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

CONTROLLED DEGRADATION OF METHACRYLONITRILE POLYMERS AND COPOLYMERS

by:

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To my mother and to the mamory of my father

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SUMMARY

This research is concerned with the preparation, characterisation and thermal degradation of methacrylonitrile based polymers and copolymers. Various methacrylonitrile homopolymers including those containing reactive chain ends and methacrylonitrile copolymers with other comonomers (e.g. methacrylic acid, styrene and maleic anhydride) were prepared, characterised and their thermal behaviour was also studied under programmed and isothermal heating experiments using TVA, TG and DTA techniques.

Polymer degradation is a complex branch of chemistry. A general description of the major types of degradation processes which may occur during thermal decomposition is given in Chapter One. This chapter also includes a brief review of the significance of polymer structure in polymer degradation.

Chapter Two details the experimental procedure of the several thermal analysis techniques employed in the present work, with special emphasis on thermal volatilisation analysis as a more versatile technique. A brief description of additional analytical methods used in identifying and quantifying degradation products is also included.

Chapter Three describes the preparation, isolation and characterisation of various homo- and copolymers of methacrylonitrile used in the present investigation. This also includes a brief description of the calculation determination of monomer feed for the preparation of copolymers of any required composition.

The experimental work regarding the thermal aspects of various methacrylonitrile polymers and copolymers is described in Chapters

Four, Five, Six, Seven and Eight.

Chapter Four is concerned, as a basis, with the thermal behaviour of high and low molecular weight methacrylonitrile polymers made using AIBN and benzoyl peroxide as initiators. It is observed that polymer simply depolymerises to monomer (as it is expected from a polymer with 1:1-disubstituted structure) in a two stage decomposition. The first stage of decomposition is attributed to the depolymerisation initiated from unsaturated chain ends and the second (and main stage in high molecular weight polymers) to unzipping after random chain scission. This chapter also contains a literature review on the thermal degradation of polymethacrylonitrile

The programmed thermal degradation of methacrylonitrile polymers and copolymers capable of colouration is detailed in Chapters Five and Six, respectively.

The thermal degradation of methacrylonitrile polymers with reactive chain-ends is the subject of Chapter Five. Programmed heating experiments were employed to investigate the effect of colouration initiated from the polymer chain ends on the thermal degradation of polymethacrylonitrile, and on the products of degradation. It has been observed, in these studies, that the end-initiated methacrylonitrile polymer samples did not simply depolymerise to monomer as has been expected[1] and observed[2] in case of a polymer made from 1:1-disubstituted monomer. Monomer yields were significantly decreased with increasing reactive chain ends. A large amount of residue, cold ring fraction, volatile liquid products (mainly monomer) and various gases (condensable and non-condensable) were found amongst the degradation products. Oligomers with various naphthyridine types of structure were suggested to be present in CRF. Formation of these other degradation products indicated towards some degradative routes other than depolymerisation.

The thermal degradation of methacrylonitrile copolymers containing small amounts of methacrylic acid is considered in Chapter Six in order to asses, the effect of thermal colouration initiated from inside the polymer chain on thermal behaviour and products of degradation. It has been observed that with increasing concentration of MAA units in the copolymer chain, there is an increase in the relative amounts of residue and cold ring fraction (formed as a result of nitrile group cyclisation[4]) together with a corresponding decrease in the monomer yield. The degradation products from MAN/MAA copolymers were almost the same as has been identified in case of end-initiated methacrylonitrile polymers.

A mechanism for the degradation products from MAN polymers with reactive chain ends and MAN/MAA copolymers has been put forward.

In Chapter Seven, the thermal stability and degradation behaviour of a set of methacrylonitrile/styrene copolymers is discussed. It was found that the thermal behaviour of these copolymer samples can be related to that of polymethacrylonitrile and polystyrene. It was concluded that the mechanism of decomposition below and above 300 °C depends upon the composition of the copolymer. A well separated two stage decomposition tends to merge into a sharp single stage degradation, with increasing ratios of styrene monomer in the copolymer. An increase in the T_{onset} and T_{max} were also observed with increasing ratios of styrene units in the copolymer.

A mechanistic route has been proposed for the formation of various degradation products from these MAN/Sty copolymers.

Chapter Seven also includes the thermal studies and proposed mechanism of formation of degradation products for a methacrylonitrile/maleic anhydride copolymer.

Chapter Eight details the isothermal colouration of MAN polymers. A set of methacrylonitrile homopolymers with reactive end structures and three methacrylonitrile copolymers containing small amounts of methacrylic acid comonomer units were used to investigate the colouration initiated from chain-ends and from inside the polymer chain. These polymer and copolymer samples were isothermally degraded in two different environments (as KBr discs and cast films) to study the effect of environment (ionic in case of KBr disc) on the extent of colouration.

In the present investigations, it has been confirmed that colouration in the methacrylonitrile polymer can only be initiated from some well defined impurity (present inside the polymer chain or at the chain-end), and the colouration is directly proportional to the number of initiating centres. It has also been observed that when the initiating centres (methacrylic acid units) are present in abundance, a side reaction (dehydration of adjacent methacrylic acid units in the chain) also occurs in the degradation of film samples, resulting in the formation of anhydride structures.

A mechanism involving initial formation of an imide has been advanced, which satisfactorily explains the observed infrared spectral changes during thermal colouration under reduced pressure. Interpretation and tentative assignments of the observed infrared data are also given.

A review of earlier work on thermal colouration of nitrile polymers is also included in Chapter.Eight.

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CHAPTER ONE

INTRODUCTION

1.1 THE DEVELOPMENT OF POLYMER SCIENCE

Polymers have existed in nature from since life began and have been used by mankind for various purposes. The main sources of these natural polymers were animals and plants.[1] Natural resins and gums have been used for thousands of years.

The first synthetic polymer, that is, made from laboratory chemicals, was Backelite, which was made from phenol and formaldehyde. Although synthetic polymeric compounds were known about in early nineteenth century[2] but it was not until 1920s that the true nature of the macromolecules became understood largely because of the efforts of Nobel laureate Staudinger. Before that time the common belief was that polymeric materials consisted of physically-associated aggregates of small molecules. Staudinger demonstrated that natural synthetic polymers are not just aggregates like colloids but are long, chain like molecules containing simple chemical units linked together by covalent bonds.

The science of high polymers arose in 1930s and the major growth of the technology of these materials started even later.[3] Carothers[4] produced a range of industrially important polymers and also developed the basic understanding of the polymerisation process and molecular weight distribution. Before the beginning of the world war II, relatively few such polymeric materials were available for the manufacture of articles required for a civilised life. The rapid increase in the range of manufactured products following world war II resulted from the development of a wide variety of polymers in the form of fibres, plastics, elastomers, adhesives and resins.

Although the polymerisation of organic compounds has been known for over a hundred years, the simultaneous polymerisation (copolymerisation) of two or more monomers was not investigated until 1911. It was soon realised that the properties of copolymers are often more useful than those of the homopolymers made from a single monomer. One of the first commercial copolymers was the copolymer of vinyl chloride and vinyl acetate (Vinylite) which was introduced in 1928. Scientific, commercial and industrial interests in macromolecules are shifting increasingly from polymerisation to copolymerisation. Synthetic copolymers are now found everywhere. 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 corresponding homopolymers.

The trend of replacing conventional materials with polymeric substitutes is still increasing and thus it is important to understand the chemical and physical properties of such materials in order to tailor them to our needs. A major contribution to understanding is the science of polymer degradation.

1.2 POLYMER DEGRADATION

1.2.1 Definition and Classification

Polymer degradation is the collective term used to describe various processes which cause a deterioration in the physical or chemical properties of polymers or their outward appearance. In a wider sense polymer degradation also includes all types of polymer reactions. Polymer degradation, according to its various modes of initiation, can be subdivided into thermal, mechanical, photochemical, radiation, biological and chemical degradation.

1.2.1.1 Thermal Degradation

The ultimate objective of thermal degradative studies of polymers is the determination of the mechanism involved. Such studies, however, also give a good insight into the nature of these materials, which is valuable in relation to their uses.

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 break down of a polymer determines the upper limit of the temperature of fabrication and the volatile products of degradation must be known in order to guarantee the safety of the workers.[5] Detailed analysis of the products of degradation of polymers are of particular interest because of well justified current concern regarding toxicity, flammability and general safety of the structural material.

It is convenient at this stage to survey briefly the types of degradation which can occur. The present work was confined to thermal degradation under high vacuum and various thermal degradation reactions occurring under these conditions may generally classified into two broad categories:[6]

(1) Chain Scission Reactions or Depolymerisation Reactions.

(2) Substituent or Non-Chain Scission Reactions.

Chain scission reactions are characterised by the breaking of the main polymer backbone. The products at any intermediate stage of the reaction are similar to the parent material. The ultimate products are monomer or other fragments closely related to it. On the other hand substituent reactions are those which occur on reactive substituent groups and do not in the first instance break the carbon backbone of polymer. Examples of both types of decomposition are found in the present work and it is therefore appropriate to discuss briefly their main features.

1.2.1.1.1 Chain Scission Reactions.

Chain scission reactions are characterised by the cleavage of a bond in the polymer backbone. These reactions may be further sub-divided into two classes which are as follows.

1.2.1.1.1a Depolymerisation.

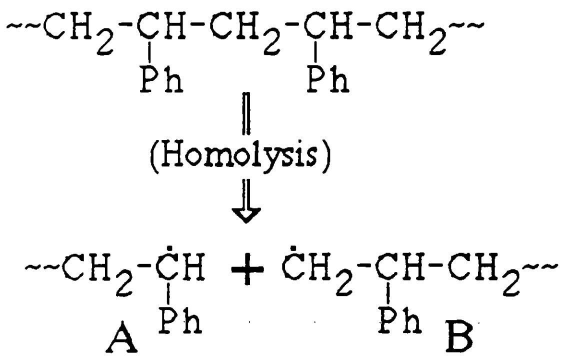
Depolymerisation is the exact reverse of the propagation step of polymerisation and results in monomer production. The reaction may be initiated from unsaturated chain ends, if present as in the case of polymethyl methacrylate[7] or by random scission of the polymer chain , as in the case of polybutadiene.[8]

1.2.1.1.1b Chain scission giving non-monomeric products

Besides depolymerisation, chain scission may sometimes result in the production of stable molecules rather than radicals. A simple example of such a reaction is the rupture of "weak links", resulting in a limited drop in the molecular weight in the case of polystyrene.[9] A more complex example involves random chain scission which results in a gradual reduction in molecular size of the polymer, the main products being various oligomers.

A large variety of addition polymers depolymerise thermally, and detailed studies have shown quite distinct behaviour. Chain scission is the predominant process occurring during the decomposition in various polymers such as poly(methyl methacrylate) (PMMA), polymethacrylonitrile (PMAN), polypropylene (PP), and polyethylene (PE), and takes place to various extents in a number of other addition polymers. Detailed studies of these reactions showed that thermal decomposition of PMMA[10] leads to quantitative monomer production whereas both PP and PE give little monomer, the products being mainly polymer chain fragments.[10–12, 8]

In general, when a polymer containing tertiary hydrogen (such as polystyrene) is thermally degraded, the degradation proceeds through a free radical mechanism by homolysis and results into the formation of macroradicals A and B:



$$\sim\sim CH_2-\underset{Ph}{CH}-CH_2-\underset{Ph}{CH}-CH_2\sim\sim \xrightarrow{\text{(Homolysis)}} \underset{A}{\sim\sim CH_2-\underset{Ph}{\dot{C}H}} + \underset{B}{\dot{C}H_2-\underset{Ph}{CH}-CH_2\sim\sim}$$

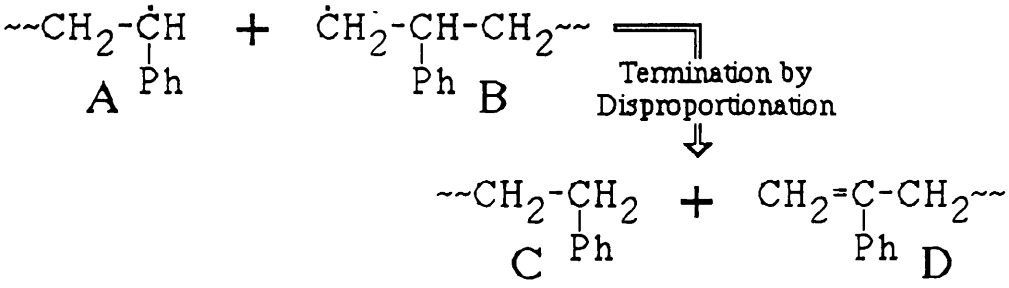
These macroradicals (A and B formed as result of homolysis) undergo through three main reactions during further degradation which are as follow:

(i) Termination by disproportionation.

(ii) Depropagation.

(iii) Chain transfer reaction
(a) Intramolecular and (b) Intermolecular.

(i)

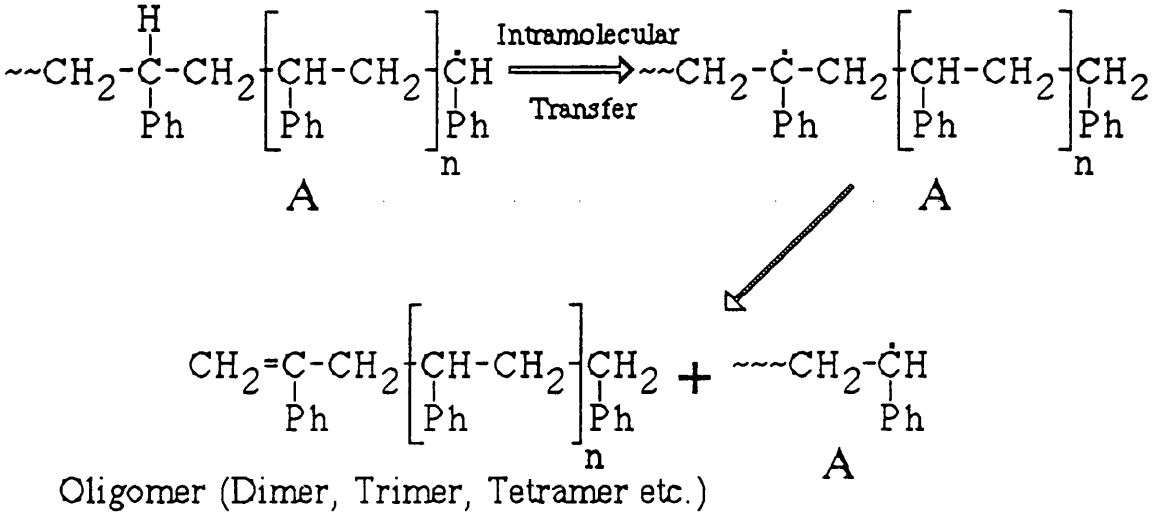


$$\underset{A}{\sim\sim CH_2-\underset{Ph}{\dot{C}H}} + \underset{B}{\dot{C}H_2-\underset{Ph}{CH}-CH_2\sim\sim} \xrightarrow{\text{Termination by Disproportionation}} \underset{C}{\sim\sim CH_2-\underset{Ph}{CH_2}} + \underset{D}{CH_2=\underset{Ph}{C}-CH_2\sim\sim}$$

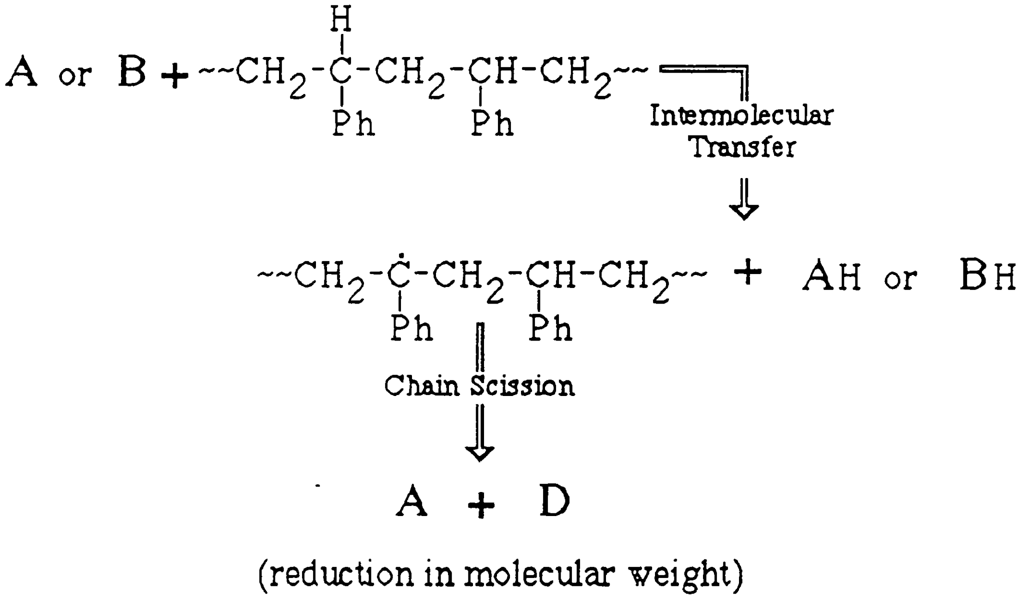
(ii).

$$A \xrightarrow{\text{Depropagation}} A + \text{Monomer}$$

(iii) a:



(iii) b:



In the first instance, it is quite possible at relatively low temperatures that the two macroradicals (A and B) simply terminate through disproportionation to produce stable macrospecies (C and D), resulting in an observed [13] molecular weight decrease.

Depolymerisation is believed to involve[5, 14] macroradical (A) and the same radical is also involved in a competing backbiting intramolecular transfer reaction leading to various oligomers (i.e., dimers, trimers, tetramers etc.). On the other hand either of the macroradicals A or B can take part in intermolecular transfer reaction and generate a new radical by breaking a polymer chain, as shown in reaction (iii)b. The effect of intermolecular transfer is a reduction in the molecular weight of the polymer.

1.2.1.1.2 Substituent Reactions

These reactions usually occur at relative low temperatures, below those at which main chain bonds are broken. Substituent reactionsdiffer from chain scission reactions mainly in that the basic mechanism of decomposition depends predominantly upon the chemical nature of the pendant substituent functional groups. The substituent reactions may be free radical, molecular or ionic in nature and can be sub-divided into three main categories:

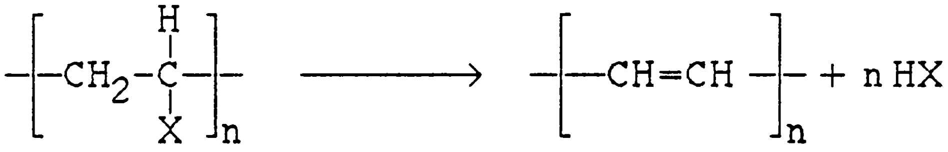
(a) Elimination reactions.

(b) Cyclisation reactions.

(c) Ester decompositions.

1.2.1.1.2a Elimination reactions

The elimination reaction can be well illustrated[15] by polyvinyl chloride (PVC), which eliminates hydrogen chloride, producing a conjugated polymer chain:



$$\left[-CH_2-\underset{X}{\overset{H}{C}}-\right]_n \longrightarrow \left[-CH{=}CH-\right]_n + n\,HX$$

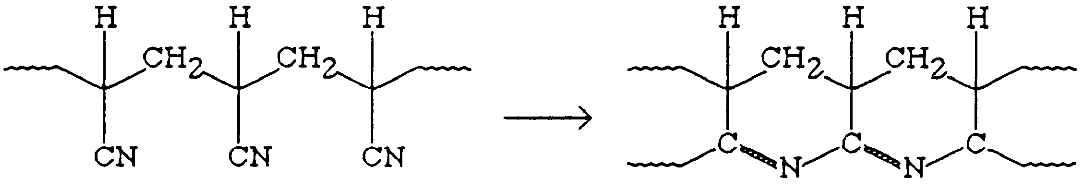
where X=Cl

Analogous processes are known where X=OH, Br or $CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}O$

The process of elimination of HCl from PVC is not clearly understood but theories have put forward that the process is ionic,[16] molecular[17] or radical[18] in nature.

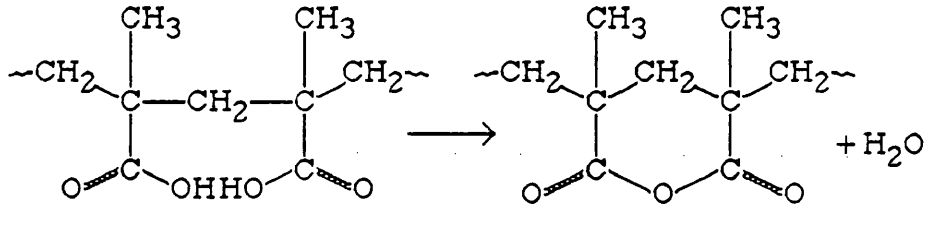
1.2.1.1.2b Cyclisation reactions

The neighbouring substituent groups or atoms, between which the cyclisation reaction takes place, may be vicinal or separated by three or more carbon atoms. This interaction results in the formation of cyclic structures in the polymer chain, and in some cases leads to a ladder like structure of considerable length. Thermal colouration in nitrile polymers[19] is a common example of this kind of reaction.

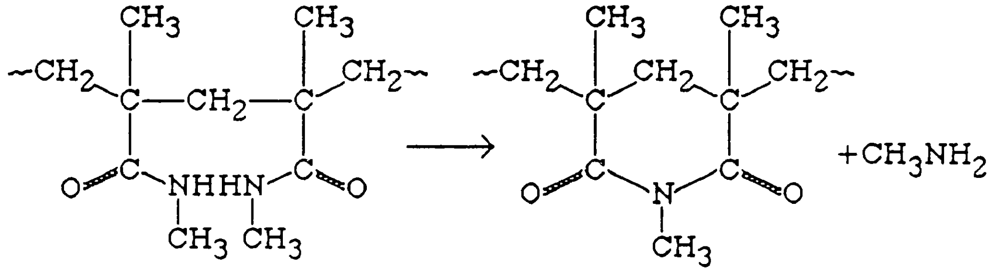


A polymer may also undergo cyclisation with concurrent elimination of small molecules, as in polymethacrylic acid[20] (A) and poly N-methacrylamide[21] (B):

(A)

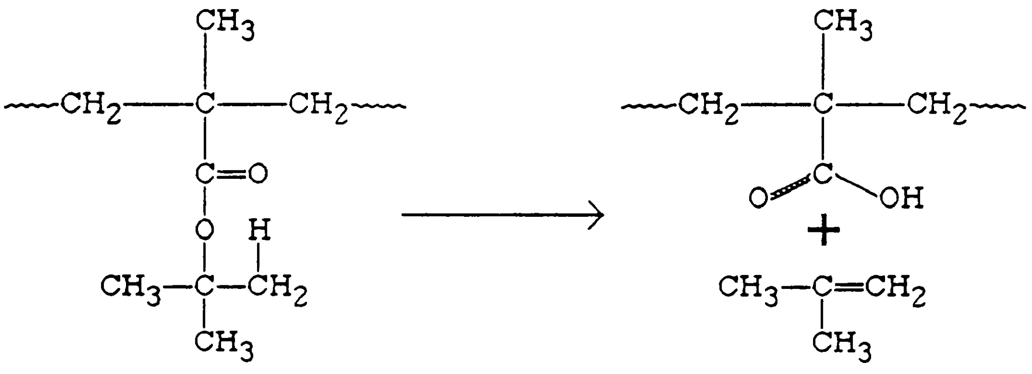


(B)



1.2.1.1.2c Ester Decomposition Reactions

These reactions involve generally formation of the parent acid together with an olefin, and have been found to take place in some (but by no means all) ester polymers as in pyrolysis of small ester molecule. A typical example of the process is given by the pyrolysis of poly(tert-butyl methacrylate) (PtBMA) which involves the formation of poly(methacrylic acid) in the residue, with evolution of isobutene.



1.2.1.1.3 Significance of Polymer Structure in Polymer Degradation.

The degradation behaviour of a polymer can often, but not always, be related to its structure. It has been established over the years[22] that the relative importance of transfer and depropagation to monomer (depolymerisation) reactions occurring during polymer degradation, depends upon mainly two factors

(i) The availability of reactive atoms (usually tertiary hydrogen) in the polymer chain.

(ii) The reactivity of the polymer, radical resulting from chain scission.

These two factors are dependent upon polymer structure. The transfer reaction is favoured by a reactive radical and is less likely to take place with a resonance stabilised or sterically hindered radical, while high yields of monomer are produced from polymers which are free from tertiary hydrogen an increase in the substitution in the polymer chain generally reduces the potential number of transfer sites and may also in some cases result in the possibility of radical stabilisation by delocalisation. A comparison of the degradation of polystyrene (PS) and poly α-methystyrene (Pα-MS) illustrates the fact that chain transfer reactions are reduced by replacement of the tertiary hydrogen in polystyrene by a methyl group, and leads to an increase in monomer yield from 50% in PS at 300-400 °C to almost 100% in Pα-MS.

In general, highly substituted radicals are more stable electronically and therefore less likely to attack the C-H bond. Steric hindrance between radical and polymer chain also increases with both substitution and size of substituent. Hence it reasonable to expect a tertiary radical with suitable substituents to be less reactive and likely to depolymerise to monomer.

1.2.1.1.3a Polymethacrylonitrile

Since polymethacrylonitrile is derived from a 1:1-disubstituted monomer, it would be expected, like poly(methyl methacrylate), poly-α-methylstyrene, poly(vinylidene cyanide) etc., to be capable of decomposing quantitatively to monomer.[23] Although the nitrile substituent could be classed as reactive, there are no reactive methylene groups present with which a condensation can occur. The elimination of hydrogen cyanide, analogous to the behaviour of PVC, resulting in the formation of polyene structures, is rather unlikely, however depolymerisation will be more favoured due to resonance stabilisation of the radical caused by the nitrile substituent. Grasssie and McNeill have demonstrated[24] that quantitative monomer yield can be obtained from a polymer (PMAN) made using an azo initiator in vacuum conditions with suitable precautions to avoid any impurity. The colouration of PMAN at relatively low temperatures is also a well known[25–27] phenomenon, and reported[26] to reduce the monomer yields, hence the thermal behaviour is not as straightforward as with PMMA.

1.2.1.1.4 Methods of Studying Polymer Degradation

A variety of methods have been reported[28] for studying the thermal degradation of polymers. The choice of method of evaluation of polymer degradation depends upon the objectives, which may differ.

In general, commercially available equipment is commonly used to carry out the thermal analysis. Probably the most widely used techniques are thermogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC). Thermal volatilisation analysis (TVA)[29–32] and evolved gas analysis (EGA), which allow the collection and further examination of the degradation products, are also used for thermal analysis.

Thermal volatilisation analysis is a more generally applicable approach which records the change in the pressure which develops in a continuously evacuated system when the polymer sample is degraded to volatile products. TVA is discussed in greater detail in subsequent chapters.

1.3 OBJECTIVES OF THE RESEARCH

This research examines the thermal stability and mechanism of degradation in vacuo of a number of polymers and copolymers of methacrylonitrile utilising several thermo analytical techniques and related examination of the degradation products. These materials include methacrylonitrile homopolymers with stable chain ends, polymethacrylonitrile with reactive end structures and various methacrylonitrile copolymers containing other comonomers such as methacrylic acid and styrene etc.

It was also intended to examine the thermal colouration in methacrylonitrile polymers and copolymers from the point of view of studying the effect of the site of the initiating centres (chain ends, or within the backbone) on the characteristic of the reaction.

CHAPTER TWO

APPARATUS AND THERMOANALYTICAL TECHNIQUES FOR POLYMER DEGRADATION

This chapter includes a brief description of the apparatus, and the techniques, both thermal and analytical, which were employed in the present work. Particular emphasis has been given to TVA which is the most versatile of all the techniques described and allows study of the all products of degradation.

2.1. THERMAL ANALYSIS

2.1.1. INTRODUCTION

There are various methods 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. These experimental techniques can be grouped together under the term "Thermal Analysis".

When a polymer degrades, a mixture of different product fractions results. Products may be volatile enough to be non-condensable at liquid nitrogen temperature (-196 ^{o}C), volatile at degradation temperature but condensable at or below ambient temperature, or involatile residual materials.

Various methods of thermal analysis have been developed, and many of them are available commercially. The method of study of thermal degradation of a polymer depends upon the objectives of the investigation. Methods of thermal analysis allow the investigation of physical phenomena (e.g. changes in crystallographic properties, melting, sublimation, absorption or evolution of heat), and chemical phenomena (e.g. degradation, decomposition, oxidation, reduction). The most important and most widely used techniques are TG, DTA and TVA.

2.1.2. THERMOGRAVIMETRY

Thermogravimetry, TG, is widely used for determining the thermal stability of polymeric materials. The conclusions drawn with regard to stability are only relevant in the context of loss of weight of the sample. There are certain reactions which occur on heating a polymer and can alter drastically the physical properties of the material without any significant change in weight loss.[33]

TG is an important technique which allows a polymer sample to be raised from ambient temperature to as high as 1500 ^{o}C, while weight loss is recorded directly as a function of temperature. Commercially available equipment for operation to 1000 ^{o}C[34] and to 1500 ^{o}C[35] have been described. TG has been used[36] for gas and solid interaction studies to 1600 ^{o}C. TG has also been coupled with mass spectrometry in a number of systems.[37–40] Simultaneous DTA and TG equipment for operation to 1500 ^{o}C has been coupled to a quadrupole mass spectrometer.[41]

In TG the polymer sample may be heated in various atmospheres or under vacuum conditions. A plot of mass as a function of temperature provides both qualitative and quantitative information including the threshold temperature T_{oneset} and temperature of maximum rate of weight loss T_{max} for the degradation process.

2.1.2.1.Derivative Thermogravimetry.

It is some times very useful be able to compare a TG curve with its first derivative. Due to the nature of the TG curves it is some times difficult to discern overlapping process, and to facilitate interpretation it is helpful to have available the derivative trace of the weight loss curve. This is known as the differential thermogravimetric (DTG) curve. Thermobalances with electronic circuits to give the first derivative automatically are commercially available. A two pen recorder permits a convenient and direct comparison of the two curves.[42]

A thermobalance module coupled with the Du Pont 950 thermoanalyser was used in this project. The degradation was carried out under dynamic nitrogen atmosphere (60ml/min). Programmed work was carried out using a heating rate of 10 ^{o}C/min, the sample being heated from ambient temperature to 500 ^{o}C. TG and DTG curves were recorded simultaneously. Samples were in powdered form and were of the order of 3-5 mg.

2.1.3. DIFFERENTIAL THERMAL ANALYSIS.

When a polymer undergoes a change in its physical state (melting point, glass transition temperature) or undergoes chemical reaction (cyclisation, degradation) there is a temperature difference between sample and inert reference material depending whether the reaction is exo or endothermic.[43] This is the basis of differential thermal analysis.

DTA involves the measurement of the temperature difference arising between sample and inert reference during programmed heating at a fixed energy output and the temperature lags are recorded. It is customary to plot endotherms downward and exotherms upward, but this convention is not universally followed.[42]

The furnace, heating programme and recording devices used for DTA were those employed in TG. Generally, in a differential thermal analysis apparatus, the sample and reference chamber are designed to permit the circulation of inert or reactive gases. For this research, a nitrogen flow of 80ml/min was used.

2.1.4. THERMAL VOLATILISATION ANALYSIS.

Thermal volatilisation analysis (TVA) is a versatile thermoanalytical technique developed in Glasgow University Chemistry Department by McNeill and coworkers.[30,32,44,45] This technique has been extensively used throughout the work. A comprehensive description of the equipment and its operation has been given below.

2.1.4.1. Principle of TVA.

In TVA, a polymer sample is heated in a continuously evacuated system. Gaseous products of degradation pass to a cold trap and the small increase in pressure is detected by a Pirani gauge placed between sample and cold trap and recorded continuously as a function of temperature or time. This pressure change gives a measure of the rate of volatilisation of products.

The basic principle of TVA is depicted schematically in Fig. 2.1 in which a Pirani gauge is placed between the heated sample and cold trap (-196 °C). The TVA apparatus can be modified by placing a second cold trap, B, at higher temperature than that of the original trap, A, between the sample and Pirani gauge, as shown in 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. The form of apparatus currently used in the present work is that illustrated in Fig. 2.3 in which a number of limbs, each with an initial cold trap and a main trap (-196 °C), are joined in parallel. The temperature of the initial trap in each limb is different and 0 °C, -45 °C, -75°C and -100 °C have been found convenient for polymer degradation.

The Pirani gauge placed after each trap monitors the passage of volatile materials through the trap as in the basic differential condensation TVA arrangement, and the addition of a Pirani gauge after the -196 °C trap allows the detection of any non-condensable products, which are lost to the pumps. In the TVA apparatus used for the present studies, a mass spectrometer was connected to the TVA line after the last Pirani gauge, which helps in detecting the non-condensable products of degradation.

2.1.4.2. TVA in Practice.

In the TVA system, the polymer sample is used in the form of a fine

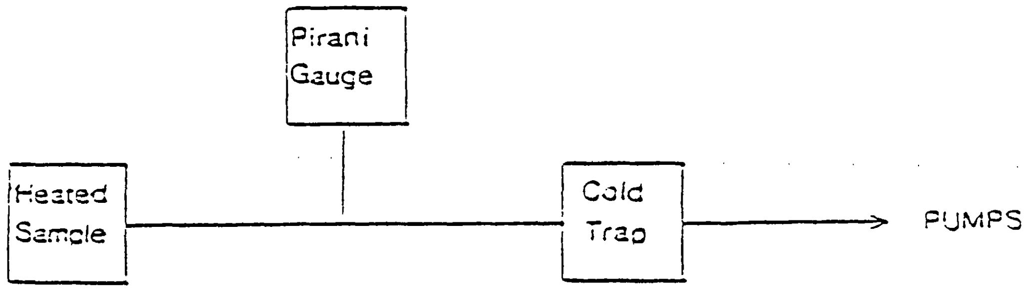
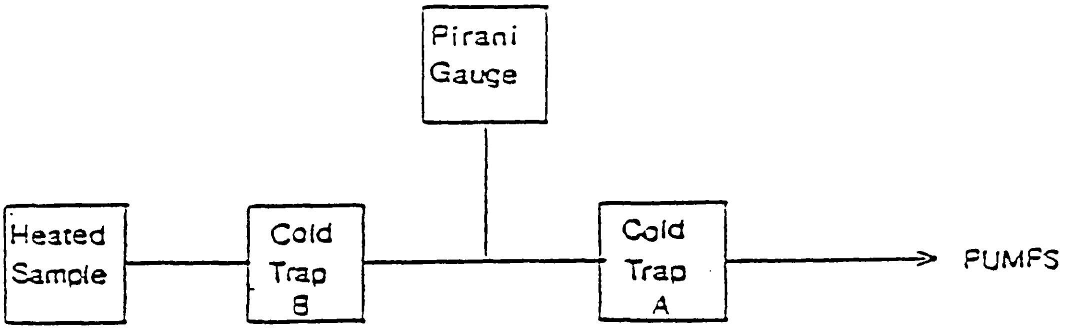


Fig. 2.1. Schematic Representation of Basic TVA System.



$T_B > T_A$

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

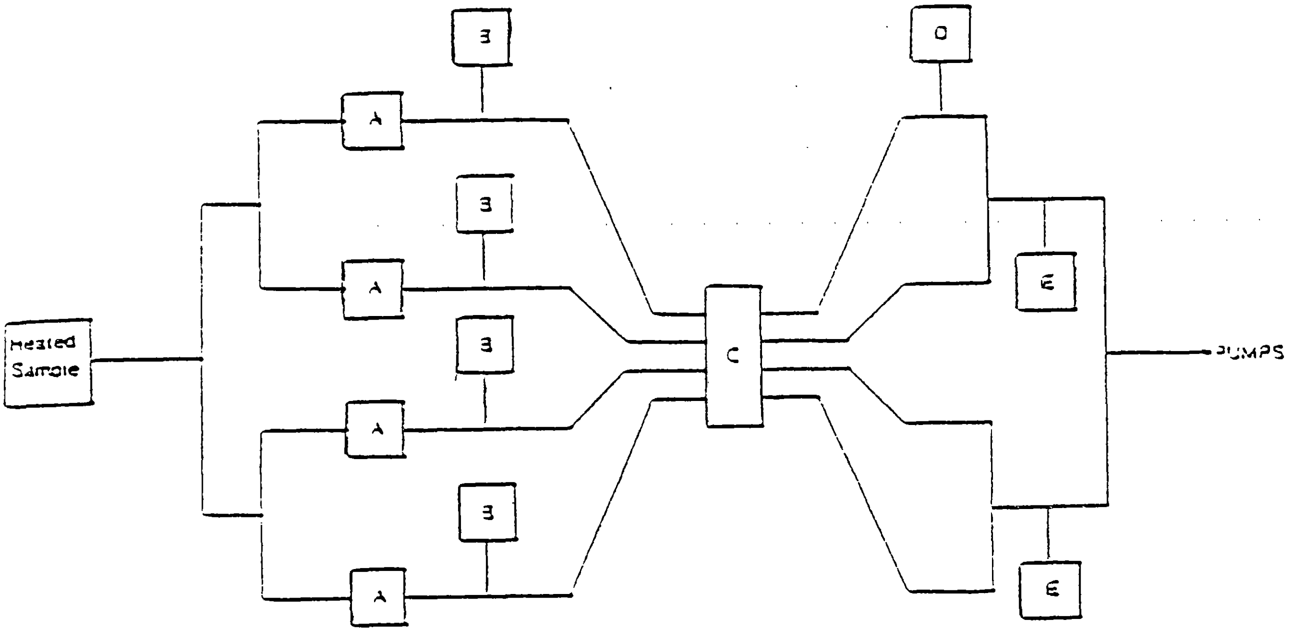


Fig. 2.3. Parallel Limb Differential Condensation TVA System.

A = 0°, -45°, -75°, -100 °C traps

B, D = Pirani gauges

C = -196 °C trap

E = Sample take off points

powder or thin film. A diagrammatic representation of the oven and degradation assembly of a typical TVA line is shown in Fig. 2.4. A Perkin Elmer F-11 gas chromatograph oven has been 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, which provides a linear increase of temperature in the range of 1^{o} to 40 ^{o}C/min. Most of the TVA work for this research was carried out by programmed mode, using a heating rate of 10 ^{o}C/min. The Pirani gauge responces and oven thermocouple output were recorded simultaneously using an BBC micro-computer through a interface developed by the computer section of Chemistry Department in Glasgow University.

The vacuum system comprised an Edwards, Speedivac EOI oil diffusion pump, backed by an Edwards Speedivac ED100 rotary pump. Pressures of 10^{-5} torr are obtainable by using this system. Edwards, G5 C2 Pirani gauge heads with Pirani model 11 or 14 control units were employed to measure the pressure. As TVA in the form used in the present work involves the comparison of the output of the five Pirani gauges attached to the line depends, for a constant pressure and gas composition, on the exact position of the gauges, and characteristics of the gauge itself. Thus it is necessary to calibrate the gauges. This was done as follows.

The line was prepared first for a TVA run with all the traps in place and pumped to high vacuum. The Pirani gauges were set on zero against the "sticking vacuum" of a vacustat gauge. The line was isolated from the pumps, dry nitrogen was introduced and the line 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 were then brought into

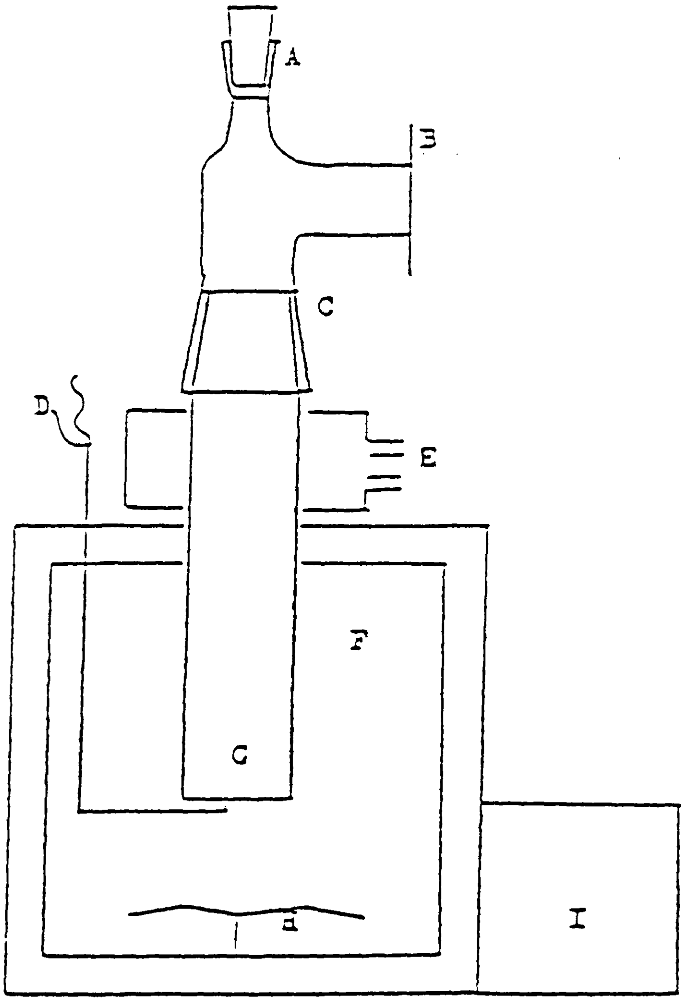


Fig. 2.4. Oven and Degradation Assembly.

A= B19 socket

B= Ground glass flange joint

C= B40 ground glass joint

D= Type K thermocouple

E= Water cooled jacket "cold ring"

F= Oven

G= Degradation tube

H= Fan

I= Programming module

coincidence by means of variable resistances. The line was then pumped down in steps, the coincidence of the output being checked at each stage. A final check was made by degrading a sample of potassium permanganate. This evolved oxygen which at the reduced pressure in use is non-condensable at -196 ^{o}C and thus passed through all five traps so that, 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, so that for quantitative analysis of degradation products calibration curves must be constructed.

The following designation for the individual trap traces of TVA curves employed in this work as standard.

————————	0 ^{o}C	(and colder traps if coincident)
··················	-45 ^{o}C	(and colder traps if coincident)
- - - - - - - -	-75 ^{o}C	(and colder traps if coincident)
— — — —	-100 ^{o}C	(and colder traps if coincident)
— · — · — ·	-196 ^{o}C	

In a single TVA experiment a considerable amount of information about product volatility and changes in product composition during the programme may be collected by means of a system with various cold traps at temperature from 0^{o} to -196 ^{o}C, in addition to data on number of stages of break down and their threshold and maximum rate temperature.[5]

When only totally volatile products and total -196 ^{o}C non-condensable products are recorded, the designation is as follows,

——————— Total volatile products

— · — · — · — Total -196 ^{o}C (non-condensable products)

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

2.1.4.3. Temperature Calibration.

The temperature recorded during the TVA experiment is that of thermocouple below the base of the degradation tube in the oven as shown in Fig. 2.4. This is always higher than the actual sample temperature of the interior of the base of the degradation tube due to a temperature differential across the tube base. To overcome these difficulties, a temperature calibration curve was obtained for the degradation tube.

A second type K thermocouple was inserted through the socket A of Fig. 2.4 until the junction was incontact with the tube base. A small bead of Apiezon L grease ws used to improve thermal contact. The system was evacuated and the oven heated in the normal fashion. Outputs from both oven and thermocouple were 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 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 and have to be repeated whenever an alteration in the position of the oven thermocouple or rewiring may alter the calibration.

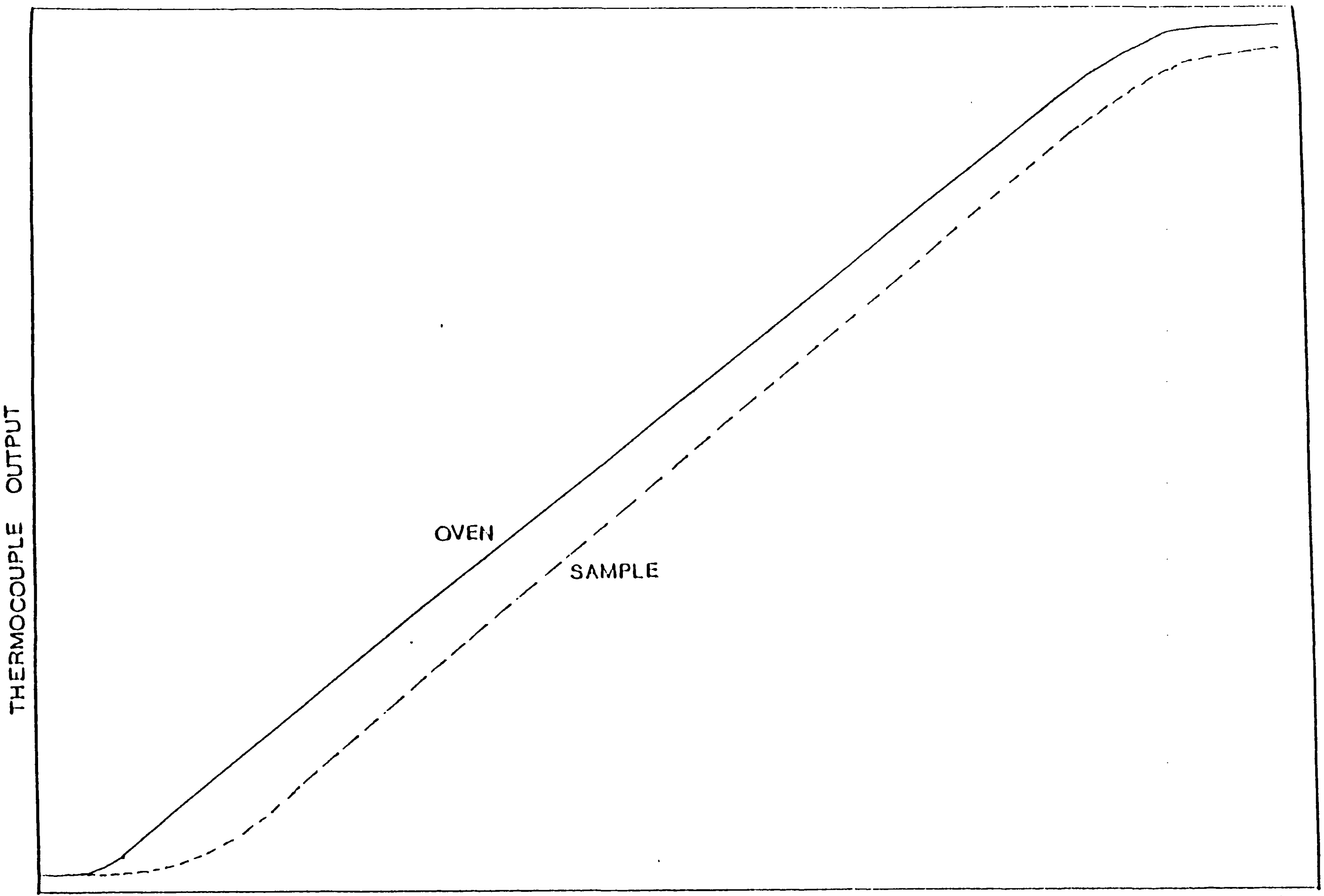


Fig. 2.5. Degradation Tube Temperature Calibration Chart.

In the present work two approaches have been used- programmed heating at 10 ^{o}C/min and isothermal heating for detailed study of colouration reaction in nitrile polymers.

2.1.4.4.Product Analysis.

A further advantage of the TVA apparatus is that the various product fractions from degradation of the polymer are available for further studies e.g. by spectroscopy. The collected volatile products from TVA degradation may be separated by controlled warming from -196 ^{o}C to ambient temperature of the trap containing degradation products, using pressure gauges of TVA system to monitor the volatilisation of each substance (Subambient TVA).[31]

The products arising from degradation of a polymer sample in the TVA apparatus can be divided into two main categories.

a. Involatile residue

b. Volatile products

2.1.4.4a. Involatile residue.

This is the involatile material left in the base of the TVA tube and it is usually insoluble. The residue may be removed from the base of the tube and analysed by IR spectroscopy. This can be achieved by grinding the insoluble material to a fine powder prior to forming a Nujol mull or KBr disc. Alternatively, a soluble residue can be dissolved in a suitable solvent and an IR spectrum can then be obtained by casting a thin film on a salt plate.

2.1.4.4b. Volatile products

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

(1) Products volatile at the degradation temperature but involatile at ambient temperature, deposited at the top of the degradation tube in the region cooled by water jacket. This type of product is described as cold ring fraction (CRF).

The cold ring fraction usually consists of high boiling chain fragments which may take the form of oils, tars and waxes. The CRF can be removed for analysis by swabbing with a tissue soaked in a suitable solvent and then depositing it on a salt plate. Alternative the CRF may be directly removed by scraping with a spatula and made into a KBr disc for IR spectroscopy.

(2) Products volatile at degradation and ambient temperatures but condensable at -196 ^{o}C, called condensables. These condensable products can be separated by subambient thermal volatilisation analysis (SATVA) (this technique is described in detail in section 1.5), and transferred to gas cell or cold finger (attached at point E in Fig. 2.3) for analysis by IR spectroscopy, mass spectrometry and gas chromatography.

3. The products volatile at liquid nitrogen temperature (-196 ^{o}C) are called non-condensable gases. Typically these are hydrogen, oxygen, carbon monoxide and methane.

The non-condensables are pumped through the cold trap system under the continuous pumping conditions of TVA system. These can be identified using an alternative closed system, which consists of IR gas cell and a cold trap to condense the less volatile substances. Such a typical system has been described by McNeill and Neil.[46] In the present studies, a quadrupole mass spectrometer was fitted on the TVA line between the main trap and pumping system (at point E in Fig. 2.3) and the non-condensables were allowed to bleed into mass spectrometer at this point.

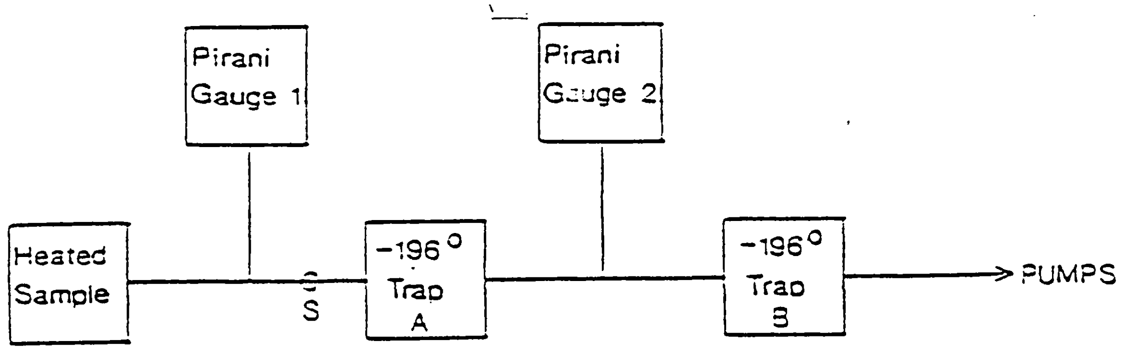
2.1.5. SUBAMBIENT THERMAL VOLATILISATION ANALYSIS.

During a TVA experiment, the degradation products can be separated into residue, cold ring fraction, condensable and non-condensable products. Valuable information on the mechanism of the degradation may be obtained by identifying the condensable products. The condensable products which are volatile at ambient temperature and condensable at -196 °C, can be further separated into different fractions. The technique through which these products are separated, was developed for use both in thermal and photodegradation studies by McNeill et al.,[31] who refer to it as subambient TVA (SATVA). This approach has also been used by Ackerman and McGill.[47-49] The technique is based on the separation of a frozen mixture using differences in component volatilities as compounds are warmed up in a controlled manner from -196 °C to ambient temperature under continuously pumped vacuum conditions.

The features of the SATVA system are shown in Fig. 2.6 The degradation products from the heated sample are condensed in the liquid nitrogen trap A while the entire system is evacuated continuously. The pressure of condensable volatile products as they evolve on degradation can be monitored using Pirani gauge 1 whilst Pirani 2 may 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, referred to as the subambient trap, as shown in Fig. 2.7, consists of a U tube and is surrounded by a pyrex glass vessel containing beads. The glass vessel is itself surrounded by a Dewar flask containing liquid nitrogen. The temperature of the U tube is measured by a thermocouple attached to it.

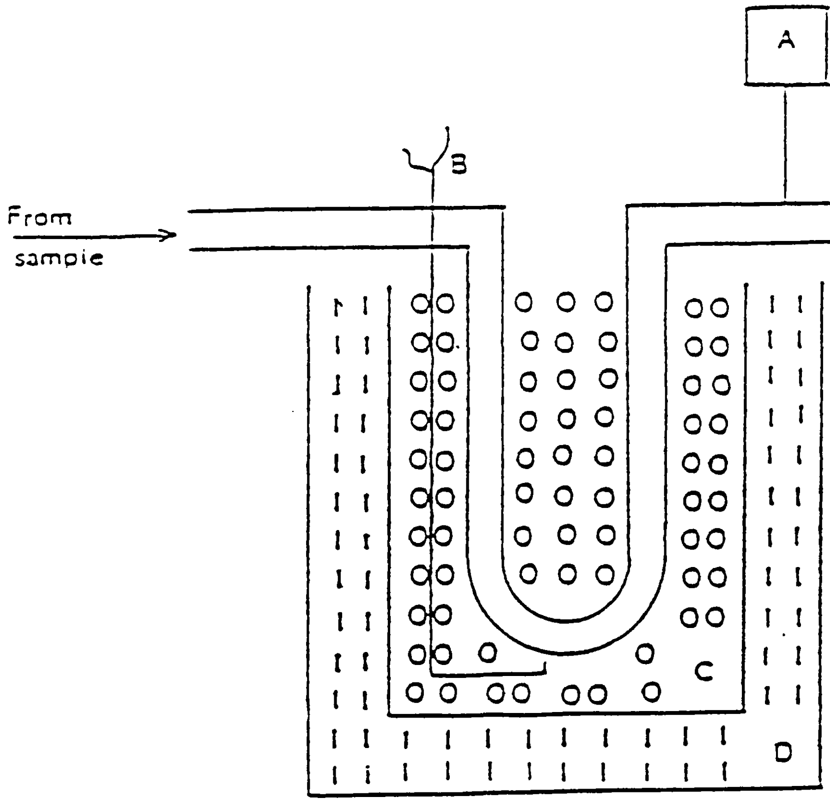
Once the condensable products have been collected, the stopcock S in Fig. 2.6 is closed, Pirani gauge 1 is switched off and the liquid nitrogen is removed from the subambient trap and placed around trap B. The subambient trap then warms up to ambient temperature. It is noticeable that the rate of warming is determined by the diameter of the surrounding jacket and the size of the bead used. Although not linear, the warming rate is reproducible for any given jacket. As the trap warms up, the condensable products distil from the trap A into trap B as the temperature becomes high enough for each product to vaporise. The pressure changes associated with the distillation of the products from trap A to trap B are measured by Pirani 2. Both Pirani output and temperature are recorded as a function of time to give a trace similar to the typical example shown in Fig. 2.8.

In general, resolution of the peaks can be enhanced by longer warm up times. This can be done by placing a chilled Dewar flask around the subambient trap. However in some cases peak overlap is unavoidable. Furthermore, a single peak may be due to simultaneous evolution of



S = Stopcock

Fig. 2.6. Principal Features for SATVA System.



A= Pirani Gauge

B= Type K Thermocouple

C= 25 mm Glass Beads in Pyrex Flask

D= Liquid Nitrogn

Fig. 2.7. Subambient Trap.

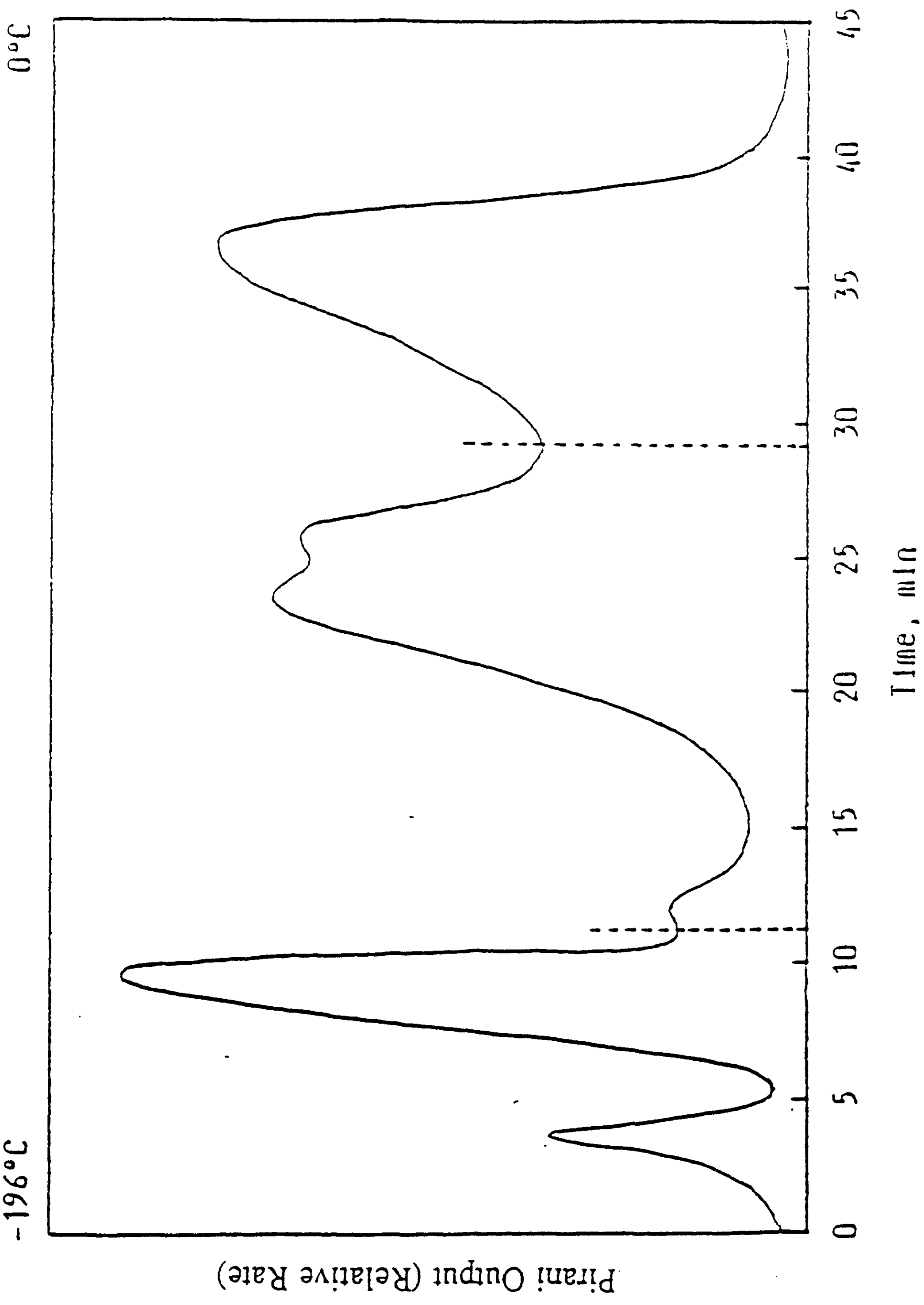


Fig. 2.8. Typical SATVA Curve.

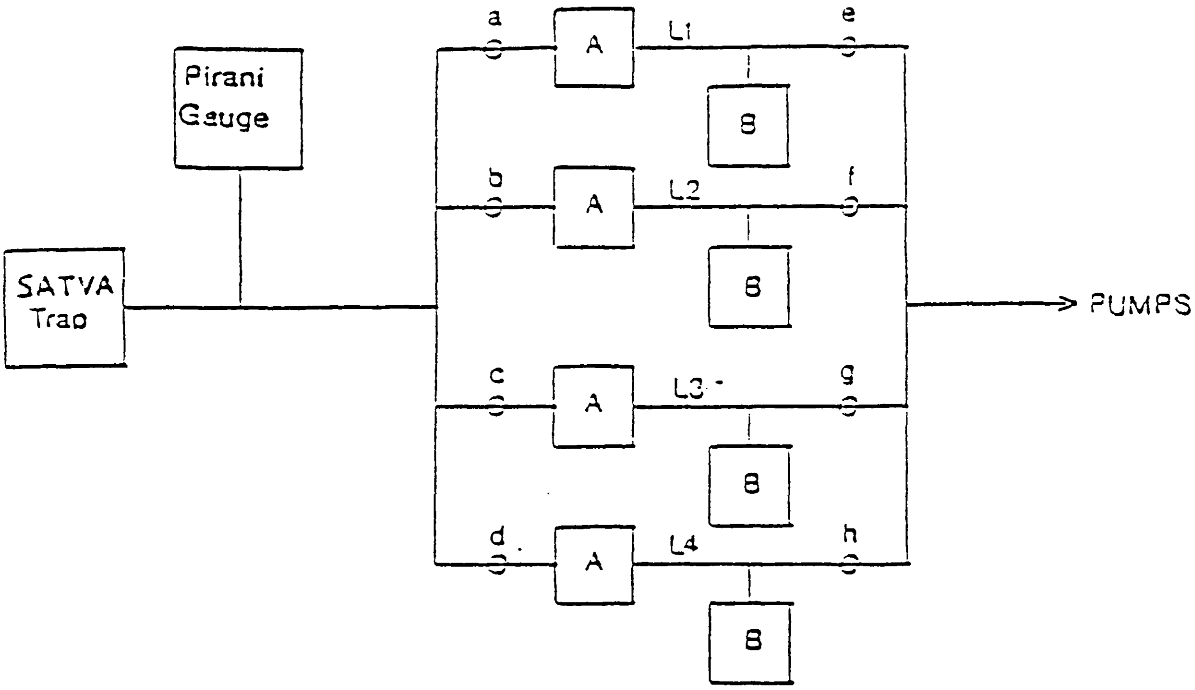
several materials of similar volatility. Despite these possible limitations, the technique is extremely useful and experimentally simple and convenient.

Isolation of products giving rise to a specific TVA peak may be achieved by use of a parallel limb system as shown in Fig.2.9. In this arrangement, taps b, c, d are initially closed and so any product distilling from B will pass down limb 1 and be condensed in the liquid nitrogen trap A. At the minimum point of the trough between subsequent SATVA peaks, tap b is opened and taps 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 pressure). Thus, the first peak product (s) are isolated in limb 1 whilst the second peak product (s) are collected in limb 2.

Further products may be collected in the limbs 3 and 4 by repeating this process in each limb. Once the products are isolated they may be removed for analysis by distilling the material from the -196 ^{o}C trap to a sample collection vessel, commonly a minimum volume gas cell or cold finger, attached to the limb at the take off points (marked B in Fig. 2.9).

2.1.6. COMPARISON OF THE TVA, TG AND DTA TECHNIQUES.

In general, for a complete understanding of thermal degradation process, no single thermal analysis technique is capable of supplying all the information required. Amongst the methods in this research TVA is the most versatile.



L1 - L4 = Limbs 1-4

A = -196 °C Trap

B = Take-off point

a - h = Stopcock

Fig. 2.9. System Employed for Isolation of Products via SATVA.

DTA analysis 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. However, it is necessary to have additional information from TG or TVA to fully interpret a DTA curve.

Although TVA, unlike TG, is only semiquantitative and is unable to record the evolution of these relatively less volatile materials which condense on the cold ring, it has several important advantages over TG. Along with providing valuable initial qualitative information, TVA can use considerably larger (but thinly distributed) samples which facilitates further analysis of all degradation products, particularly when coupled with SATVA.

Continuous evacuation of the degradation zone also aids the diffusion of volatile products from the sample and limits the possibility of secondary decomposition process.[50]

It is notoriously difficult to compare directly the temperatures of decomposition as recorded by different thermal analytical techniques due to the effects of the sample sizes and form, atmosphere and instrumental vagaries.[51]

In the present work, TG and DTA were performed under nitrogen atmosphere and TVA under high vacuum. In general, a T_{onset} or T_{max} temperature obtained from TG under atmospheric pressure will be higher than that obtained from the TVA due to earlier evolution of volatile in latter, high vacuum techniques. As TG measures all volatile products while TVA does not record CRF materials, this sometimes results genuine differences in T_{onset} and T_{max}.

2.2 ANALYTICAL TECHNIQUES

In conjunction with and in addition to the thermoanalytical techniques employed, a number of other analytical techniques were used in the present work which are mentioned as follows.

2.2.1. INFRARED SPECTROSCOPY.

Infrared spectra were obtained on a Philip PU 9800 FT-IR, Perkin Elmer 983 with P.E. 3600 data system and a Perkin Elmer 257 grating spectrometer.

Spectra of undegraded polymers, copolymers and involatile residues of degradation products were run as KBr discs. CRF spectra were obtained by dissolution in a suitable solvent and casting a film onto a salt plate (NaCl).

Volatile gaseous products of degradation were studied using gas cells equipped with 25 mm NaCl window as shown in Fig. 2.10.

Liquid degradation products separated by SATVA were collected in cold finger (Fig. 2.11) and examined as a film between two sodium plates. After the assignment of infrared absorption bands, the identification of degradation products was carried out by comparison of authentic samples.[54]

2.2.2. ELEMENTAL ANALYSIS.

The elementary analysis of polymers for carbon, hydrogen and nitrogen

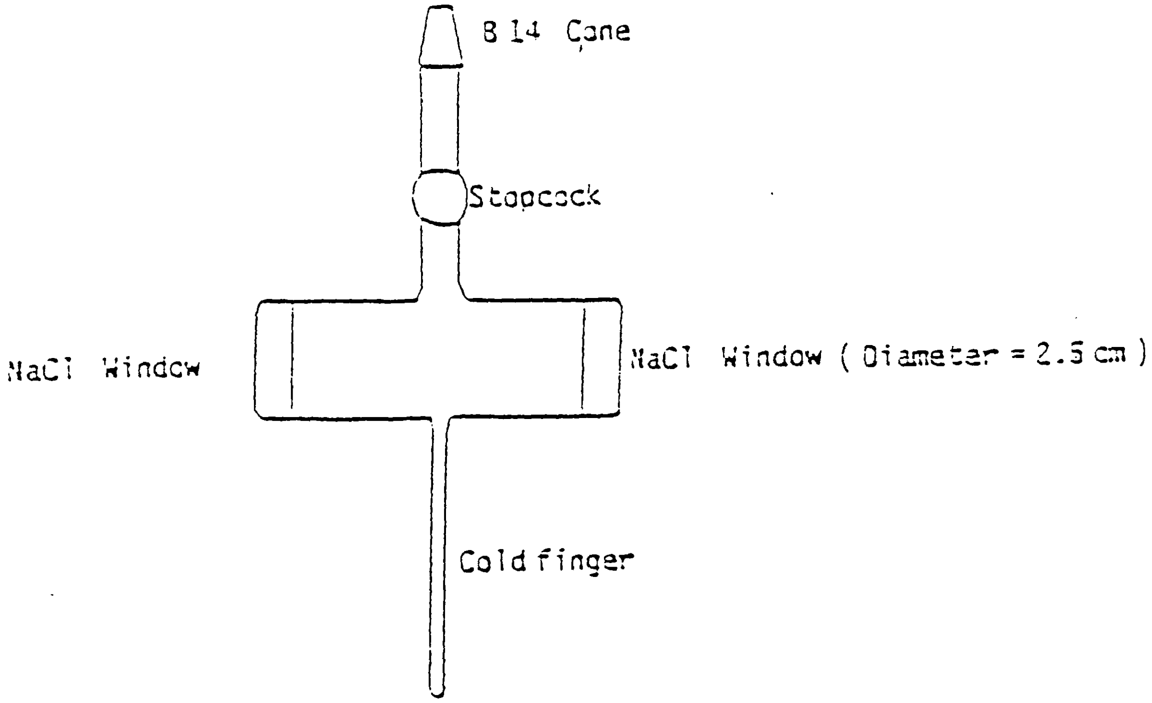


Fig. 2.10. Gas Cell for IR and Mass Spectrometric Analysis.

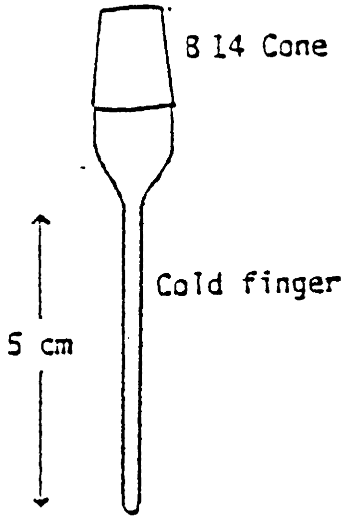


Fig. 2.11. Cold Finger for Liquid Fraction Collection and GC-MS Analysis.
Product.

was performed using a Carlo Ebra model 1106 Elemental Analyser.

2.2.3. MASS SPECTROMETRY.

A modified low resolution Kratos MS12 mass spectrometer with a VG Micromass DS 55 data handling system and a high resolution Kratos MS 9025 mass spectrometer with a Micromass DS 90 data handling system were used for identification of degradation products in the present work. In addition mass spectral analyses for TVA and SATVA systems were also obtained using a Leda-Mass quardrupole type mass spectrometer which was in turn linked to an APC computer for data storage and analysis. Non-condensable gaseous products evolved from the degradation may be bled into the mass spectrometer during the heating process. In addition, during fractionation of condensable products by SATVA, at each peak material may be bled into the mass spectrometer as it is evolved.

2.2.4. GAS CHROMATOGRAPHY-MASS SPECTROMETRY

In the present work, a Perkin Elmer Sigma 3 chromatograph interfaced to a Kratos MS 30 mass-spectrometer with DS 90 data handling system were used for separation and identification of volatile liquid products from polymer degradation.

By using this technique, excellent results have been obtained. Various columns which were used for the separation of the volatile liquid products are listed in Table 2.1.

Table 2.1. Columns used for the Separation of Volatile Liquid Degradation Products.

COLUMN	BP-10	DB-5
Column Packing	14% Cyanopropyl-dimethylsiloxane	5% Phenyl silicone
Polarity	Slightly polar	Polar
Length (mm)	25.0	15.0
Inside diameter (mm)	0.330	25.0
Film thickness (µm)	0.50	1.0
Gas carrier	He	He

2.2.5. GEL PERMEATION CHROMATOGRAPHY.

A service from the Polymer Supply & Characterisation Centre was the source to obtain number-average molecular weight ($\overline{M}n$) of various polymers studied. The following conditions and columns were used during gel permeation chromatography (GPC).

Columns	P.L. gel X mixed bed-B. 30cm, 10 microns.
Solvent	Dimethylformamide with 100 ppm LiBr.
Flow rate	1.0 ml/min.
Temperature	80 ^{o}C (nominal).
Detector	Refractive index (at 80 ^{o}C).

CHAPTER THREE

SYNTHESIS AND CHARACTERISATION OF HOMOPOLYMERS AND COPOLYMERS OF METHACRYLONITRILE

This chapter includes the preparation, purification, isolation and characterisation of various nitrile homopolymers and copolymers of methacrylonitrile. In the present investigation, various homopolymers have been synthesised, in particular, a set of methacrylonitrile polymers with reactive end structures for studying the colouration reaction[24] in a systematic manner. Methacrylonitrile homopolymers with reactive chain ends will be referred as end-initiated methacrylonitrile polymer, etc. and abbreviated to EIPMAN etc., with in the text.

Two different sets of methacrylonitrile copolymers with various ratios of the comonomer units were also prepared using methacrylic acid (MAA) and styrene, respectively, as other comonomer. These copolymers will be abbreviated in the text as COMAN/MAA and COMAN/Sty etc., respectively.

One copolymer of methacrylonitrile with maleic anhydride was also synthesised

3.1 SYNTHESIS

3.1.1 PURIFICATION OF MATERIALS

3.1.1.1 Methacrylonitrile

Methacrylonitrile (Aldrich Ltd.) was purified after being degassed by repeated freezing and thawing under vacuum by double distillation by the usual high vacuum line cold distillation technique, first into a tube calibrated in tenths of a cubic centimeter and finally into a dilatometer containing a known amount of the initiator.

