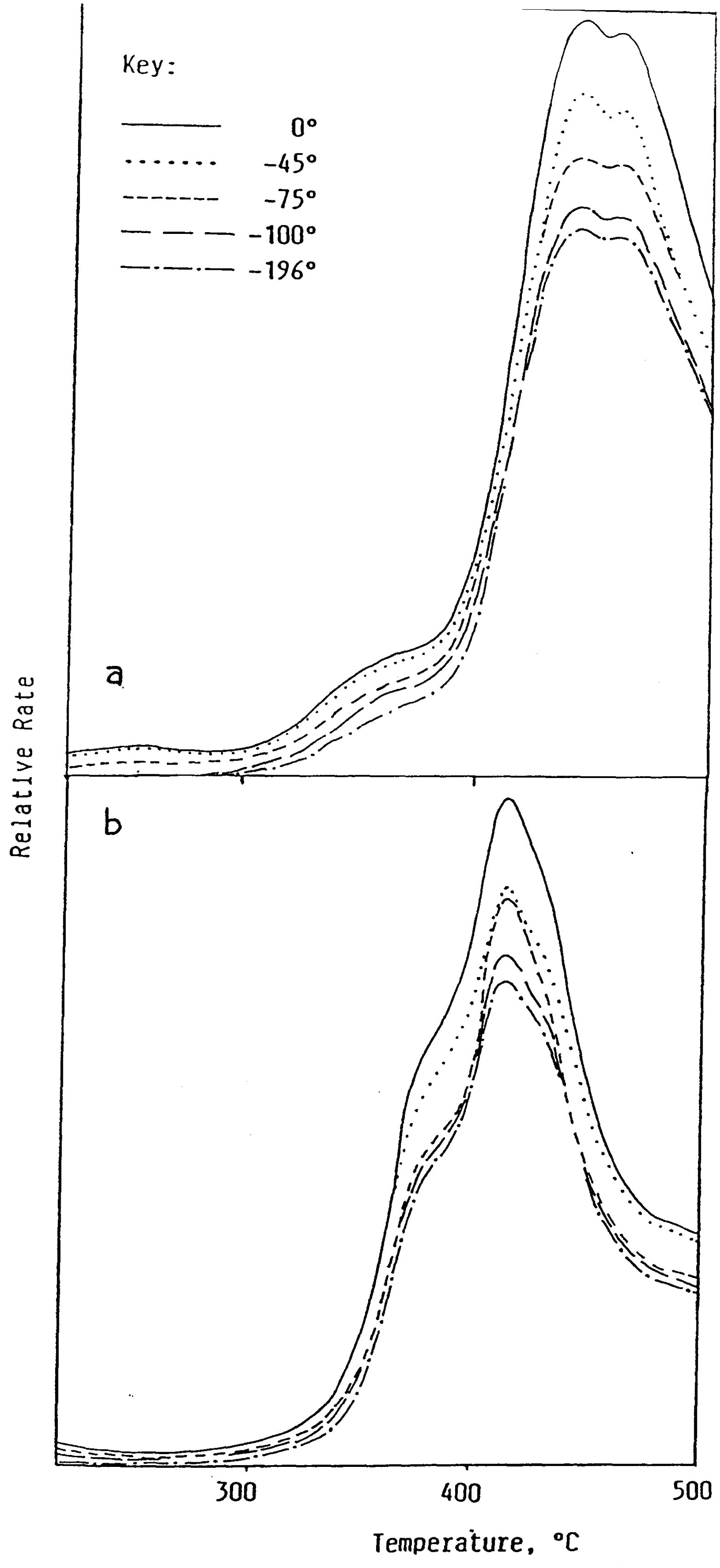


**Fig. 7.16.** TVA curves (vacuum, heating rate 10$^{O}$C/min) for cobalt polyacrylate samples.

a. CoPA* ; b. CoPA

400-480 $^{o}$C. After the first peak, a more extensive release of volatile products begins and shows a shoulder prior to the main peak of decomposition. The separation of traces, in the case of cobalt polyacrylate, at the higher temperatures is indicative of a variety of products. In the case of CoPA$^{*}$, the first peak of degradation may be mainly related to dehydration and decarboxylation processes of unreacted acid groups. Above 300 $^{o}$C, the shoulder shows partial degradation which evolves the non-condensable products due to the formation of intermediate species and their decomposition. Two-stage decomposition at the main peak of both polymers is consistent with formation of metal carbonate and its decomposition to metal oxide.

The TVA data for zinc and cobalt polyacrylate are summarised in *Table 7.4*. Quantitative measurements of the main product fractions and carbon dioxide were carried out using the same experimental approach already described in previous chapters.

The high yield of carbon dioxide from degradation of the zinc and cobalt polyacrylate samples is due to the instability of the corresponding metal carbonate at 500 $^{o}$C under vacuum.

In all cases, the separation of the TVA traces at the main decomposition is clearly indicative of the presence of a variety of products of differing volatilities.

### *3.3.1. Subambient TVA*

The condensable volatile product fraction from each polymer sample, made by polymerisation, was separated by subambient TVA. The corresponding SATVA curves are illustrated in *Figs.7.17* and *7.18*.

**Table 7.4.** TVA data for degradation of zinc and cobalt polyacrylate samples made by both routes.

| polymer | $T_{onset}$ $^{o}C$ | $T_{max}$ $^{o}C$ | Wt % residue, ~500 $^{o}C$ | Wt % CRF, ~500 $^{o}C$ | Wt % total volatile products, 500$^{o}C$ (incl. $CO_2$) | Wt % $CO_2$ |
|---|---|---|---|---|---|---|
| ZnPA | 340 | 480 | 53 | 12.5 | 34.5 | 21.0 |
| ZnPA* | 375 | 480 | 71 | 11.8 | 17.2 | 14.6 |
| CoPA | 260 | 170,380, 415 | 55 | ~1 | 44.0 | 24.3 |
| CoPA* | 300 | 245,365, 440,450 | 44.3 | trace | 55.7 | 25.9 |

* Polymers prepared from poly(acrylic acid) by neutralisation.

### *3.3.2. Product Analysis*

The volatile products of degradation of the polymer salts to 500 °C under normal TVA conditions were investigated by the techniques already described in the previous chapters.

Each degradation left a black involatile residue, which was found by IR spectroscopy to consist mainly of metal oxide.

The cold ring fraction (CRF) materials from the degradation of zinc salts were light blue solids, amounting to about 12 % of the original sample weight. The ir spectra of these fractions do not provide a good insight into the structural rearrangements which can take place since these fractions consist of *zinc metal* as a major product. The mass spectrometric analyses were consistent with the presence of zinc metal and various short chain fragments, containing carbonyl and carboxylic acid groups and including small amounts of the monomer and dimer salts. The corresponding identified products are listed in *Table 7.5*.

The CRF materials from the cobalt polyacrylate samples were yellow solids and it is particularly striking that the yields of CRF products from CoPA and CoPA* are very low, of the order of 1% of the sample weight or less. The mass spectra were consistent with the presence of fragments containing carbonyl and carboxylic groups; no monomer salt or other oligomer was found . This may be a result of stronger ionic forces reducing the mobility required in the chain for intramolecular transfer as already mentioned for magnesium and calcium salts in previous chapter.

Less volatile products collected as a liquid fraction, the last peak in the SATVA separation were further investigated by GC-MS. Instrumental conditions during the GC-MS analysis for liquid fraction of the polymers were as follows;

Injector temperature 250 $^{o}$C, voltage 70 ev, column temperature initially 60 $^{o}$C for 5 min then programmed at 2-5$^{o}$/min to about 200 $^{o}$C, helium gas flow rate 12 ml/min. The chromatograms for the GC-MS investigations of these fractions from the degradation of ZnPA and CoPA, shown in *Figs. 7.19* and *7.20.*

All the products identified in the degradation of zinc and cobalt polyacrylate samples using IR, MS, GC and GC-MS are listed in *Tables 7.6* and *7.7*, respectively.

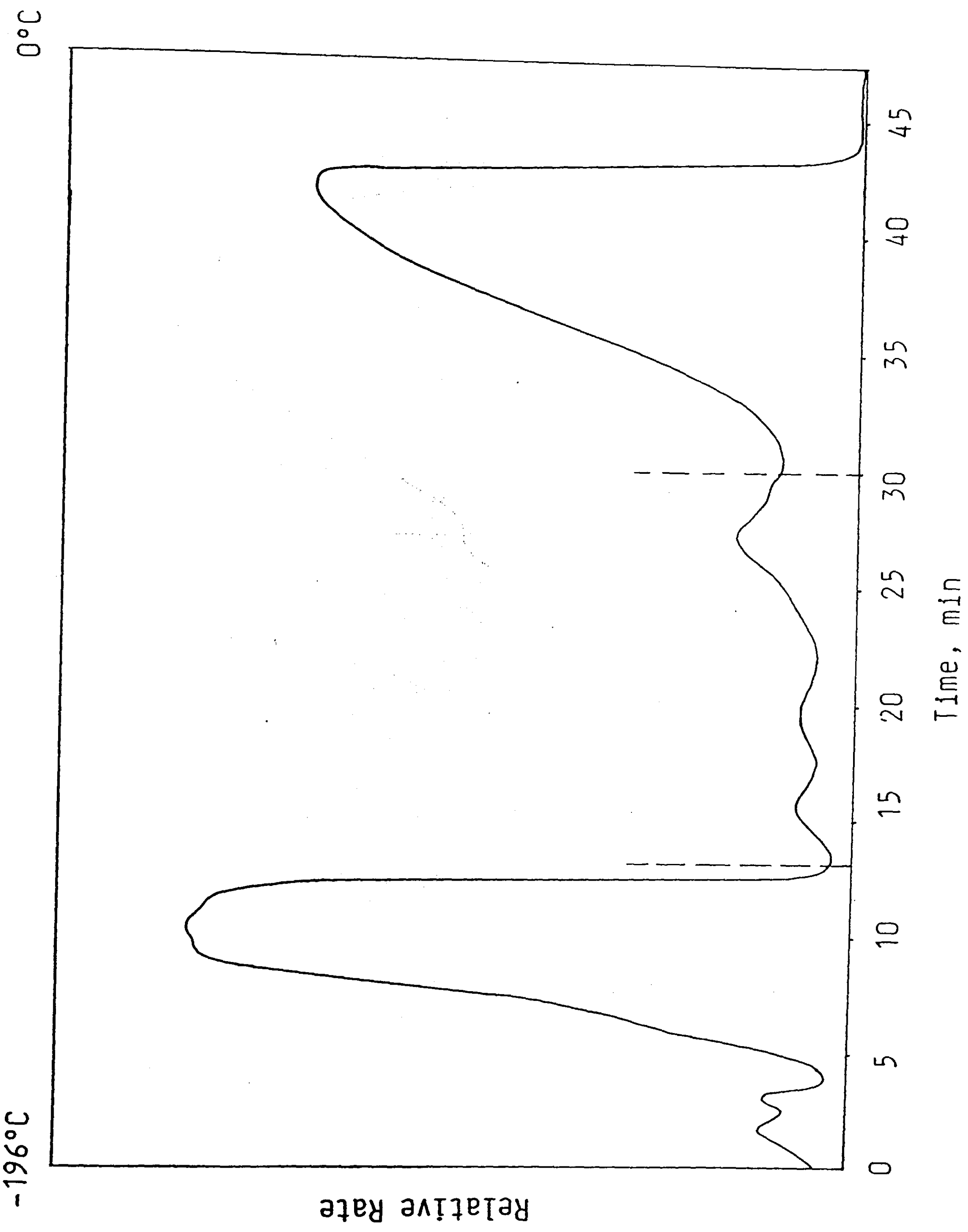


**Fig. 7.17.** SATVA curve of condensable product fraction from degradation to 500 °C under TVA conditions of zinc polyacrylate.

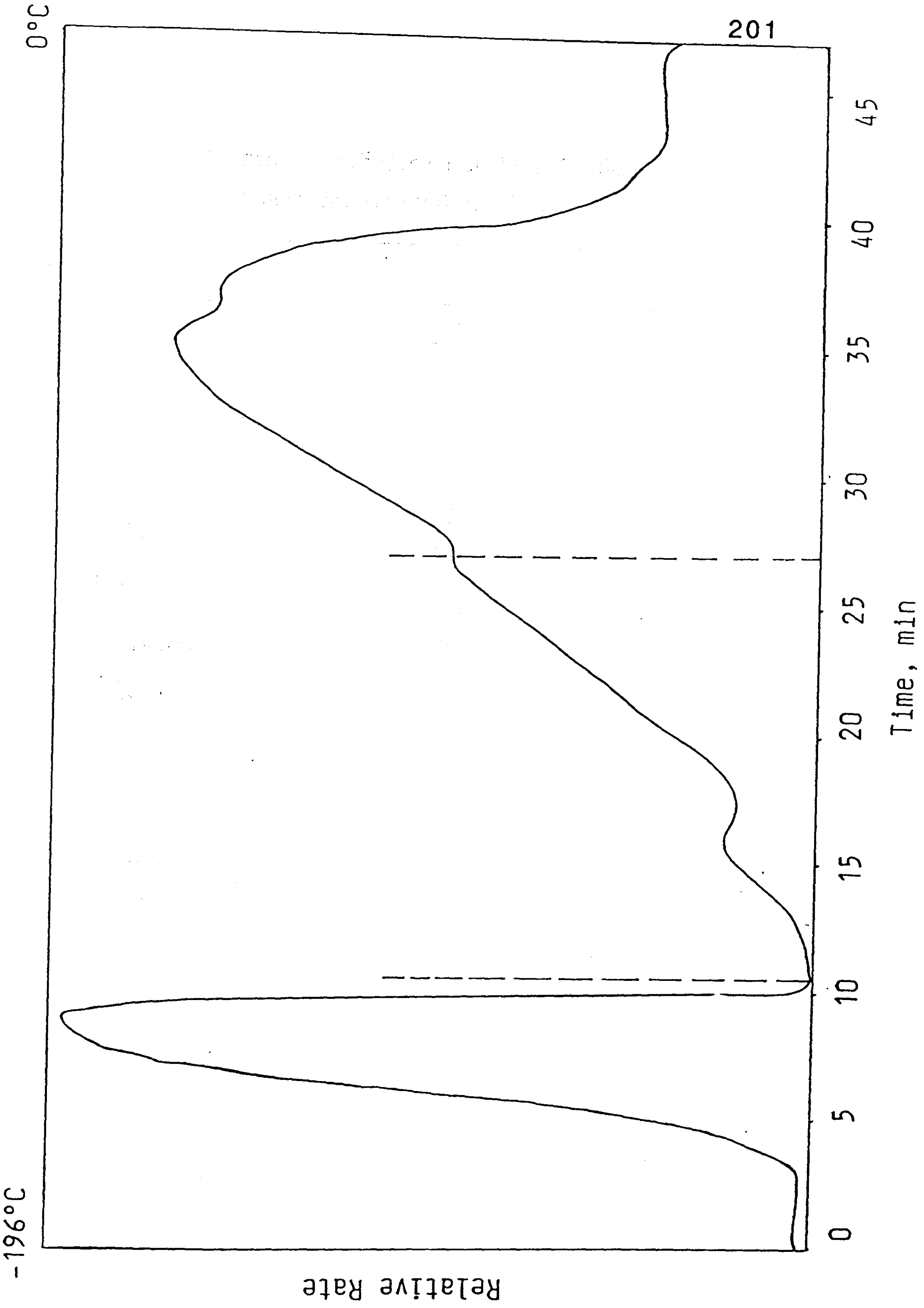
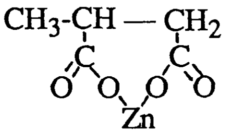
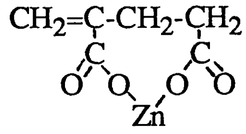
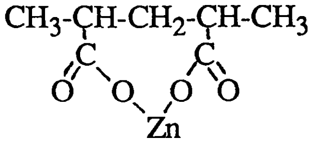
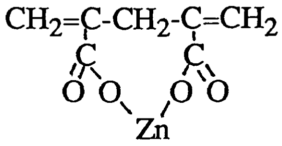
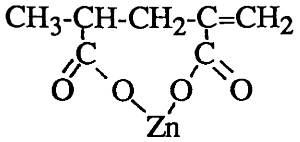
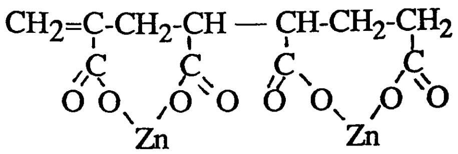
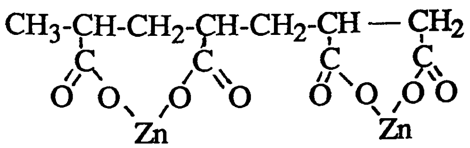


**Fig.7.18.** SATVA curve of condensable product fraction from degradation to 500 °C under TVA conditions of cobalt polyacrylate.

**Table 7.5.** Products identified in the cold ring fraction from degradation to 500 °C of ZnPA

| compounds | m/e |
|---|---|
| ZnO | 81 |
|  | 195 |
|  | 207 |
|  | 223 |
| Zinc metal | 65 |
|  | 219 |
|  | 221 |
|  | 400 |
|  | 402 |

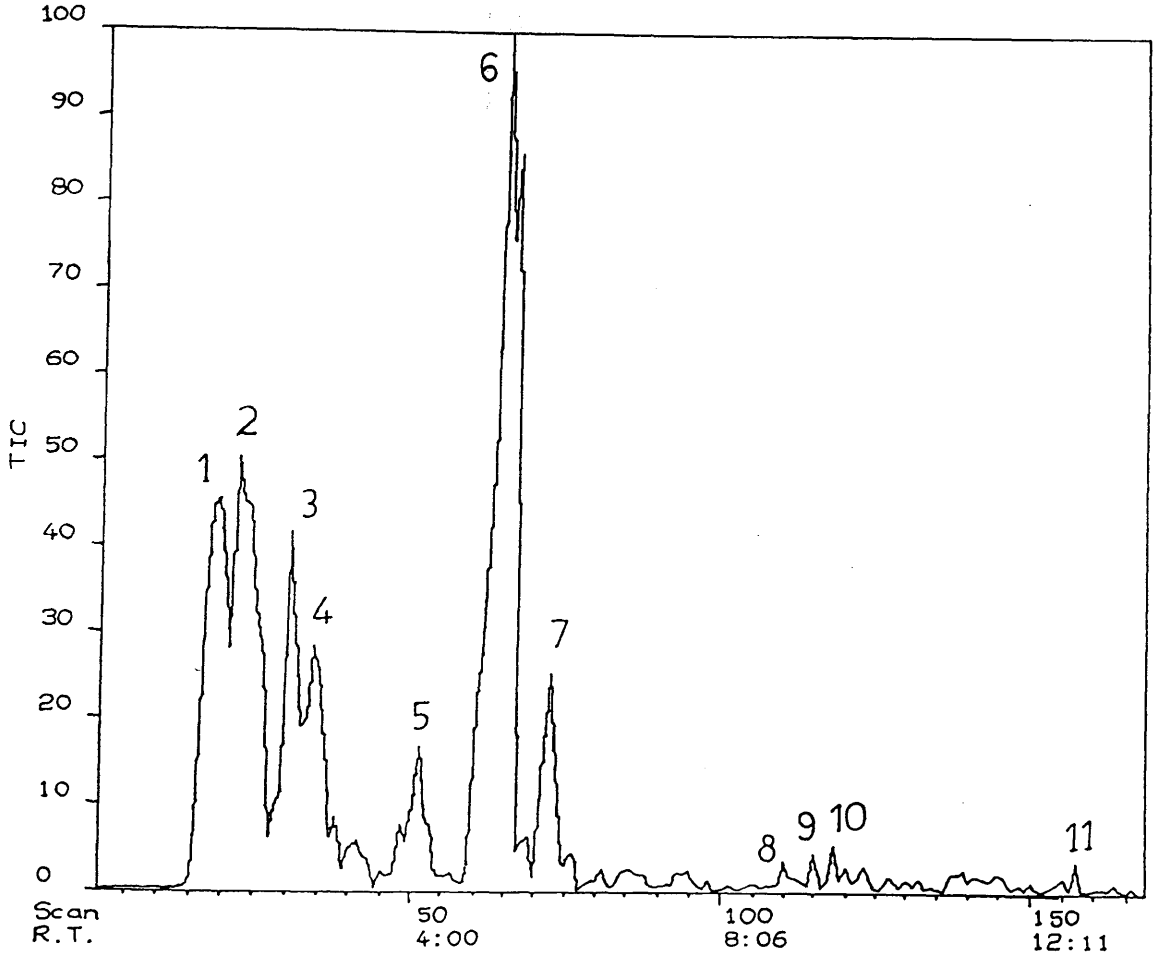


**Fig. 7.19.** GC-MS chromatogram of the less volatile liquid fraction of zinc polyacrylate,prepared by polymerisation. Assignments: **1** methyl vinyl ketone, **2** methyl vinyl ketone and methylene chloride (impurity), **3** methyl ethyl ketone, **4** benzene, **5** diethyl ketone, **6** toluene, **7** acrylic acid, **8** xylene, **9** ethyl benzene, **10** xylene, **11** ethyl n-butyl ketone.

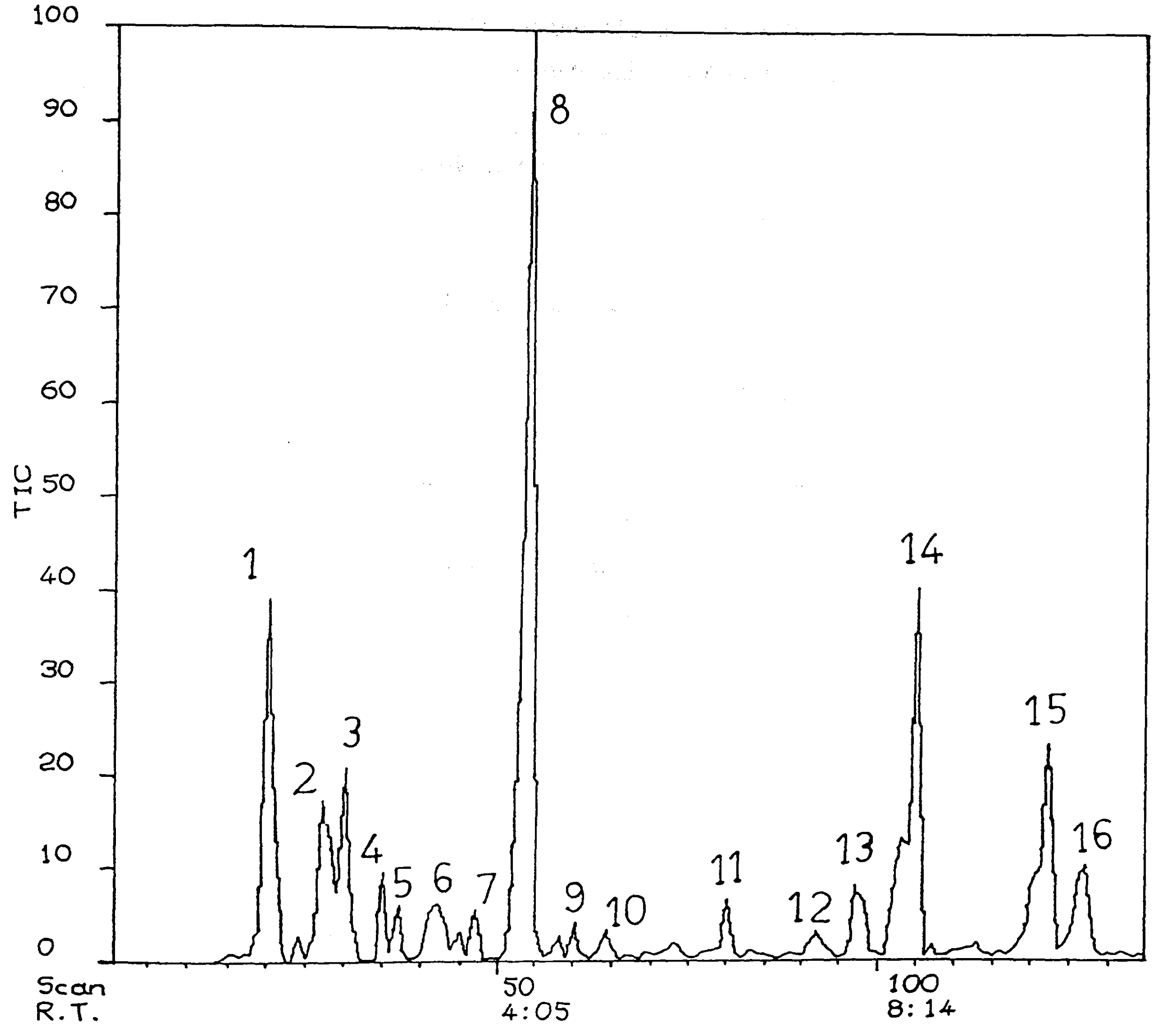


**Fig. 7.20.** GC-MS chromatogram of the less volatile liquid fraction of cobalt polyacrylate,prepared by polymerisation. Assignments: **1** acetone, **2** methyl ethyl ketone, **3** benzene, **4** diethyl ketone, **5** methyl propenyl ketone, **6** methyl n-propyl ketone, **7**, **8** toluene, **9** methyl isopropyl ketone, **10** methyl n-propyl ketone, **11** methyl n-butyl ketone, **12** cyclopentanone, **13**, **14**, **15** xylene, **16** unknown.

**Table 7.6.** Products of degradation of zinc polyacrylate to 500 $^{o}$C at 10$^{o}$C/min under TVA conditions.

| Non-condensable products at -196 $^{o}$C | Condensable volatile products at -196 $^{o}$C | | | CRF (yellow solid) | Residue (black) |
|---|---|---|---|---|---|
| | Gases | Liquid Fraction | | | |
| IR | IR, MS | IR, MS | GC-MS | IR, MS | IR |
| CO<br>$CH_4$ | $CO_2$*<br>$C_2H_4$<br>Ketene<br>Propene<br>1-Butene<br>Acetone<br>Diethyl ketone<br>Xylene<br>Methyl vinyl ketone<br>Toluene<br>Benzene<br>Cyclopentene<br>Cyclopentanone<br>1,3-Butadiene<br>Acetaldehyde<br>Acrolein | Acrylic acid<br>$H_2O$<br>Mesitylene | Toluene<br>Methyl vinyl ketone<br>Methyl ethyl ketone<br>Benzene<br>Acrylic acid<br>Diethyl ketone<br>Xylene<br>Ethyl benzene<br>Ethyl n-butyl ketone | Zinc metal as a major product together with small amount of short chain fragments such as monomer and dimer salts. | ZnO as a major product. |

* Major

**Table 7.7.** Products of degradation of cobalt polyacrylate to 500 °C at 10°C/min under TVA conditions.

| Non-condensable products at -196 °C | Condensable volatile products at -196 °C | | | | CRF (yellow solid) | Residue (black) |
|---|---|---|---|---|---|---|
| | Gases | | Liquid Fraction | | | |
| IR | IR, MS | IR, MS | GC | GC-MS | IR, MS | IR |
| CO<br>$CH_4$ | $CO_2$*<br>Ketene<br>Propene<br>Acetone*<br>Benzene<br>Toluene<br>Xylene<br>Propanal<br>Acetaldehyde<br>Cyclopentene<br>Acrolein<br>Diethyl ketone<br>$CH_3OH$[a] | $H_2O$<br>$CH_3OH$[a]<br>Acetic acid[b] | Acetone<br>Methyl ethyl ketone<br>Toluene<br>Xylene<br>Butanal<br>Diethyl ketone<br>Cyclopentanone<br>Benzene<br>Propanal<br>Mesitylene<br>$CH_3OH$[a] | Toluene<br>Xylene<br>Acetone<br>Benzene<br>Methyl ethyl ketone<br>Diethyl ketone<br>Methyl n-propyl ketone<br>Methyl n-butyl ketone<br>Methyl propenyl ketone<br>Methyl isopropyl ketone<br>Cyclopentanone | CRF consisted of fragments containing carbonyl and carboxylic groups, no monomer salt or oligomer was found. | Metal oxide as a principal product. |

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* Major

a. Impurity (solvent).

b. Impurity from starting material.

## *4. CONCLUSIONS*

According to the TG, DTG, DTA and TVA data which have already been discussed, the thermal behaviour of zinc acrylate is similar to that of the alkaline earth metal salts of acrylic acid.

When heated, zinc and cobalt acrylate samples polymerise prior to degradation . The thermal stability of the zinc monomer salt is higher than that of the cobalt salt. It is found that zinc and cobalt acrylate decompose to zinc oxide and cobalt carbonate as the major products of the respective involatile residue under TVA conditions.

The thermal behaviour of zinc and cobalt polyacrylate shows many similarities to the behaviour of the calcium and magnesium salts of poly(acrylic acid). The thermal stability of the divalent metal salts of poly(acrylic acid) increases in the sequence; Ca > Mg > Zn > Co.

The solid residue of Zn and Co polyacrylate samples consisted mainly of the respective oxide as in the case of the Mg salt.

The structure of the cold ring fraction material from degradation of zinc polyacrylate, as for the calcium and magnesium salts, is consistent with the presence of small amounts of the monomer salt. A zinc mirror became visible on the head connection of the TVA tube as CRF. The formation of zinc metal during the degradation is due to reduction of zinc oxide in the presence of carbon.

It is found that the thermal stability of zinc and cobalt polyacrylate samples is greater than that of the corresponding monomer salts. The mechanism of degradation of these materials are similar to that of the magnesium and calcium polyacrylate which already discussed in Chapter Six.

# CHAPTER EIGHT

## THERMAL DEGRADATION OF ACRYLIC ACID / STYRENE COPOLYMER

### *1. INTRODUCTION*

Acrylic acid monomer and polymer have been already discussed in Chapters One and Four, respectively, in terms of physical and chemical properties, particularly thermal behaviour. This chapter considers the thermal degradation of acrylic acid / styrene copolymers.

Styrene is a monomer which can be polymerised by all known addition polymerisation mechanisms, such as radical[145], cationic[145], anionic[146], and with transition metal containing catalysts.[147] Styrene readily copolymerises with a variety of other monomers. Styrene monomer can generate enough free radicals during heating that high conversion and high molecular weight polymer can be prepared without chemical initiators. Free radicals for the polymerisation reaction form from two monomer molecules by a Diels Alder reaction.[148] Polystyrenes are mostly prepared industrially by radical polymerisation.[149]

Polystyrene is a thermoplastic with many desirable properties. It is clear, transparent, easily coloured and fabricated. It has reasonably good mechanical and thermal properties, but is slightly brittle and softens below 100 $^{o}$C. It is quite resistant to alkalis, halide acids and oxidising and reducing agents. Since styrene polymers are nonpolar, resistant to water, and easy to fabricate, they are the products of choice for electronic, medical, food packaging, optical, appliance, and automotive applications. Use of styrene polymers in packaging is enhanced by their resistance to gamma radiation in the 2 to 3 µrad range used for sterilisation.