3.1.1.2. Methacrylic Acid

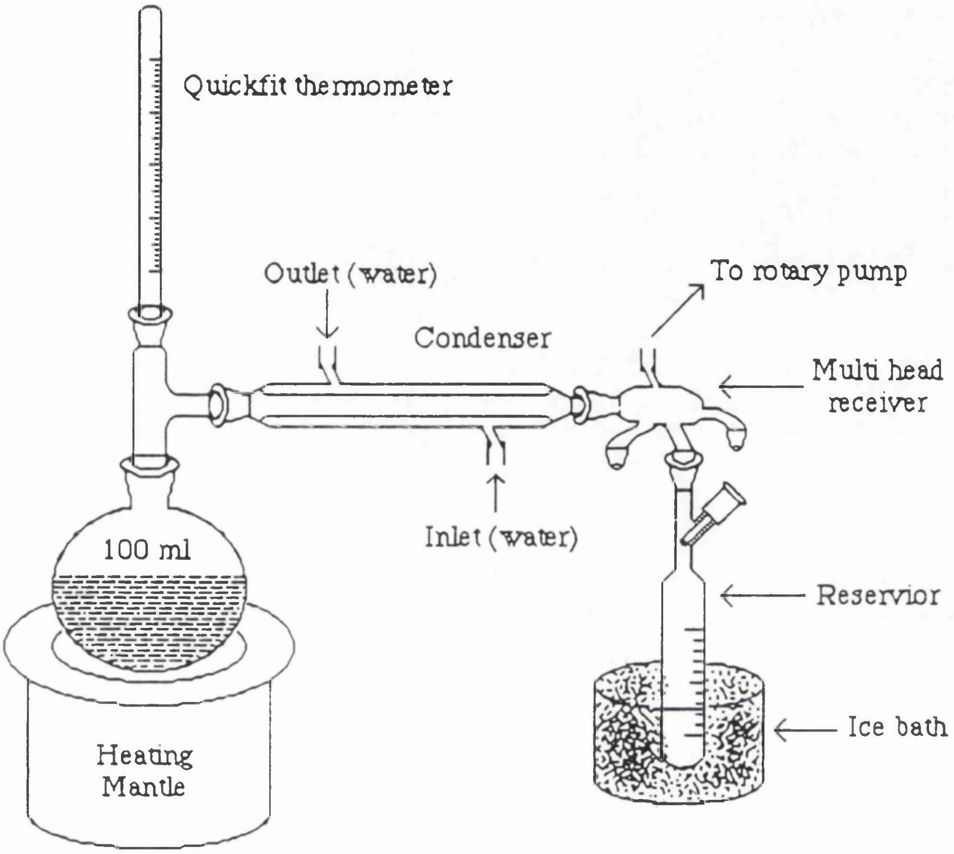
Methacrylic acid (Aldrich Ltd.) is usually supplied inhibited with 1000 ppm hydroquinone and 250 ppm hydroquinone monomethyl ether etc., and was purified to remove inhibitor before use.

Distillation was carried out at a reduced pressure at 60 ^{O}C in a 250 ml round bottomed flask fitted with a thermometer and condenser in which the multi head receiver was connected to the rotary pump as shown in Fig. 3.1. Boiling stones were used to avoid bumping. The first and last part of the distillate was rejected and only the middle fraction was collected for experimental purposes, it was stored at -15 ^{O}C prior to use.

3.1.1.3. Styrene.

When selecting a purification scheme for styrene monomer, it is

FIGURE 3.1 Apparatus for Methacrylic Acid Distillation.



necessary to consider its chemical reactivity towards the drying agents.[53]

For instance, violent polymerisation results from contact with strong acids such as phosphorus pentoxide and strong bases such as lithium aluminum hydride, while rapid polymerisation occurs in the presence of sodium metal.

Styrene monomer was washed twice with 5% aqueous sodium hydroxide in a separating funnel to remove inhibitor, then washed three times with distilled water to remove any traces of sodium hydroxide. It was dried over anhydrous calcium chloride during storage for 48 hours. It was then dried over finely divided anhydrous calcium sulphate for five hours and then overnight with calcium hydride in a refrigerator. Due to the tendency of the pure styrene to polymerise, it was finally distilled under high vacuum and degassed immediately prior to use.

3.1.1.4. Maleic Anhydride.

Maleic anhydride (Aldrich Ltd.) was purified by recrystallisation from chloroform, the solution being filtered hot to remove the insoluble impurities. The fine crystals were dried under vacuum and then kept over silica gel in a desiccator prior to use.

3.1.1.5 INITIATOR

3.1.1.5a. 2,2'- *Azobisisobutyronitrile*

2,2'-*Azobisisobutyronitrile* (AIBN) (BDH) was purified by recrystallising twice from absolute methanol, the solution being filtered hot to remove insoluble products of decomposition of the initiator.[54] The crystals were filtered off, dried under vacuum and kept in the dark at 0 °C.

3.1.1.5b. Benzoyl Peroxide

Benzoyl peroxide (BPO) was purified by dissolving the solid in the minimum volume of cold chloroform, removing the small aqueous layer, and pouring the solution into methanol. The fine crystals which precipitated were dried under vacuum at room temperature.

2.1.1.5c 4,4'-Azobis (4-cyanovaleric acid)

4,4'-Azobis(4-cyanovaleric acid) (ACVA) (Aldrich Ltd.) was used without any further purification.

3.1.2. PREPARATION OF METHACRYLONITRILE POLYMERS AND COPOLYMERS

Various homopolymers of methacrylonitrile with different initiators and copolymers with methacrylic acid, styrene and maleic anhydride were prepared by free radical polymerisation. The polymerisation reaction was carried out under vacuum. The procedure for preparation of various polymers and copolymers is described in detail as follows.

3.1 2.1 Preparation of Methacrylonitrile Homopolymers

Various homopolymers of methacrylonitrile using different initiators such as AIBN, BPO or ACVA were synthesised using the following procedure.

A dilatometer with known bulb volume and calibrated stem was used as a polymerisation vessel. Prior to use, the dilatometer was washed with cleaning fluid, distilled water, Analar acetone, and dried by pumping to high vacuum. It was also flamed out to remove any volatile materials adsorbed on the glass. An appropriate amount of initiator was introduced through a funnel into the reaction dilatometer. Any initiator sticking to the surface of the funnel stem was washed down with Analar acetone, which was then pumped off under high vacuum. Purified methacrylonitrile monomer kept in a graduated reservoir under vacuum was degassed thoroughly, then distilled by the usual high vacuum line cold distillation technique into the dilatometer, containing initiator, the first and last part of the distillate being rejected. The dilatometer was sealed off under vacuum.

3.1.2.2.Preparation of Methacrylonitrile Copolymers

3.1.2.2a. Methacrylonitrile/Methacrylic Acid Copolymers

Once the appropriate amount of methacrylonitrile had been distilled into the dilatometer containing initiator as described in the case of the homopolymer, the dilatometer containing initiator and methacrylonitrile monomer was then removed from the vacuum system and a measured quantity of pure methacrylic acid was added. This procedure was adopted since methacrylic acid cannot easily be distilled due to its low volatility and strong tendency to polymerise when freed from inhibitor. The mixture was finally degassed and sealed off under vacuum.

3.1.2.2b. Methacrylonitrile/Styrene Copolymers

Both monomers (methacrylonitrile and styrene) already purified, were distilled in turn by the high vacuum line cold distillation technique into a dilatometer containing initiator which was finally sealed off under vacuum.

3.1.2.2c. Methacrylonitrile/Maleic Anhydride Comonomer

A measured amount of recrystallised maleic anhydride monomer dissolved in a calculated amount of Analar acetone was poured into the dilatometer already containing an appropriate amount of purified initiator (AIBN). The mixture (maleic anhydride, acetone solution also containing AIBN initiator) was degassed and after a pressure of 10 $^{-5}$ torr was obtained, a suitable amount of methacrylonitrile was distilled under vacuum into the dilatometer which was then sealed off.

3.1.3. POLYMERISATION

The dilatometer was warmed up to room temperature for a few minutes to make the reaction mixture homogeneous. Polymerisation was carried out in a thermostat controlled ± 0·1 °C at the selected temperature. The progress of the polymerisation reaction was monitored by observing the fall in the level of reaction liquid in the graduated stem of the dilatometer.

The relationship between contraction and extent of polymerisation for methacrylonitrile, obtained by Grassie and Vance,[55] is given in Table 1.[55] It is assumed that the same relationship also holds for copolymerisations of methacrylonitrile in which a small proportion of an other monomer is present

Table 1[55]

Dilatometric Relationship

Temperature °C	% polymerisation / % contraction*
20	3.22
30	3.12
40	3.00
50	2.98
60	2.88
70	2.78
80	2.68

*Based on volume at 20 °C

The volume of contraction corresponding to extent of polymerisation reaction in any given case was obtained using the data of Table 1[55] and the equation.

$$Vc = V [1 + 0.001 (t - 20)] \%$$

where V = Volume of the monomer at 20 ^{o}C

t = Polymerisation temperature, ^{o}C

% = Extent of polymerisation required

F = % polymerisation/ % contraction (Table 1)

In general polymerisation was carried out up to 10% in case of pure polymers (homopolymers) and 5% in various polymers with exception of maleic anhydride copolymer, for which it was 12%.

Polymers (mostly homopolymers) with high molecular weights tend to separate during polymerisation and gradually form a tough gelatinous plug at the bottom of the dilatometer. There is no gel effect,[55] but the formation of this gelatinous material is undesirable due to the following reasons. Firstly, there may be the possibility of crosslinking and secondly, the attempts to dissolve the gelatinous plug in hot solvent may result in contamination of the polymer due to the reaction with oxygen present in the atmosphere, while the initiator and monomer are present at this stage. This difficulty can be overcome by shaking and stirring the reaction mixture during polymerisation. One way which was utilised in the present investigation to avoid gel formation consisted of placing the reaction dilatometer in a specially designed thermostated glass cylinder in which water was made to circulate from bottom to top and keep the dilatometer always shaking. Readings for following the extent of polymerisation were made by stopping the circulating water at the required intervals.

The polymerisation data for various homo- and copolymers of methacrylonitrile are given in Table 3.1

3.1.4 ISOLATION AND PURIFICATION OF MAN POLYMERS AND COPOLYMERS

All MAN homopolymers were precipitated by pouring the cooled reaction mixture (or mixture + acetone in case of less soluble polymers) into about ten times its volume of methanol. The polymer (PMAN) was dissolved in Analar acetone and again precipitated in Analar methanol for further purification. It was finally dried under vacuum at 40 ^{o}C.

Since the solubility changes towards precipitant as the proportion of methacrylic acid alters in copolymers of methacrylonitrile/methacrylic acid, it is difficult to isolate these copolymers in methanol. Petroleum ether was found to be the most satisfactory precipitant for this purpose. Methanol was also used as non-solvent for methacrylonitrile/styrene copolymers, whereas ethanol was found to be a more suitable precipitant for the methacrylonitrile/maleic anhydride copolymer.

3.2 COPOLYMER COMPOSITIONS

In order to evaluate the influence of a comonomer on the thermal degradation and colouration in methacrylonitrile polymers, it was felt desirable to study a range of composition in various copolymers. Copolymers of methacrylonitrile with other comonomers (methacrylic acid, styrene and maleic anhydride) with the required compositions were synthesised by determining the monomer feed for each comonomer using the published reactivity ratios and the copolymer

TABLE3.1 Polymerisation Data for Various Polymers and Copolymers of Methacrylonitrile.

Polymers & Copolymers	Initiator	Temp. of polymerisation	Percentage conversation
PMAN 16	AIBN 0.200%	60 °C	12
PMAN 59	AIBN 0.025%	60 °C	10
PMAN 49	BPO 0.020%	60 °C	10
EIPMAN 1	ACVA 0.2%	60 °C	10
EIPMAN 2	ACVA 0.5%	60 °C	9
EIPMAN 3	ACVA 1.0%	60 °C	10
EIPMAN 4	ACVA 1.5%	70 °C	10
EIPMAN 5	ACVA 2.0%	80 °C	8
COMAN/MAA 1	AIBN 0.7%	60 °C	5
COMAN/MAA 2	AIBN 0.7%	60 °C	5
COMAN/MAA 3	AIBN 0.7%	60 °C	5
COMAN/Sty 1	AIBN 0.7%	80 °C	5
COMAN/Sty 2	AIBN 0.7%	80 °C	6
COMAN/Sty 3	AIBN 0.7%	80 °C	6
COMAN/Sty 4	ACVA 0.7%	80 °C	5
COMAN/MalAn	AIBN 0.7%	60 °C	12

composition equation:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \frac{\left(r_1[M_1] + [M_2]\right)}{\left([M_1] + r_2[M_2]\right)} \qquad (3.1)$$

or

$$\frac{d[M_1]}{d[M_2]} = \frac{r_1\left([M_1]/[M_2]\right) + 1}{1 + r_2\left([M_2]/[M_1]\right)} \qquad (3.2)$$

where M_1 and M_2 are the two types of monomers and r_1 and r_2 are their respective reactivity ratios. The reactivity ratio may be defined as the ratio of the rate constant for a given radical adding its own monomer to that for its adding the other monomer.

In the form (3.1) and (3.2), the copolymer composition equation is expressed in terms of molar concentrations of the two monomers, $[M_1]$ and $[M_2]$. For practical application to copolymer formation, it is more convenient to express the equation in terms of mole fractions of one of the monomers.

By defining F_1 and F_2 as the mole fraction of monomers 1 and 2, respectively, in the copolymer, and f_1 and f_2 as the mole fraction of the respective monomers in the monomer feed, the molar proportion of the two monomers at any given instance may be represented as:

$$F_1 = \frac{d[M_1]}{d([M_1]+[M_2])}, \quad F_2 = \frac{d[M_2]}{d([M_1]+[M_2])}, \quad \frac{F_1}{F_2} = \frac{d[M_1]}{d[M_2]} \qquad (3.3)$$

when

$$f_1 = \frac{[M_1]}{[M_1]+[M_2]}, \quad f_2 = \frac{[M_2]}{[M_1]+[M_2]}, \quad \frac{f_1}{f_2} = \frac{[M_1]}{[M_2]} \qquad (3.4)$$

Using (3.3) and (3.4), the copolymer equation can be modified as (3.5)[3] or (3.6)

$$F1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1 2 + 2 f_1 f_2 + r_2 f_2^2} \qquad (3.5)^3$$

$$\frac{F_1}{1 - F_1} = \frac{r_1 f_1/(1-f_1) + 1}{1 + r_2(1-f_1)/f_1} \qquad (3.6)$$

The values of the reactivity ratios (r_1 and r_2) for methacrylonitrile/methacrylic acid and methacrylonitrile/styrene systems are available,[25,57] and are given below

For MAN/MAA system (calculated at 65 °C)[25]
$r_1=0.62 \pm 0.05$ and $r_2=1.64 \pm 0.05$

For MAN/Sty system (calculated at 80 ^{o}C)[57]
$r_1=0.26 \pm 0.05$ and $r_2 = 0.38 \pm 0.05$

The required monomer feed (f_1) for a particular copolymer was directely calculated from (3.5), taking F_1 as the required mole fraction of methacrylonitrile in the copolymer.

Monomer feed composition was also determined from the graph obtained by plotting a series of values of F_1 vs f_1 in (3.6). The F_1 vs f_1 curves for the MAN/MAA and MAN/Sty systems are reproduced in Figs. 3.2 and 3.3 respectively.

The copolymerisation data for MAN/MAA and MAN/Sty copolymers are listed in Table 3.2.

3.3 CHARACTERISATION

All polymers and copolymers of methacrylonitrile were characterised by various means such as elemental analysis, molecular weight determination by gel permeation chromatography (GPC) and infrared spectroscopy.

3.3.1 Elemental Analysis

The percentage of carbon., hydrogen and nitrogen from elemental analysis was obtained using a Carlo-Erba CHN Elemental Analyser. The percentage of oxygen in the case of methacrylonitrile copolymers with methacrylic acid and maleic anhydride was calculated by difference.

TABLE 3.2 Copolymerisation Composition Data for Various Copolymers of Methacrylonitrile.

Copolymer	Temp. of polymerisation	MAN composition ratios*	
		In monomer	In copolymer
COMAN/MAA 1	60 °C	72	45
COMAN/MAA 2	60 °C	41	25
COMAN/MAA 3	60 °C	16	10
COMAN/Sty 1	80 °C	35	10
COMAN/Sty 2	80 °C	1.21	1.0
COMAN/Sty 3	80 °C	0.042	.0.1
COMAN/Sty 4	80 °C	35	10
COMAN/MalAn	60 °C	1	3

* (molar ratios) Methacrylonitrile/Methacrylic Acid or
Methacrylonitrile/Styrene

Figure 3.2 Copolymer Composition Curve for the System Methacrylonitrile/Methacrylic Acid.

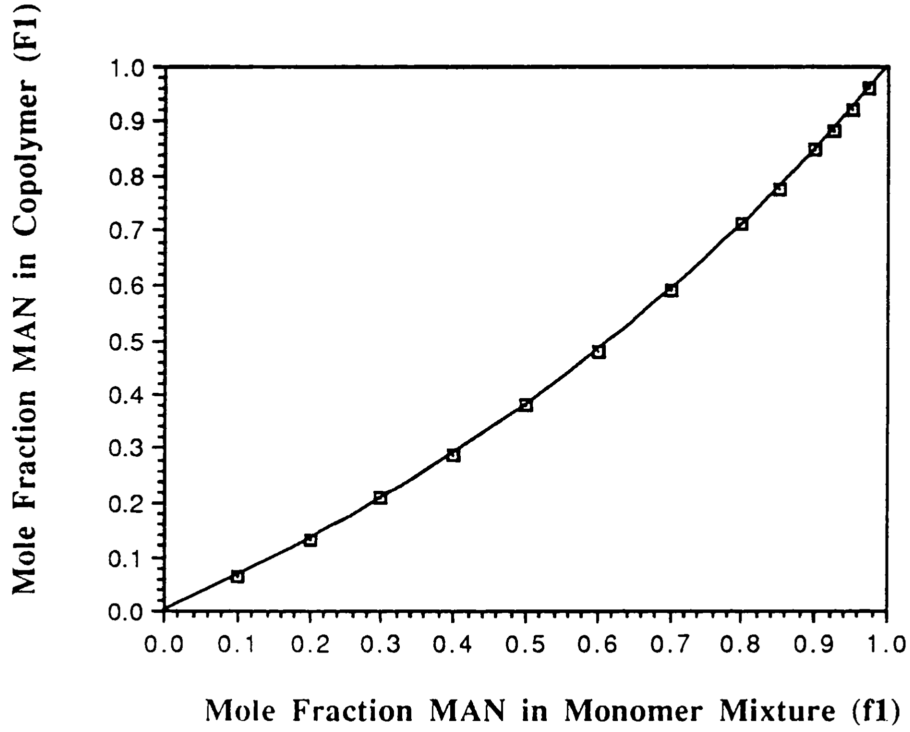
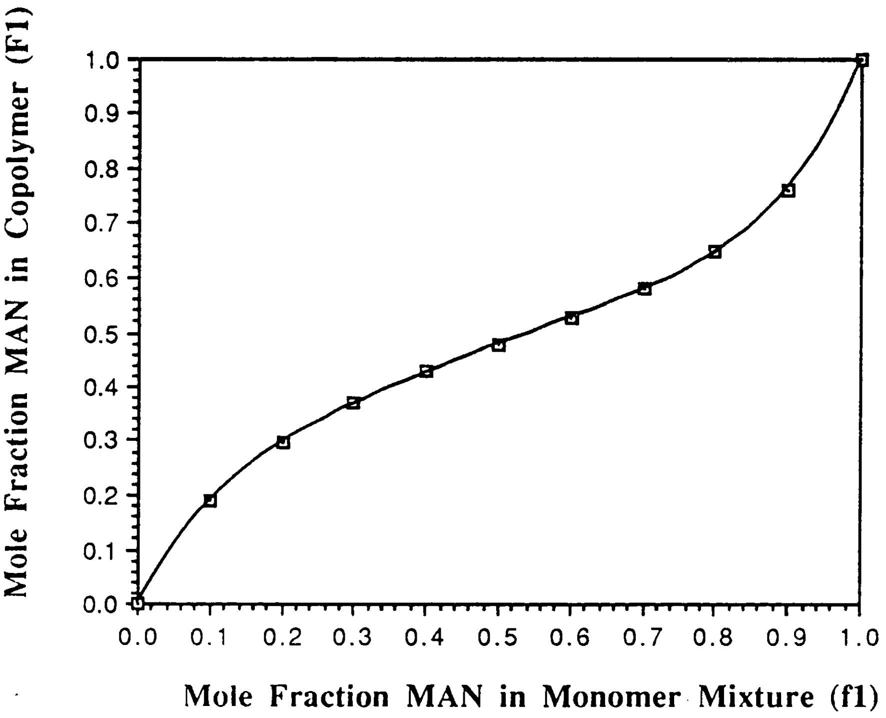


Figure 3.3 Copolymer Composition Curve for the System Methacrylonitrile/Styrene.



The elemental compositions (wt. % based on repeat units) of various methacrylonitrile polymers and copolymers are shown in Table 3.3. The microanalysis results are in good agreement with the theoretical values for each polymer sample.

3.3.2 Molecular Weight Measurements

Number-average molecular weights ($\overline{Mn}$) of the various homopolymers and copolymers of methacrylonitrile were obtained using gel-permeation chromatography through the services of Polymer Supply and Characterisation Centre, Rapra Technology Limited. The GPC results are summarised in Table 3.4.

3.3.4 Infrared Spectroscopy

All the polymers and copolymers of methacrylonitrile were also characterised by the FT-IR technique. The spectra are presented in Figs. 3.4 and 3.5., whilst the characteristic bands and their assignments are given in Table 3.5. The spectra of end-initiated MAN polymers and MAN/MAA copolymer are shown in Chapter Eight Figs. 8.1–8.6.

The IR spectrum of methacrylonitrile monomer differs from that of the homopolymer in the appearance of extra bands at 3010, 1623 and 965 cm^{-1}, which are due to υ(=C–H), υ(C=C) and δ(=C–H) respectively, and disappeared during the course of polymerisation.

In case of various methacrylonitrile end-initiated homopolymers and copolymers with methacrylic acid, the band at 1736 cm^{-1} (corresponding to acidic carbonyl stretching) shows relatively stronger

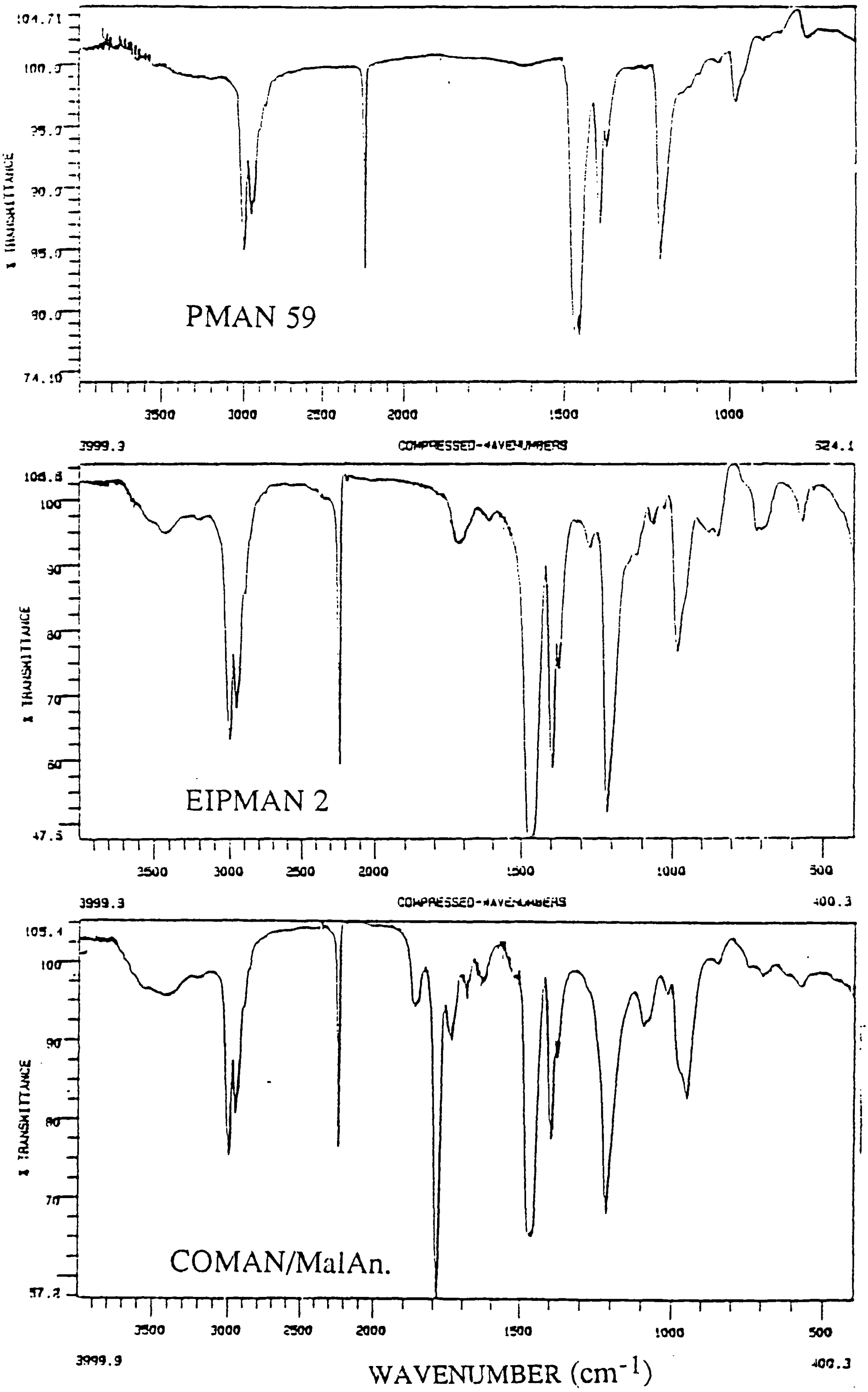


Fig. 3.4. FT-IR Spectra of Methacrylonitrile Homopolymers and Copolymer with Maleic Anhydride.

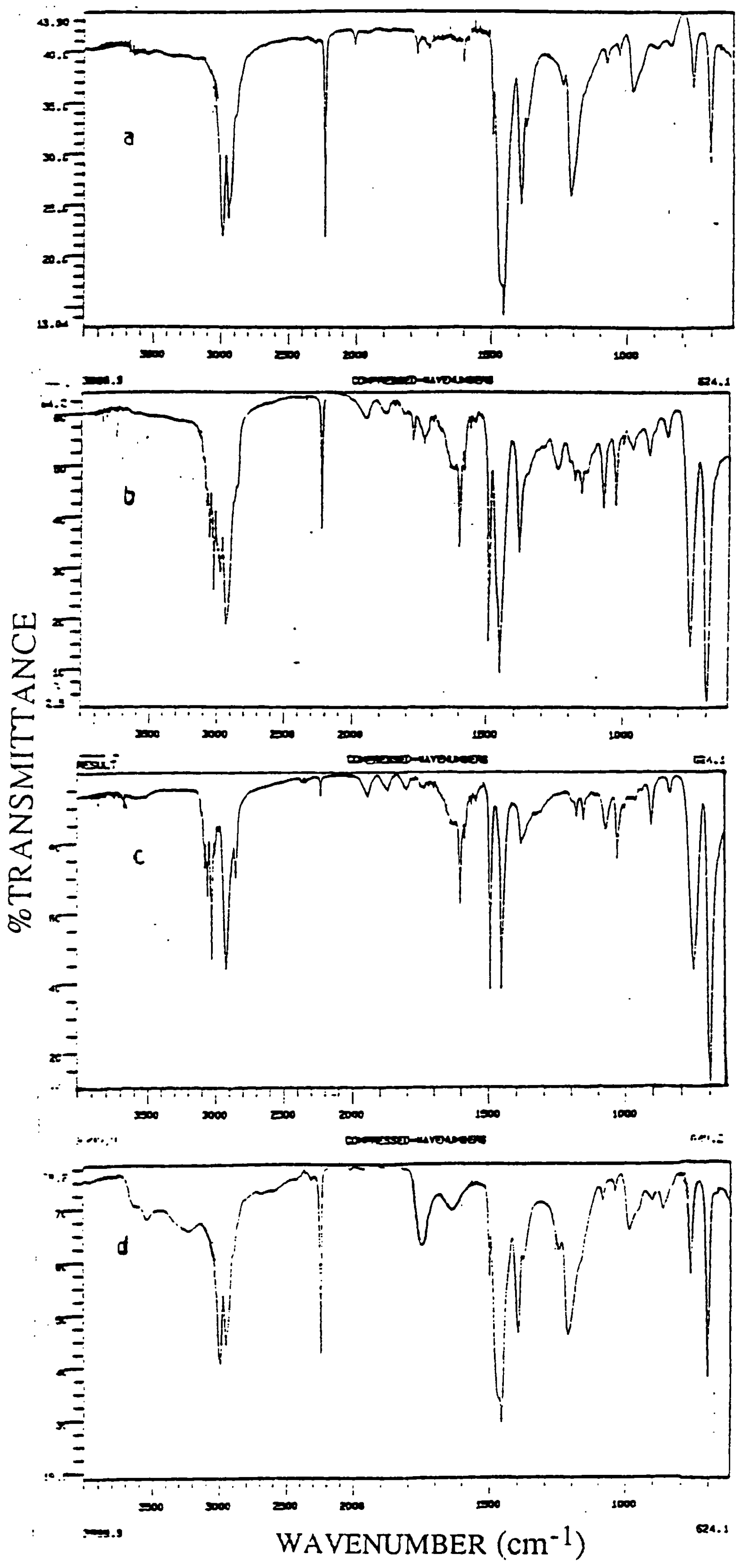


Fig. 3.5. FT-IR Spectra of Various Methacrylonitrile/Styrene Copolymers.

(a) COMAN/Sty 1(b) COMAN/Sty 2(c) COMAN/Sty 3(d) COMAN/Sty 4 absorption with decreasing molecular weight (in EIPMAN) or by increasing ratios of MAA units (in COMAN/MAA), respectively. A broad band in the 3280–2500 cm^{-1} spectral region is also noticeable in MAN/MAA copolymer which is due to the acidic O–H group of the methacrylic acid units. A medium intensity band at 1808 cm^{-1} and a strong band at 1760 cm^{-1} in the IR spectrum of COMAN/MalAn confirms the presence of cyclic anhydride units in the copolymer chain.

In case of COMAN/Sty, the characteristic IR band corresponding to styrene units (i.e., bands at 2820, 1600, 736 and 699 cm^{-1} etc.) become more significant with increasing proportion of styrene monomer, as expected.

TABLE 3.3 Elemental Analysis for Various Methacrylonitrile Polymers and Copolymers.

Polymer or Copolymer	Calculated				Observed			
	%C	%H	%N	%O	%C	%H	%N	%O
PMAN 28	71.64	7.46	20.90	——	71.58	7.53	20.87	——
PMAN 58	71.64	7.46	20.90	——	71.61	7.48	20.89	——
PMAN 49	71.64	7.46	20.90	——	71.55	7.43	20.84	——
EIPMAN 1	71.64	7.46	20.90	——	71.59	7.46	20.76	——
EIPMAN 2	71.61	7.45	20.86	——	71.55	7.42	20.72	——
EIPMAN 3	71.58	7.45	20.79	——	71.53	7.48	20.59	——
EIPMAN 4	71.45	7.45	20.59	——	71.35	7.46	20.48	——
EIPMAN 5	71.30	7.45	20.37	——	71.27	7.38	20.35	——
COMAN/MAA1	71.20	7.45	20.31	1.03	71.2	7.40	20.18	1. 2
COMAN/MAA2	70.87	7.44	19.87	1.82	70.5	7.35	19.56	2.1
COMAN/MAA3	69.84	7.41	18.52	4.23	69.38	7.42	18.36	4.4
COMAN/Sty 1	74.33	7.48	18.10	——	74.15	7.55	17.96	——
COMAN/Sty 2	84.20	7.61	8.18	——	83.05	7.74	8.26	——
COMAN/Sty 3	91.05	7.68	1.27	——	90.53	7.75	1.38	——
COMAN/Sty 4	74.33	7.48	18.10	——	73.85	7.55	17.86	——
COMAN/MalAn	64.21	5.69	14.05	16.05	64.35	5.7	14.31	15.64

TABLE 3.4. Molecular Weight Data for Various Homopolymers and Copolymers of Methacrylonitrile.

Polymer or Copolymer	$\overline{Mn}$ by GPC	$\overline{Mw}/\overline{Mn}$
PMAN 16	16000	1.713
PMAN 59	59000	1.822
PMAN 46	46000	1.780
EIPMAN 1	29020	2.183
EIPMAN 2	13800	1.981
EIPMAN 3	10980	1.852
EIPMAN 4	7150	1.780
EIPMAN 5	4260	1.327
COMAN/MAA 1	7325	2.010
COMAN/MAA 2	10720	1.980
COMAN/MAA 3	12830	1.953
COMAN/Sty 1	6990	1.397
COMAN/Sty 2	18010	1.630
COMAN/Sty 3	20210	1.784
COMAN/Sty 4	7918	1.393
COMAN/MalAn	25180	1.831

TABLE 3.5. Assignments of the Principle Peaks Present in the IR Spectra of Polymers and Copolymers of Methacrylonitrile

Infrared band (cm^{-1})	Assignment
2993—2845 s,m	Saturated C–H asymmetric and symmetric stretching for (CH_3) and (CH_2)
2235 s	Nitrile C≡N Stretching
2021 w	C=C=N Ketene imine stretching
1468 s	(CH_2) C–H Bending or scissoring
1454 s	(CH_3) C–H asymmetric deformation
1395 s	(CH_3) C–H symmetric deformation
1215 s	Distortion or backbone skeletal
980 s	(CH_3) Rocking
Extra bands present in various EIPMAN and COPMAN/MAA	
1735 s	>C=O Carbonyl C=O stretching
3250—2580 br	O–H stretching of acidic -OH group
Extra bands present in various methacrylonitrile/styrene copolymers	
3082, 3060 and 3026 m	Aromatic C–H stretching
2975 s and 2920 s	Saturated C–H stretch.
1600 s,1584 w and 1495 s	Aromatic ring C=C stretching
760 s and 700 s	Out of plane C–H deformation for mono-substituted ring
Extra bands present in methacrylonitrile/maleic anhydride copolymers	
1864 m and 1795 s	Typical cyclic anhydride C=O stretching
1225 s	Cyclic anhydride C–O–C sretching

Key: m=medium, s = strong, w = weak

CHAPTER FOUR

THERMAL DEGRADATION OF POLYMETHACRYLONITRILE

4.1 INTRODUCTION

The degradation behaviour of a polymer can often but not always be related to its structure. Polymethacrylonitrile (PMAN) which is derived from a 1:1 disubstituted monomer, would be expected by comparison with the behaviour of other polymers of this kind, to be capable of decomposing quantitatively to monomer.[6] The main features of thermal behaviour of polymethacrylonitrile have been known for many years, but certain aspects of degradation products and their mechanisms of formation still remain the subject of discussion. A brief survey of the literature is given here regarding the thermal behaviour of PMAN.

4.2 LITERATURE REVIEW OF THERMAL DEGRADATION OF POLYMETHACRYLONITRILE.

Early work on the thermal degradation of polymethacrylonitrile was carried out by Kern and Fernow.[58] They pyrolysed polymethacrylonitrile in air and reported a monomer yield of the order of 80% when polymer was heated to 350 °C. They also found that polymer softened at 110-120 °C and colouration was observed in the 120–220 °C temperature range. Monomer production was observed above 220 °C.

Beaman[59] prepared polymethacrylonitrile anionically and found the physical and chemical properties of the polymer to correspond with those reported by Kern and Fernow.[58]

Grassie and Vance[60] thermally degraded polymethacrylonitrile under high vacuum conditions. They confirmed Kern and Fernow's observation, but these authors were not able to obtain more then 65% yield of monomer. McCartney[61] also reported colouration in nitrile polymers when heated or when base is added to the polymer solution. Pendant nitrile groups cyclisation was suggested to be the reason for colouration.

The thermal behaviour of polymethacrylonitrile was extensively examined by Grassie and McNeill.[24-26, 62] They found[24] that the colouration which occurs in polymethacrylonitrile, can be avoided by careful purification of the monomer and polymerisation in the presence of 2,2'-azobisisobutyronitrile under vacuum. Such polymers depolymerised to give quantitative yield of monomer and hence can be studied without the complication colouration.

Grassie and McNeill[25] also studied the colouration reaction in polymethacrylonitrile in much detail. Copolymers of different compositions of methacrylonitrile with small amount of methacrylic acid were used for this purpose and isothermal studies at 140 °C were carried out. These authors established from these studies that colouration reaction is initiated by certain types of impurities (which were methacrylic acid in these cases) and propagated through adjacent nitrile group resulted in formation of conjugated double bond of naphthyridine type structures.

In their further investigations,[26, 62] Grassie and McNeill reported the presence of some structural abnormalities in the polymer chain called ketene-imine structures, ($-CH_2-C(CH_3)=C=N-$), presumely formed during the polymerisation by reaction of the growing polymer radical through the cyanide group as ($-CH_2-C(CH_3)=C=N-$). These ketene-imine structures, were reported to disappear on heating to 120 °C in a second order reaction whose rate is strongly dependent upon the viscosity of the medium.

From these studies,[24–26,62] these authors finally concluded that polymethacrylonitrile undergoes three quite distinct reactions in the temperature ranges 20-120,120--220 °C and above 220 °C. In the lower temperature ranges ketene-imine structures disappear with a limited decrease in molecular weight. Above the softening point rapid colouration occurs and is attributed to progressive linking up of adjacent nitrile groups to from conjugated structure.

Above 220 °C depolymerisation was reported to occur and monomer yields approaching 100% can be attain provided the colouration reaction is suppressed by careful purification of monomer from which the polymer is prepared. The depolymerisation process was proposed[26] to be similar to that of poly(methyl methacrylate).

Nakamura et al.[63] investigated by various thermoanalytical techniques the intramolecular samples using various radically initiated and anionically initiated homopolymers along with methacrylonitrile/methacrylic acid copolymers.

It was reported that anionically initiated polymethacrylonitrile sample and MAN/MAA copolymers degrade in a single stage whereas radically initiated polymers were observed to decompose in two stages with an inflection point at about 330 °C. For radically initiated samples, the first stage of thermal degradation was thought to be at the unsaturated chain ends formed as a result of termination by disproportionation and the second stage decomposition at higher temperature due to random chain scission in the polymer. The anionically initiated samples without terminal double bonds were reported to be decomposed exclusively by random scission in a single stage.

Grassie and McGuchan[64] made comparative studies of thermal behaviour of polyacrylonitrile with that of its α- substituted polymers (polymethacrylonitrile etc). These authors noticed a two stage degradation for radically polymerised low molecular weight polymethacrylonitrile during their TG and DTA analysis. This behaviour (two stage decomposition) of PMAN was also reported by McNeill[45] when he thermally degraded PMAN by thermal volatilisation analysis (TVA).

During their comparative studies,[64] Grassie and McGuchan also mentioned that even when some colouration occurred in PMAN, no exothermicity due to nitrile cyclisation was observed which might have been expected by analogy with PAN. In case of PMAN it was suggested that the exothermicity attributed to cyclisation was masked by endothermic fusion and depolymerisation. It was concluded that the preferred degradation process in PMAN is depolymerisation to monomer.

Bashir et al.[65] have recently claimed intermolecular linking of C=N groups in PMAN is more important than the intramolecular reaction, in both base induced and thermal colouration in PMAN, basing their reasoning mainly on the absence of a DSC exotherm in PMAN compared with PAN. The absence of an exotherm, however does not establish that crosslinking is occurring.

4.3 AIM OF THIS WORK

In the present work, the programmed thermal degradation of high and low molecular weight polymethacrylonitrile (PMAN) has been investigated using TVA, DTA, TG and DTG technique to provide a basis for a series of studies of different type of PMAN and copolymers of methacrylic acid, styrene and maleic anhydride using the same experimental approach.

Quantitative measurements of the main product fractions (liquid fraction and residue) have been made. The condensable products from the TVA degradation have been analysed by IR, MS and GC-MS techniques.

Non-condensable products during TVA degradation were identified by using the mass spectrometer attached to TVA apparatus.

4.4 PROGRAMMED THERMAL DEGRADATION

The thermal behaviour of two polymethacrylonitrile samples (high and low molecular weight) prepared by bulk polymerisation using AIBN initiator, and a sample of polymethacrylonitrile made with benzoyl peroxide initiator have been investigated using TVA, DTA, TG and DTG techniques. The poly(methacrylonitrile) samples were prepared as described in chapter three and their origin is listed in Table 4.1.

4.4.1. THERMAL VOLATILISATION ANALYSIS.

The polymers were examined as 50 mg powder samples in a TVA

TABLE 4.1 Origin of the Methacrylonitrile Homopolymers used in this Investigation.

Polymer	Initiator	Temperature of polymerisation	$\overline{M}$n by GPC
PMAN 16	AIBN O.200%	60 °C	16320
PMAN 59	AIBN 0.025%	60 °C	59710
PMAN 49	BPO 0.020%	60 °C	49080

$\overline{M}$n	Number-average molecular weight
AIBN	2-2'-Azobis-isobutyronitrile
BPO	Benzoyl peroxide

system under vacuum conditions as described in chapter two. Programmed heating was carried out at a rate of 10 ^{o}C/min. The TVA curves for the polymers PMAN 16 ($\bar{M}n$=16000, AIBN initiated) PMAN 59 ($\bar{M}n$= 59,0000, AIBN initiated) and PMAN 49 ($\bar{M}n$=49,000, BPO initiated) are shown in Fig. 4.1 (a, b and c) respectively.

It is clear from TVA curves of PMAN 16 PMAN 59 and PMAN 49 that in each case decomposition begins at above 250 ^{o}C and appreciable rate of break down is observed near 315 ^{o}C and 380 ^{o}C. All polymers show a two stage decomposition but the decrease in the height of first degradation peak (T_{max} 310–320 ^{o}C) with increasing molecular weight being particularly noticeable. In all three samples of PMAN, -196 ^{o}C and -100 ^{o}C traces are well separated from rest of the traces (0, –45 and -75 ^{o}C) and near the base line until 300 ^{o}C, after which these show a very small response. This indicates the formation of some non-condensables at the later stage of degradation.

On the basis of TVA data, results for PMAN 59 and PMAN 49 are almost the same, not just in respect of $T1_{max}$ at 318 ^{o}C, and $T2_{max}$ at 381 ^{o}C and 377 ^{o}C respectively, but also in the character of their degradation products as shown by their volatility in TVA system. However low molecular-weight PMAN 16 shows a more distinct two stage decomposition and a relatively lower $T1_{onset}$ at 250 ^{o}C which is 263 ^{o}C and 257 ^{o}C for PMAN 59 and PMAN 49 respectively. Comparative data for TVA analysis for these polymers are given in Table 4.2.

Gravimetric data were obtained during TVA experiment in which the polymer sample was placed in a thin glass flat bottomed sample tube weighed before and after the TVA experiment. The sample tube was placed in side the tube and in contact with its flat base. Data are shown

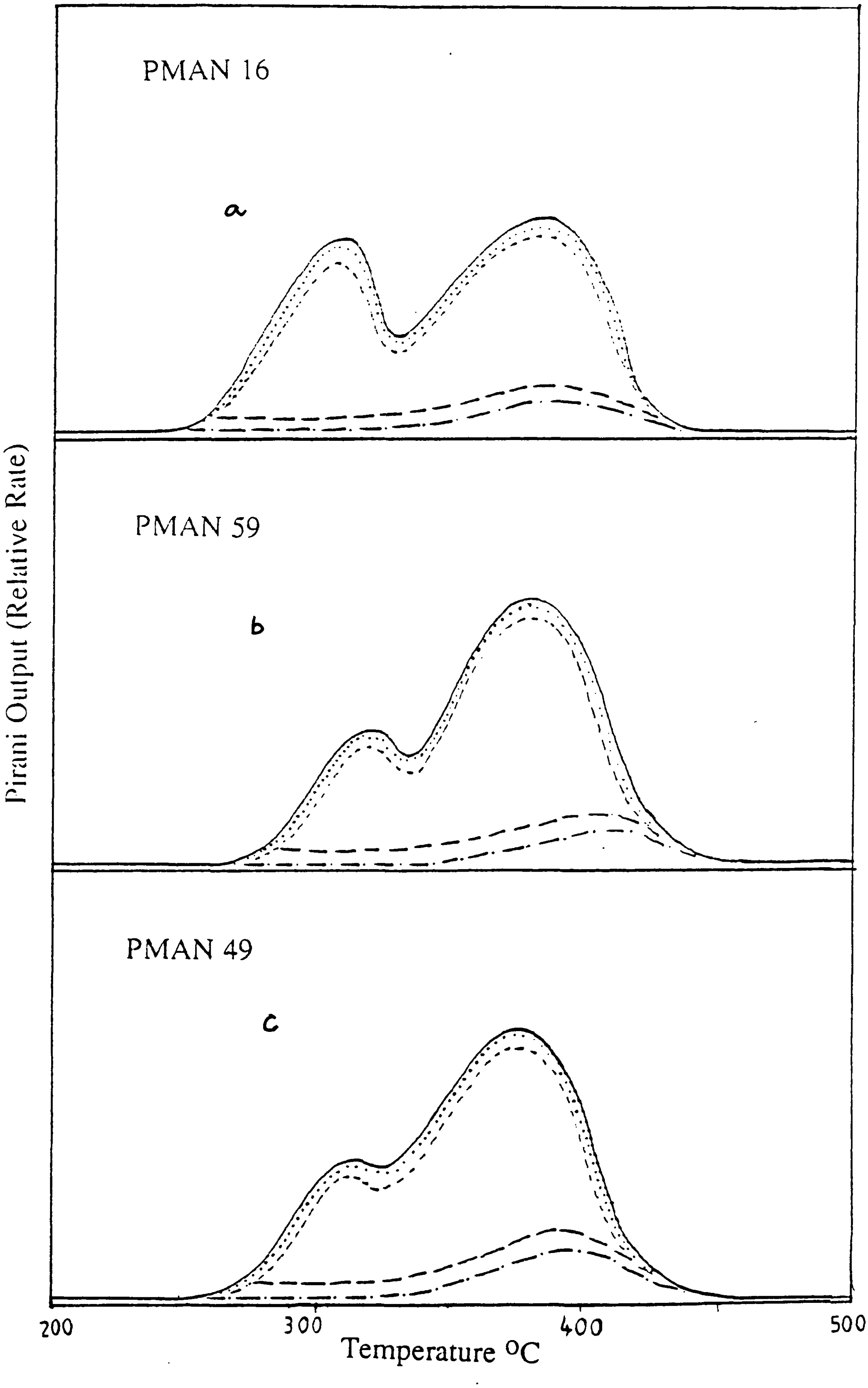


Fig. 4.1. TVA Curves for Various MAN Homopolymers under Vacuum, Heated at 10 °C/min to 500 °C.

Key: 0 °C —, -45 °C ····, -75 °C - - , -100 °C – – , -196 °C – · – ·

TABLE 4.2 Comparative TVA Data for Polymethacrylonitrile Samples.

Polymer	$T1_{onset}$ (^{o}C)	$T1_{max}$ (^{o}C)	$T2_{onset}$ (^{o}C)	$T2_{max}$ (^{o}C)
PMAN 16	250	309	330	381
PMAN 59	261	320	334	381
PMAN 49	257	315	335	377

in Table 4.3.

4.4.1.1.Subambient thermal volatilisation analysis.

Condensable volatile degradation products from polymer samples degraded to 500 ^{o}C using TVA technique, collected in a liquid nitrogen trap (−196 ^{o}C) in the vacuum system, were separated by SATVA[31] method, (subambient thermal volatilisation analysis) by allowing the trap to warm up from -196 ^{o}C to ambient temperature in a controlled manner, with continuous removal of volatile products monitored by following the pressure changes using a Pirani gauge. A quadrupole mass spectrometer was also coupled to system and products were bled into it, as they volatilised from the cold trap.

The SATVA traces for this product fraction from PMAN 59 and PMAN 49 are shown in Figs. 4.2 and 4.3, respectively. The SATVA trace for PMAN 16 was identical to SATVA trace of PMAN 59.

4.4.1.2 Product analysis.

The various degradation products consisting mainly of liquid fraction, together with small amount of condensable gases and non-condensable gases were examined after degradation of each sample under TVA conditions. The -196 ^{o}C condensable products of degradation, separated by SATVA technique were collected in gas cells and cold finger. The non-condensable gases were bled to the quadrupole mass spectrometer during the TVA experiment. The degradation products were examined by IR, MS and GC-MS since the interpretation was difficult as each fraction contains a mixture of products so it was required to use several techniques. In this investigation condensable gaseous products were

TABLE 4.3 Gravimetric Data for Polymethacrylonitrile Degradation in the TVA System under Vacuum Using Programmed Heating to 500 ^{o}C.

Polymer	Liquid Fraction	Gaseous Products	Residue
PMAN 16	99%	> 1%	> 1%
PMAN 59	98%	< 1%	> 1%
PMAN 49	94%	2%	4%

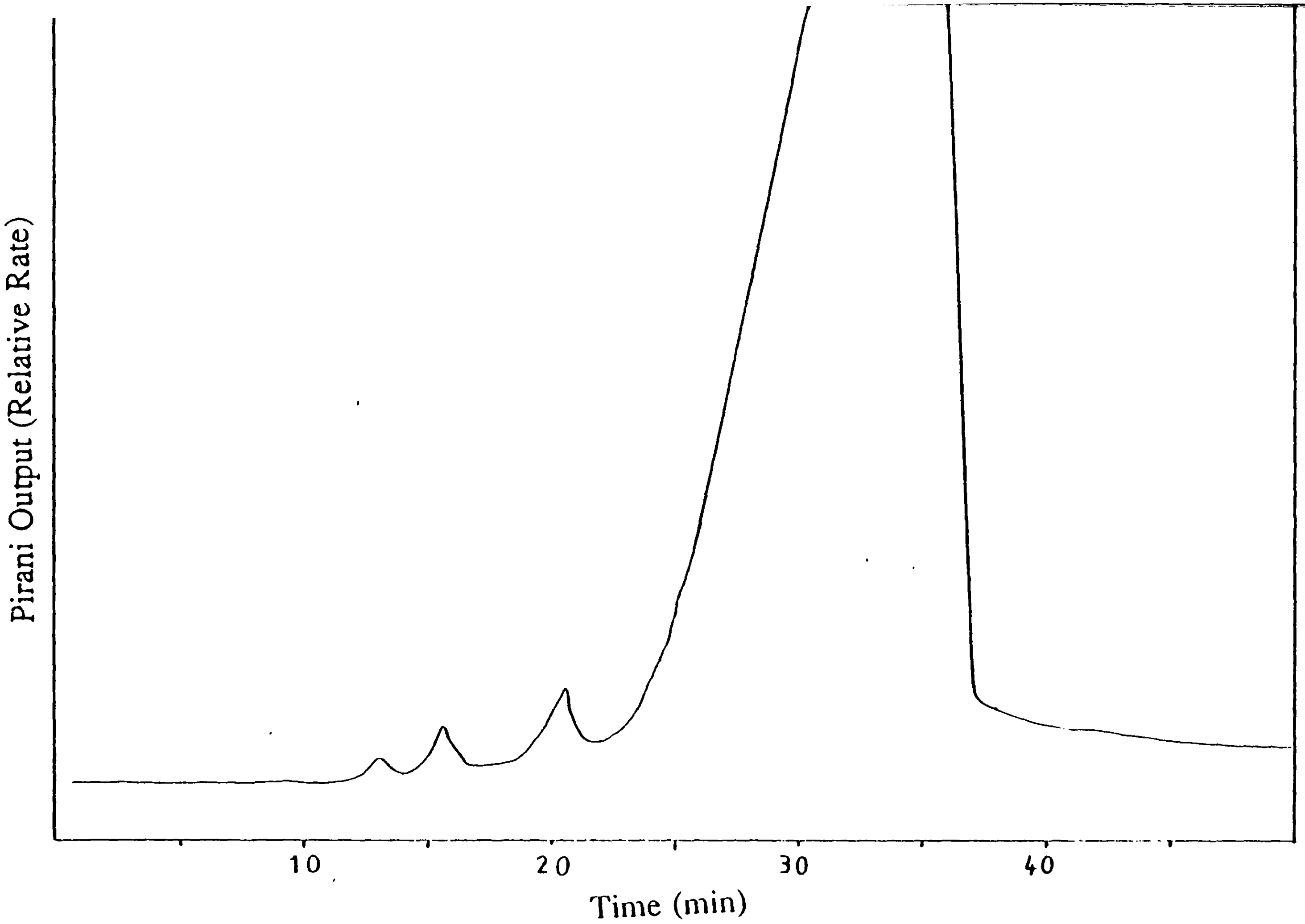


Fig. 4.2. SATVA Curve for Condensable Product Fraction from Degradation to 500 ^oC under TVA Conditions of PMAN 59.

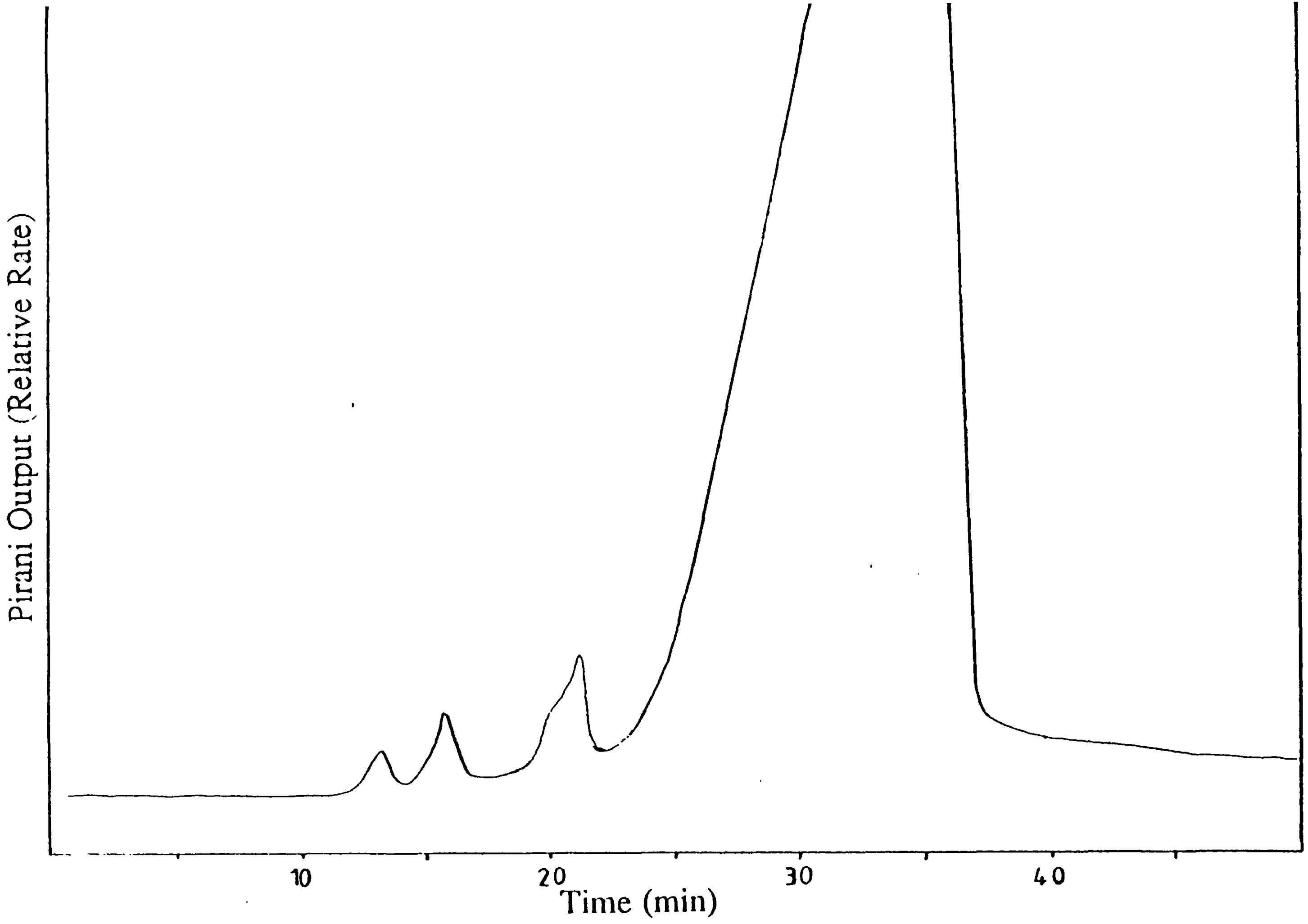


Fig. 4.3. SATVA Curve for Condensable Product Fraction from Degradation to 500 ^{o}C under TVA Conditions of PMAN 49.

analysed by IR and MS while the liquid fraction was examined by GC-MS as well. The degradation products identified by these techniques are listed in Table 4.4.

4.4.1.2a Residue.

There was no significant amount of residue left in case of PMAN 16 and PMAN 59. A small black char was obtained as residue from degradation of PMAN 46.

4.4.1.2b Cold Ring Fraction.

No cold ring fraction (CRF) was obtained during thermal degradation of any of the polymethacrylonitrile samples used in this investigation.

4.4.1.2c Condensable products as liquid fraction

The IR spectra of the liquid fractions from degradation of each of the homo polymers discussed in this chapter, Fig 4.4 suggests that only the monomer (methacrylonitrile) is present. The liquid fractions were also subjected to GC-MS.

Instrumental conditions during GC-MS were as follows.

Injector temperature 250 ^{o}C, Voltage 70 ev, column temperature initially 50 ^{o}C for 10 min to 200 ^{o}C, helium gas flow rate 10 ml/min.

Monomer was confirmed as the only major product in all three cases. Trace amounts of other products such as 2-cyanobutane and 4-cyano-2methyl-1-pentene were also identified. A typical GC trace is reproduced in Fig. 4.5.

TABLE 4.4 Total Degradation Products Identified from Poly (methacrylonitrile) Samples to 500 ^{o}C using TVA Conditions.

Polymer	Non-condensable gases	Condensables		Residue
		Gases	Liquid fraction	
PMAN 16	Methane	Isobutene Hydrogen-cyanide Ethane	Methacrylonitrile	Absent
PMAN 59	Methane	Isobutene Hydrogen-cyanide Ethene	Methacrylonitrile	Absent
PMAN 46	Methane	Carbon dioxide Isobutene Hydrogen cyanide Propene	Methacrylonitrile	Black char

All products except monomer were found in trace amount

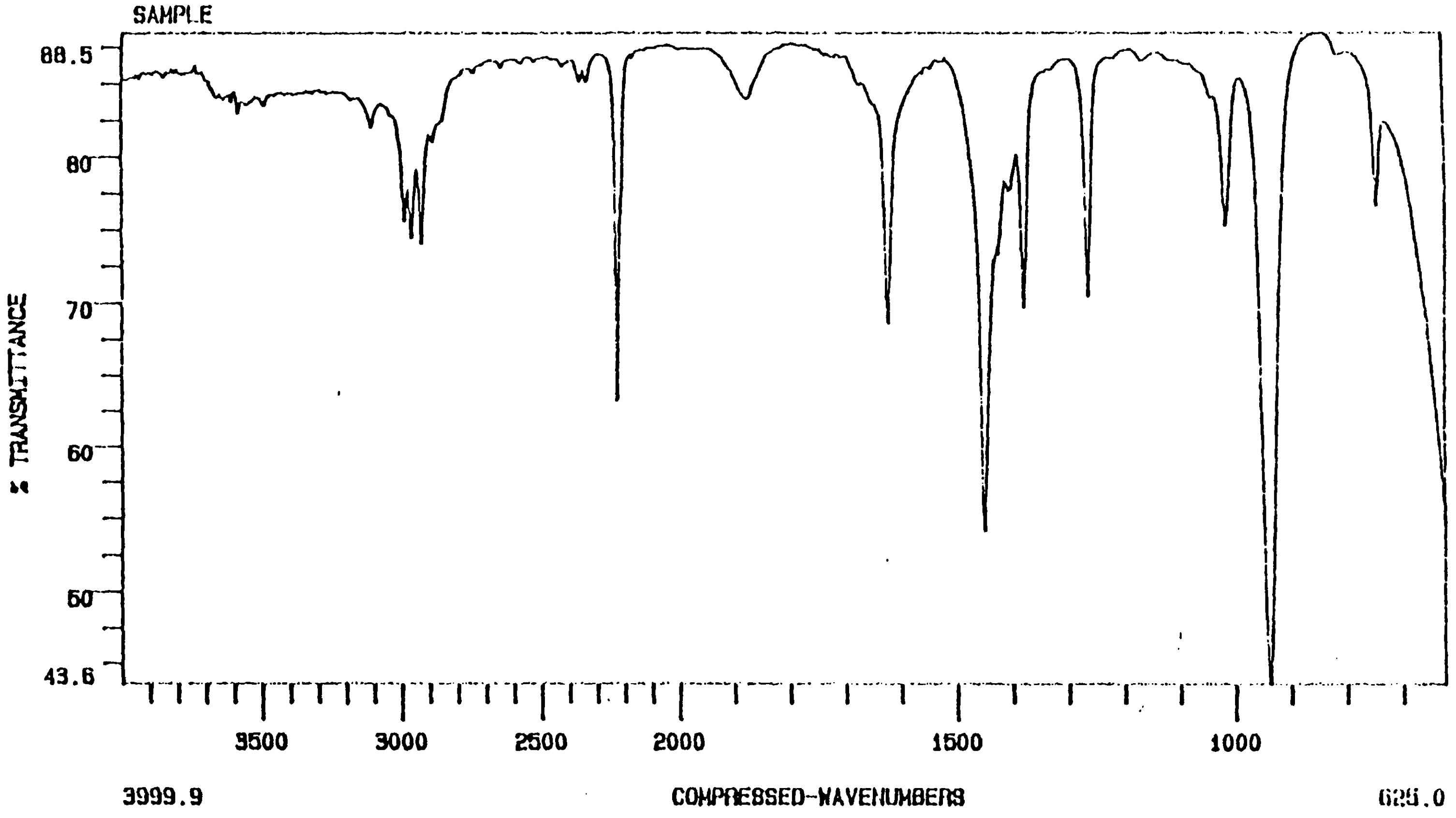


Fig. 4.4. Infrared Spectrum of Liquid Fraction from Degradation of PMAN 16 to 500 °C under TVA Conditions.

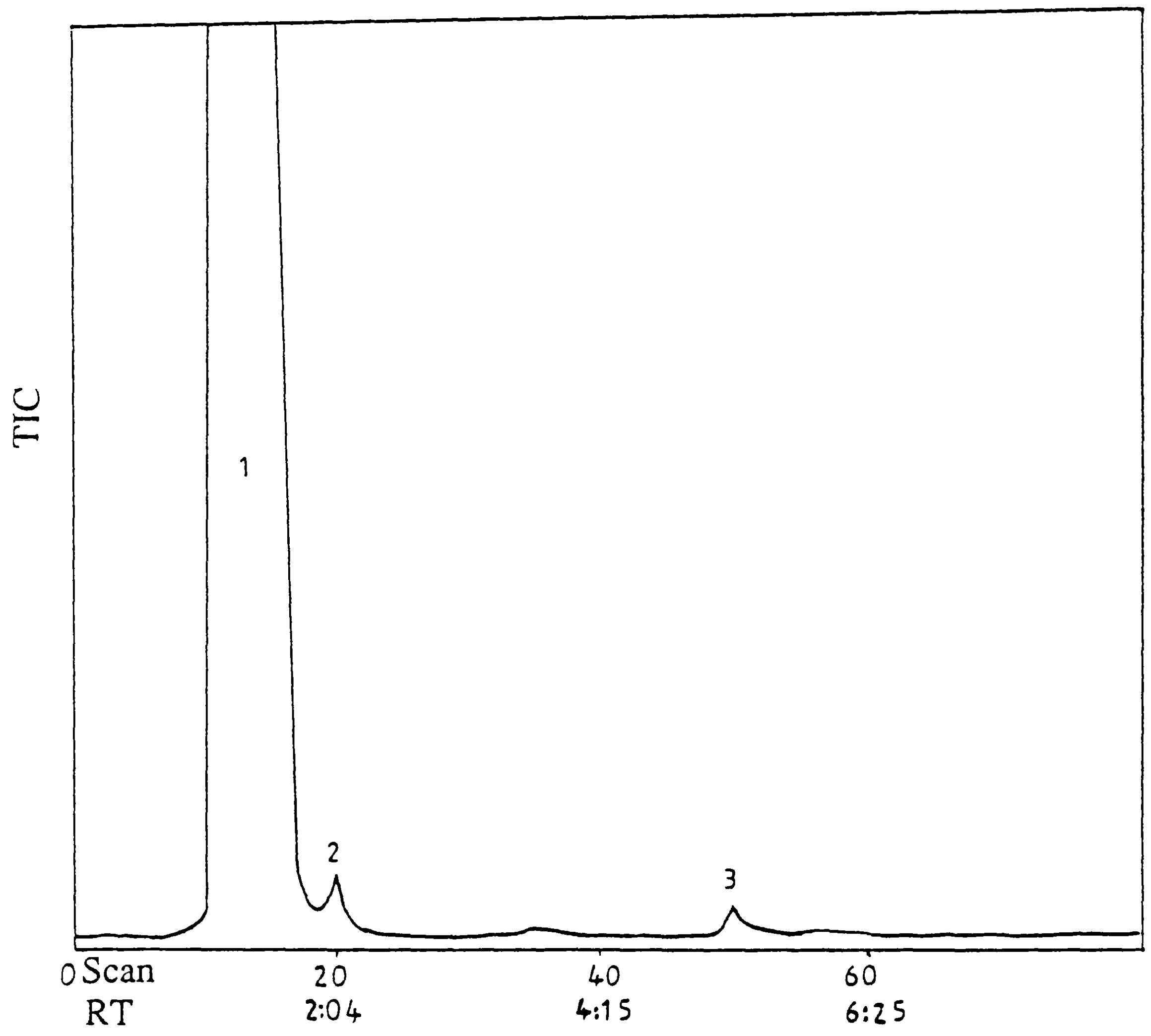


Fig. 4.5. GC-MS Chromatogram of Liquid Fraction from Degradation of PMAN 49 to 500 °C under normal TVA Conditions.

ASSIGNMENTS

1. Methacrylonitrile, 2. 2-Cyanobutane,
3. 2-Cyano-4-methyl-1-butene

4.4.1.2d Condensable products as gases

The condensable gaseous products of the degradation of the polymer samples to 500 °C were examined by IR spectroscopy and mass spectrometry, and were found to consist of mainly ethylene, hydrogen cyanide and isobutene, in the case of PMAN 16 and PMAN 59. Carbon dioxide was also identified as condensable gaseous product along with the ethene, hydrogen cyanide and isobutene in the case of PMAN 59. Mass spectra of various fractions are shown in Fig. 4.6 and products identified are listed in Table 4.4.

4.4.1.2e Non-condensable gases.

Methane was found to be the only non-condensable by on-line mass spectrometry. The mass spectrum obtained is also included in Fig. 4.6.

4.4.2 THERMOGRAVIMETRY.

The thermogravimetric (TG) and differential thermogravimetric (DTG) curves for these three homopolymers were obtained under dynamic nitrogen at a heating rate of 10 °C/min. The curves, illustrated in Fig.4.7, indicate that break down occurs in two stages with an inflection point at 330 °C. In the case of the relative low molecular weight polymer (PMAN 16), the first stage of break down (330 °C) accounts for about 50% weight loss while in case of two other polymer samples (PMAN 59 & PMAN 49), the weight loss for first stage is not more than 20%.

The overall weight loss for AIBN initiated polymers (PMAN 16 & PMAN 59) is almost 100%, while the benzoyl peroxide initiated

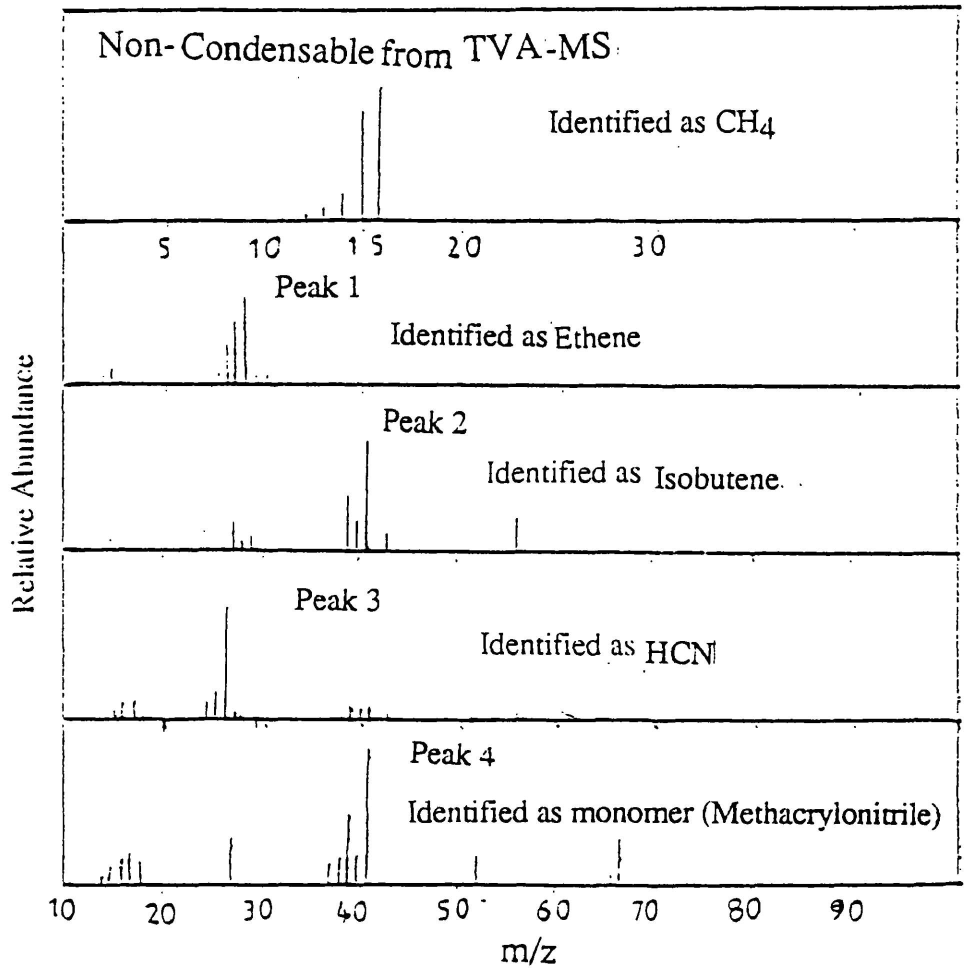


Fig. 4.6. Mass Spectra of Various Fractions from Degradation of PMAN 59 to 500 °C under normal TVA Conditions.

polymer shows 94% weight loss.

The DTG curves in Fig. 4.7 show $T1_{max}$ at 320 ^{o}C and 318 ^{o}C, and $T2_{max}$ at 384 ^{o}C and 380 ^{o}C for PMAN 59 and PMAN 46 respectively. PMAN 16 shows $T1_{max}$ at 312 ^{o}C which is a bit lower than other two homopolymers and may be due to the relatively low molecular weight. Although the TVA and TG results for these polymers are in reasonable agreement, the small discrepancy between the TVA and TG maxima can be explained by the efficient product removal under vacuum.

4.4.3 DIFFERENTIAL THERMAL ANALYSIS.

The thermal stability of the polymers were also examined by differential analysis (DTA) in the range of 25 ^{o}C to 500 ^{o}C under dynamic nitrogen. The DTA curves for PMAN 16, PMAN 59 and PMAN 49 are reproduced in Fig. 4.8. In the case of PMAN 16, the DTA curve shows two distinct endotherms at 325 ^{o}C and 385 ^{o}C while in case of PMAN 59 and PMAN 49, DTA curves show a broad endothermic shoulder followed by a main endotherm at 375 ^{o}C.

The features revealed by DTA are consistent with the pattern of behaviour shown in TVA and TG, indicating that the first stage of the two stage degradation process is more prominent in the low molecular weight polymer.