## 2. *PREVIOUS WORK ON THERMAL DEGRADATION OF POLYSTYRENE*

Polystyrene degrades at elevated temperatures to a mixture of volatile products about half of which is styrene. The characteristic odor of the monomer serves as an identification for the polymer.[2] A number of recent monographs have provided additional information about thermal behaviour of polystyrene which reflect a discrepancy in views.[150-156]

The thermal degradation of polystyrene depends mainly upon whether the temperature is below or above *300 $^oC$*. Under vacuum, polystyrene usually begins to exhibit significant molecular weight decrease at about 300 $^oC$, but molecular weight reductions by random chain are observed at lower temperatures. Rates of degradation depend on the technique by which the polymer was prepared.[157] Anionically polymerised polystyrene is initially more stable than that produced thermally or from free-radical initiators such as benzoyl peroxide or AIBN.

In general, it is clearly evident that the thermal degradation mechanism of polystyrene proceeds by a free-radical chain mechanism by homolysis, in which the steps involve generation of free radicals, propagation (during which inter- and intramolecular chain transfers are very active), and a first-order termination.[157,159,160] Initiation at a chain end with a benzyl group produces a tolyl radical ($\cdot CH_2$-$C_6H_5$) and a primary polystyryl radical. At unsaturated end groups,$\alpha$-methyl styryl and secondary polystyryl radicals are formed.[153] The tolyl and $\alpha$-methyl styryl radicals abstract hydrogen to yield the toluene and $\alpha$-methyl styrene. In polystyrene made by the anionic route, the benzylic end ($\sim\sim CH_2$-$CH_2$-$C_6H_5$ ) has also been identified as a site for initiation of depolymerisation.[155,162] *Lehrle* and his co-workers[163] have shown that three series of propagation reactions for the chain-end polystyryl radicals account for the major volatile products observed. They are explained as ß-scission, intramolecular hydrogen abstraction (back biting) followed by ß-scission farther from the chain end. Formation of styrene and a polystyrene radical one unit shorter (unzipping) results from the scission of carbon-carbon bond beta to the chain end. Then styrene dimer and another polystyryl radical can be formed from intramolecular hydrogen abstraction. Finally, the formation of styrene trimer can probably be related to the last stage which is again ß-scission farther from the chain end after the back-biting.

There is general agreement that the termination step in the degradation of polystyrene in the range 30-350 °C is first order. It has been shown[159,163] that volatile radicals escaping from the polymer provide the predominant route for radical elimination.

*McNeill et al*[164] have recently studied the thermal behaviour of polystyrene in detail in this laboratory. They investigated the degradation of several polystyrene samples anionically prepared using sodium naphthalenide and compared the behaviour with that of a polystyrene sample made by the free radical route. A detailed product analysis for degradation at 300°, 350° and 420 °C was carried out using the GC-MS technique. They also studied the volatile liquid to cold ring fraction ratio for these two main products over a wide range of extent of degradation. It is found that the ratio falls sharply, is dependent on the initial molecular weight of the polymer and finally reaches a constant value. It is concluded from isothermal heating at 300 °C that intramolecular transfer is initially impeded by the high melt viscosity and intermolecular hydrogen transfer is favoured. They showed that intramolecular transfer becomes more important, indicated by the production of CRF, after the first 25 % of weight loss.

## *3. THERMAL BEHAVIOUR OF STYRENE/ACRYLIC ACID COPOLYMER*

The main features of the thermal degradation of poly(acrylic acid) and polystyrene have been known for many years, but littile attention has been paid to the corresponding copolymers, such as styrene/acrylic acid copolymer.

### *3.1. Previous Work On The Thermal Degradation Of ST/AA Copolymer*

*Suchock-Galas et al*[165], who studied the thermal and thermooxidative degradations of copolymer of styrene-acrylic acid and their sodium salts, have shown that thermal resistance is independent to the amount of introduced acid.

*Bukin*[166] and *Jegrovo*[167] have investigated the thermal behaviour of styrene ionomers (styrene-methacrylic acid and the sodium salt). They suggested that the thermal stability of the ionomers may or may not be dependent on the amount and kind of the metal ion present.

*Suchock-Galas*[168] Studied the correlation between the thermal stabilities of styrene-methacrylic acid copolymers and their sodium salts and the amount of acid or salt present into the copolymer. He degraded the copolymers using TG and DTA techniques. He showed that the initial decomposition temperatures and temperatures of the main decomposition of the copolymers of styrene and methacrylic acid remain almost constant, independently of the amount of MAA and sodium methacrylate introduced.

*Liggat*[68] Studied the thermal degradation of styrene-methacrylic acid copolymers containing 18, 44 and 72 mole % methacrylic acid using TG and TVA techniques, as a part of his research in this Department. He has shown that the TVA data for the copolymers indicate that the main decomposition of the copolymer is stabilised relative to polystyrene and destabilised relative to PMAA and the temperature of the major peak for the various samples lies between that of polystyrene and PMAA.

In the subsequent discussion, the thermal behaviour of two copolymer samples of styrene/acrylic acid containing 40 and 45 mole % acrylic acid, prepared as described in Chapter 3, has been studied using DTA, TG and TVA.

The degradation studies were carried out using two approaches, programmed heating at 10 °C/min to 500 °C and isothermal heating, at 300° and 340 °C.

### *3.2. PROGRAMMED HEATING EXPERIMENTS*

#### *3.2.1. Thermal Volatilisation Analysis*

The styrene-acrylic acid copolymers were examined as 70 mg powder samples in a TVA system under vacuum as previously described, including the modifications used[154] to increase the accessibility for study of the CRF of products volatile at degradation temperature but not at ambient temperature. Programmed heating was at a rate of 10°/min. The TVA curves for both copolymers are shown in *Fig. 8.1*.

Both copolymers show a two stage decomposition and from inspection of the separation of the traces, it is evident that product composition is different at each stage, the product volatility becoming greater as the degradation temperature rises. Non-condensable products are formed at about 275 °C, in which temperature region the presence of materials covering a wide range of volatilities is indicated.

It is clear from the TVA curves that in each case decomposition begins above 140 °C. There is no major difference in behaviour between these copolymer samples on the basis of the TVA data. The TVA results for both ionomers are almost similar, not only in respect of presence of a degradation peak below 275 °C, but also in the character of the degradation products, as revealed by their volatility in the TVA system. The main decomposition for both copolymers appears in the temperature region between 325-450$^{o}$C and the maximum rate of volatilisation ($T_{max}$) occurs at about 390 $^{o}$C. The major peak in the TVA curve of polystyrene is due almost entirely to styrene and has no associated -196 $^{o}$C non-condensable products whilst the major peak of poly(acrylic acid), due to the fragmentation of the anhydro-polymer shows a major contribution from -196 $^{o}$C non-condensable products.

The implication of the evolution of water and -196 $^{o}$C non-condensable gases from the copolymers is that these copolymers contain neighbouring carboxyl groups which cyclise exactly as in poly(acrylic acid) to form anhydride ring structures.

Gravimetric data were obtained under TVA conditions in experiments in which the copolymer sample was placed in a thin glass sample bottle and weighed as described in previous chapters. Quantitative measurement of carbon dioxide evolution was carried out using the calibration method previously described.[90]

### *3.2.2. Subambient Thermal Volatilisation Analysis*

Condensable volatile degradation products from the copolymer samples degraded to 500$^{o}$C using the TVA technique, collected in a liquid nitrogen trap in the vacuum system, were separated by the SATVA method. The SATVA traces for the products from the copolymers are shown in *Figs. 8.2* and *8.3*. Products collected in different fractions as indicated.

### *3.3. Product Analysis*

In this study, the degradation products have been examined by infrared spectroscopy, mass spectrometry and GC-MS techniques.

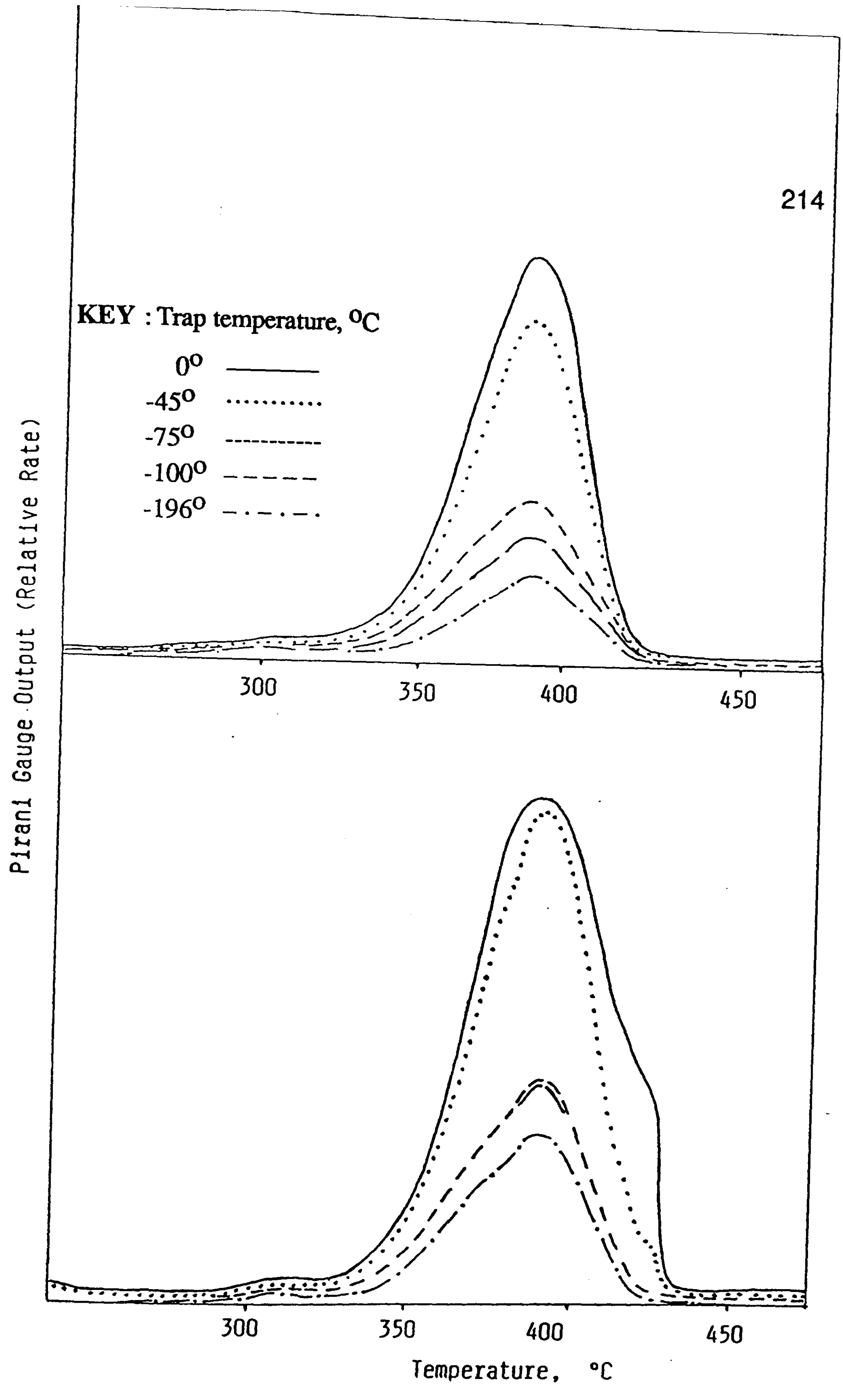


**Fig. 8.1.** TVA curves (vacuum, heating rate 10 °C/min) for styrene/acrylic acid copolymer samples:

**a.** ST/AA copolymer containing 40% of acid units.

**b.** ST/AA copolymer consisting of 45% of acid units.

### *3.3.1. Residue*

There was no significant amount of involatile fraction left in this experiment.

### *3.3.2. Cold Ring Fraction*

Cold ring fraction (light brown solid material) products which condensed on the inserted cold finger, were removed using a volatile solvent. These were examined by IR, MS and GC-MS. The corresponding ir spectra (Fig.8.5) are rather similar to the spectrum of the

**Table 8.1.** TVA data for degradation of styrene/acrylic acid copolymer samples contain 40 and 45% acid units.

| Polymer | $T_{onset}$ °C | Initial temp. for non-condensable gases, °C | $T_{max}$ °C | Wt% residue at ~ 500 °C | Wt% CRF at ~ 500 °C | Wt% of condensable volatile products at ~500 °C (incl. $CO_2$) | Wt% $CO_2$ |
|---|---|---|---|---|---|---|---|
| ST/AA copolymer* | 175 | 285 | 395 | 4 | 51.6 | 44.4 | 4.4 |
| ST/AA copolymer** | 140 | 275 | 390 | 1.5 | 57.5 | 41.0 | 6.4 |

* Copolymer consisting of 40% acrylic acid units.

** Copolymer containing 45% acrylic acid units.

copolymer, showing bands at 1625, 1700 and 1760 $cm^{-1}$ due to the carbon-carbon double bond and hydrogen-bonded and nonbonded carbonyl group absorptions, respectively. The characteristic bands of anhydride type structure at 1805, 1760 (shoulder) and 1030 $cm^{-1}$ and bands due to oligomeric structure of styrene are also present. Mass spectrometry data indicated that the CRF consists of monomer and other high boiling products such as dimer and trimer containing the monomer units; products identified are listed in *Table 8.2*. The cold ring fraction was also subjected to GC-MS and a 15 m capillary column DB-5 was used for separation. Instrumental conditions during the GC-MS analysis for CRF of the copolymers were as follows;

Injector temperature 280 $^{o}C$, voltage 70 ev, column temperature initially 190 $^{o}C$ for 5 min then programmed at 5 $^{o}C$/min to 300 $^{o}C$, helium gas flow rate 18 ml/min. The corresponding chromatogram is illustrated in *Fig. 8.4.*

### *3.3.3. Non-condensable Gases*

Methane and carbon monoxide were established as non-condensables.

### *3.3.4. Condensables as Gaseous Products*

The condensable gaseous products were examined by ir spectroscopy and mass spectrometry. These products were clearly found to consist of carbon dioxide as a major product together with toluene, acetone, ketene, benzene, methanal, 1-butene, acrolein, cyclopetene, methyl ethyl ketone, cyclopentanone and methyl n-propyl ketone.

### *3.3.5. Condensables as Liquid Fraction*

The ir spectrum is consistent with the styrene spectrum. There is a clear indication of carbon-carbon double bond, monosubstituted aromatic and vinyl group absorptions

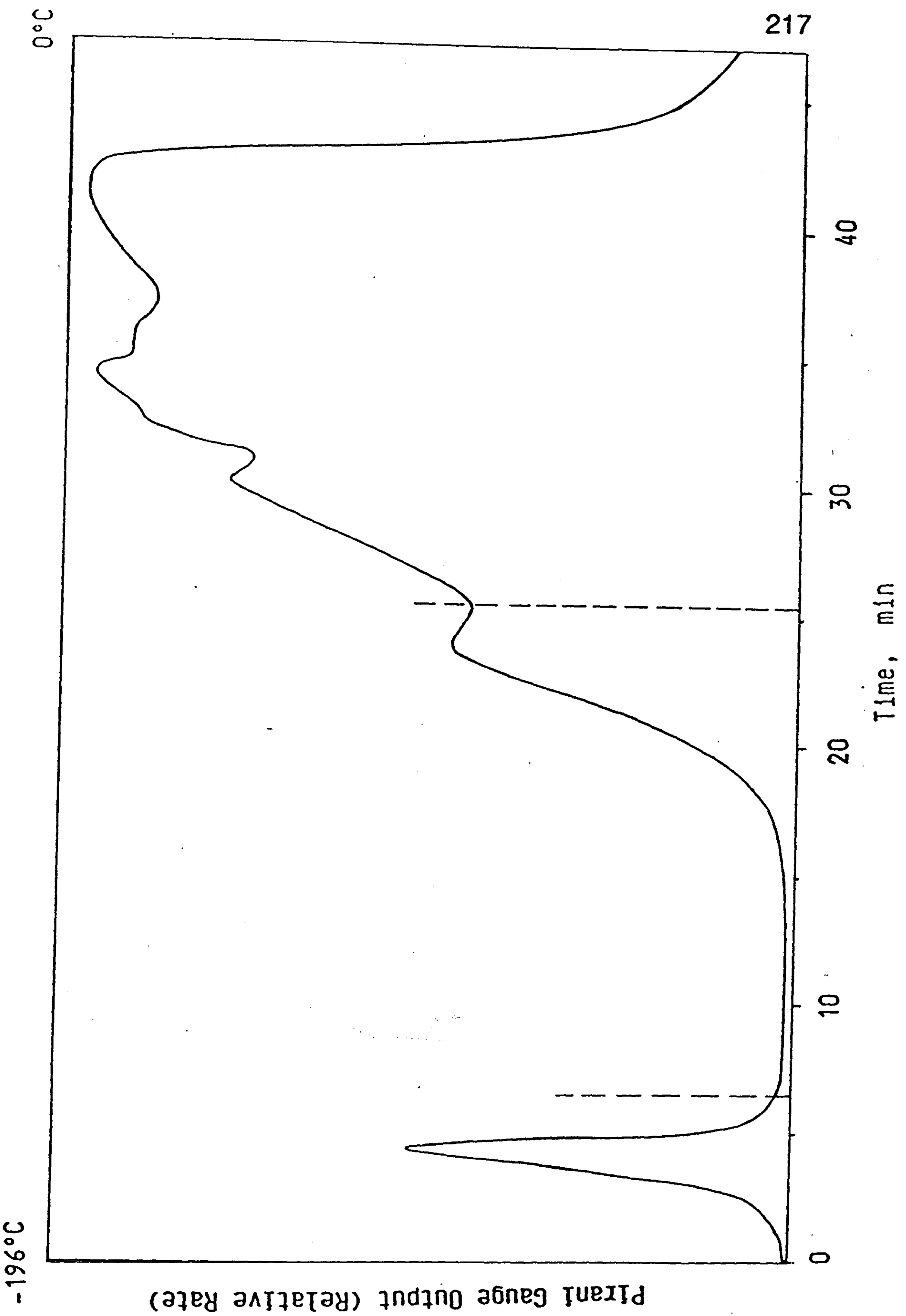


**Fig. 8.2.** SATVA curve of the condensable product fraction from degradation of ST/AA copolymer consisting of 40% acrylic acid units to 500 °C under TVA conditions.

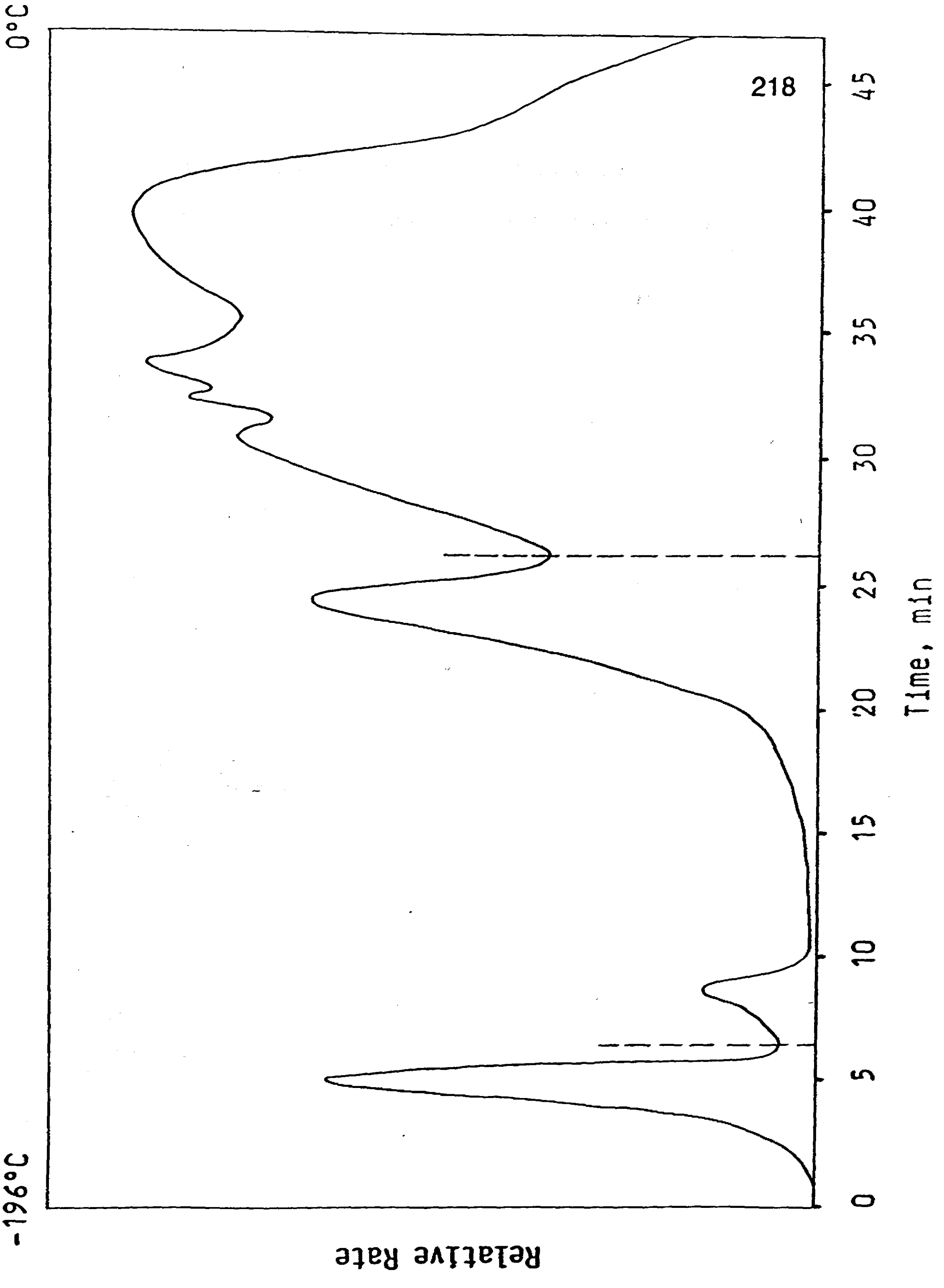
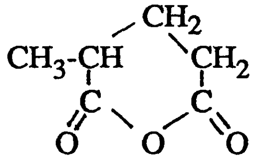
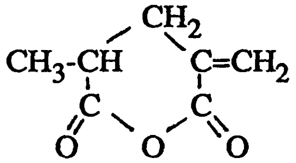
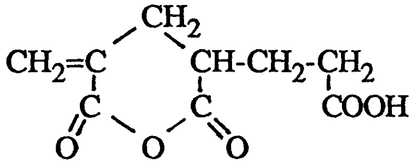
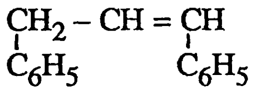
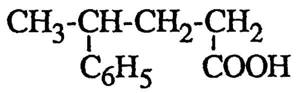
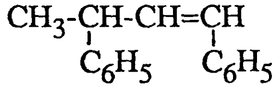
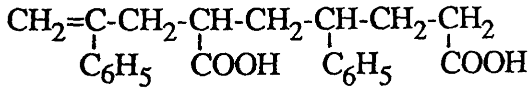


**Fig. 8.3.** SATVA curve of the condensable product fraction from degradation of ST/AA copolymer consisting of 45% acrylic acid units to 500 °C under TVA conditions.

**Table 8.2.** Products identified in the cold ring fraction from degradation of ST/AA copolymer* under TVA conditions.

| Product | m/e |
|---|---|
|  | 128 |
|  | 140 |
|  | 196 |
|  $\underset{C_6H_5}{CH_2}-CH=\underset{C_6H_5}{CH}$ | 194 |
|  $CH_3-\underset{C_6H_5}{CH}-CH_2-\underset{COOH}{CH_2}$ | 178 |
|  $CH_3-\underset{C_6H_5}{CH}-CH=\underset{C_6H_5}{CH}$ (styrene dimer) | 208 |
|  $CH_2=\underset{C_6H_5}{C}-CH_2-\underset{COOH}{CH}-CH_2-\underset{C_6H_5}{CH}-CH_2-\underset{COOH}{CH_2}$<br>(two units of each type) | 352 |

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* Copolymer containing 40% acrylic acid units.

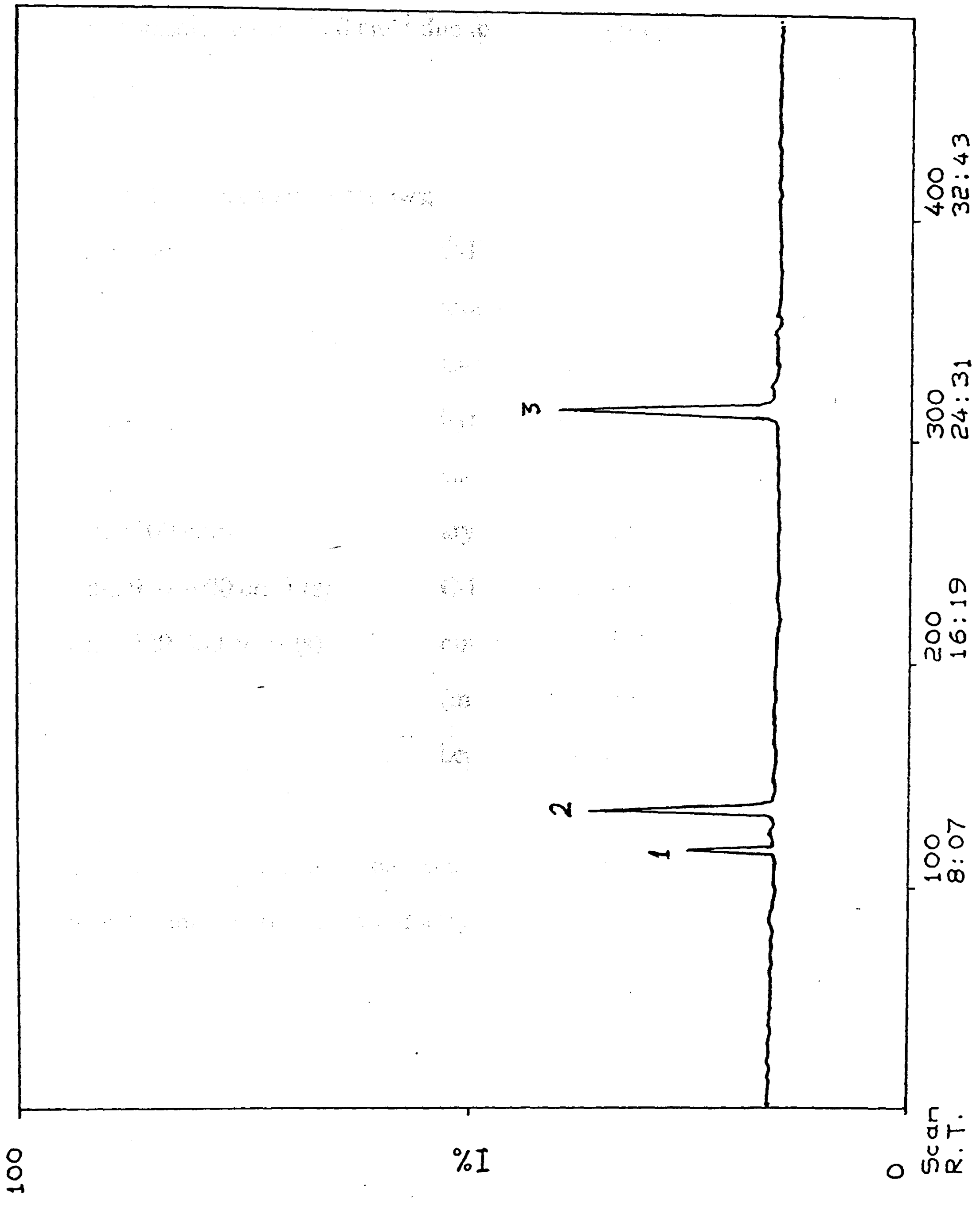


**Fig. 8.4.** GC-MS chromatogram of the cold ring fraction of ST/AA copolymer containing 40% acid units. Assignments: **1** 1,3 diphenyl propane, **2** styrene dimer, **3** styrene trimer.

together with strong absorption at 1700 cm$^{-1}$ due to carbonyl group. The ir spectrum is reproduced in *Fig. 8.5*.

The most significant absorptions are as follows;

| | |
|---|---|
| 3040-3010 cm$^{-1}$ (w) | C-H stretching (aryl-H) |
| 2000-1800 cm$^{-1}$ (w) | aromatic overtone |
| 1625 cm$^{-1}$ | C=C conjugated with aromatic ring |
| 1740, 1700 cm$^{-1}$ | hydrogen-bonded and nonbonded carbonyl group |
| 1600, 1580 and1500 cm$^{-1}$ | aryl-H vibration frequencies |
| 995-985 (s) and 940--900 cm$^{-1}$ (s) | C-H stretching of vinyl group |
| 770-730 (s) and 720-680 cm$^{-1}$ (s) | out of plane C-H bending vibrations (mono-substitution patterns of the benzene ring) |

Mass spectrometric analysis confirms styrene as a principal product in the volatile liquid fraction together with benzene, toluene andα-methyl styrene.

The last fractions of the SATVA separation, were also subjected to GC-MS and the corresponding chromatograms are illustrated in *Figs. 8.6* and *8.7*. Toluene, α-methyl styrene, ethyl benzene, benzoic acid , allyl benzene, acrylic acid and benzaldehyde are the volatile products next in importance to styrene, respectively, to 500 $^{o}$C in the TVA system under vacuum using programmed heating. The degradation products are listed in order of importance in *Table 8.3* and *8.4*.