4.5 MECHANISM OF DEGRADATION.

Poly (methyl methacrylate) (PMMA) and other polymers of this kind which are derived from 1:1 disubstituted monomers,[5] give high monomer yields. Due to the resemblance of PMAN with PMMA, it

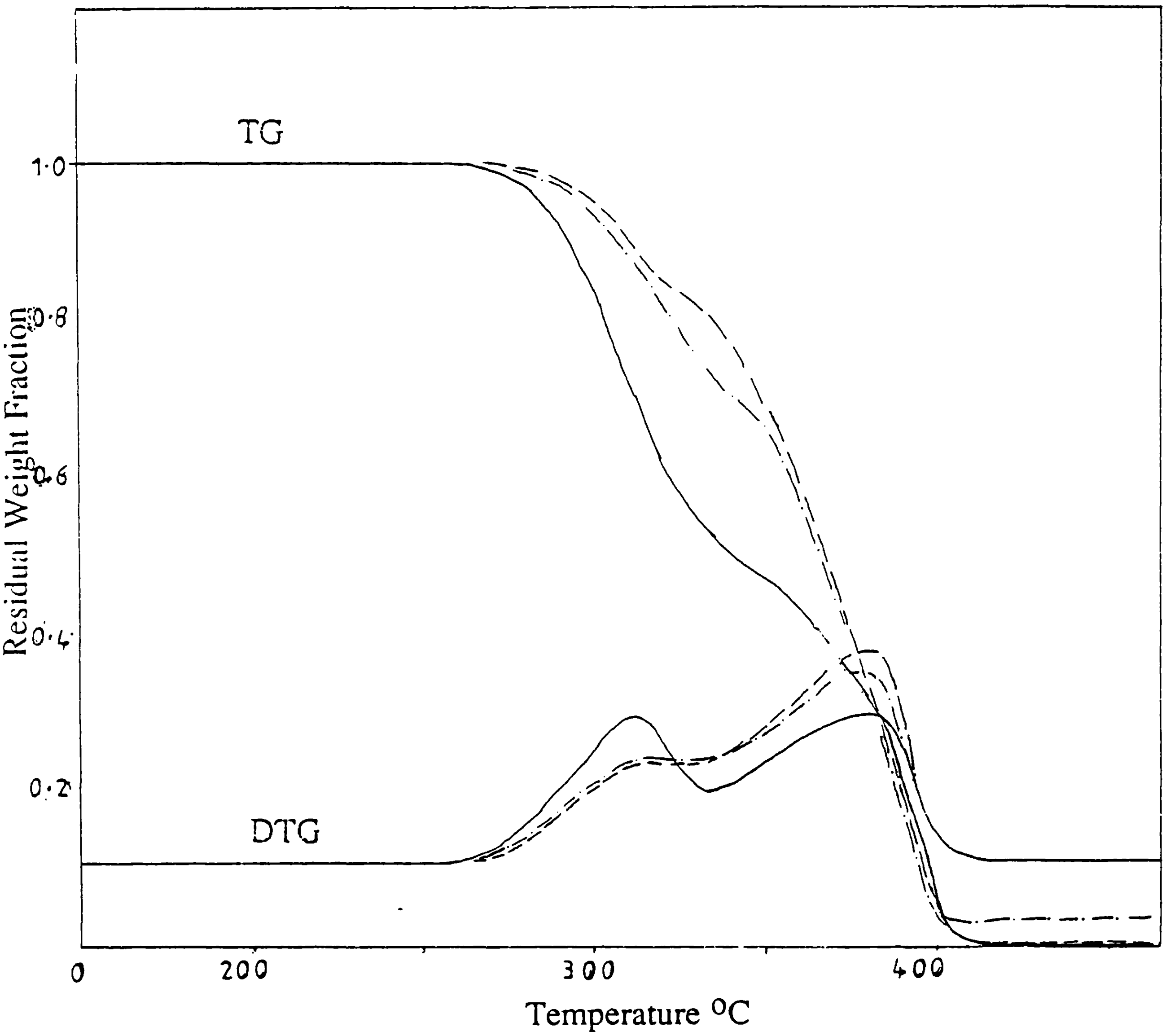


Fig. 4.7. TG and DTG Curves (Dynamic Nitrogen Atmosphere, Heating Rate 10 °C/min.) for Various MAN Homopolymers.

Keys: (a) PMAN 16 —— (b) PMAN 59 — — (c) PMAN 49 — · —

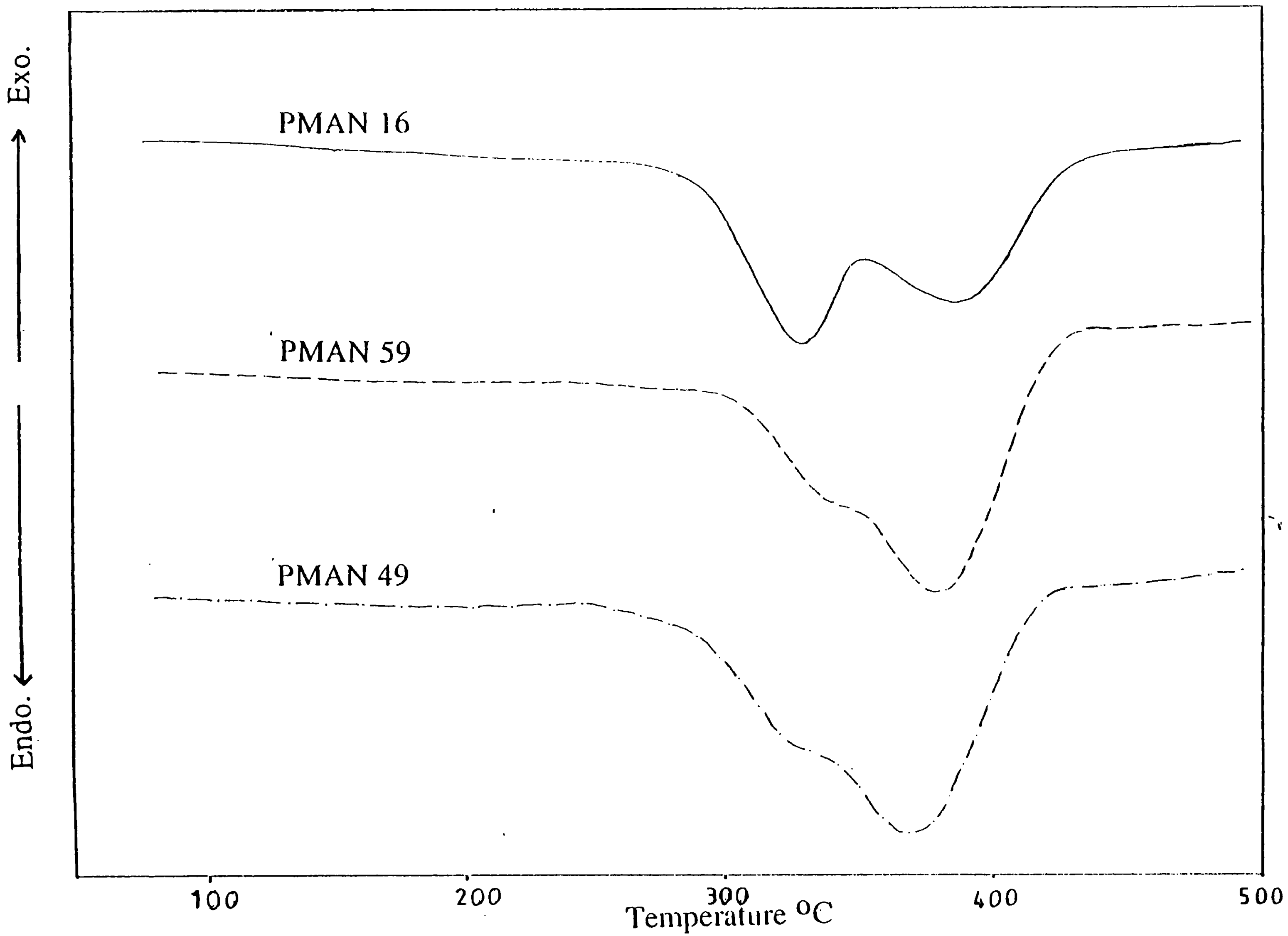


Fig. 4.8. DTA Curves (Dynamic Nitrogen Atmosphere, Heating Rate 10 °C/min.) for Various MAN Homopolymers.

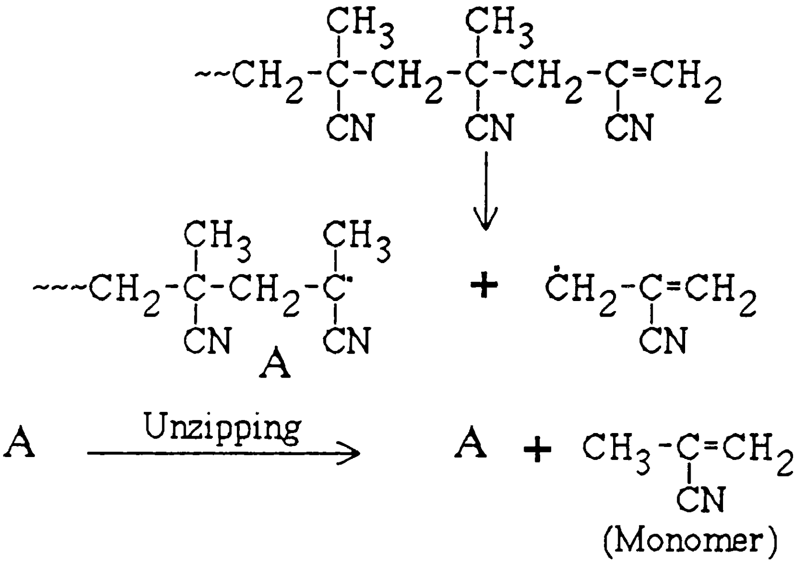
could be expected that PMAN would degrade to monomer. Grassie and McNeill[24–26, 62] in fact showed that high percentage yields of monomer were obtained by degrading PMAN prepared from carefully purified monomer polymerised with an azo initiator.

The TVA behaviour of PMMA was reported[66] to show two peaks varying in sizes with varying molecular weight, yet monomer was found to be The only product of degradation.[56] The first and lower temperature peak was attributed to monomer production by initiation at unsaturated chain ends formed during the termination step by disproportionation, and the second and main TVA peak was associated with monomer production by random chain scission.

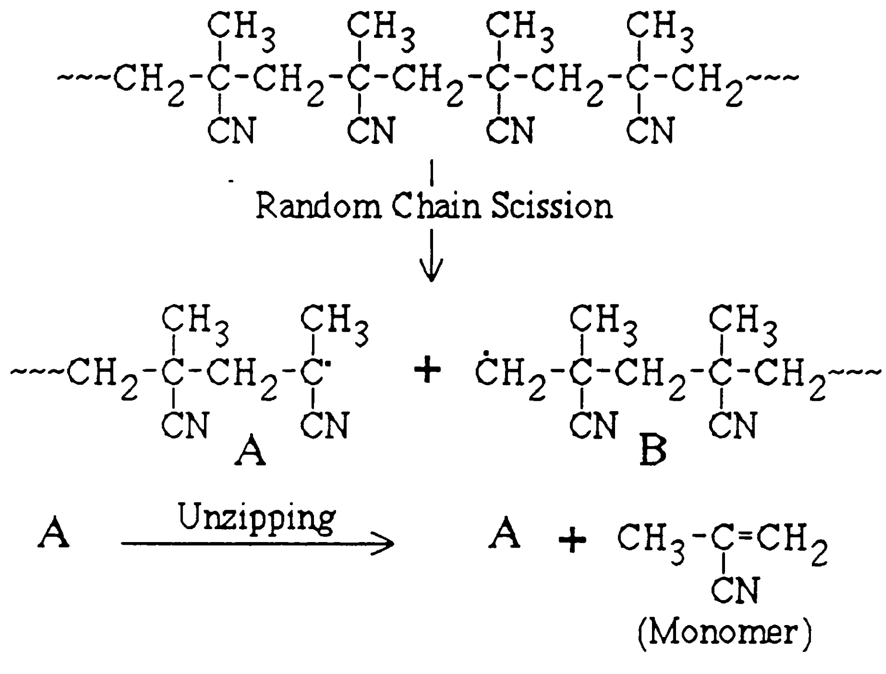
In the present investigation, the TVA behaviour of PMAN has been found to be similar to that of PMMA and monomer is also the only important product, hence a similar explanation can be presented for monomer production.

Scheme 1.1 Mechanism of Degradation for Methacrylonitrile Homopolymers Made With AIBN and BPO Initiators (PMAN 16, PMAN 58 and PMAN 49)

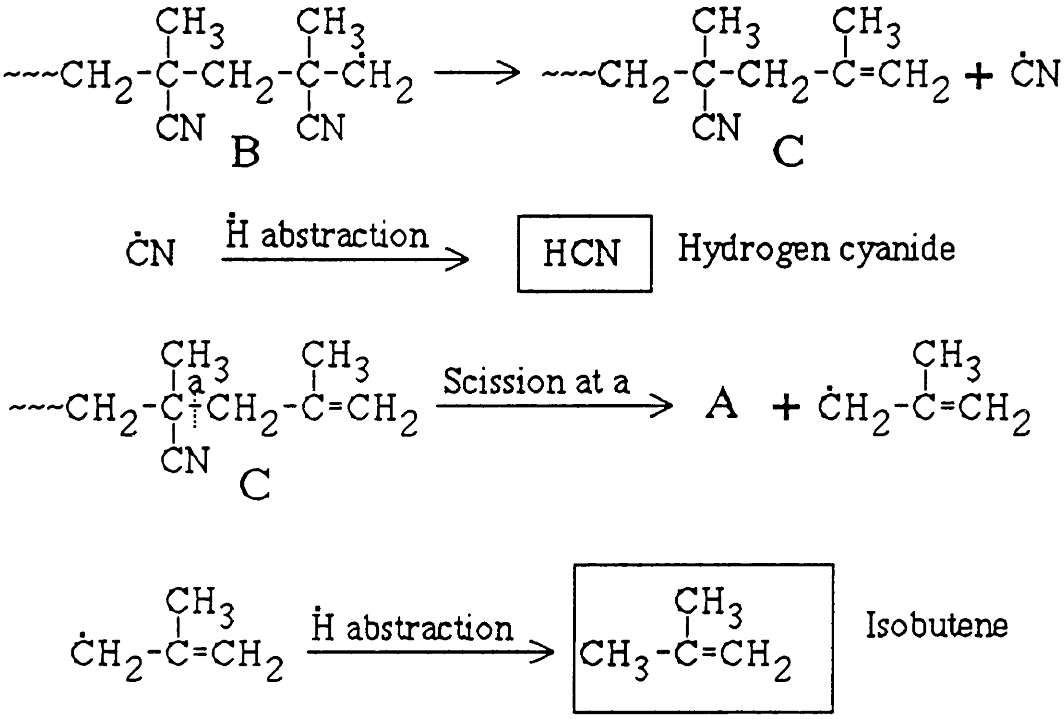
(i) First stage of degradation (from unsaturated chain ends)



(ii) Second stage of degradation (from random chain scission)



(iii) Mechanism of formation of other condensable products



$$\sim\sim\sim CH_2-\overset{CH_3}{\underset{CN}{C}}-CH_2-\overset{CH_3}{\underset{CN}{C}}-\dot{C}H_2 \;\; \text{B} \longrightarrow \sim\sim\sim CH_2-\overset{CH_3}{\underset{CN}{C}}-CH_2-\overset{CH_3}{C}=CH_2 \;\; \text{C} + \dot{C}N$$

$$\dot{C}N \xrightarrow{\dot{H}\text{ abstraction}} \boxed{HCN} \text{ Hydrogen cyanide}$$

$$\sim\sim\sim CH_2-\overset{CH_3}{\underset{CN}{C}}\overset{a}{\vdots}CH_2-\overset{CH_3}{C}=CH_2 \;\; \text{C} \xrightarrow{\text{Scission at a}} \text{A} + \dot{C}H_2-\overset{CH_3}{C}=CH_2$$

$$\dot{C}H_2-\overset{CH_3}{C}=CH_2 \xrightarrow{\dot{H}\text{ abstraction}} \boxed{CH_3-\overset{CH_3}{C}=CH_2} \text{ Isobutene}$$

CHAPTER FIVE

DEGRADATION BEHAVIOUR OF METHACRYLONITRILE POLYMERS WITH REACTIVE CHAIN ENDS

5.1 INTRODUCTION

A brief survey of the thermal behaviour of polymethacrylonitrile (PMAN) has been given in Chapter Four. Grassie and McNeill have carried out a detailed study[24-26, 62] of the thermal degradation of PMAN especially the colouration which develops above 120 °C. These authors concluded[27] that the colouration in PMAN occurs due to adjacent nitrile group cyclisation initiated from some well-defined impurities present in the polymer chain or mixed physically with the polymer.

Nothing has been reported about the degradation volatile products of coloured polymer, when polymer was heated to 500 °C, and the mechanistic route of their formation.

For a systematic investigation of the effect of colouration (in PMAN) on the degradation behaviour, two types of polymers have been utilised.

(i) Homopolymers (PMAN) which are capable of undergoing initiation of colouration from polymer chain ends [end-initiated polymethacrylonitrile (EIPMAN)].

(ii) Methacrylonitrile copolymers with a known amounts of methacrylic acid comonomer units present in the polymer chain which can act as initiating centres for colouration.

In this chapter, the first type of polymer [end-initiated polymethacrylonitrile (EIPMAN)] has been utilised and for this purpose five homopolymers (PMAN) have been synthesised using 4,4'-azobis-(4-cyanovaleric acid) as initiator. These homopolymers are capable of initiating colouration from chain ends containing an acidic group. The origin of the polymers used in this investigation is listed in Table 5.1.

The methacrylonitrile copolymers with methacrylic acid comonomer units will be discussed in Chapter Six.

5.2 PROGRAMMED HEATING

5.2.1 THERMOGRAVIMETRY

The TG and DTG curves for various end-initiated methacrylonitrile polymer samples were obtained under dynamic nitrogen at a heating rate of 10 °C/min. The TG and DTG curves for the five polymers investigated are reproduced in Figs. 5.1—5.5.

All five polymers show a similar pattern of degradation. An initial weight loss of 5-10% is observed at temperature ranges 250 °C to 300°C, after which follows the main decomposition above 320 °C. It is obvious from the TG and DTG curves that a gradual weight loss is observed upto 500 °C indicating the presence of some kind of stable material decomposing very slowly at that higher temperature. The

TABLE 5.1 Data for the End-Initiated Methacrylonitrile Homopolymers used in this Investigation.

Polymer	Initiator	Temperature of polymerisation	$\overline{M}n$ by GPC
EIPMAN* 1	ACVA** 0.2%	60 °C	29020
EIPMAN 2	ACVA 0.5%	60 °C	13800
EIPMAN 3	ACVA 1.0%	70 °C	7150
EIPMAN 4	ACVA 1.5%	80 °C	4864
EIPMAN 5	ACVA 2.0% +S***	60 °C	3721

EIPMAN*	End-initiated poly(methacrylonitrile)
ACVA**	4, 4'- Azobis (4- cyanovaleric acid)
S***	Suitable amount of solvent (Acetone) used to dissolve the initiator to give homogeneity.
$\overline{M}n$	Number-average molecular weight

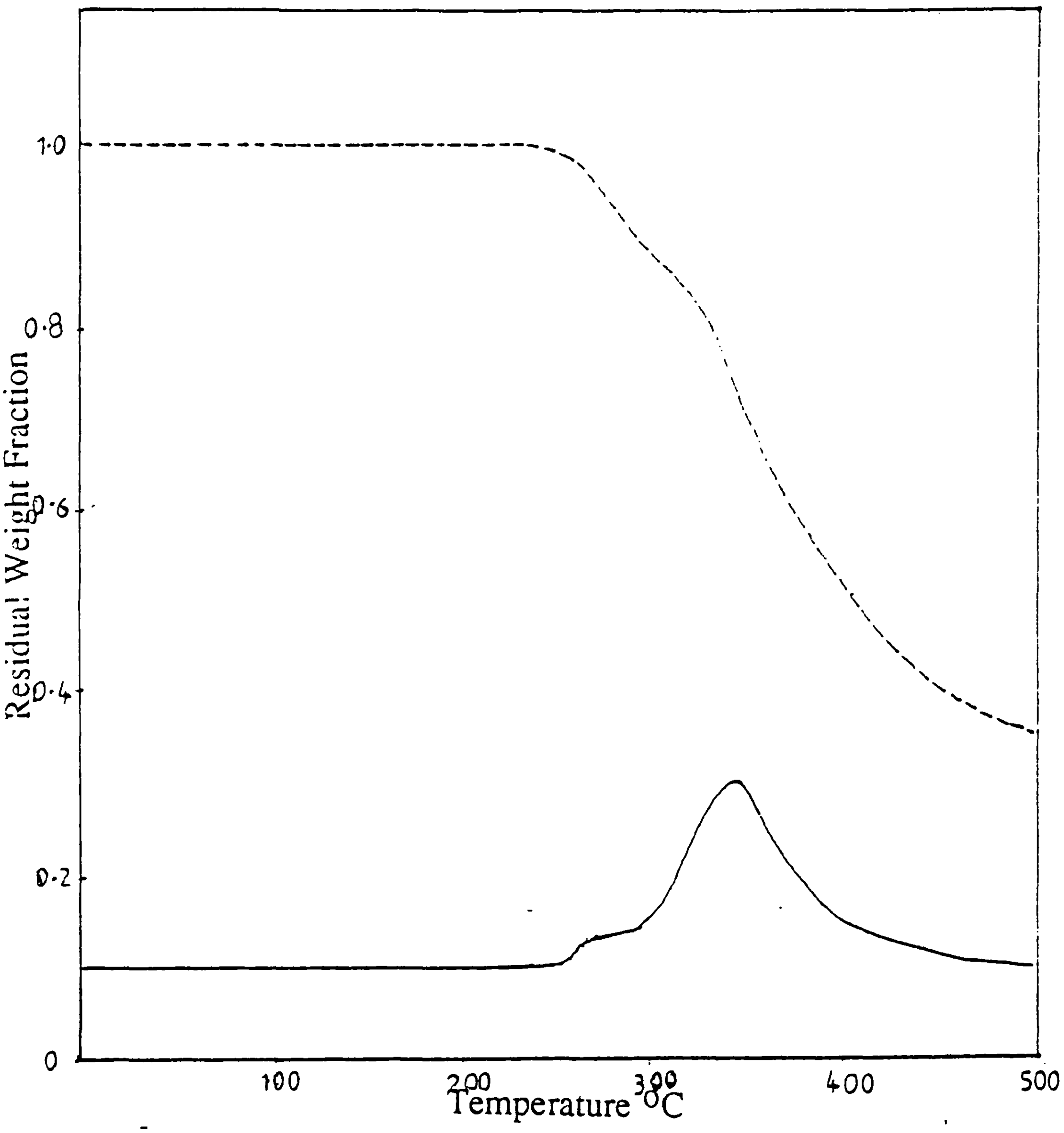


Fig. 5.1. TG and DTG Curves (Dynamic Nitrogen Atmosphere, Heating Rate 10 °C/min.) for EIPMAN 1.

Keys: TG — — — DTG ————

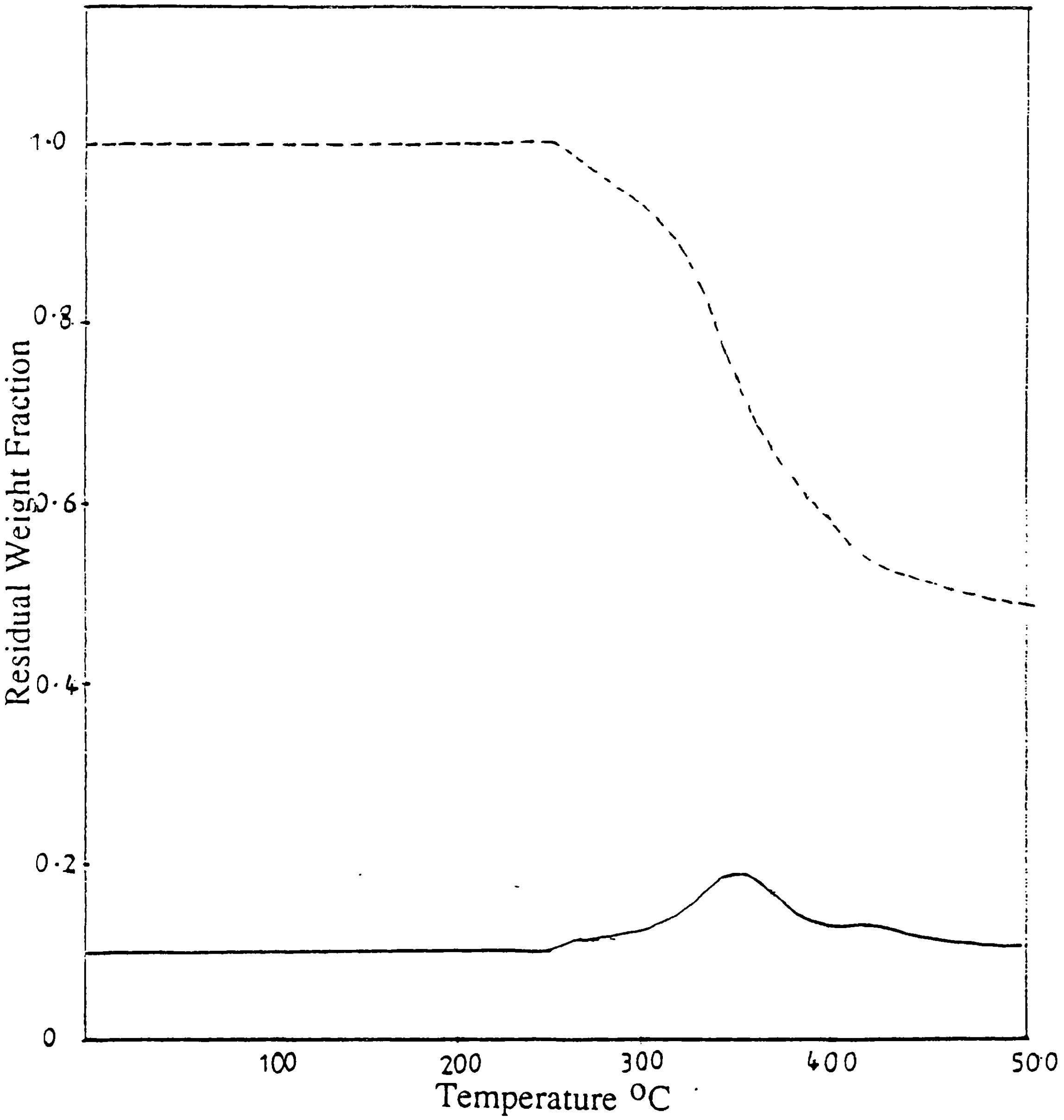


Fig. 5.2. TG and DTG Curves (Dynamic Nitrogen Atmosphere, Heating Rate 10 ^{0}C/min.) for EIPMAN 2.

Keys: TG — — — DTG ————

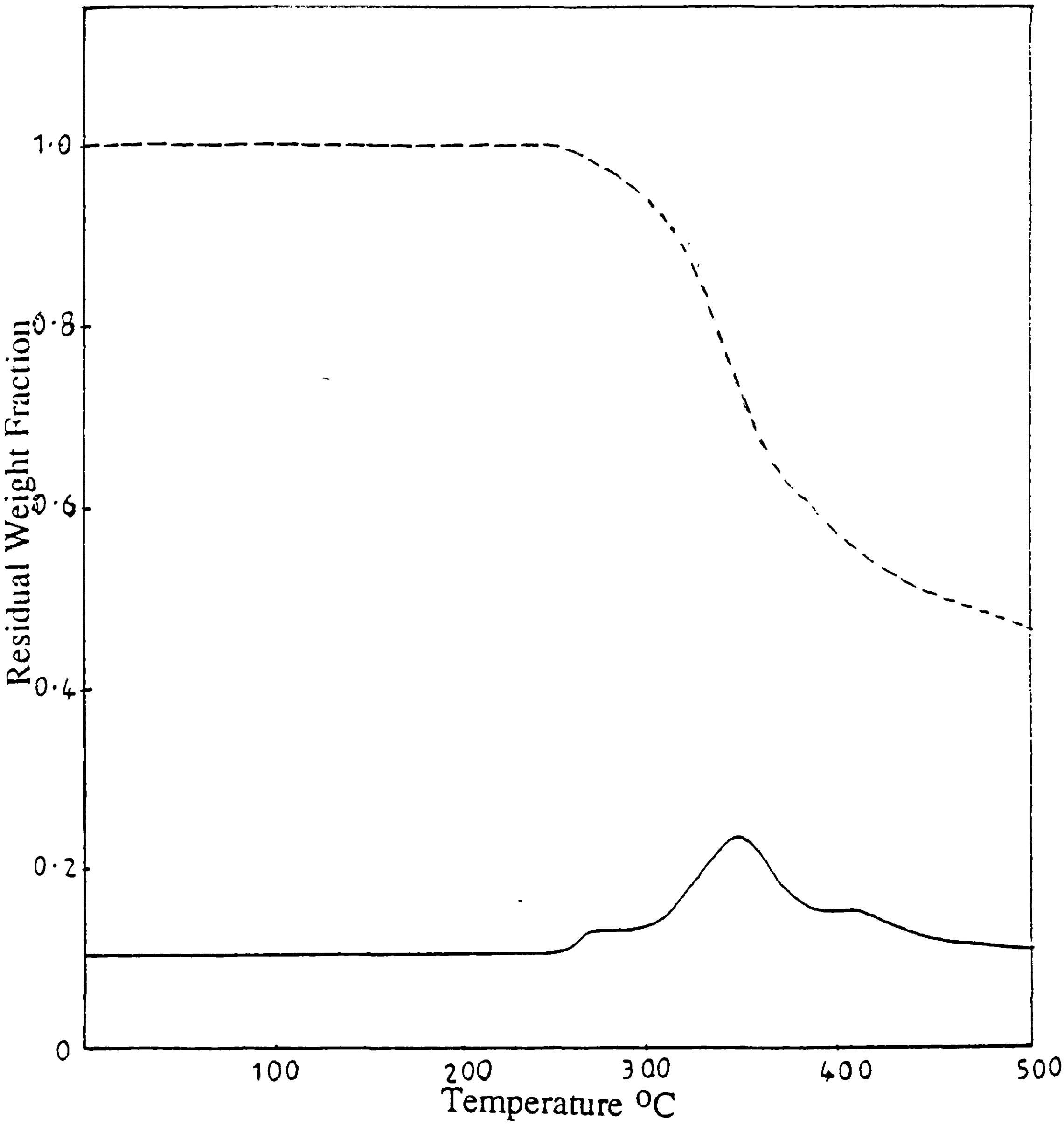


Fig. 5.3. TG and DTG Curves (Dynamic Nitrogen Atmosphere, Heating Rate 10 °C/min.) for EIPMAN 3.

Keys: TG — — — DTG ————

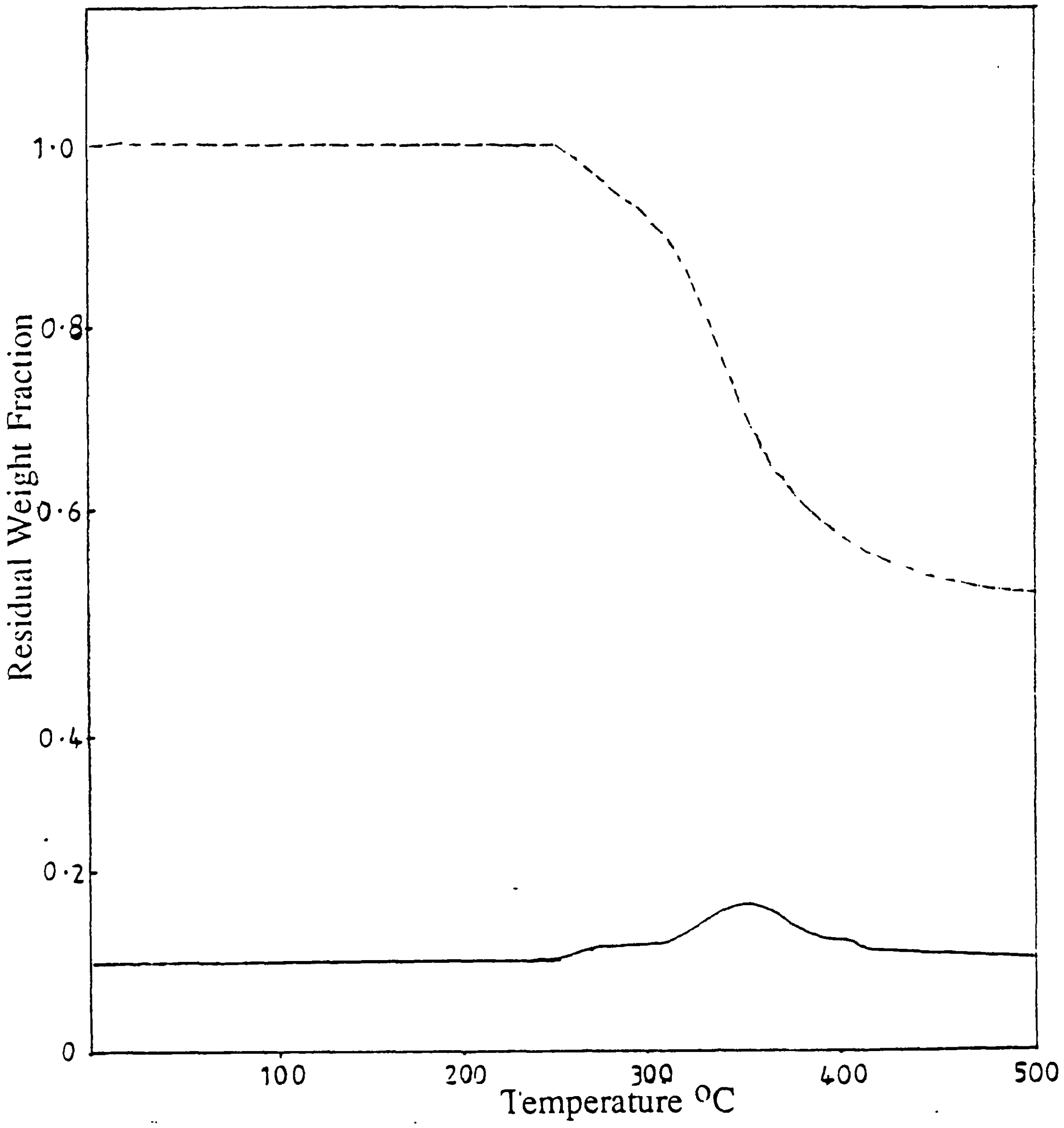


Fig. 5.4. TG and DTG Curves (Dynamic Nitrogen Atmosphere, Heating Rate 10 °C/min.) for EIPMAN.4.

Keys: TG — — — DTG ————

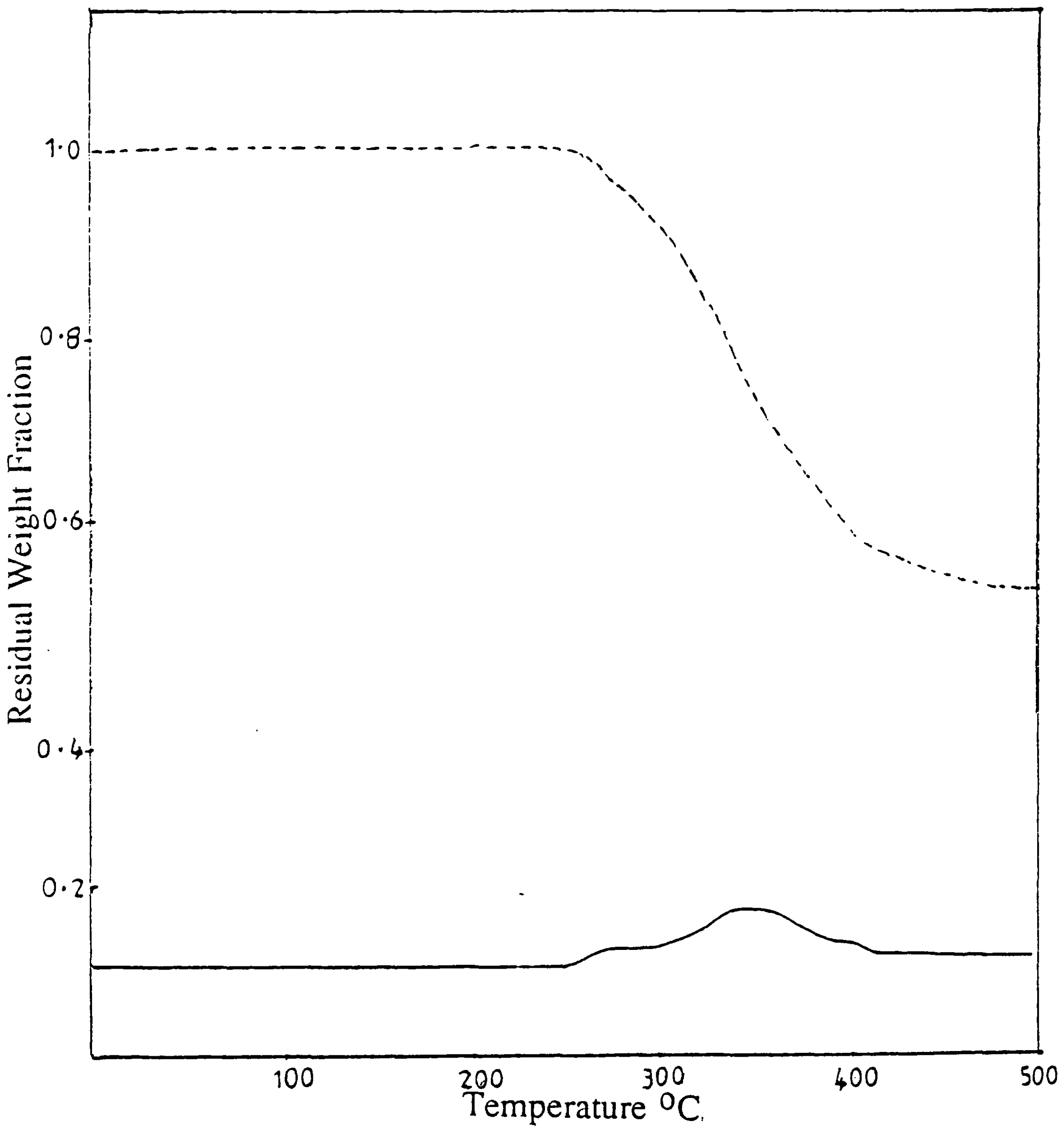


Fig. 5.5. TG and DTG Curves (Dynamic Nitrogen Atmosphere, Heating Rate 10 °C/min.) for EIPMAN 5.

Keys: TG — — — DTG ————

DTG curves show $T_{(max)}$ for the main decomposition in the temperature region 340 ^{o}C to 360 ^{o}C. The main features of TG, DTG and DTA data are listed in Table 5.2.

5.2.2 DIFFERENTIAL THERMAL ANALYSIS.

DTA curves for the five end-initiated polymethacrylonitrile samples used in this investigation were obtained under dynamic nitrogen at a heating rate of 10 ^{o}C/min are reproduced in Fig. 5.7. Although all DTA curves are generally featureless showing a single endothermic peak in the temperature ranges 350–365 ^{o}C which confirms the nature of the bond scission process, but some exothermic response is noticeable in case of low mlecular weight end-initiated methacrylonitrile polymers (i.e. EIPMAN 4 & 5). A small (but reproduceable) exothermic broadening "A" (in Fig. 5.7) starting with an exothermic drift (A') near temperature ranges at 212 ^{o}C with a small T_{max} around 308 ^{o}C, indicating the nitrile cyclisation as it has reported [67, 68] in case of polyacrylonitrile (PAN).The intensity of exothermic response in the present studies is not as significant as it has reported[68] in case of PAN and may be masked by endothermic fusion and depolymerisation. The main features of thermal behaviour established by DTA are summarised in Table 5.2.

5.2.3 THERMAL VOLATILISATION ANALYSIS.

Various end-initiated polymethacrylonitrile samples were examined as 50 mg powder samples in a TVA system under vacuum using programmed heating at a heating rate of 10 ^{o}C/min to 500 ^{o}C. The TVA curves for all five polymers (EIPMAN 1, EIPMAN 2, EIPMAN3,

TABLE 5.2. DTG, TG and DTA Data for End-Initiated Methacrylonitrile Polymer Samples used in this Investigation.

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
	278	255-300	16				
EIPMAN 1	342	300-390	44	64	350	309-412	Endotherm
	425	392-500	6				
	275	250-295	7				
EIPMAN 2	348	295-392	36	54	355	302-410	Endotherm
	425	392-500	11				
	282	248-299	6				
EIPMAN 3	347	300-410	34	52	352	297-395	Endotherm
	440	410-500					
	285	245-303	8			273-305	Exo. Br*
EIPMAN 4	349	305-420	37	49	357	307-412	Endotherm
	445	420-500	4				
	284	251-305	9			212-283	Exo. Dr.**
EIPMAN 5	351	307-422	33	47	308	288-312	Exo. Br
	443	422-500	5		361	312-414	Endotherm

Exo. Br* Exothermic Broadening

Exo. Dr.** Exothermic Drift

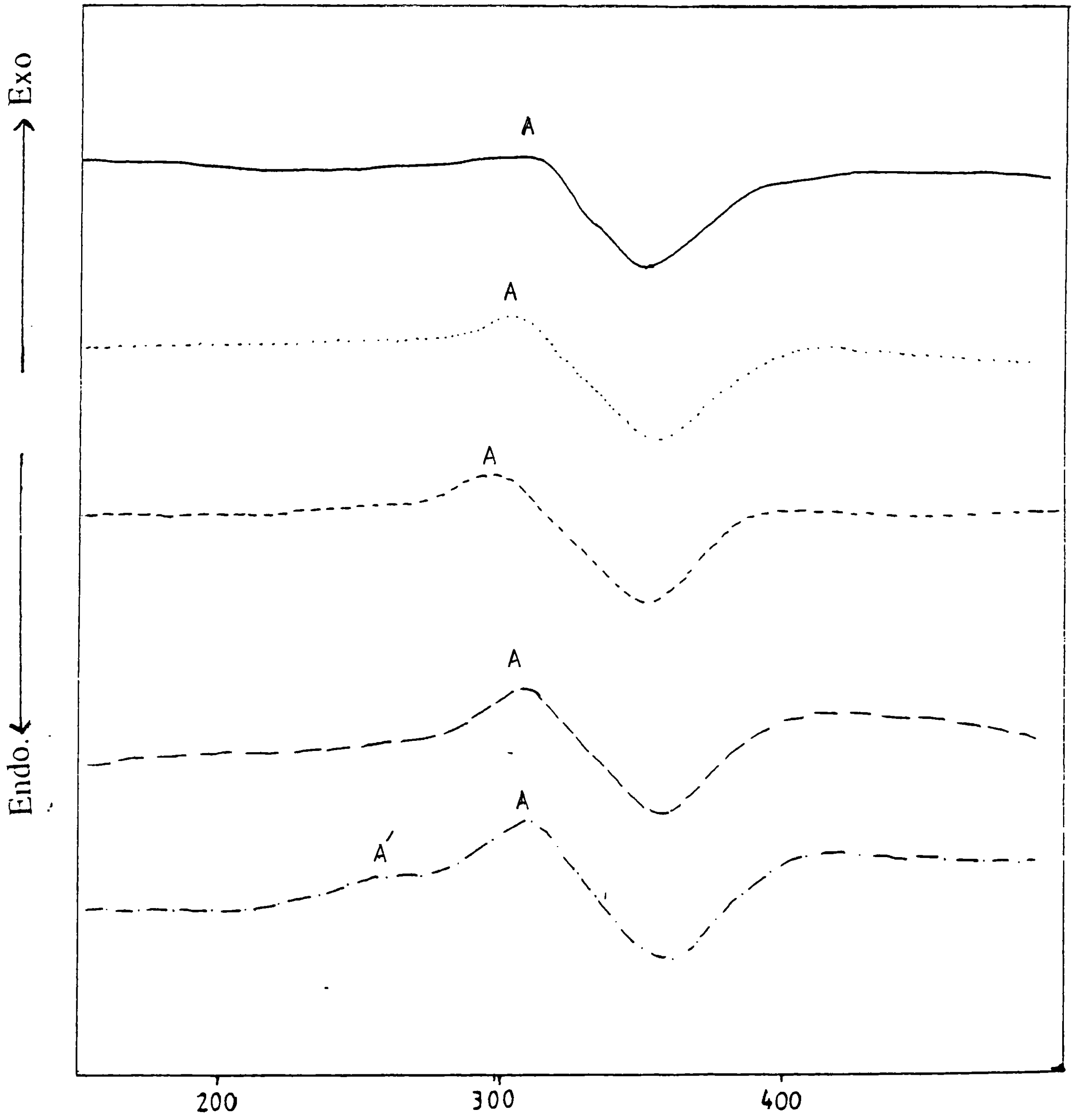


Fig. 5.6. DTA Curves (Dynamic Nitrogen Atmosphere, Heating Rate 10 °C/min.) for Various End-initiated Methacrylonitrile Polymers.

EIPMAN 1 —— EIPMAN 2 ······· EIPMAN 3 - - - -
" 4 — — — " 5 —·—·

EIPMAN 4, & EIPMAN 5) are shown in Figs. 5.7 (a, b, c, d & e) respectively. All five TVA traces for these end-initiated methacrylonitrile polymer samples are quite similar and show a two stage decomposition. The first and the main stage of decomposition which starts above 240 °C, shows a broad peak and then follows a gradual decomposition above 450 °C. The first and main broad decomposition stage tends to split into two separate T_{max} with increasing molecular weight and this behaviour is quite noticeable in case of EIPMAN 1 which is relatively higher molecular weight in the series of end-initiated polymer samples investigated. All the TVA curves show a large response due to non-condensable products indicated by the -196 °C traces. Non-condensable gases were bled to the quadrupole mass spectrometer attached to the TVA system and were identified as mainly methane and hydrogen. A trace amount of carbon monoxide was also detected as a non-condensable product in polymers with lower molecular weights. From mass spectrometric studies carried out during the TVA experiment, methane was found to be the only non-condensable gas evolved during the main decomposition stage (i.e. temperature ranges 250 °C to 400 °C). Hydrogen and carbon monoxide together with methane were detected at the later stage of the degradation (above 420 °C).

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

The TVA data for the end-initiated polymers investigated are summarised in Table 5.3.

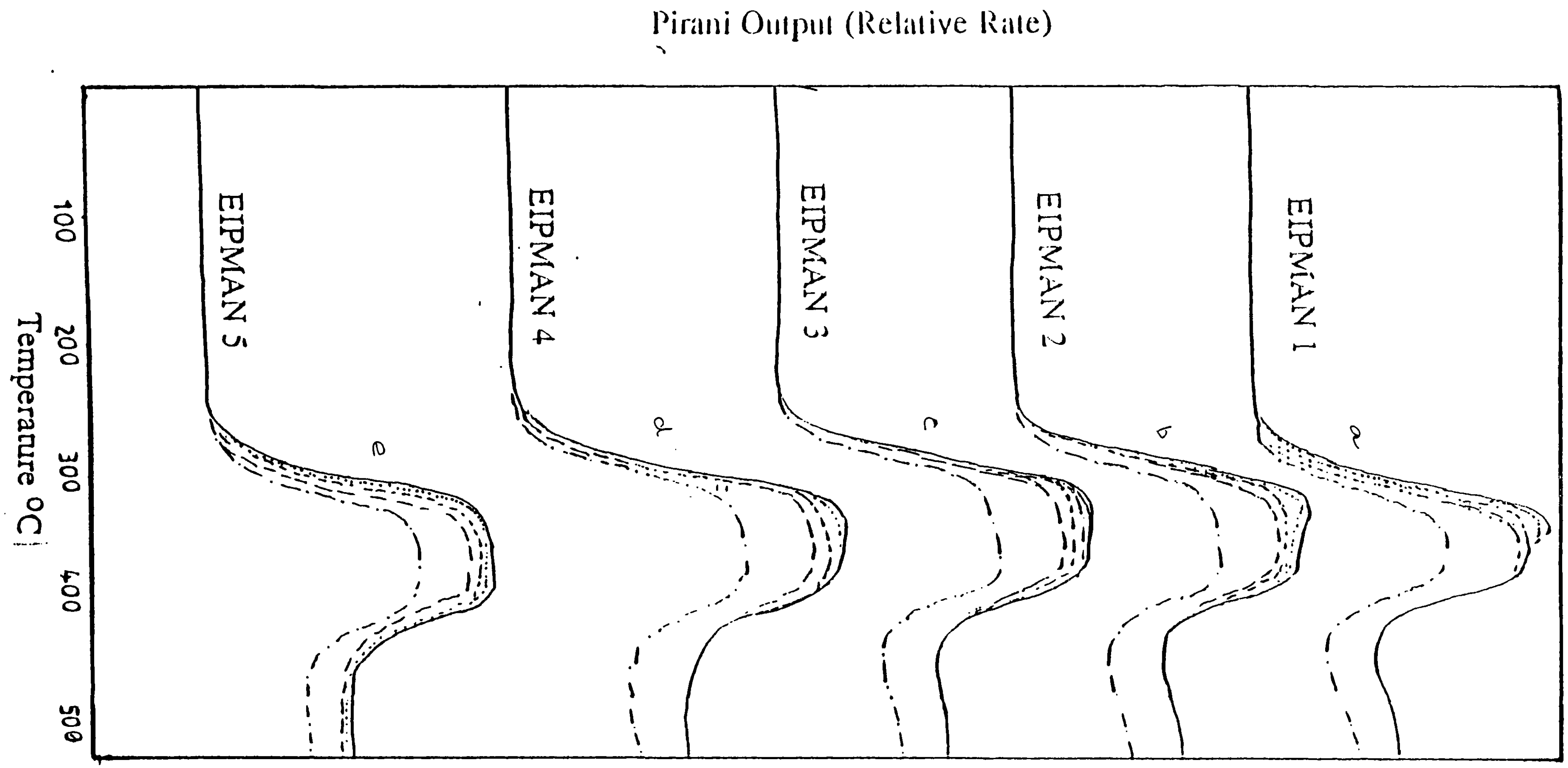


Fig. 5.7. The TVA Curves (Vacuum, heating Rate 10 °C/min. to 500 °C) for Various End-initiated Methacrylonitrile Polymers.

Key: 0 °C —, -45 °C ····, -75 °C - - , -100 °C — — , -196 °C — · — ·

TABLE 5.3. TVA Data for Degradation of End-Initiated Methacrylonitrile Polymer Samples

Polymer	T_{onset} ^oC	T_{max} ^oC	Wt. % Residue at ~500 ^oC	Wt. % CRF at ~500 ^oC	Wt% L.F at ~500 ^oC
EIPMAN 1	248	325–357	31.5	4.5	54
EIPMAN 2	245	318–365	41	8	47
EIPMAN 3	240	320–355	43	10.5	38
EIPMAN 4	240	325-370	46	13.	33
EIPMAN 5	246	330–385	48	14	28

5.2.3.1 Subambient Thermal Volatilisation Analysis.

Condensable volatile products from the TVA experiment were collected in a liquid nitrogen trap in the vacuum system, and were separated by the SATVA[31] method. The SATVA traces for the five end-initiated polymers used in this investigation are reproduced in Figs. 5.8, 5.9, 5.10, 5.11 and 5.12. Products corresponding to each SATVA peak were collected separately for identification by various other techniques such as IR, MS and GC-MS.

5.2.3.2 Product Analysis

The various degradation products, namely residue, cold ring fraction (CRF), liquid fraction, and condensable gaseous products, were examined after degradation of 50 mg of each polymer sample to 500 ^{o}C under TVA conditions. Non-condensable gases were examined and identified by mass spectrometry by bleeding them into a quadrupole mass spectrometer coupled to the TVA system during TVA experiment.

Mass spectrometric analysis were also carried out for condensable degradation products (condensable gases and liquid fraction) during the SATVA separation by bleeding the warmed up products into the quadrupole mass spectrometer coupled with the system.

The gaseous fractions separated by SATVA were also characterised by IR spectroscopy. The less volatile liquid fraction was collected and subjected to GC-MS investigation

5.2.3.2.1 Residue

Each polymer degradation left a black involatile residue, which was

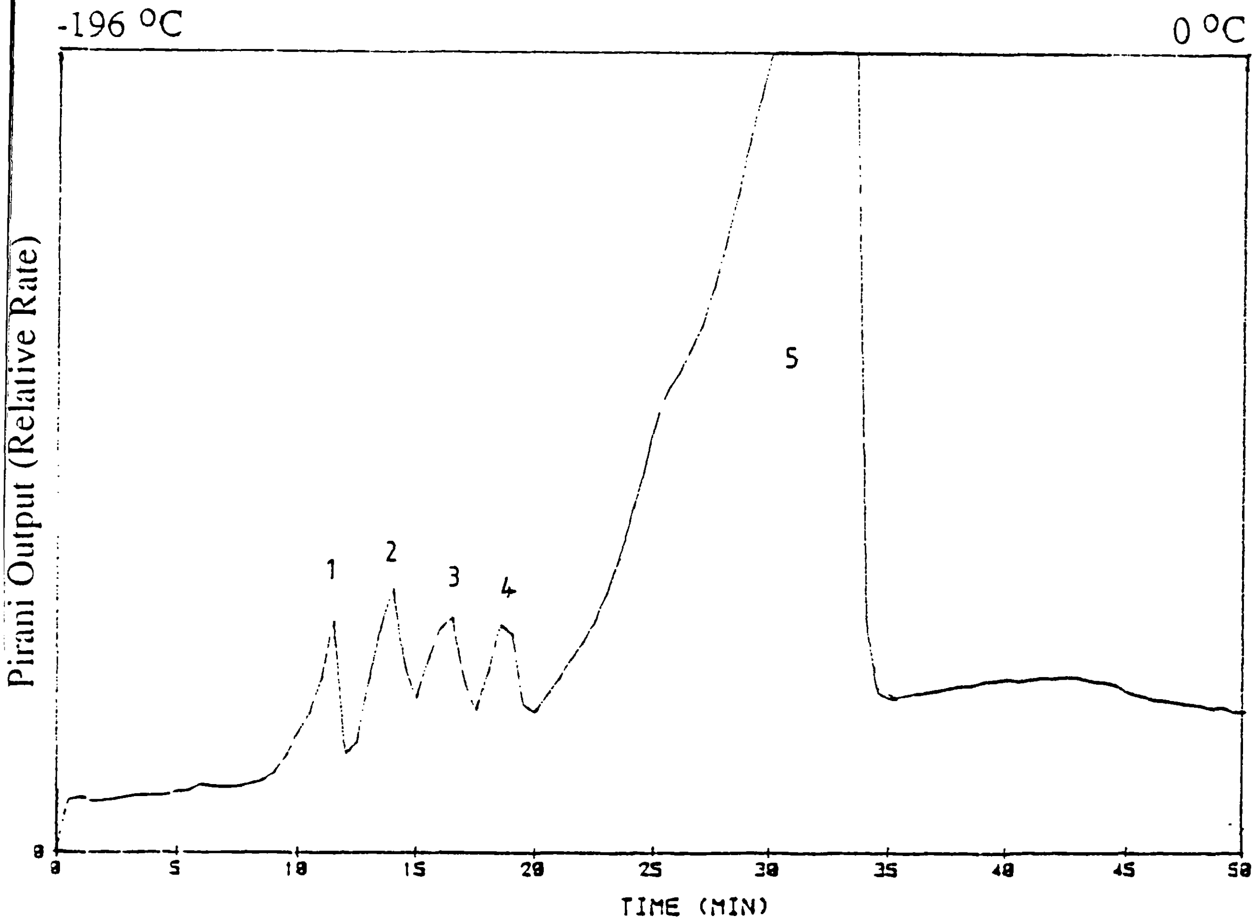


Fig. 5.8. SATVA Warm-up from -196 ^{o}C to Room Temperature of Condensable Volatile Products of Degradation to 500 ^{o}C under TVA Conditions of EIPMAN 1.

Peak 1	Ethane
Peak 2	Propane
Peak 3	Isobutene and Ammonia
Peak 4	Hydrogen cyanide and Ammonia
Peak 5	Collected as liquid fraction ; mainly monomer (Methacrylonitrile

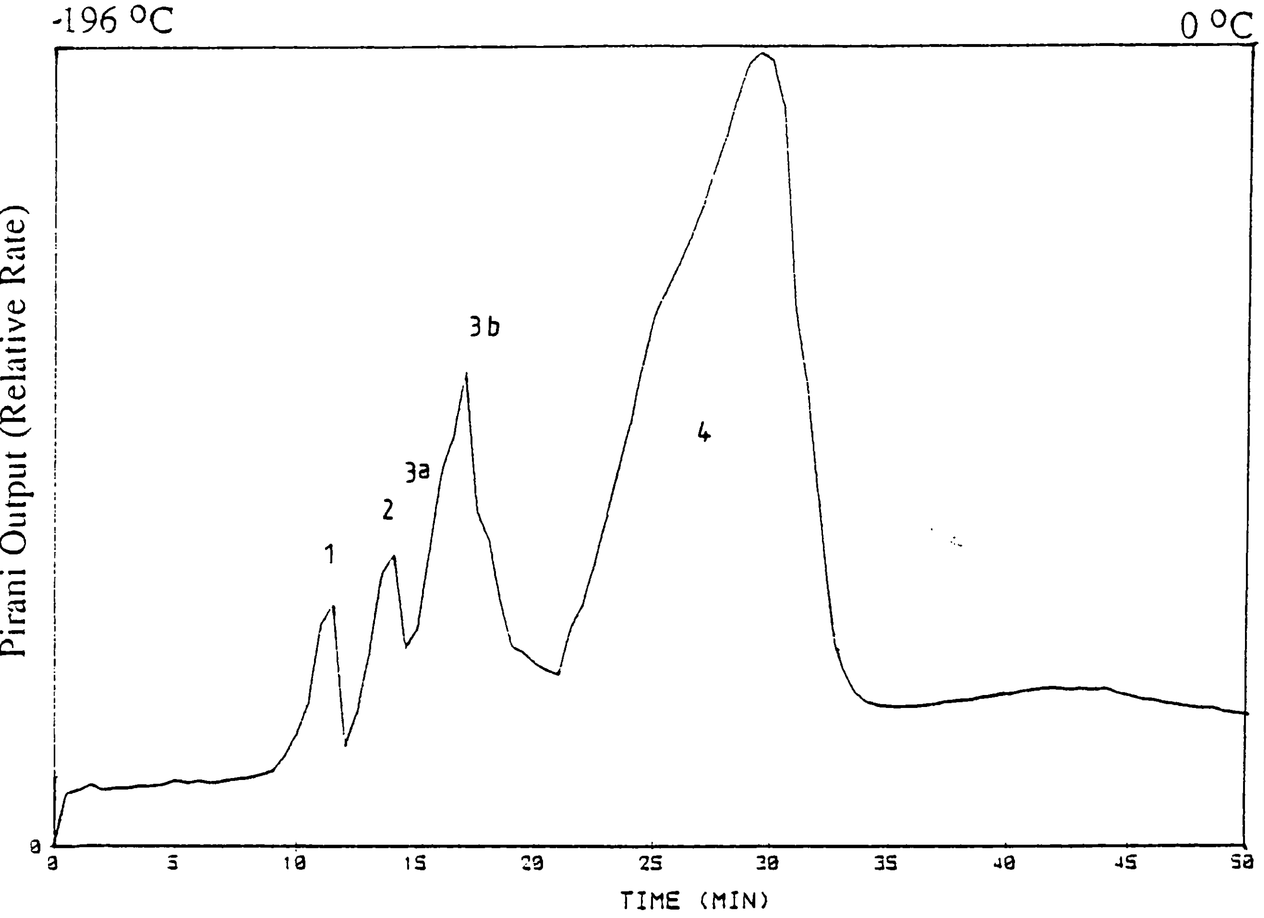


Fig. 5.9. SATVA Warm-up from -196 °C to Room Temperature of Condensable Volatile Products of Degradation to 500 °C under TVA Conditions of EIPMAN 2.

Peak 1	Ethane
Peak 2	Propane
Peak 3a	Isobutene and Ammonia
Peak 3b	Hydrogen cyanide and Ammonia
Peak 4	Collected as liquid fraction ; mainly monomer (Methacrylonitrile)

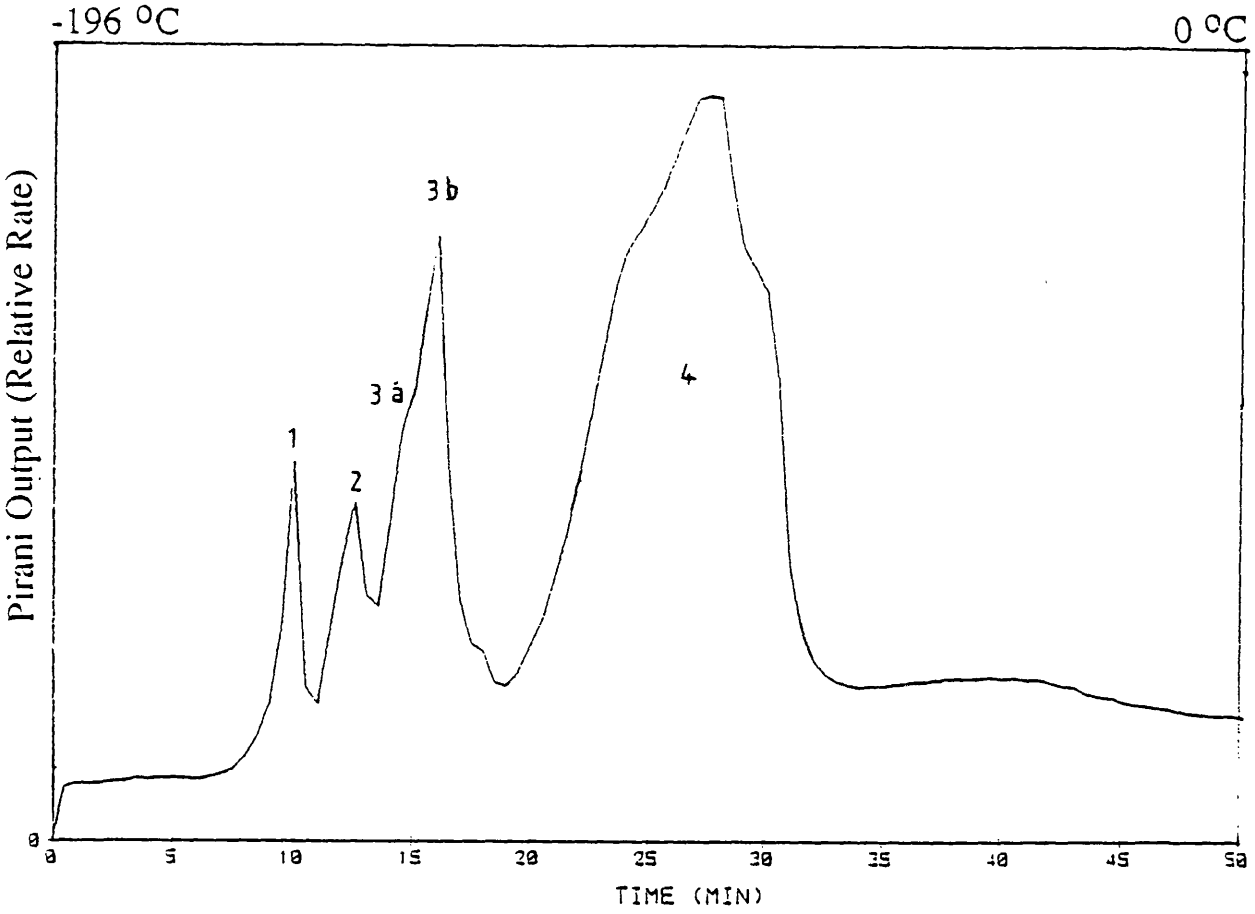


Fig. 5.10. SATVA Warm-up from -196 °C to Room Temperature of CondensableVolatile Products of Degradation to 500 °C under TVA Conditions of EIPMAN 3.

Peak 1	Ethane
Peak 2	Propane
Peak 3a	Isobutene and Ammonia
Peak 3b	Hydrogen cyanide and Ammonia
Peak 4	Collected as liquid fraction ; mainly monomer (Methacrylonitrile

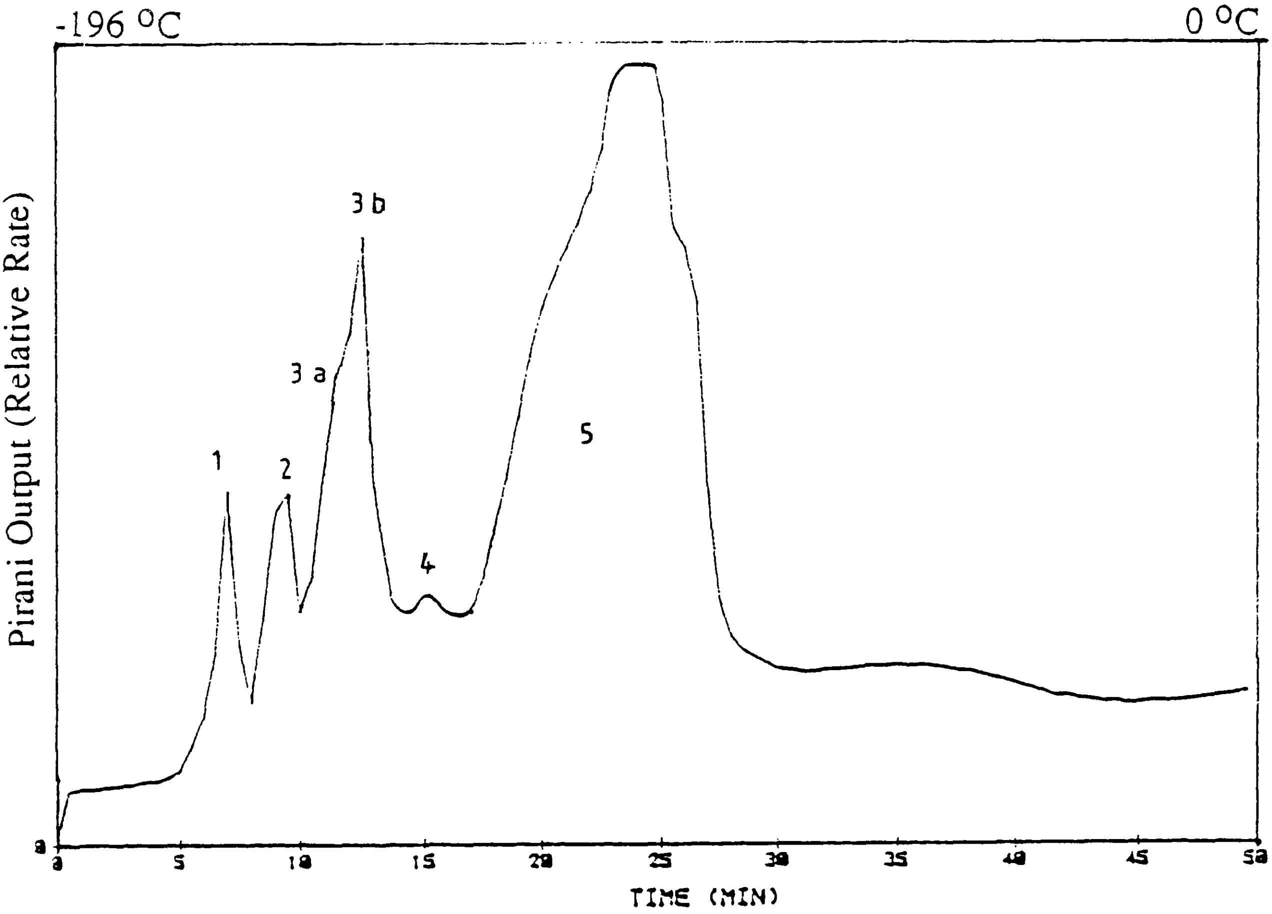


Fig. 5.11. SATVA Warm-up from -196 °C to Room Temperature of Condensable Volatile Products of Degradation to 500 °C under TVA Conditions of EIPMAN 4.

Peak 1	Ethane
Peak 2	Propane
Peak 3a	Isobutene and Ammonia
Peak 3b	Hydrogen cyanide and Ammonia
Peak 4	Hydrogen cyanide and Ammonia and Isopentene
Peak 5	Collected as liquid fraction ; mainly monomer (Methacrylonitrile)

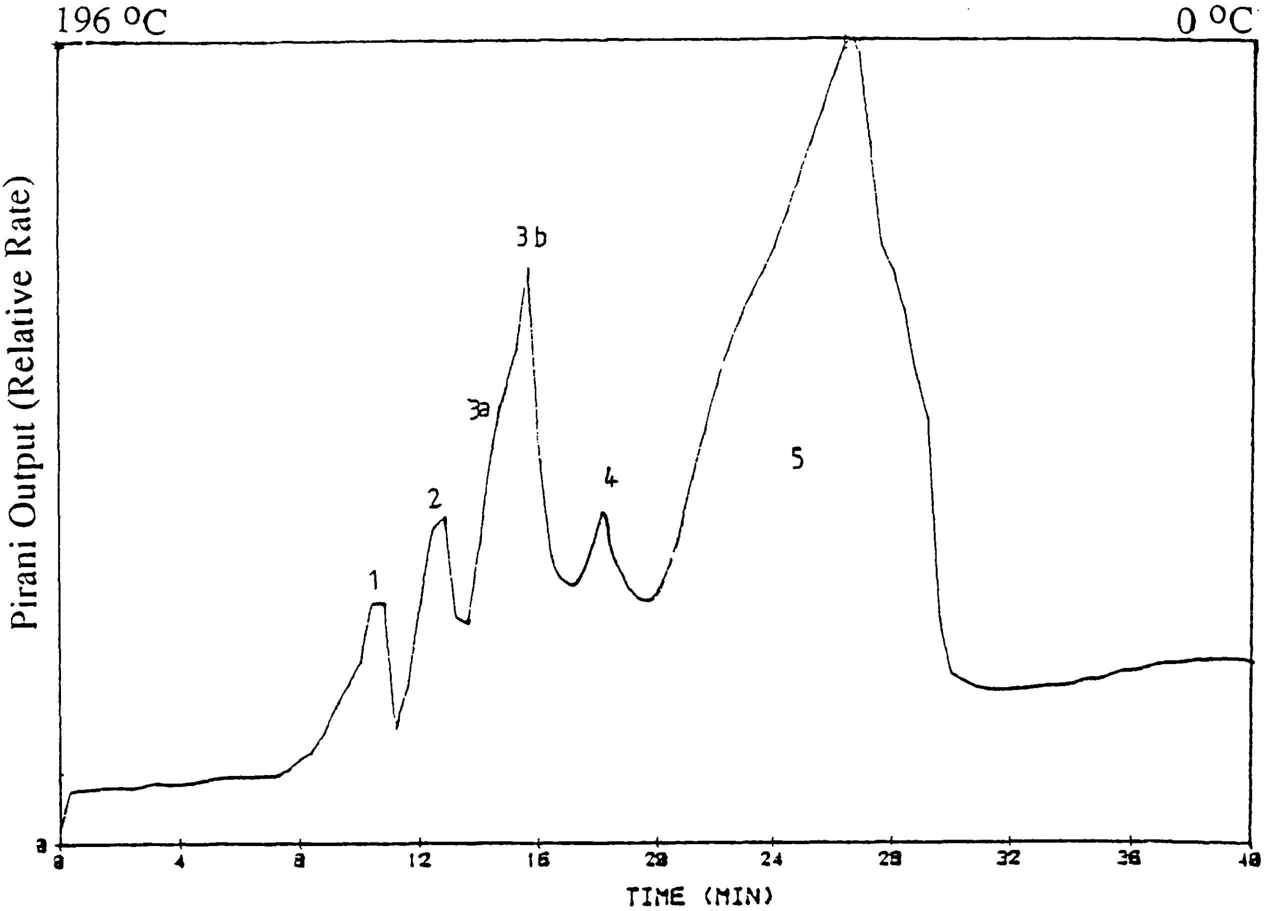


Fig. 5.12. SATVA Warm-up from -196 °C to Room Temperature of Condensable Volatile Products of Degradation to 500 °C under TVA Conditions of EIPMAN 5.