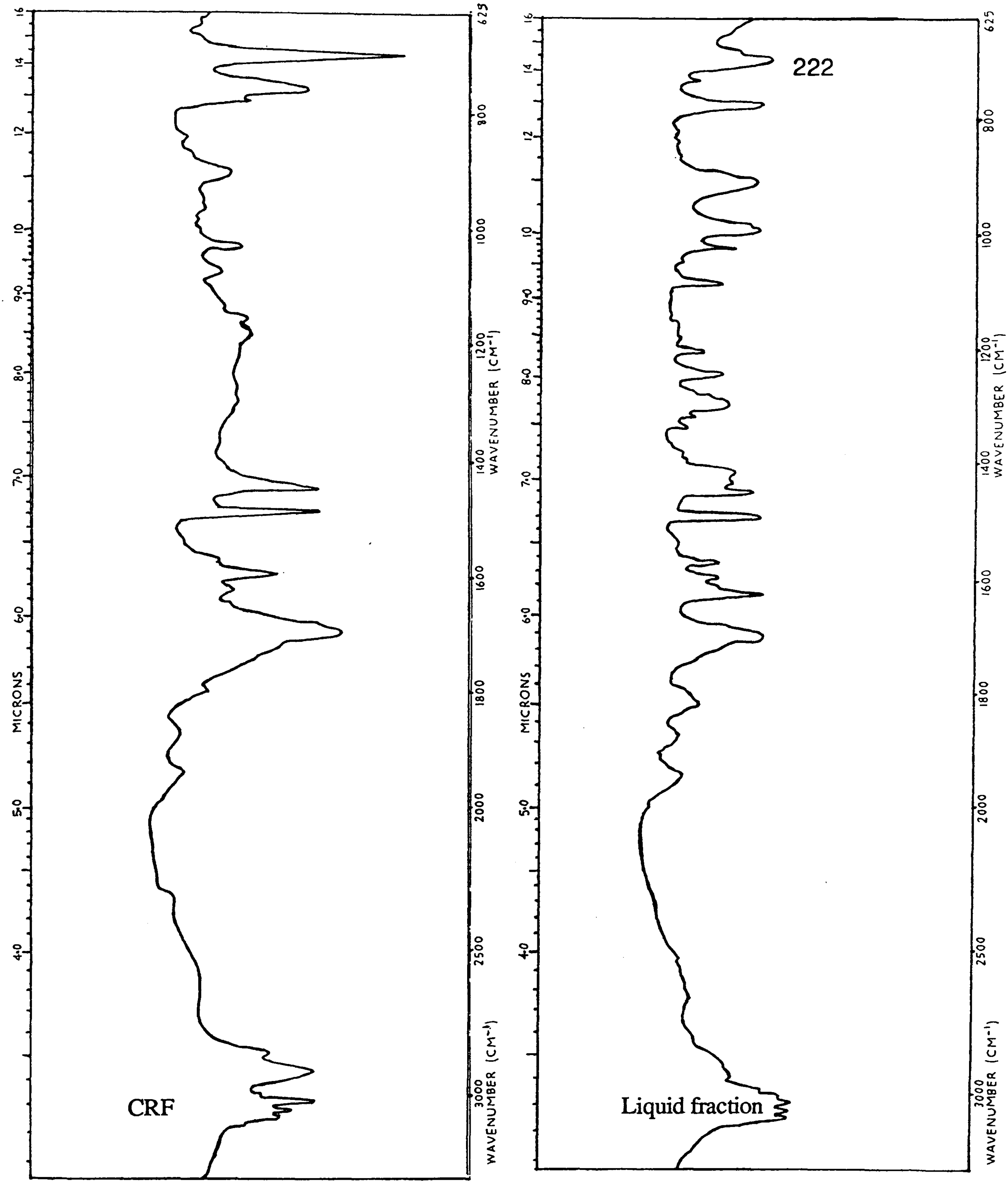


**Fig. 8.5.** Infrared spectra of CRF and liquid fraction of styrene/acrylic acid copolymer sample containing 40% acrylic acid units.

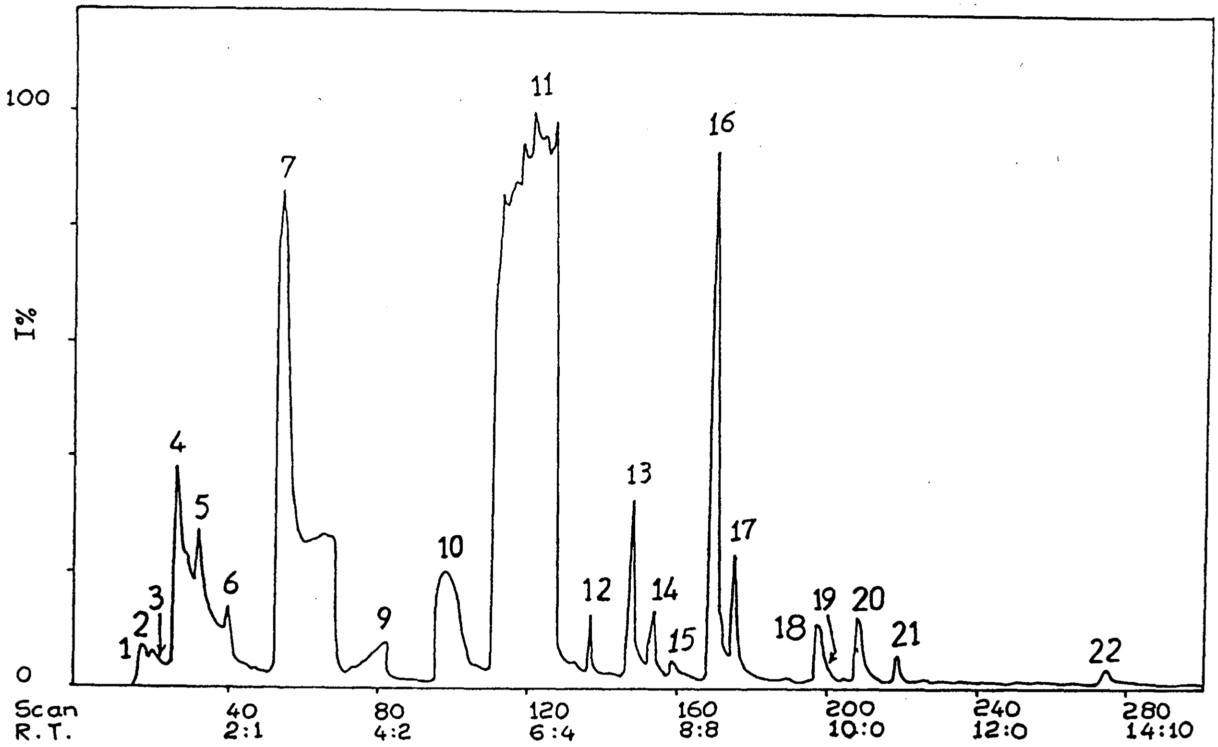


**Fig. 8.6.** GC-MS chromatogram of the less volatile liquid fraction of ST/AA copolymer containing 40% acrylic acid units. Assignments: **1** acetaldehyde, **2** methanol, **3** acetone, **4** butanoic acid, **5** unknown, **6** 3-methyl-2-pentanone, **7** acrylic acid + toluene, **8** toluene, **9** isobutyric acid, **10** ethyl benzene,**11** styrene,**12** cumene,**13** allyl benzene, **14** n-propyl benzene,**15** isopropyl benzene, **16**α-methyl styrene, **17** unknown, **18** cyclopropyl benzene, **19** 2,3-di-hydroindene, **20** 4-phenyl-butene-1, **21** n-butyl benzene, **22** α-methyl dihydro naphthalene.

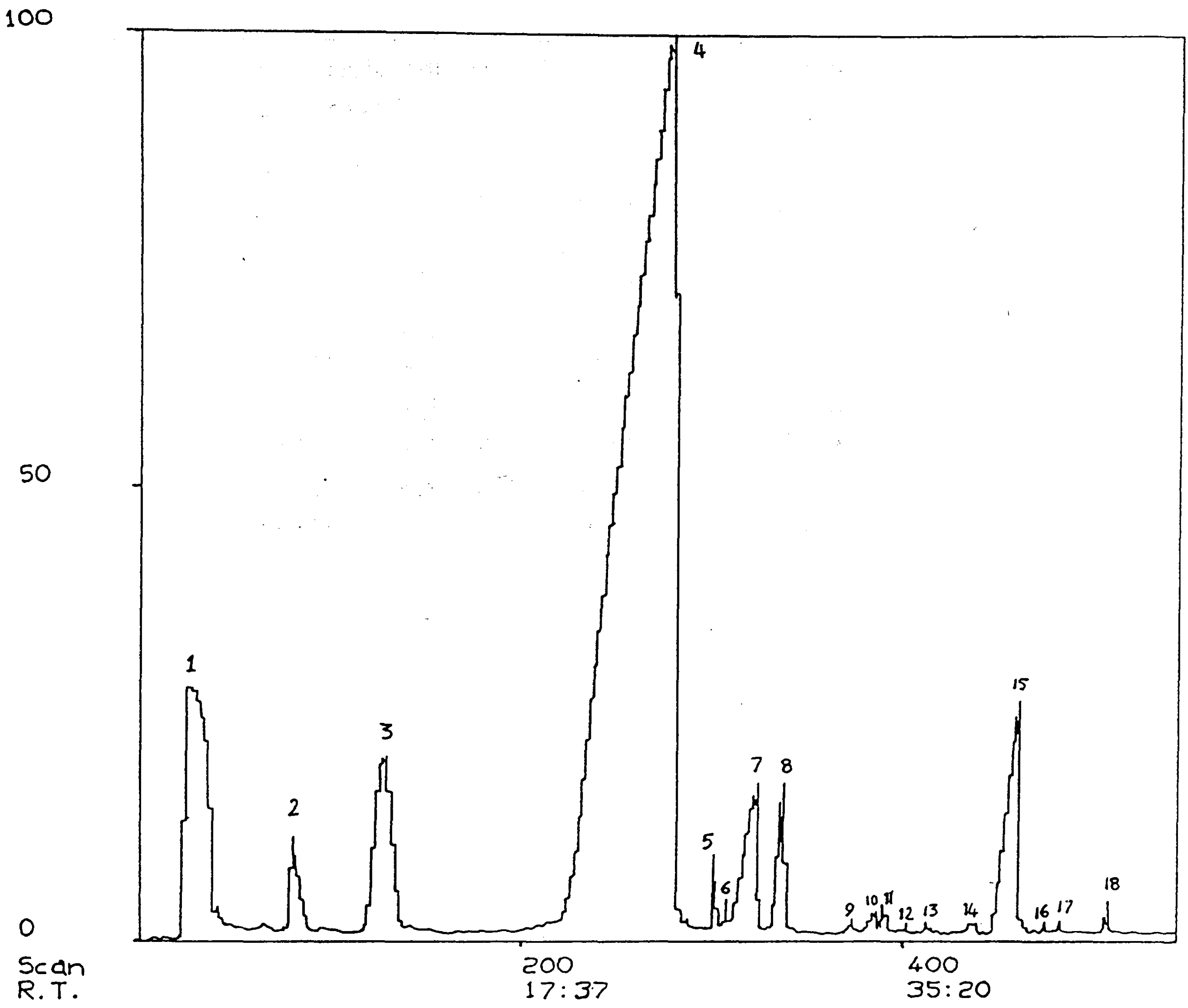


**Fig. 8.7.** GC-MS chromatogram of the less volatile liquid fraction of ST/AA copolymer containing 45% acrylic acid units. Assignments: **1** air, **2** methyl ethyl ketone + acrylic acid **3** toluene, **4** styrene, **5** allyl benzene, **6** n-propyl benzene, **7** benzaldehyde, **8** α-methyl styrene, **9** indane, **10** unknown, **11** 4-phenyl-1- butene **12** n-butyl benzene **13** 1-phenyl-2-butene, **14** unknown **15** unknown, **16** α-methyl dihydro naphthalene **17** divinyl benzene, **18** naphthalene.

**Table 8.3.** Products of degradation of ST/AA copolymer*
to 500 °C at 10 °C/min under TVA conditions.

| Non-condensable products at -196 °C | condensable volatile products at -196 °C | | | CRF (light brown solid) | Residue (black) |
|---|---|---|---|---|---|
| | Gases | Liquid Fraction | | | |
| IR | IR, MS | IR, MS | GC-MS | IR, MS | IR |
| CO<br>$CH_4$ | $CO_2$**<br>Ketene<br>1-Butene<br>Toluene<br>Acrolein<br>Acetone | Styrene**<br>Benzene<br>Toluene<br>Methanol[a] | Styrene**<br>Toluene<br>α-Methyl styrene<br>Acrylic acid<br>Ethyl benzene<br>Allyl benzene<br>Cumene<br>n-Propyl benzene<br>Isopropyl benzene<br>Cyclopropyl benzene<br>4-Phenyl-butene-1<br>Isobutyric acid<br>n-Butyl benzene<br>Acetaldehyde<br>Acetone<br>2,3-Dihydro indene<br>3-Methyl-2-pentanone<br>α-Methyl dihydro naphthalene | Short chain fragments including dimer and trimer of styrene, acrylic acid, together with anhydride structures and one and two units of each type. | Char |

---

a. Impurity from solvent.

* ST/AA copolymer containing 40% acrylic acid units.

** Major product

**Table 8.4.** Products of degradation of ST/AA copolymer* to 500 °C at 10 °C/min under TVA conditions

| Non-condensable products at -196 °C | condensable volatile products at -196 °C | | | CRF (light brown solid) | Residue (black) |
|---|---|---|---|---|---|
| | Gases | Liquid Fraction | | | |
| IR | IR, MS | IR, MS | GC-MS | IR, MS | IR |
| CO<br>$CH_4$ | $CO_2$**<br>Acetone<br>Toluene<br>Ketene<br>Benzene<br>Cyclopentane<br>Methyl ethyl ketone<br>Cyclopentanone<br>Methyl n-propyl ketone<br>Methanol[a] | Styrene**<br>Benzene<br>Toluene<br>α-Methyl styrene | Styrene**<br>Toluene<br>Benzoic acid<br>Benzaldehyde<br>α-Methyl styrene<br>Methyl ethyl ketone<br>Acrylic acid<br>Allyl benzene<br>n-Propyl benzene<br>Indane<br>4-Phenyl-butene-1<br>n-Butyl benzene<br>Divinyl benzene<br>α-Methyl dihydronaphthalene<br>1-Phenyl-2-butene | Short chain fragments such as dimer and trimer of styrene, acrylic acid, and one and two units of each type together with anhydride type structures. | Char |

a. Impurity.

* ST/AA copolymer sample containing 45% acrylic acid units.

** Major product.

## *3.4. ISOTHERMAL EXPERIMENTS*

In this investigation, the styrene/acrylic acid copolymer with 40% acrylic acid units was degraded isothermally under vacuum at 300$^{o}$ and 340 $^{o}$C. The isothermal data were obtained by degrading 160 mg of sample. The choice of these temperatures for isothermal heating was due to the thermal behaviour of poly(acrylic acid) and polystyrene on one hand and $T_{onset}$ temperature of the main decomposition of the copolymer on the other hand.

### *3.4.1. Isothermal Heating At 300 $^{o}$C*

The copolymer sample was heated isothermally at 300 $^{o}$C for different periods of time and the results are listed in *Table 8.5*. The weight loss % was plotted against time and the corresponding curve is shown in *Fig. 8.8*.

The degradation products of the degraded copolymer sample were collected and fractionated by SATVA technique after isothermal heating at this temperature for 3 hr.

#### *3.4.1.1. Product Analysis*

Product analysis was carried out using the same experimental approach already applied in programmed experiment.

#### *3.4.1.1a. Residue*

The involatile residue was a dark brown solid material. The ir spectrum (Fig. 8.9a) is consistent with partially degradation and shows the characteristic anhydride ring bands at 1805, 1760 (shoulder) and 1030 cm$^{-1}$ formed in anhydro poly(acrylic acid).

**Table 8.5.** Isothermal heating data for degradation of ST/AA copolymer* at 300 $^{o}$C for different periods of time under TVA conditions.

| Time (hr) | Weight loss (%) | Residue | | CRF | | Volatile products | | Ratio of volatile/CRF products |
|---|---|---|---|---|---|---|---|---|
| | | weight (g) | % | weight (g) | % | weight (g) | % | |
| 1/2 | 6.66 | 0.15 | 93.4 | 0.003 | 1.8 | 0.008 | 4.8 | 2.7 |
| 1 | 10.3 | 0.143 | 89.7 | 0.005 | 3.1 | 0.0115 | 7.2 | 2.3 |
| 1.5 | 13 | 0.14 | 87 | 0.008 | 5.2 | 0.012 | 7.8 | 1.5 |
| 2 | 15.2 | 0.136 | 84.8 | 0.011 | 6.7 | 0.0136 | 8.5 | 1.3 |
| 2.5 | 19.6 | 0.13 | 80.4 | 0.014 | 8.7 | 0.0175 | 10.9 | 1.3 |
| 3 | 21.7 | 0.125 | 78.3 | 0.017 | 10.9 | 0.0172 | 10.7 | 1 |

* ST/AA copolymer sample containing 40% acrylic acid units.

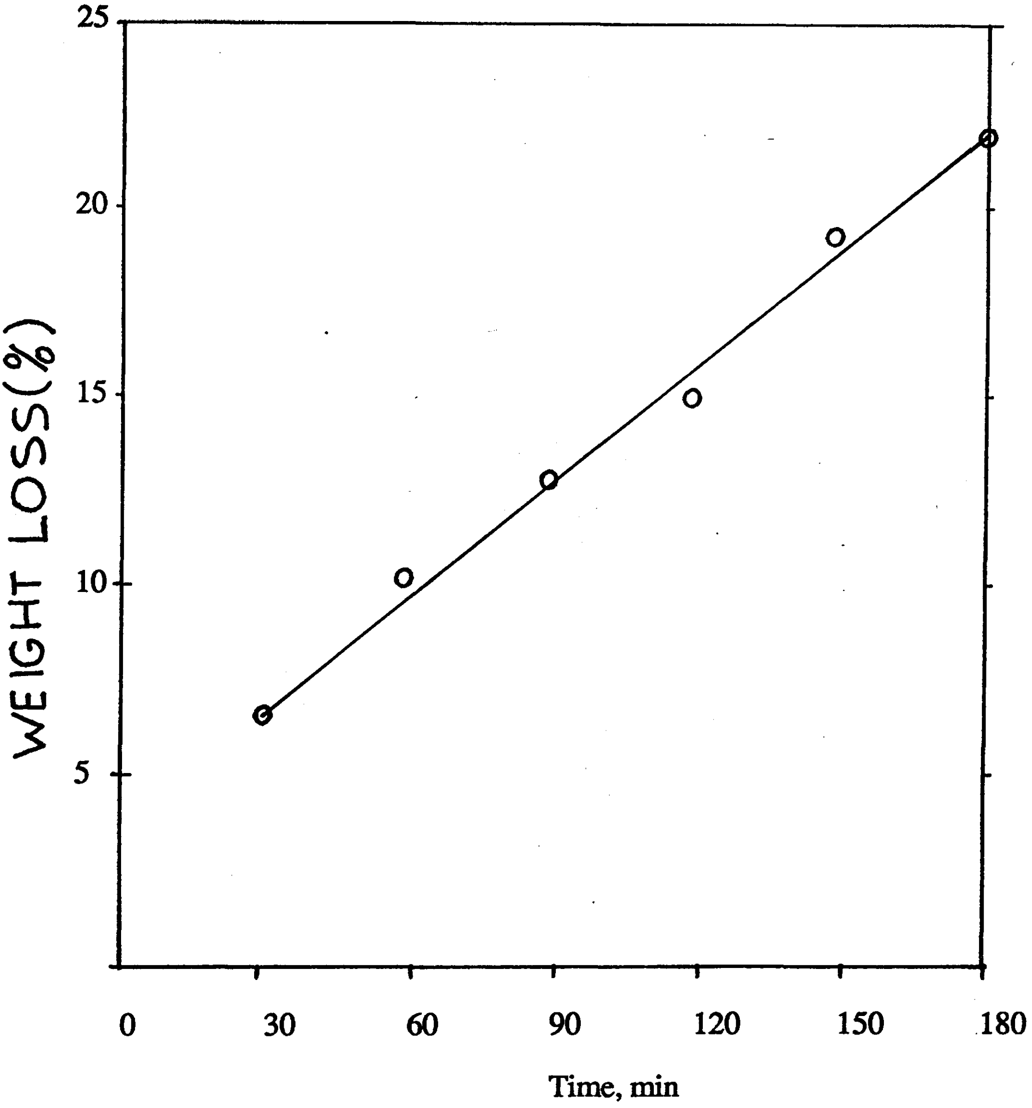


**Fig. 8.8.** Weight loss curve vs time for ST/AA copolymer sample containing 40% acrylic acid units, degraded isothermally at 300 °C under TVA conditions.

### *3.4.1.1b. Cold Ring Fraction*

The cold ring fraction obtained from isothermal degradation at 300 $^{o}$C was a brownish solid material. This fraction was collected on the inserted cold finger then removed by a suitable solvent for further investigation.

The infrared spectrum and mass spectrometry data are consistent with the presence of short chain fragments such as styrene and acrylic acid dimer together with anhydride structures and structures including one unit of each type. The corresponding ir spectrum is reproduced in *Fig. 8.9b*. Some of the products identified by mass spectrometry are listed in order of importance in *Table 8.6*.

The strong absorptions in the ir spectrum of the cold ring fraction are due to carbonyl, aromatic, vinyl groups, carbon-carbon double bonds and the anhydride type structures.

### *3.4.1.1c. Condensable Volatile Products as Gases.*

Carbon dioxide was found as a major product together with acetone, toluene, methyl ethyl ketone and cyclopentanone.

It is evident that the total weight loss is about 22% of the original sample weight. A gradual increase in CRF and volatile fraction as a function of time is observed.

The volatile/CRF product ratio determinations for the copolymer obtained isothermally at 300 $^{o}$C under normal TVA conditions are listed in Table 8.5. The data are based on gravimetric determinations of residue and cold ring fraction, the volatile fraction being calculated by difference from the initial sample weight. In this investigation, the values of the ratio decrease from nearly 3 to reach a value of unity. These results imply that in

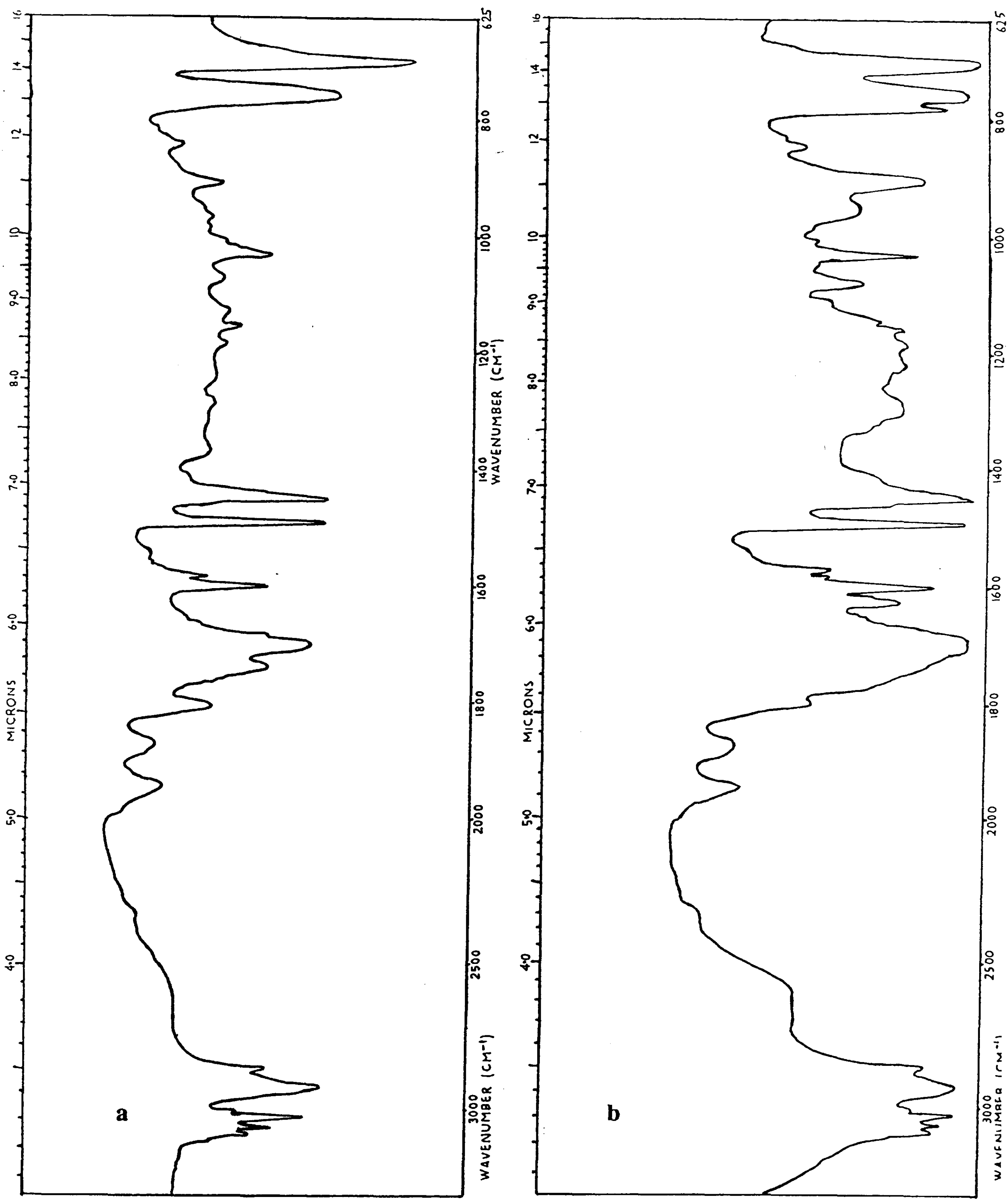
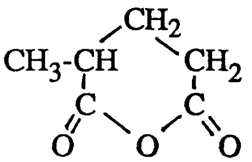
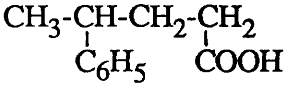
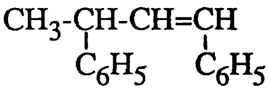
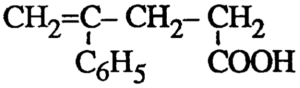
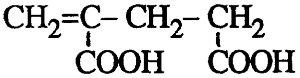
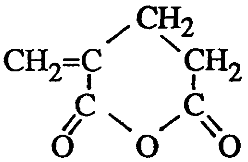
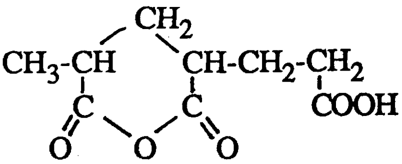


**Fig. 8.9.** Infrared spectra of the involatile residue and the CRF from isothermal degradation of styrene/acrylic acid copolymer sample containing 40% AA units at 300 °C. **a.** Residue, **b.** CRF

**Table 8.6.** Some of the products identified in the cold ring fraction of ST/AA copolymer* using isothermal heating at 300 °C under TVA conditions.

| Product | m/e |
|---|---|
|  | 128 |
|  $CH_3\text{-}\underset{C_6H_5}{CH}\text{-}CH_2\text{-}\underset{COOH}{CH_2}$ | 178 |
|  $CH_3\text{-}\underset{C_6H_5}{CH}\text{-}CH{=}\underset{C_6H_5}{CH}$ (styrene dimer) | 208 |
|  $CH_2{=}\underset{C_6H_5}{C}\text{-}CH_2\text{-}\underset{COOH}{CH_2}$ | 176 |
|  $CH_2{=}\underset{COOH}{C}\text{-}CH_2\text{-}\underset{COOH}{CH_2}$ | 144 |
|  | 126 |
|  | 198 |

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* ST/AA copolymer containing 40 mole % acrylic acid.

the early stages of copolymer degradation the volatile fraction production due to dehydration and decarboxylation processes greatly exceeds CRF production, but finally after 3 hr, CRF production equals volatile formation.

### *3.4.2. Isothermal Heating at 340 $^{o}C$ ($T_{onset}$)*

The resulting residue from isothermal degradation at 300 $^{o}$C was degraded isothermally beyond this temperature at 340 $^{o}$C for 3 hr continuously, to investigate the further structural changes in the copolymer. Degradation products were collected, separated by SATVA and analysed by IR, MS and GC-MS techniques.

### *3.4.2.1. Product Analysis*

#### *3.4.2.1a. Residue*

The involatile fraction was a dark brown material left as residue which mainly consisted of carbon as a char amounting to less than 1% of the initial sample weight.

#### *3.4.2.1b. Cold Ring Fraction*

The cold ring fraction was a brownish material. The corresponding ir spectrum (Fig. 8.10) indicates similar absorptions as were observed in the previous experiment at 300$^{o}$C. This fraction consisted of short chain fragments such as dimer and trimer of styrene and acrylic acid including also fragments containing either one or two units of each type, together with anhydride structures. The CRF quantity amounted to 63.3% of the initial sample weight. Products identified by mass spectrometry are listed in *Table 8.7.*

#### *3.4.2.1c.Condensable Volatile as Gaseous Products*

Carbon dioxide, toluene, ketene, propene and traces of benzene were established by IR

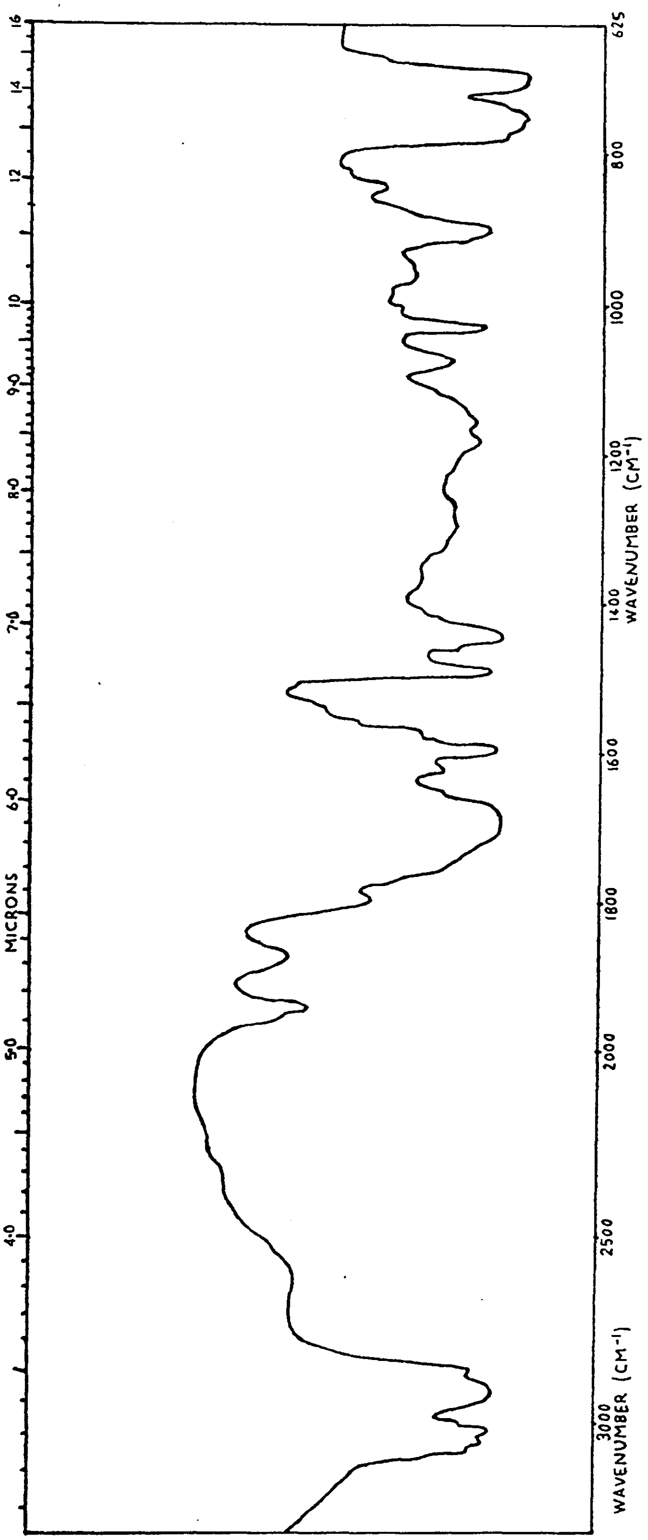


**Fig. 8.10.** Ir spectrum of CRF of ST/AA copolymer sample containing 40% acrylic acid units degraded isothermally at 340 °C.

and MS as condensable gaseous products. Less carbon dioxide was evolved than in the previous experiment. This result implies that most of the carboxyl groups have already been decomposed via dehydration and decarboxylation processes at 300 °C.

### *3.4.2.1d.Condensable Volatile as Liquid Fraction*

The less volatile liquid fraction was analysed using the GC-MS technique. The chromatogram is reproduced in *Fig. 8.11*.Styrene was found as the principal product together with $\alpha$-methyl styrene and toluene next in importance in this fraction.

CRF production became significant in degradation at 340 °C, approximately double the amount of the volatile fraction and almost 35.8% of the initial sample weight.

## *3.5. THERMOGRAVIMETRY*

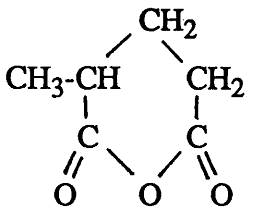
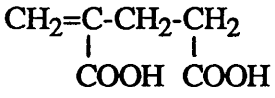
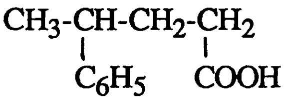
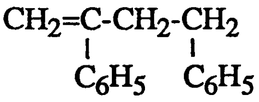
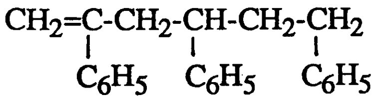
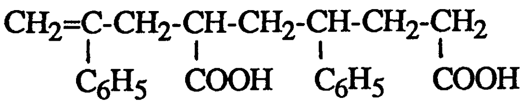
The TG and DTG curves of the copolymers obtained under dynamic nitrogen at heating rate of 10 °C/min, illustrated in *Fig. 8.12*. The TG curves for both copolymer samples have been presented on the same diagram to facilitate comparison. It is clear that the copolymer containing 45% acrylic acid units shows an initial weight loss below 200 °C amounting to 7% weight loss which is probably due to release of water or solvent as impurity.

The main decomposition appears at temperatures about 385° and 395 °C with 98 and 99% weight losses (to 500 °C) for styrene/acrylic acid copolymer samples containing 45 and 40% of acrylic acid units , respectively.

### *3.5.1. Isothermal Heating using TG*

The styrene/acrylic acid copolymer sample containing 40% acid units was also heated

**Table 8.7.** Products identified in the cold ring fraction of ST/AA copolymer* using isotherml heating at 340 °C under TVA conditions.

| Product | | m/e |
|---|---|---|
|  | | 128 |
|  $CH_2{=}\underset{COOH}{\underset{\mid}{C}}\text{-}CH_2\text{-}\underset{COOH}{\underset{\mid}{CH_2}}$ | (acrylic acid dimer) | 144 |
|  $CH_3\text{-}\underset{C_6H_5}{\underset{\mid}{CH}}\text{-}CH_2\text{-}\underset{COOH}{\underset{\mid}{CH_2}}$ | (saturated mixed dimer) | 178 |
|  $CH_2{=}\underset{C_6H_5}{\underset{\mid}{C}}\text{-}CH_2\text{-}\underset{C_6H_5}{\underset{\mid}{CH_2}}$ | (styrene dimer) | 208 |
|  $CH_2{=}\underset{C_6H_5}{\underset{\mid}{C}}\text{-}CH_2\text{-}\underset{C_6H_5}{\underset{\mid}{CH}}\text{-}CH_2\text{-}\underset{C_6H_5}{\underset{\mid}{CH_2}}$ | (styrene trimer) | 312 |
|  $CH_2{=}\underset{C_6H_5}{\underset{\mid}{C}}\text{-}CH_2\text{-}\underset{COOH}{\underset{\mid}{CH}}\text{-}CH_2\text{-}\underset{C_6H_5}{\underset{\mid}{CH}}\text{-}CH_2\text{-}\underset{COOH}{\underset{\mid}{CH_2}}$<br>(two units of each type) | | 352 |

* ST/AA copolymer consisting of 40% acrylic acid units.

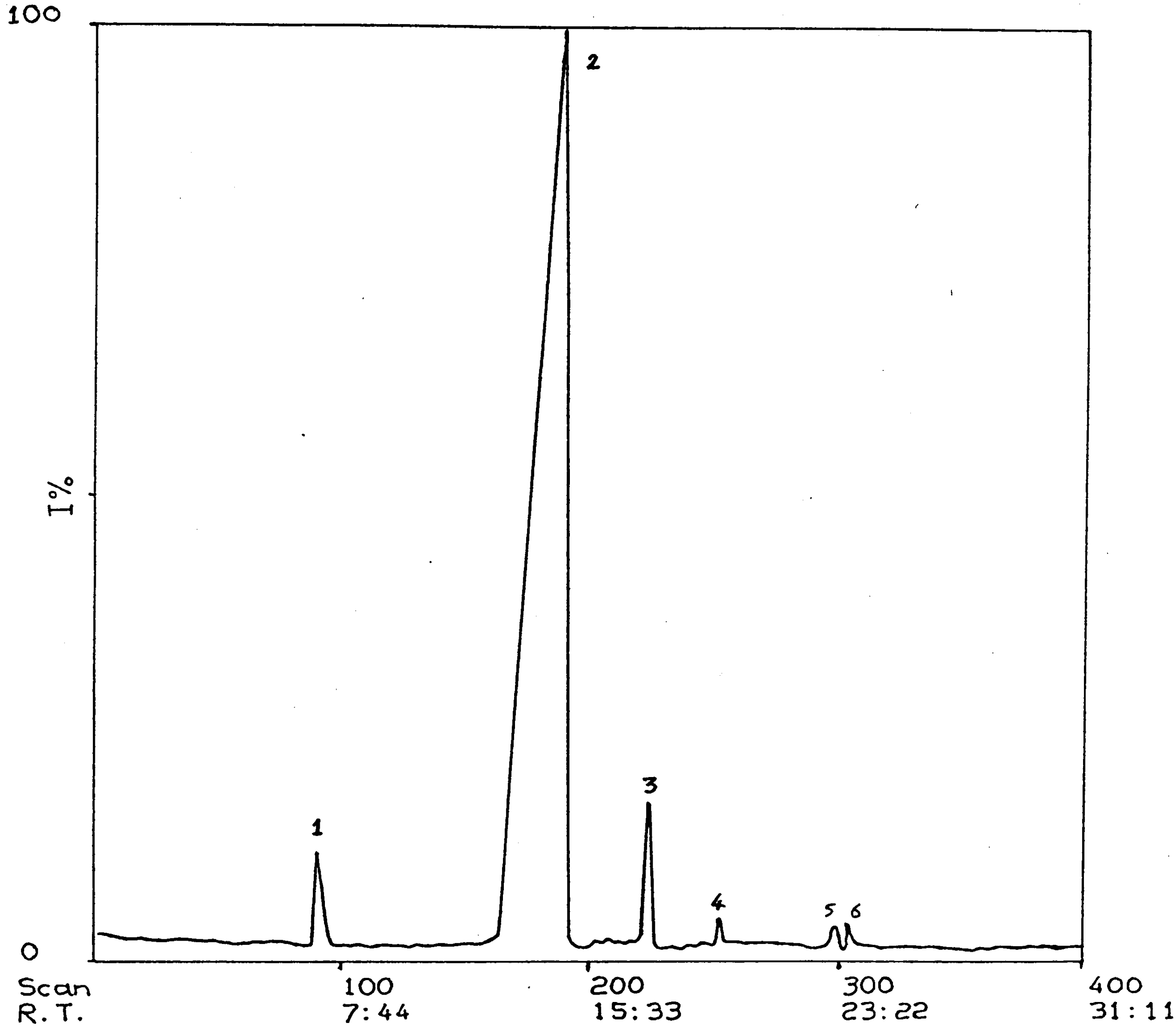


**Fig. 8.11.** GC-MS chromatogram of the less volatile liquid fraction of ST/AA copolymer containing 40% acrylic acid units, heated isothermally at 340 °C.

Assignments: **1** toluene, **2** styrene, **3**α-methyl styrene, **4** toluene, **5**α-methyl dihydro naphthalene, **6** divinyl benzene.

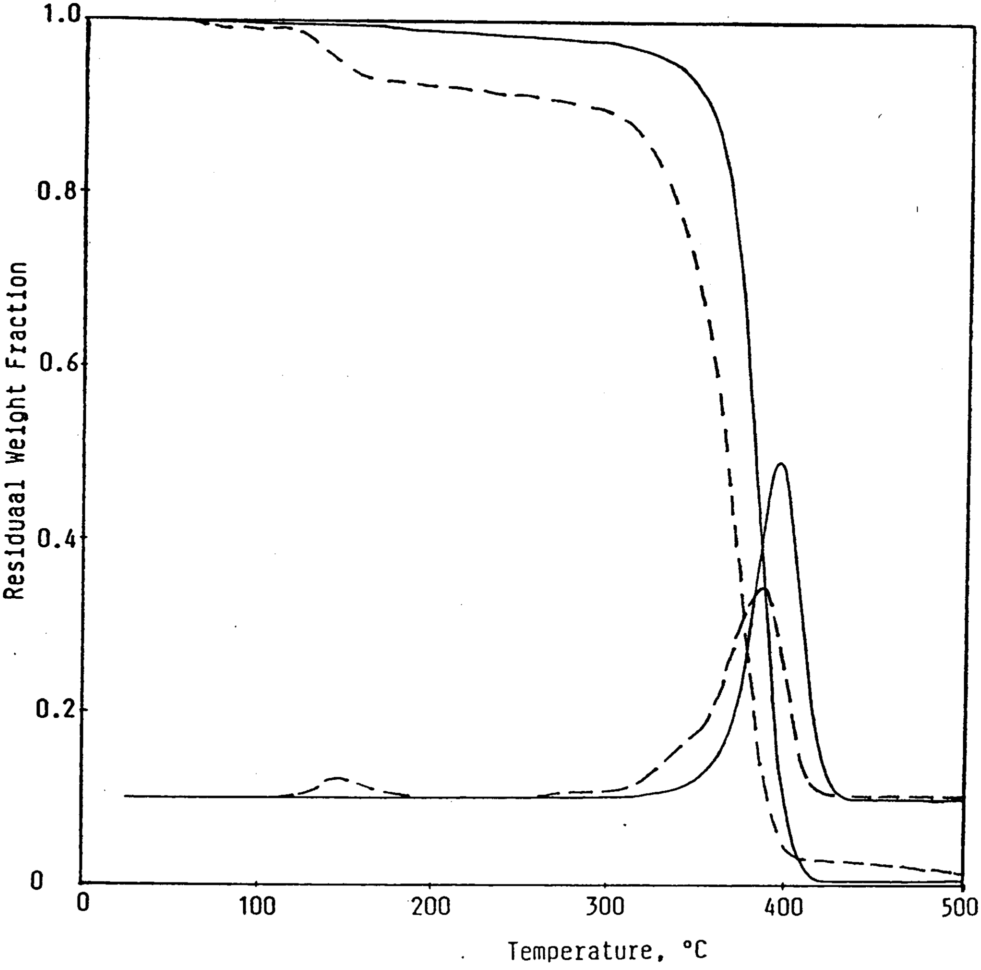


**Fig. 8.12.** TG and DTG curves (dynamic nitrogen atmosphere, heating rate 10 °C/min) for ST/AA copolymer samples.

——— ST/AA copolymer containing 40% acid units.

-------- ST/AA copolymer containing 45% acid units.

isothermally at 300 $^{o}$C for 3 hr using thermogravimetry. The isothermal data are in close agreement with TVA. The overall weight loss was about 26% of the original sample weight, compared with 22% found in the isothermal heating experiment at 300 $^{o}$C under vacuum. The TG curve is illustrated in *Fig. 8.13*.

### *3.6. DIFFERENTIAL THERMAL ANALYSIS*

The DTA curves of the ionomers were recorded in the range 25-485 $^{o}$C under nitrogen atmosphere, shown in *Fig. 8.14*. The DTA curve of the copolymer sample containing 40% acrylic acid units indicates an exothermic effect at 150 $^{o}$C which is probably due to structural changes.

The main step of decomposition of both copolymer samples is observed at temperature about 390 $^{o}$C. The DTA, TG and DTG results are consistent and are summarised in *Table 8.8*.

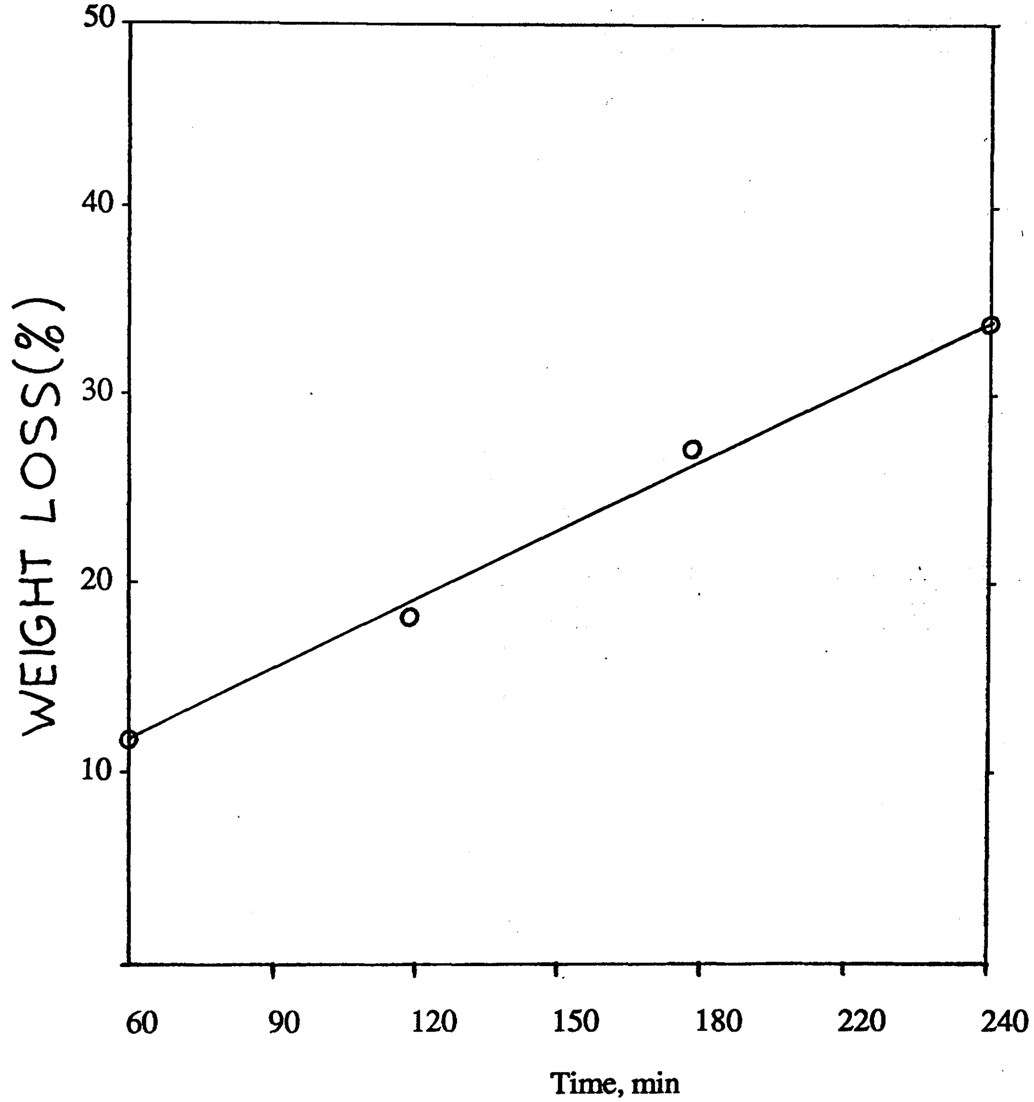


**Fig. 8.13.** Weight loss curve vs time for ST/AA copolymer sample containing 40 mole % acrylic acid degraded isothermally at 300 °C under nitrogen atmosphere using TG.

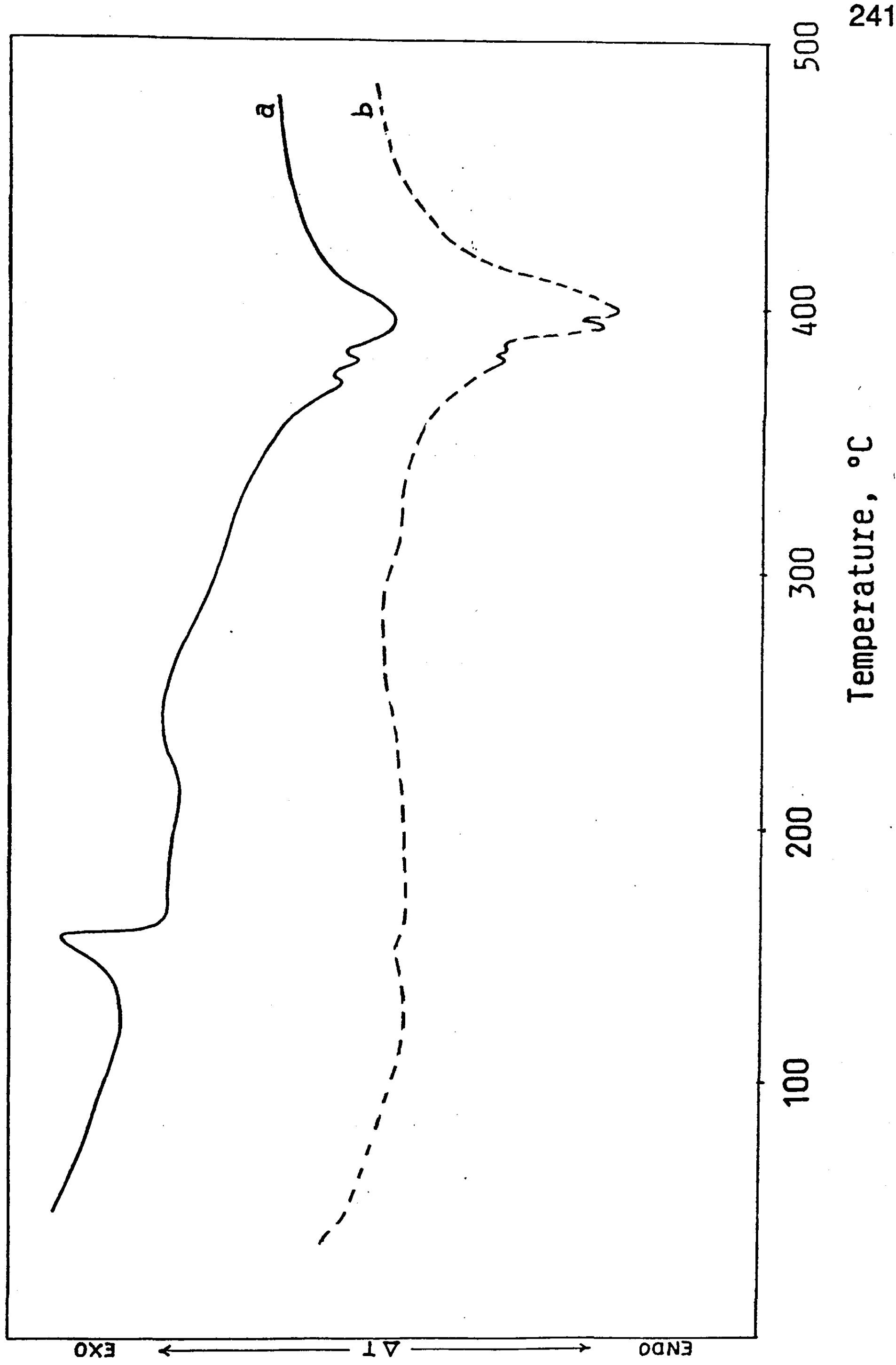


**Fig. 8.14.** DTA curve (dynamic nitrogen atmosphere, heating rate 10 °C/min) for ST/AA copolymer samples.

——— ST/AA copolymer containing 40% acid units.

-------- ST/AA copolymer containing 45% acid units.

**Table 8.8.** DTA, TG and DTG data for styrene/acrylic acid copolymer samples.

| | DTG | | TG | | DTA | | |
|---|---|---|---|---|---|---|---|
| Polymer | Peak temp., $^oC$ | Temp. range, $^oC$ | Wt% loss for stage | Total Wt% loss in the range 25-500 $^oC$ | Peak temp., $^oC$ | Temp. range, $^oC$ | Thermal effect |
| ST/AA* copolymer | _ | 25-350 | 8 | | | | |
| | | | | 100 | | | |
| | 390 | 350-430 | 92 | | 395 | 350-450 | endo |
| ST/AA** copolymer | 145 | 25-175 | 7 | | 155 | 135-165 | exo |
| | | | | 97 | | | |
| | 385 | 175-425 | 90 | | 390 | 300-450 | endo |

* Copolymer containing 40% of acrylic acid units.

** Copolymer containing 45% of acrylic acid units.

## *4. MECHANISM OF DEGRADATION*

The thermal degradation of polystyrene and poly(acrylic acid) have been subjects of study for many years. The thermal behaviour and mechanism of degradation of PAA has already been discussed in Chapter Four. Before attention is focused on mechanism of degradation of the copolymer, recent studies on the degradation mechanism of polystyrene will be discussed.

It can be concluded from many investigations of the mechanism of decomposition of thermally and anionically polymerised polystyrene that the processes occurring can be grouped into low-temperature (below 300 °C) and high-temperature decomposition (above 300 °C).

### *4.1. Degradation Mechanism of PS Below and Above 300 °C*

The degradation of polystyrene takes place at temperatures below 300 °C results in a decrease in molecular weight without evolution of volatile products.[169,170] Under these conditions, radically polymerised polystyrene degrades more rapidly due to irregularities such as head-to-head links and unsaturation which contribute to the instability of the polymer.[151] Some homolytic chain scissions also occur which are followed by hydrogen abstraction at temperatures lower than 300 °C.

It has been reported[152,169] that in polystyrene made by free radical route, a small amount of "weak links" is present. The number of weak links is a very small fraction of the total number of links in the polymer chain and they break down by heating the polymer at low temperature (below 250 °C), but their scissions are not the principal reason for the decrease in the degree of polymerisation.

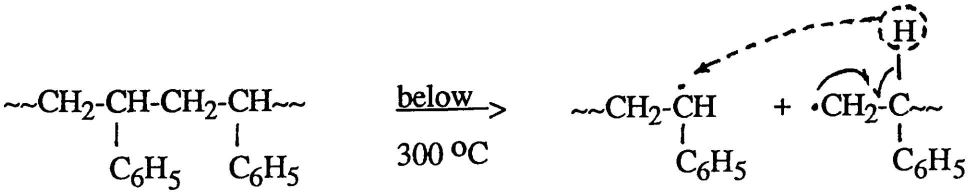
Between 280° and 300 °C, where weight loss is still negligible, free radicals can be generated by random chain scission. These radicals with their greatly hindered mobility either recombine or they may undergo disproportionation, to produce a double bond on one chain end.[158]

The volatile products evolve significantly at temperatures higher than 300 °C. Above 300°C, the quantities of high boiling volatile products, of which a major constituent is monomer, show a sharp increase up to 420 °C at which the maximum rate of decomposition occurs, under programmed heating (10°/min).

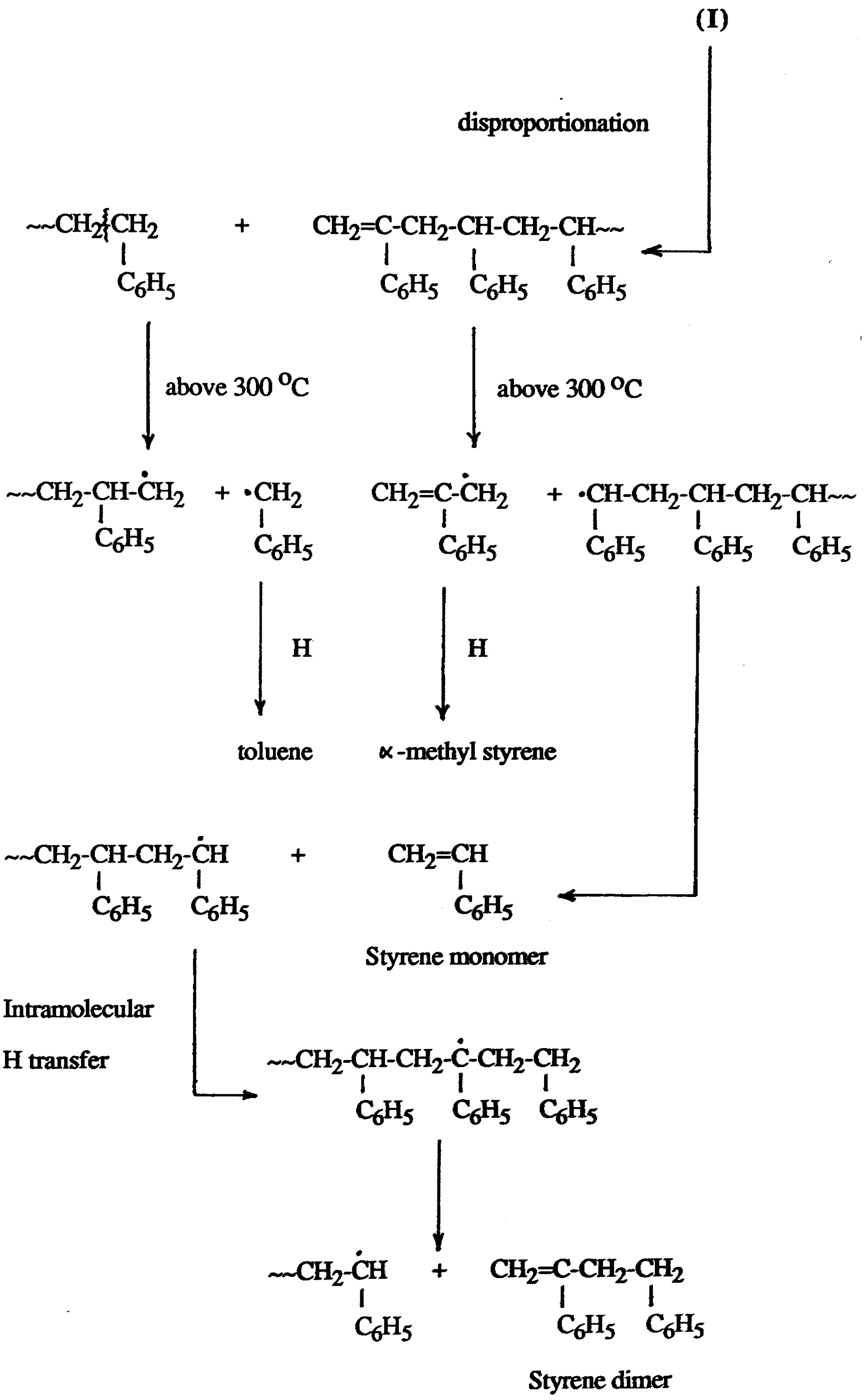
The evolution of short chain fragments such as dimer, etc., has been explained[171] as a consequence of intramolecular chain transfer occurring during the depolymerisation steps (ß-scission). The most frequent reaction is ß-scission, which mainly involves the normal chain end radical and produces styrene.[159]

At temperatures above 300 °C, polystyrene degrades to evolve a mixture of volatile products including monomer as a major component together with progressively smaller amounts of oligomers.[157,159,160] Much smaller amounts of toluene, α-methyl styrene and 1,3-diphenyl propane are found.[161] Investigation of the cold ring fraction from polystyrene degradation indicates the presence of benzylic and unsaturated end structures.[154]

McNeill et al[164] have proposed the following mechanism for the degradation of polystyrene samples below and above 300 °C;



$$\sim\sim CH_2-\underset{C_6H_5}{\underset{|}{CH}}-CH_2-\underset{C_6H_5}{\underset{|}{CH}}\sim\sim \xrightarrow[300\ ^{o}C]{below} \sim\sim CH_2-\underset{C_6H_5}{\underset{|}{\dot{C}H}} + \cdot CH_2-\underset{C_6H_5}{\underset{|}{\overset{H}{\overset{|}{C}}}}\sim\sim \qquad (I)$$


(I)
disproportionation
above 300 °C
above 300 °C
H
H
toluene
α-methyl styrene
Styrene monomer
Intramolecular
H transfer
Styrene dimer

## *4.2. DEGRADATION MECHANISM OF ST/AA COPOLYMER*

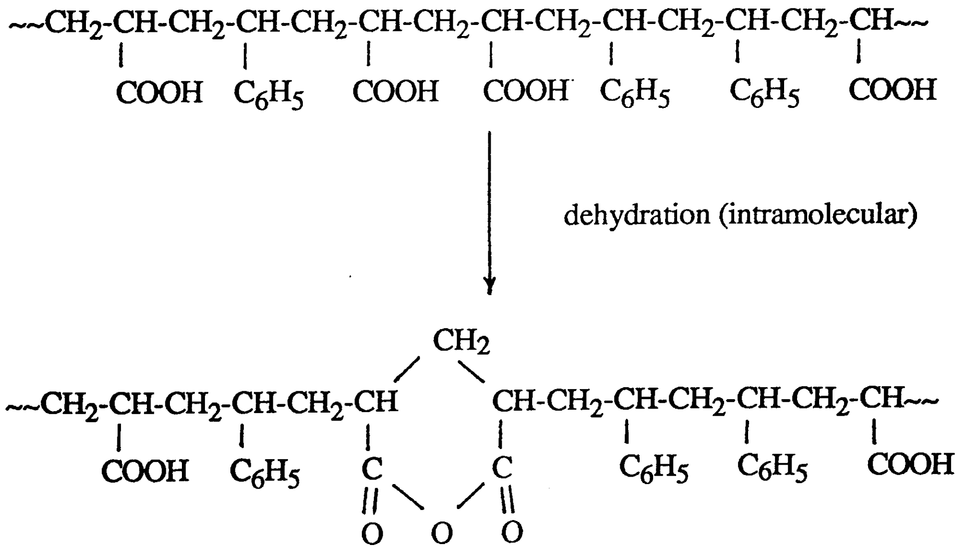
As has already been discussed, heating ST/AA copolymer samples to 500 °C under TVA conditions leads to formation of the volatile and CRF products amounting to about 96% of the initial sample weight, the main component of which is styrene monomer. The high boiling materials formed in the degradation are dimer, trimer etc. A general degradation mechanism can be proposed based on the random sequence arrangement of styrene/acrylic acid copolymer as follows;

### *4.2.1. Mechanism Due To Decomposition Below 300 °C*

At these temperatures dehydration and decarboxylation of the acrylic acid units occurs, together with some scission of the polymer backbone.