Peak 1	Ethane
Peak 2	Propane
Peak 3a	Isobutene and Ammonia
Peak 3b	Hydrogen cyanide and Ammonia
Peak 4	Hydrogen cyanide and Ammonia and Isopentene
Peak 5	Collected as liquid fraction ; mainly monomer (Methacrylonitrile)

analysed by IR spectroscopy. The IR spectra of these residual fractions from five end-initiated methacrylonitrile polymer samples were totally identical to each other (Fig. 5.13) showing a broad and featureless band in the high wavenumber IR spectral region which is characteristic of black (residual) samples. The presence of a strong band at 1600 cm^{-1} (which is usually assigned to C=C and C=N stretching) may be associated with extented conjugated systems.

The percentage residue left after the degradation was considerable (30 to 48% of initial sample weights), and observed to increase with decrease in molecular weight.

5.2.3.2.2 Cold ring fraction.

Cold ring fraction (light yellow brown waxy) products which were collected on the upper part of the TVA tube, were removed using a volatile solvent. These fractions were examined by IR and mass spectrometry.

The IR spectra for all five end-initiated polymers studied were almost similar (Fig. 5.14) showing peaks at

3324 cm^{-1} (m)	3177 cm^{-1} (m)	(N-H) (Stretching) Asymmetric & symmetric for primary amines
2925 cm^{-1} (s)	2853 cm^{-1} (m)	Saturated C-H stretch
2214 cm^{-1} (w)		$C\equiv N$ Stretch
1628 cm^{-1} (s)–1618 cm^{-1}		C=N Stretch,
1448 cm^{-1} (s),	1386 cm^{-1} (m)	C-H Deformation
710 cm^{-1} (w)		C-H Out of plane deformation

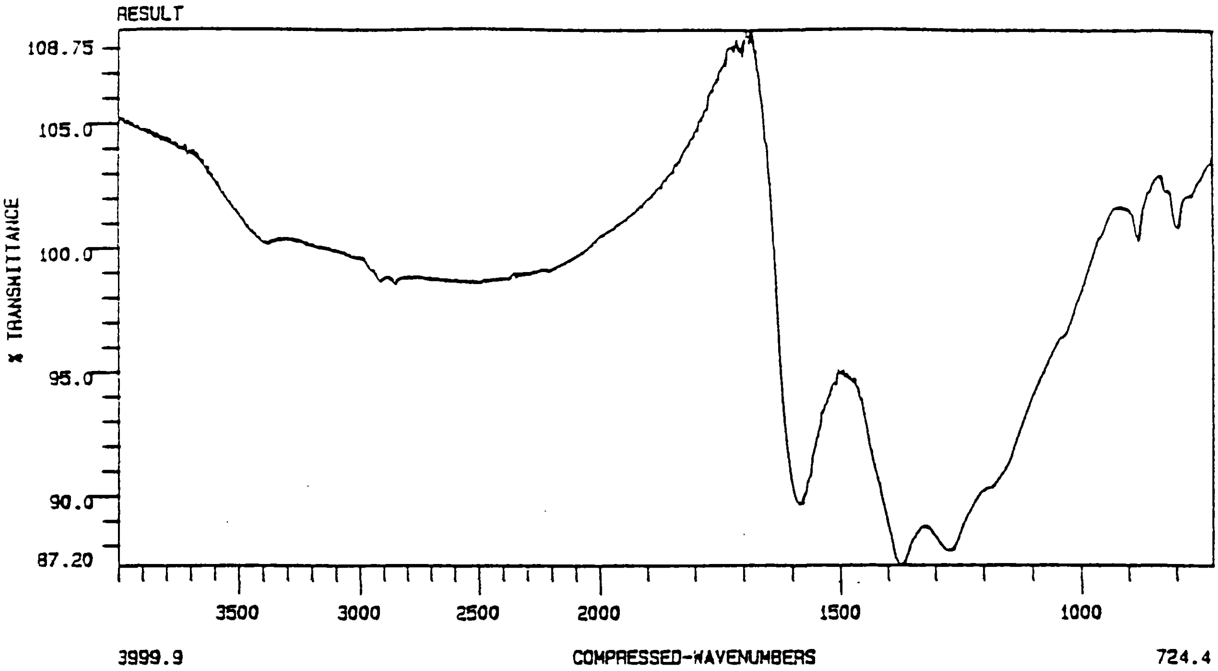


Fig. 5.13. IR Spectrum of the Residual Fraction from Degradation of End-initiated Methacrylonitrile Polymers to 500 °C under TVA Conditions.

The spectra of these fractions (CRF) are markedly different from those of corresponding homopolymers especially due to presence of the bands at 3324 cm^{-1}, 3177 cm^{-1} and 733 cm^{-1} which are not present in the homopolymers spectra, and are due to primary amine (N-H) stretching and unsaturated (C–H) out of plane deformation respectively. The strong band in the region 1628–1618 cm^{-1} may be attributed to cyclic (-C=N-) structures in the CRF which are absent in the undegraded homopolymers. The above mentioned bands suggested that fractions of these end-initiated polymethacrylonitrile samples contain some amino (NH_2) substituted heterocyclic fused ring structures beside short chain fragments.

The mass spectrometric studies of these fractions (CRF) supported IR results and various amino and methyl substituted heterocyclic (nitrogen containing) structures together with MAN short chain fragments (trimers, tetramers) were identified. Mass spectrometric results for the five polymers studied are shown in Figs. 5.15, and the products identified from these cold ring fractions of end-initiated methacrylonitrile polymers (EIPMAN 1, EIPMAN 2, EIPMAN 3, EIPMAN 4, &EIPMAN 5) by mass spectrometry are listed in Tables (5.4, 5.5, 5.6, 5.7, and 5.8) respectively. Products are listed according to relative abundance. The assignment of the mass spectral peaks for the compounds identified is based on the fact[69] that the presence of a conjugated system (i.e. like pyridyle ring structures identified in CRF), tend to give rise to an abundant molecular-ion peak. It is well known[69] that the stabilising effect of aromatic (pyridyle in this case) π electron system and the difficulty of cleaving a benzoid (or pyridyle) ring mean that the molecular-ion is usually observed, and often abundant, in the spectra of this class of compounds.

During present studies, in the light of above mentioned facts, the major

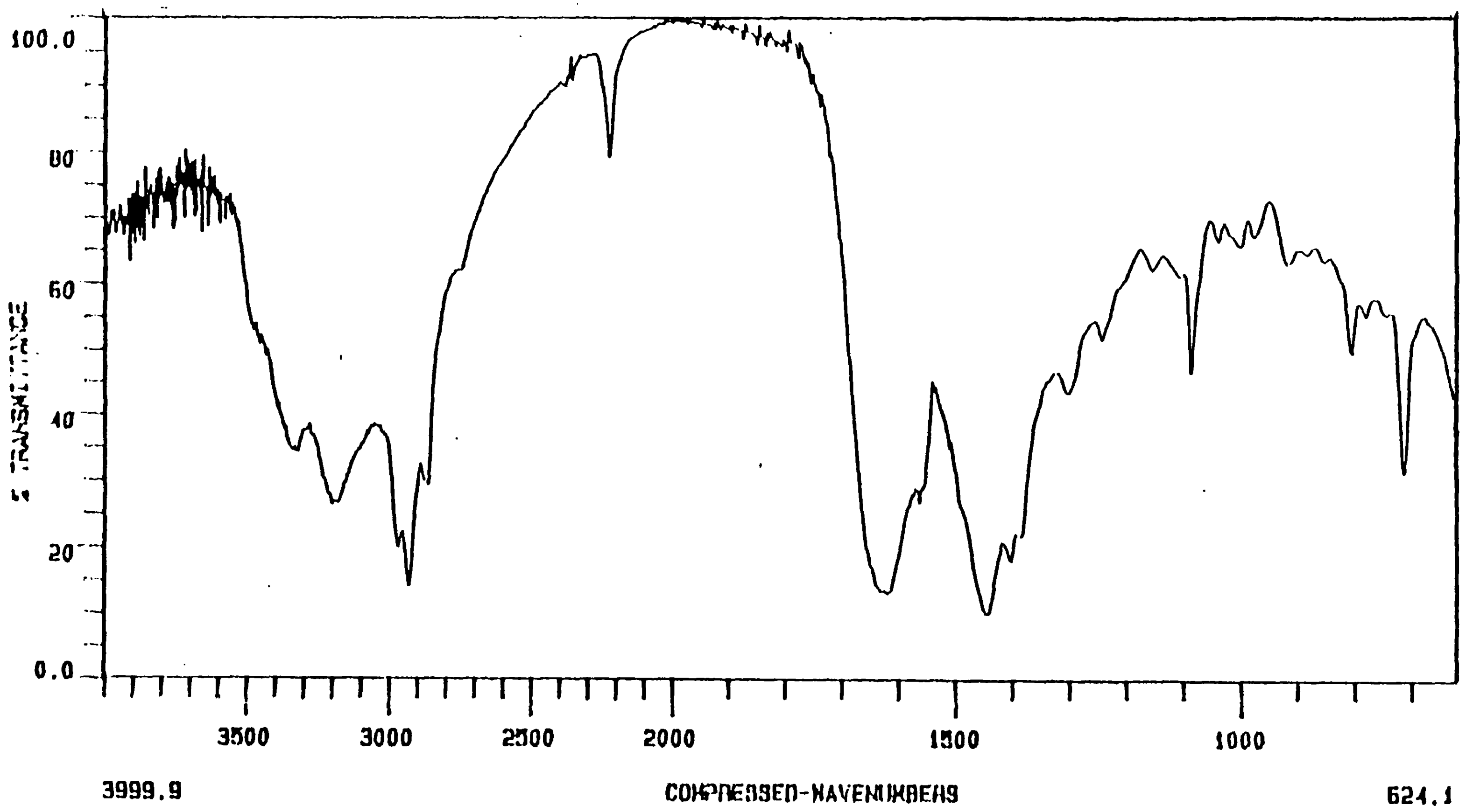


Fig. 5.14. The IR Spectrum of the Cold Ring Fraction from Degradation of End-initiated Methacrylonitrile Polymers to 500 °C under TVA Conditions.

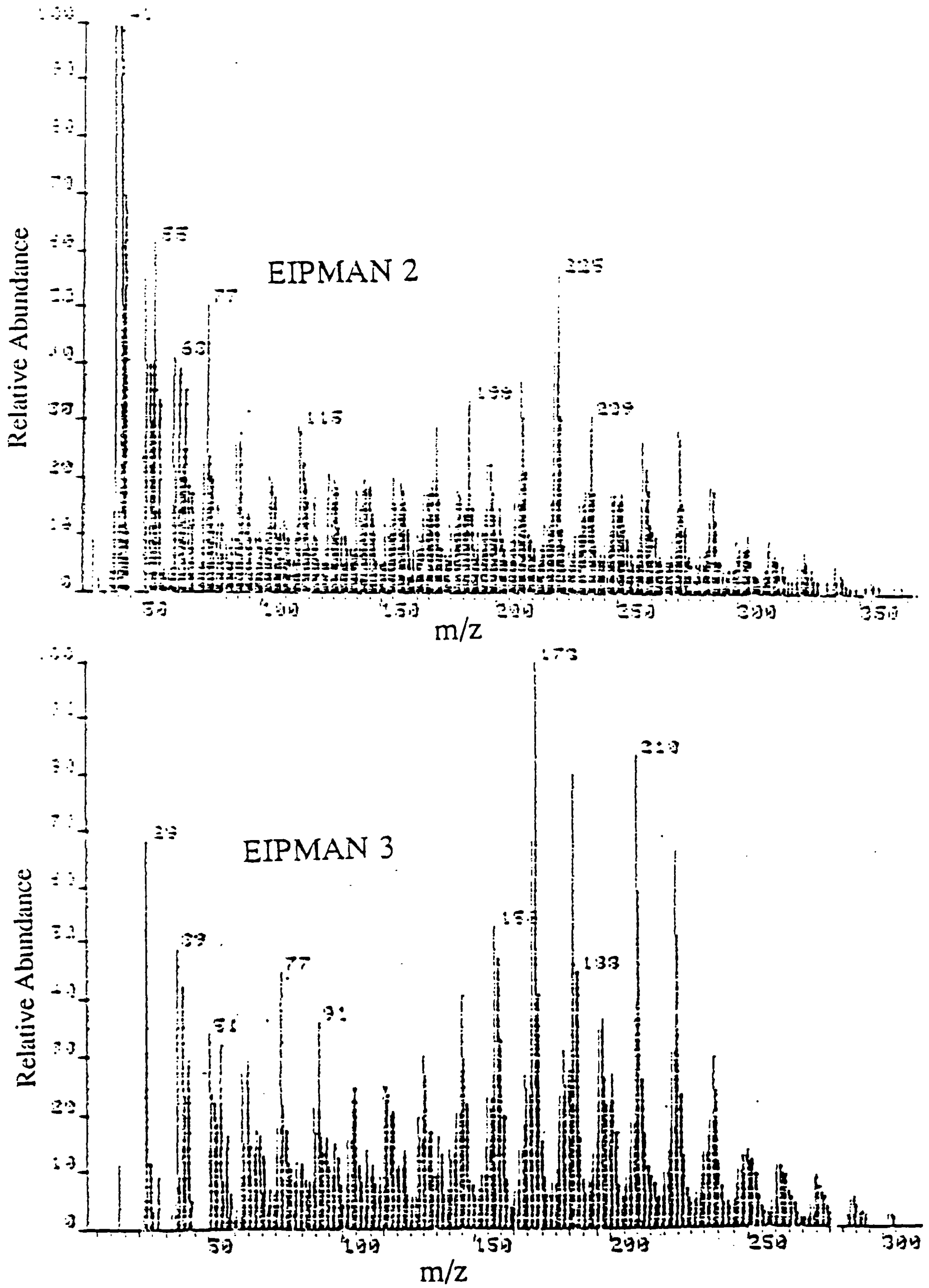
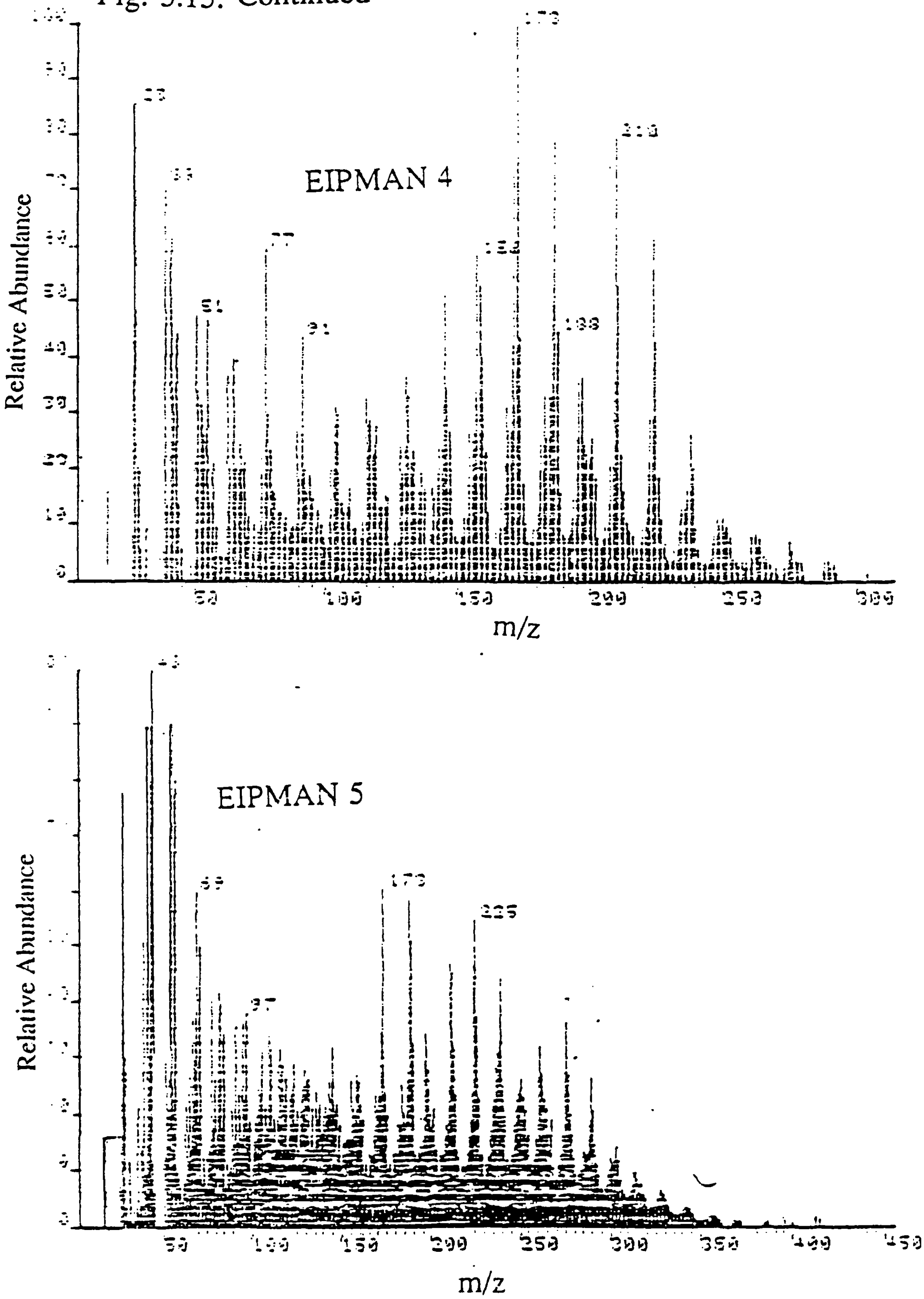


Fig. 5.15. Mass Spectrometric Results of Cold Ring Fraction from Degradation of End-initiated Methacrylonitrile Polymers to 500 ^{o}C under TVA Conditions.

(CONTINUED)

Fig. 5.15. Continued



(or most prominent) mass spectral peaks of cold ring fractions mass spectra have been assigned as the molecular-ion peaks of the compounds identified. The small peaks around major (molecular-ion) peaks have regarded as daughter-ions for the same or other higher molecular ion.

5.2.3.2.3 Condensables as liquid fraction.

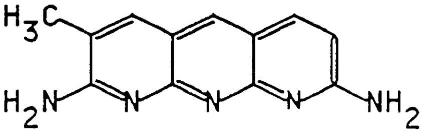
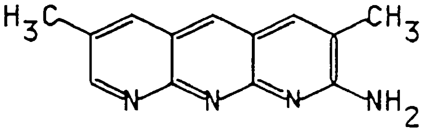
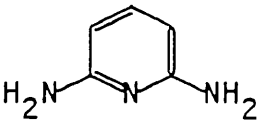
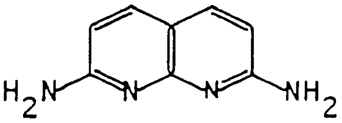
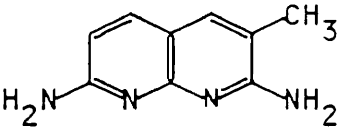
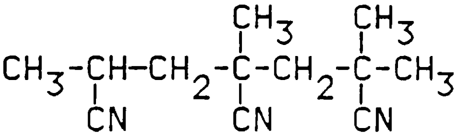
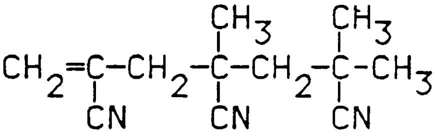
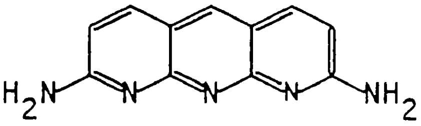
In all five end-initiated polymethacrylonitrile samples used in this investigation, the IR spectra for liquid product fractions were identical and indistinguishable from that of monomer (methacrylonitrile). Further investigation of these fractions was carried out by subjecting them to GC-MS. The chromatograms of these fractions (liquid fractions) for all five end-initiated polymers studied are illustrated in Figs. 5.16–5.20.

From GC-MS data for the liquid fractions of these five end-initiated homopolymers, it was concluded that in addition to the methacrylonitrile, which is dominant product of the total liquid fraction, the other products identified are 2-cyanobutane, 2-cyanopropane, 1-cyano-2-propene, 1-cyano-1-propene, acetonitrile and 2-cyano-2-butene in order of importance.

5.2.3.2.4 Condensables products as gases.

The condensable gaseous products from degradation of the all end-initiated methacrylonitrile polymers were examined by IR spectroscopy and mass spectrometry. Mass spectrometric studies were carried out during SATVA process by a quadrupole mass spectrometer coupled with the system, as gaseous products warmed up. Gaseous products were also examined by IR spectroscopy, by collecting in gas cells after SATVA separation. Corresponding mass spectra and infrared spectra

TABLE 5.4. Products Identified in the Cold Ring Fraction from Degradation of EIPMAN 1 Sample under normal TVA Conditions. (Products are listed According to Relative Abundance.)

Product	m/e
	225
	224
	109
	160
	174
 $CH_3-\underset{CN}{CH}-CH_2-\overset{CH_3}{\underset{CN}{C}}-CH_2-\overset{CH_3}{\underset{CN}{C}}-CH_3$	203
 $CH_2=\underset{CN}{C}-CH_2-\overset{CH_3}{\underset{CN}{C}}-CH_2-\overset{CH_3}{\underset{CN}{C}}-CH_3$	201
	211

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TABEL 5.4. CONTINUED

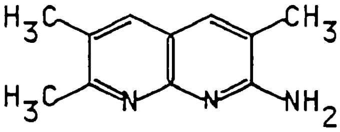
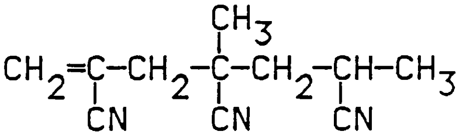
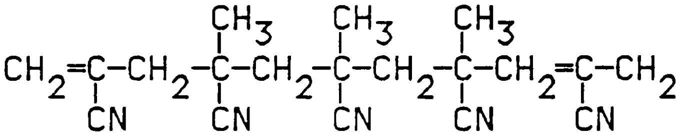
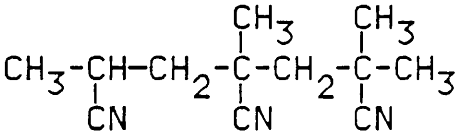
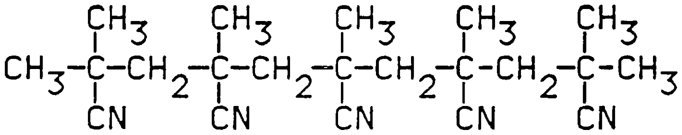
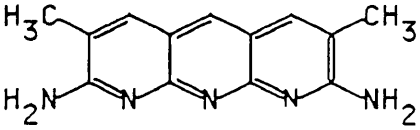
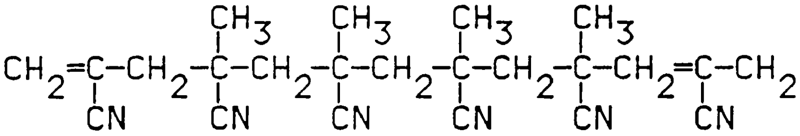
  $CH_2{=}\underset{CN}{C}{-}CH_2{-}\overset{CH_3}{\underset{CN}{C}}{-}CH_2{-}\underset{CN}{CH}{-}CH_3$	187
 $CH_2{=}\underset{CN}{C}{-}CH_2{-}\overset{CH_3}{\underset{CN}{C}}{-}CH_2{-}\overset{CH_3}{\underset{CN}{C}}{-}CH_2{-}\overset{CH_3}{\underset{CN}{C}}{-}CH_2{=}\underset{CN}{C}{-}CH_2$	319
 $CH_3{-}\underset{CN}{CH}{-}CH_2{-}\overset{CH_3}{\underset{CN}{C}}{-}CH_2{-}\overset{CH_3}{\underset{CN}{C}}{-}CH_3$	203
 $CH_3{-}\overset{CH_3}{\underset{CN}{C}}{-}CH_2{-}\overset{CH_3}{\underset{CN}{C}}{-}CH_2{-}\overset{CH_3}{\underset{CN}{C}}{-}CH_2{-}\overset{CH_3}{\underset{CN}{C}}{-}CH_2{-}\overset{CH_3}{\underset{CN}{C}}{-}CH_3$	351
	239
 $CH_2{=}\underset{CN}{C}{-}CH_2{-}\overset{CH_3}{\underset{CN}{C}}{-}CH_2{-}\overset{CH_3}{\underset{CN}{C}}{-}CH_2{-}\overset{CH_3}{\underset{CN}{C}}{-}CH_2{-}\overset{CH_3}{\underset{CN}{C}}{-}CH_2{=}\underset{CN}{C}{-}CH_2$	386

TABLE 5.5. Products Identified in the Cold Ring Fraction from Degradation of EIPMAN 2 Sample under normal TVA Conditions. (Products are listed According to Relative Abundance.)

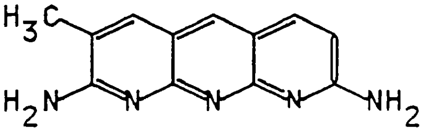
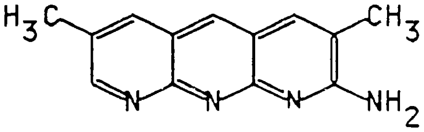
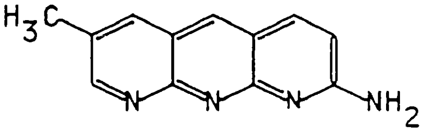
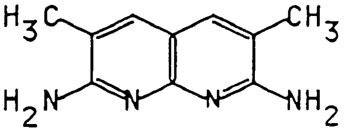
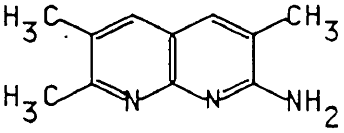
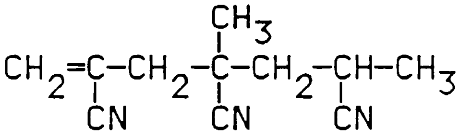
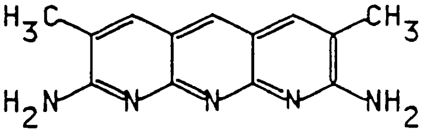
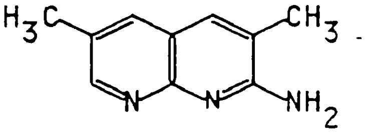
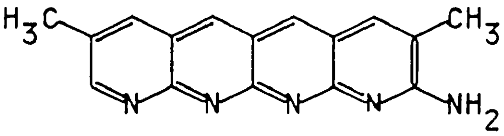
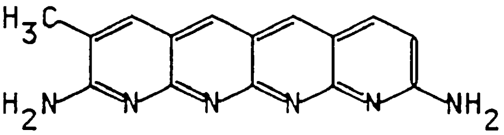
Product	m/e
	225
	224
	210
	188
  $\mathrm{CH_2{=}\underset{CN}{C}{-}CH_2{-}\overset{CH_3}{\underset{CN}{C}}{-}CH_2{-}\underset{CN}{CH}{-}CH_3}$	187
	239
	173
	275
	276

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TABLE 5.5. CONTINUED

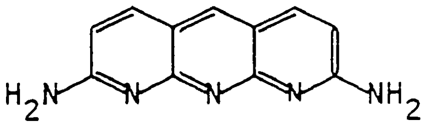
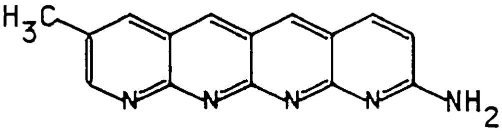
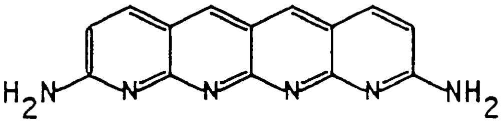
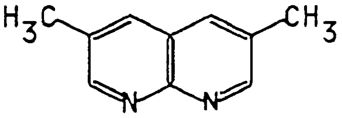
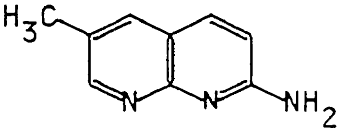
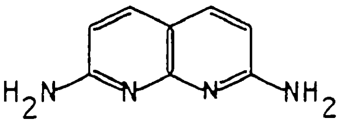
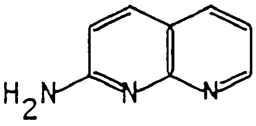
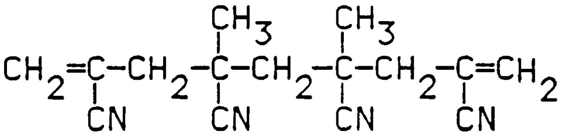
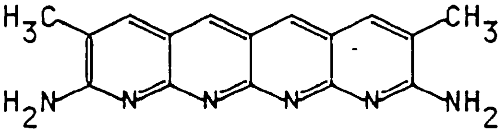
	211
	261
	262
	158
	159
	160
	145
 $CH_2{=}\underset{CN}{C}{-}CH_2{-}\underset{CN}{\overset{CH_3}{C}}{-}CH_2{-}\underset{CN}{\overset{CH_3}{C}}{-}CH_2{-}\underset{CN}{C}{=}CH_2$	252
	290

TABLE 5.6. Products Identified in the Cold Ring Fraction from Degradation of EIPMAN 3 Sample under normal TVA Conditions. (Products are listed According to Relative Abundance.)

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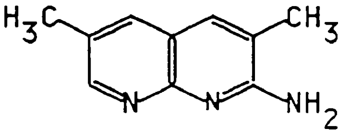
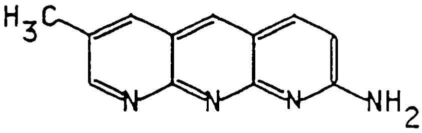
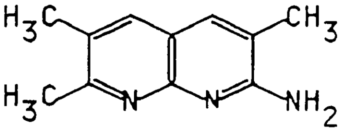
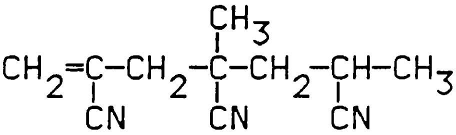
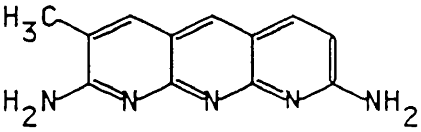
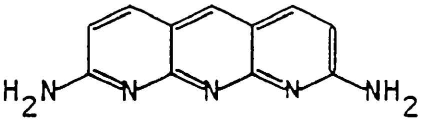
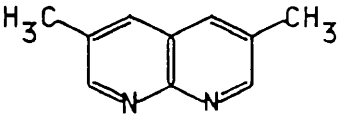
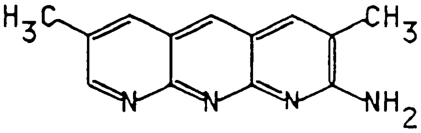
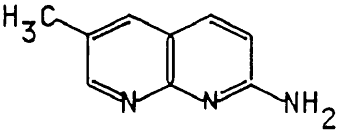
	173
	210
  $CH_2{=}\underset{CN}{C}-CH_2-\overset{CH_3}{\underset{CN}{C}}-CH_2-\underset{CN}{CH}-CH_3$	187
	225
	211
	158
	224
	159

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TABLE 5.6 CONTONUED

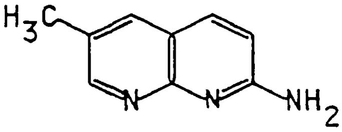
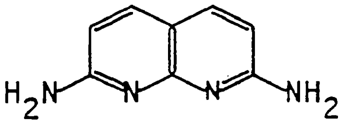
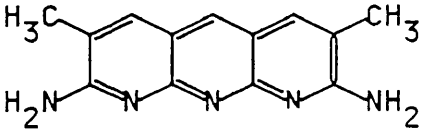
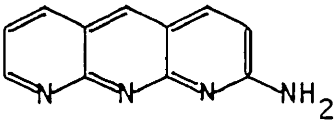
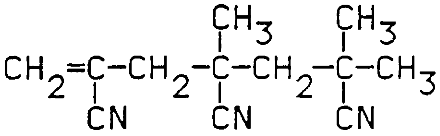
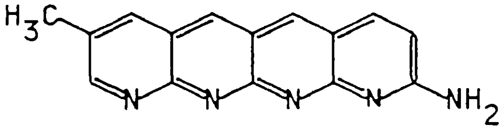
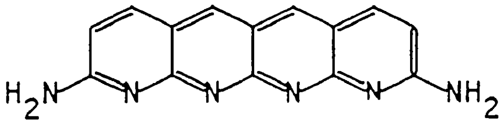
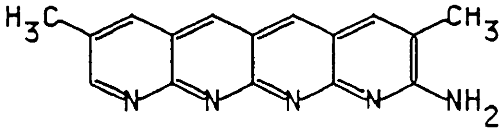
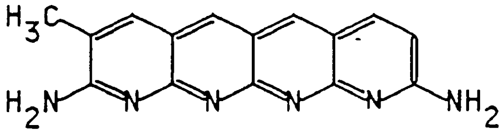
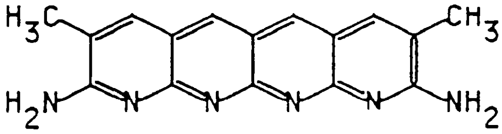
	159
	145
	239
	196
 $CH_2{=}C(CN){-}CH_2{-}C(CH_3)(CN){-}CH_2{-}C(CH_3)(CN){-}CH_3$	201
	261
	262
	275
	276
	290

TABLE 5.7. Products Identified in the Cold Ring Fraction from Degradation of EIPMAN 4 Sample under normal TVA Conditions. (Products are listed According to Relative Abundance.)

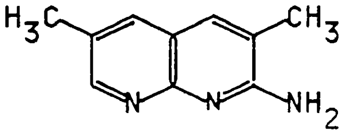
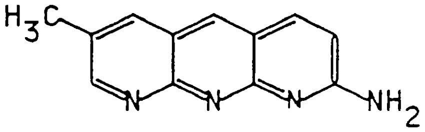
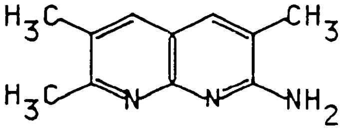
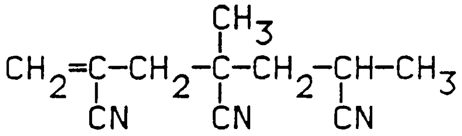
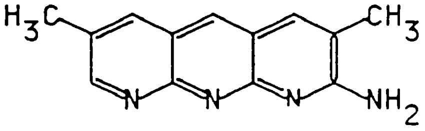
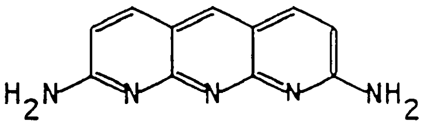
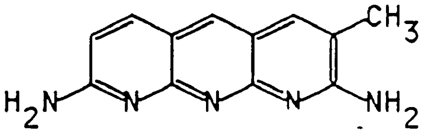
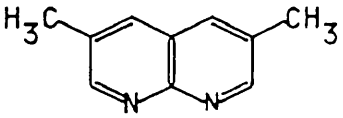
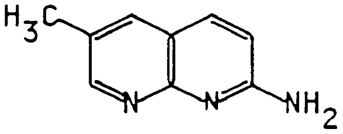
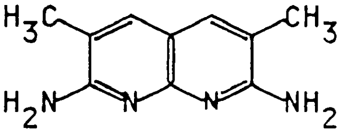
Product	m/e
	173
	210
  $CH_2{=}\underset{CN}{C}{-}CH_2{-}\underset{CN}{\overset{CH_3}{C}}{-}CH_2{-}\underset{CN}{CH}{-}CH_3$	187
	224
	211
	225
	158
	159
	188

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TABLE 5.7 CONTINUED

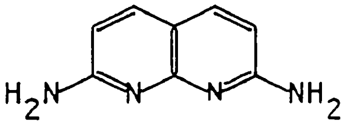
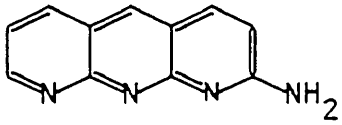
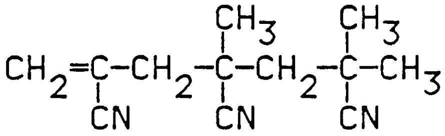
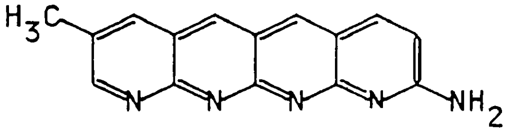
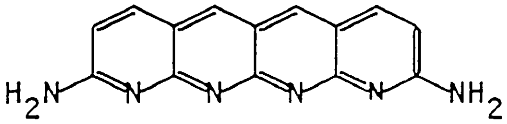
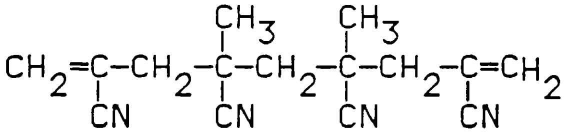
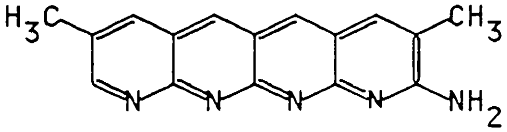
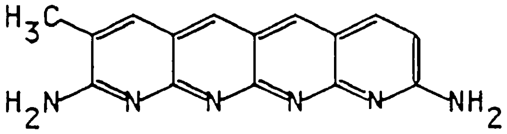
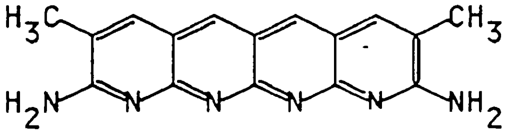
	145
	196
 $CH_2{=}\underset{CN}{C}{-}CH_2{-}\overset{CH_3}{\underset{CN}{C}}{-}CH_2{-}\overset{CH_3}{\underset{CN}{C}}{-}CH_3$	201
	261
	262
 $CH_2{=}\underset{CN}{C}{-}CH_2{-}\overset{CH_3}{\underset{CN}{C}}{-}CH_2{-}\overset{CH_3}{\underset{CN}{C}}{-}CH_2{-}\underset{CN}{C}{=}CH_2$	252
	275
	276
	290

TABLE 5.8. Products Identified in the Cold Ring Fraction from Degradation of EIPMAN 5 Sample under normal TVA Conditions. (Products are listed According to Relative Abundance.)

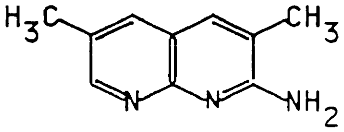
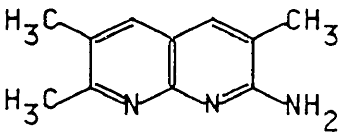
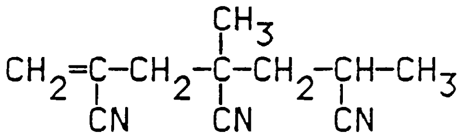
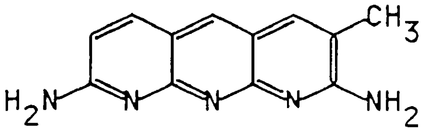
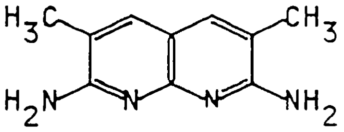
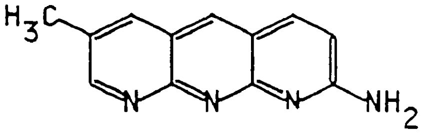
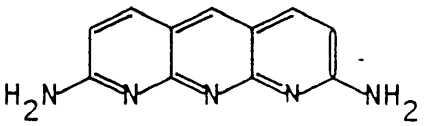
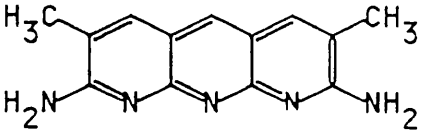
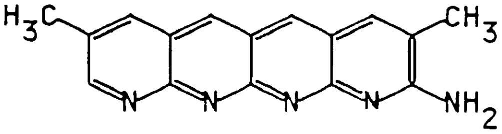
Product	m/e
	173
  $CH_2{=}\underset{CN}{C}{-}CH_2{-}\overset{CH_3}{\underset{CN}{C}}{-}CH_2{-}\underset{CN}{CH}{-}CH_3$	187
	225
	188
	210
	211
	239
	275

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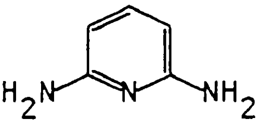
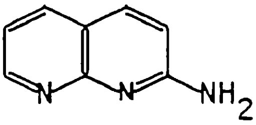
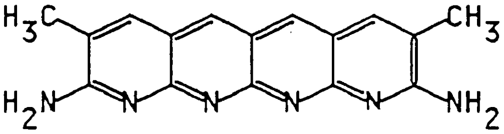
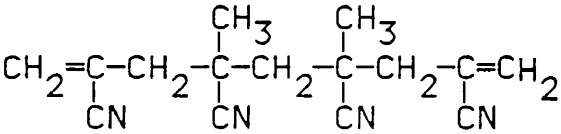
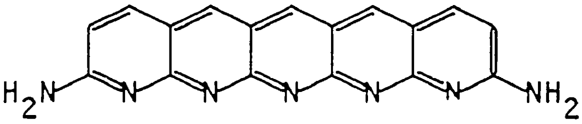
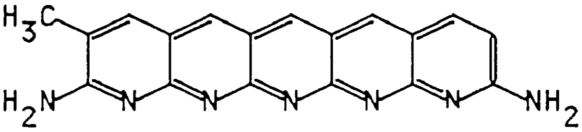
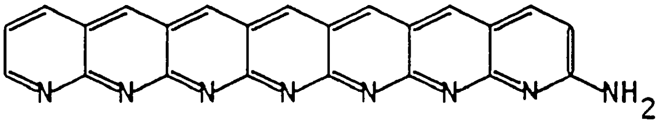
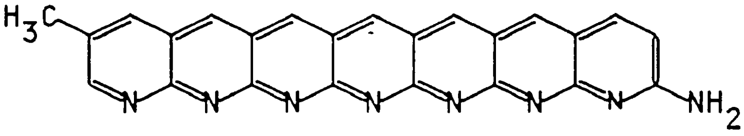
TABLE 5.8 CONTINUED

	109
	145
	290
 $CH_2{=}\underset{CN}{C}{-}CH_2{-}\underset{CN}{\overset{CH_3}{C}}{-}CH_2{-}\underset{CN}{\overset{CH_3}{C}}{-}CH_2{-}\underset{CN}{C}{=}CH_2$	252
	313
	327
	400
	414

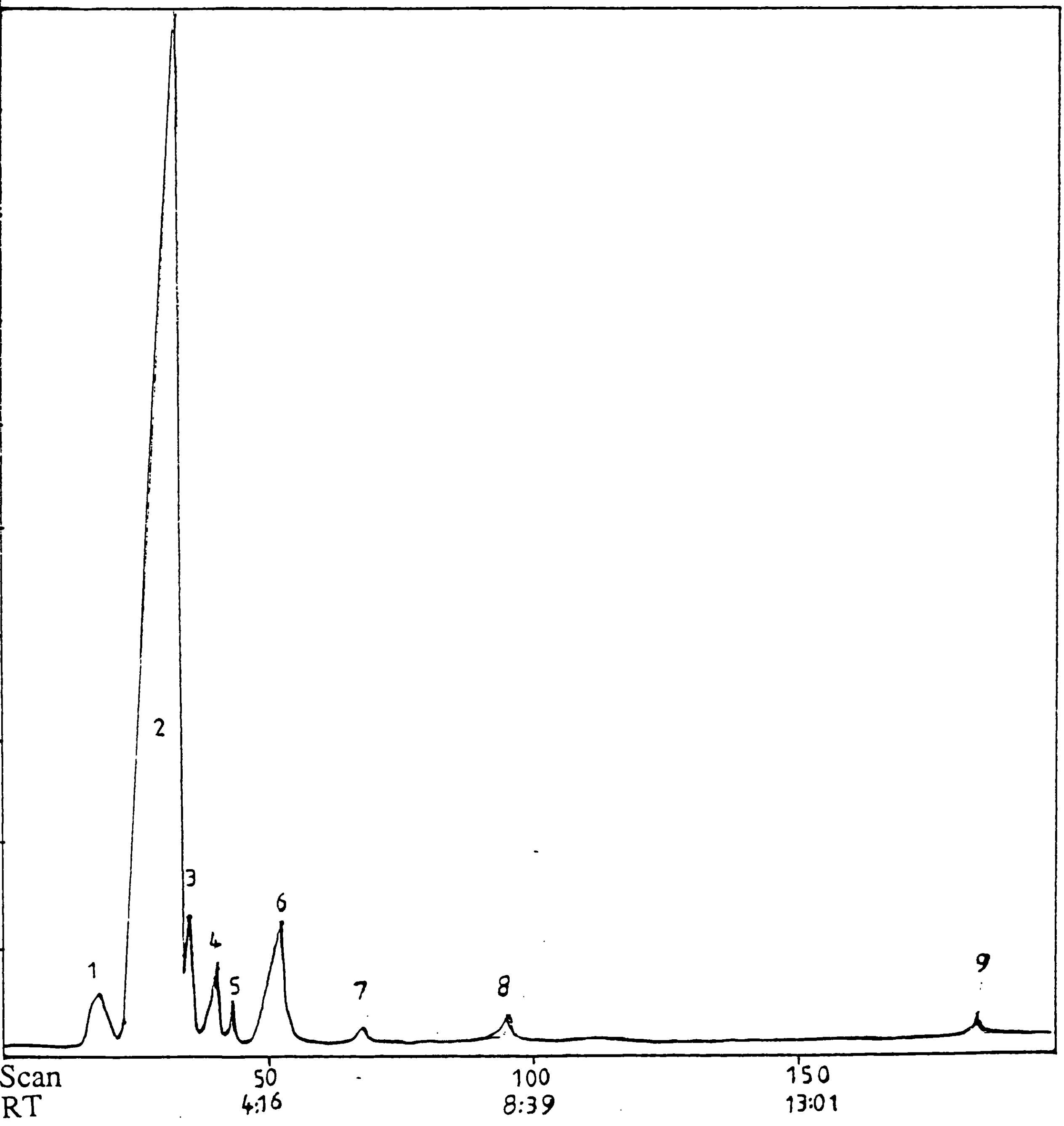


Fig. 5.16. GC-Data for the Less Volatile Fraction from Degradation of EIPMAN 1 in the TVA System under Vacuum at 10 ^{o}C/min.

ASSIGNMENTS

1. Acetonitrile **2.** Methacrylonitrile **3.** 2-Cyanopropane
4. 1-Cyano-2-propene, **5.** 1-Cyano-1-propene,
6. 2-Cyanobutane, **7.** 2-Cyano-2-butene,
8. 2-Cyano-2-methylpentane, **9.** Unknown.

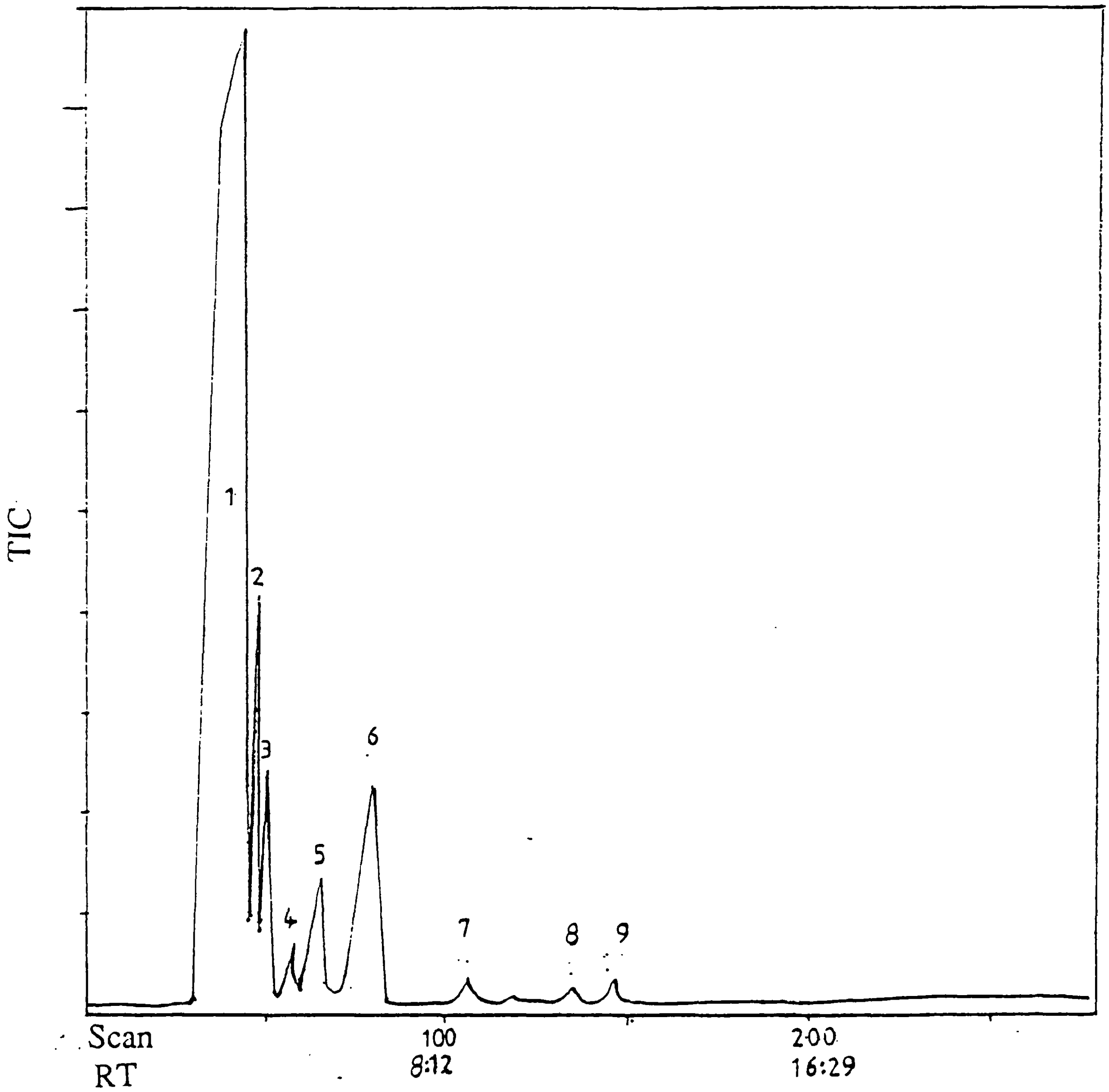


Fig. 5.17. GC-Data for the Less Volatile Fraction from Degradation of EIPMAN 2 in the TVA System under Vacuum at 10 ^{o}C/min.

ASSIGNMENTS

1. Methacrylonitrile, **2.** 2-Cyanopropane, **3.** 1-Cyano-2-propene,
4. 1-Cyano-1-propene, **5.** 2-Cyano-1-propene, **6.** 2-Cyanobutane,
7. 2-Cyano-2-butene, **8.** 4-Cyano-2-methyl-1-pentene **9.** Unknown

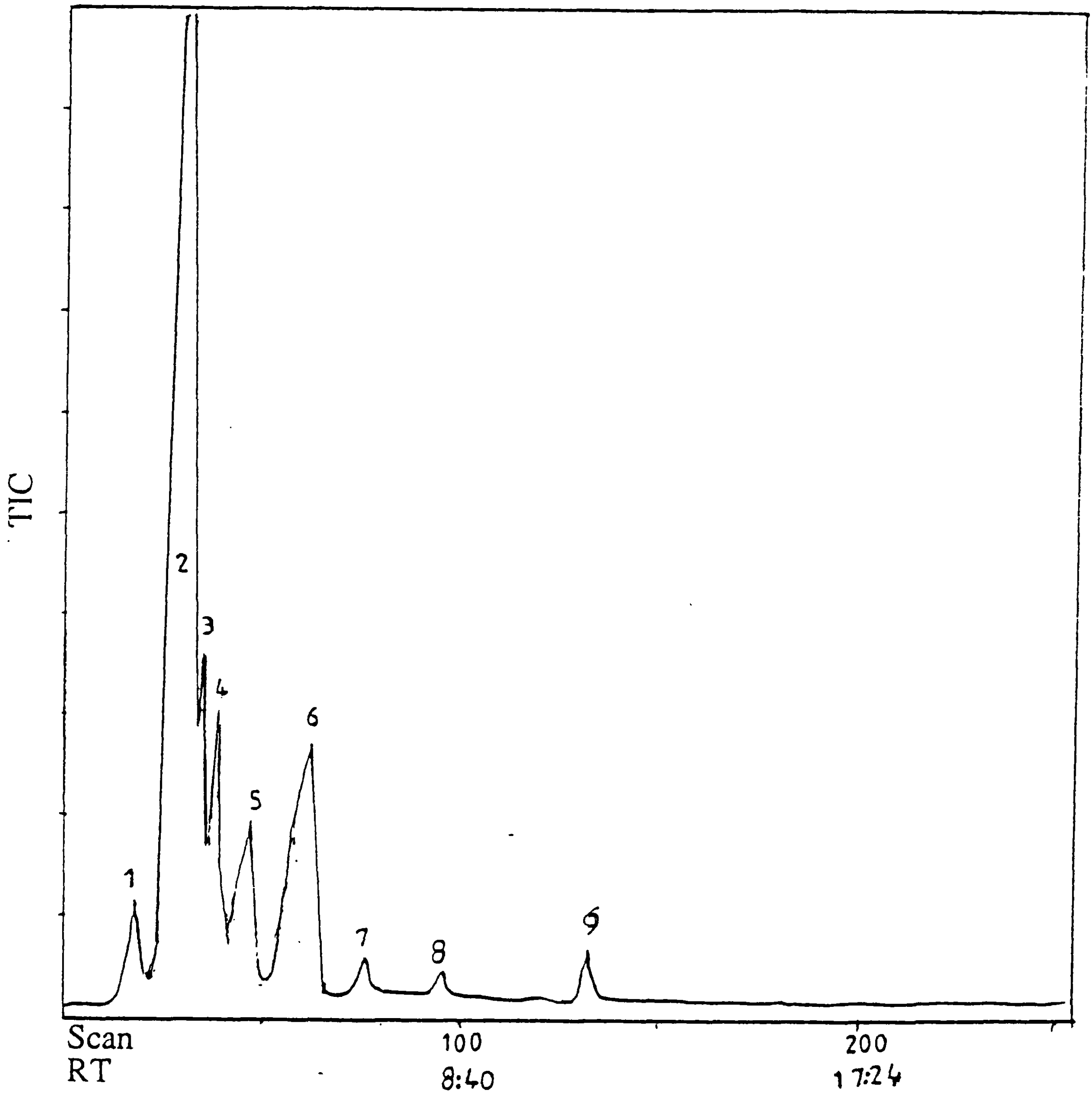


Fig. 5.18. GC-Data for the Less Volatile Fraction from Degradation of EIPMAN 3 in the TVA System under Vacuum at 10 ^{o}C/min.

ASSIGNMENTS

1. Acetonitrile, **2.** Methacrylonitrile, **3.** 2-Cyanopropane,
4. 1-Cyano-2-propene, **5.** 1-Cyano-1-propene, **6.** 2-Cyanobutane,
7. 2-Cyano-2-butene, **8.** 4-Cyano-2-methyl-1-pent~~y~~ene, **9.** Unknown.

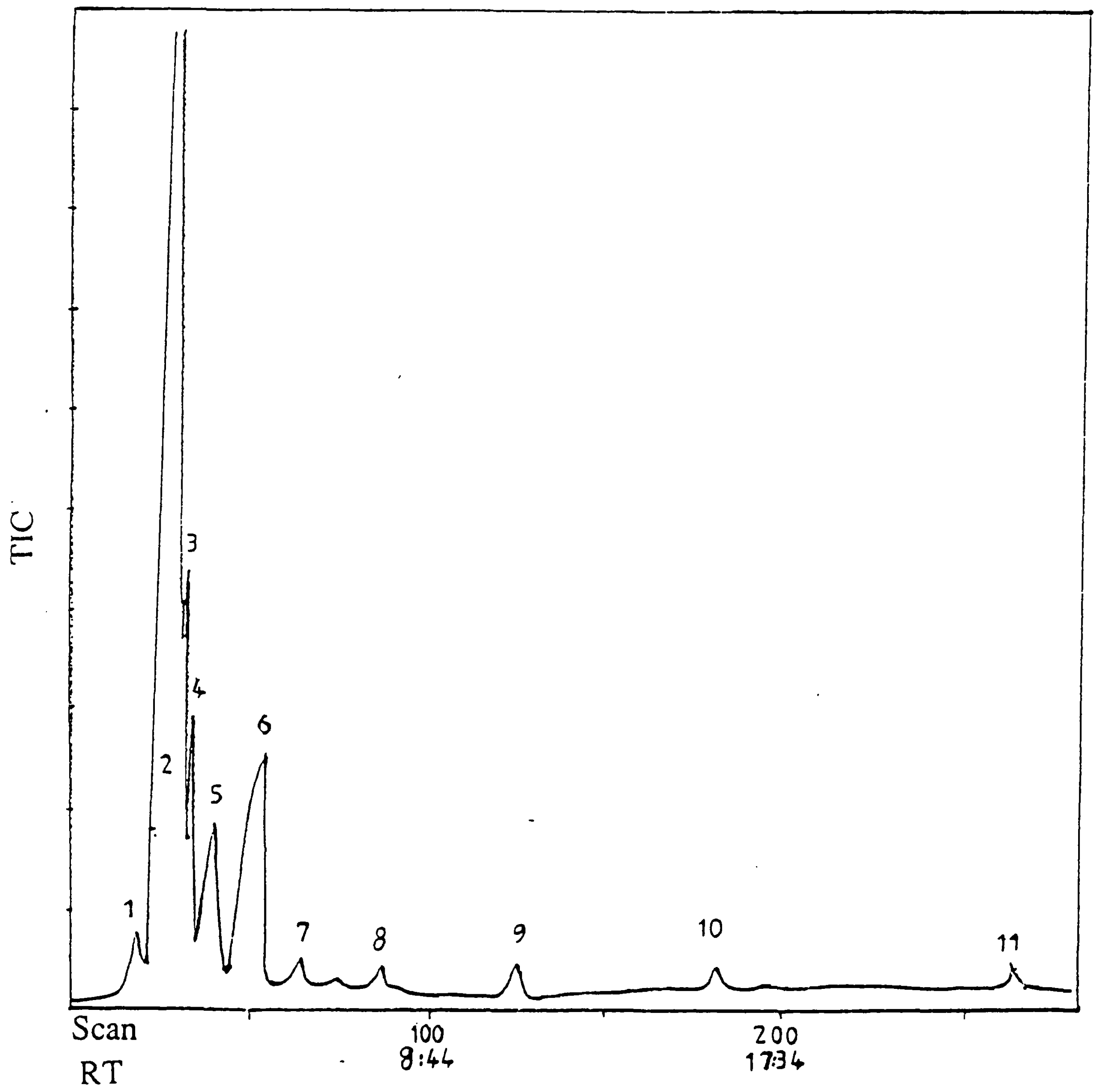


Fig. 5.19. GC-Data for the Less Volatile Fraction from Degradation of EIPMAN 4 in the TVA System under Vacuum at 10 °C/min.

ASSIGNMENTS

1. Acetonitrile, **2.** Methacrylonitrile, **3.** 2-Cyanopropane,
4. 1-Cyano-2-propene **5.** 1-Cyano-1-propene, **6.** 2-Cyanobutane,
7. 2-Cyano-2-butene, **8.** 4-Cyano-2-methyl-1-pent~~y~~ene, **9.** Unknown,
10. 3, 4-Dimethylpyrrole, **11.** Unknown,
12. MAN dimer with extra methyl group.

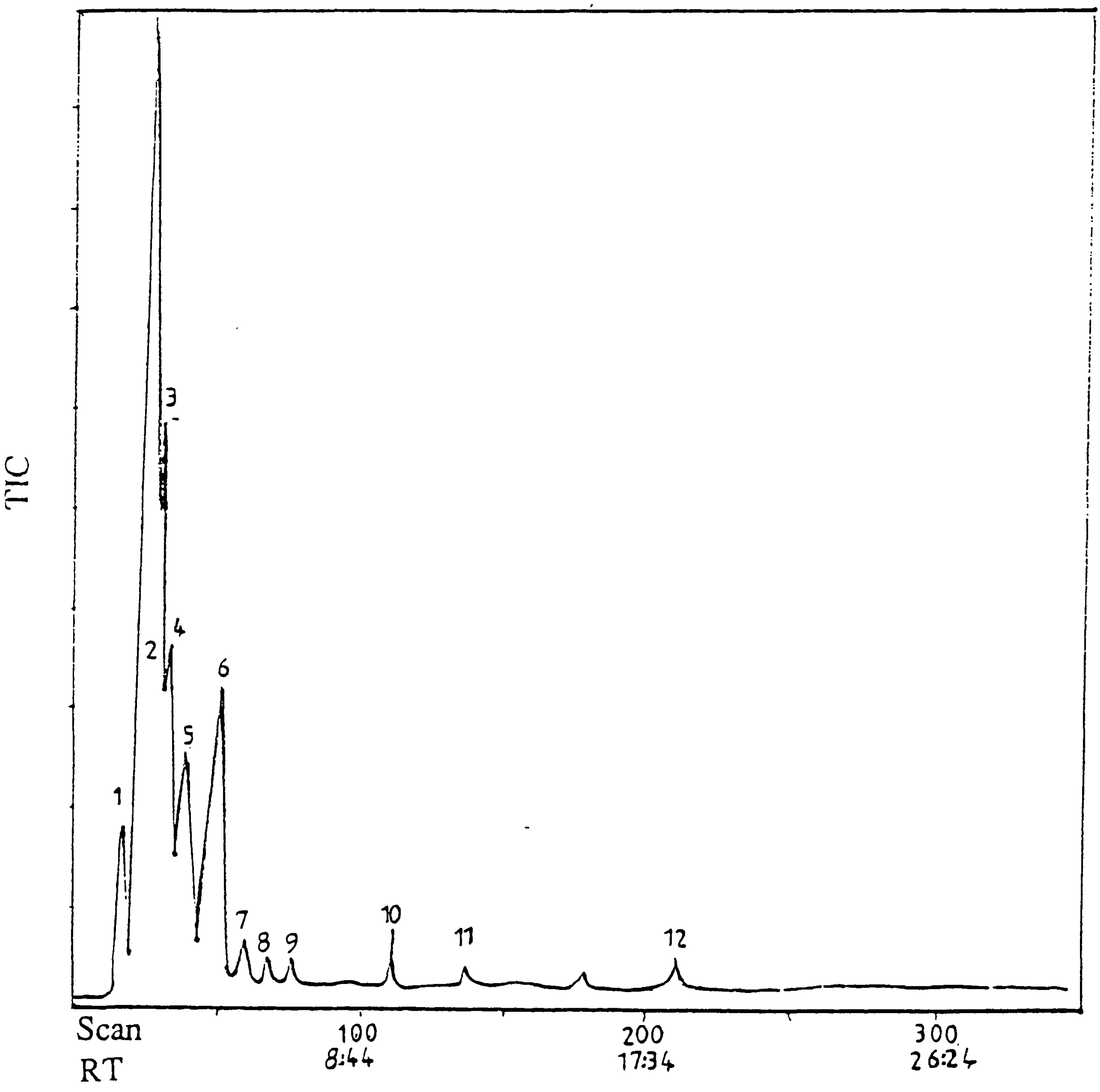


Fig. 5.20. GC-Data for the Less Volatile Fraction from Degradation of EIPMAN 5 in the TVA System under Vacuum at 10 °C/min.

ASSIGNMENTS

1. Acetonitrile, **2.** Methacrylonitrile, **3.** 2-Cyanopropane,
4. 1-Cyano-2-propene **5.** 1-Cyano-1-propene, **6.** 2-Cyanobutane,
7. 2-Cyano-2-butene, **8.** 2-Cyano-4-methyl-1-pentne,
9.2-Cyano-4-methyl-1-pentene, **10.** Unknown, **11.** 3,4-Dimethylpyrrole.
12. MAN dimer with extra methyl group.

are reproduced in Figs. 5.21 and 5.22 respectively.

The gaseous products identified are mainly ammonia, carbon dioxide, propane, isobutene and hydrogen cyanide. It may be significant that the amount of ammonia, carbon dioxide and propane were observed to increase with decreasing molecular weight of the polymer sample.

The gaseous products for each end-initiated polymer sample studied are listed in Tables 5.9, 5.10, 5.11, 5.12, and 5.13 respectively.

5.2.3.2.5 Non-condensable gases.

In all five end-initiated polymers studied, formation of non-condensable was observed above 250 ^{o}C during TVA studies. Methane was identified as main non-condensable gas by a quadrupole mass spectrometer coupled with TVA system. Small amounts of hydrogen and carbon monoxide gases were also detected above 400 ^{o}C. A typical mass spectrum of the non-condensables gases is included in Fig. 5.23.

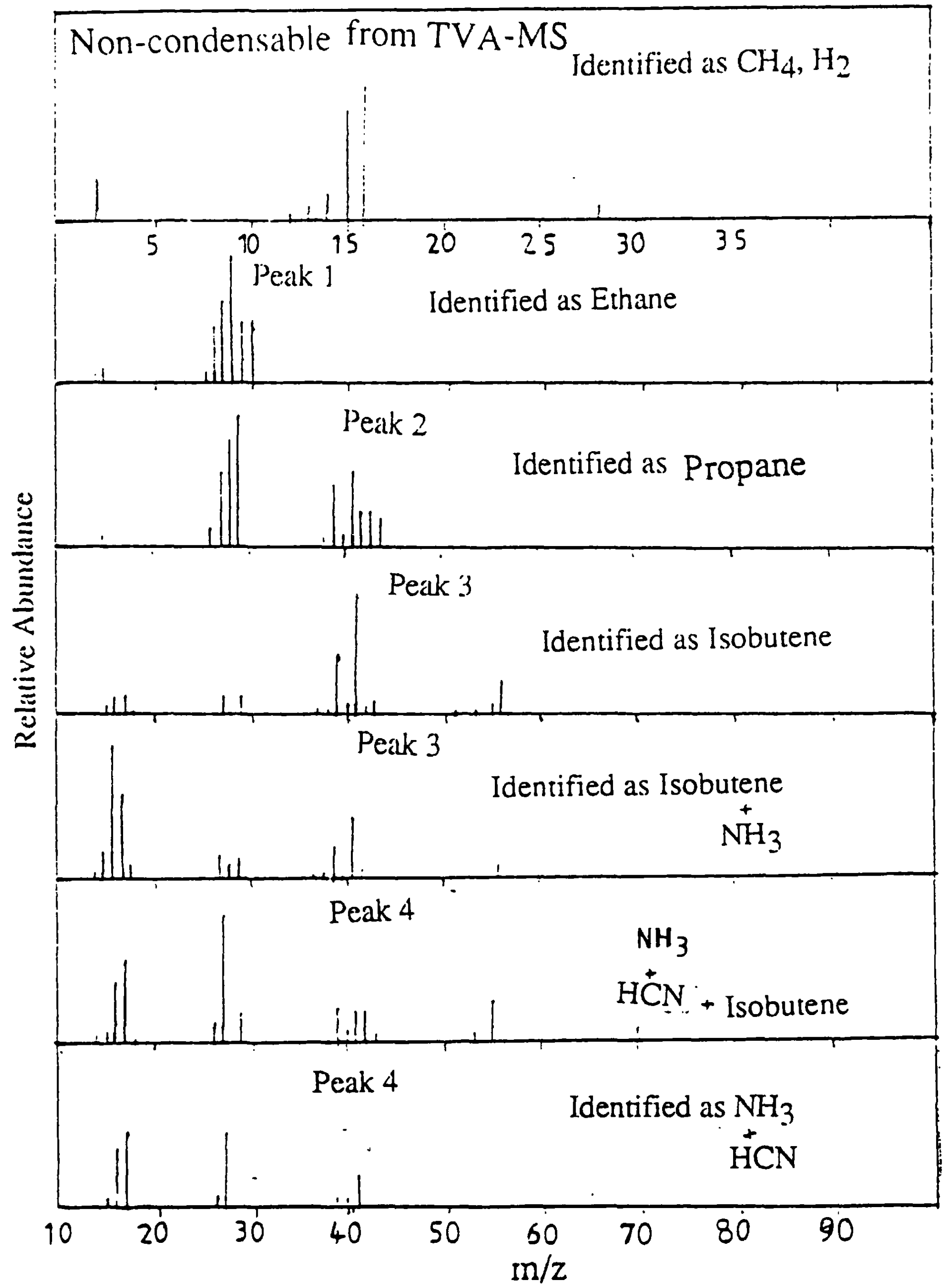


Fig. 5.21. Mass Spectrometric Results of Condensable Gases (from SATVA) and Non-condensable Gases (from Degradation in the TVA System under Vacuum at 10 °C/min to 500 °C) for the End-initiated Methacrylonitrile Polymers.

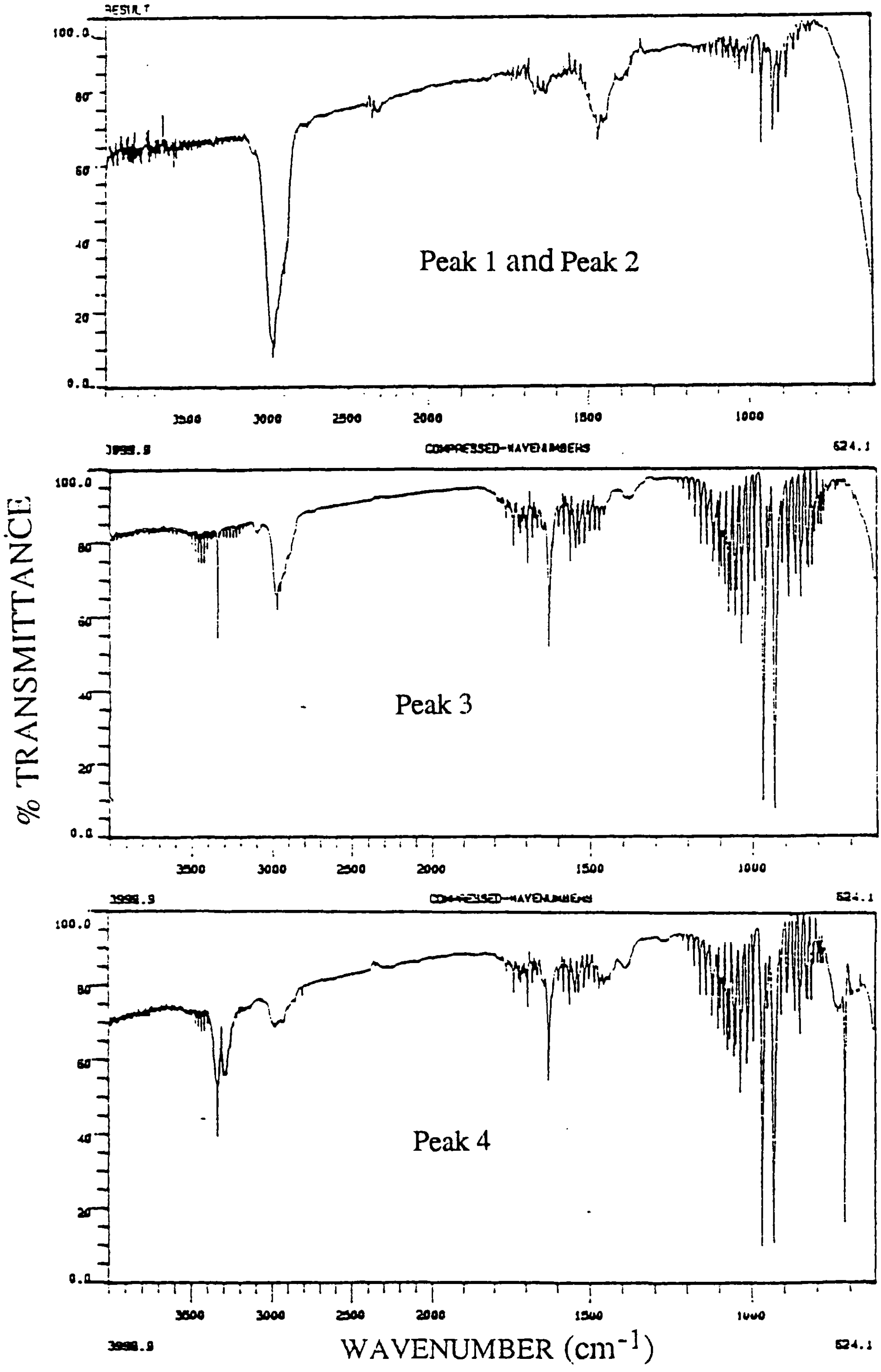


Fig. 5.22. The IR Spectra of Condensable Gases for the Degradation of End-initiated Methacrylonitrile Polymers under Vacuum at 10 °C/min to 500 °C.