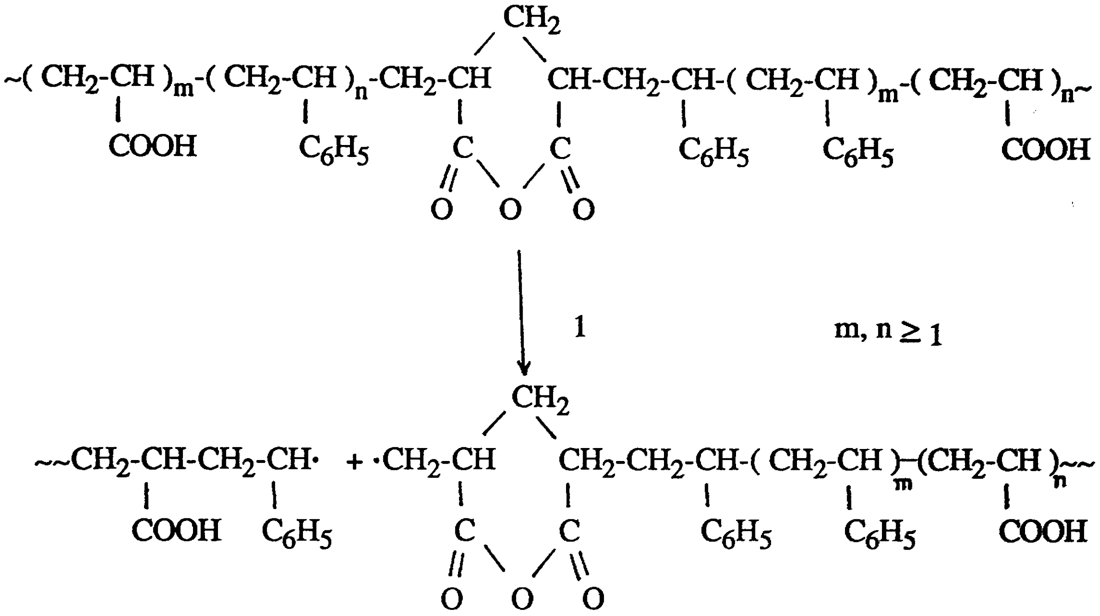
#### *4.2.1.1. Dehydration*

This reaction can occur at about 200 °C by intra- or intermolecular reaction of carboxyl groups, as described in Chapter Four;



### *4.2.1.2. Chain Scission*

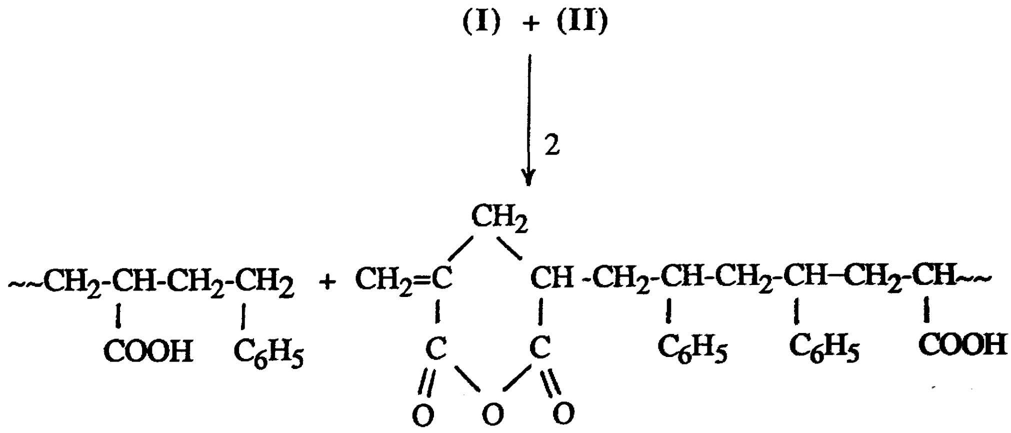
Some chain scissions occur, resulting in a decrease in molecular weight as in reactions 1 and 2. Decarboxylation is also evident at temperatures above 200 °C.



(I)

(II)

Since no significant volatiles based on styrene compounds are observed at temperatures below 300 °C, then the macroradicals (I) and (II) do not depolymerise in this temperature region, but undergo disproportionation as in reaction 2.

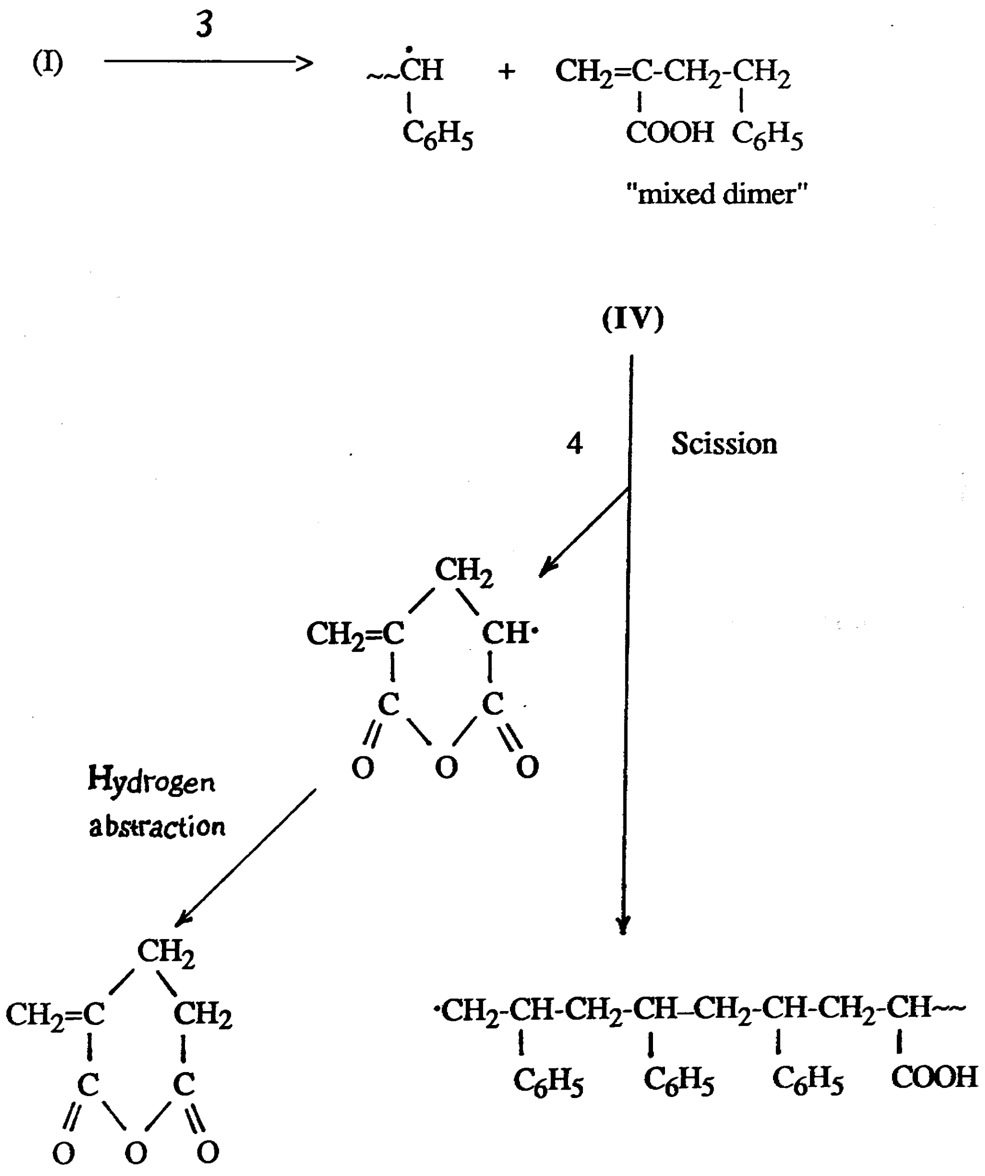


(III)

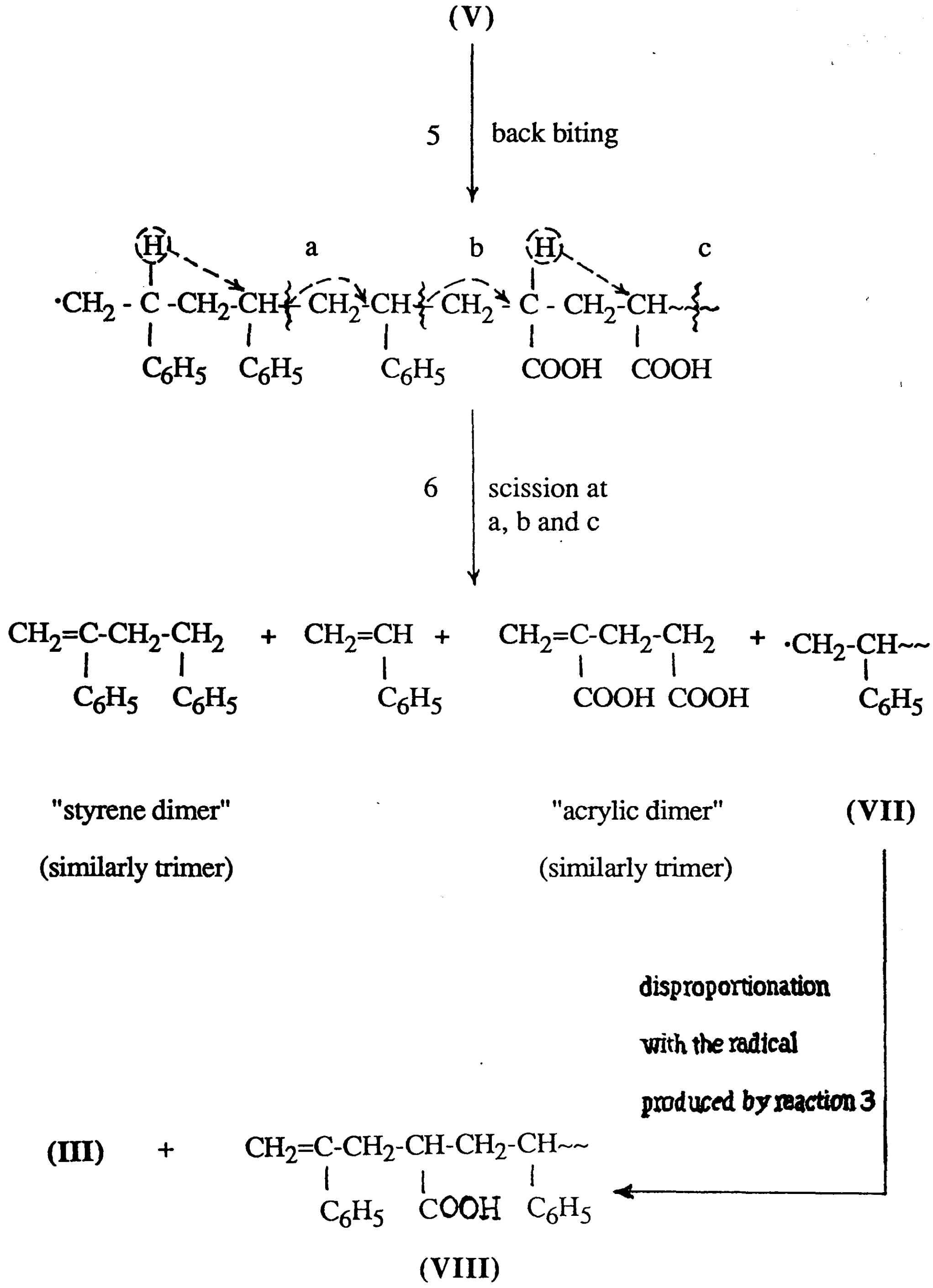
(IV)

### *4.2.2. Mechanism Based on Decomposition Above 300 $^oC$*

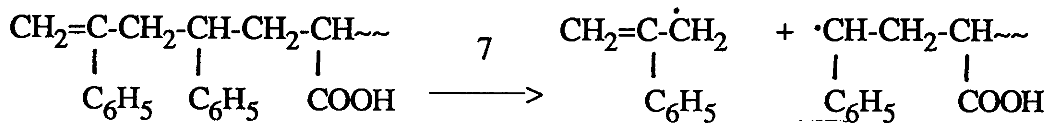
At temperatures higher than 300 $^oC$, significant amounts of cold ring fraction and volatile products are observed. The evolution of dimers, trimers, etc. together with styrene and acrylic acid monomers and also fragments with one unit of each type (mixed dimer) has been assumed by depropagation and intramolecular transfer (back biting) as in reactions 3 to 6;



(V)



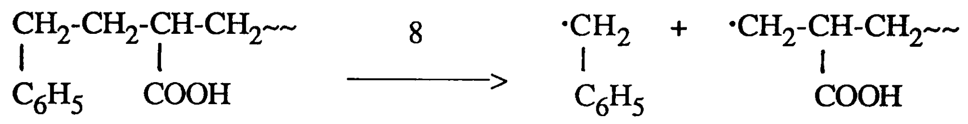
The unsaturated chain end (VIII) has been proposed in various investigations to be the site at which depolymerisation is initiated in polystyrene by the formation of the macroradical (I) in reaction 7;



$$\underset{C_6H_5}{CH_2=\underset{|}{C}}\text{-}CH_2\text{-}\underset{C_6H_5}{\underset{|}{CH}}\text{-}CH_2\text{-}\underset{COOH}{\underset{|}{CH}}\sim\sim \xrightarrow{7} CH_2=\underset{C_6H_5}{\underset{|}{C}}\text{-}\dot{C}H_2 + \cdot\underset{C_6H_5}{\underset{|}{CH}}\text{-}CH_2\text{-}\underset{COOH}{\underset{|}{CH}}\sim\sim$$

(IX) (I)

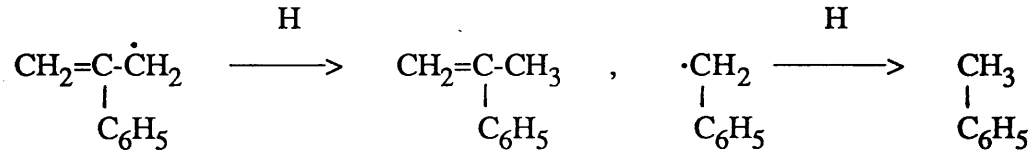
Alternatively, decomposition of benzylic ends (III) occurs as in reaction 8;



$$\underset{C_6H_5}{\underset{|}{CH_2}}\text{-}CH_2\text{-}\underset{COOH}{\underset{|}{CH}}\text{-}CH_2\sim\sim \xrightarrow{8} \underset{C_6H_5}{\underset{|}{\cdot CH_2}} + \cdot CH_2\text{-}\underset{COOH}{\underset{|}{CH}}\text{-}CH_2\sim\sim$$

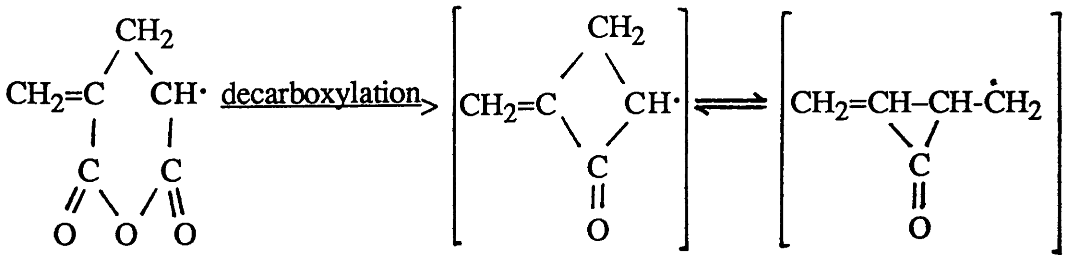
(X)

The minor products such as α-methyl styrene and toluene result when radicals (IX) and (X) abstract a hydrogen atom, respectively, as follows;



$$CH_2=\underset{C_6H_5}{\underset{|}{C}}\text{-}\dot{C}H_2 \xrightarrow{H} CH_2=\underset{C_6H_5}{\underset{|}{C}}\text{-}CH_3\ ,\quad \underset{C_6H_5}{\underset{|}{\cdot CH_2}} \xrightarrow{H} \underset{C_6H_5}{\underset{|}{CH_3}}$$

The anhydride radical produced by the reaction 4 can also undergo decarboxylation to give cyclic ketonic intermediate species,



(X)

At high temperatures, the intermediate species (X) can decompose to produce a various products such as ketones, ketene and hydrocarbons, see Chapters Four and Five.

The recent publications[150-160] have furnished new insight into the mechanism of degradation of polystyrene which are useful to give further information about the other products like ethyl benzene, indane etc.

## *5. CONCLUSIONS*

It can be concluded from degradation behaviour of styrene/acrylic acid copolymer that the mechanism of decomposition below and above 300 °C, depends upon the composition of ionomer. The presence of polar components, such as acrylic acid, in the copolymer structure causes reduction in $T_{max}$ which is lower than that for polystyrene or poly(acrylic acid).

This investigation has contradiction to that performed by Liggat[68], who studied the thermal degradation of styrene-methacrylic acid copolymers with the 18, 44 and 72 mole % of methacrylic acid in the copolymers. He has shown that the $T_{max}$ of the decomposition of the copolymers is stabilised relative to PS and destabilised relative to PMMA.

There is no significant change observed in the main decomposition temperature of the copolymer samples, this may be due to the contents of acid units which are not very different in the composition of the copolymers. It is found that the thermal stability of the copolymer depends upon the amounts of the acrylic acid units introduced.

It is clear from the TVA, TG and DTA data that a small change in the composition of the copolymer samples causes a decrease in the $T_{max}$ temperature of the major peak of decomposition of the copolymer sample. These results are inconsistent with those obtained by Suchock-Galas[165], Bukin[166] and Jegorov et al[167], who showed that the thermal stability of styrene-methacrylic acid copolymers and their sodium salts are practically independent of the amount of acid and salt units introduced into the copolymer.

The formation of various degradation products can be explained as the basis of the randomly located acrylic acid units in the backbone of the copolymer structure.

The degradation data indicate that the initial decomposition in this copolymer is mainly due to dehydration and decarboxylation processes together with some chain scission.

The formation of glutaric type anhydride structures within the copolymers by the cyclisation of neighbouring acrylic acid units is apparent from the mass spectrometry data of the CRF of the copolymer degraded to 500 $^{o}$C and isothermally at 300$^{o}$ and 340 $^{o}$C under TVA conditions, in addition, the ir spectra of the residue at 300 $^{o}$C and CRF at both isothermal experiments are consistent with the presence of the anhydro-polymer structure in which initially formed.

Dehydration, decarboxylation and intermolecular hydrogen transfer (fall in the molecular weight) can be considered as the main processes occurring at temperatures below 300$^{o}$C.

At temperatures higher than 300 $^{o}$C, further chain scissions followed by intra- and intermolecular hydrogen transfer become predominant. Formation of the cyclic ketonic transient species as sources of various degradation products can be considered from decomposition of the anhydro-polymer structure.

# CHAPTER NINE

## STUDIES ON THE THERMAL BEHAVIOUR OF STYRENE/ACRYLIC ACID SALT COPOLYMERS (Na and K)

### *1. INTRODUCTION*

Copolymerisation is commonly used in industry to obtain a desired set of physical properties in a polymeric material. The thermal behaviour of copolymers is of interest since a copolymer may have degradation properties considerably different from those of the corresponding homopolymers. The presence of a comonomer may either stabilise or destabilise the copolymer relative to the homopolymers. It is therefore important to understand how such materials break down on heating. The degradation behaviour of ionomers has not been extensively studied.

### *2. THERMAL DEGRADATION OF STYRENE/ACRYLIC ACID SALTS*

#### *2.1. Previous Work on Thermal Degradation of ST/AA salts*

The thermal and thermooxidative degradations of copolymers of styrene-acrylic acid and their sodium salts obtained have been studied by *Suchocka-Galas* and his co-workers.[168]

*Wlochowicz et al*[172] have investigated the dependence of glass transition temperature on the heating rate and the composition for styrene-zinc acrylate copolymers by differential scanning calorimetry. They showed using thermogravimetry that the thermal decomposition of the ionomers is a three-stage process and determined the order and activation energy for each stage of decomposition. It was found that the ionic groups present in ST/ZnA copolymers lower the activation energy of decomposition, i.e.

decrease the thermal stability of copolymer.

In this study, copolymers of styrene/acrylic acid salts (Na and K) were prepared by neutralisation of the ST/AA copolymer containing 40 mole% acid units with the respective hydroxide as described in Chapter Three and their thermal behaviour studied by TVA, TG and DTA techniques supported by product analysis. Programmed heating at $10^{o}$/min to 500 $^{o}$C and isothermal heating at $300^{o}$ and 340 $^{o}$C were applied as parts of the degradation studies.

### *2.2. PROGRAMMED HEATING EXPERIMENTS*

#### *2.2.1. Thermal volatilisation Analysis*

The copolymer samples were of the order of 60-70 mg and in the form of a powder. All analyses were performed using a TVA system as described in Chapter 8. ***Fig.9.1*** shows the TVA curves obtained for the copolymers.

The main decomposition appears in the temperature range from 400 to 480 $^{o}$C having $T_{max}$ at about 435 $^{o}$C. TVA shows two stages clearly for Na salt and in both samples the products differ at higher temperature.

It is to be observed, however, that the $T_{max}$ temperature of the major peak for the both copolymer samples lies between that of polystyrene and the corresponding poly(acrylic acid) salts. In addition, the ionomers have a peak on their TVA curves below 250 $^{o}$C which is probably due to the release of precipitant or water taken up by them.

The thermal stability of these ionomers seems to be dependent on the amount of introduced acid units (already discussed in Chapter Eight) and the degree of neutralisation. There is notmuch difference in thermal behaviour of these copolymer

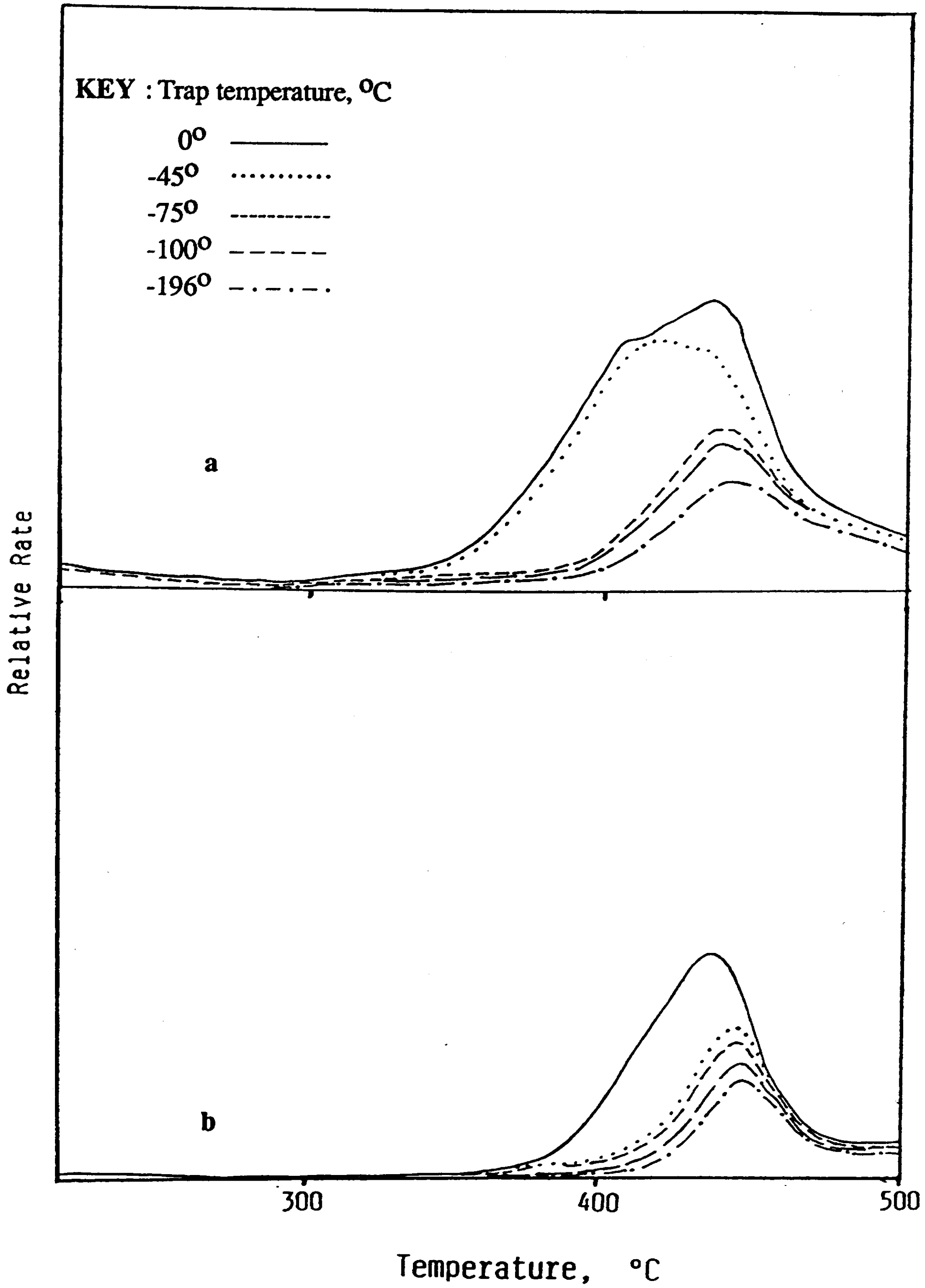


Fig. 9.1. TVA curves (vacuum, heating rate 10 °C/min) for styrene/acrylic acid salt copolymer samples: a. ST/NaA copolymer, b. ST/KA copolymer.

samples on the basis of the TVA data. In degradation above 275° and 355 °C, the volatile material produced consists of substances non-condensable at liquid nitrogen trap (-196 °C) for sodium and potassium salts, respectively.

Gravimetric data, *Table 9.1*, were obtained under normal TVA conditions using the same experimental approach as described in the previous chapter.

### *2.2.2. Subambient Thermal Volatilisation Analysis*

Products from degradation of ionomer samples to 500 °C, collected in a -196 °C trap and fractionated by the SATVA technique, gave the curves indicated in *Figs. 9.2* and *9.3*.

### *2.2.3. Product Analysis*

Infrared spectroscopy, mass spectrometry and GC-MS techniques were used to examine the degradation products. The last fraction of the SATVA separation as a liquid was subjected to GC-MS. Instrumental conditions were similar to the case of ST/AA copolymers already discussed in the previous chapter.

### *2.2.3.1. Residue*

Metal carbonate is the main component in the involatile fraction. The corresponding ir spectra are illustrated in *Fig. 9.4*.

### *2.2.3.2. Cold Ring Fraction*

Ir spectra of the cold ring fractions are consistent with the presence of short chain fragments of the respective copolymer. The spectra of the CRF contain features of both polystyrene and the metal polyacrylates. These show different significant bands, *Fig.9.5*, in the 3100-2850, 2000-1600, 1600-1500 $cm^{-1}$ regions and a group of bands below 900 $cm^{-1}$ which are produced by aromatic ring systems related to styrene as a main component.

The characteristic bands in the 1610-1550 and 1430-1350 $cm^{-1}$ range produced by carboxylate ions ( $-CO_2^-$ ) are due to the antisymmetrical and symmetrical stretching of carbonyl group. The characteristic bands at 1805, 1760 (shoulder) and 1030 $cm^{-1}$, due to anhydride structures, imply that some acrylic acid units are left unreacted in the chain after the neutralisation process.

The cold ring fractions tended to separate into two parts, an upper part soluble in dichloromethane ($CH_2Cl_2$) giving an ir spectrum ( film cast on NaCl disc) rather similar to styrene based compounds and a lower, insoluble part giving a spectrum (KBr disc) closely resembling that of the acrylate salts. The spectra are shown in Fig. 9.6.

The presence of short chain fragments of polystyrene, such as dimer, trimer and tetramer (trace) together with one and two units (trace) of each type were also confirmed by mass spectrometry in the cold ring fractions. Products identified for the CRF of ST/KA copolymer sample are listed in order of importance in *Table 9.2*.

#### *2.2.3.3. Non-condensables as gaseous products*

Methane and carbon monoxide were established as non-condensables.

#### *2.2.3.4. Condensable gases*

The condensable gaseous products were identified by IR and MS consisted of carbon dioxide and acetone as major products together with small amounts of ethylene, propene, 1-butene, acrolein, acetaldehyde, methyl ethyl ketone, benzene, toluene, cyclopentene and cyclopentadiene.

**Table 9.1.** TVA data for degradation of styrene/acrylic acid salt copolymer samples containing 40 mole% salt units.

| copolymer | Initial temp. for non-condensable gases, °C | $T_{max}$ °C | Wt% residue at ~ 500 °C | Wt% CRF at ~ 500 °C | Wt% of condensable volatile products at ~500 °C (incl. $CO_2$) | Wt% $CO_2$ |
|---|---|---|---|---|---|---|
| ST/NaA | 275 | 435 | 13.2 | 21.5 | 65.3 | 7.6 |
| ST/KA | 355 | 435 | 16.5 | 23.7 | 59.8 | 8.3 |

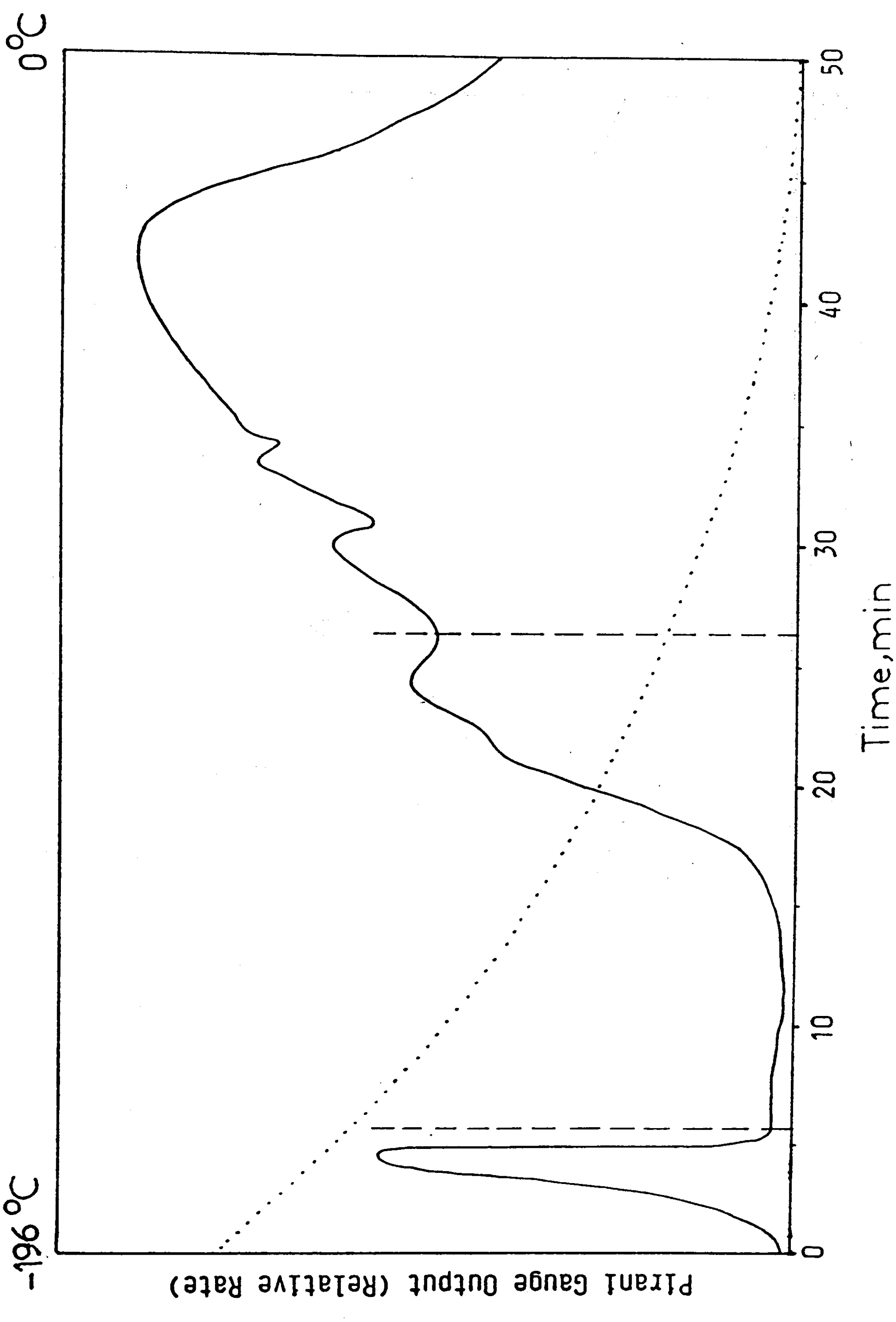


**Fig. 9.2.** SATVA curve of the condensable product fraction from degradation of ST/NaA copolymer containing 40 mole% salt units to 500 °C under TVA conditions.