TABLE 5.9 Products of Degradation of PMAN 1 Heated to 500 °C at 10 °C/min Under TVA Conditions.

Non-condensable products at -196 °C	Condensable Volatile products at -196 °C		CRF	Residue
	Gases	Liquid Fraction		
MS	IR , MS	IR , MS , GC-MS	IR , MS	IR
Methane Hydrogen	Ethene* Ethane Propane Isobutene Isopentene* Hydrogen-cyanide Ammonia	Acetonitrile Methacrylonitrile 2-Cyanopropane 1-Cyano-2-propene 1-Cyano-1-propene 2-Cyanobutane 2-Cyano-2-butene 2-Cyano-4-methylpantane	Amino & methyl substituted heterocyclic (nitrogen containing) fussed ring structures & various type of oligomers.	Black char

* Products only identified by MS (i.e. not by IR spectroscopy.)

TABLE 5.10 Products of Degradation of PMAN 2 Heated to 500 °C at 10 °C/min Under TVA Conditions.

Non-condensable Products at -196 °C	Condensable Volatile Products at -196 °C		CRF	Residue
	Gases	Liquid Fraction		
MS	IR , MS	IR , MS , GC-MS	IR , MS	IR
Methane Hydrogen	Ethene* Ethane Propane Isobutene Isopentene* Hydrogen-cyanide Ammonia	Methacrylonitrile 2-Cyanopropane 1-Cyano-2-propene 1-Cyano-2-butene 1-Cyano-1-propene 2-Cyanobutane 2-Cyano-2-butene 4-Cyano-2-methyl-1-pentene	Amino & methyl substituted heterocyclic (nitrogen containing) fussed ring structures & various type of oligomers .	Black char

* Products only identified by MS (i.e. not by IR spectroscopy.)

TABLE 5.11 Products of Degradation of PMAN 3 Heated to 500 °C at 10 °C/min Under TVA Conditions.

Non-condensable products at -196 °C	Condensable Volatile products at -196 °C		CRF	Residue
	Gases	Liquid Fraction		
MS	IR , MS	IR , MS , GC-MS	IR , MS	IR
Methane	Ethene*	Acetonitrile	Amino & methyl substituted heterocyclic (nitrogen containing) fussed ring structures & various type of oligomers.	Black char
Hydrogen	Ethane	Methacrylonitrile		
	Propane	2-Cyanopropane		
	Isobutene	1-Cyano-2-propene		
	Isopentene*	1-Cyano-1-propene		
	Hydrogen-cyanide	2-Cyanobutane		
		2-Cyano-2-butene		
	Ammonia	4-Cyano-2-methyl-2-pentene		

* Products only identified by MS (i.e. not by IR spectroscopy.)

TABLE 5.12 Products of Degradation of PMAN 4 Heated to 500 °C at 10 °C/min Under TVA Conditions.

Non-condensable products at -196 °C	Condensable Volatile products at -196 °C		CRF	Residue
	Gases	Liquid Fraction		
MS	IR , MS	IR , MS , GC-MS	IR , MS	IR
Carbon-monoxide Methane Hydrogen	Ethene* Ethane Propane Isobutene Propene* Isopentene* Hydrogen-cyanide Ammonia	Acetonitrile Methacrylonitrile 2-Cyanopropane 1-Cyano-2-propene 1-Cyano-1-propene 2-Cyanobutne 2-Cyano-2-butene 2-Cyano-4-methyl-1-butene 3,4-Dimethylpyrrole Saturated MAN dimer with extra methyl (CH_3) group	Amino & methyl substituted heterocyclic (nitrogen containing) fussed ring structures & various type of oligomers.	Black char

* Products only identified by MS (i.e. not by IR spectroscopy.)

TABLE 5.13 Products of Degradation of PMAN 5 Heated to 500 °C at 10 °C/min Under TVA Conditions.

Non-consable products at	Condensable Volatile products at -196 °C		CRF	Residue
-196 °C	Gases	Liquid Fraction		
MS	IR , MS	IR , MS , GC-MS	IR , MS	IR
Carbon-monoxide Hydrogen	Ethene* Ethane Propane Isobutene Propene* Isopentene* Hydrogen-cyanide Ammonia	Acetonitrile Methacrylonitrile 2-Cyanopropane 1-Cyano-2-propene 1-Cyano-1-propene 2-Cyanobutane 2-Cyano-2-butene 2-Cyano-4-methyl-1-pentene 4-Cyano-2-methyl-1-pentene 3,4- Dimethylpyrrole Saturated MAN dimer with extra methyl (CH3) group	Amino &methyl substituted heterocyclic (nitrogen containing) fussed ring structures & various type of oligomers.	Black char

* Products only identified by MS (i.e. not by IR spectroscopy.)

CHAPTER SIX

THERMAL DEGRADATION OF METHACRYLONITRILE/METHACRYLIC ACID COPOLYMERS

6.1 INTRODUCTION

The effect of colouration initiated from the polymer chain end on the thermal degradation of polymethacrylonitrile, and on the products of degradation has been investigated in Chapter Five. It has been observed, in these studies, that the end-initiated methacrylonitrile polymer samples did not simply depolymerise to monomer as expected[6] and observed[24] in case of a polymer made from 1:1 disubstituted monomer, but due to the presence of terminal acidic group (-COOH) which is capable of initiating colouration, various types of other degradation products beside monomer were identified. Formation of these other degradation products indicates some other degradative routes as well (beside depolymerisation). In this chapter another approach in which the effect of colouration initiated from within the polymer chain (rather than colouration initiated from the polymer chain end) has been employed. For this purpose three copolymers of methacrylonitrile containing small amounts of methacrylic acid comonomer units have been synthesised and their thermal degradation has been studied. The origin of the copolymers used in this investigation is listed in Table 6.1.

TABLE 6.1 Data for the Methacrylonitrile/Methacrylic Acid Copolymers Used in this Investigation.

Polymer	Initiator	Composition*		$\overline{M}n$ by
		In monomer	In copolymer	GPC
COMAN/MAA 1	AIBN	72	45	7325
COMAN/MAA 2	AIBN	41	25	10720
COMAN/MAA 3	AIBN	17	10	12830

Composition* Molar ratios (Methacrylonitrile/Methacrylic acid)

$\overline{M}n$ Number-average molecular weight

6.2 PROGRAMMED HEATING

6.2.1 THERMOGRAVIMETRY

The TG and DTG curves for the methacrylonitrile/methacrylic acid copolymers (COMAN/MAA) were obtained under dynamic nitrogen at a heating rate of 10 ^{o}C/min and are reproduced in Figs. 6.1−6.3.

All three copolymers show a similar pattern of degradation. DTG studies show a main decomposition peak which follows a small decomposition curve at the later stage of degradation. The DTG curves for the main decomposition peak which starts around 250 ^{o}C and shows T_{max} in the temperature region 360 ^{o}C to 375 ^{o}C. It is obvious from the TG and DTG curves that a further more gradual weight loss is observed after 500 ^{o}C indicating the presence of some kind of stable material decomposing very slowly at that higher temperature. TG curves for these copolymer samples have shown a significant amount of residue (around 35−45%) after programmed heating to 500 ^{o}C, and this is observed to increase with increasing methacrylic acid comonomer units. This behaviour of increase in residue with increasing colouration initiating sites was also observed in case of end-initiated PMAN in Chapter Five.

The main features of the TG and DTG data are summarised in Table 6.2.

6.2.2 DIFFERENTIAL THERMAL ANALYSIS.

DTA curves for the three methacrylonitrile/methacrylic acid copolymer samples used in this investigation, were obtained under dynamic

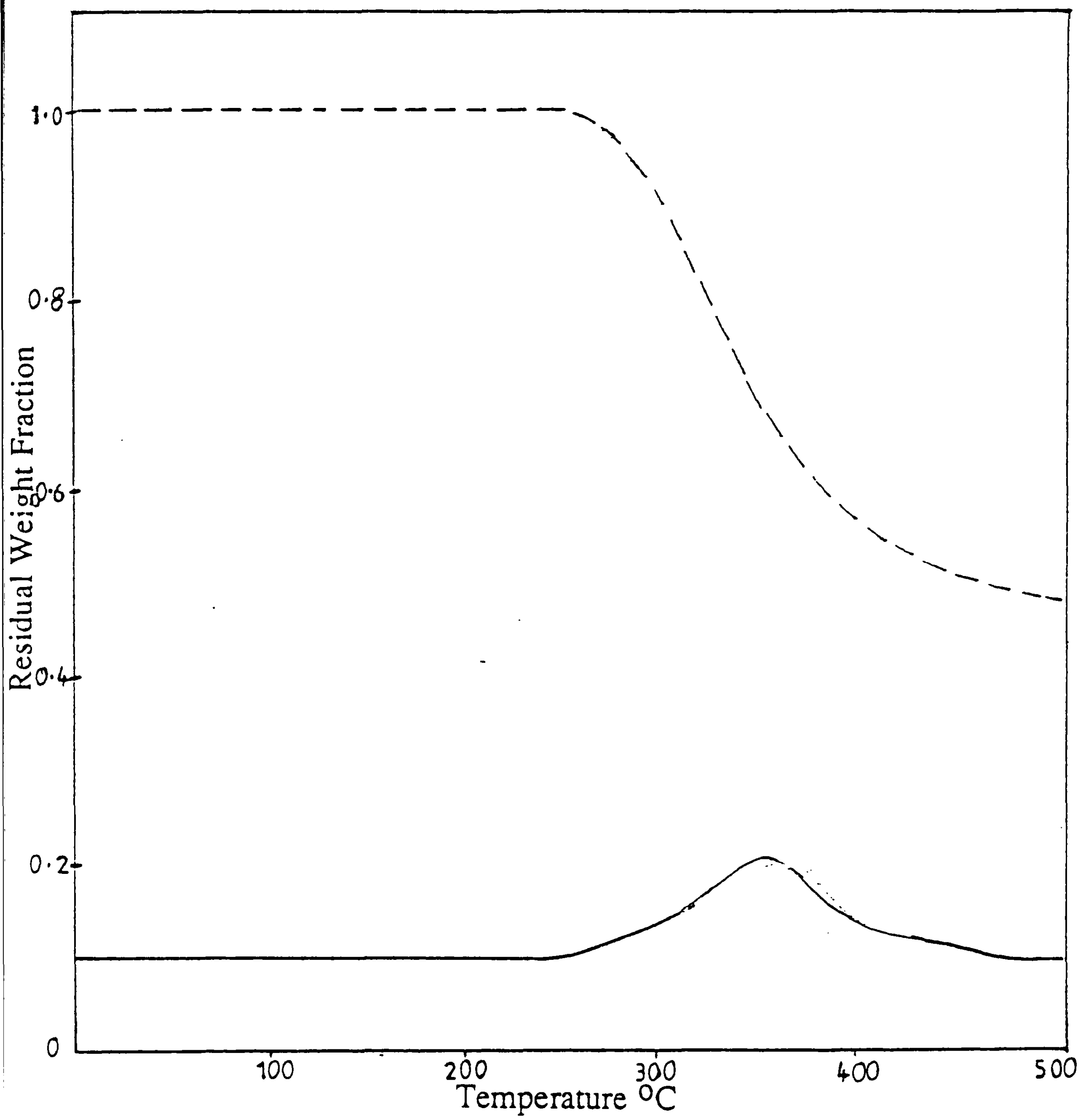


Fig. 6.1. TG and DTG Curves (Dynamic Nitrogen Atmosphere, Heating Rate 10 °C/min.) for COMAN/MAA 1.

Keys: TG — — — DTG ————

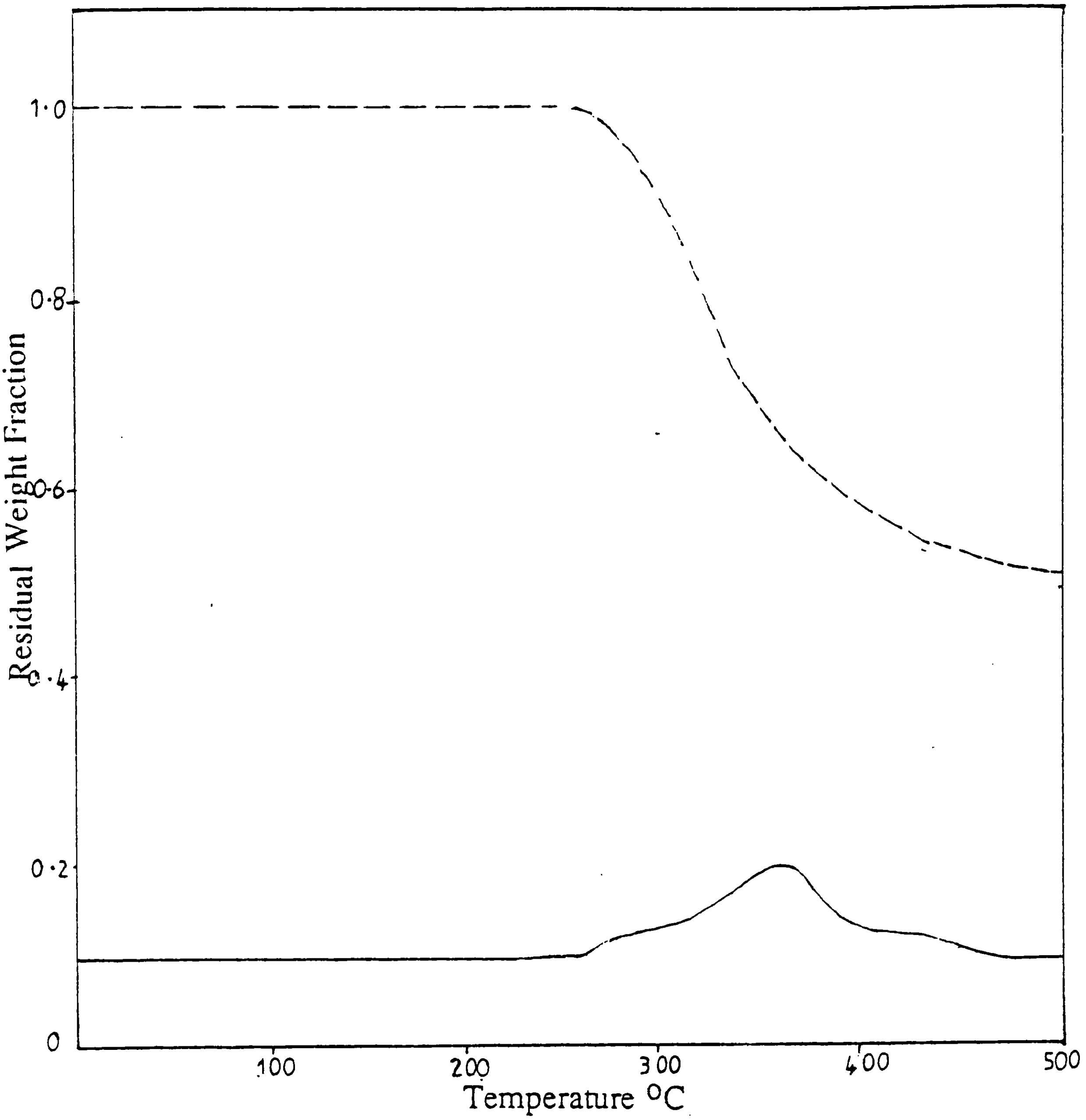


Fig.. 6.2. TG and DTG Curves (Dynamic Nitrogen Atmosphere, Heating Rate 10 °C/min.) for COMAN/MAA 2.

Keys: TG — — — DTG ————

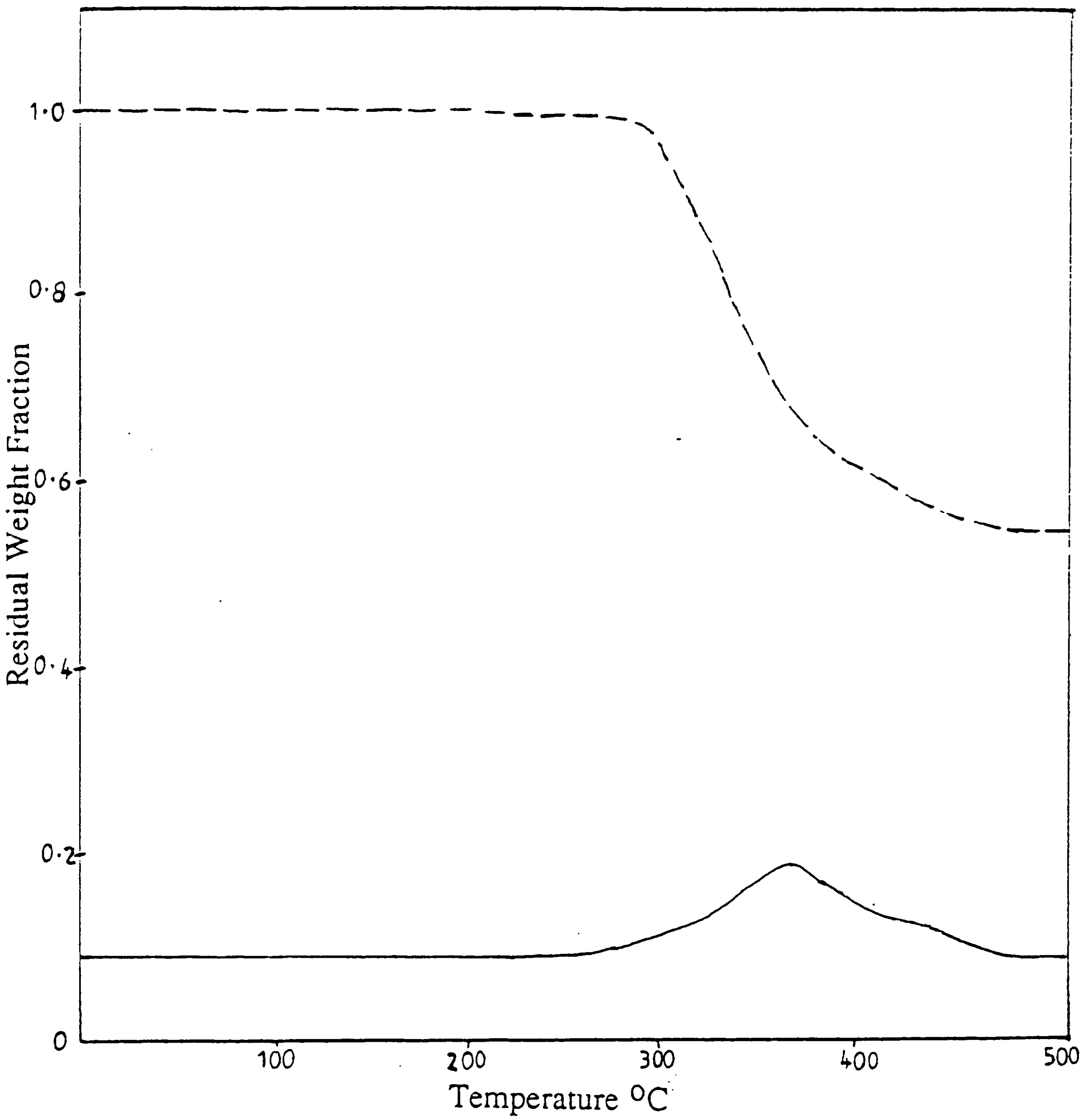


Fig. 6.3. TG and DTG Curves (Dynamic Nitrogen Atmosphere, Heating Rate 10 °C/min.) for COMAN/MAA 3.

Keys: TG — — — DTG ————

nitrogen at a heating rate of 10 ^{o}C/min, are reproduced in Fig. 6.4.

The DTA curves for the copolymers are mainly featureless showing an endotherm around 365 ^{o}C, and do not exhibit any significant exothermic response. A slight exothermic broadening "A" (in Fig. 6.4) around 325 ^{o}C is reproducible as has already observed in low molecular weight end-initiated methacrylonitrile polymers (i.e. EIPMAN 4 & 5), but is not significant enough to attribute to nitrile cyclisation as in the case of polyacrylonitrile.[67,68] The actual exothermicity in the present studies (in case of end-initiated polymethacrylonitrile polymers and methacrylonitrile polymers with methacrylic acid comonomer units) may be masked by endothermic fusion and depolymerisation.

The main features of the DTA data are also listed in Table 6.2.

6.2.3 THERMAL VOLATILISATION ANALYSIS.

The sample size was 50 mg for each copolymer. All degradations were performed using programmed heating at 10 ^{o}C/min to 500 ^{o}C under normal TVA conditions as described in Chapter Two. The TVA traces for the copolymers (COMAN/MAA 1, COMAN/MAA 2, AND COMAN/MAA 3) are reproduced in Fig. 6.5 (a, b and c).

These TVA traces for all copolymers show an almost similar pattern of degradation. It is clear that in each case decomposition begins around 250 ^{o}C, which is the threshold temperature for the main decomposition peak with a T_{max} around 360 ^{o}C. After the main decomposition peak (from 440 ^{o}C), a gradual decomposition follows, indicating the presence of some relatively stable material slowly decomposing at this

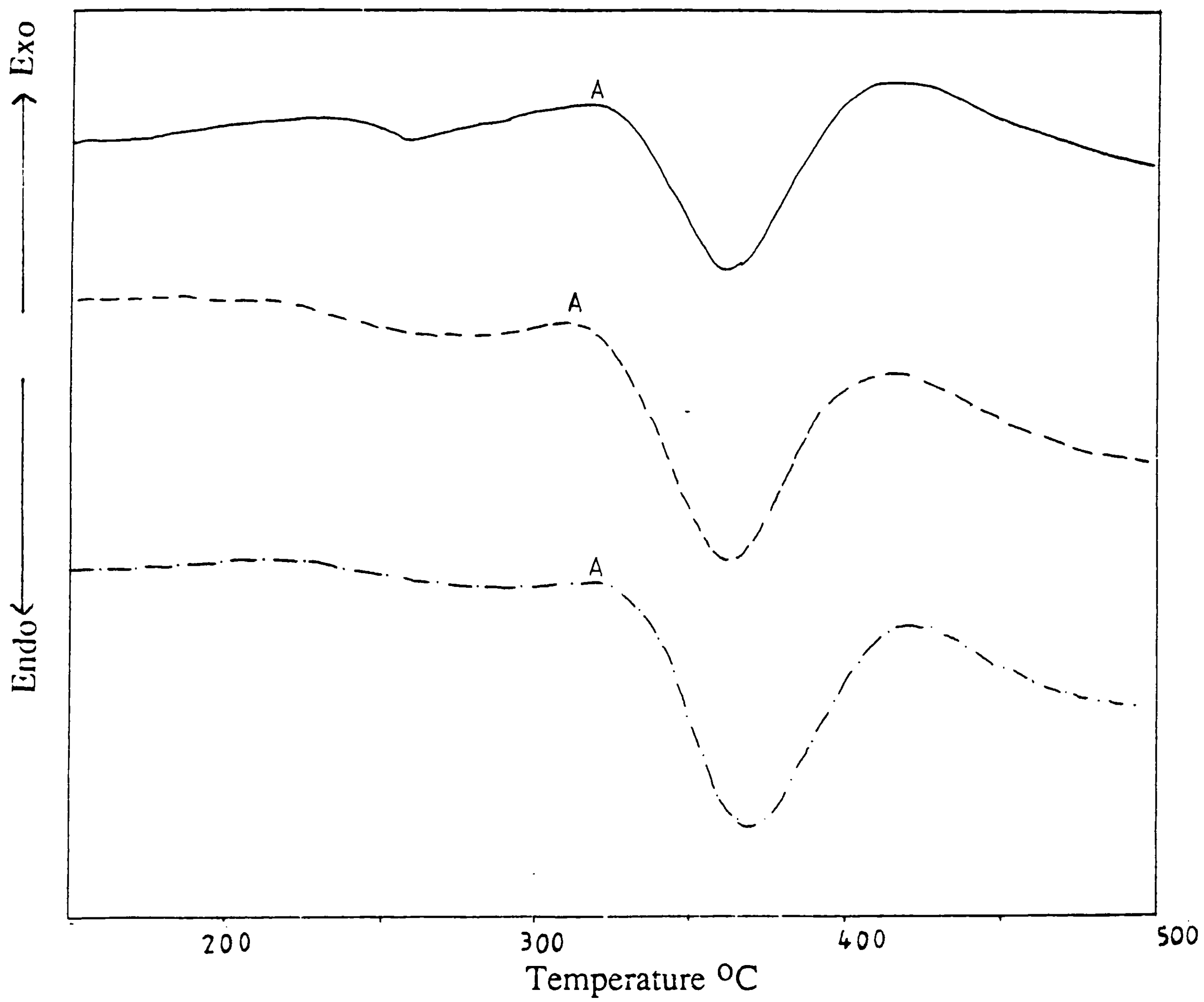


Fig. 6.4. DTA Curves (Dynamic Nitrogen Atmosphere, Heating Rate 10 °C/min.) for Various MAN/MAA copolymers.

(a) COMAN/MAA 1 —— (b) COMAN/MAA 2 — —

(c) COMAN/MAA 3 — · —

TABLE 6.2 DTG, TG and DTA Data for Methacrylonitrile/Methacrylic acid Copolymer Samples used in this Investigation.

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
						300-330	Exo.Br*
MAN/MAA 1	355	255-390	44	52	362	318-420	Endotherm
		392-500	8				
						295-328	Exo.Br*
MAN/MAA 2	359	261-398	39	48	365	318-420	Endotherm
		390-500	9				
						298-325	Exo.Br*
MAN/MAA 3	365	266-392	38	45	369	312-415	Endotherm
		385-500	7				

Exo. Br* Exothermic Broadening

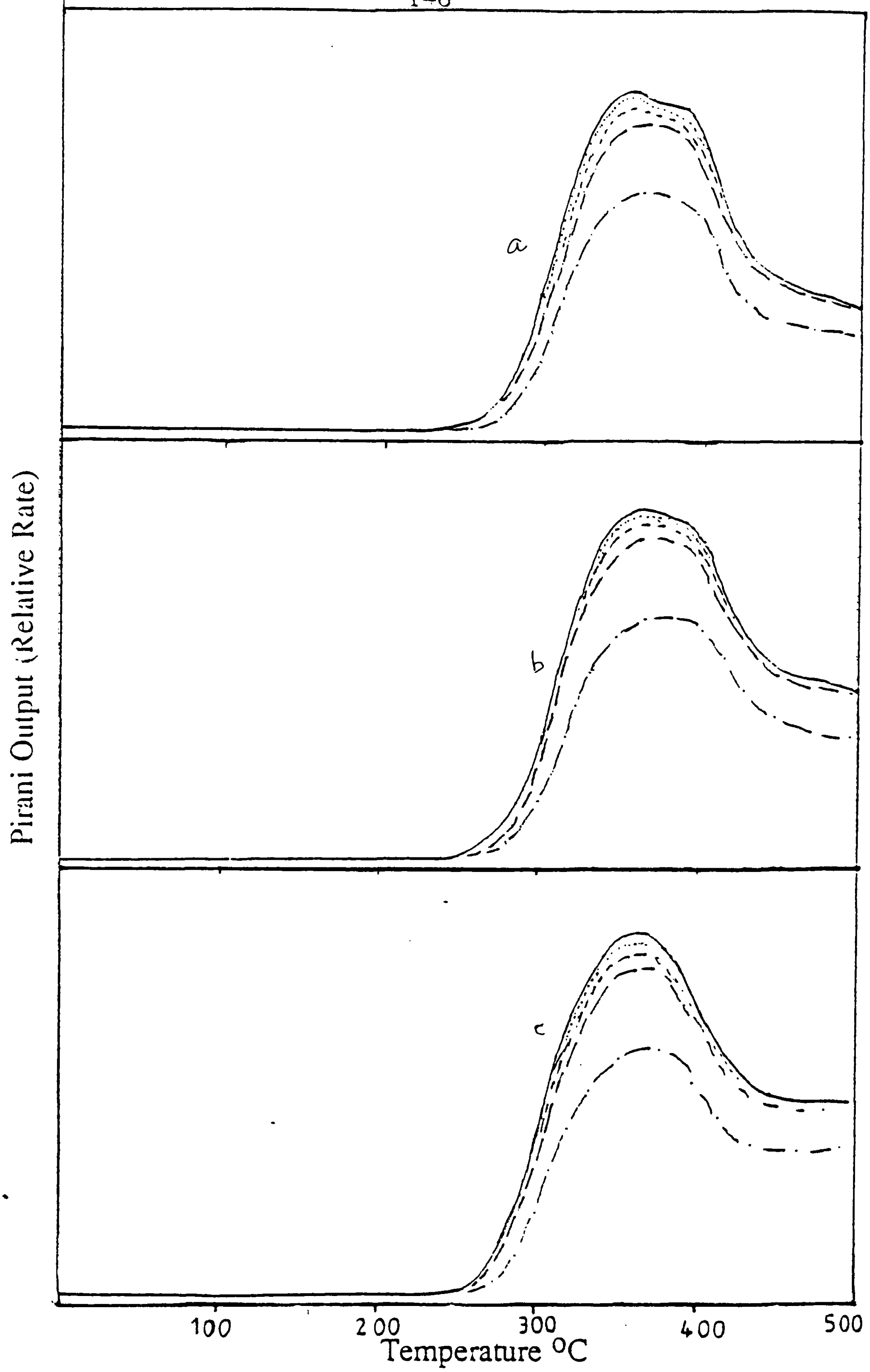


Fig. 6.5. TVA Curves (Cacuum, Heating Rate 10 °C/min.) for Various MAN/MAA Copolymers to 500 °C.

(a) COMAN/MAA 1 (b) COMAN/MAA 2 (c) COMAN/MAA3

Key: 0 °C —, -45 °C ····, -75 °C - - , -100 °C — — , -196 °C — · — ·

higher temperature.

Close examination of these TVA traces shows lack of coincidence among all Pirani traces (i.e. 0, -45, -75, -100, and -196 ^{o}C), indicating formation of a variety of degradation products with significant amounts of non-condensables which were identified as mainly methane by on-line mass spectrometry during the TVA experiment.

The TVA data for methacrylonitrile/methacrylic acid copolymers investigated are summarised in Table 6.3.

6.2.3.1 Subambient Thermal Volatilisation Analysis.

Condensable volatile 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 reproduced in Figs. 6.6, 6.7 and 6.8. Mass spectrometric studies were also performed simultaneously during SATVA separation using a quadrupole mass spectrometer attached to the system. Assignments of materials present, based on IR and MS investigation, are shown in Tables 6.4, 6.5 and 6.6.

6.2.3.2 Product Analysis

The degradation products of the copolymers heated to 500 ^{o}C under normal TVA conditions were investigated by the same techniques already described in Chapter Four. These were examined as four main

TABLE 6.3. TVA Data for Degradation of Methacrylonitrile/Methacrylic Acid Copolymer Samples

Polymer	T_{onset} ^{o}C	T_{max} ^{o}C	Wt. % Residue at ~500 ^{o}C	Wt. % CRF at ~500 ^{o}C	Wt. % L.F at ~500 ^{o}C
MAN/MAA 1	248	358	45	16	26
MAN/MAA 2	246	362	48	24	15
MAN/MAA 3	256	368	52	31	6

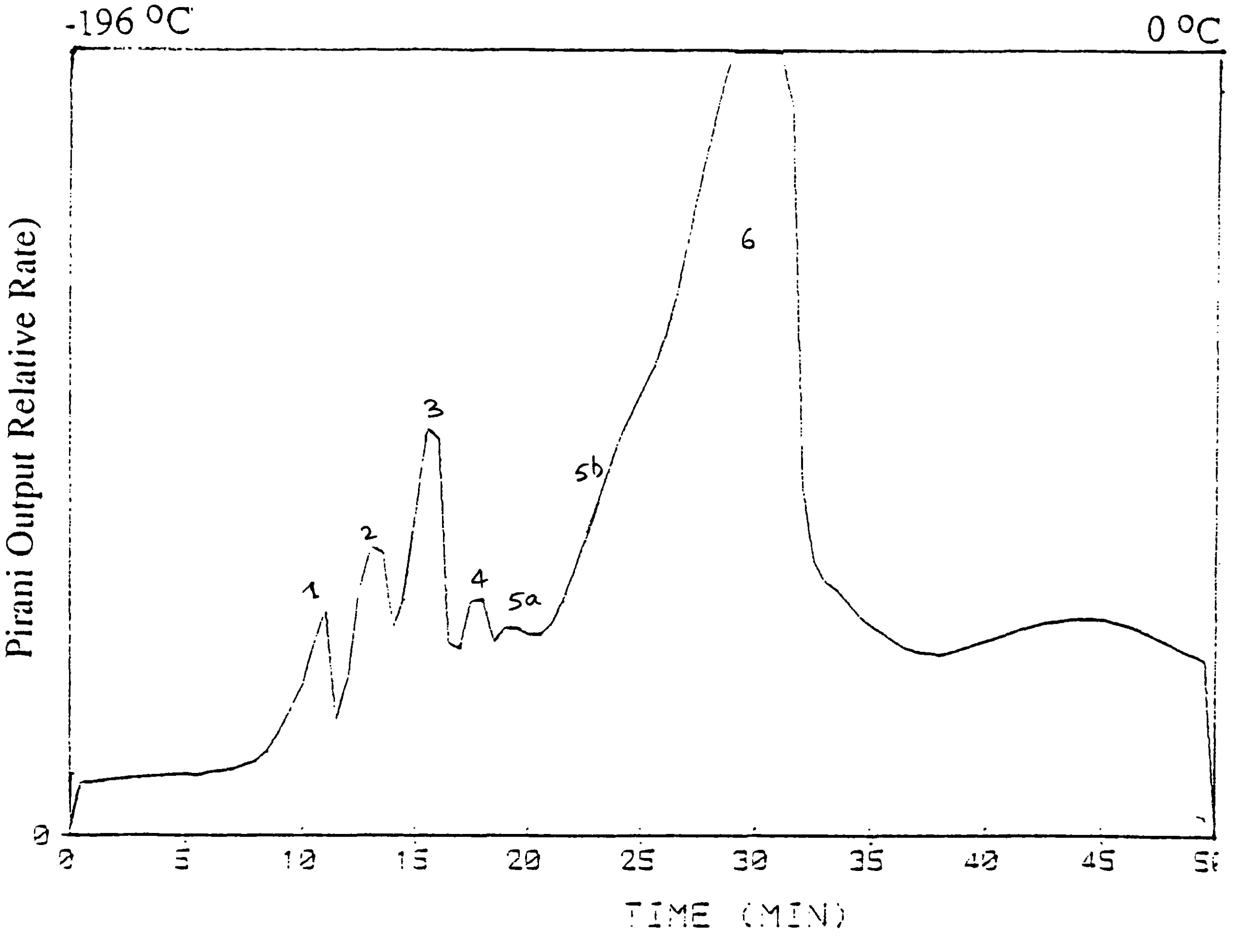


Fig. 6.6. SATVA Curve for Condensable Product Fraction from Degradation to 500 °C under TVA Conditions of COMAN/MAA 1.

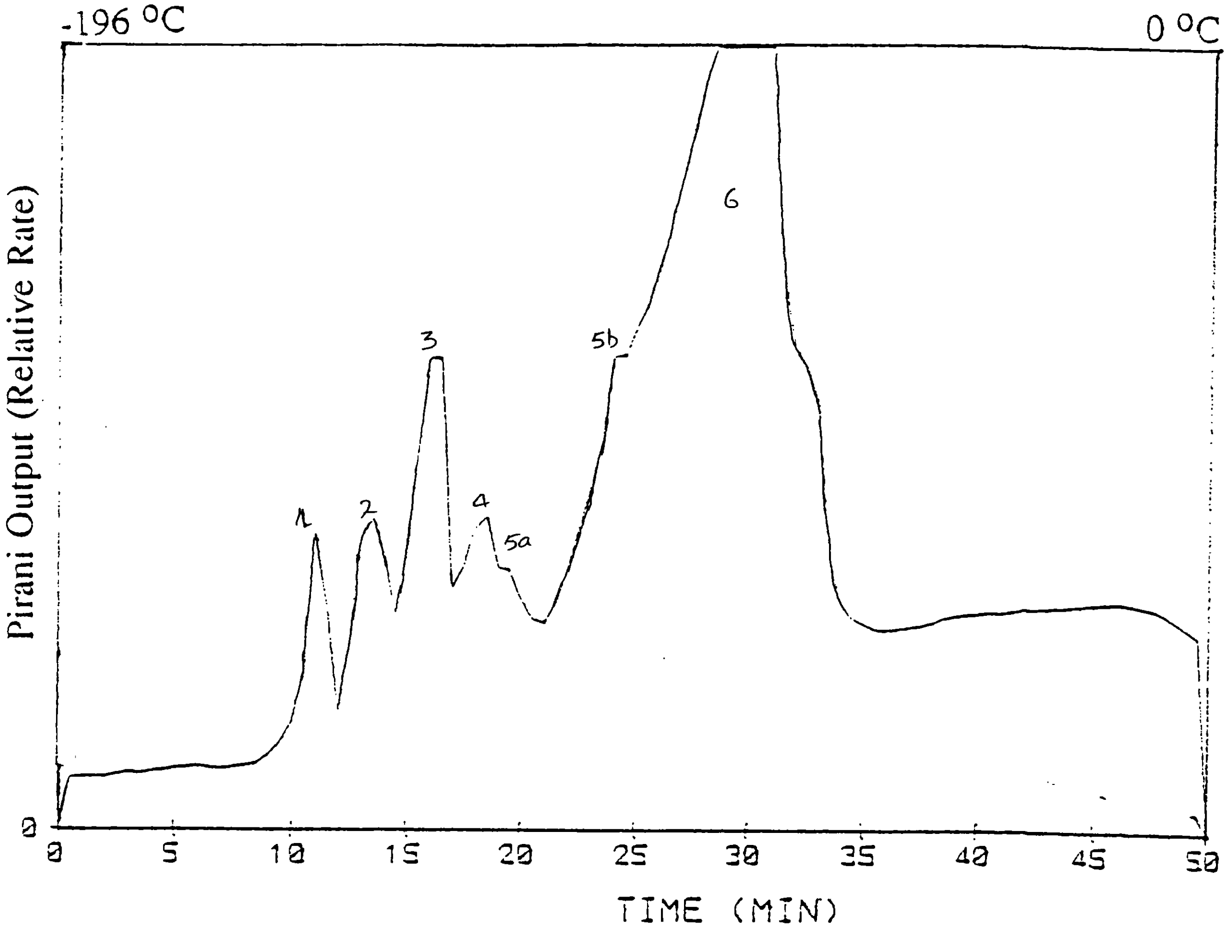


Fig. 6.7. SATVA Curve for Condensable Product Fraction from Degradation to 500 °C under TVA Conditions of COMAN/MAA 2.

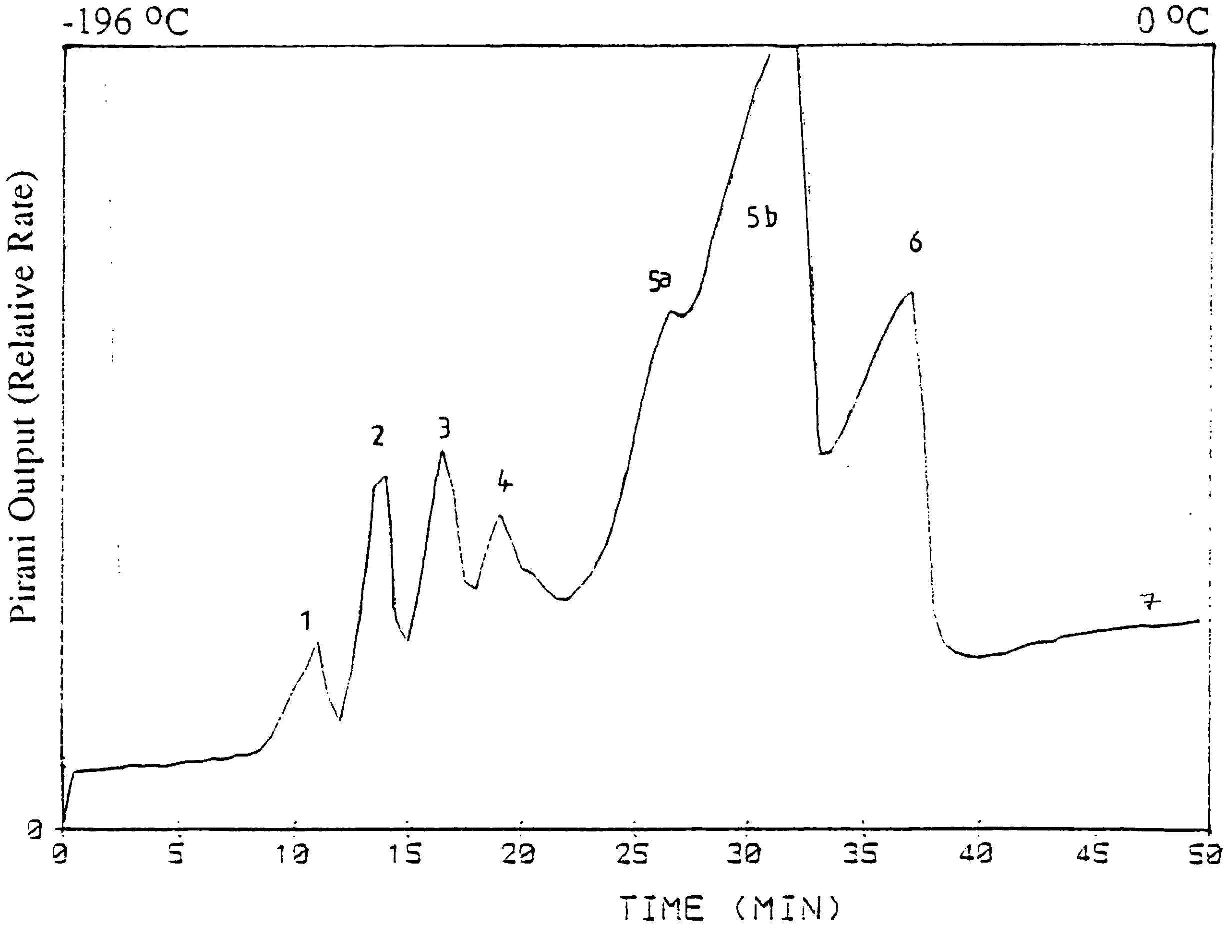


Fig. 6.8. SATVA Curve for Condensable Product Fraction from Degradation to 500 °C under TVA Conditions of COMAN/MAA 3.

TABLE 6.4 Assignment of Volatile Products of COMAN/MAA 1 Sample Degraded to 500 °C in the TVA System under Vacuum using Programmed Heating and Separated by SATVA (MS Ion Peaks are in Order of Abundance)

Peak No	Compound	IR	MS
1	Ethane	2976, 2895, 1464, 822 cm^{-1}	28, 27, 30, 26
2	Propane	2968, 2887, 1471	29, 28, 44, 43
2	Carbon dioxide	3701, 2364, 688 cm^{-1}	44, 28, 16, 12
3	Isobutene	3086, 2945,1458, 1381, 890	41, 56, 39, 55, 28
3	Ammonia	3340, 1626, 1046,967, 932,	17,16,15, 14 868 cm^{-1}
4	Ammonia	3340, 1630, 1046,967	17,16,15, 14 930, 868
4	2-Methyl- 1-butene	2975, 1645, 1459, 1388,	55, 39, 42, 70, 29 890 cm^{-1}
5a	Hydrogen cyanide	3334, 3300, 714, 700	27, 16, 12, 28
5a	Ammonia	3340, 1630, 1046,967	17,16,15, 14 930, 868
5b	Methacrylonitrile	3102, 2228, 1625,937 cm^{-1}	41, 39, 67, 40
6	Methacrylonitrile	3102, 2228, 1625,937	41, 39, 67, 40
6	Water *	3400, 1640 cm^{-1}	18,17,16

* In trace amount

TABLE 6.5 Assignment of Volatile Products of COMAN/MAA 2 Sample Degraded to 500 °C in the TVA System under Vacuum using Programmed Heating and Separated by SATVA (MS Ion Peaks are in Order of Abundance)

Peak No	Compound	IR	MS
1	Ethane	2976, 2895, 1464, 822 cm^{-1}	28, 27, 30, 26
2	Propane	2968, 2887, 1471	29, 28, 44, 43
2	Carbon dioxide	3701, 2364, 688 cm^{-1}	44, 28, 16, 12
3	Isobutene	3086, 2945,1458, 1381, 890	41, 56, 39, 55, 28
3	3-Methyl-1-butene *	2967, 1647, 1469, 909	55, 27, 42, 70, 393
3	Ammonia	3340, 1626, 1046,967, 932, 868 cm^{-1}	17,16,15, 14
4	Ammonia	3340, 1630, 1046,967	17,16,15, 14
			930, 868
4	2-Methyl-1-butene	2975, 1645, 1459, 1388,	55, 39, 42, 70, 29
			890 cm^{-1}
5a	Hydrogen cyanide	3334, 3300, 714, 700	27, 16, 12, 28
5a	Ammonia	3340, 1630, 1046,967	17,16,15, 14
			930, 868
5b	Methacrylonitrile	3102, 2228, 1625,937 cm^{-1}	41, 39, 67, 40
6	Methacrylonitrile	3102, 2228, 1625,937	41, 39, 67, 40
6	Water	3400, 1640 cm^{-1}	18,17,16

* In trace amount

TABLE 6.6 Assignment of Volatile Products of COMAN/MAA 3 Sample Degraded to 500 ^{o}C in the TVA System under Vacuum using Programmed Heating and Separated by SATVA (MS Ion Peaks are in Order of Abundance)

Peak No	Compound	IR	MS
1	Ethane	2976, 2895, 1464, 822 cm^{-1}	28, 27, 30, 26
2	Propane	2968, 2887, 1471	29, 28, 44, 43
2	Carbon dioxide	3701, 2364, 688 cm^{-1}	44, 28, 16, 12
3	Isobutene	3086, 2945,1458, 1381, 890	41, 56, 39, 55, 28
3	3-Methyl-1-butene *	2967, 1647, 1469, 909	55, 27, 42, 70, 393
3	Ammonia	3340, 1626, 1046,967, 932, 868 cm^{-1}	17,16,15, 14
4	Ammonia	3340, 1630, 1046,967	17,16,15, 14 930, 868
4	2-Methyl-1-butene	2975, 1645, 1459, 1388,	55, 39, 42, 70, 29 890 cm^{-1}
5a	Hydrogen cyanide	3334, 3300, 714, 700	27, 16, 12, 28
5a	Ammonia	3340, 1630, 1046,967	17,16,15, 14 930, 868
5b	Methacrylonitrile	3102, 2228, 1625,937 cm^{-1}	41, 39, 67, 40
6	Methacrylonitrile	3102, 2228, 1625,937	41, 39, 67, 40
6	Water	3400, 1640 cm^{-1}	18,17,16
7	Water	3400, 1640 cm^{-1}	18,17,16

* In trace amount

fractions, consisting of the involatile residue, the cold ring fraction, the condensable volatile fraction, and the non-condensable gases.

6.2.3.2.1 Residue

The black involatile material (residue) left after the degradation of the copolymers was analysed by IR spectroscopy. The IR spectra were identical, as shown in Fig. 6.9, and indicate the presence of some complex structures (propably extended fused ring heterocyclic) showing strong absorption at 1610–1600 cm^{-1}, which is attributed to C=C, C=N ring str~~i~~etching.

The percentage residue left after the degradation was quite significant, and observed to increase with increasing methacrylic acid contents.

6.2.3.2.2 Cold ring fraction.

Cold ring fraction products waxy and varying in colour from light yellow brown to dark brown, which were collected on the upper part of the TVA tube, were analysed by IR and mass spectrometry.

The IR spectra for cold ring fractions of all copolymers studied were almost similar (Fig. 6.10) showing different intensities of C≡N (nitrile) absorption at 2214 cm^{-1} indicating presence of oligomers (which were later also identified by mass spectrometry) depending on the proportion of MAA comonomer units.

These IR spectra suggest that the CRF products are mainly amino (NH_2) and methyl (CH_3) substituted nitrogen containing heterocyclic

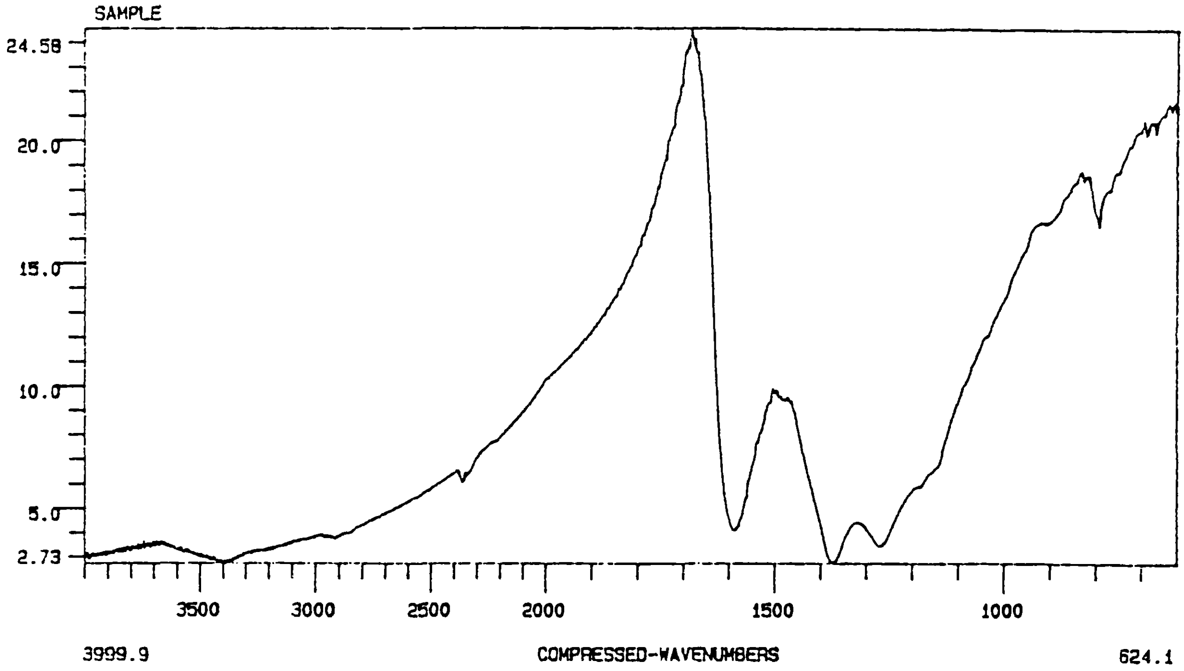


Fig. 6.9. IR Spectrum of the Residual Fraction from Degradation of MAN/MAA Copolymers to 500 °C under TVA Conditions. %TRANSMITTANCE

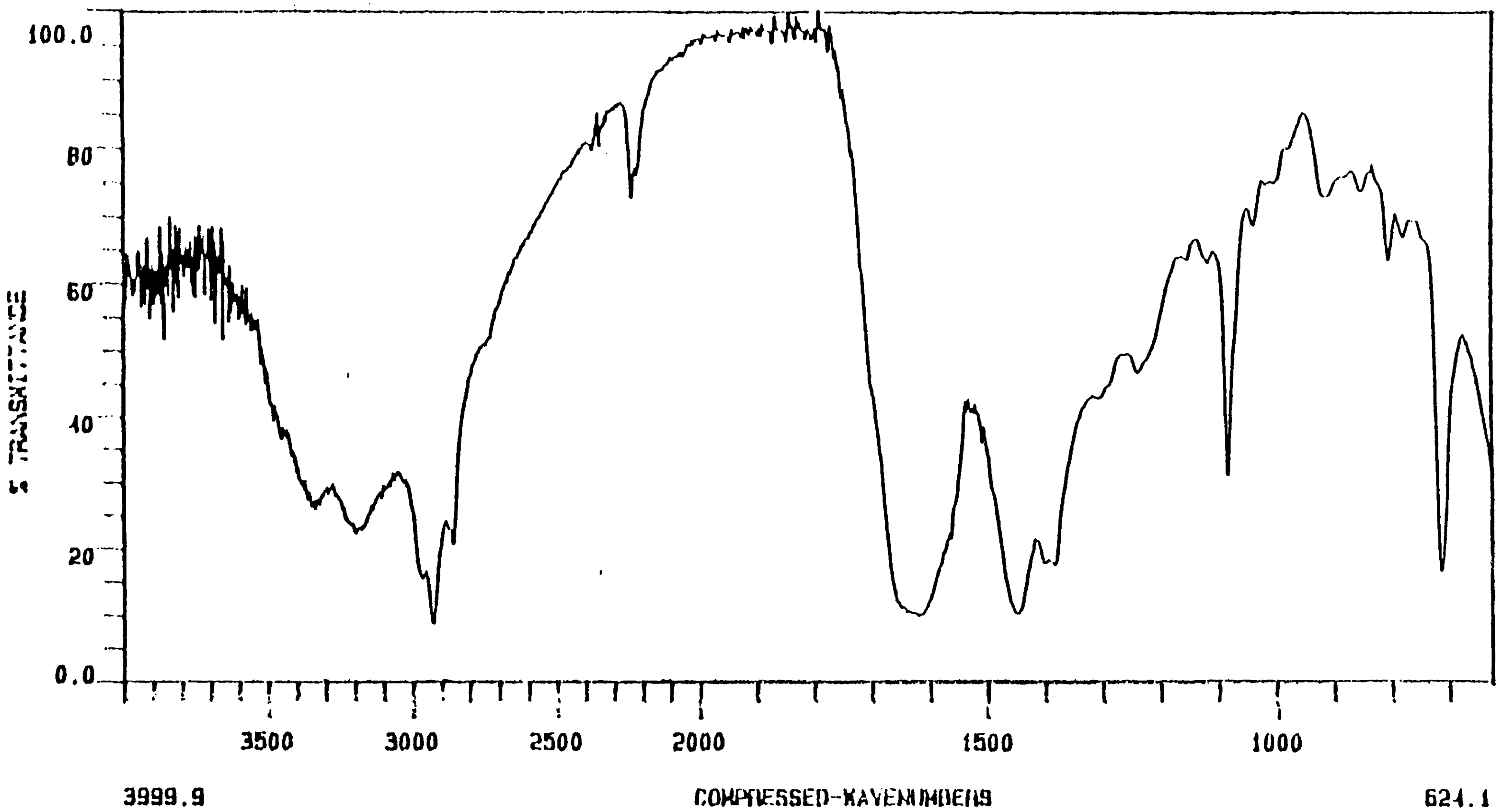


Fig. 6.10. IR Spectrum of the Cold Ring Fraction from Degradation of MAN/MAA Copolymers to500 ^{o}C under TVA Conditions.

fused ring structures together with small (and varying) amounts of methacrylonitrile oligomers.

The mass spectrometric studies of these fractions supported the IR results and various methyl and amino substituted heterocyclic (nitrogen containing) structures were identified. The basis for the assignment of the mass spectral peaks for the methyl and amino substituted heterocyclic (nitrogen containing) structures is the same as already discussed in Chapter Five (section 5.2.3.2.2).

Mass spectrometric results for the cold ring fractions of the copolymers are shown in Fig. 6.11 (a, b & c), and the products identified are listed in Tables 6.7, 6.8 and 6.9 respectively. Products are listed according to relative abundance.

6.2.3.2.3 Condensable Products as liquid fraction.

The IR spectra (Fig. 6.12 a & b) for liquid product fractions corresponding to (last SATVA peaks) from first two copolymers of the series (COMAN/MAA 1 & COMAN/MAA 2) were almost identical and indistinguishable from that of monomer (methacrylonitrile), but small peaks at 3400 and 1640 cm^{-1} region in the IR spectrum of COMAN/MAA 2 suggested the presence of a trace amount of water. Mass spectrometric studies performed during SATVA separation confirmed this conclusion.

Peaks 6 & 7 in the SATVA trace (Fig. 6.8) were collected separately as liquid fractions for COMAN/MAA 3. The IR spectrum for first part of liquid fraction (peak 6) of COMAN/MAA 3 (Fig. 6.12 c) was identical to that of the liquid fraction of COMAN/MAA 2, and hence identified

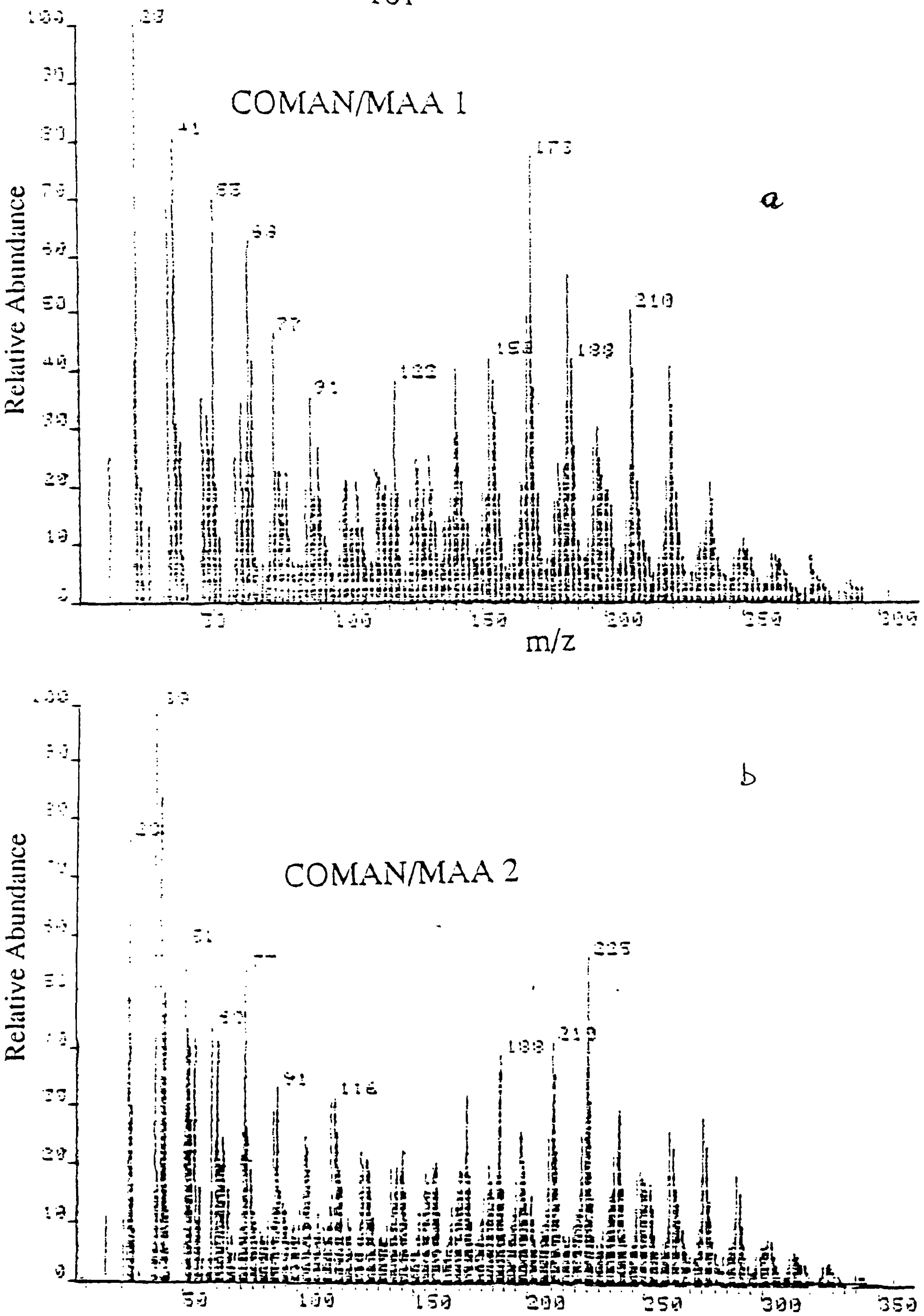


Fig. 6.11. Mass Spectrometric Results of Cold Ring Fraction from Degradation of MAN/MAA Copolymers to 500 ^{o}C under TVA Conditions.

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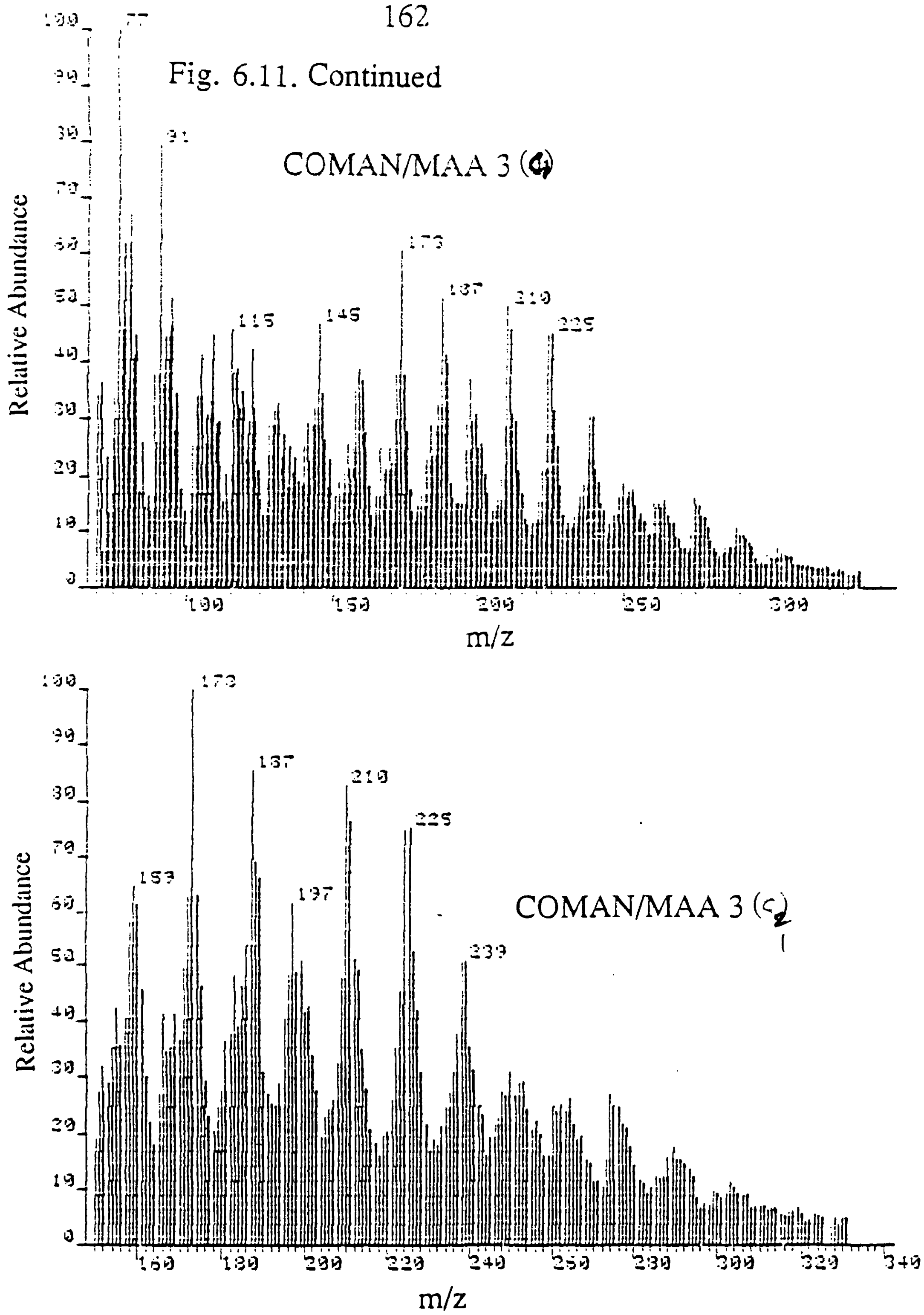
Fig. 6.11. Continued



COMAN/MAA 3 (c_1)

COMAN/MAA 3 (c_2)

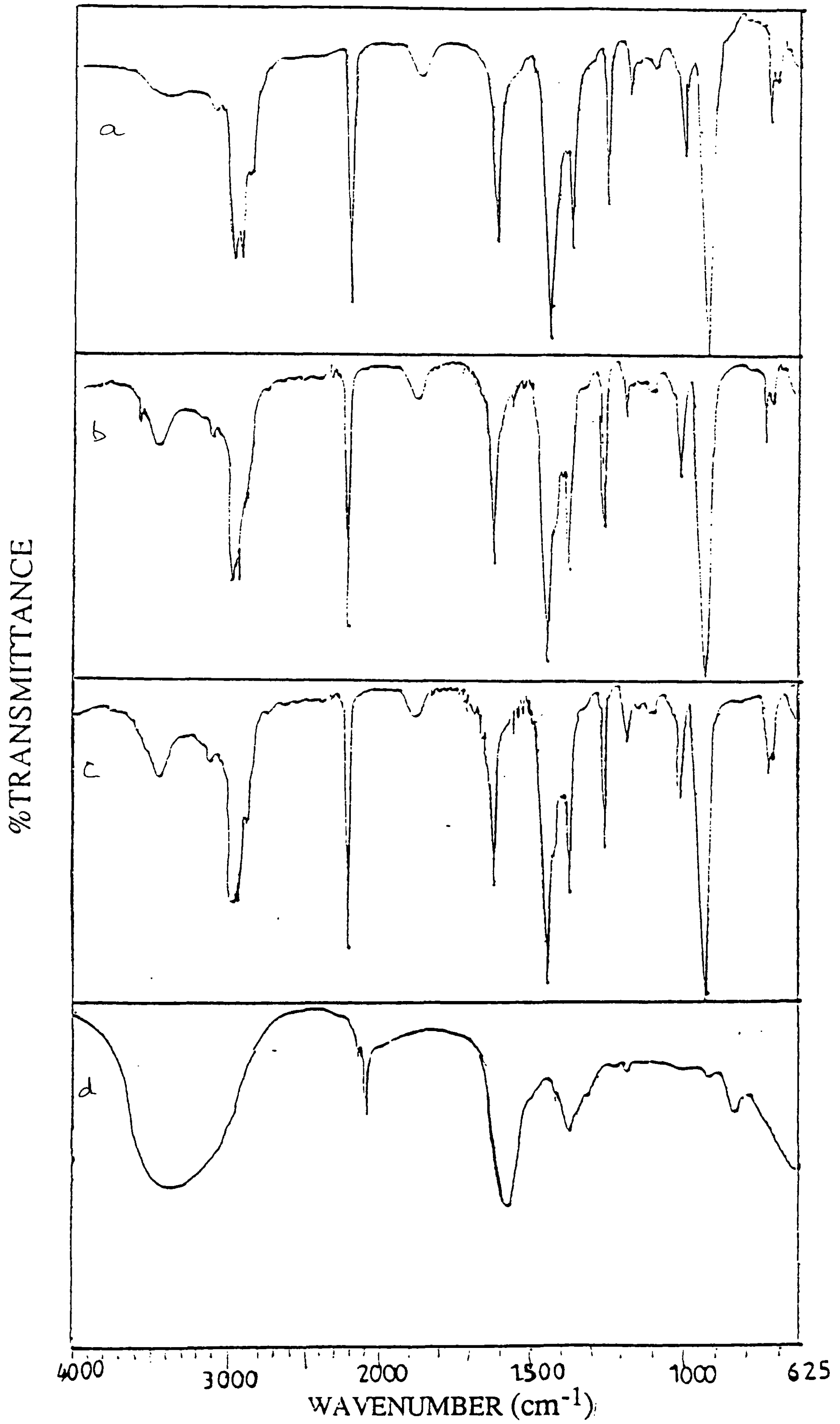


Fig. 6.12. IR Spectra for Liquid Product Fractions from Degradation of MAN/MAA Copolymers to 500 °C under TVA Conditions.
(a) COMAN/MAA 1 (b) COMAN/MAA 2
(c) COMAN/MAA 3 (peak 6) (d) COMAN/MAA 3 (peak 7)

TABLE 6.7. Products Identified in the Cold Ring Fraction from Degradation of COMAN/MAA 1 Sample under normal TVA Conditions. (Products are listed According to Relative Abundance.)

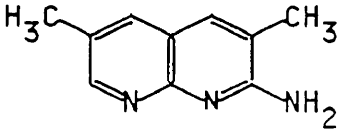
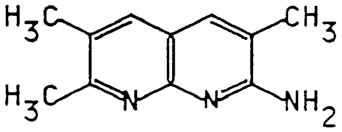
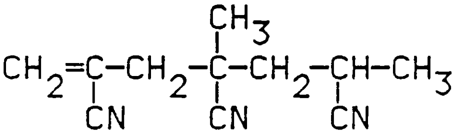
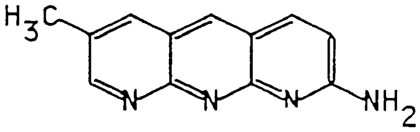
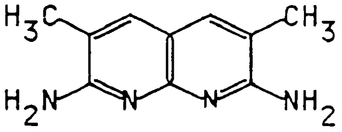
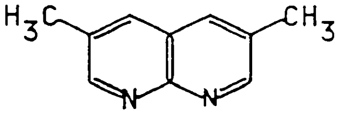
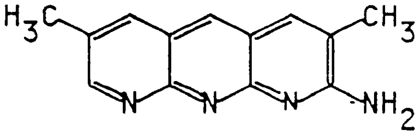
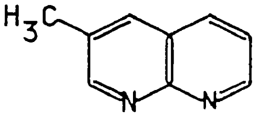
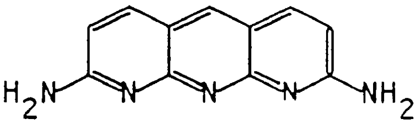
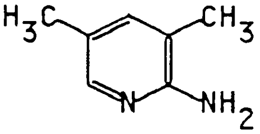
Product	m/e
	173
  $CH_2{=}C(CN){-}CH_2{-}C(CH_3)(CN){-}CH_2{-}CH(CN){-}CH_3$	187
	210
	188
	158
	224
	145
	211
	122

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TABLE 6.7. CONTINUED

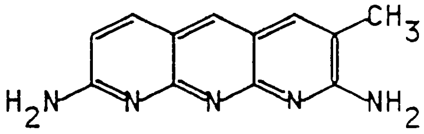
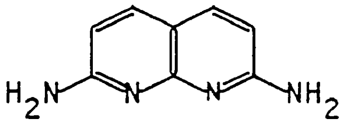
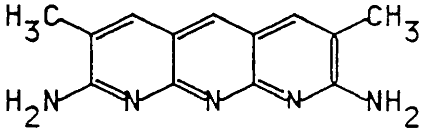
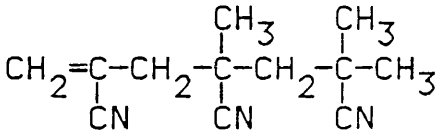
	225
	160
	239
 $CH_2{=}\underset{CN}{C}-CH_2-\overset{CH_3}{\underset{CN}{C}}-CH_2-\overset{CH_3}{\underset{CN}{C}}-CH_3$	201

TABLE 6.8. Products Identified in the Cold Ring Fraction from Degradation of COMAN/MAA 2 Sample under normal TVA Conditions. (Products are listed According to Relative Abundance.)