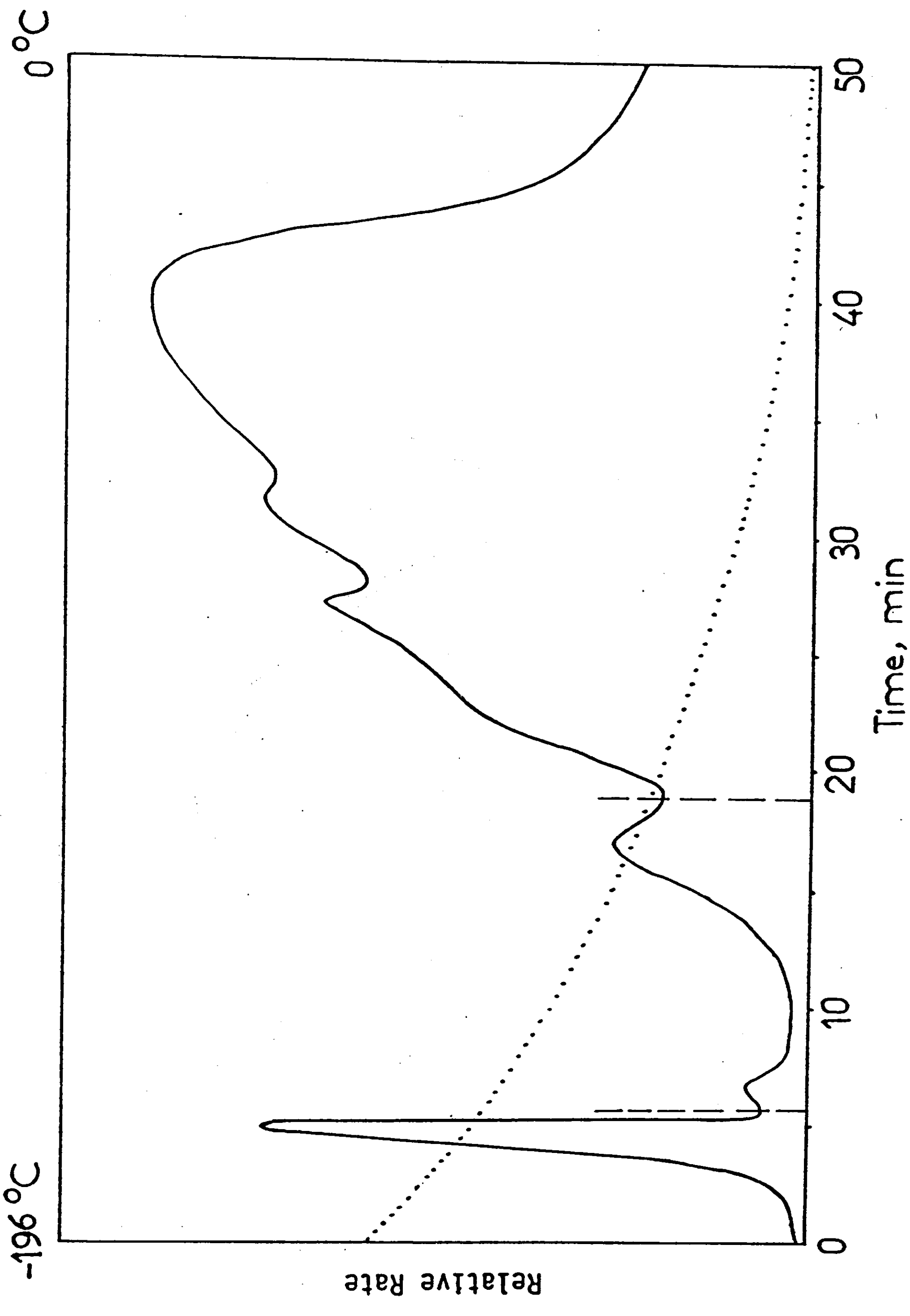


**Fig. 9.3.** SATVA curve of the condensable product fraction from degradation of ST/KA copolymer containing 40 mole% salt units to 500 °C under TVA conditions.

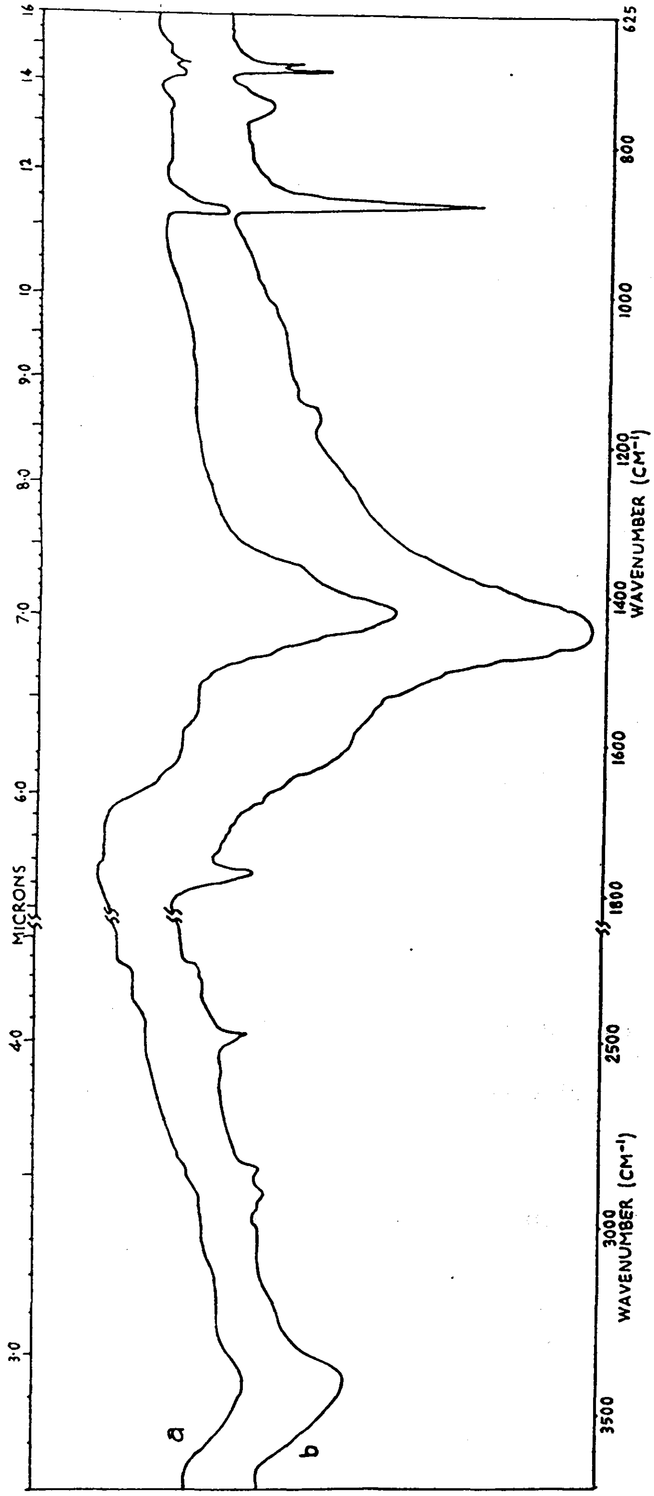


**Fig. 9.4.** Ir spectra of residues of styrene/acrylic acid salt copolymer samples.

a. ST/NaA copolymer; **b.** ST/KA copolymer.

### *2.2.3.5. Condensables as liquid fraction*

The ir spectra of liquid fractions from degradation of the ionomer samples are clearly indicative of styrene as a principal component together with different kinds of styrene-based compounds ( see *Fig. 9.7.*).

These fractions were subjected to GC-MS and the corresponding chromatograms are reproduced in *Figs. 9.8* and *9.9*. It is observed that toluene, α-methyl styrene and methyl ethyl ketone are the volatile products next in importance to styrene.

The products of degradation of the styrene/acrylic acid salt copolymers (Na and K) to 500 °C under TVA conditions are listed in *Tables 9.3* and *9.4*.

### *2.2.4. THERMOGRAVIMETRY*

The TG and DTG curves for both copolymer samples obtained under dynamic nitrogen atmosphere at 10°/min heating rate, are shown in *Fig. 9.10*.

Fig. 9.10 shows clearly a single stage decomposition above 400 °C with $T_{max}$ at about 420 °C. The TG curves show that the weight losses to 200 °C are 15 and 7.5 % for ST/NaA and ST/KA ionomers, respectively, due to the loss of water which both absorb from the atmosphere. Total weight loss at 500 °C is about 82% for both copolymers.

The results show clearly that these copolymers are more stable than polystyrene and less stable than the corresponding salt homopolymers. Data are summarised in *Table 9.5*.

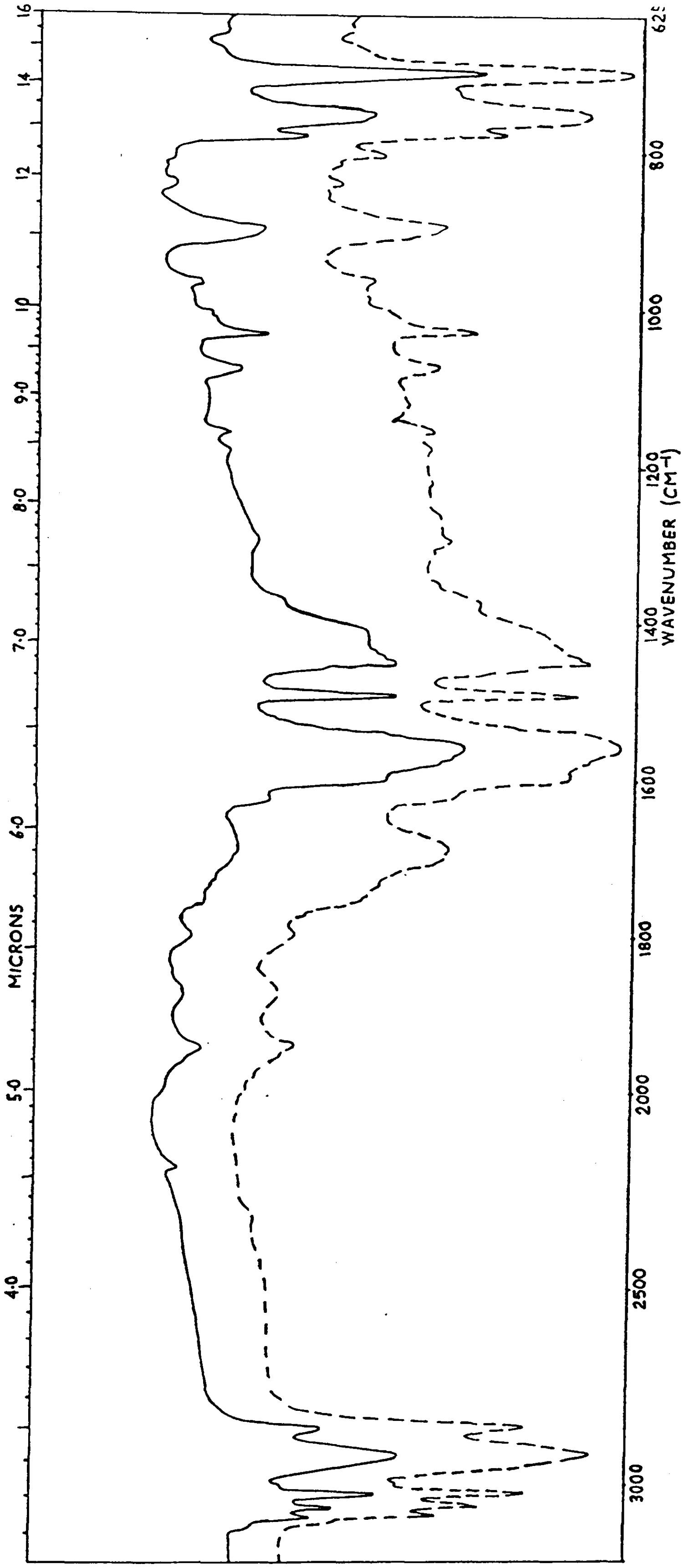
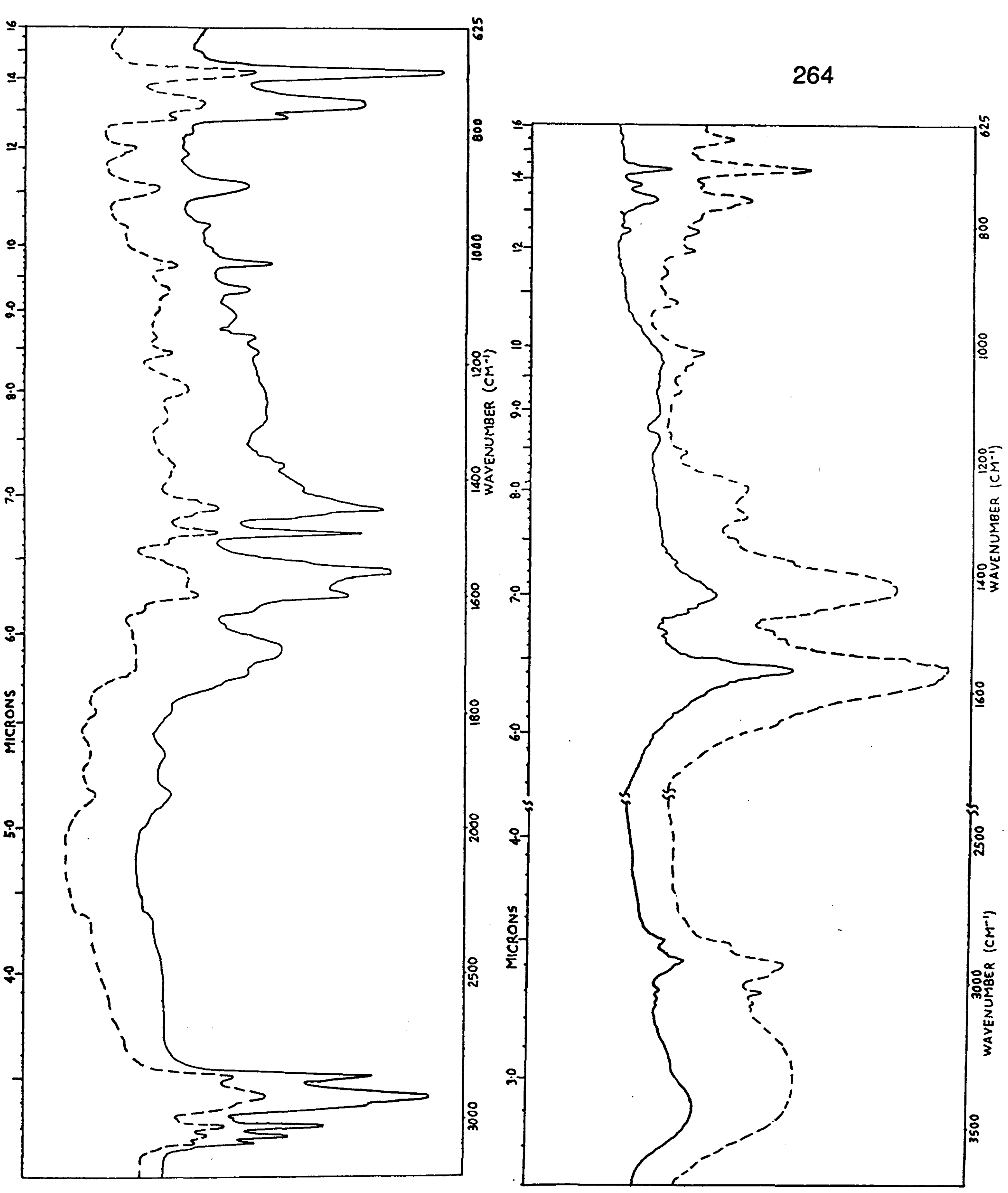


**Fig. 9.5.** Ir spectra of the cold ring fraction of styrene/acrylic acid salt copolymer samples.

----- ST/NaA copolymer; ——— ST/KA copolymer.



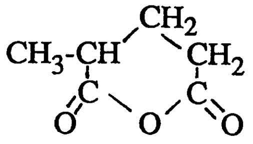
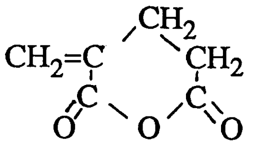
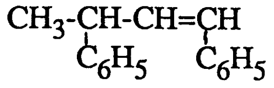
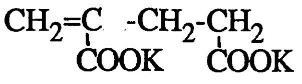
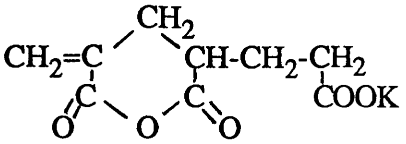
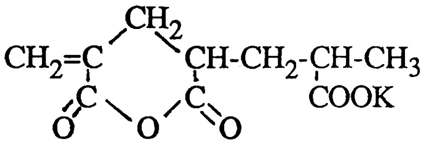
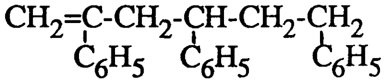
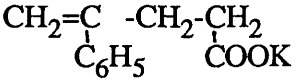
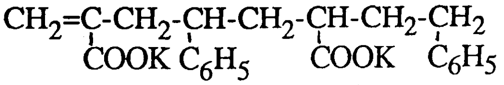
upper part

lower part

**Fig. 9.6.** Ir spectra of upper and lower parts of the cold ring fraction of styrene/acrylic acid salt copolymer samples.

—— ST/NaA copolymer; ----- ST/KA copolymer.

**Table 9.2.** Products identified in the cold ring fraction from degradation of ST/KA copolymer under TVA conditions to 500 °C.

| Product | m/e |
|---|---|
| $CH_2=CH-COOK$ | 110 |
|  | 128 |
|  | 126 |
|  $CH_3-\underset{C_6H_5}{CH}-CH=\underset{C_6H_5}{CH}$ (styrene dimer) | 208 |
|  $CH_2=\underset{COOK}{C}-CH_2-\underset{COOK}{CH_2}$ (salt dimer) | 220 |
|  | 236 |
| Saturated " " " | 238 |
|  | 250 |
| Saturated " " " | 252 |
|  $CH_2=\underset{C_6H_5}{C}-CH_2-\underset{C_6H_5}{CH}-CH_2-\underset{C_6H_5}{CH_2}$ (styrene trimer) | 312 |
|  $CH_2=\underset{C_6H_5}{C}-CH_2-\underset{COOK}{CH_2}$ (mix dimer) | 214 |
|  $CH_2=\underset{COOK}{C}-CH_2-\underset{C_6H_5}{CH}-CH_2-\underset{COOK}{CH}-CH_2-\underset{C_6H_5}{CH_2}$<br>(two units of each type) | 428 |

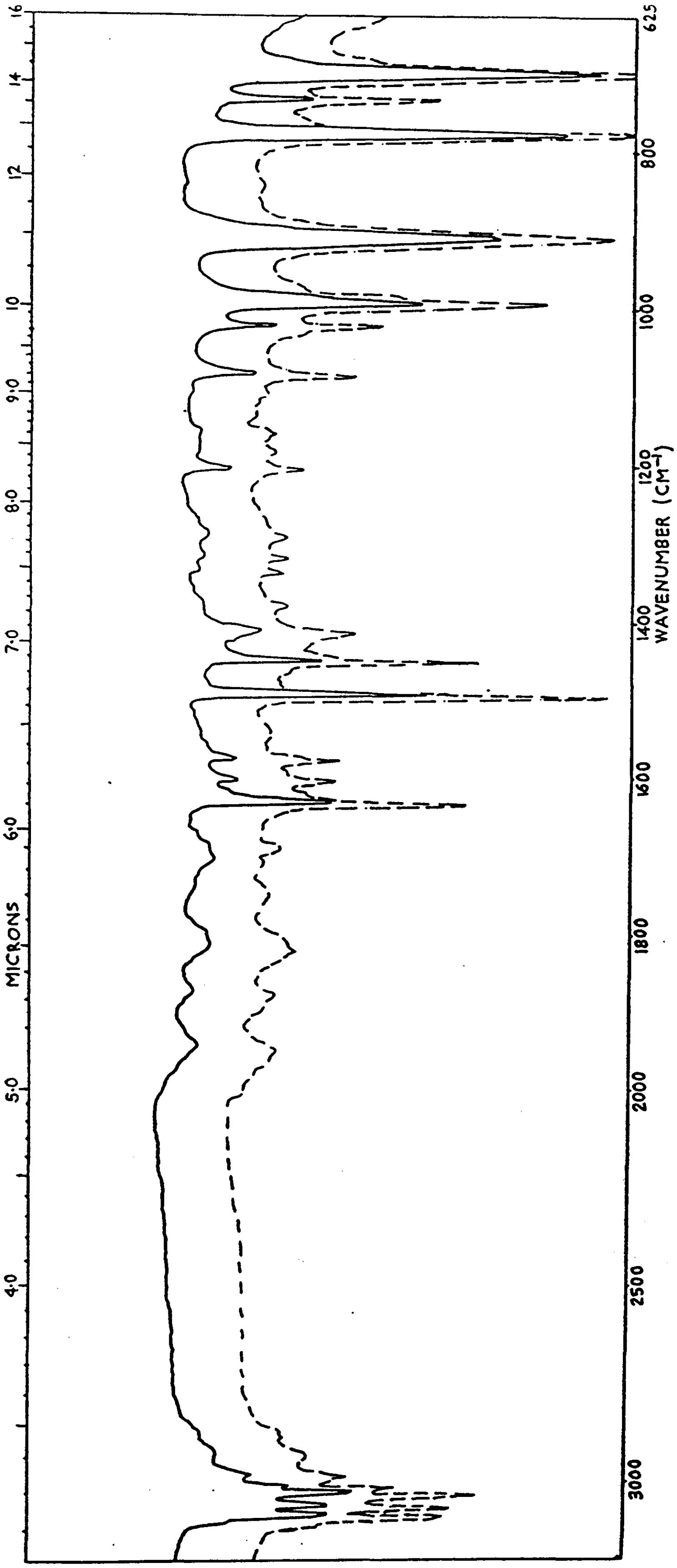


**Fig. 9.7.** Infrared spectra of liquid fractions of products separated by SATVA after degradation of styrene/acrylic acid salt copolymer samples to 500 $^{o}$C by TVA.

—— ST/NaA copolymer; ----- ST/KA copolymer.

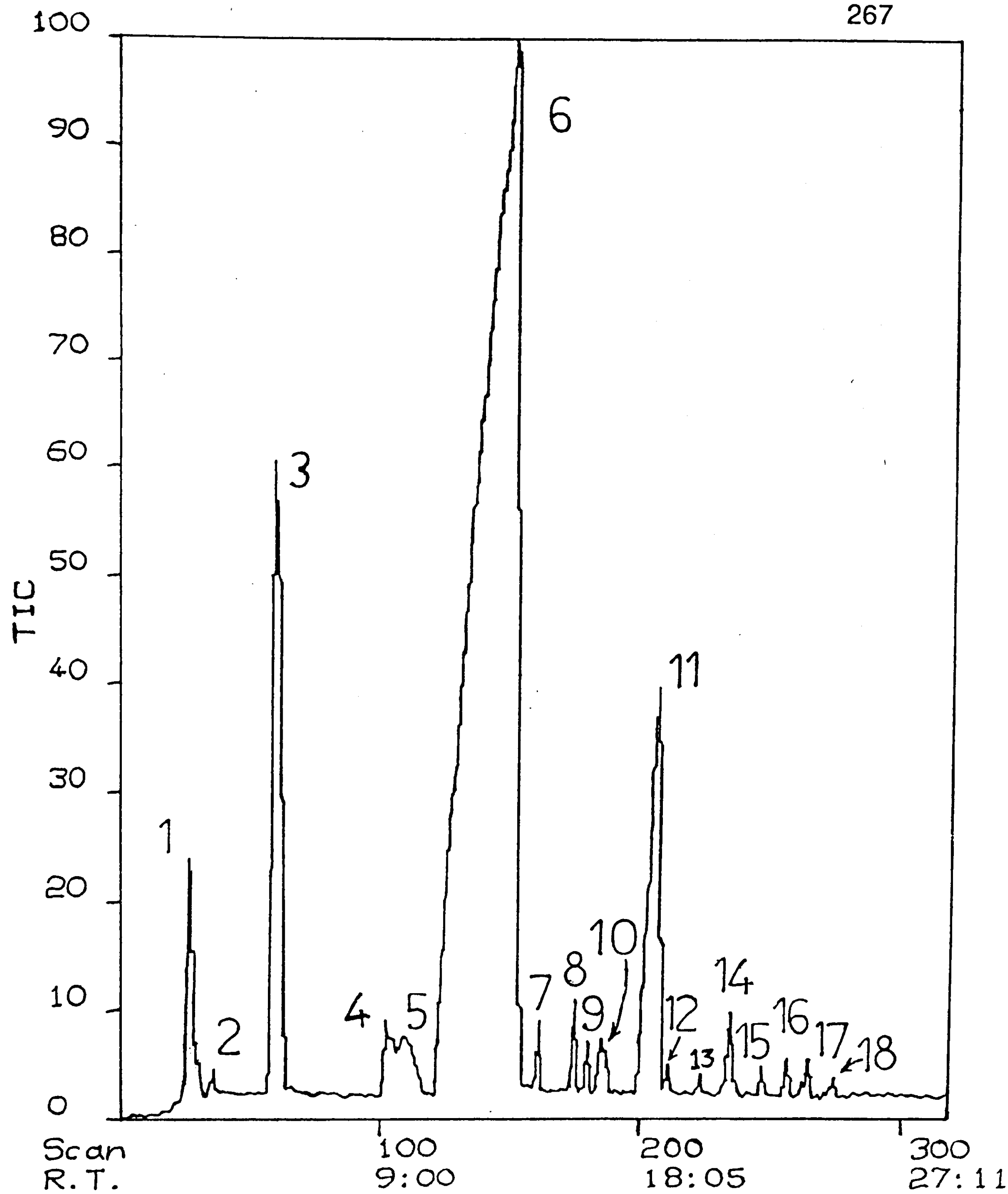


Fig.9.8. GC-MS chromatogram of the liquid fraction of products separated by SATVA after degradation of ST/NaA copolymer to 500 °C by TVA. Assignments: **1** Methyl ethyl ketone and Acetone, **2** Benzene, **3** Toluene, **4** Ethyl benzene, **5** Xylene, **6** Styrene, **7** Cumene, **8** Allyl benzene, **9** n-Propyl benzene, **10** Benzaldehyde, **11** α-Methyl styrene, **12** Cyclopropyl benzene, **13** 1-Methyl indane, **14** Indane, **15** 4-Phenyl butene-1, **16** ß-Methyl benzene, **17** 2-Methyl propenyl benzene, **18** 2-Methyl indane.