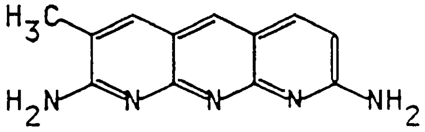
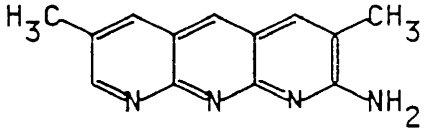
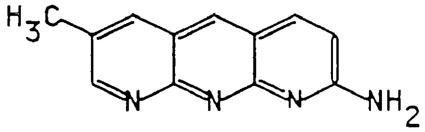
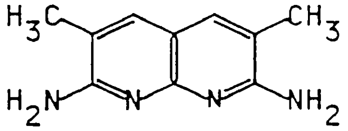
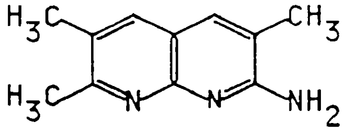
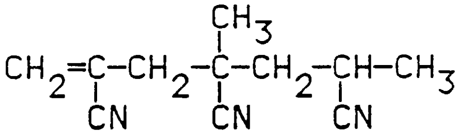
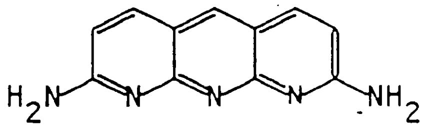
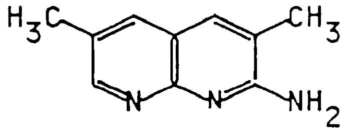
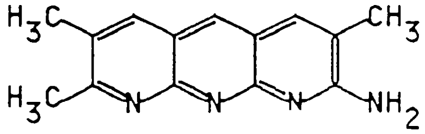
Product	m/e
	225
	224
	210
	188
  $CH_2{=}\underset{CN}{C}{-}CH_2{-}\underset{CN}{\overset{CH_3}{C}}{-}CH_2{-}\underset{CN}{CH}{-}CH_3$	187
	211
	173
	239

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TABLE 6.8 CONTINUED

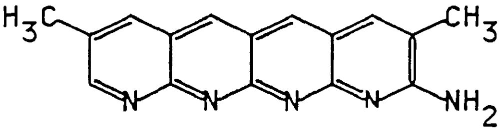
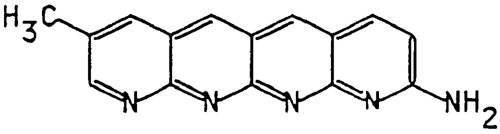
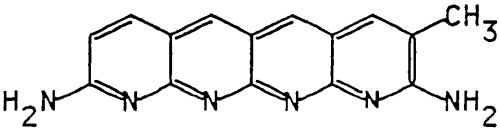
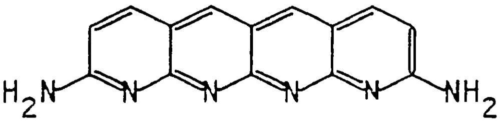
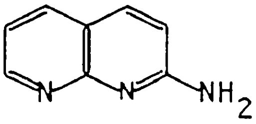
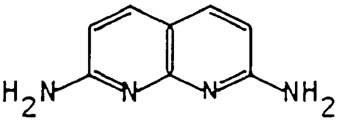
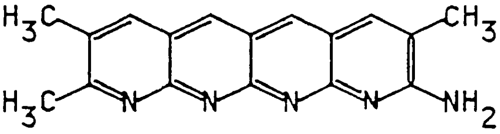
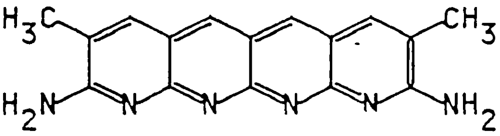
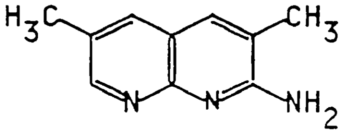
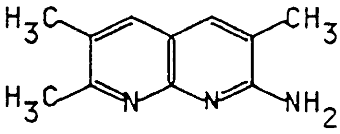
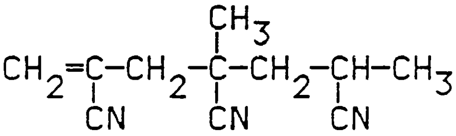
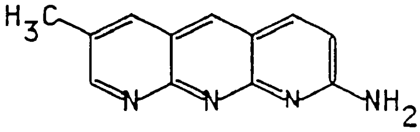
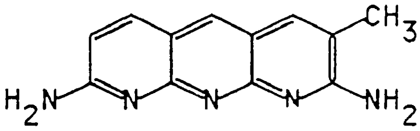
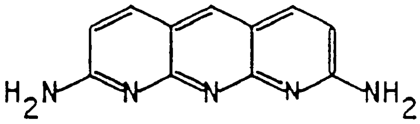
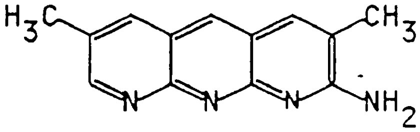
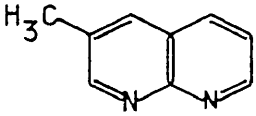
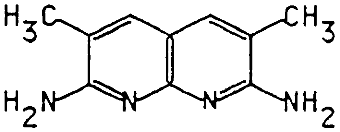
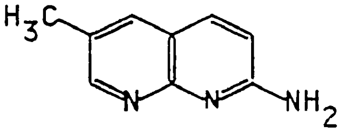
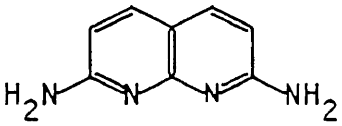
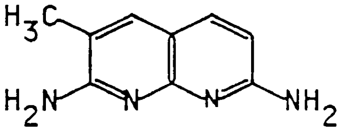
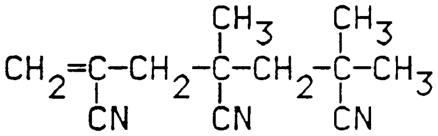
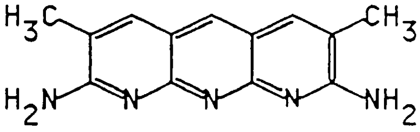
	275
	261
	276
	262
	145
	160
	289
	290

TABLE 6.9. Products Identified in the Cold Ring Fraction from Degradation of COMAN/MAA 3 Sample under normal TVA Conditions. (Products are listed According to Relative Abundance.)

Product	m/e
	173
  $CH_2{=}\underset{CN}{C}{-}CH_2{-}\overset{CH_3}{\underset{CN}{C}}{-}CH_2{-}\underset{CN}{CH}{-}CH_3$	187
	210
	225
	211
	224
	145
	188

CONTINUED

TABLE 6.9 CONTINUED

	159
	160
	174
 $CH_2{=}\underset{\vert\atop CN}{C}-CH_2-\overset{CH_3\atop\vert}{\underset{\vert\atop CN}{C}}-CH_2-\overset{CH_3\atop\vert}{\underset{\vert\atop CN}{C}}-CH_3$	201
	239

as mainly monomer containing a trace amount of water. Water was also identified as the main component of the last part of the liquid fraction (peak 7).

These liquid fractions [last fractions in case of COMAN/MAA 1 & 2, and second fraction (peak 6) in case of COMAN/ MAA 3] were subjected to GC-MS for further investigation. The chromatograms are illustrated in Figs. 6.13–6.15.

From the GC-MS data, it was concluded that in addition to methacrylonitrile, which is the dominant product of the total liquid fraction, the other products present are 2-cyanobutane, 2-cyanopropane, 1-cyano-1-propene, 1-cyano-2-propene, acetonitrile, 2-cyano-1-butene and 2-cyano-2-butene , in order of their importance. The products identified in the liquid fractions by GC-MS are listed in Tables 6.10.

6.2.3.2.4 Condensable products as gases.

The condensable gaseous products from degradation of the copolymers, separated by SATVA and collected in gas cells, were examined by IR spectroscopy and mass spectrometry. The gaseous products identified were mainly ammonia, carbon dioxide, propane, isobutene and hydrogen cyanide. Ammonia and carbon dioxide were observed to increase with increasing contents of methacrylic acid comonomer.The IR results for the gaseous products are shown in Figs. 6.16 and 6.17. Mass spectrometric (SATVA-MS) results for all condensables, including condensable gases, are shown in Fig. 6.17.

The gaseous products identified for each copolymer sample are listed in Tables 6.4, 6.5, and 6.6 respectively.

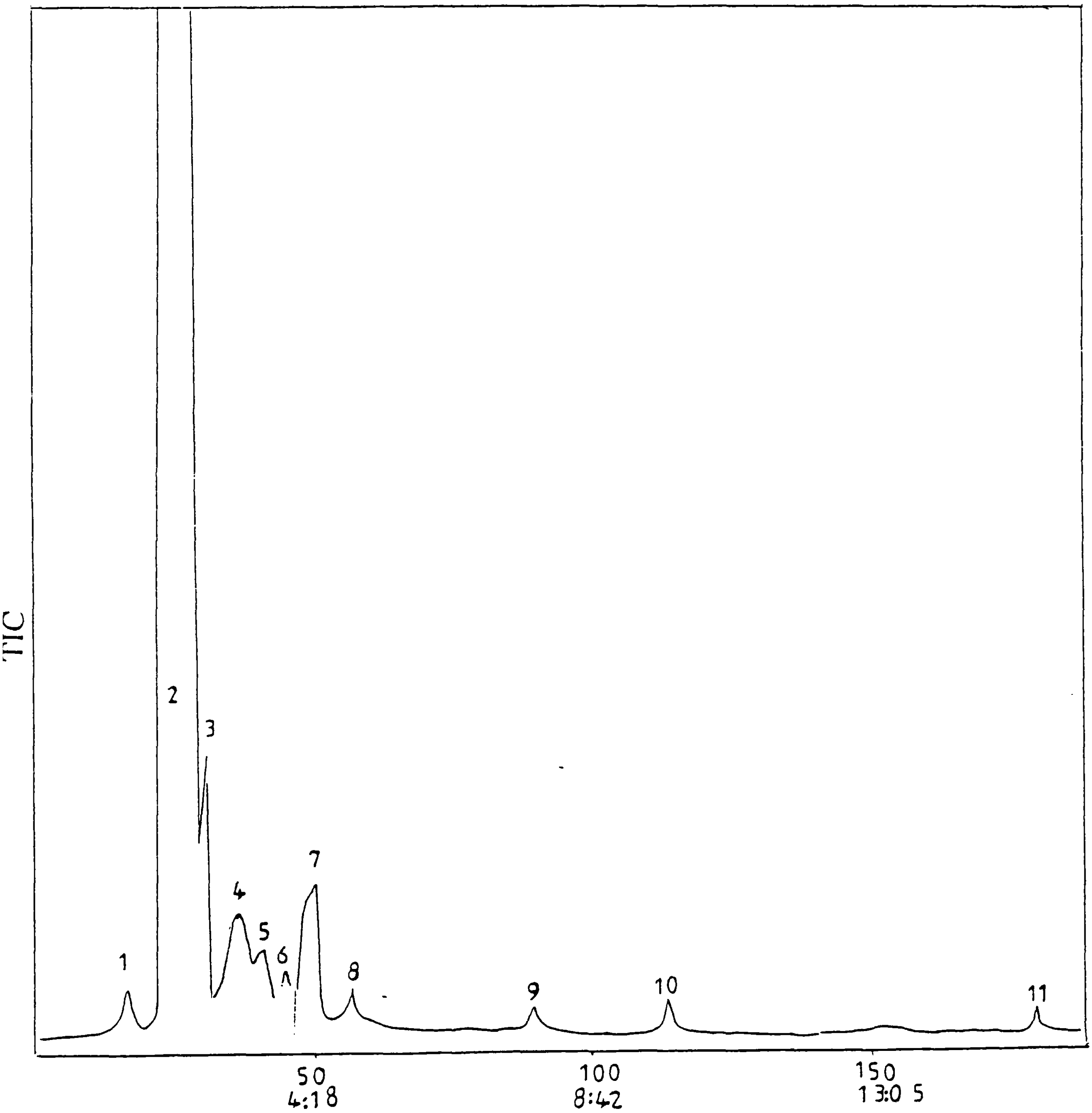


Fig. 6.13. GC-MS Chromatogram of Liquid Fraction from Degradation of COMAN/MAA 1 to 500 ^{o}C under TVA Conditions.

ASSIGNMENTS

1. Acetonitrile, **2.** Methacrylonitrile, **3.** 2-Cyanopropane,
4. 1-Cyano-2-propene **5.** 1-Cyano-1-propene, **6.**2-Cyano-1-butene,
7. 2-Cyanobutane, **8.** 2-Cyano-2-butene,
9. 4-Cyano-2-methyl-1-pentene, **10.** Unknown,
11.MAN dimer with less methyl group.

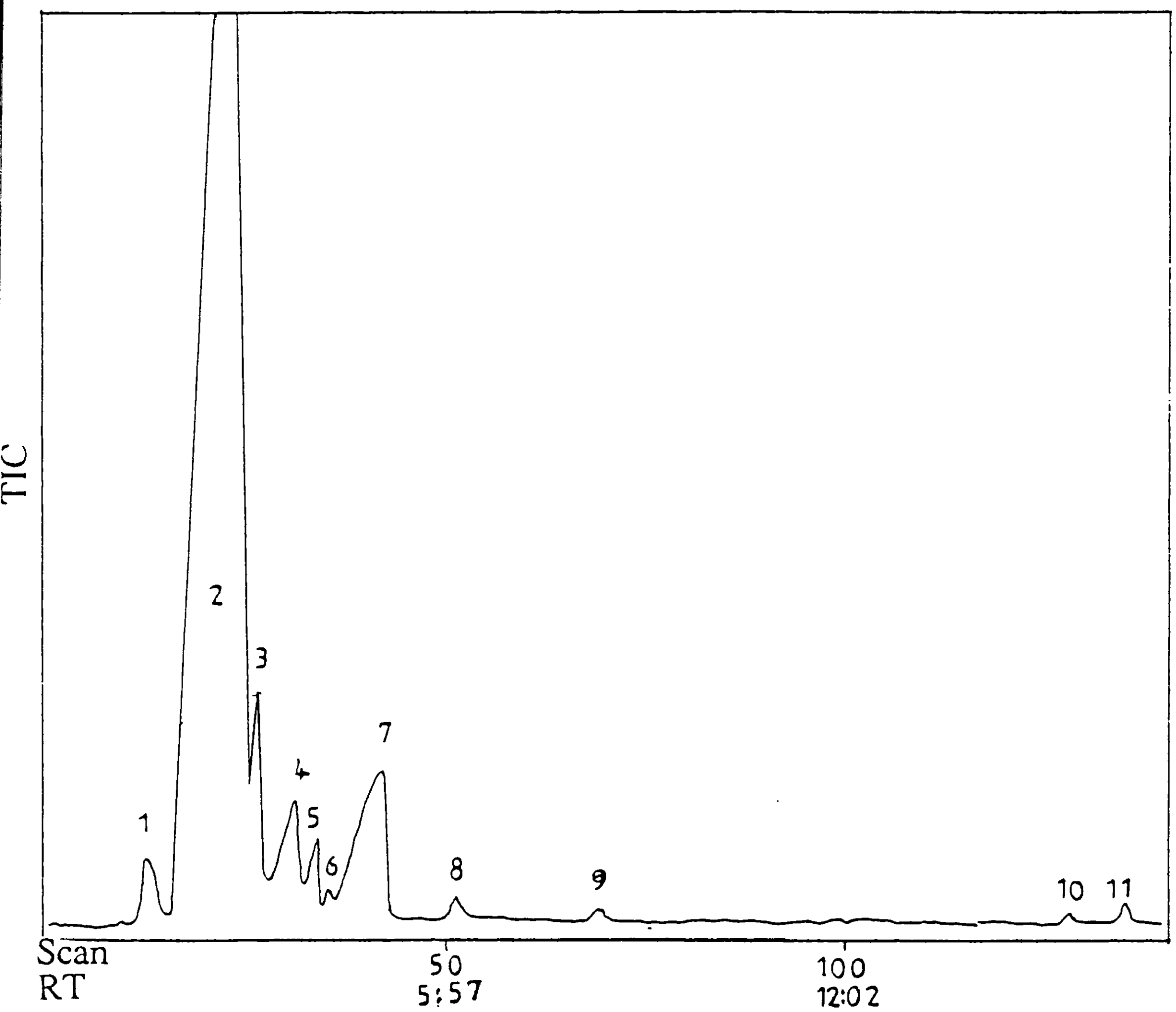


Fig. 6.14. GC-MS Chromatogram of Liquid Fraction from
Degradation of COMAN/MAA 2 to 500 °C
under TVA Conditions.

ASSIGNMENTS

1. Acetonitrile, **2.** Methacrylonitrile, **3.** 2-Cyanopropane,
4. 1-Cyano-2-propene **5.** 1-Cyano-1-propene, **6.**1-Cyano-2-butene,
7. 2-Cyanobutane, **8.** 2-Cyano-2-butene,
9. 2-Cyano-4-methylpentane, **10.** MAN dimer,
11.MAN dimer with extra methyl group.

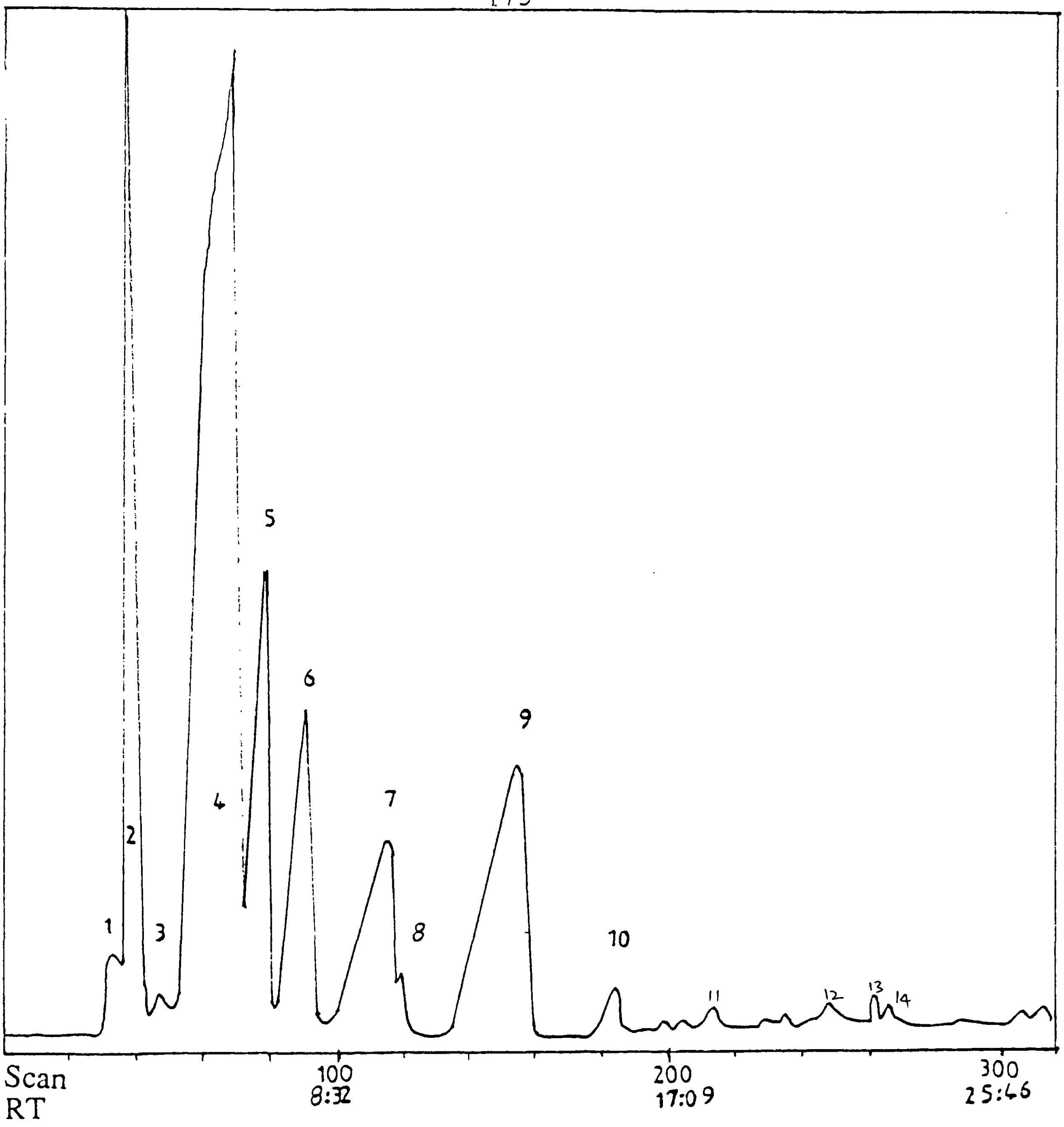


Fig. 6.15. GC-MS Chromatogram of Liquid Fraction from Degradation of COMAN/MAA 3 to 500 °C under TVA Conditions.

ASSIGNMENTS

1. Acetonitrile, **2.** Solvent, **3.** Cyanoethane, **4.** Methacrylonitrile, **5.** 2-Cyanopropane, **6** 1-Cyano-2-propene, **7.** 1-Cyano-1-propene, **8.** 2-Cyano-1-butene, **9.** 2-Cyanobutane, **10.** 2-Cyano-2-butene, **11.** 2-Cyano-4-methylpentane, **12.** Unknown, **13.** MAN dimer, **14.**MAN dimer with extra methyl group.

TABLE 6.10. GC-MS Results for Condensable Volatile Fraction Products Evolved from Methacrylonitrile/Methacrylic Acid Copolymers(1, 2 & 3) Heated to 500 ^{o}C under normal TVA Condition

Common products found in all copolymers	Methacrylonitrile, 2-Cyanobutane, Acetonitrile 2-Cyanobutane, 1-Cyano-1-propene, 1-Cyano-2-propene, 2-Cyano-2-butene

COMAN/MAA 1	COMAN/MAA 2	COMAN/MAA 3
2-Cyano-1-butene	1-Cyano -2-butene	1-Cyanoethane
4-Cyano-2-methyl-1-pentene	2-Cyano-4-methyl-1-pentene	2-Cyano -1-butene
MAN dimer with one less methyl (CH_3) group	MAN dimer	2-Cyano-4-methylpentane
	MAN dimer with one extra methyl (CH_3) group	MAN dimer
		MAN dimer with one extra methyl group

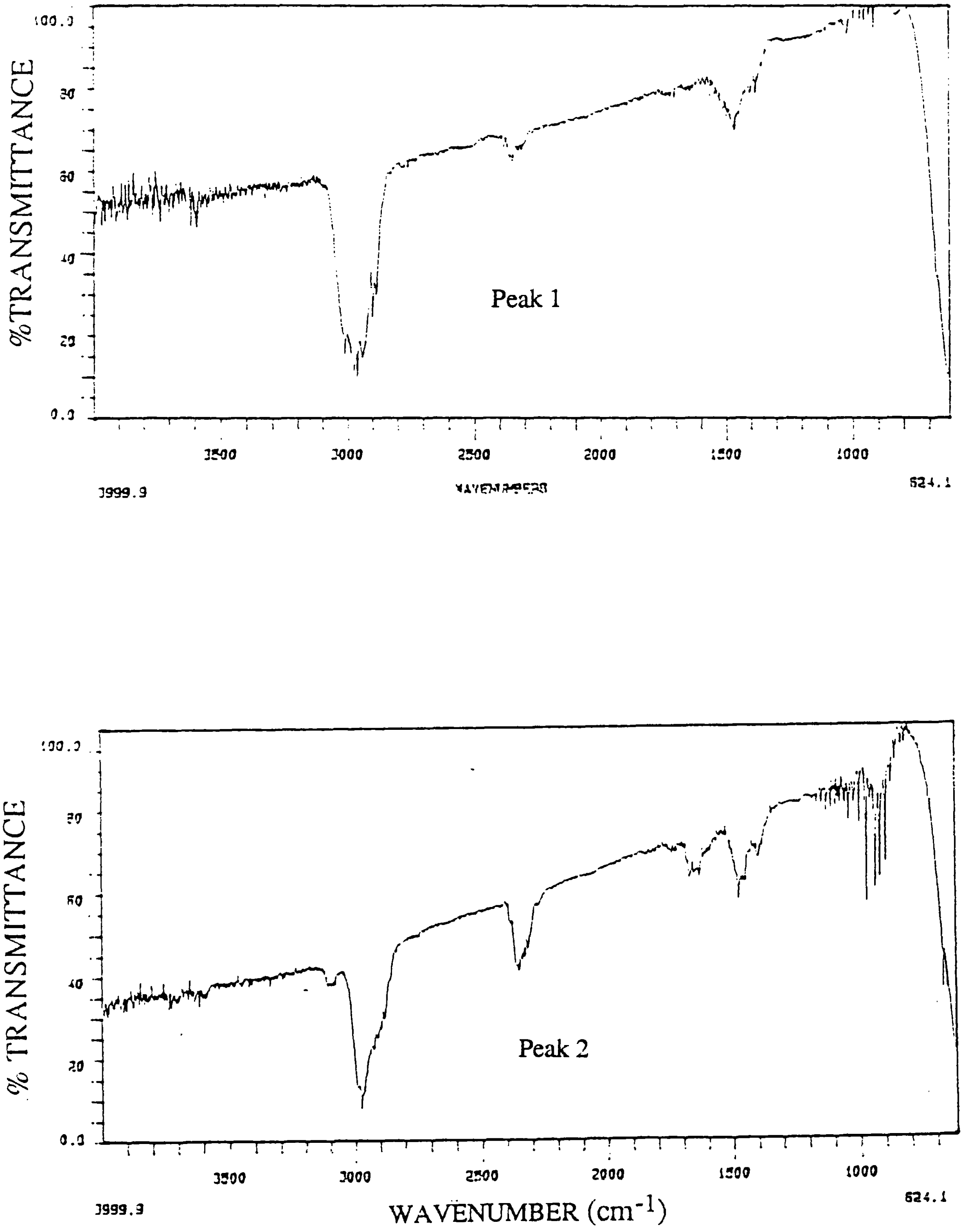
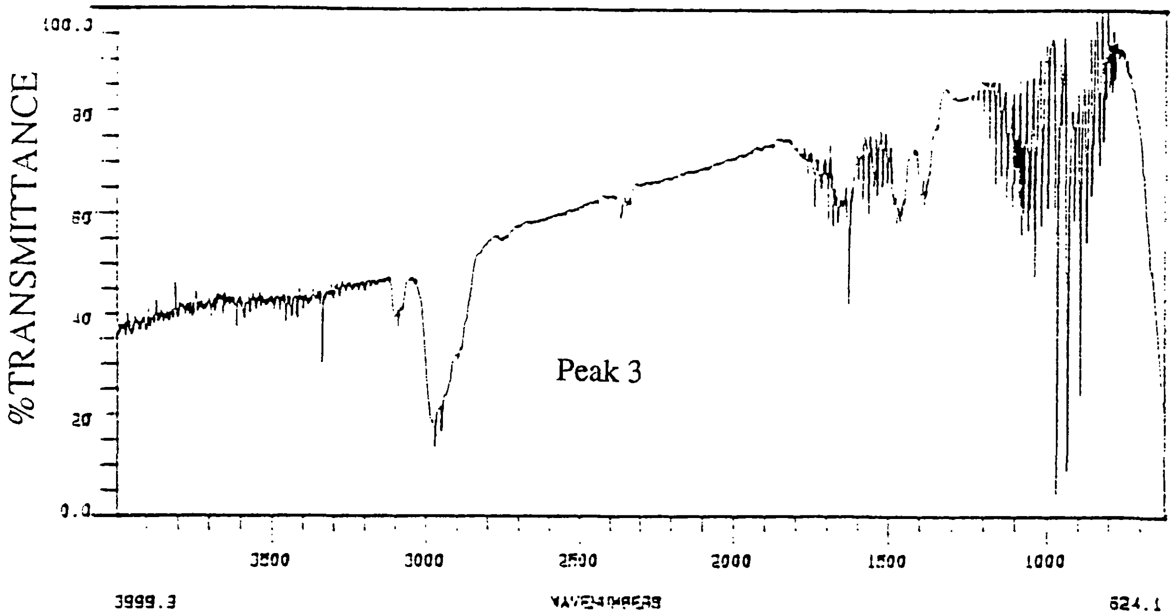
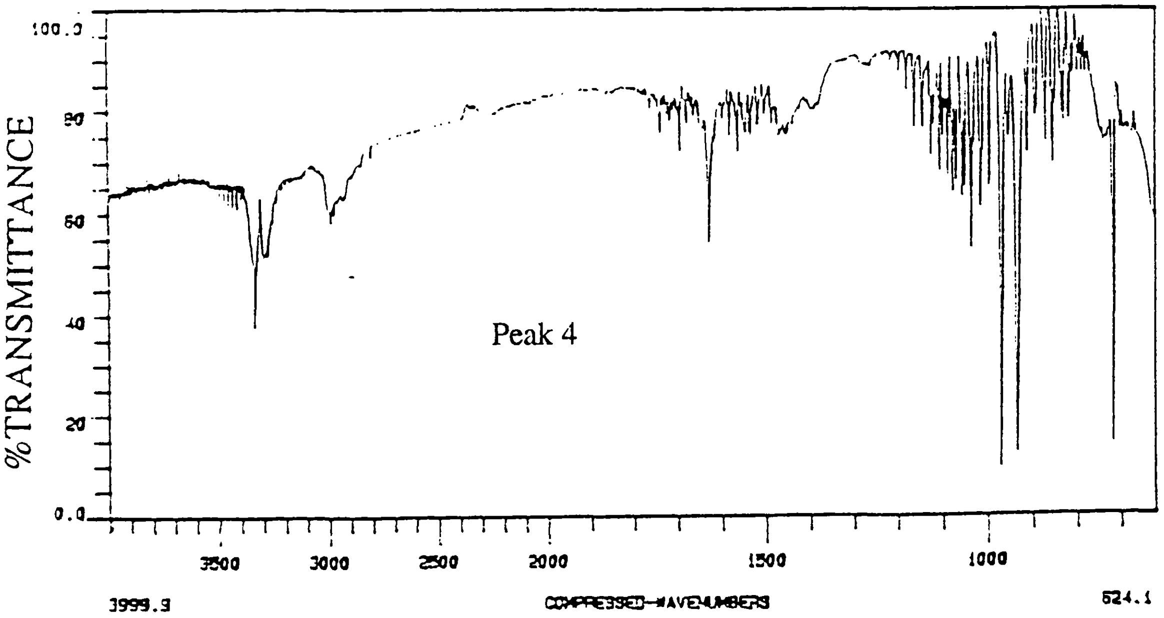


Fig. 6.16. IR Spectra of the Gaseous Products at Peak 1, 2, 3 & 4 in the SATVA Trace for MAN/MAA 3.

(CONTINUED)

Fig. 6.16. Continued





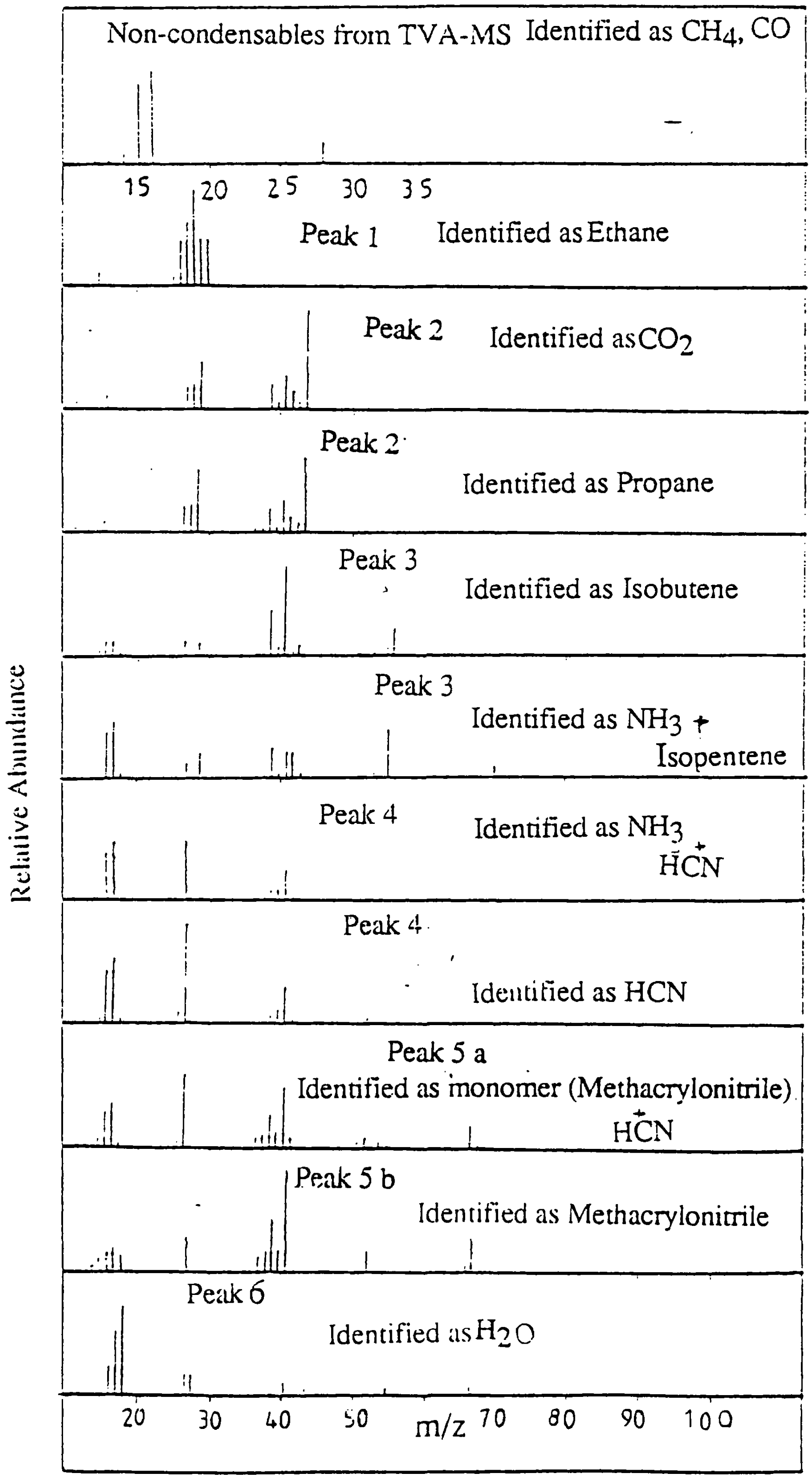


Fig. 6.17. Mass Spectrometric (SATVA-MS) Results for all Volatile Condensable Products, Including Non-Condensable Gases from Degradation of COMAN/MAA 3 to 500 °C under TVA Conditions.

6.2.3.2.5 Non-condensable gases.

Methane was identified as main non-condensable degradation product when mass spectrometric studies were carried out during the thermal volatilisation analysis process. Small amounts of carbon monoxide and hydrogen were also detected above 400 ^{o}C. A typical mass spectrum of the non-condensable gases is included in Fig. 6.17.

6.3 DEGRADATION MECHANISM

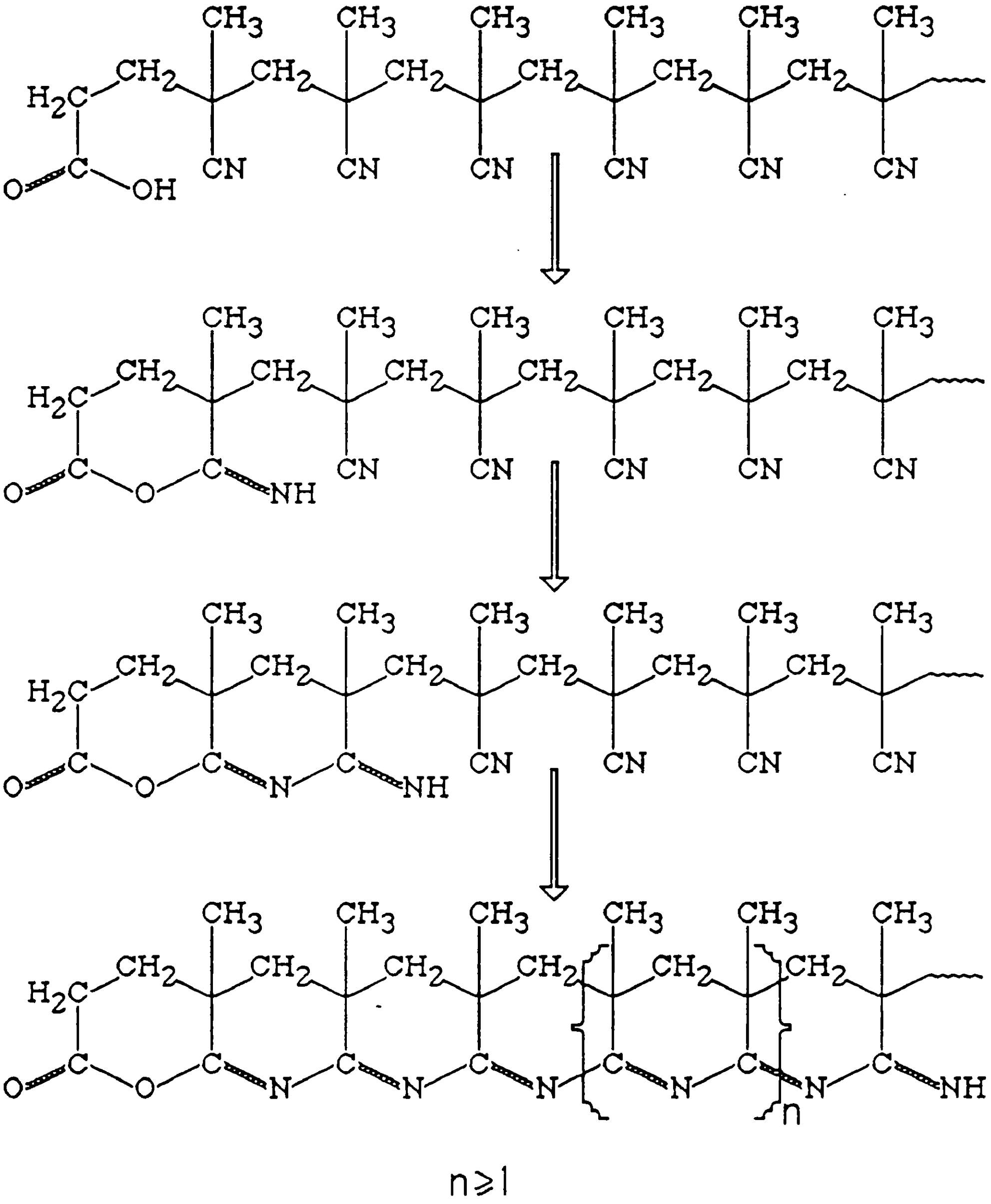
The degradation mechanism for the decomposition of methacrylonitrile homopolymers made using AIBN and BPO initiators has already been discussed in Chapter Four. It has been established[66,5] over the years that polymers like polymethacrylonitrile which are made from 1:1 disubstituted monomer depolymerise to monomer, and the depolymerisation reaction may start from an unsaturated chain end (produced during termination by disproportionation reaction) at relatively low temperature or from radical A produced by random chain scission at higher degradation temperature as shown in Scheme 4.1 in Chapter Four.

It has already been reported[27] that in presence of certain types of impurities, colouration begins at around 150 ^{o}C in polymethacrylonitrile, and adjacent nitrile group cyclisation is believed to responsible for the colouration. The mechanistic route for the formation of coloured material has been already proposed[27] as shown in Scheme 6.1.

The colouration in polymethacrylonitrile will be discussed in more detail in Chapter Eight. Here in this chapter, a mechanistic route has been put forward which accounts for the production of various products identified from the thermal degradation of methacrylonitrile polymer samples capable of colouration (various end-initiated polymethacrylonitrile and methacrylonitrile polymers containing methacrylic acid comonomer unit s) .

TVA traces for various end-initiated polymethacrylonitrile (EIPMAN) and COMAN/MAA have shown that volatilisation (0, -45,and -75 ^{o}C

SCHEME 6.1



Pirani response) starts above 250 °C. Monomer production by unzipping initiated from unsaturated chain end is the most probable reaction occurring at this stage. Above 275-280 °C, the -196 °C response indicates production of non-condensable gases. This may be due to aromatisation of cyclised structures as shown in Scheme 6.2.

Homolytic chain scission of the backbone is believed to occur above 300°C, producing macroradicals A and B, which in turn fragment into various degradation products as shown in Schemes 6.3-6 6.

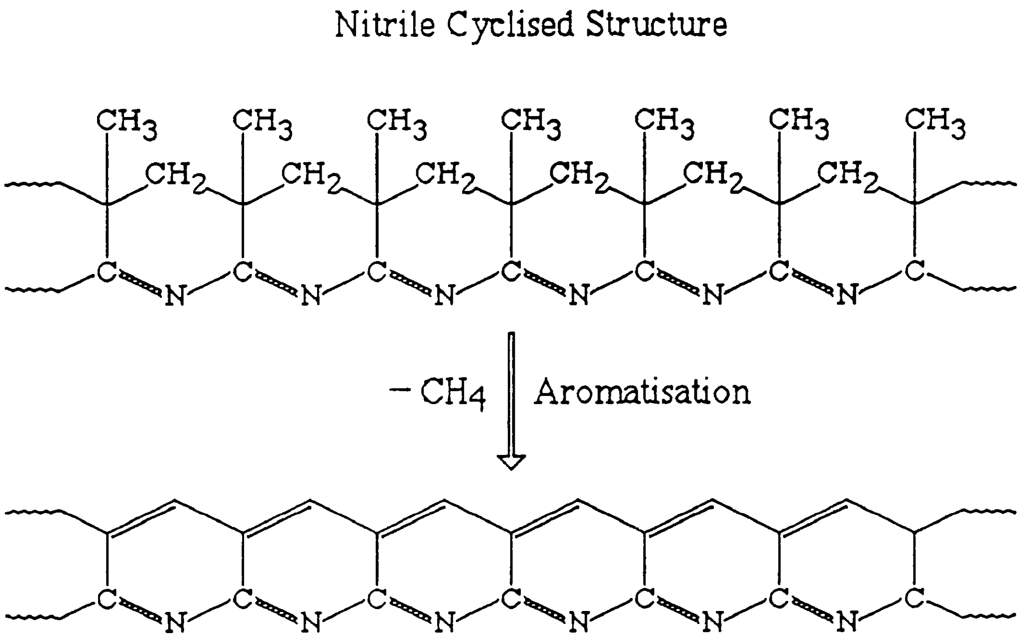
In scheme 6.3, macroradical A depolymerises to monomer whereas macro radical B produces intermediate species C, D and E via reactions 1a, 1b and 1c, respectively. Intermediate species C is believe to be produced by C-CN bond cleavage (reaction 1a), and further on scission at b and H-abstraction produces isobutene as already has shown in Chapter Four (Scheme 4.1). Hydrogen abstraction (reaction 1b) and methylation (reaction 1c) of macroradical B result in intermediate species D and E respectively.

In scheme 6.4 fragmentation of the intermediate species D is proposed to produce 2-cyanopropane and propane through routes 2a and 2b, respectively. In both routes macroradical B also generates as by-products.

Scheme 6.5 illustrates the possible route of formation of 2-Cyanobutane (which is the second most important product in the liquid fraction) and other significant products of the liquid fraction such as 1-cyano-1-propene and 1-cyano-2-propene.

Scheme 6.6 explains the route of formation of ammonia which is an important degradation product .

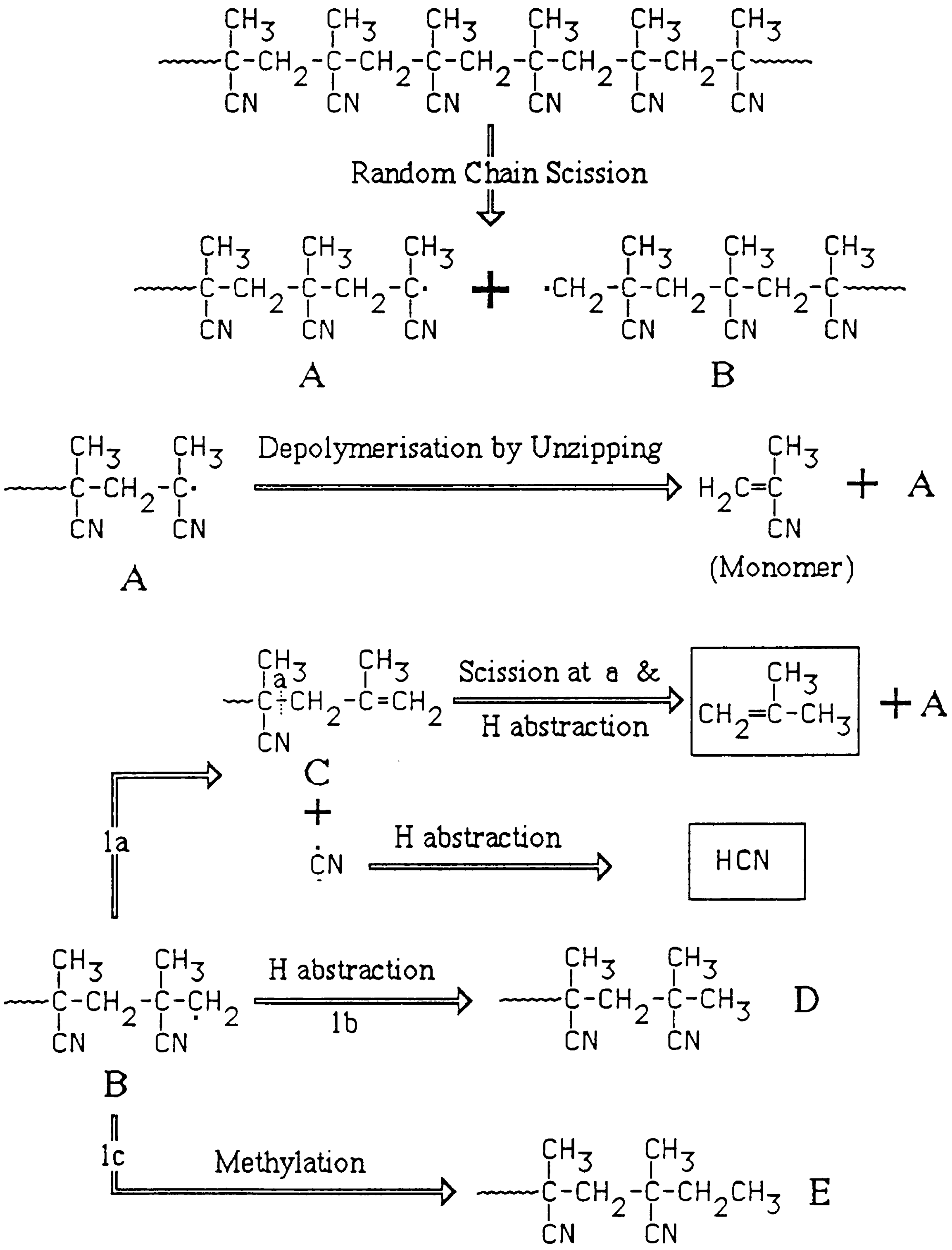
SCHEME 6.2



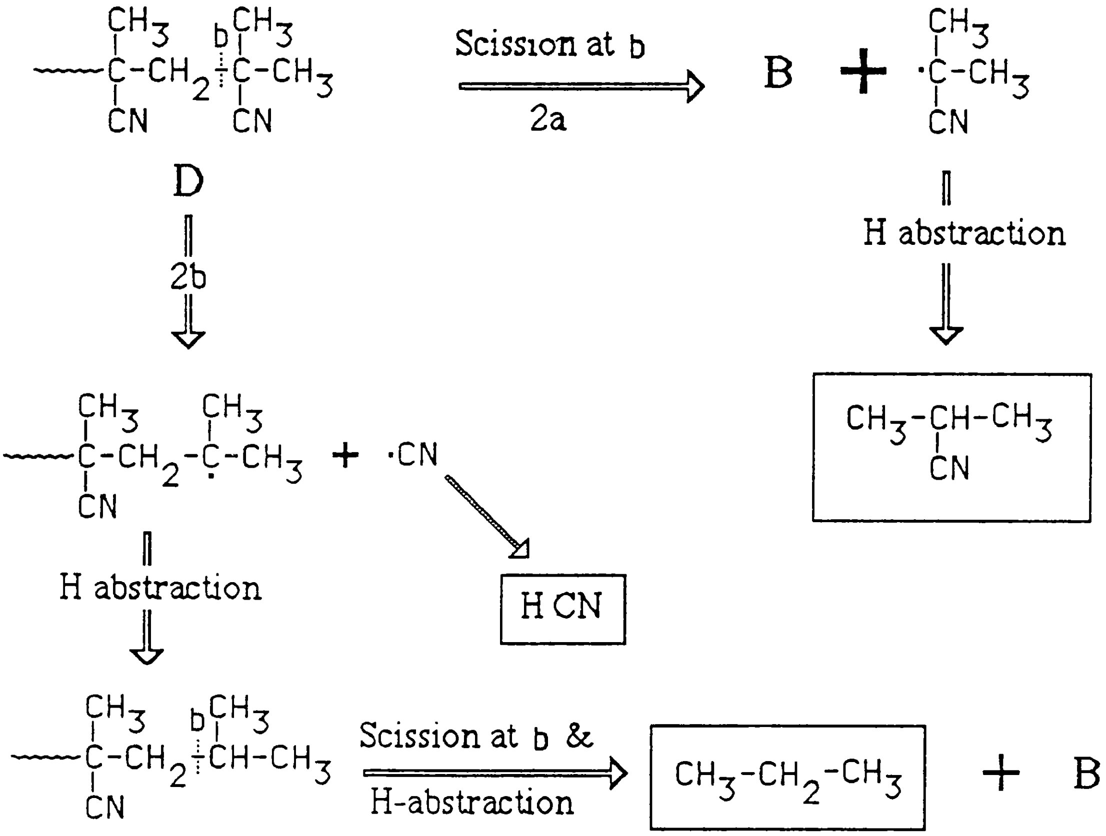
Formation of various types of products identified in the CRF is explained in Scheme 6.7. Various amino and methyl substituted fused ring heterocyclic structures are proposed to form by partial and selective aromatisation of nitrile cyclised polymer as shown in Scheme 6.7a. Formation of different oligomers found in the CRF is believed to occur from scission of macro species D at a* or b* as explained in scheme 6.7b. Scission at a* followed by removal of H radical results into various dimers, trimers and tetramers etc., as shown in scheme 6.7b. Different oligomers containing extra methyl group results from scission at b* followed by hydrogen abstraction as shown in Scheme 6.7b.

Formation of some other products (oligomers with one less methyl group) identified in CRF is also proposed in Scheme 6.7 b.

SCHEME 6.3

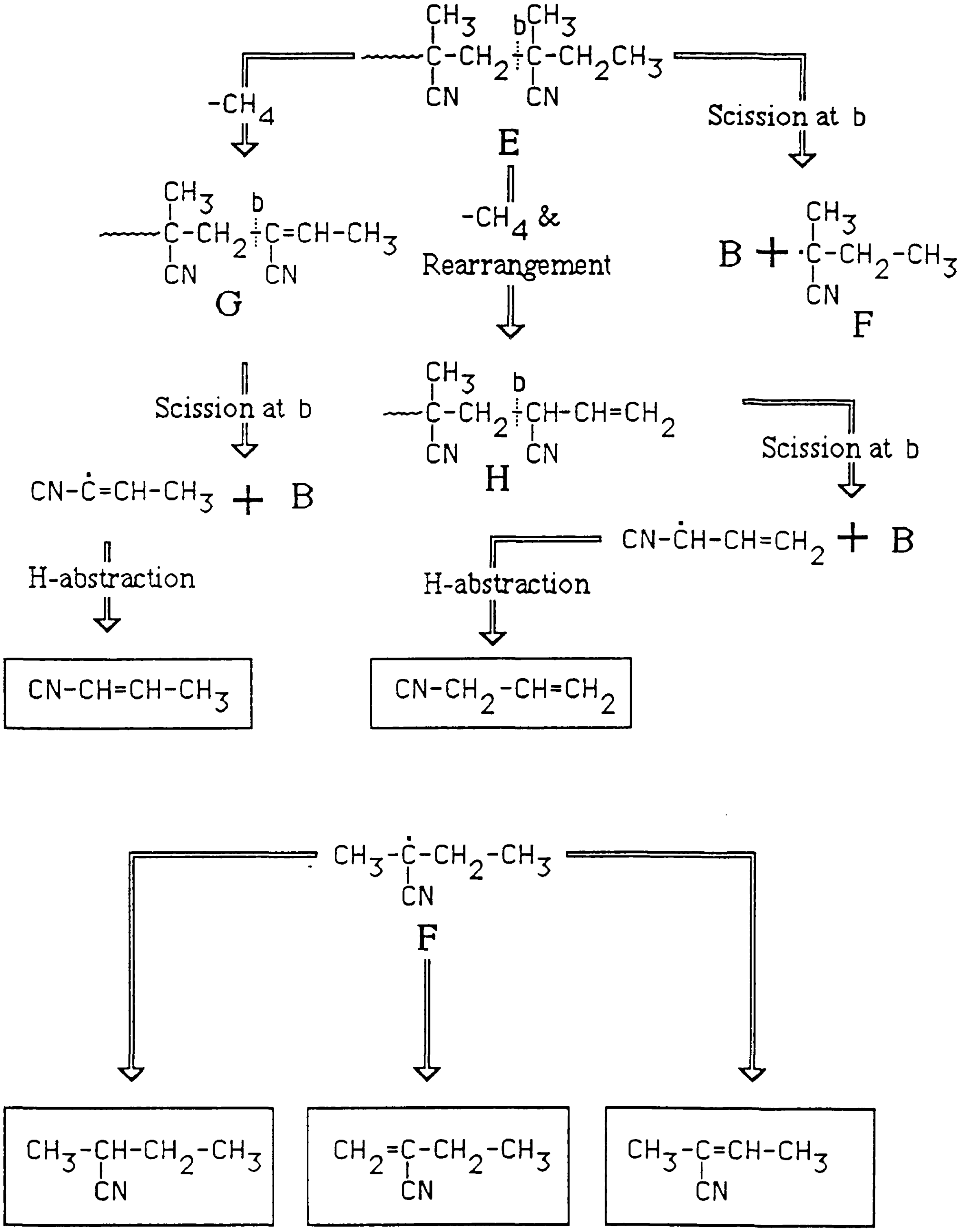

Random Chain Scission
A
B
Depolymerisation by Unzipping
(Monomer)
+ A
Scission at a &
H abstraction
C
+
ĊN
H abstraction
HCN
1a
H abstraction
1b
D
1c
Methylation
E

SCHEME 6.4

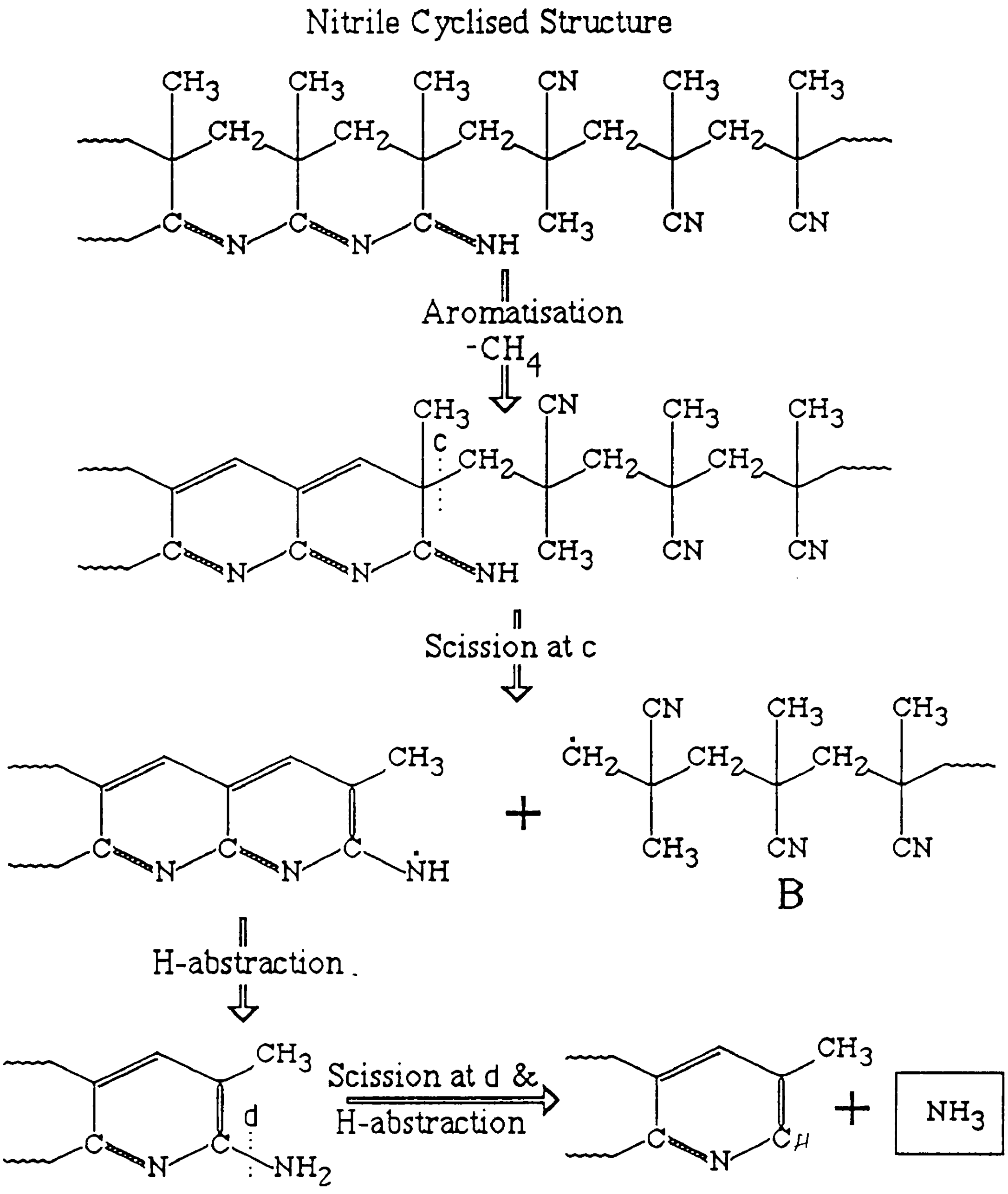


b
Scission at b
2a
B
D
2b
H abstraction
·CN
HCN
CH3-CH-CH3 CN
H abstraction
Scission at b &
H-abstraction
CH3-CH2-CH3
B

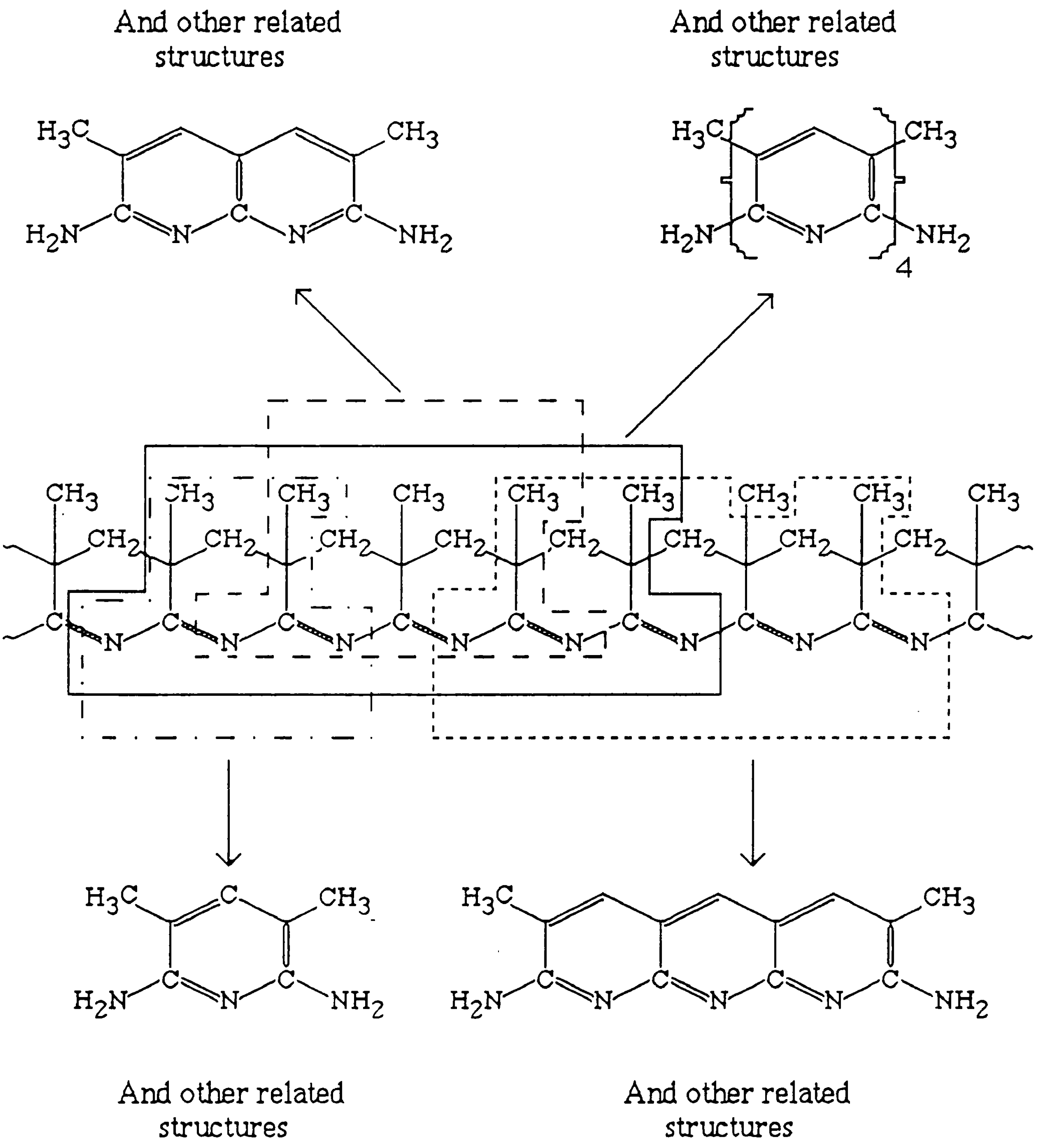
SCHEME 6.5


E
G
H
F
B
b
-CH4
-CH4 & Rearrangement
Scission at b
H-abstraction
CN-CH=CH-CH3
CN-CH2-CH=CH2
CN-Ċ=CH-CH3 + B
CN-ĊH-CH=CH2 + B
CH3-CH(CN)-CH2-CH3
CH2=C(CN)-CH2-CH3
CH3-C(CN)=CH-CH3

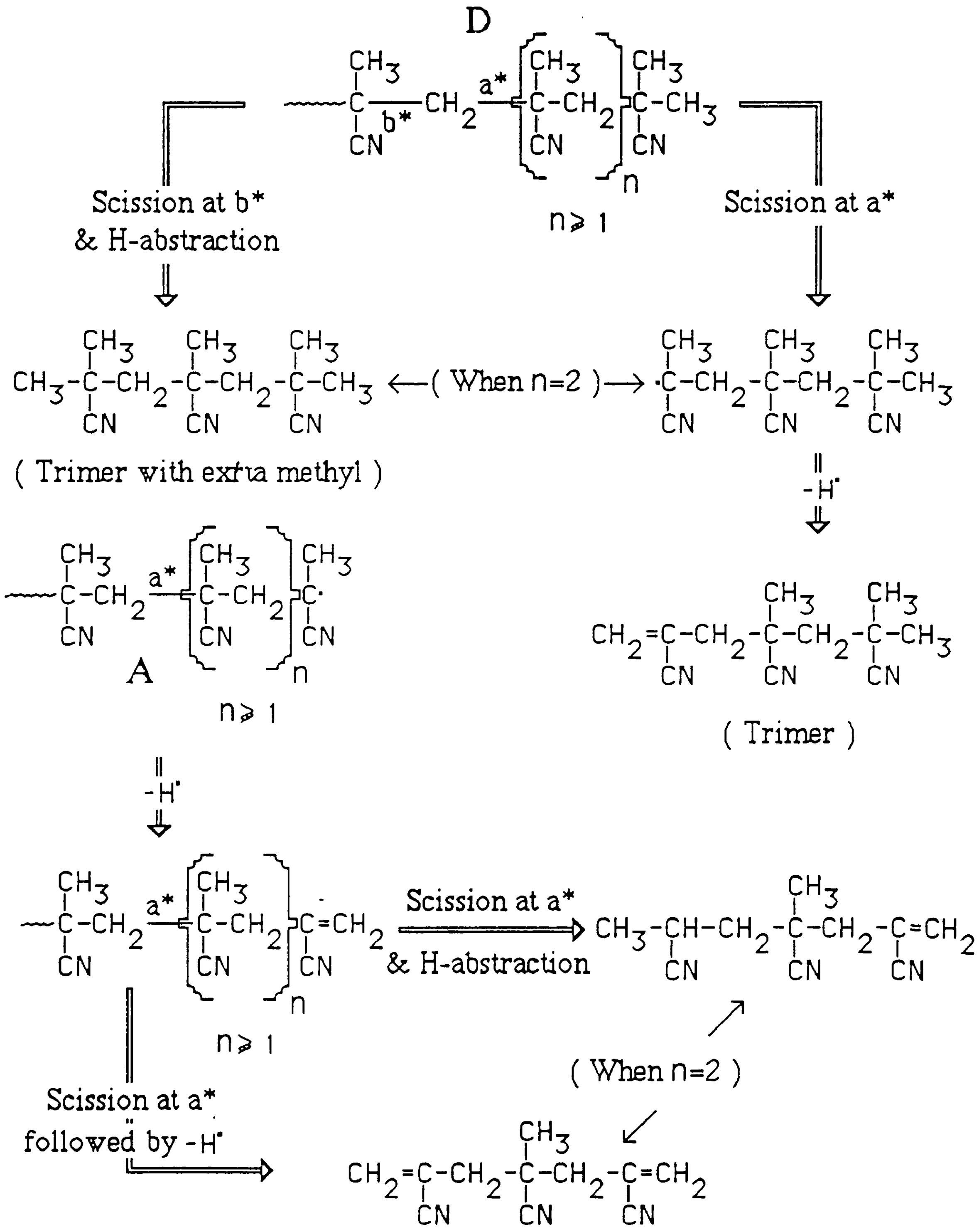
SCHEME 6.6


Nitrile Cyclised Structure
Aromatisation
$-CH_4$
c
Scission at c
+
B
H-abstraction.
d
Scission at d &
H-abstraction
+
NH_3

SCHEME 6.7a


And other related structures
And other related structures
And other related structures
And other related structures
4

SCHEME 6.7b


D
a*
b*
n
n ≥ 1
Scission at b*
& H-abstraction
Scission at a*
(When n=2)
(Trimer with extra methyl)
-H·
A
(Trimer)
Scission at a*
& H-abstraction
(When n=2)
Scission at a*
followed by -H·

CHAPTER SEVEN

CHAPTER SEVEN

THERMAL DEGRADATION OF METHACRYLONITRILE/STYRENE COPOLYMERS

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 comonomer may either stabilise or destabilise the copolymer relative to the homopolymers.

In this chapter, the thermal behaviour of a set of methacrylonitrile/styrene copolymers (with different molar composition) have been investigated. The effect of presence of an acidic comonomer (methacrylic acid) on the thermal behaviour and on the degradation products had already been investigated in Chapter Six. One copolymer of methacrylonitrile and maleic anhydride has also been included in this chapter to see the effect of presence of anhydride monomer on the thermal stability and on the products of degradation.

The origin of the five copolymers (four copolymers of methacrylonitrile with styrene comonomer and one with maleic anhydride) is given in Table 7.1.

7.1 INTRODUCTION

Styrene is a monomer which can be polymerised by all known addition polymerisation mechanisms, such as radical,[70] cationic,[70] anionic[71] and transition metal containing catalysts.[72] Styrene monomer can also generate enough free radicals during heating and high molecular weight polymer can also be prepared without chemical initiator. Polystyrenes are mostly prepared industrially by radical polymerisation.[73]

Polystyrene is a thermoplastic which can be easily coloured and fabricated, and posseses excellent insulating properties. It has reasonably good mechanical and thermal properties, but is brittle and softens below 100 °C. Since styrene polymers are non-polar, resistant to water and easy to fabricate, they are used for electronics, medical, food packing, optical appliance and automotive applications.

7.1.2 PREVIOUS WORK ON THE THERMAL DEGRADATION OF POLYSTYRENE

Polystyrene degrades at elevated temperatures to a mixture of volatile products about half of which is styrene. A number of recent comunications have provided additional information about the thermal degradation behaviour of polystyrene which reflect a discrepancy in views.[74-77,14,79]

Polystyrene begins to show significant molecular weight decrease around 300 °C, but formation of volatile products is not observe at low temperatures. The method by which the polymer was prepared plays an important role on the degradation rate.[80] Anionically prepared polystyrene is initially more stable than that produced thermally or from free-radical initiators such as benzoyl peroxide or AIBN.

Generally, the thermal degradation mechanism of polystyrene involves a homolytic chain scission mechanism. The main steps involved in the process are generation of free radicals, propagation (during which inter- and intramolecular chain reactions are very active), and first order termination.[80-82] Initiation at a chain end by a benzyl group results into a tolyl radical ($^{\bullet}CH_2$-C_6H_5) and a primary polystyryl radical. α-Methyl styryl and secondary polystyryl radicals are formed from the unsaturated ends.[77] The tolyl and α-methyl styryl radicals yield toluene and α-methyl styrene by hydrogen abstraction. In case of anionically prepared polystyrene, the benzylic end (~~CH_2-CH_2-C_6H_5) has also been identified as a site for depolymerisation initiation.[14,83] It has been shown[84] that a series of three propagation reactions [which are β-scission, intramolecular hydrogen abstraction (backbiting) followed by β-scission further from chain end] for the chain end polystyryl radicals accounts for the major volatile products observed. Finally the formation of various short chain fragments can be explained/related by intermolecular transfer reactions, reducing chain size to the extent that short chains can volatilise at high temperature.

There is a general agreement that the termination step in the degradation of polystyrene in the range 300–350 ^{o}C is first order. It has been shown[81,84] that volatile radical escaping from the polymer provides the predominant route for radical elimination.

McNeill et al.[13] have carried out a detailed study of thermal behaviour of several polystyrene samples prepared anionically using sodium naphthalenide and compared with polystyrene samples made by the free radical route. Isothermal degradation at 300, 350 and 420 ^{o}C was

TABLE 7.1 Data for the Methacrylonitrile/Methacrylic Acid Copolymers used in this Investigation.

Polymer	Initiator	Temperature of polymerisation	Composition In copolymer	$\overline{M}$n by GPC
COMAN/Sty 1	AIBN	80 ^{o}C	10 : 1	6986
COMAN/Sty 2	AIBN	80 ^{o}C	1 : 1	18010
COMAN/Sty 3	AIBN	80 ^{o}C	1 : 10	20210
COMAN/Sty 4	ACVA	80 ^{o}C	10 : 1	7918
COMAN/Ml.An.	AIBN	80 ^{o}C	3 : 1	21180

Composition	Molar ratio (Methacrylonitrile/Styrene)
$\overline{M}$n	Number-average molecular weight
AIBN	2,2'-Azobisisobutyronitrile
ACVA	4,4'-Azobis(4-cyanovaleric acid)

performed over a wide range of extent of degradation and it was found that the ratio of volatile liquid to the cold ring fraction falls sharply, is dependent on the initial molecular weight of the polymer and finally reaches a constant value. It was concluded from isothermal heating at 300 ^{o}C intramolecular transfer is initially impeded by the high melt viscosity and intermolecular hydrogen transfer (which leads to a fall in molecular weight) is favoured

7.2 THERMAL DEGRADATION

Thermal degradation of these copolymers (a set of four methacrylonitrile/styrene copolymers and one methacrylonitrile/maleic anhydride copolymer) has been studied by using TVA, TG, DTG and DTA techniques. Degradation products were also examined after each TVA experiment.

7.2.1 PROGRAMMED HEATING EXPERIMENTS

7.2.1.1 Thermal Volatilisation Analysis

The sample size was 50 mg for each copolymer. These copolymer samples were degraded to 500 ^{o}C at a heating rate of 10 ^{o}C/ min. under the normal conditions of TVA as described in Chapter Two. Mass spectrometric studies during TVA operation (TVA-MS) were also carried out for detection of any non-condensable gases as described previously.

The TVA curves for all copolymers are reproduced in Fig. 7.1, which indicated that there are discrepancies among the degradation pattern of the various methacrylonitrile/styrene copolymers studied.

COMAN/Sty 1: The TVA trace for copolymer 1 (having 10:1 methacrylonitrile/styrene molar ratio) shows a two stage decomposition. The first stage of degradation starts above 260 ^{o}C with a T_{max} around 325 ^{o}C, whereas the second stage of decomposition (which extends over a wide range of temperature between 330 to 500 ^{o}C) shows a T_{max} value at 412 ^{o}C.

COMAN/Sty 2: The TVA curve for COMAN/Sty 2 consists of a broad single decomposition peak. The onset of evolution of volatile products occurs around 300 ^{o}C and reaches a broad maximum in the temperature range 390–420 ^{o}C. The separation of traces (0, -45, -75 ^{o}C etc.) in the main step of degradation is indicative of variety of products. The TVA data are in good agreement with the TG, DTG and DTA results.

COMAN/Sty 3: In case of COMAN/Sty 3, the TVA trace comprises a relatively sharp and well resolved single peak having T_{max} around 423^{o}C. It is clear from the TVA curve that no significant amount of volatile material is given off below 320 ^{o}C.

COMAN/Sty 4: Like COMAN/Sty 1, the copolymer sample (COMAN/Sty 4) also has the same molar composition ratio of methacrylonitrile/styrene (10:1), but has made from ACVA initiator rather then AIBN, and shows quite different thermal behavior. The TVA trace for COMAN/Sty. 4 shows a single broad decomposition curve with a small initial shoulder in the temperature range 280-320^{o}C, before the T_{max} is reached. The volatile material, including non-condensables, appears above 260 ^{o}C, and the maximum rate of volatilisation in case of COMAN/Sty 4 occurs at a temperature of around 370-385 ^{o}C.

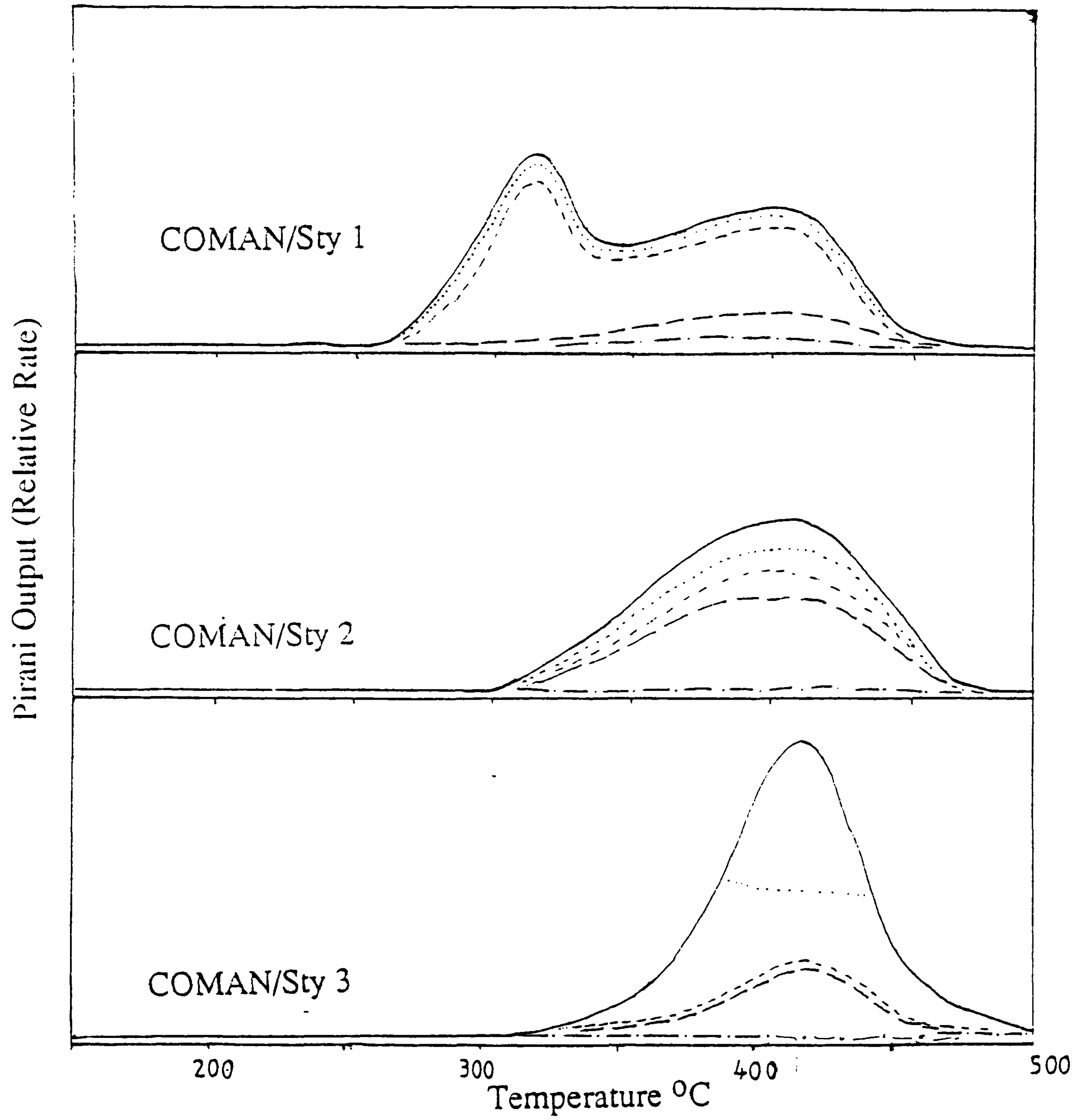
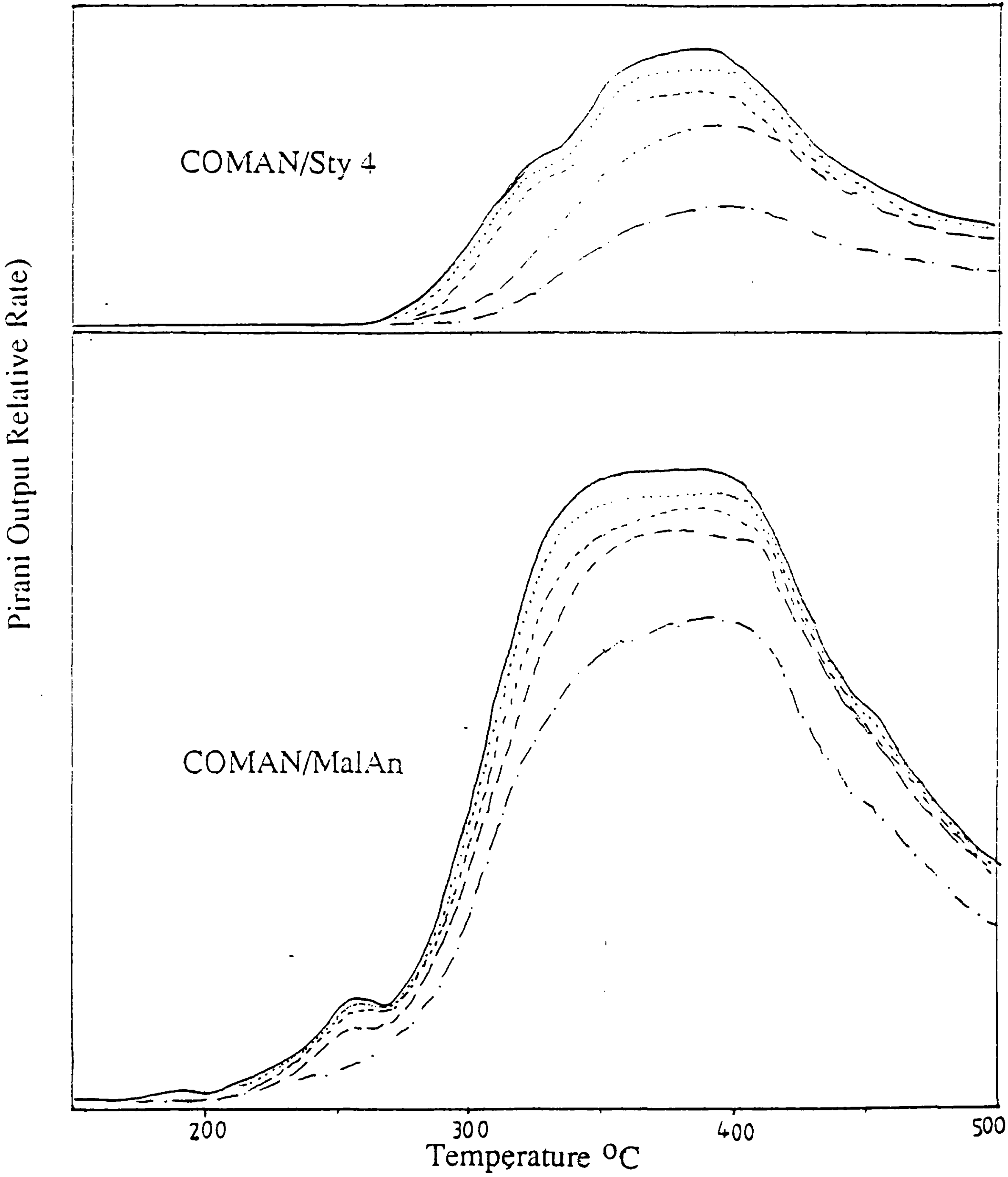


Fig. 7.1. The TVA Curves (Vacuum, Heating Rate 10 ^{0}C/min.) for Various MAN/Sty Copolymers and MAN/MalAn Copolymer.

Key: 0 ^{0}C —, -45 ^{0}C ····, -75 ^{0}C - - , -100 ^{0}C — — , -196 ^{0}C — · — .

(CONTINUED)

Fig. 7.1. Continued



The TVA trace for COMAN/MalAn is somewhat similar to the TVA curves of high molecular methacrylonitrile polymers with acidic ends (e.g. EIPMAN 1 & 2) with an additional small peak around 200-275 ^{o}C, which is mainly due to decarboxylation of anhydride units present in the polymer chain. The second, and main decomposition peak which is broad in nature, appears to involve a further two stages (showing not well resolved T_{max} at 350 and 410 ^{o}C). Then follows a gradual decomposition of some relatively stable material above 450 ^{o}C.

Close inspection of TVA traces of this set of methacrylonitrile/styrene copolymers suggested that

(i) A well separated two stage decomposition (in case of COMAN/Sty 1), tends to merge into a sharp single stage (in case of COMAN/Sty 3), with increasing styrene monomer ratio in the copolymer.

(ii) An increase in T_{onset} and T_{max} is well noticeable as proportion of styrene monomer increases

The main features of thermal behaviour established by TVA studies are summarised in Table 7.2.

7.2.1.1.1 Subambient Thermal Volatilisation Analysis.

Condensable volatile degradation products from the copolymer sample 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[73] already described in Chapter Two. Mass spectrometric studies during SATVA separation (SATVA-MS) were also carried out for instantaneous product identification. The SATVA traces for products

TABLE 7.2. TVA Data for the Degradation of the Various Methacrylonitrile Copolymer Samples Investigated.

Polymer	T_{onset} °C	T_{max} °C	Wt. % Residue at ~500 °C	Wt. % CRF at ~500 °C	Wt. % L.F at ~500 °C
COMAN/Sty 1	258	325 & 412	2	12	85
COMAN/Sty 2	305	415	1	18	78
COMAN/Sty 3	314	423	2	29	67
COMAN/Sty 4	264	385	10	45.2	38.2
CMAN/MalAn	207	350--410	45	33	14

CRF	Cold ring fraction
LF	Liquid fraction

from all the copolymers studied are reproduced in Figs. 7.2-7.6.

Assignment for materials present based on IR and MS (SATVA-MS) investigation are shown in Tables 7.8– 7.12.

7.2.1.1.2 PRODUCT ANALYSIS

The various degradation products namely residue, cold ring fraction, liquid fraction and condensable gases were examined after degradation.of 50 mg of each copolymer sample to 500 ^{o}C under normal TVA conditions. Non-condensable gases evolved (if any) from degradation of each copolymer sample were instantaneously analysed by mass spectrometry by bleeding them into a quadrupole mass spectrometer coupled with the system during the TVA experiment. Instantaneous mass spectrometric analysis during SATVA separation (SATVA-MS) was also carried out by bleeding the warmed up degradation products into the quadrupole mass spectrometer coupled with the system. Cold ring fractions from degradation of all copolymers, were also analysed by mass spectrometry. All degradation products except non-condensables were examined by IR spectroscopy. Condensable liquid products collected in a cold finger were also subjected to GC-MS.

7.2.1.1.2a Residue.

There was no significant amount of residue left after the degradation of copolymers MAN/Sty 1, 2 and 3, but a 10% and 42% of residue was obtained from degradation of COMAN/Sty 4 and COMAN/MalAn samples, respectively. The IR spectrum (Fig. 7.7) of the residue (which

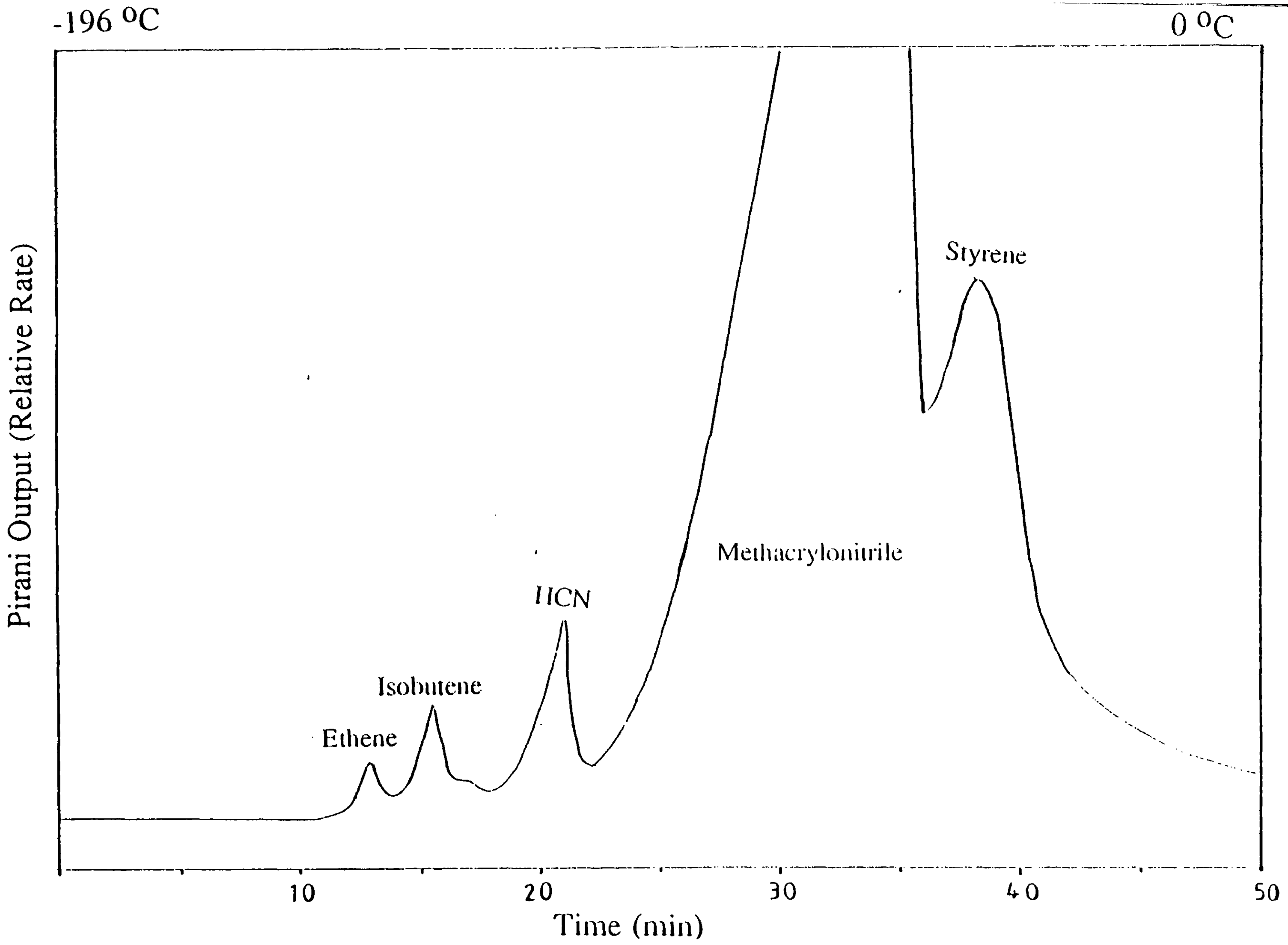


Fig. 7.2. SATVA Curve for Condensable Product Fraction from Degradation of COMAN/Sty 1 to 500 °C under Normal TVA Conditions.

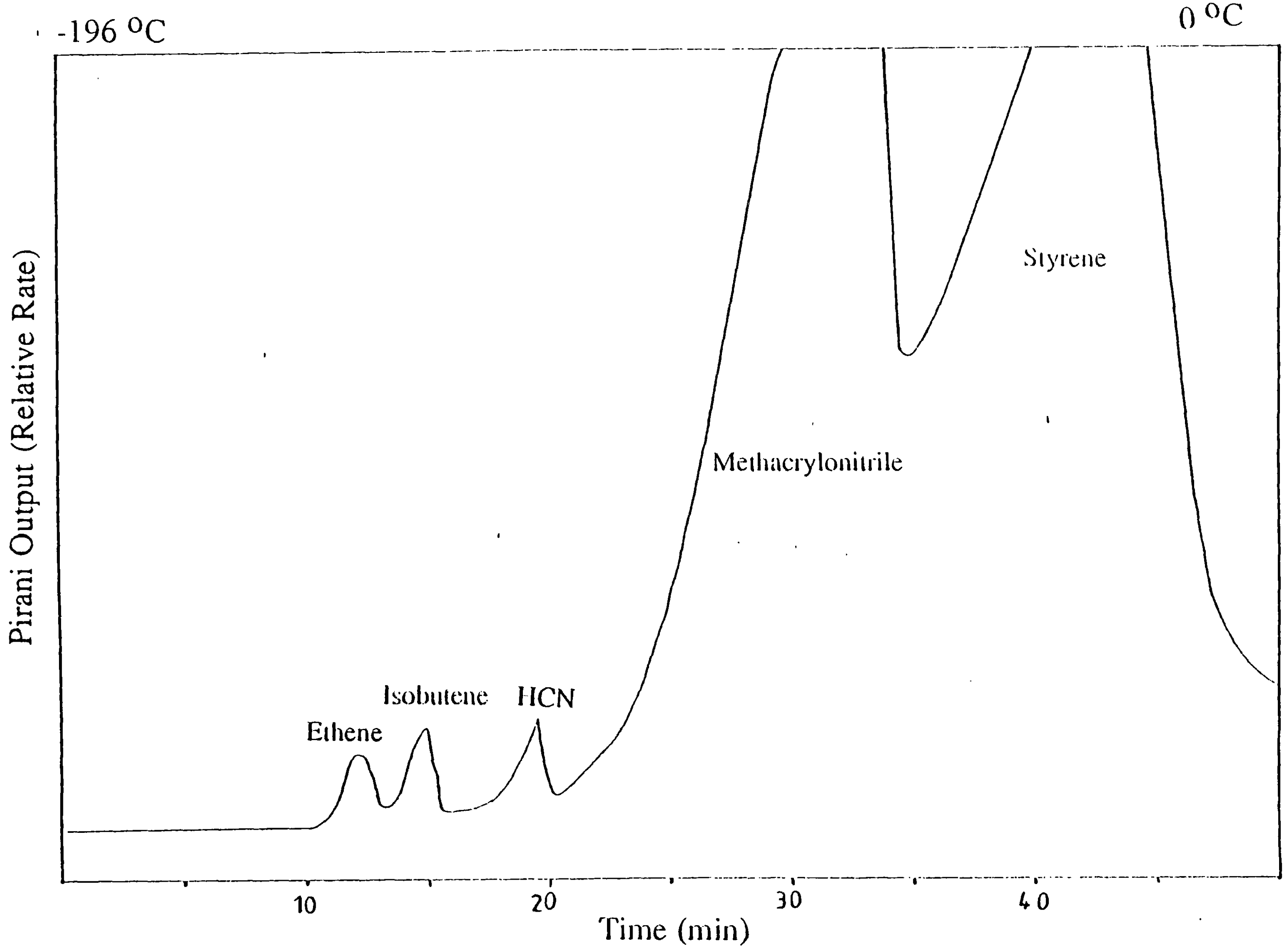


Fig. 7.3. SATVA Curve for Condensable Product Fraction from Degradation of COMAN/Sty 2 to 500 °C under normal TVA Conditions.

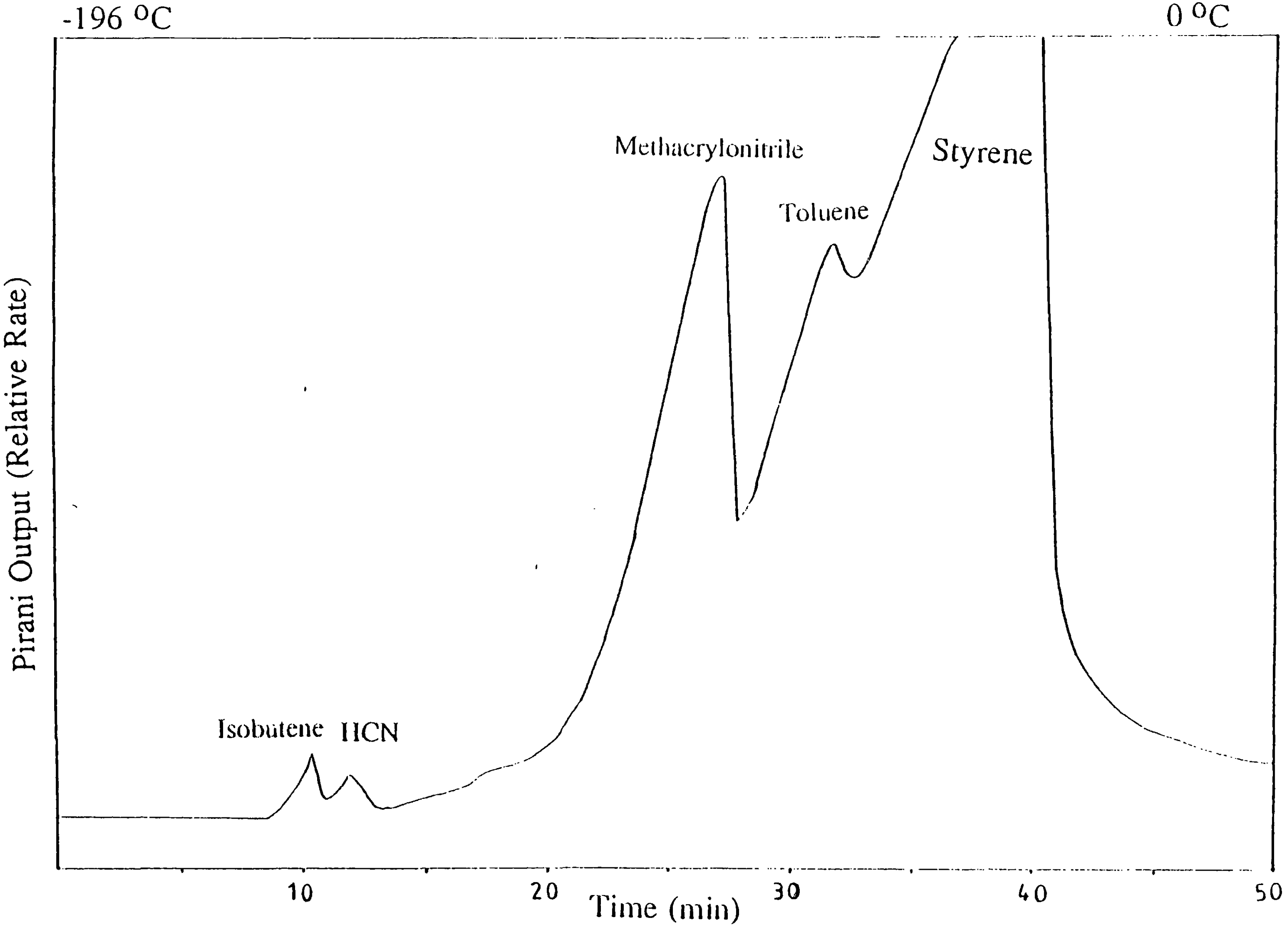


Fig. 7.4. SATVA Curve for Condensable Product Fraction from Degradation of COMAN/Sty 3 to 500 ^{o}C under normal TVA Conditions.

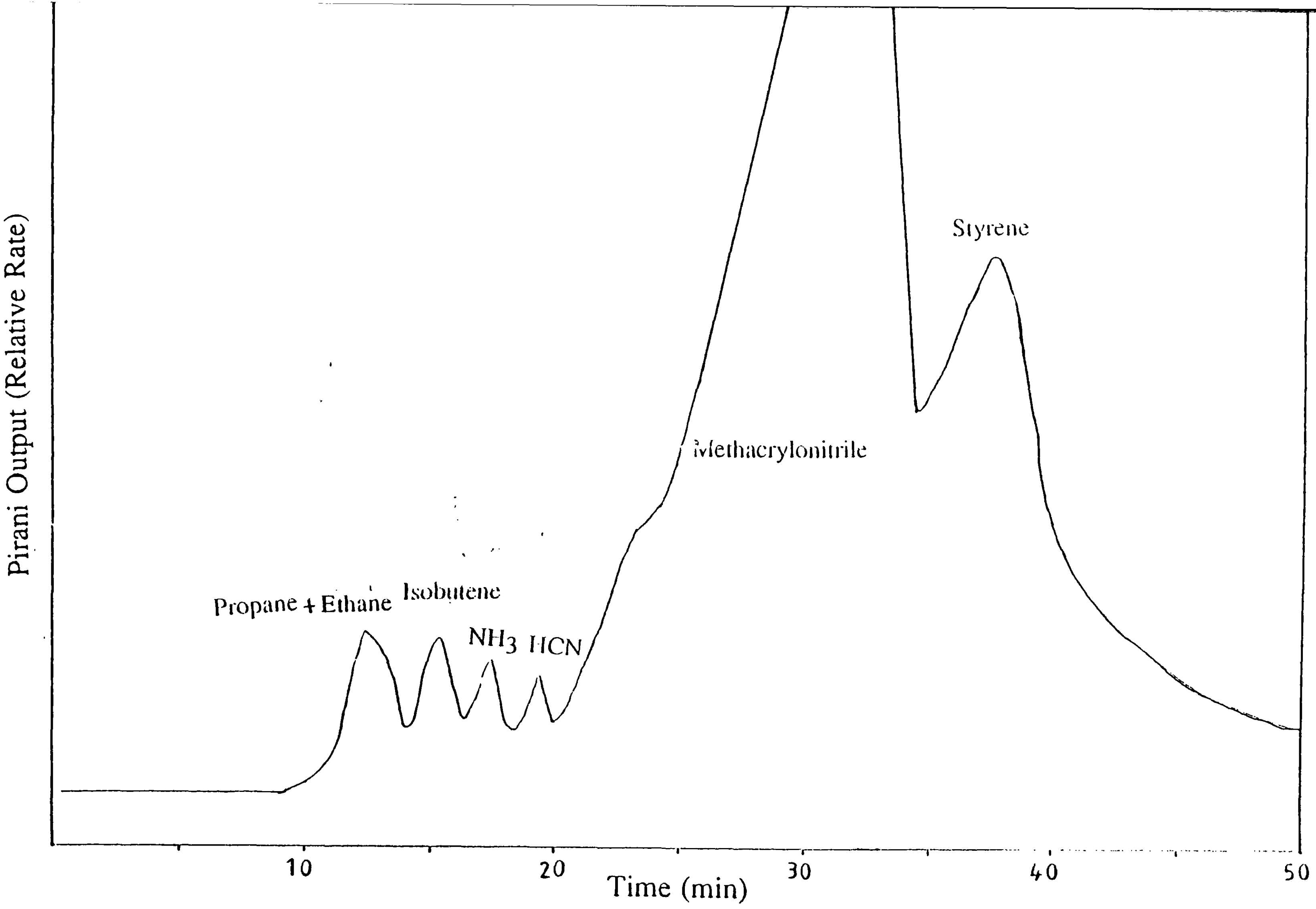


Fig. 7.5. SATVA Curve for Condensable Product Fraction from Degradation of COMAN/Sty 4 to 500 ^{o}C under normal TVA Conditions.

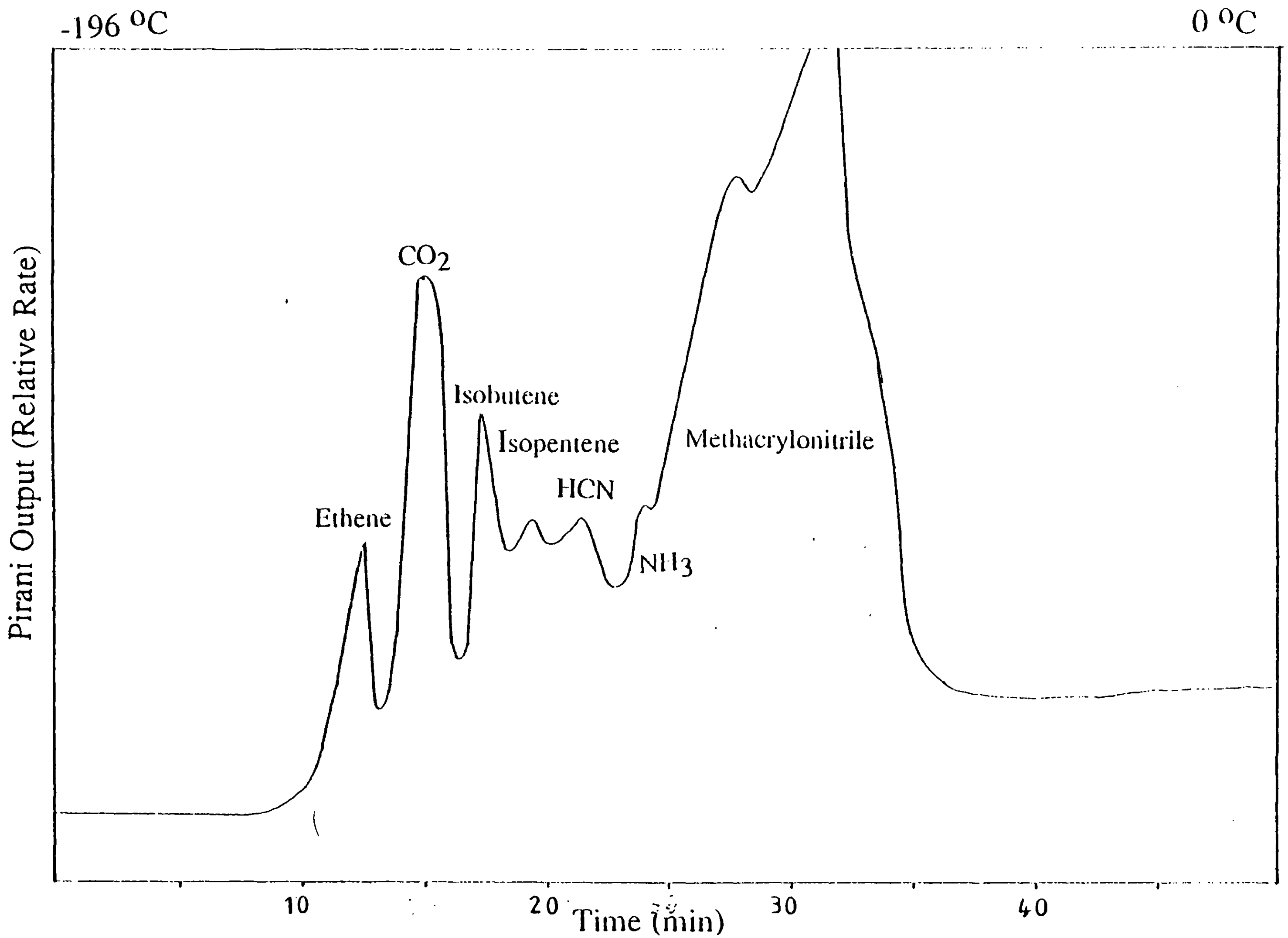


Fig. 7.6. SATVA Curve for Condensable Product Fraction from Degradation of COMAN/MalAn to 500 °C under normal TVA Conditions.

is poorly resolved and difficult to assign), is almost identical to IR spectra obtained from residues of various end-initiated methacrylonitrile homopolymers and copolymers of MAN/MAA. The high wavenumber region of the IR spectrum shows a broad and featureless band which may be associated with the extended conjugated systems

7.2.1.1.2b Cold ring fraction.

Cold ring fraction products (varying in colour from dark brown to colourless waxy) which were collected on the upper part of the TVA tube, were analysed by IR and mass spectrometry.

The IR spectra for cold ring fractions obtained from various MAN/Sty copolymers made from AIBN initiator (MAN/Sty copolymers 1, 2 & 3) were similar to their corresponding copolymers (Fig. 7.8) but showing one extra peak around 1630 cm^{-1}, indicating various lengths of oligomers, also containing C=C unsaturation. A decrease in C≡N (nitrile) absorption at 2214 cm^{-1} in cold ring fractions IR spectra with increasing ratios of styrene monomer (as also in the corresponding copolymer IR spectra) indicated oligomers with different proportions of the two (methacrylonitrile & styrene) monomer units.

In case of COMAN/Sty 4 (made from ACVA initiator with 10:1 methacrylonitrile/styrene ratio) and COMAN/MalAn, the IR spectra (Fig. 7.8 d & e) show peaks at 3187 and 3327 cm^{-1} corresponding to NH_2 stretching. A strong and broad peak at 1660–1600 cm^{-1} is also observed in.the IR spectrum of the CRF from these two copolymers as has already been reported in the case of the CRF from all ACVA

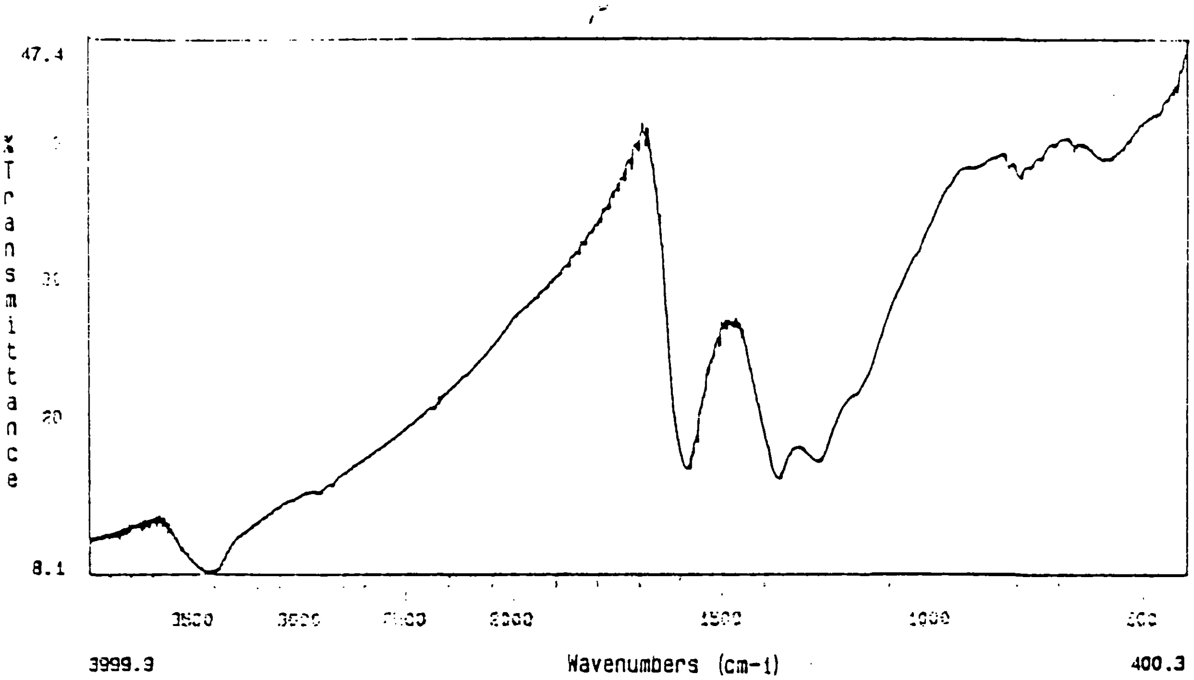


Fig. 7.7. IR Spectrum of the Residual Fraction From Degradation to 500 oC under TVA Conditions of MAN/MalAn Copolymer.

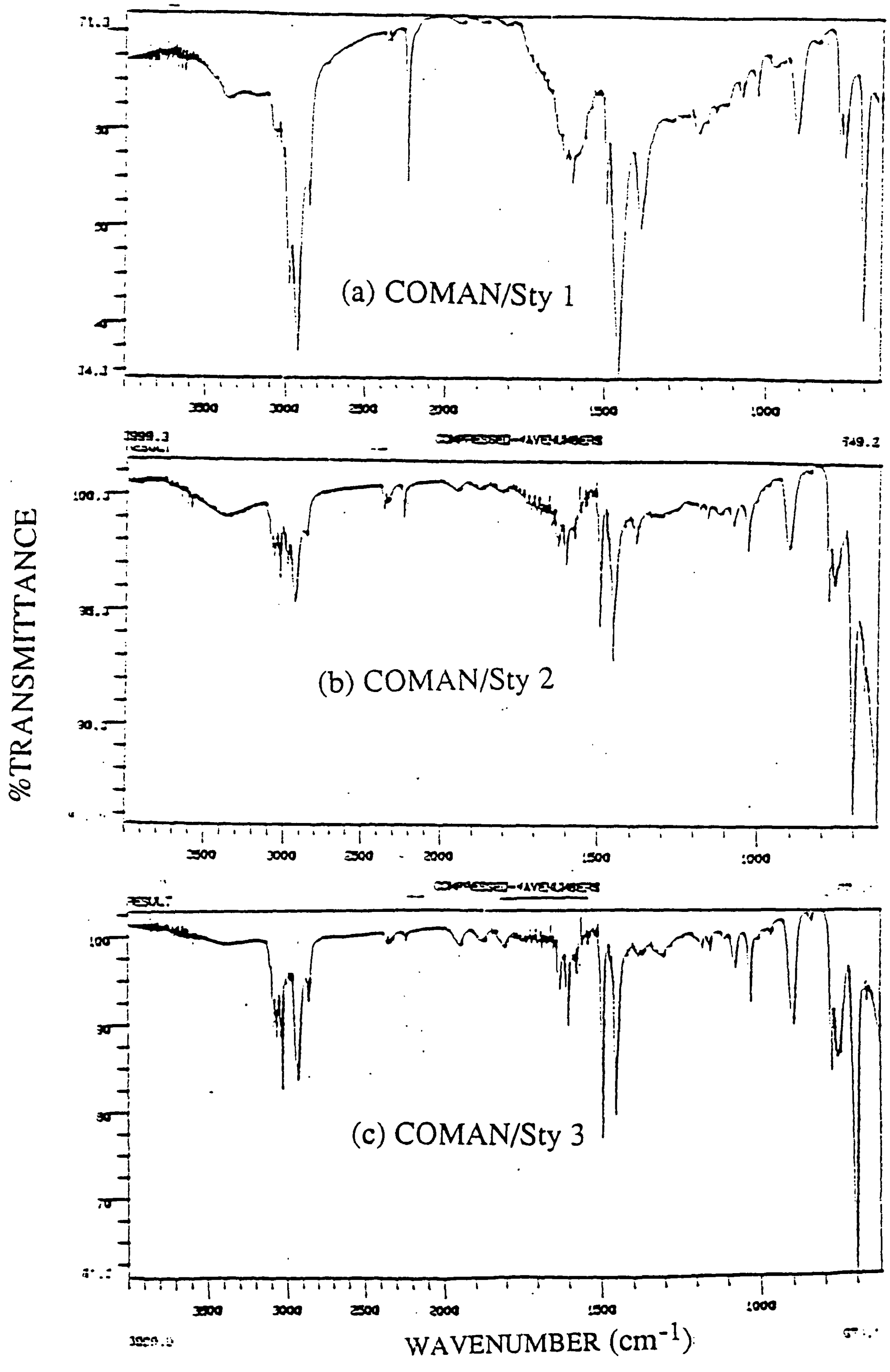
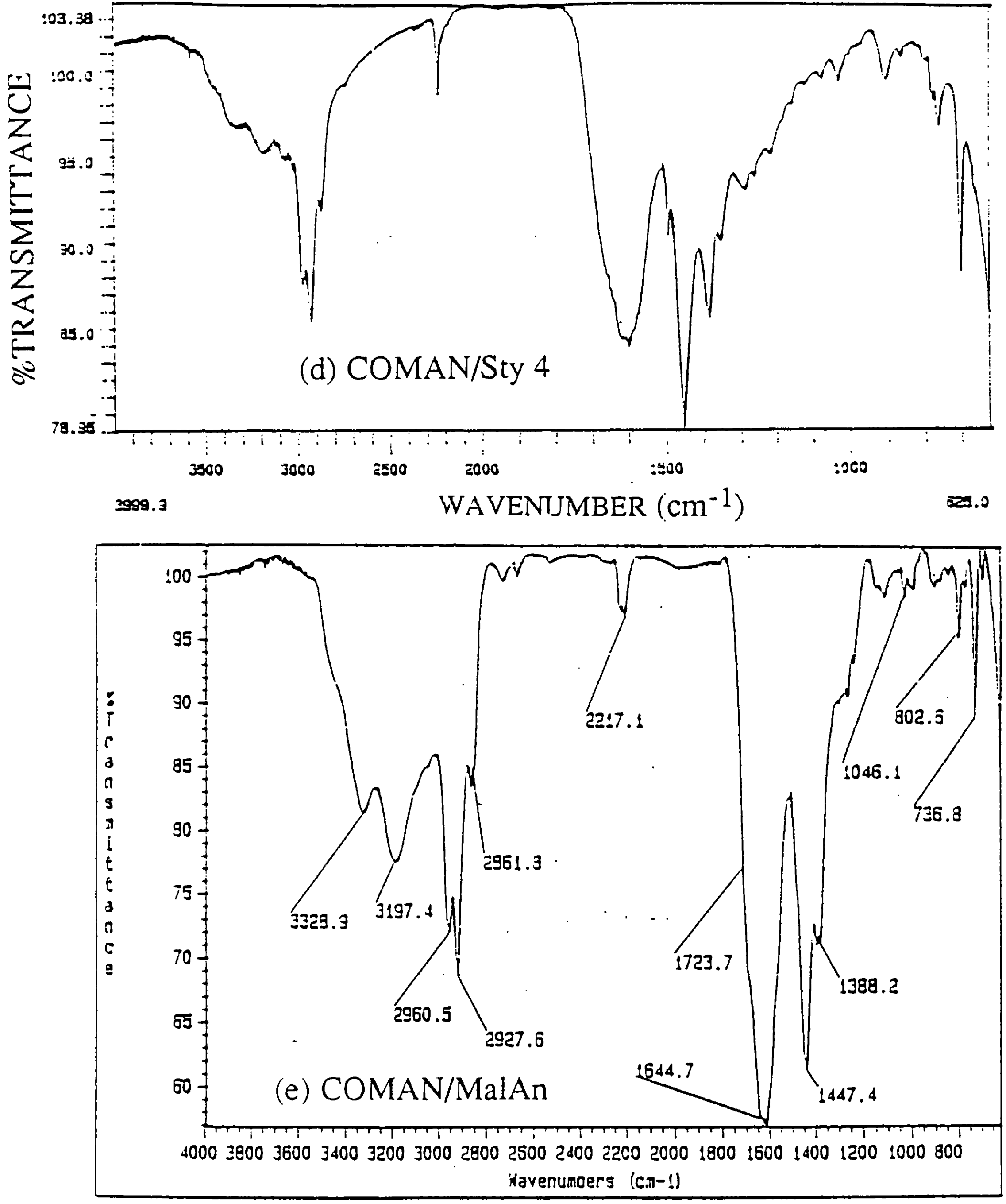


Fig. 7.8. IR Spectra of the Cold Ring Fraction from.Degradation of Various MAN/Sty Copolymers.to 500 °C under TVA Conditions.

(CONTINUED)

Fig. 7.8. Continued



initiated methacrylonitrile polymers and methacrylonitrile/methacrylic acid copolymers, indicating the presence of some amino and methyl substituted conjugated (hydronaphthyridine and naphthyridine) structures. A strong band at 1700 cm^{-1} is also present in the the IR spectrum of the CRF from COMAN/MalAn indicating the presence of some C=O containing structures.

Some of the products identified from these fractions (CRF) from the various copolymers, studied by mass spectrometry are listed in Tables 7.3–7.6.

TABLE 7.3. Products Identified in the Cold Ring Fraction from Degradation of COMAN/Sty 1 Sample under normal TVA Conditions. (Products are Listed According to Relative Abundance.)

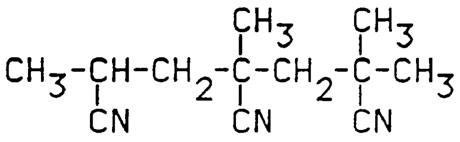
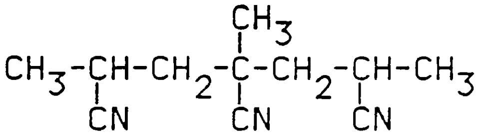
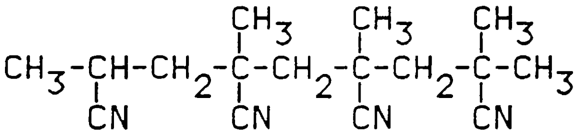
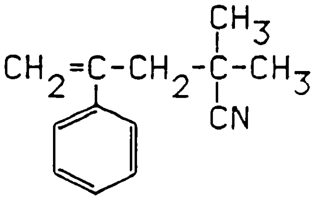
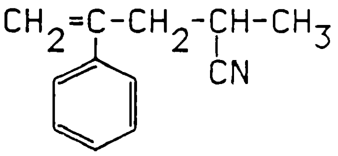
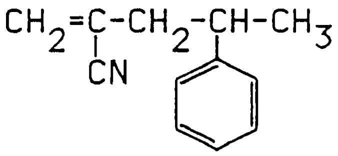
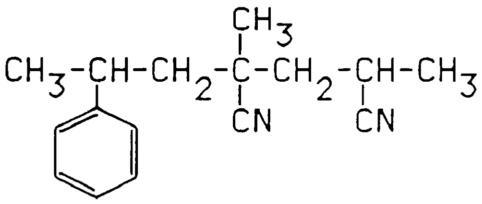
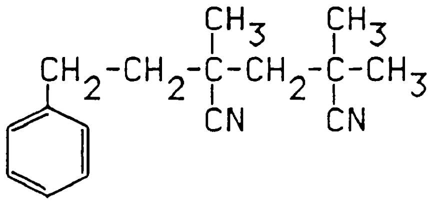
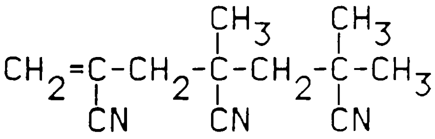
Product	m/e
 $CH_3\text{-}\underset{CN}{CH}\text{-}CH_2\text{-}\overset{CH_3}{\underset{CN}{C}}\text{-}CH_2\text{-}\overset{CH_3}{\underset{CN}{C}}\text{-}CH_3$	203
 $CH_3\text{-}\underset{CN}{CH}\text{-}CH_2\text{-}\overset{CH_3}{\underset{CN}{C}}\text{-}CH_2\text{-}\underset{CN}{CH}\text{-}CH_3$	189
 $CH_3\text{-}\underset{CN}{CH}\text{-}CH_2\text{-}\overset{CH_3}{\underset{CN}{C}}\text{-}CH_2\text{-}\overset{CH_3}{\underset{CN}{C}}\text{-}CH_2\text{-}\overset{CH_3}{\underset{CN}{C}}\text{-}CH_3$	270
	185
 	171
 	240
 $CH_2\text{=}\underset{CN}{C}\text{-}CH_2\text{-}\overset{CH_3}{\underset{CN}{C}}\text{-}CH_2\text{-}\overset{CH_3}{\underset{CN}{C}}\text{-}CH_3$	201

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TABLE 7.3 CONTINUED

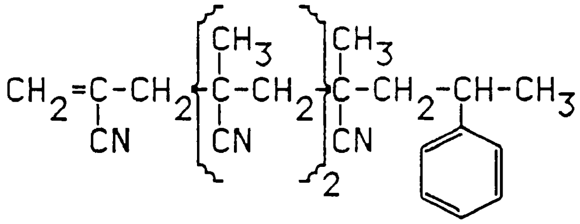
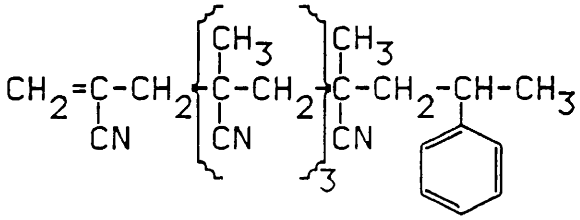
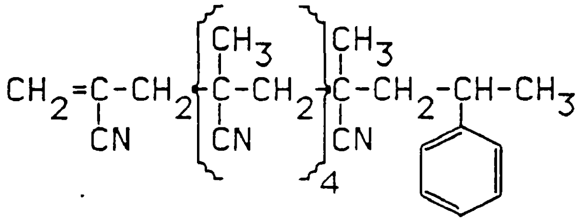
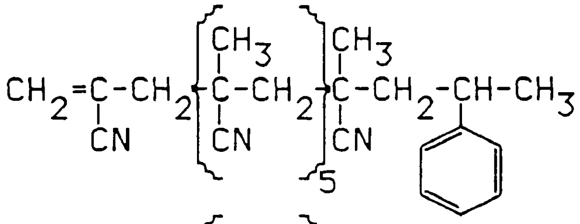
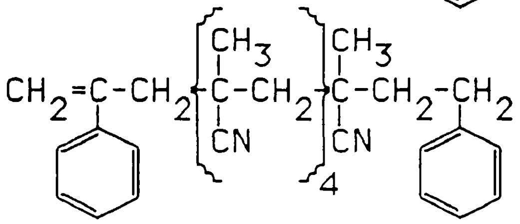
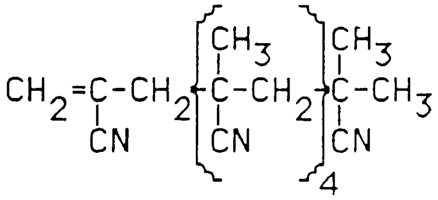
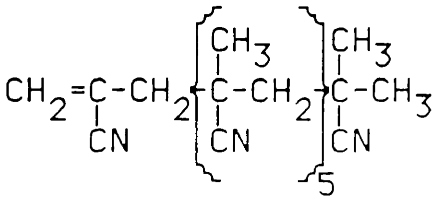
	or other isomer(s)	372
	or other isomer(s)	439
	or other isomer(s)	506
	or other isomer(s)	573
	or other isomer(s)	543
 $\mathrm{CH_2{=}C(CN){-}CH_2{-}[C(CH_3)(CN){-}CH_2]_4{-}C(CH_3)(CN){-}CH_3}$		402
 $\mathrm{CH_2{=}C(CN){-}CH_2{-}[C(CH_3)(CN){-}CH_2]_5{-}C(CH_3)(CN){-}CH_3}$		469

TABLE 7.4. Products Identified in the Cold Ring Fraction from Degradation of COMAN/Sty 2 Sample under normal TVA Conditions. (Products are Listed According to Relative Abundance.)

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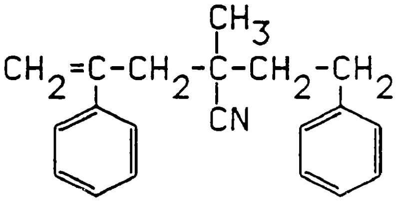
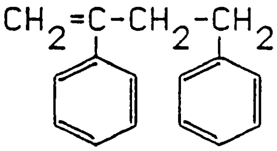
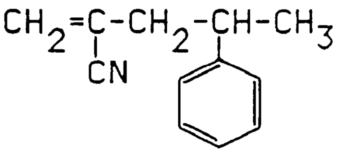
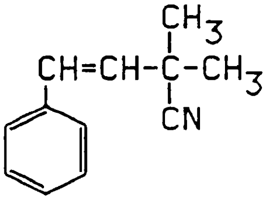
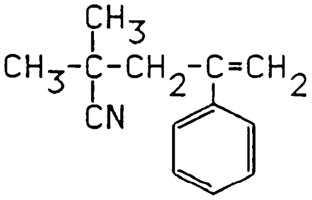
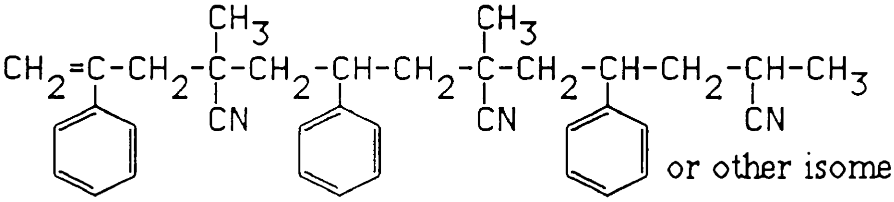
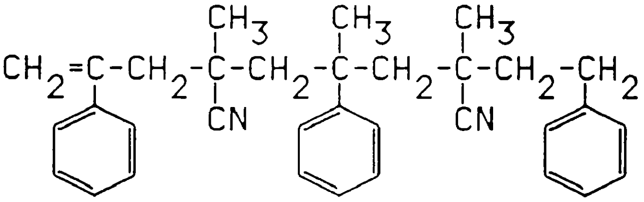
	or other isomer(s)	275
		208
		171
		185
	or other isomer(s)	513
	or other isomer(s)	446

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TABLE 7.4 CONTINUED

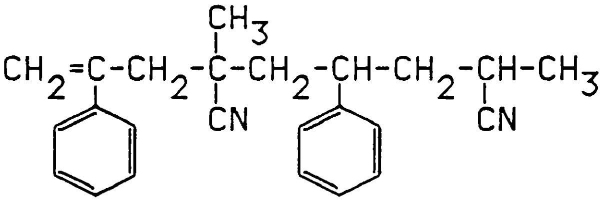
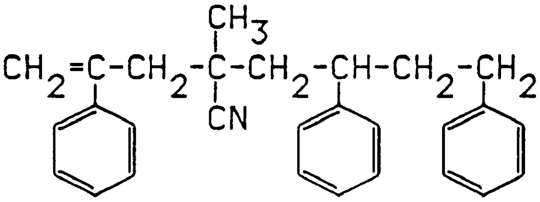
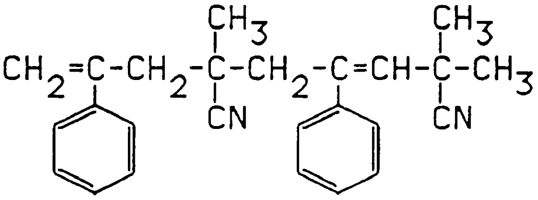
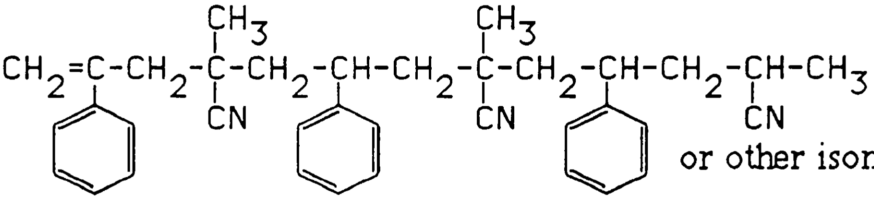
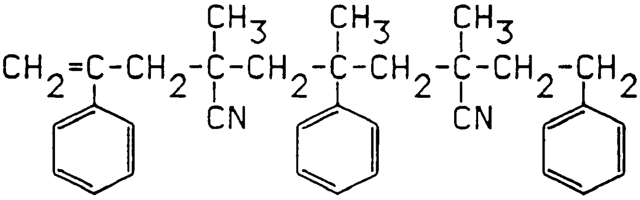
	or other isomer(s)	342
	or other isomer(s)	379
	or other isomer(s)	354
	or other isomer(s)	513
	or other isomer(s)	446

TABLE 7.5. Products Identified in the Cold Ring Fraction from Degradation of COMAN/Sty 3 Sample under normal TVA Conditions. (Products are Listed According to Relative Abundance.)

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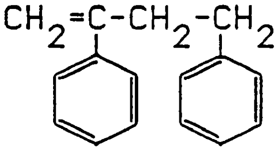
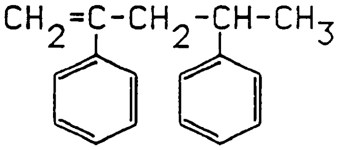
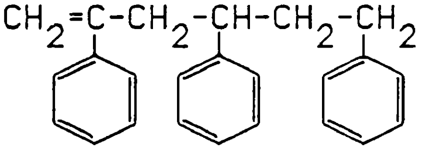
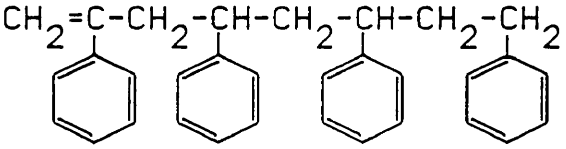
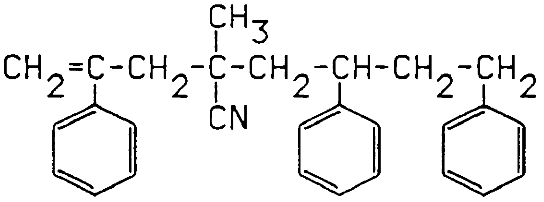
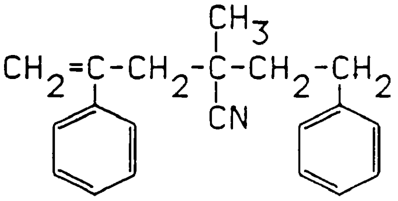
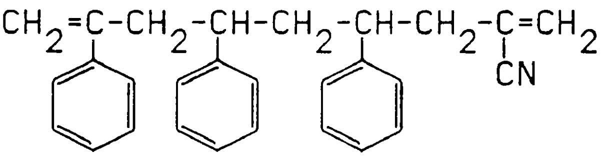
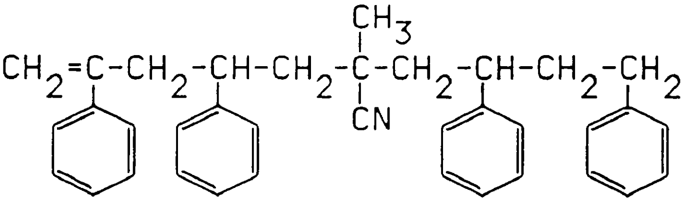
	208
	222
	312
	416
 or other isomer(s)	379
 or other isomer(s)	275
 or other isomer(s)	377
 or other isomer(s)	483

TABLE 7.6. Products Identified in the Cold Ring Fraction from Degradation of COMAN/Sty 4 Sample under normal TVA Conditions. (Products are Listed According to Relative Abundance.)

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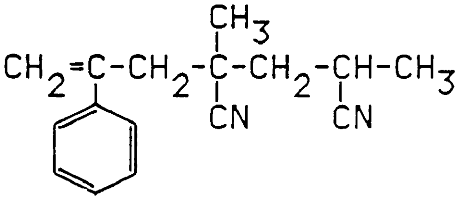
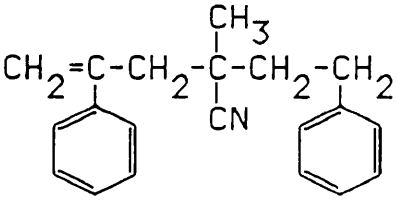
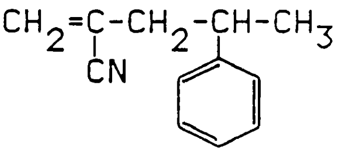
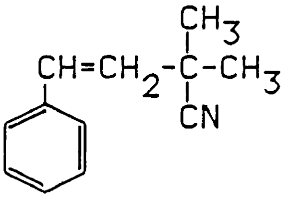
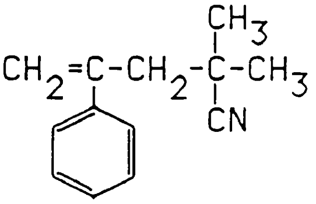
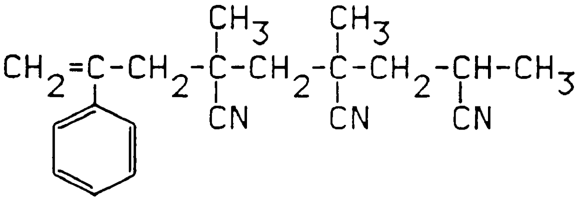
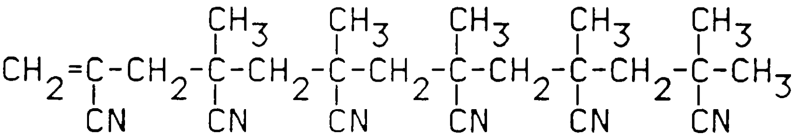
	or other isomer(s)	238
	or other isomer(s)	275
		171
		185
	or other isomer(s)	305
 $CH_2=C(CN)-CH_2-C(CH_3)(CN)-CH_2-C(CH_3)(CN)-CH_2-C(CH_3)(CN)-CH_2-C(CH_3)(CN)-CH_2-C(CH_3)(CN)-CH_3$		402

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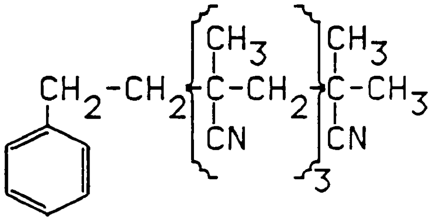
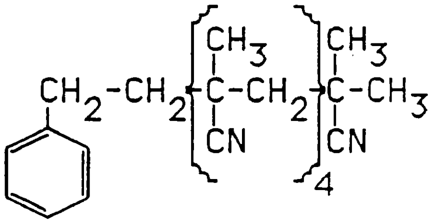
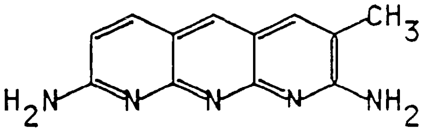
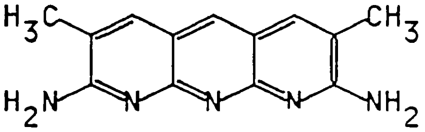
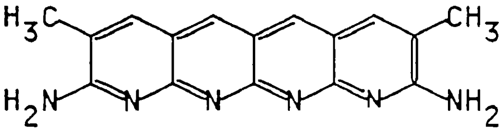
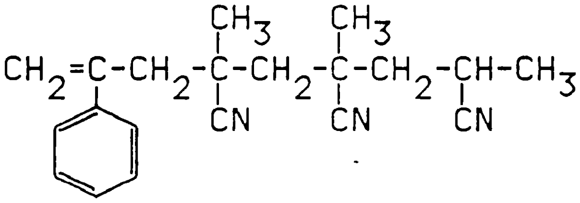
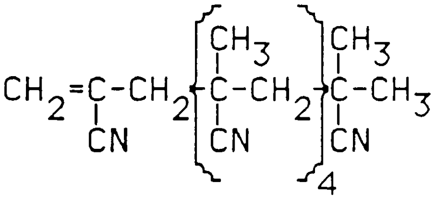
TABLE 7.6 CONTINUED

	or other isomer(s)	374
	or other isomer(s)	441
		225
		239
		290
	or other isomer(s)	305
		402

7.2.1.1.2c Condensable Products as Liquid Fraction.

The IR spectra (Fig. 7.9 a, b, c & d) for liquid fractions from degradation of various MAN/Sty copolymer samples show altering intensities of characteristic peaks for the two monomers (methacrylonitrile and styrene). There is a clear indication of carbon-carbon double bond at 1620 and 1600 cm^{-1}, mono-substituted aromatic vinyl group absorption at 736 cm^{-1} together with characteristic absorption at 2230 cm^{-1} due to the nitrile($C\equiv N$) group.

The most significant absorptions are as followes

3080—3020 cm^{-1} (s)	C-H stretching (Aryl)**
3010 cm^{-1}	C-H stretching (unsaturated)*
2990—2945 and 2885 cm^{-1}	C-H stretching (saturated)* asymmetric and symmetric
2230 cm^{-1} (s)	$C\equiv N$ stretching*
1950—1690 cm^{-1}	Substituted aromatic ring**
1630 cm^{-1}	C=C stretch.(vinyl group)
1600, 1576 &1495 cm^{-1} (s)	Aryl C=C ring stretching mode
1455 & 1380 cm^{-1} (s)	Saturated C-H deformation*
940 cm^{-1} (s)	C-H out of plane deformation of vinyl group*
990 & 910 cm^{-1} (s)	C-H out of plane deformation of vinyl group.**
700 & 777 cm^{-1} (s)	Out of plane C-H deformation (mono-substituted patterns of the benzene ring)

---

* Absorption corresponding to Methacrylonitrile

** Absorption corresponding to Styrene

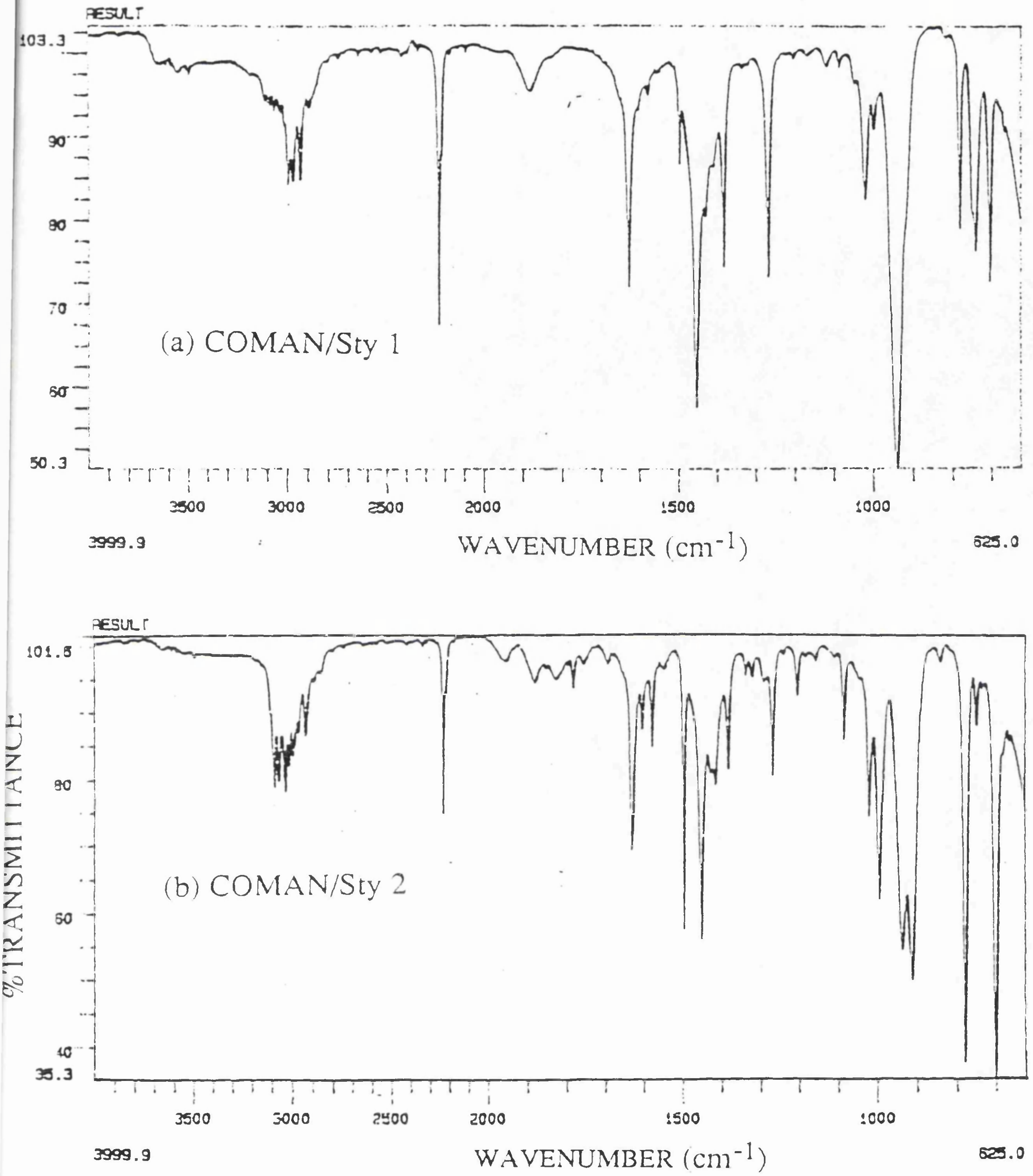
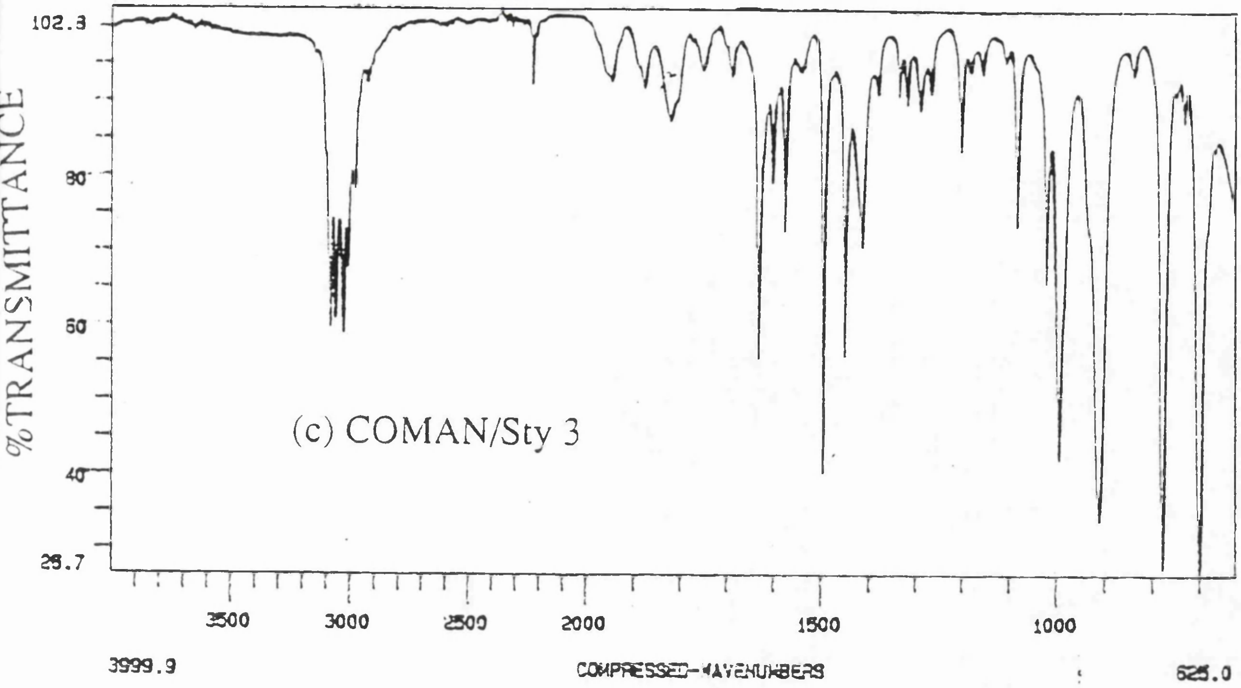


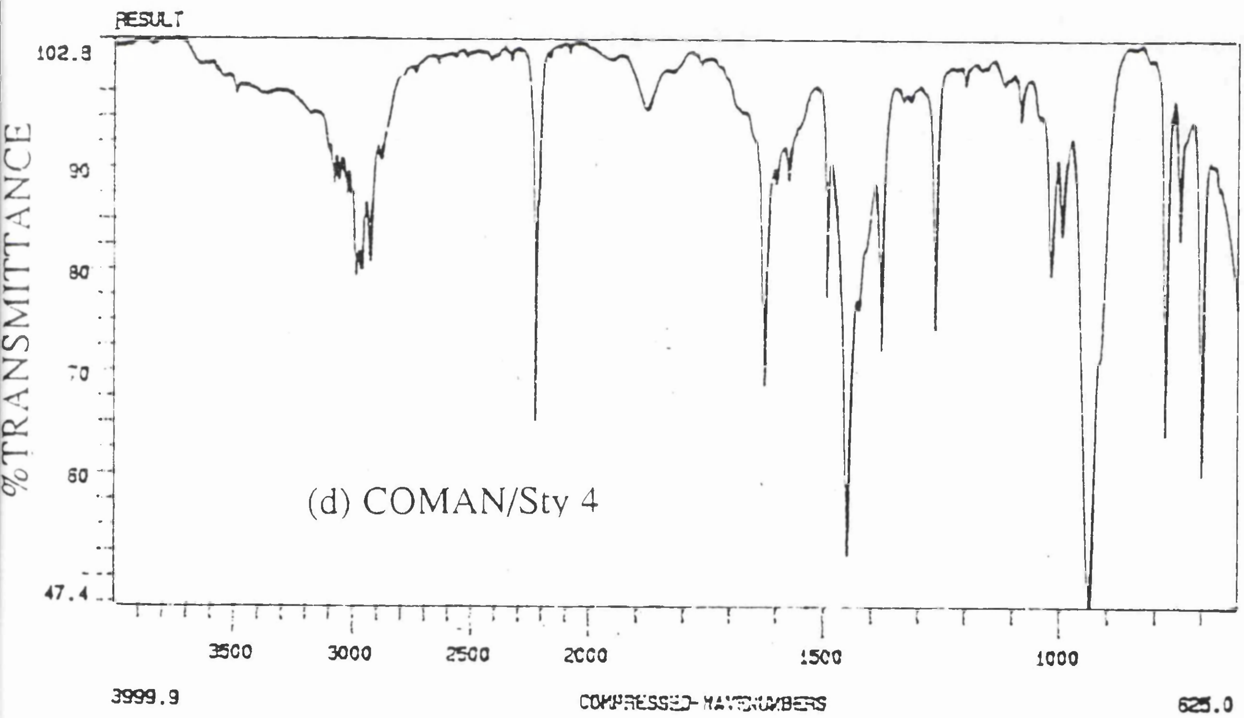
Fig. 7.9. The IR Spectra for Liquid Fractions from Degradation of Various MAN/Sty Copolymers to 500 °C under TVA Conditions.