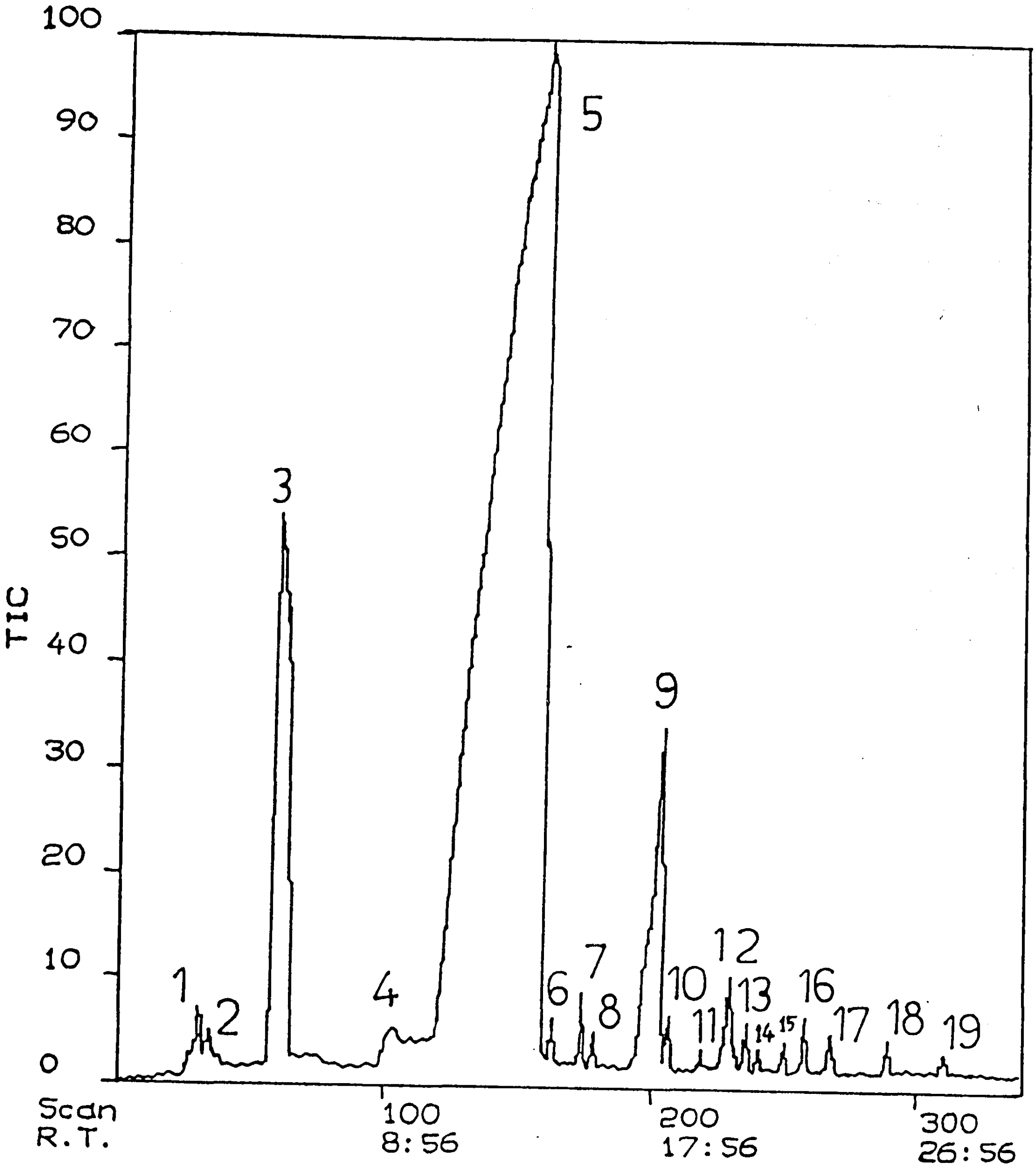


**Fig.9.9.** GC-MS chromatogram of the liquid fraction of products separated by SATVA after degradation of ST/KA copolymer to 500 °C by TVA. Assignments: **1** Methyl ethyl ketone, **2** Benzene, **3** Toluene, **4** Ethyl benzene, **5** Styrene, **6** Cumene, **7** Allyl benzene, **8** n-Propyl benzene, **9**α-Methyl styrene, **10** Cyclopropyl benzene, **11** 1-Phenyl-2-butene, **12** Indane, **13** Unknown, **14** 4-Phenyl butene-1, **15** Methallyl benzene, **16** 2-Methyl propenyl benzene, **17** 2-Methyl indane, **18** 1-Methyl indane, **19**α-Methyl dihydronaphthalene.

### *2.2.5. DIFFERENTIAL THERMAL ANALYSIS*

The DTA curves, *Fig. 9.11*, for both ionomers were obtained under nitrogen atmosphere in the range 25-485 $^{o}$C. The endothermic effect at about 370 $^{o}$C prior to the main decomposition may possibly be due to dehydration and decarboxylation of acrylic acid units left unreacted during neutralisation of acrylic acid/styrene copolymer with the respective bases. The DTA data are consistent with TG and TVA. The corresponding data are given in *Table 9.5*.

## *2.3. ISOTHERMAL EXPERIMENTS*

In this study, the copolymer samples were degraded isothermally at 300 $^{o}$C (ST/NaA copolymer only) and 340 $^{o}$C, under vacuum (TVA) and dynamic nitrogen atmosphere (TG). These temperatures are close to $T_{onset}$ for non-condensables evolution in degradation of ST/NaA and ST/KA ionomers, respectively, under programmed heating conditions.

### *2.3.1. Isothermal Heating at 300 $^{o}$C*

Only the styrene/sodium acrylate copolymer sample was used. It was heated isothermally at this temperature for different periods of time. Data are listed in *Table 9.6*.

It is to be observed, however, that overall weight loss after 2.5 hr is about 13.5 and 12% under vacuum (TVA) and nitrogen (TG), respectively. Of interest is the observed constancy in weight of the CRF throughout the experiment, amounting to about 2% of the original sample weight. Traces of non-condensable products were observed.

The volatile degradation products were collected and separated by SATVA technique. Product analysis was carried out by IR, MS and GC-MS (liquid fraction only) techniques.

**Table 9.3.** Products of degradation of ST/NaA copolymer to 500 $^{o}$C at 10 $^{o}$C/min under TVA conditions.

| Non-condensable products at -196 $^{o}$C | condensable volatile products at -196 $^{o}$C | | CRF (light brown solid) | Residue (black) |
|---|---|---|---|---|
| | Gases | Liquid Fraction | | |
| IR | IR, MS | GC-MS | IR, MS | IR |
| CO<br>$CH_4$ | $CO_2$*<br>Acetone<br>Ketene<br>Toluene<br>Propene<br>Methyl ethyl ketone | Styrene*<br>Toluene<br>α-Methyl styrene<br>Methyl ethyl ketone<br>Ethyl benzene<br>Xylene<br>Allyl benzene<br>Indane<br>Acetone<br>Cumene<br>Benzaldehyde<br>n-Propyl benzene<br>2-Methyl propenyl benzene<br>ß-Methyl styrene<br>2-Methyl indane<br>Cyclopropyl benzene<br>4-Phenyl butene-1 | Short chain fragments of PS, such as dimer, trimer and also monomer and dimer of acrylic acid salt together with mixed dimer and anhydride structures. | Metal carbonate as a major product. |

* Major product

**Table 9.4.** Products of degradation of ST/KA copolymer to 500 °C at 10 °C/min under TVA conditions.

| Non-condensable products at -196 °C | condensable volatile products at -196 °C | | CRF (light brown solid) | Residue (black) |
|---|---|---|---|---|
| | Gases | Liquid Fraction | | |
| IR | IR, MS | GC-MS | IR, MS | IR |
| CO<br>$CH_4$ | $CO_2$*<br>Acetone<br>Ketene<br>Cyclopentene<br>Propene<br>1-Butene<br>Acetaldehyde<br>Acrolein<br>Toluene<br>Benzene<br>Cyclopentadiene<br>Methanol** | Styrene*<br>Toluene<br>α-Methyl styrene<br>Ethyl benzene<br>Indane<br>Allyl benzene<br>Cyclopropyl benzene<br>Cumene<br>Benzene<br>Methyl ethyl ketone<br>n-Propyl benzene<br>2-Methyl propenyl benzene<br>2-Methyl indane<br>4-Phenyl butene-1<br>1-Methyl indane<br>α-Methyl dihydro naphthalene<br>1-Phenyl butene-2 | Short chain fragments of PS including dimer, trimer and traces of tetramer. Compounds with anhydride structures together with monomer and dimer of the metal acrylate and also one and two units(traces) of each type are also present | Metal carbonate as a major product |

* Major product

** Impurity

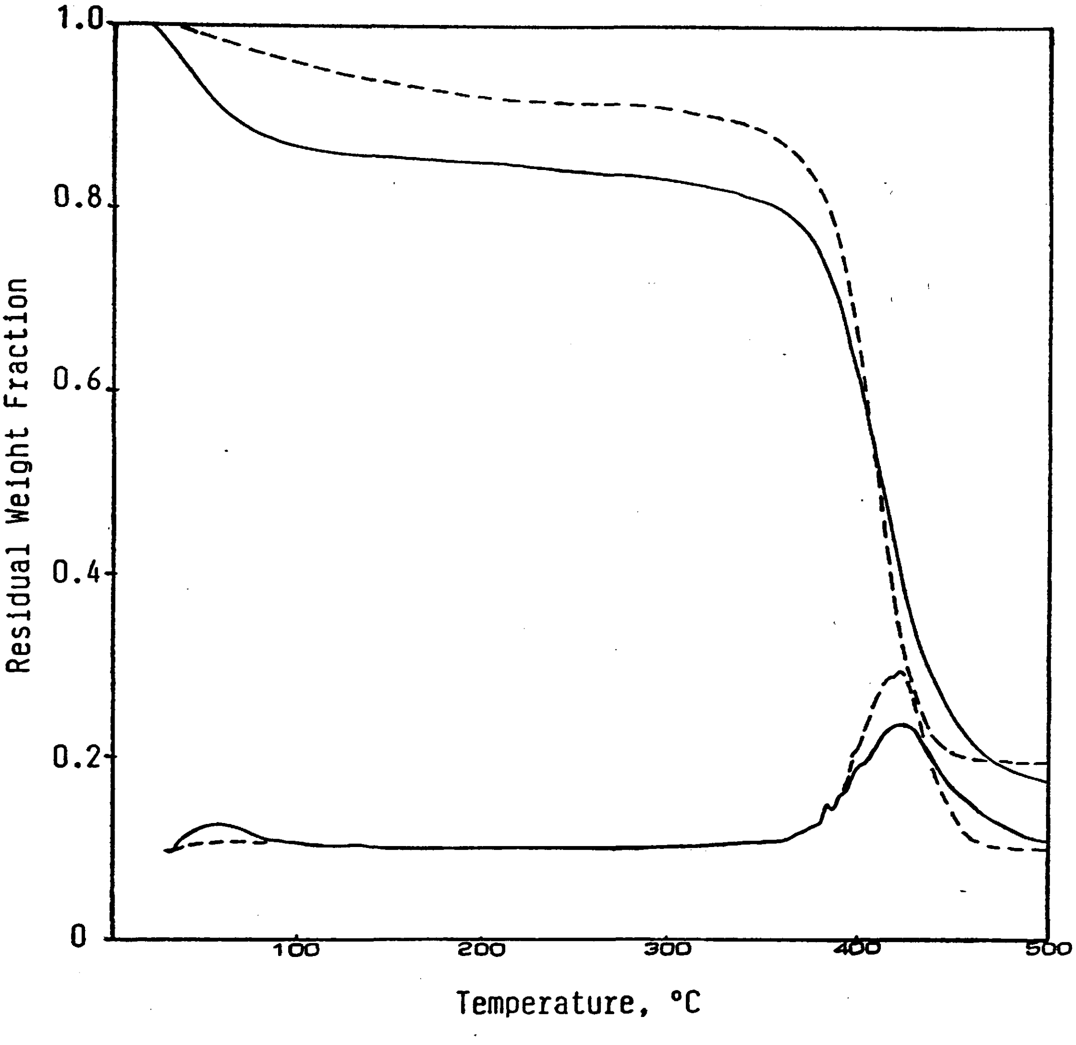


**Fig. 9.10.** TG and DTG curves (dynamic nitrogen atmosphere, heating rate 10 °C/min) for ST/AA salt copolymer samples.

——— ST/NaA copolymer sample.

------- ST/KA copolymer sample.

### *2.3.1.1. Residue*

*Fig. 9.12* shows the ir spectrum of the yellow solid involatile fraction which is similar to partially degraded (incompletely degraded) copolymer.

### *2.3.1.2. Cold Ring Fraction*

The brownish solid material was collected on the inserted cold finger and examined by infrared and mass spectrometry. The data indicate the presence of fragments which consist mainly of dimer and trimer of styrene together with traces of products with one and two units of each type.

### *2.3.1.3. Condensables Detected as Gases and Liquid Fraction*

Acetone was observed as a major gaseous product together with carbon dioxide, methyl ethyl ketone, diethyl ketone, toluene, acetaldehyde and methanol (solvent) (see *Table 9.7.*). A gradual increase in weight of volatile fraction is observed as a function of time (Table 9.6).

The less volatile fraction collected as liquid was analysed by GC-MS and styrene was identified as a principal component. The corresponding data and chromatogram are shown in Table 9.7 and *Fig. 9.13*, respectively.

### *2.3.2. Isothermal Heating at 340 $^{o}C$*

As already mentioned, this temperature corresponds to the onset of evolution of non-condensable products under programmed heating, for the ST/KA copolymer sample. ST/NaA ionomer was also degraded at 340 $^{o}$C isothermally under the same conditions for comparison of the degradation data.

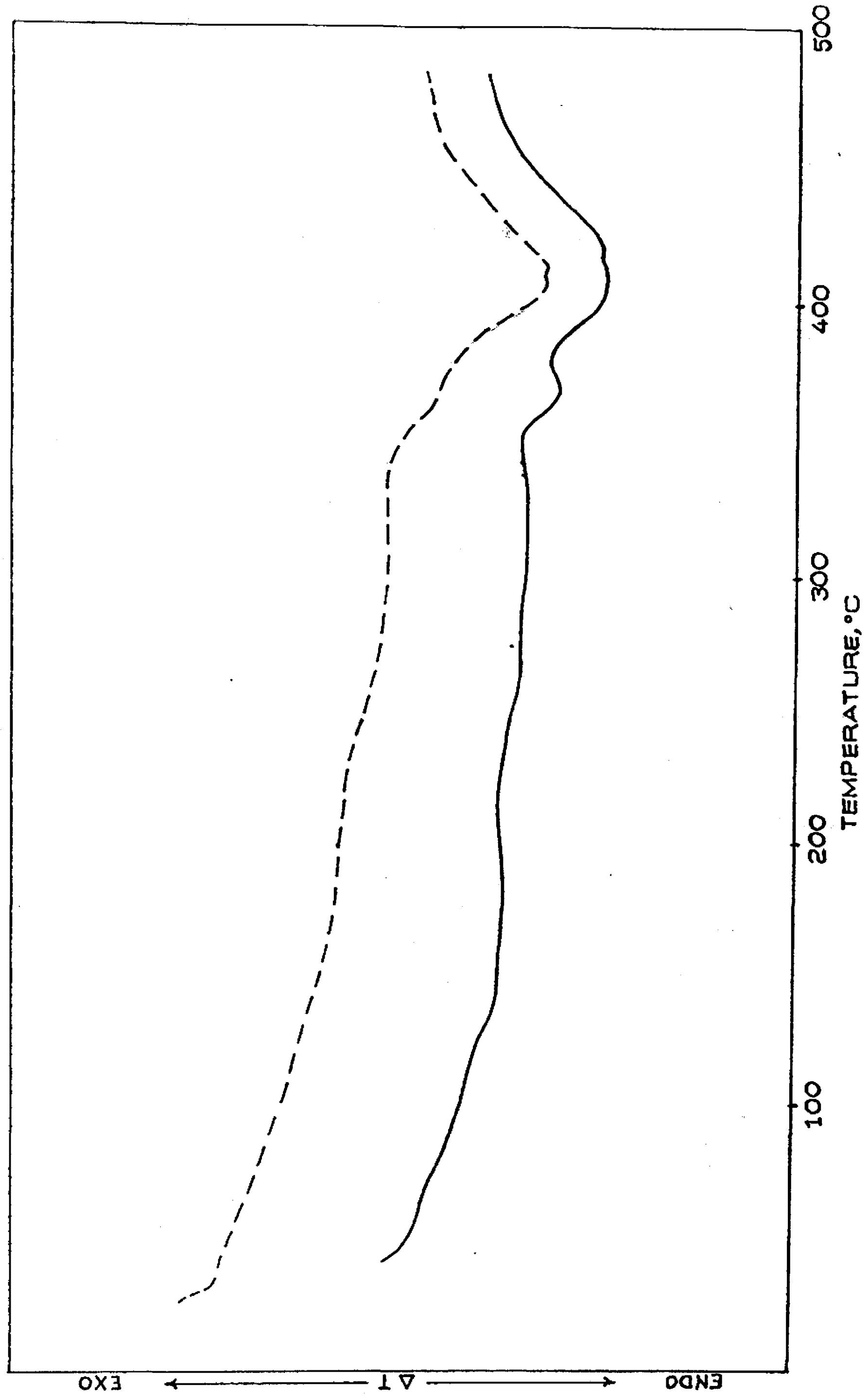


**Fig. 9.11.** DTA curve (dynamic nitrogen atmosphere, heating rate 10 °C/min) for ST/AA salt copolymer samples.

——— ST/NaA copolymer.

-------- ST/KA copolymer.

**Table 9.5.** DTA, TG and DTG data for styrene/acrylic acid salt copolymer samples.

| | DTG | | TG | | DTA | | |
|---|---|---|---|---|---|---|---|
| Co-polymer | Peak temp., °C | Temp. range, °C | Wt% loss for stage | Total Wt% loss in the range | Peak temp., °C 25-500 °C | Temp. range, °C | Thermal effect |
| ST/NaA | — | 25-350 | 19 | 83 | 370[a] | 355-375 | endo |
| | 420 | 350-500 | 64 | | 417 | 375-450 | endo |
| ST/KA | — | 25-350 | 11.5 | 80.5 | 370[b] | 355-375 | endo |
| | 420 | 350-500 | 69 | | 412 | 375-450 | endo |

a. A weak peak.

b. Shoulder.

**Table 9.6.** Isothermal heating data for degradation of ST/NaA copolymer at 300 $^{0}C$ for different periods of time under TVA conditions.

| Time (hr) | Weight loss (%) | Residue (wt%) | CRF (wt%) | Volatile products (wt%) | Ratio of volatile/CRF products |
|---|---|---|---|---|---|
| 1/2 | 7.2 | 92.8 | 1.9 | 5.3 | 2.8 |
| 1 | 11.5 | 88.5 | 1.9 | 9.6 | 5.1 |
| 1.5 | 13.3 | 86.7 | 1.9 | 11.4 | 6 |
| 2 | 13.5 | 86.5 | 1.9 | 11.6 | 6.2 |
| 2.5 | 13.6 | 86.4 | 1.9 | 11.7 | 6.25 |

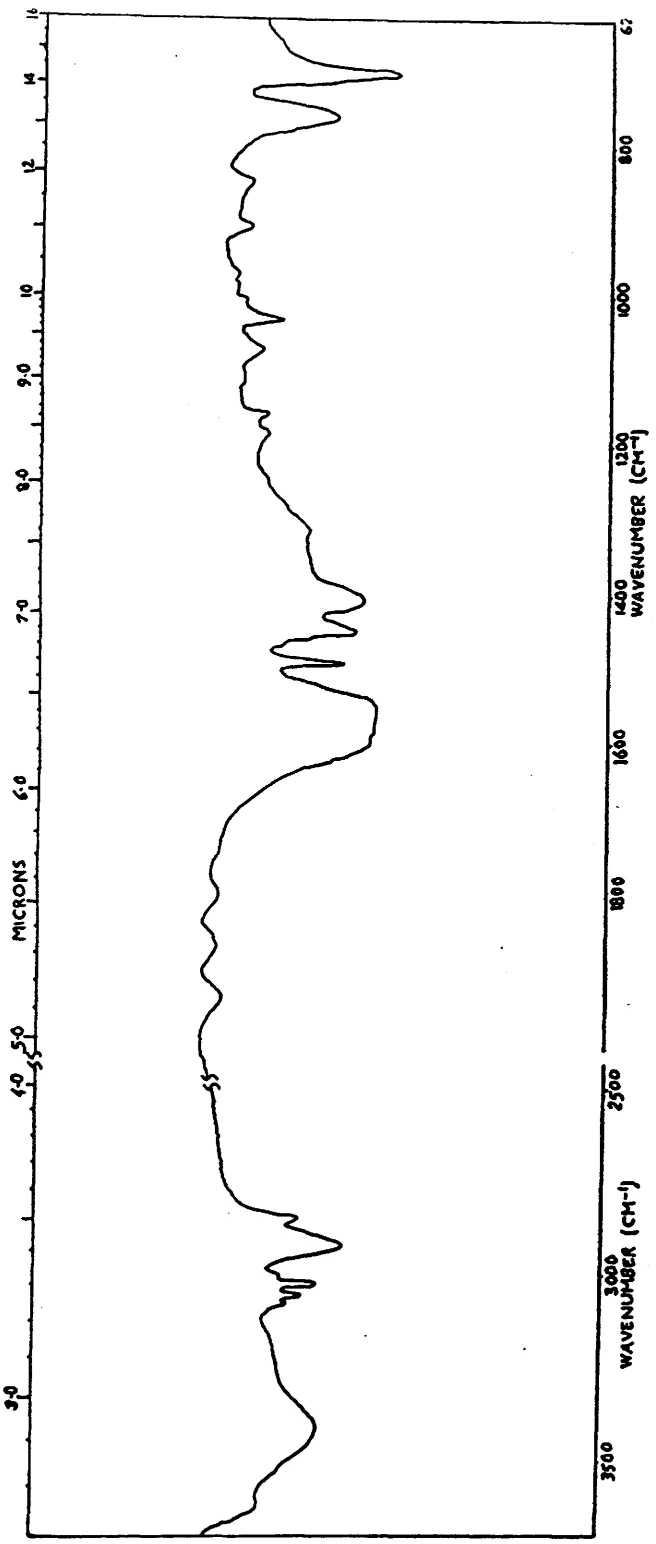


**Fig. 9.12.** Ir spectra of the yellow involatile fraction of styrene/sodium acrylate copolymer sample, heated isothermally at 300 °C.

**Table 9.7.** Products of degradation of ST/NaA copolymer sample, degraded isothermally at 300 °C for 2.5 hr.

| Gaseous condensable | Liquid fraction (brownish solid) | CRF (yellow solid) | Residue |
|---|---|---|---|
| IR, MS | GC-MS | IR, MS | IR |
| Acetone *<br>$CO_2$<br>Methyl ethyl ketone<br>Diethyl ketone<br>Acetaldehyde<br>Toluene<br>Methanol ** | Styrene *<br>Methyl ethyl ketone<br>Acetone<br>α-Methyl styrene<br>Toluene<br>Benzaldehyde<br>Ethyl benzene<br>Allyl benzene<br>Acetophenone<br>Dihydro indene | Short chain fragments of polystyrene such as dimer and trimer together with one and two units (traces) of each type. | Partially degraded copolymer |

* Major product.

** Impurity from solvent.

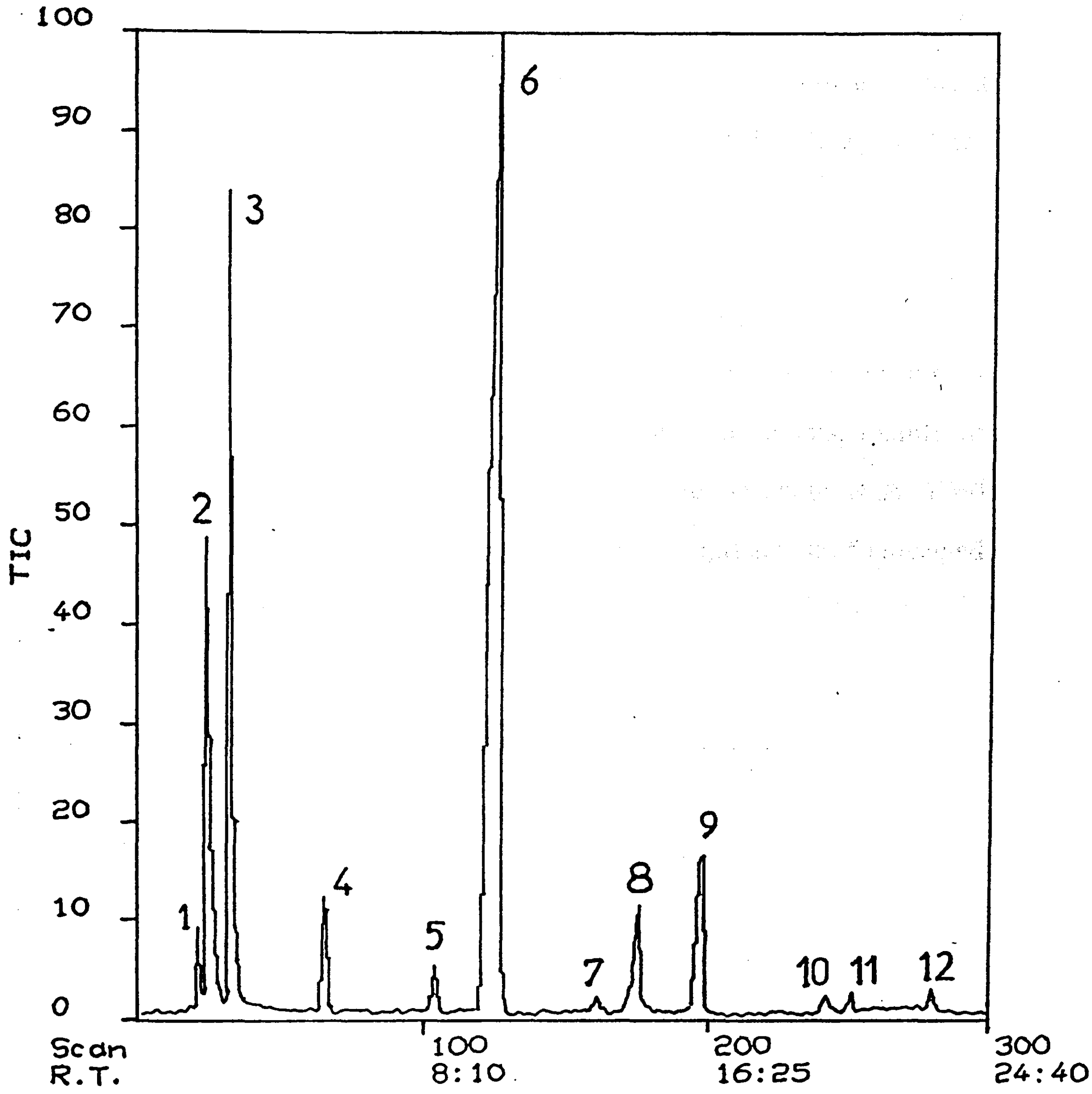


**Fig. 9.13.** GC-MS chromatogram of the liquid fraction of ST/NaA copolymer sample, degraded isothermally at 300 °C for 2.5 hr.

Assignments: **1** Air, **2** Acetone, **3** Methyl ethyl ketone, **4** Toluene, **5** Ethyl benzene, **6** Styrene, **7** 2,3-dihydro indene, **8** Benzaldehyde, **9**α-Methyl styrene, **10** Allyl benzene, **11** Unknown, **12** Acetophenone.

### *2.3.2.1. Product Analysis*

Degradation products for both ionomer samples were collected after isothermal heating at 340 $^{o}$C for 2.5 hr, then separated by SATVA and analysed using IR, MS and GC-MS techniques.

#### *2.3.2.1a. Residue*

The dark brown involatile fractions remaining as residues after isothermal heating at 340$^{o}$C were examined by ir spectroscopy and were found to consist mainly of undegraded copolymer (*Fig. 9.14.*). The appearance of bands at about 1805, 1760 (shoulder) and 1030 cm$^{-1}$ due to anhydride result `from the degradation of unreacted acid units initially present in the copolymer.

#### *2.3.2.1b. Cold Ring Fraction*

*Fig. 9.15* shows the ir spectra of both copolymers, in which bands due to aromatic ring, vinyl group conjugated with aromatic ring and carboxylate ion are clearly displayed.

Mass spectrometric data are consistent with the presence of high boiling fragments including styrene oligomer, together with traces of products containing one and two units of each type in the case of ST/NaA copolymer only.

#### *2.3.2.1c. Condensables as Gaseous Products*

Acetone and carbon dioxide were established as major gaseous products for ST/KA and ST/NaA ionomers, respectively. Apart from these, ethene, propene, toluene, benzene, ketene and 1-butene were also identified as minor condensable gases.

### *2.3.2.1d. Liquid Fraction*

The less volatile condensable fractions as liquid were subjected to GC-MS and the corresponding chromatograms are reproduced in *Figs. 9.16* and *9.17*. There are similarities in the behaviour of both ionomer samples.

Gravimetric data obtained from isothermal degradation of ST/KA copolymer at 340 °C are shown in *Table 9.8*. *Table 9.9*. shows the data for both copolymers facilitating comparison.

Products identified by IR, MS and GC-MS techniques from isothermal heating of ST/NaA and ST/KA ionomers at 340 °C for 2.5 hr are given in *Tables 9.10* and *9.11*, respectively.

[illegible] spectra of the [illegible] acid salt copolymer samples [illegible]

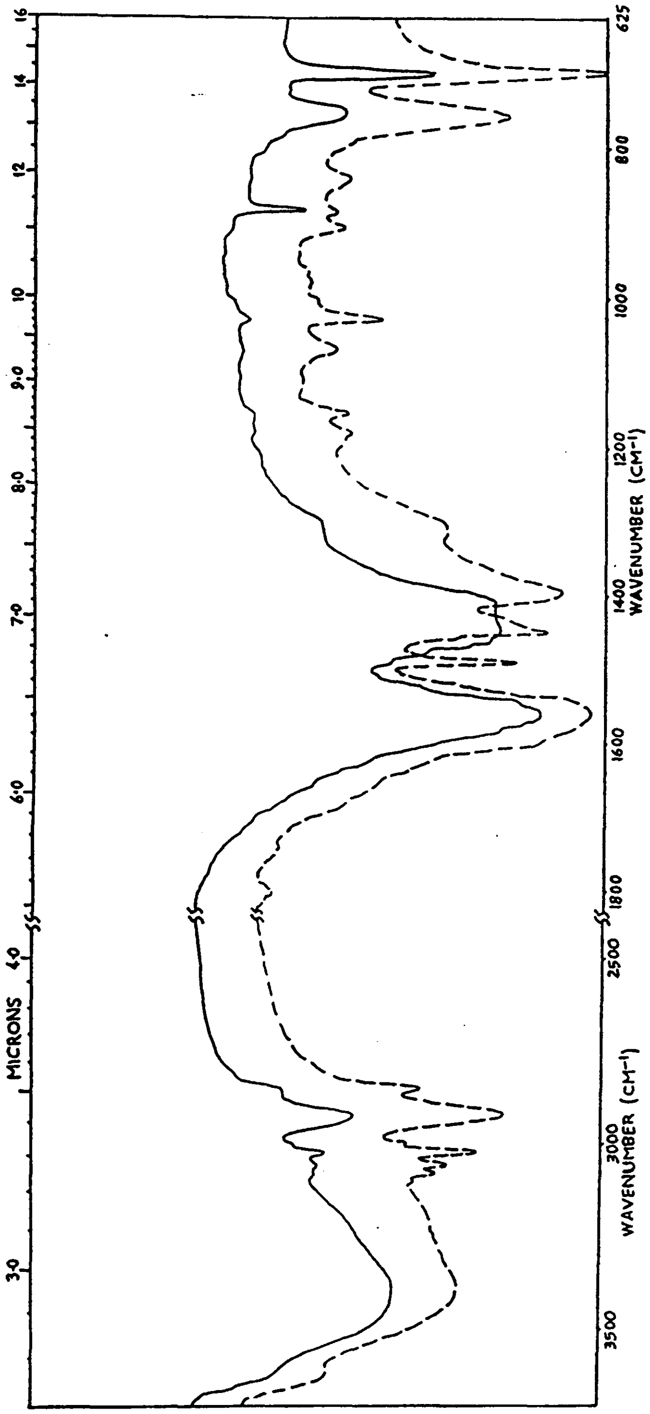


**Fig. 9.14.** Ir spectra of the involatile fractions of styrene/acrylic acid salt copolymer samples, heated isothermally at 340 °C for 2.5 hr.

—— ST/NaA copolymer, ---- ST/KA copolymer.

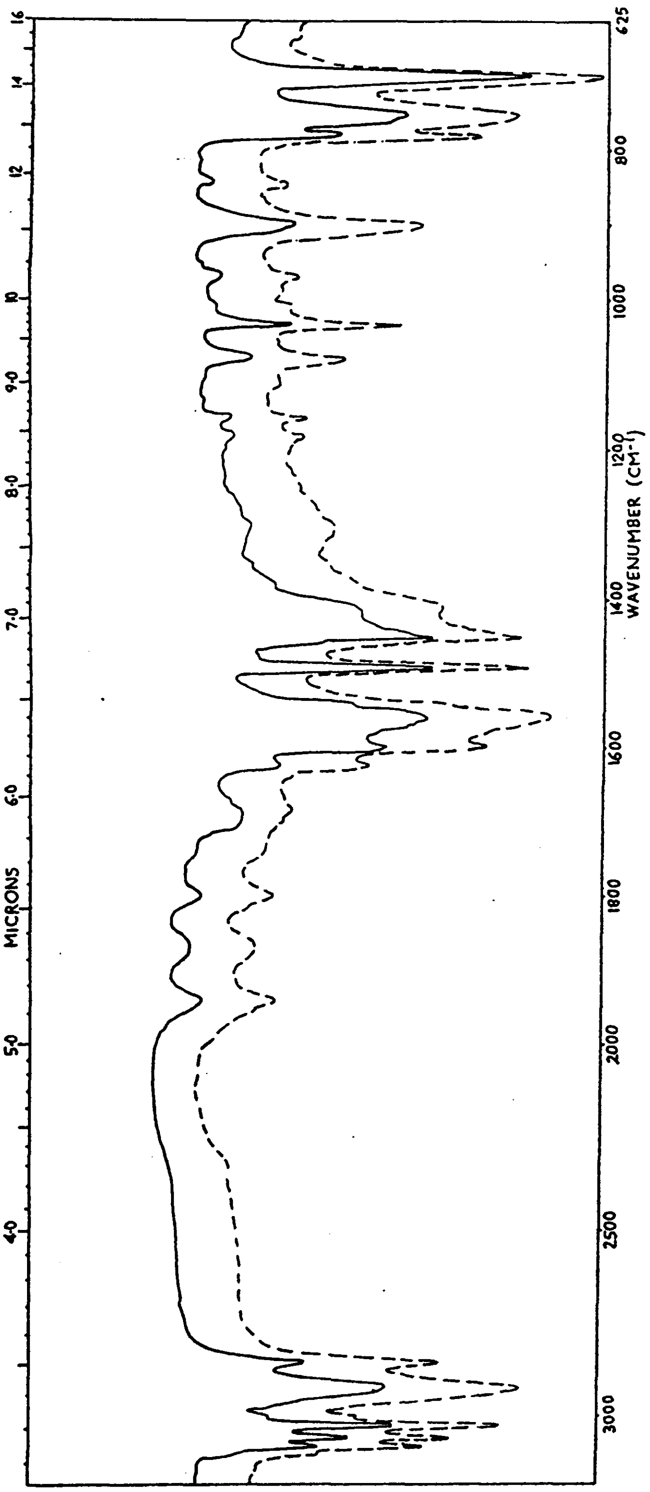


**Fig. 9.15.** Ir spectra of the cold ring fractions of styrene/acrylic acid salt copolymer samples, heated isothermally at 340 °C for 2.5 hr.

—— ST/NaA copolymer, - - - - ST/KA copolymer.

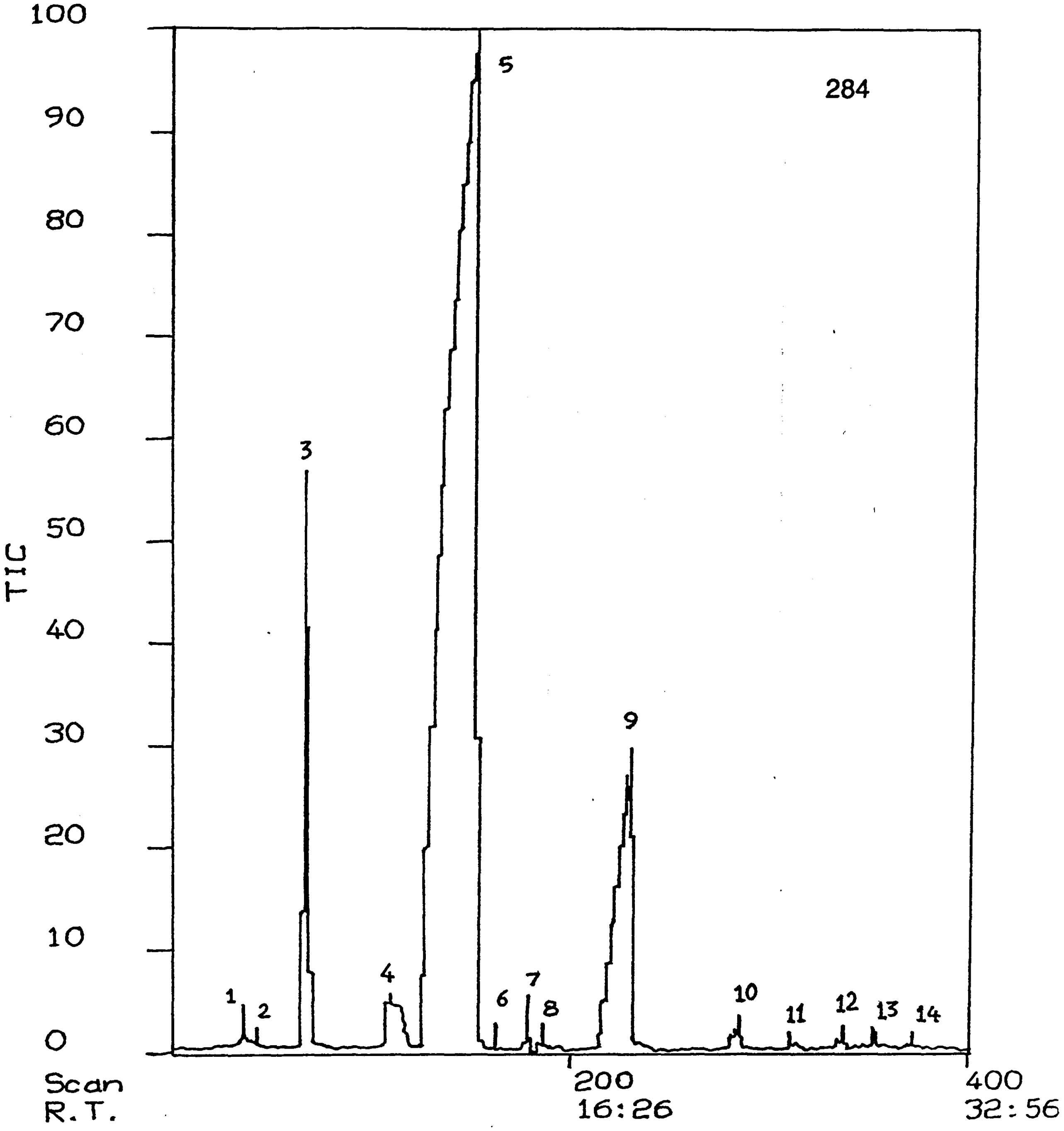


**Fig. 9.16.** GC-MS chromatogram of the liquid fraction of ST/NaA copolymer sample, degraded isothermally at 340 $^{o}$C for 2.5 hr.

Assignments: **1** 2-Methyl propane nitrile (initiator), **2** Benzene, **3** Toluene, **4** Ethyl benzene, **5** Styrene, **6** Isopropyl benzene, **7** Cyclopropyl benzene, **8** n-Propyl benzene, **9** $\alpha$-Methyl styrene, **10** 2,3-Dihydro indene (indan), **11** 4-Phenyl butene-1, **12** Methallyl benzene, **13** 1-Methyl indan, **14** Unknown.

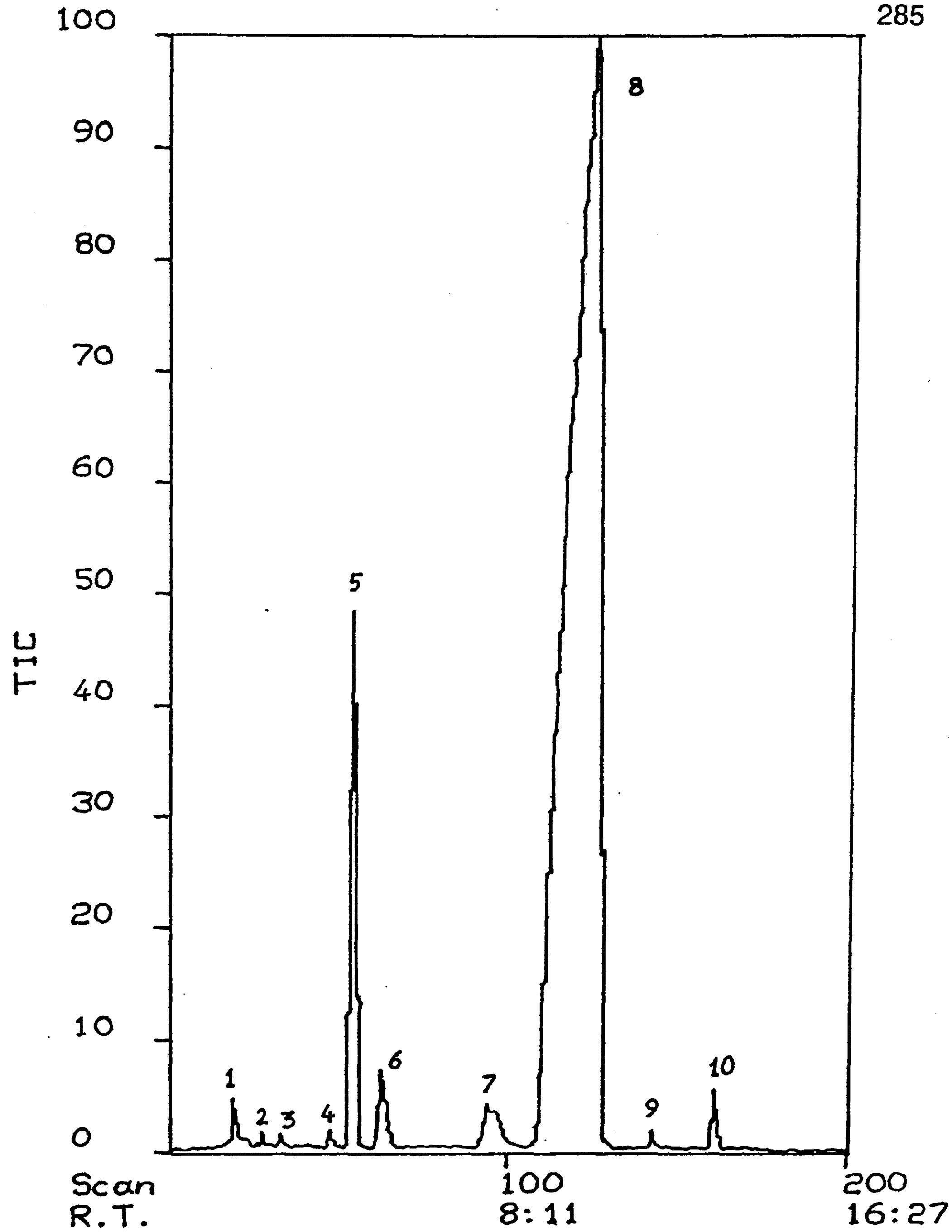


**Fig. 9.17.** GC-MS chromatogram of the liquid fraction of ST/KA copolymer sample, heated isothermally at 340 °C for 2.5 hr.

Assignments: **1** Acetone, **2** Initiator fragment, **3** Benzene, **4** Mesityl oxide, **5** Toluene, **6** Mesityl oxide, **7** Ethyl benzene, **8** Styrene, **9** Allyl benzene, **10**α-Methyl styrene.

**Table 9.8.** Isothermal heating data for degradation of ST/KA copolymer at 340 $^{o}C^{*}$ for different periods of time under TVA conditions

| Time (hr) | Weight loss (%) | Residue (wt%) | CRF (wt%) | Volatile products (wt%) | Ratio of volatile/CRF products |
|---|---|---|---|---|---|
| 1/2 | 11.6 | 88.4 | 1.2 | 10.4 | 8.6 |
| 1 | 18 | 82 | 3.3 | 14.7 | 4.5 |
| 1.5 | 23 | 77 | 4.6 | 18.4 | 4 |
| 2 | 28.2 | 71.8 | 5.4 | 22.8 | 4.2 |
| 2.5 | 30.2 | 69.8 | 7.2 | 23 | 3.2 |

* The onset temperature for non-condensables.

**Table 9.9.** Isothermal heating data for degradation of both copolymers at 340 $^{o}$C for different periods of time under TVA conditions.

| Time (hr) | Total wt loss (%) | Residue (wt%) | CRF (wt%) | Volatile products (wt%) | Ratio of volatile/CRF products |
|---|---|---|---|---|---|
| 2.5* | 59.5 | 40.5 | 16 | 43.5 | 2.7 |
| 2.5** | 30.2 | 69.8 | 7.2 | 23 | 3.2 |

* ST/NaA copolymer sample had already been heated isothermally at 300 $^{o}$C for 2.5 hr.

** ST/KA copolymer sample.

**Table 9.10.** Products of degradation of ST/NaA copolymer degraded isothermally at 340 °C ** for 2.5 hr.

| Non-condensable products at -196 °C | condensable volatile products at -196 °C | | CRF (light brown solid) | Residue (black) |
|---|---|---|---|---|
| | Gases | Liquid Fraction | | |
| IR | IR, MS | GC-MS | IR, MS | IR |
| CO | $CO_2$* | Styrene * | High boiling fragments of PS, such as dimer, trimer together with one and two units (traces) of each type. | Undegraded copolymer |
| $CH_4$ | Propene | α-Methyl styrene | | |
| | Ketene | Toluene | | |
| | | Ethyl benzene | | |
| | | 2,3-Dihydroindene | | |
| | | Cyclopropyl benzene | | |
| | | Methallyl benzene | | |
| | | n-Propyl benzene | | |
| | | Isopropyl benzene | | |
| | | Benzene | | |
| | | 4-Phenyl butene-1 | | |
| | | 1-Methyl indane | | |

* Major product.

** This sample had already been heated at 300 °C for 2.5 hr.

**Table 9.11.** Products of degradation of ST/KA copolymer degraded isothermally at 340 °C for 2.5 hr.

| Non-condensable products at -196 °C | condensable volatile products at -196 °C | | CRF (light brown solid) | Residue (black) |
|---|---|---|---|---|
| | Gases | Liquid Fraction | | |
| IR | IR, MS | GC-MS | IR, MS | IR |
| CO | $CO_2$* | Styrene * | High boiling fragments of PS, such as dimer, trimer together with one and two units (traces) of each type. | Undegraded copolymer |
| $CH_4$ | Acetone * | Toluene | | |
| | Ethylene | Mesityl oxide | | |
| | 1-Butene | Ethyl benzene | | |
| | Benzene | α-Methyl styrene | | |
| | Toluene | Acetone | | |
| | | Allyl benzene | | |
| | | Benzene | | |

* Major product

## *3. MECHANISM OF DEGRADATION*

The degradation behaviour of the alkali metal salts (Na and K) of PAA and styrene-acrylic acid copolymer has already been discussed in Chapters 5 and 8, respectively.

The degradation mechanism of the alkali metal salts is explicable in terms of main chain and side group scission reactions, accompanied to a limited extent by intramolecular transfer of the macroradicals. The mechanism of degradation of polystyrene involves chain scission, depolymerisation to monomer and both intra- and intermolecular transfers (as briefly described in Chapter Eight). Below 300 °C, only scission and disproportionation of the macroradicals occurs.

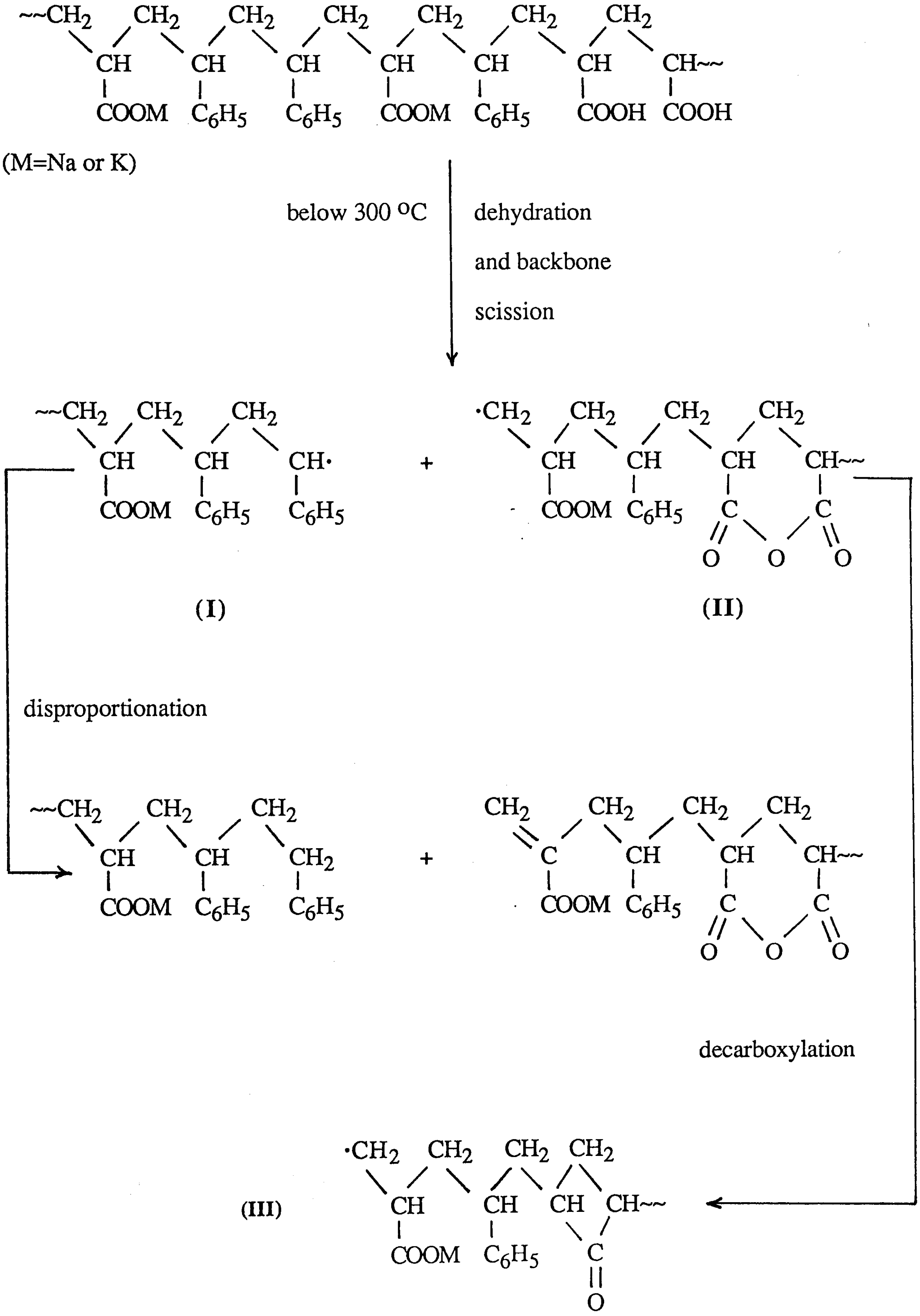
Contributions of features from both mechanisms (either PS or the alkali metal salts of PAA) might be expected to occur during the decomposition of styrene-acrylic acid salt copolymers.

The presence of the ionic groups causes an increase in the thermal stability of the copolymer relative to the parent styrene/acrylic acid copolymer.

The main features of the degradation of styrene/acrylic acid salt (Na and K) copolymers depend on composition and the distribution of the ionic groups along the chain, and they are summarised as follows;

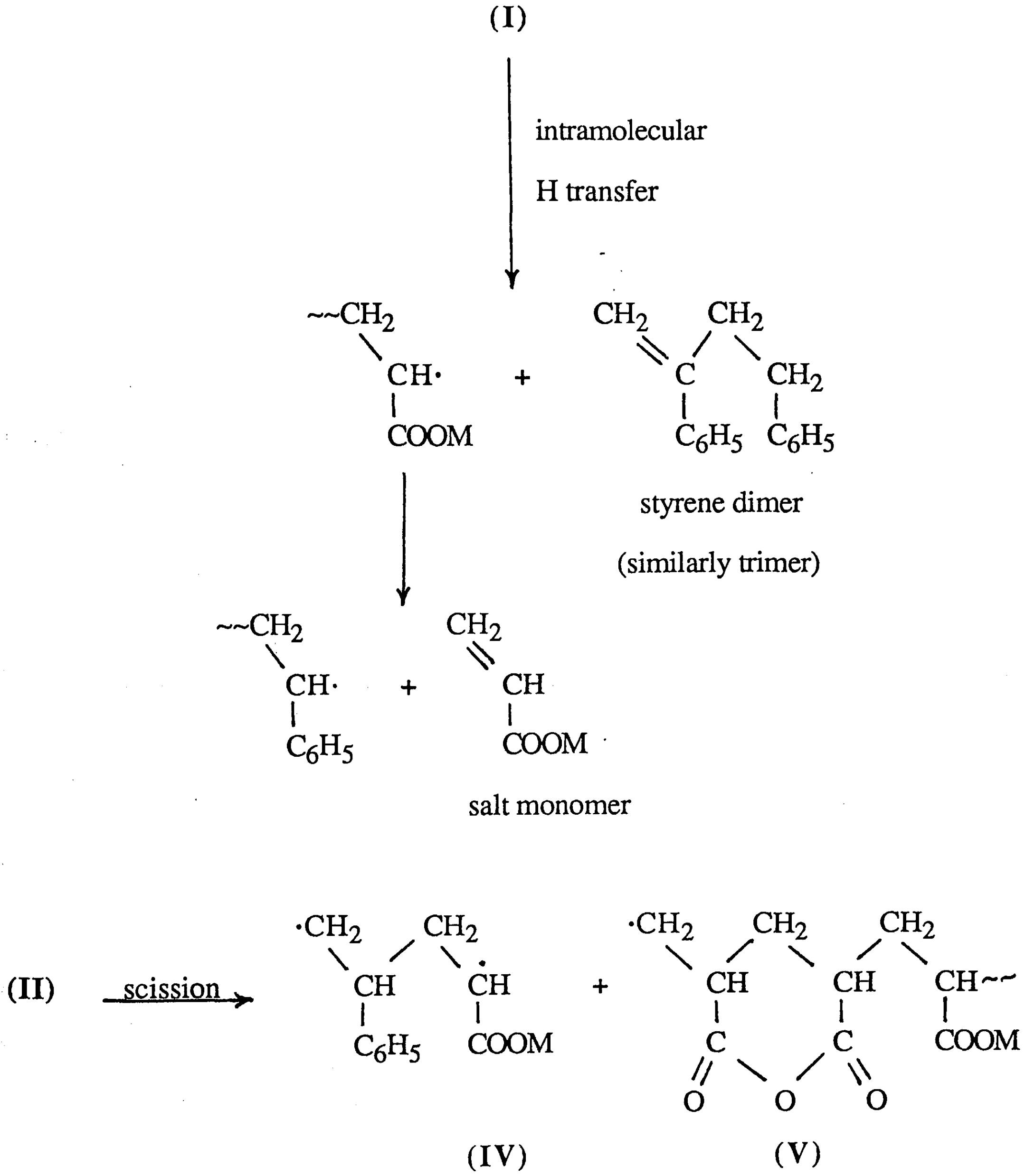
### *a. Below 300 °C*

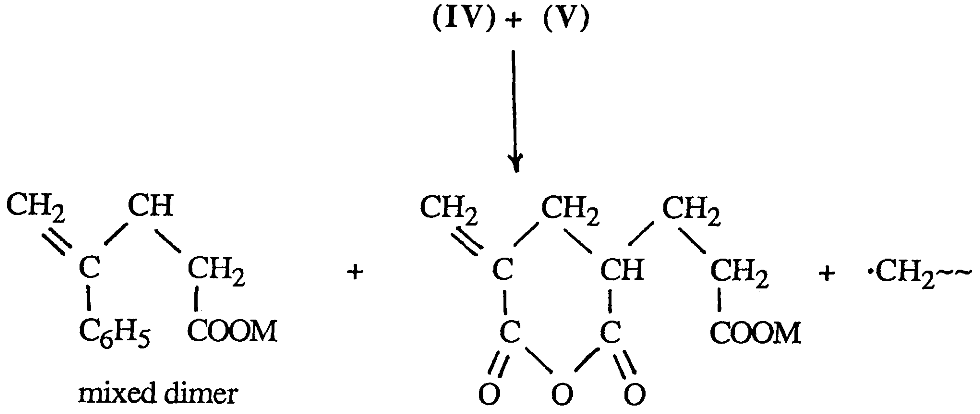
At temperatures below 300 °C, dehydration and decarboxylation of the acrylic acid units left possibly unreacted during neutralisation of the styrene/acrylic acid copolymer accompanied by some chain scission can be proposed as main reactions.


(M=Na or K)
below 300 °C
dehydration and backbone scission
(I)
(II)
disproportionation
decarboxylation
(III)

### *b. Above 300 $^oC$*

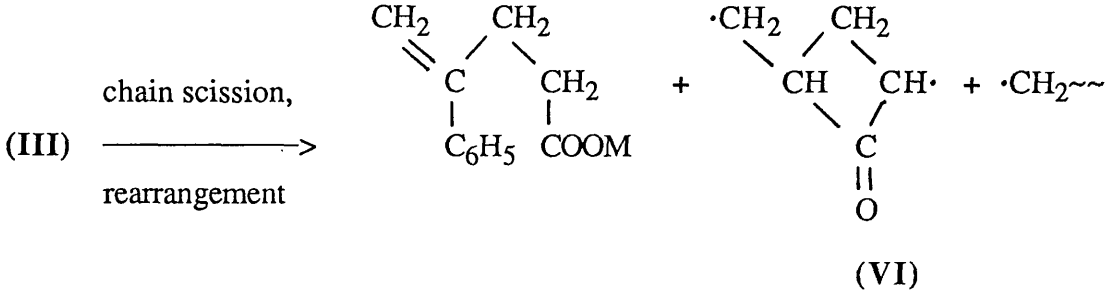
Further main chain and side group scission reactions followed by intra- and intermolecular transfer might be expected at temperatures higher than 300 $^oC$, in leading to oligomer (dimer or trimer) of styrene and a little of the salt monomer together with mixed dimer or one and two units of each type.





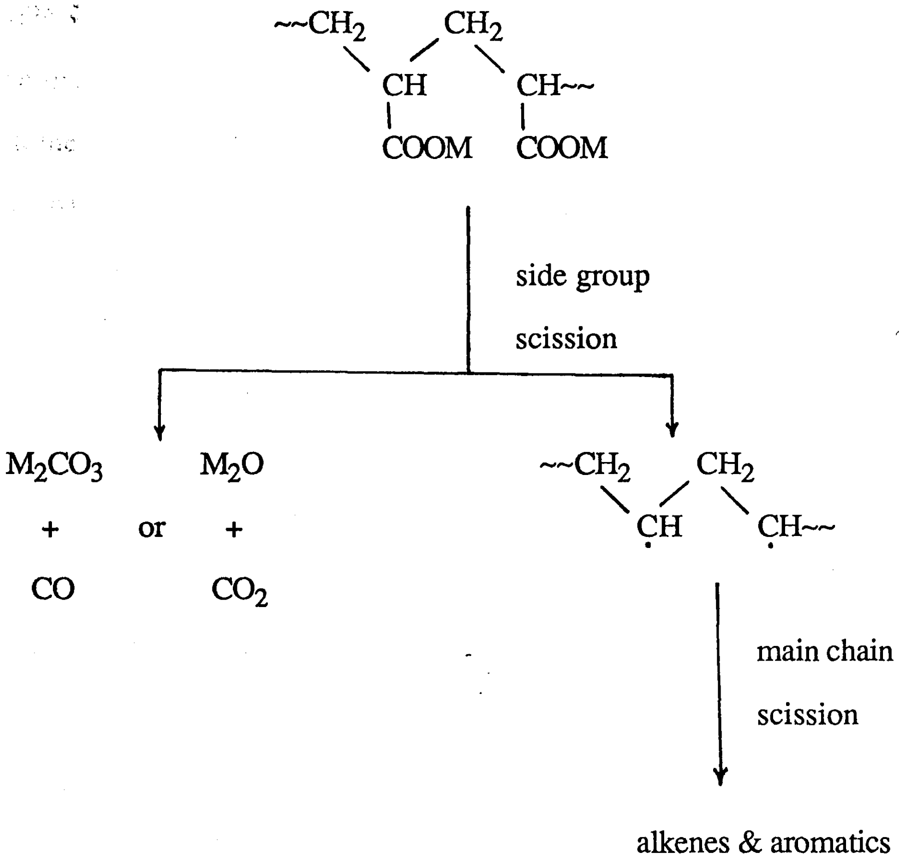
(similarly two units of each type)

Macroradical (III) may undergo backbone scission and rearrangement



The intermediate species (VI) may also form from side group splitting and main chain scissions of neighbouring carboxylate groups along the backbone. Formation of a variety of carbonyl containing degradation products, such as acyclic ketones, can be explained by further reactions of the intermediates (see Chapter Five, mechanism section).

Main and side group scissions from neighbouring carboxylate groups lead to the formation of metal carbonate, metal oxide, carbon dioxide and carbon monoxide, while secondary reactions of the backbone following several such scissions can also explain the formation of unsaturated hydrocarbons.



The minor products such α-methyl styrene, toluene and the other styrene-based compounds results from a similar mechanism as described in Chapter Eight in case of polystyrene.

## *4. CONCLUSIONS*

Although the thermal behaviour of the sodium and potassium salts of styrene-acrylic acid copolymer is rather similar, there is a significant difference from the parent acid copolymer on the basis of TVA, TG and DTA data.

The temperature of the maximum rate of evolution of volatile products from the major degradation process of the copolymer samples is markedly higher than that of polystyrene and the styrene-acrylic acid copolymers. This increase in stability results from the inhibition of the depolymerisation and chain transfer reactions of the styrene sequences blocked by acrylate units within the copolymers due to the presence of metal acrylate units randomly distributed in the chain.

It seems that the thermal stability of these ionomers is dependent on the amount of introduced salt units and the degree of neutralisation of the styrene-acrylic acid copolymer by the respective bases.

This result is in close agreement with that reported by Wlochowicz[172], who indicated that the thermal stability of styrene/acrylic acid salt (Zn) copolymer is dependent on the ionic groups present in the copolymer but inconsistent with those obtained by other investigators[165-167], who believe that the thermal stability of the styrene-acrylic(methacrylic) acid copolymers and their sodium salts are independent of the amount of the salt units introduced.

A mechanism similar to that of the styrene/acrylic acid copolymer can be proposed for the degradation of these copolymers, but it is clear that features of the mechanisms of degradation both of polystyrene and the alkali metal salts of PAA contribute to the decomposition of the ionomers.

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