(CONTINUED)

Fig. 7.9. Continued



(c) COMAN/Sty 3



(d) COMAN/Sty 4

The liquid fraction, the last fraction from the SATVA separation, was also in each case subjected to GC-MS investigation and the corresponding chromatograms are illustrated in Figs. 7.10-7.14. In all the methacrylonitrile/styrene copolymers, toluene, α-methylstyrene, ethyl benzene and allyl benzene are the volatile products next in importance to the two monomers, when these copolymer samples were degraded to 500 ^{o}C under normal TVA conditions. In the case of MAN/Sty copolymer 4, trace amounts of 2-cyanobutane and 1-cyano-2-propene were also identified, and these two products were also found as minor products in the case of all methacrylonitrile polymers capable of colouration (i.e. all ACVA initiated methacrylonitrile polymers and methacrylonitrile polymers containing methacrylic acid comonomer units). The degradation products from all the copolymers are listed in order of importance in Tables 7.7-7.11.

7.2.1.1.2d Condensable Products as Gases.

The condensable gaseous products were examined by IR spectroscopy and mass spectrometry. In case of COMAN/Sty 1, 2, and 3, hydrogen cyanide, isobutene and ethene were identified as condensable gases. Ammonia, propene and a trace amount of isopentene were also amongst the gaseous products identified in the case of COMAN/Sty 4. Carbon dioxide was identified as the major component in the condensable gases from degradation of methacrylonitrile/maleic anhydride copolymer. Isobutene, hydrogen cyanide, isopentene, ammonia and a trace amount of isoprene were also amongst the condensable gases from COMAN/MalAn. The infrared spectra of condensable gaseous products for COMAN/MalMn are shown in Fig. 7.15.

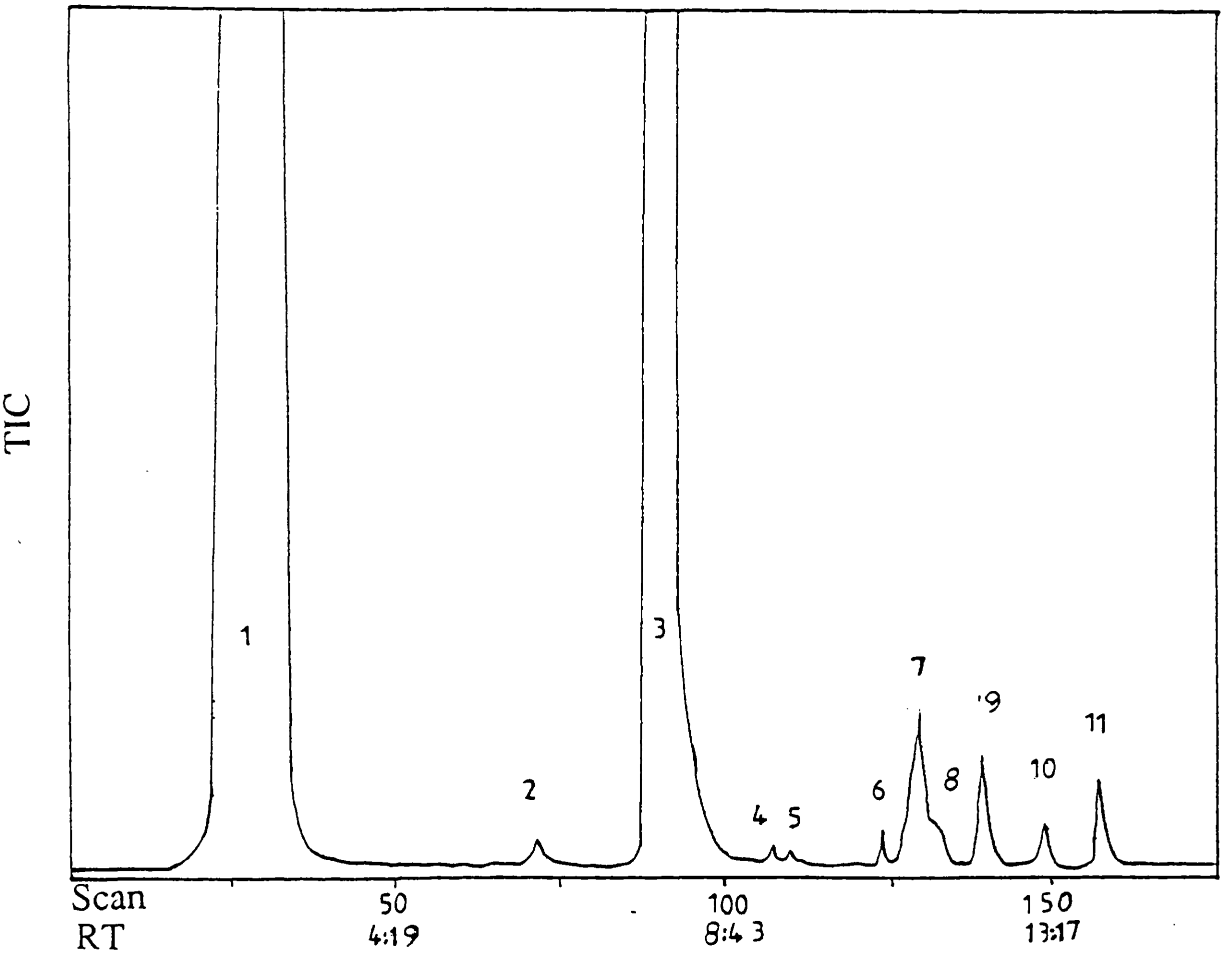


Fig. 7.10. GC-MS Chromatogram of Liquid Fraction from Degradation of COMAN/Sty 1 to 500 ^{o}C under normal TVA Conditions.

ASSIGNMENTS

1. Methacrylonitrile, **2.** Toluene, **3.** Styrene, **4.** α-Methylstyrene,
5. β-Methylstyrene, **6.** 2-Phenyl-1-butene, **7.** Unknown,
8. 4-Cyano-2,4-dimethyl-1-pent~~y~~ene, **9.** Unknown
10. 4-Phenyl-2-methylbutene, **11.** 3-Phenyl-2-propanenitrile,

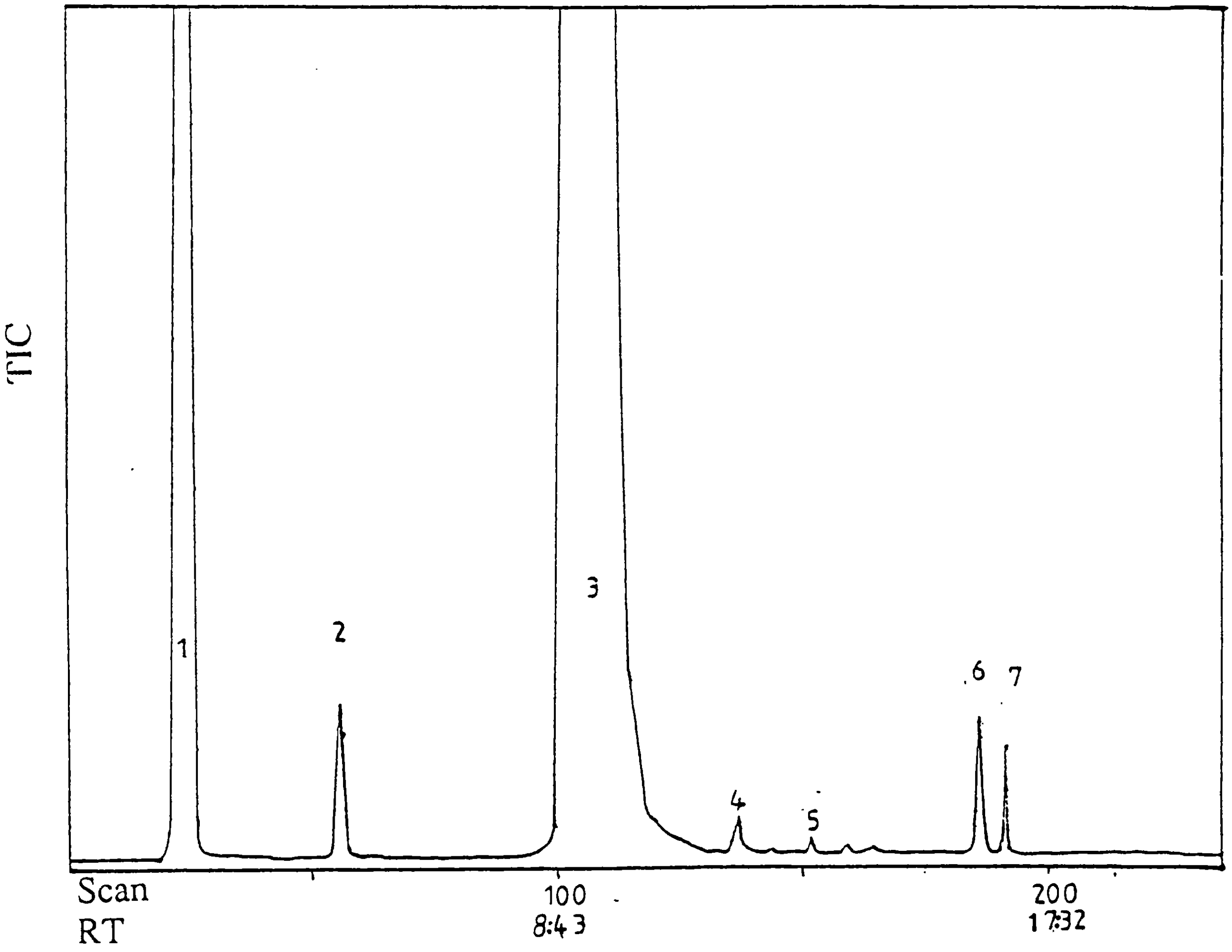


Fig. 7.11. GC-MS Chromatogram of Liquid Fraction from Degradation of COMAN/Sty 2 to 500 °C under normal TVA Conditions.

ASSIGNMENTS

1. Methacrylonitrile, **2.** Toluene, **3.** Styrene, **4.** α-Methylstyrene,
5. 4-Phenyl-1-butene, **6.** 4-Phenyl-2-methylbutene, ,
7. 3-Phenyl-2-propanenitrile

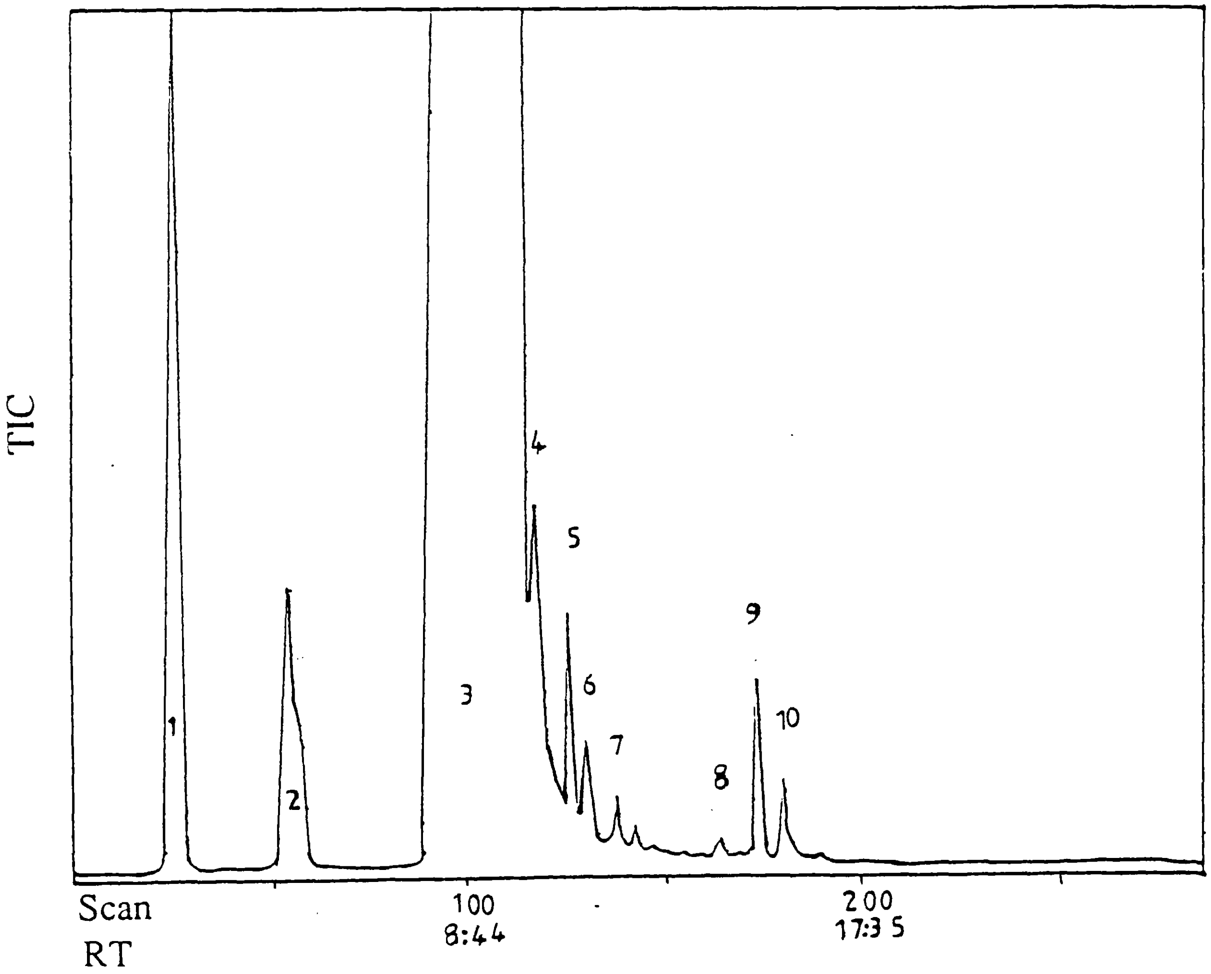


Fig. 7.12. GC-MS Chromatogram of Liquid Fraction from Degradation of COMAN/Sty 3 to 500 °C under normal TVA Conditions.

ASSIGNMENTS

1. Methacrylonitrile, **2.** Toluene, **3.** Styrene, **4.** Allylbenzene,
5. α-Methylstyrene, **6.** Unknown, **7.** β-Methylstyrene,
8. 4-Phenyl-1-butene, **9.** 4-Phenyl-2-methylbutene,
10. 3-Phenyl-2-propanenitrile,

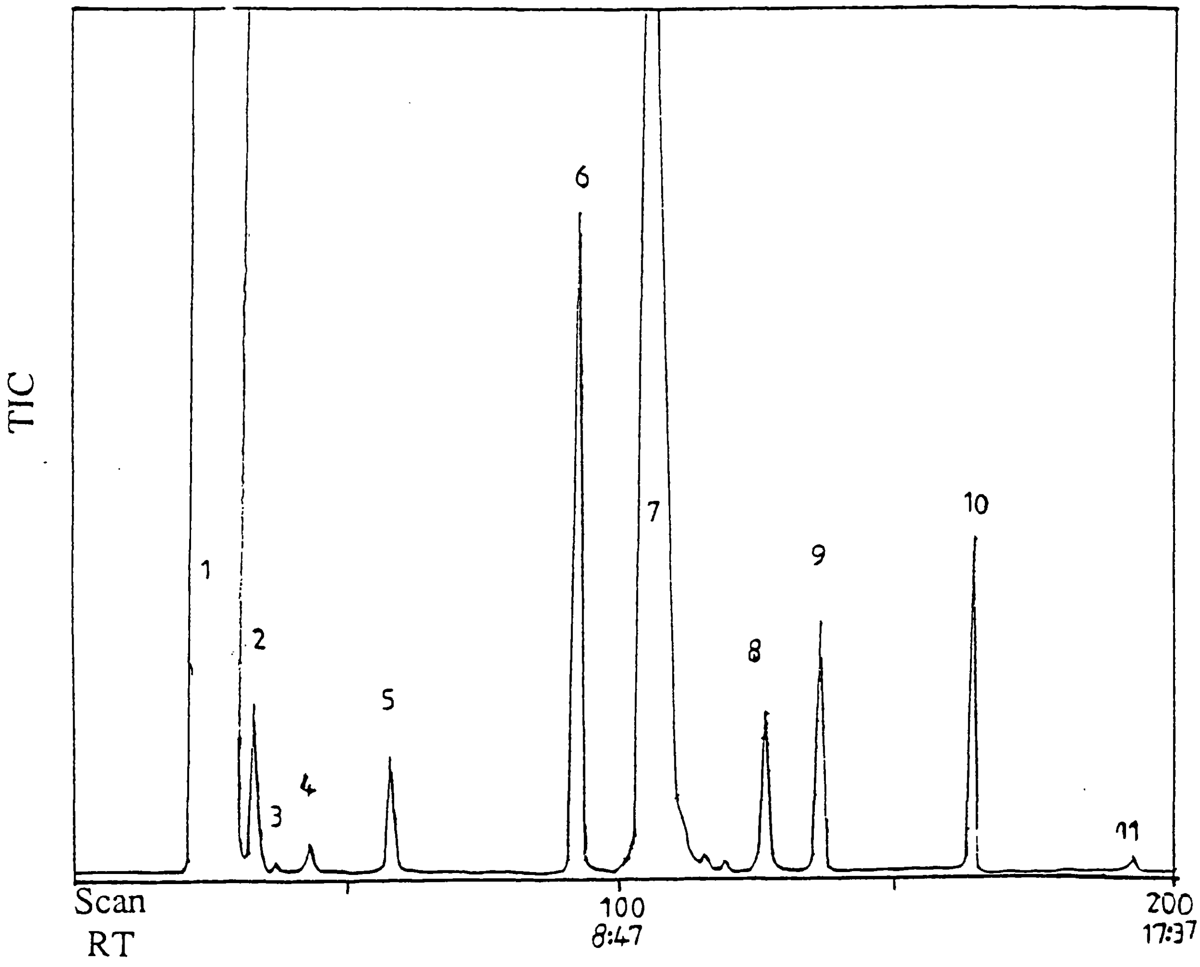


Fig. 7.13. GC-MS Chromatogram of Liquid Fraction from Degradation of COMAN/Sty 4 to 500 ^{o}C under normal TVA Conditions.

ASSIGNMENTS

1. Methacrylonitrile, **2.** 1-Cyano-2-propene, **3.** 2-Cyano-1-butene, **4.** 2-Cyanobutane, **5.** Toluene, **6.** Ethylbenzene, **7.** Styrene, **8.** Propylbenzene, **9.** α-Methylstyrene,**10.** 4-Phenyl-2-butene **11.** 4-Phenyl-2-methylbutene.

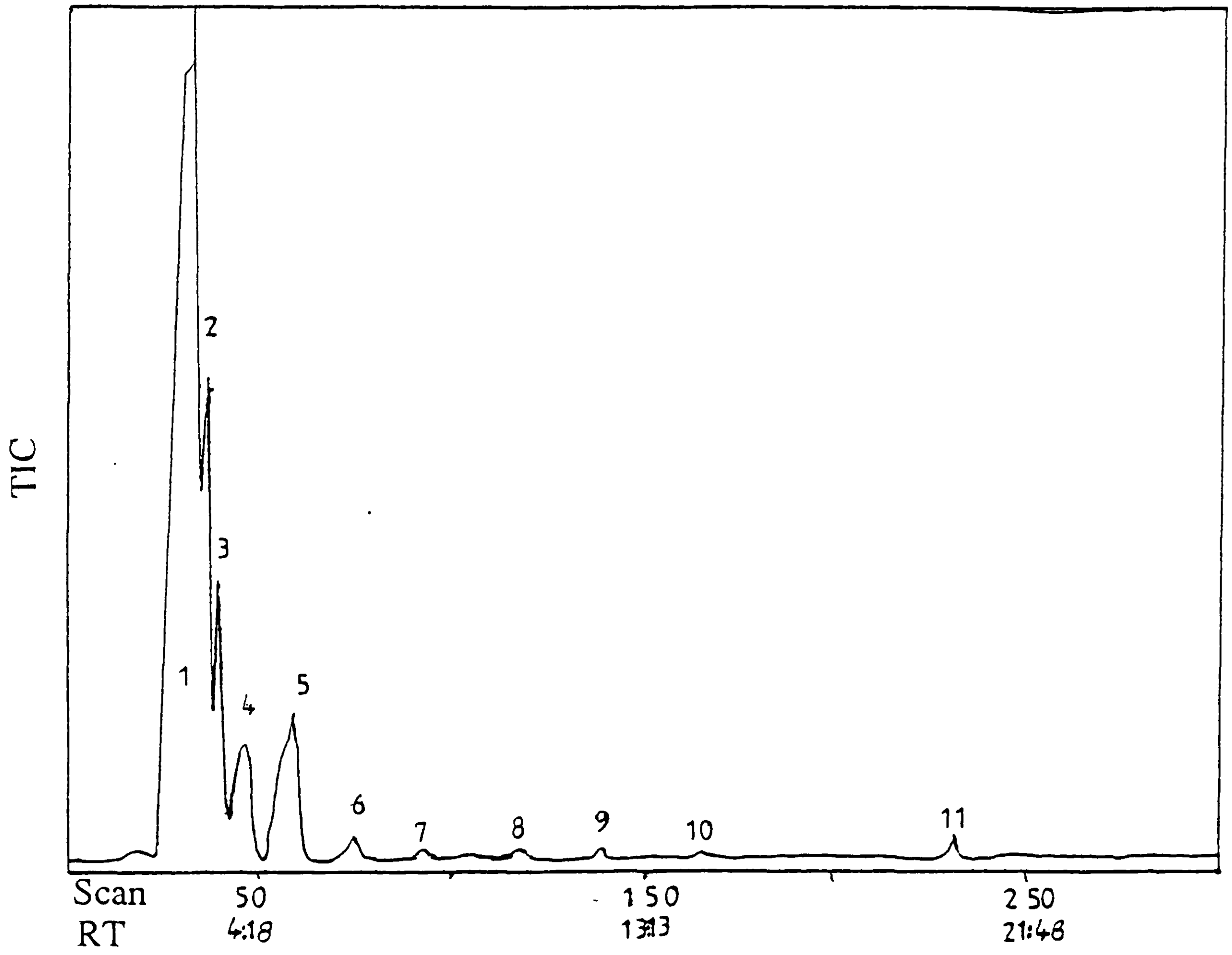


Fig. 7.14. GC-MS Chromatogram of Liquid Fraction from Degradation of COMAN/MalAn to 500 ^{o}C under normal TVA Conditions.

ASSIGNMENTS

1. Methacrylonitrile, **2.** 2-Cyanopropane, **3.** 1-Cyano-2-propene, **4.** 1-Cyano-1-propene, **5.** 2-Cyano-1-but~~y~~ene, **6.** 2-Cyanobutane, **7.** 2-Cyano-2-butene, **8.** 2-Cyano-4-methyl-1-pent~~y~~ene, **9.** Unknown **10.** Unknown, **11.** Maleic anhydride

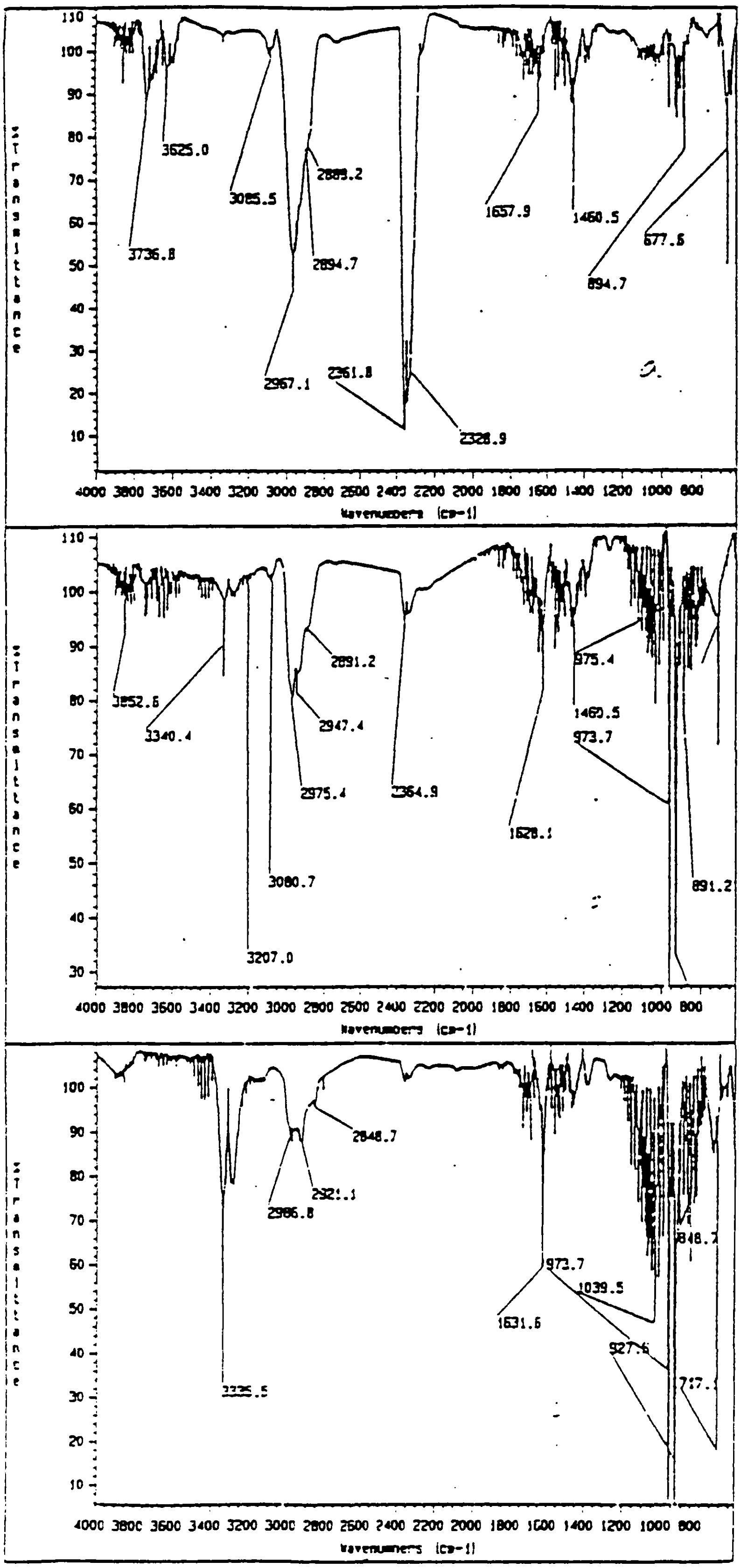


Fig. 7.15. The Infrared Spectra of Condensable Gaseous Products from Degradation of COMAN/MalAn to 500 °C under normal TVA Conditions.

Condensable gases from all copolymers investigated, identified by IR spectroscopy and on-line mass spectrometry are listed in Tables 7.7–7.11.

7,2.1.1.2e Non-condensable Gases.

In all methacrylonitrile/styrene copolymers, methane was the only non-condensable gas identified. In case of COMAN/MalAn, carbon monoxide was also identified as a non-condensable product by on-line mass spectrometry.

7.2.1.2 THERMOGRAVIMETRY

The TG and DTG curves for the copolymers were obtained under dynamic nitrogen at a heating rate of 10 ^{o}C/min and are reproduced in Figs. 7.16–7.20.

These curves show that copolymer MAN/Sty 1 decomposes in a two step degradation, whereas copolymers MAN/Sty 2 & 3 degrade in a single stage. In the case of copolymer MAN/Sty 1 (which is a low molecular weight polymer with 90% of methacrylonitrile units in the polymer chain), the decomposition starts around 265 ^{o}C and and there are two rate maxima at 337 and 420 ^{o}C, respectively. The copolymers MAN/Sty 2 & 3 (with around 50 and 90% styrene monomer units in the copolymer chain respectively) exhibit weight loss at relatively higher temperatures (starting at 313 and 320 ^{o}C respectively), and show T_{max} around 427 and 440 ^{o}C.

The copolymer MAN/Sty 4 (made using ACVA initiator, with about 90

TABLE 7.7. Products of Degradation of COMAN/Sty 1 Heated 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
	Gases	Liquid Fraction	
MS	IR , MS	IR , MS , GC-MS	IR , MS
Methane	Ethene Isobutene Hydrogen cyanide	Methacrylonitrile** Toluene, Styrene* α–Methylstyrene β–Methylstyrene 2-Phenyl-1-butene 4-Cyano-2,4- dimethyl-1-pentene 4-Phenyl-2-methyl-1-butene 3-Phenyl-2-propenenitrile	Mainly short chain fragments of MAN, but few chain fragments containing styrene monomer units

** Product found in most abundance

* Product found second in importance

TABLE 7.8. Products of Degradation of COMAN/Sty 2 Heated 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
	Gases	Liquid Fraction	
MS	IR , MS	IR , MS , GC-MS	IR , MS
Methane	Ethene Isobutene Hydrogen cyanide	Methacrylonitrile* Toluene, Styrene* α–Methylstyrene 4-Phenyl-1-butene 4-Phenyl-2-methylbutene 3-Phenyl-2-propenenitrile	Short chain fragments containing styrene & MAN monomer units

* Product found in most abundance

TABLE 7.9 Products of Degradation of COMAN/Sty 3 Heated 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
	Gases	Liquid Fraction	
MS	IR , MS	IR , MS , GC-MS	IR , MS
Methane	Isobutene Hydrogen cyanide	Methacrylonitrile* Toluene, Styrene** Allyle benzene α–Methylstyrene β–Methylstyrene 4-Phenyl-1-butene 4-Phenyl-2-methylbutene 3-Phenyl-2-propenenitrile	Mainly short chain fragments of styrene, but few chain fragments containing MAN monomer units

** Product found in most abundance

* Product found second in importance

TABLE 7.10. Products of Degradation of COMAN/Sty 4 Heated to 500 °Cat 10 °C/min Under TVA Conditions.

Non-condensable products - at -196 °C	Condensable Volatile products at -196 °C		CRF
	Gases	Liquid Fraction	
MS	IR , MS	IR , MS , GC-MS	IR , MS
Methane	Ethane Propene Isobutene Isopentene⋆ Hydrogen cyanide Ammonia	Methacrylonitrile** 1-Cyano-1-propene 2-Cyano-1-butene 2-Cyanobutane Toluene, Ethylbenzene Styrene* 1-Phenylpropane α–Methylstyrene 2-Phenyl-1-butene 4-Phenyl-2-methylbutene	Mainly short chain fragments of MAN, but few chain fragments containing styrene monomer units

** Product found in most abundunce

* Product found second in importance

⋆ Product found second in trace amount

TABLE 7.11 Products of Degradation of COMAN/MalAn Heated to 500 °C at 10 °C/min under TVA Conditions.

Non-condensable Products - at -196 °C	Condensable Volatile Products at -196 °C		CRF
	Gases	Liquid Fraction	
MS	IR , MS	IR , MS , GC-MS	IR , MS
Methane Carbon monoxide	Ethene Carbon dioxide* Propene Isobutene Isopentene Hydrogen cyanide Ammonia	Methacrylonitrile* 2-Cyanopropane 1-Cyano-2-propene 1-Cyano-1-propene 2-Cyano-1-butene 1-Cyanobutane 2-Cyano-2-butene 1-Cyano-2-propene 2-Cyano-4-methyl-1-pentene Maleic anhydride	Mixture of short chain fragments of MAN, some fragments containing C=O group & methyl & amino substituted heterocyclic structures.

* Product found in most abundance

% of methacrylonitrile monomer units in the copolymer chain) shows weight loss from near 275 °C and decomposes in a single stage with a shoulder around 345–360 °C and maximum rate of volatilisation at 385 °C.

TG and DTG curves for MAN/MalAn show three stage decomposition and weight loss begins above 200 °C. There is a small peak in the temperature range 220–270 °C (with T_{max} at 262 °C), which proceeds the main decomposition stage having T_{max} at 385 °C. The main decomposition stage is followed by gradual decomposition with a further small peak at 430 °C.

The main features of thermal behaviour, established by TG and DTG, are summarised in Table 7.13.

7.2.1.3 DIFFERENTIAL THERMAL ANALYSIS.

DTA curves for the five copolymer samples used in this investigation were obtained under dynamic nitrogen at a heating rate of 10 °C/min.. These curves are reproduced in Fig. 7.21.

None of the DTA curves of the copolymer samples show any exothermic effect. Generally all curves only show an endotherm in the temperature range 400–460 °C corresponding to the main step of decomposition. In the case of COMAN/MalAn, a slight endothermic effect prior to the main decomposition may possibly be due to decarboxylation of anhydride units. The DTA data are consistent with TG and TVA. The corresponding data are included in Table 7.12.

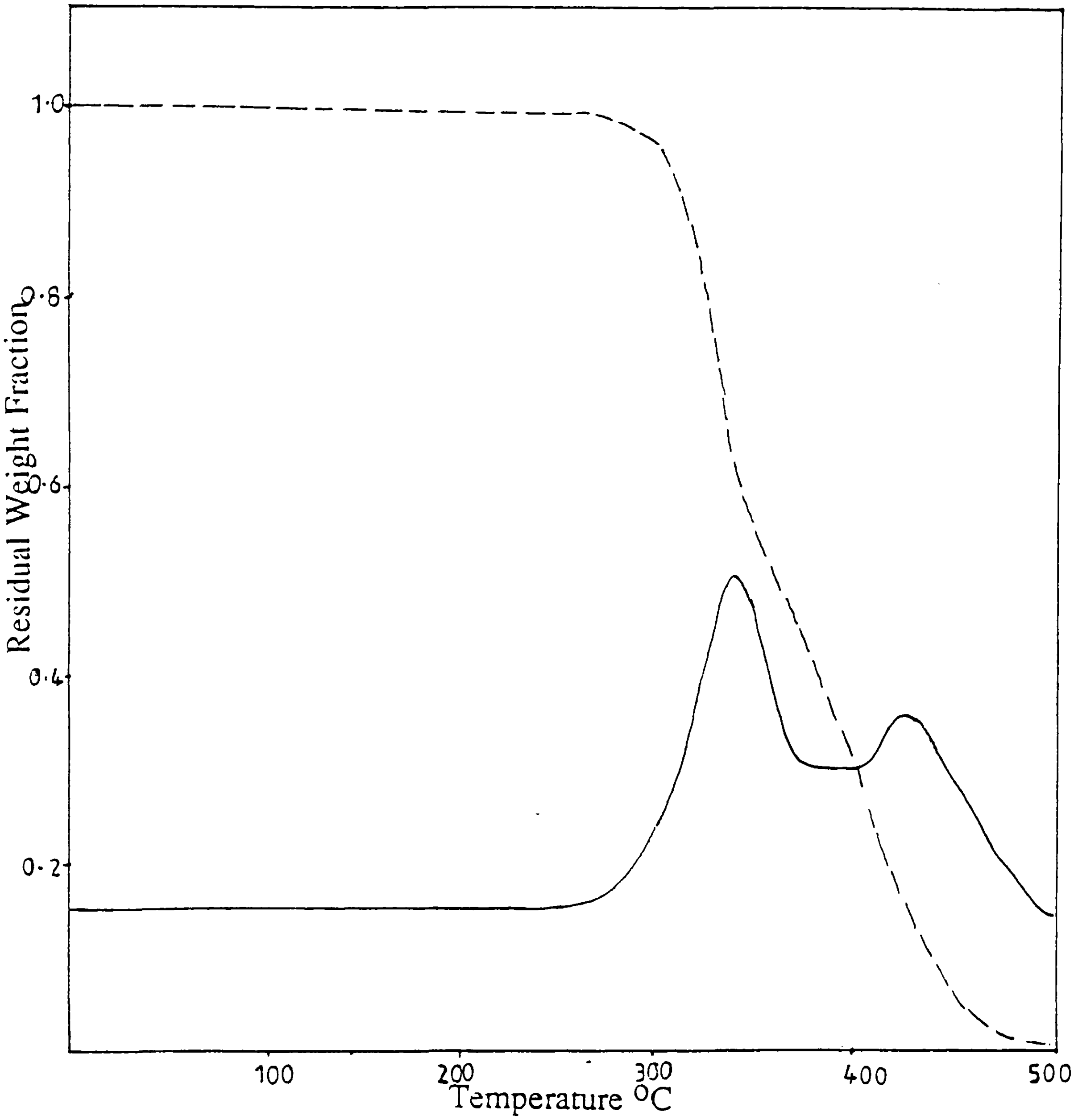


Fig. 7.16. TG and DTG Curves (Dynamic Nitrogen Atmosphere, Heating Rate 10 °C/min.) for COMAN/Sty 1.

Keys: TG — — — DTG ————

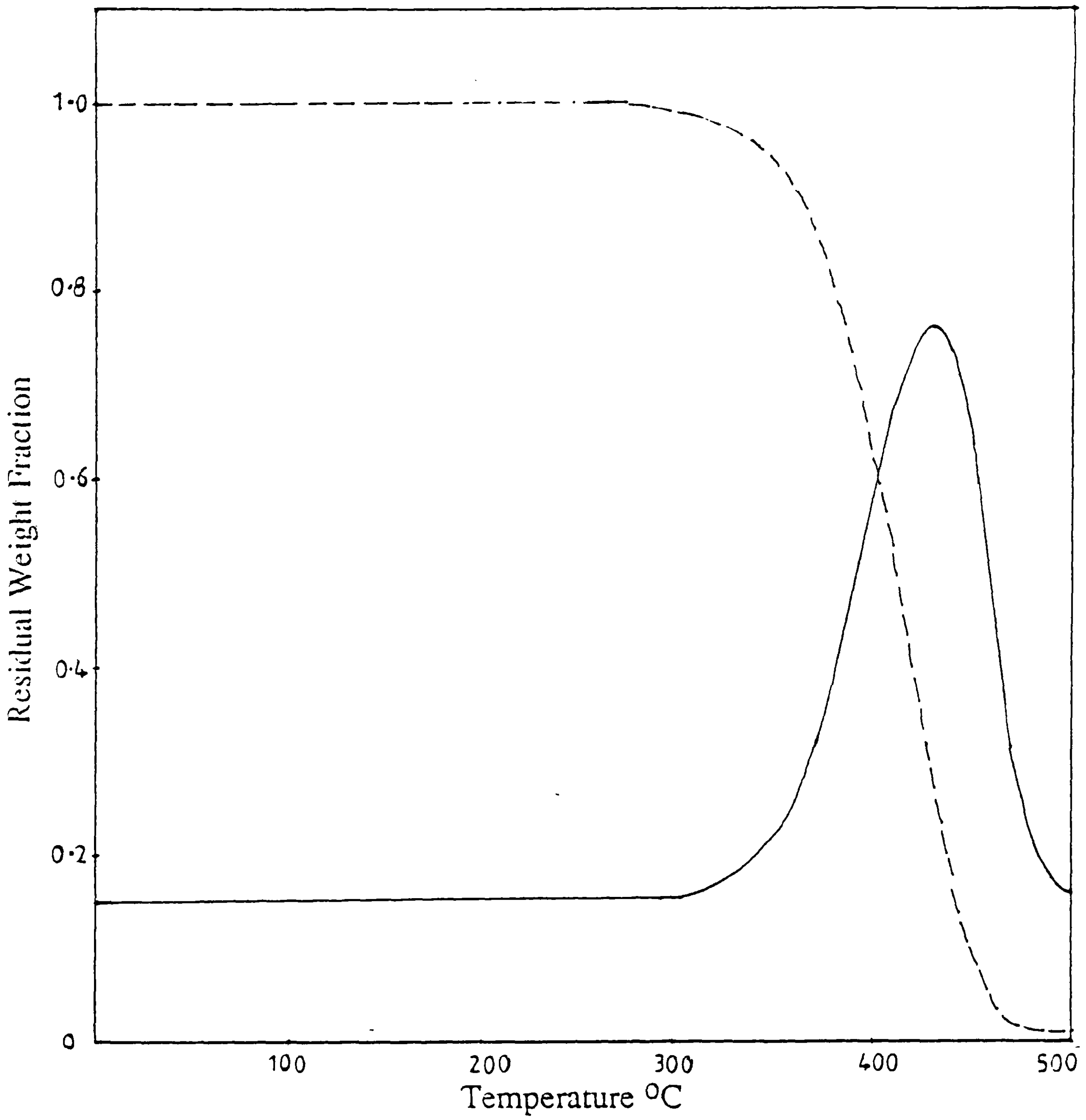


Fig. 7.17. TG and DTG Curves (Dynamic Nitrogen Atmosphere, Heating Rate 10 °C/min.) for COMAN/Sty 2.
Keys: TG — — — DTG ————

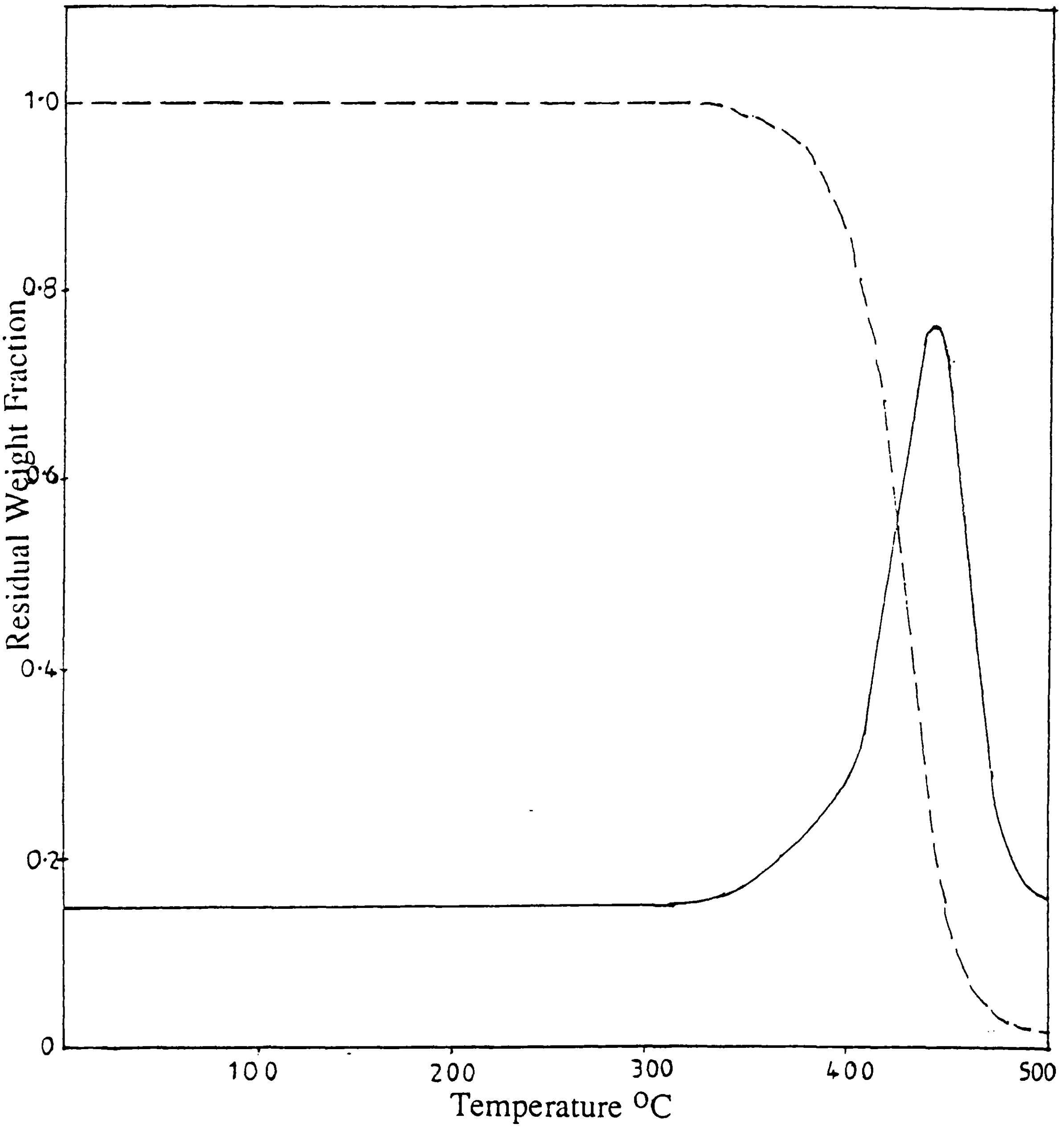


Fig. 7.18. TG and DTG Curves (Dynamic Nitrogen Atmosphere, Heating Rate 10 °C/min.) for COMAN/Sty 3.

Keys: TG — — — DTG ————

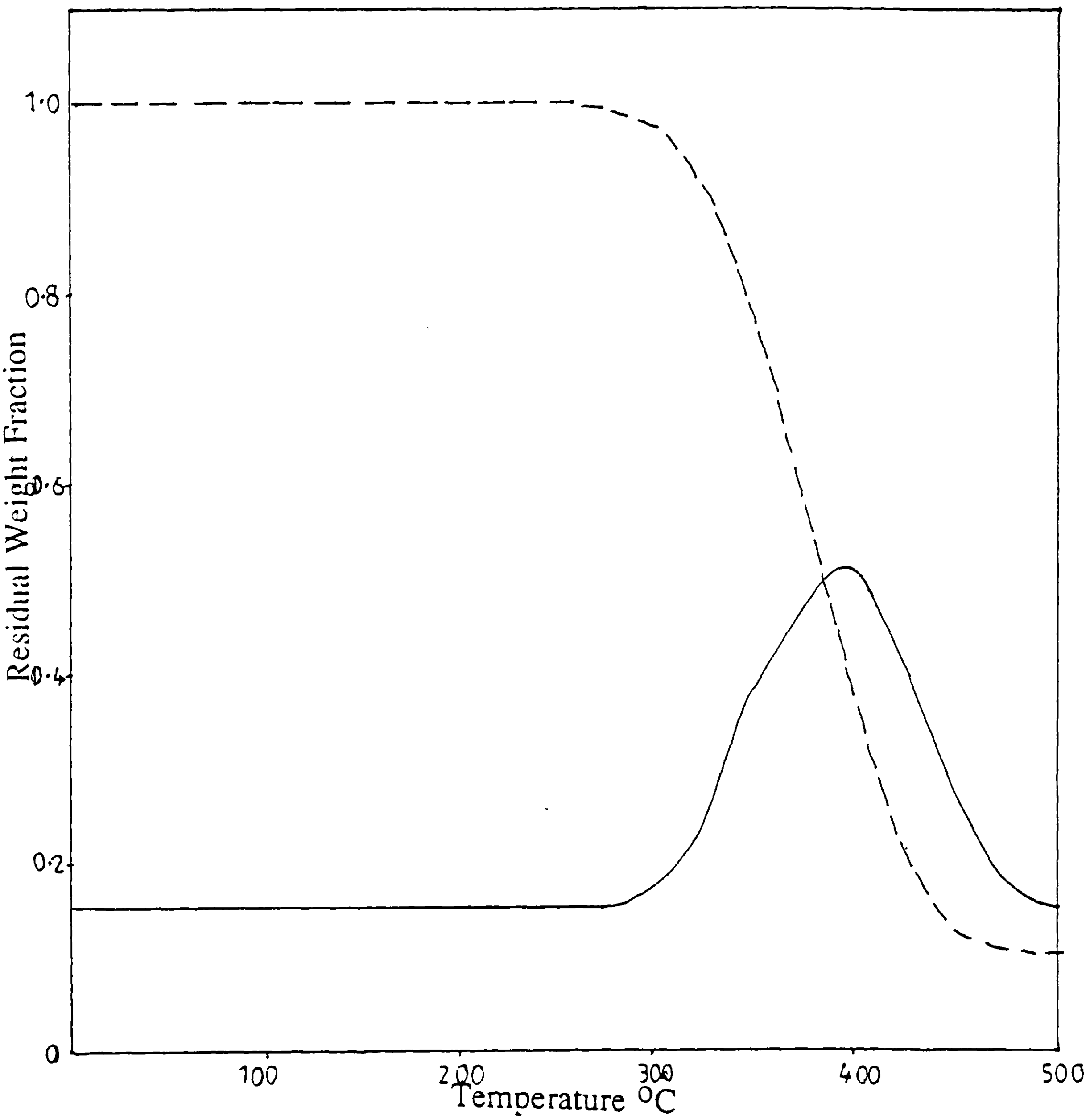


Fig. 7.19. TG and DTG Curves (Dynamic Nitrogen Atmosphere, Heating Rate 10 °C/min.) for COMAN/Sty 4.

Keys: TG — — — DTG ————

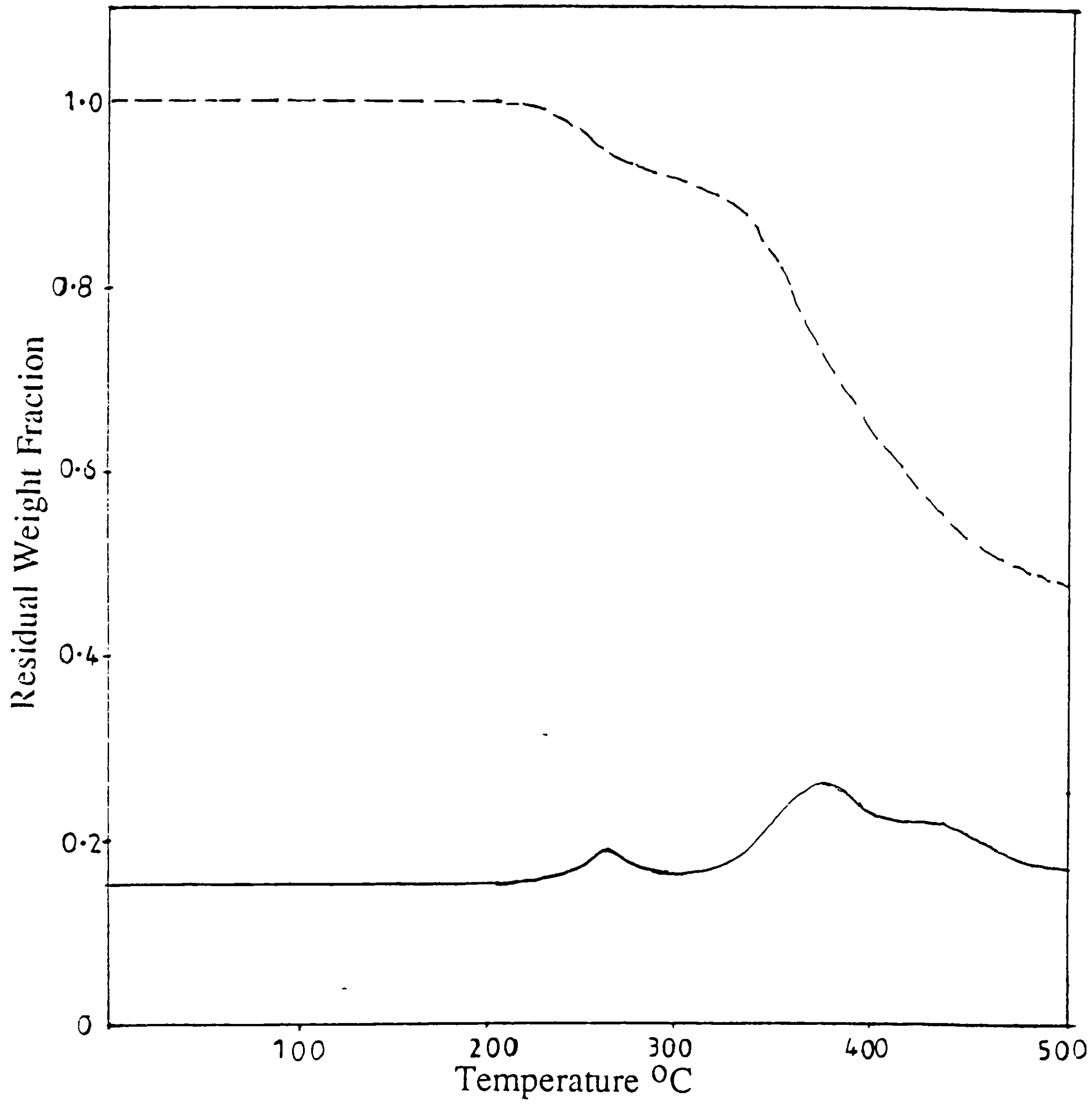


Fig. 7.20. TG and DTG Curves (Dynamic Nitrogen Atmosphere, Heating Rate 10 °C/min.) for COMAN/MalAn.

Keys: TG — — — DTG ————

TABLE 7.12. DTG, TG and DTA Data for Methacrylonitrile Copolymer Samples used in this Investigation.

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
COMAN/Sty 1	337	265-373	56		347	268-380	Endotherm
	420	375-500	42	98	421	382-472	Endotherm
COMAN/Sty 2	427	313-500	99	99	434	318-478	Endotherm
COMAN/Sty 3	440	320-500	96	96	444	335-488	Endotherm
COMAN/Sty 4	393	275-500	80	80	402	395-500	Endotherm
	262	213-281	15				
COMAN/MIAn	385	295-500	37	55	393	260-432	Endotherm

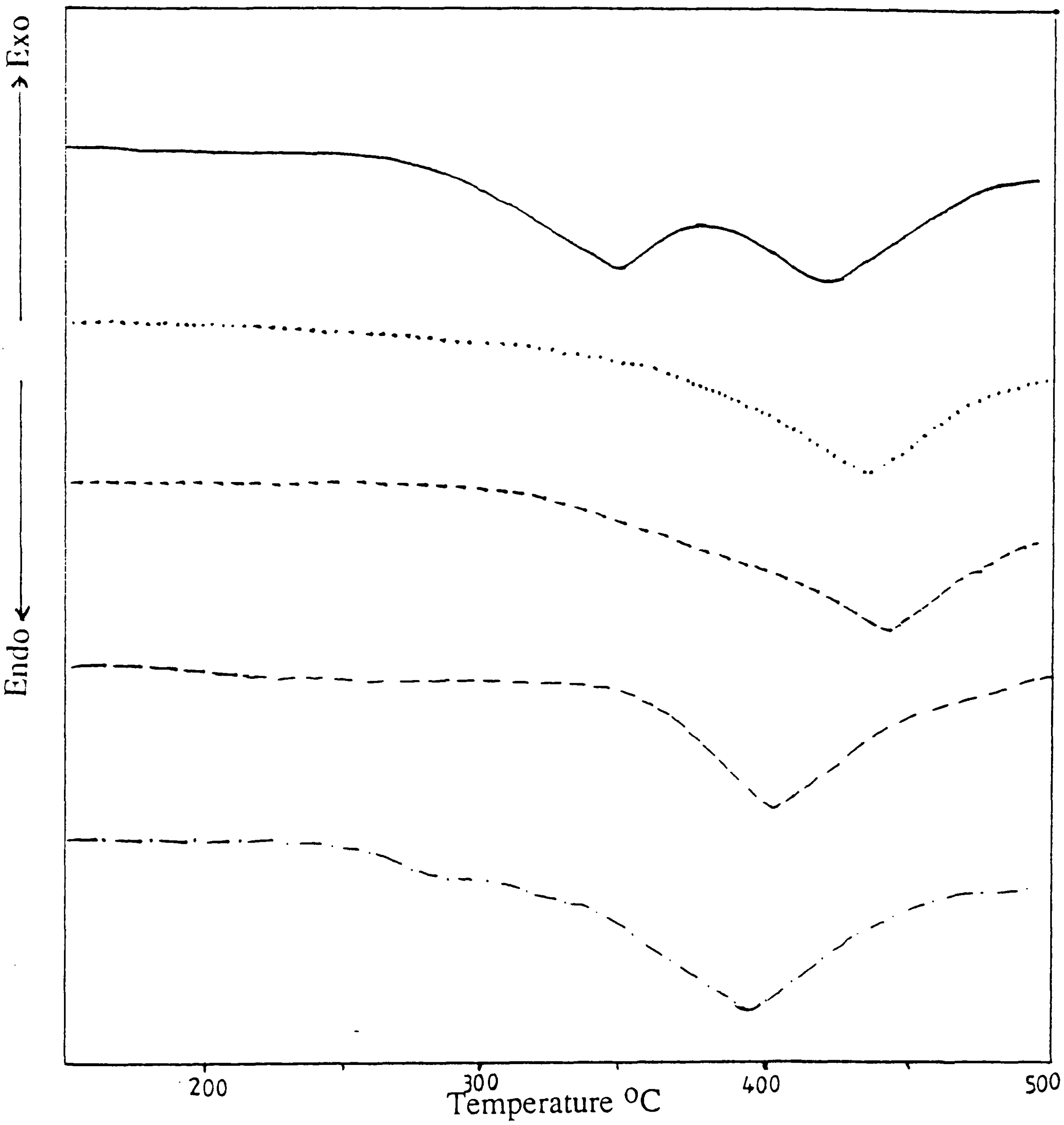


Fig. 7.21. DTA Curves (Dynamic Nitrogen Atmosphere, Heating Rate 10 oC/min to 500 °C) for Various MAN/Sty Copolymers and MAN/MalAn copolymer.

Keys: COMAN/Sty 1 ———— COMAN/Sty 2 ··················

COMAN/Sty 3 -------- COMAN/Sty 4 — — — — —

COMAN/MalAn —·—·—·—

7.4 DEGRADATION MECHANISM

The main features of degradation of polystyrene, established by various workers over many years, have been considered already in this chapter section (7.1.2).It is established[13] that the observed molecular weight decrease below 300 ^{o}C may be due to formation of macro species (C) and (D) from random chain scission (reaction 1) followed by disproportionation (reaction 2 of Scheme 7.1). The chain ends (C) and (D) must be stable at temperatures below 300 ^{o}C since there has not been significant volatilisation observed below this temperature region in polystyrene degradation.

Above 300 ^{o}C, initiation of production of volatile products from polystyrene degradation results from homolysis at random (reaction 1 Scheme 7.1) or near (C) and (D) type ends.The latter possibility results in the formation of toluene and α-methylstyrene as shown in reaction 3 &4 of Scheme 7.1.

It is believed[5,14] that only macroradical A is involved in depropagation, and the same radical is also involved in a competing backbiting intramolecular transfer reaction,which leads to oligomers (dimer, trimer,etc) as shown in Scheme 7.1 and 7.5.

The mechanistic route for the formation of other minor products such as allylbenzene and β–methylstyrene (1-Phenylpropene) etc has already proposed[13] to derive only from head to head linkages as shown in Scheme 7.2a. The results of the present investigations working with styrene and methacrylonitrile copolymers have suggested that simultaneous transfer of methyl group (CH_3) to a B type macroradical during random homolysis could also be a probable route for the formation of these materials like allylbenzene, β–methylstyrene and 2-phenylbutene as shown in Scheme 7.2b.

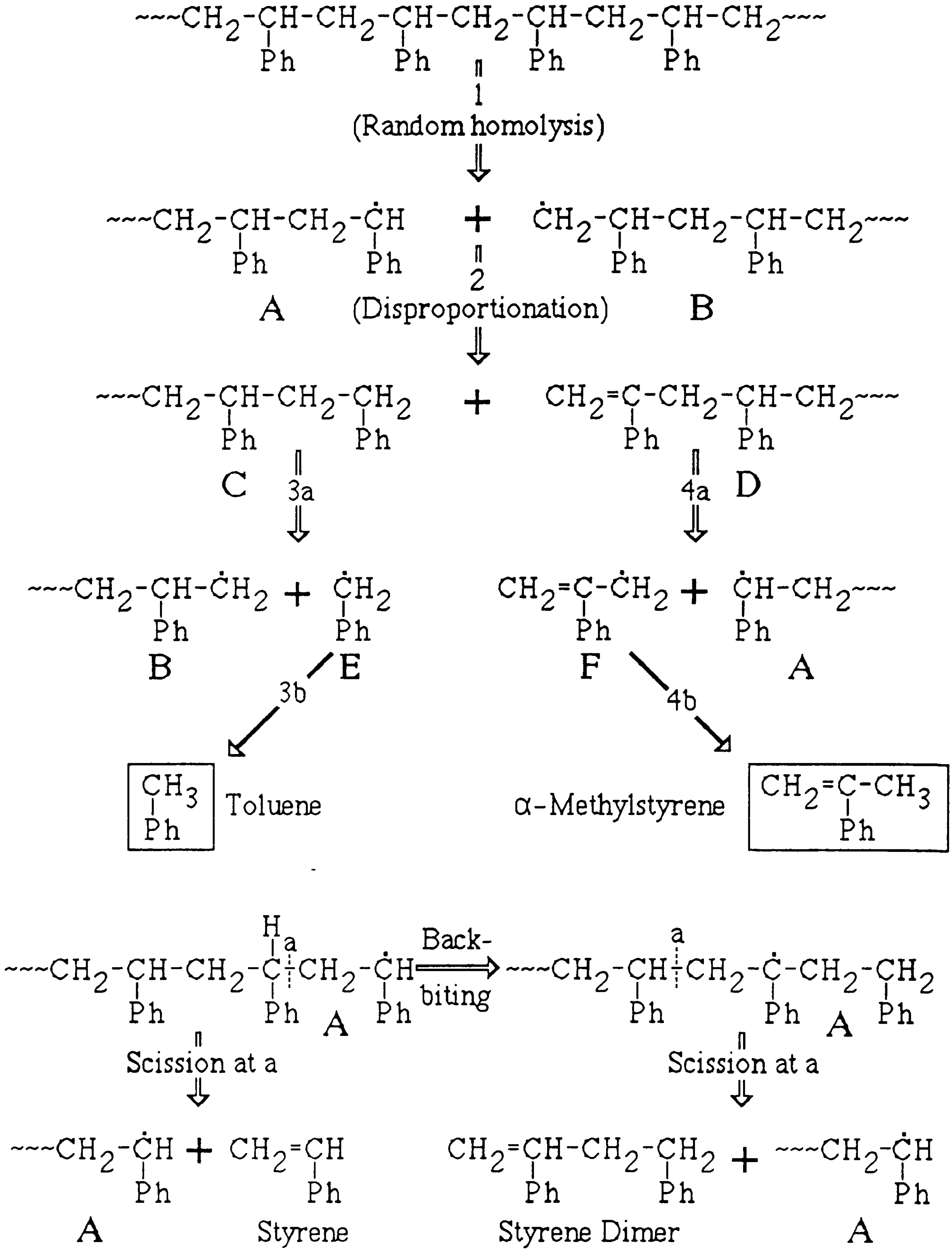
Scheme 7.3 and 7.4 illustrate the possible route of the formation of two other minor products (4-phenyl-2-methylbutene and 1-phenyl-2-propenenitrile) respectively, which are found in liquid fractions from most of the methacrylonitrile/styrene copolymers studied.

Elimination of nitrile (CN) radical (which eventually forms hydrogen cyanide by hydrogen abstraction) from macroradicals K, results into an intermediate macrospecies L (Scheme 7.3) which produces isobutene and 4-phenyl-2-methylbutene by scission at points a and b, respectively. In Scheme 7.4, simultaneous nitrile group (CN) transfer from macroradical A to the macroradical B during random homolysis of a MAN/STY copolymer chain is suggested to be the most likely route for the production of 3-phenyl-2-propenenitrile (cinnamonitrile).

The possible formation route for the various types of oligomers found in cold ring fractions from these MAN/Sty copolymers is shown Schemes 7.5 and 7.6. Scheme 7.5 corresponds for the styrene oligomers (trimers tetramers etc) formation, whereas Scheme 7.6 explains the mechanistic route of formation for the oligomer containing both monomer (methacrylonitrile & styrene)units.

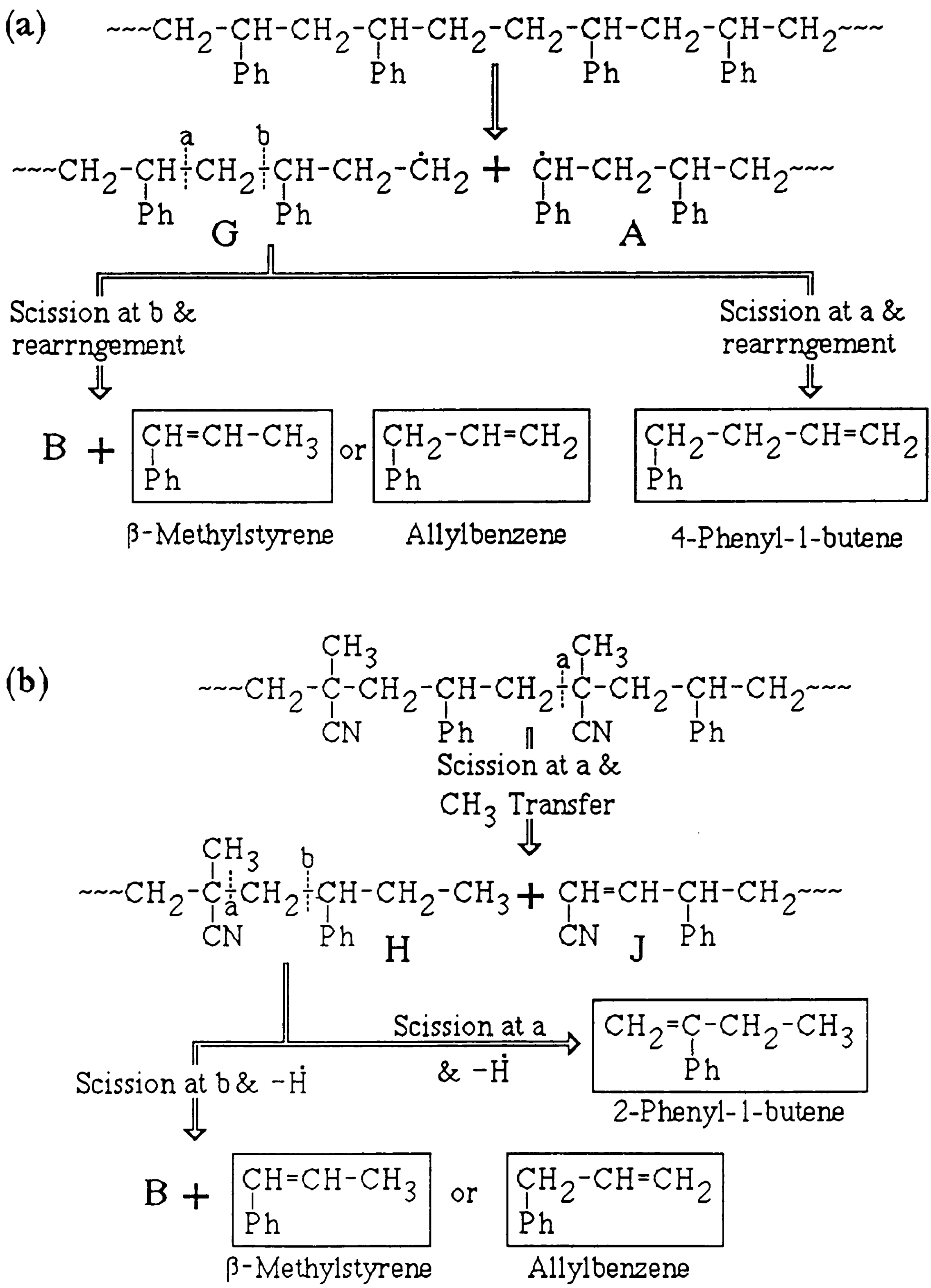
Scheme 7.7 explains the possible formation route for the various degradation products from methacrylonitrile/maleic anhydride.

SCHEME 7.1

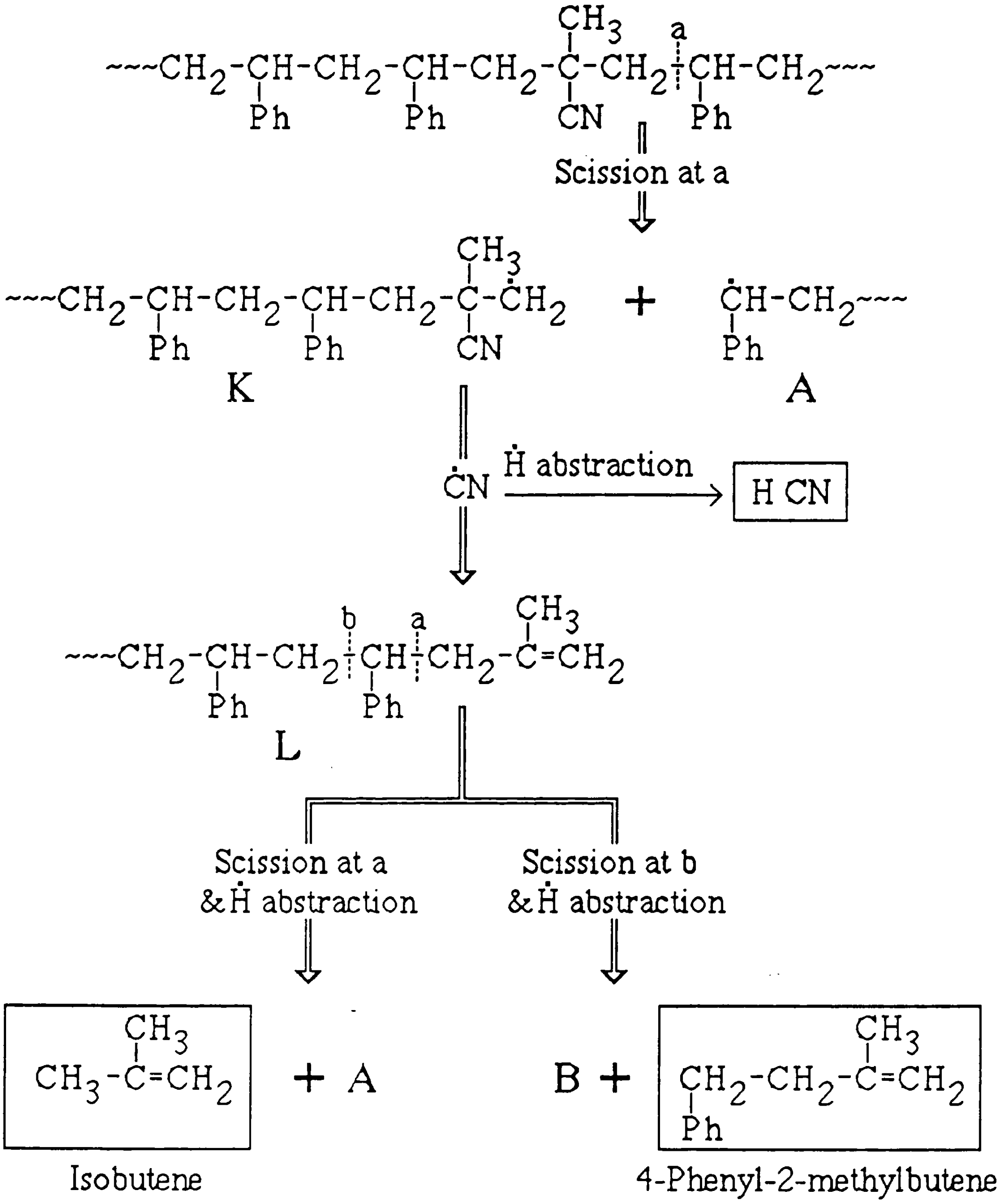


1
(Random homolysis)
A
2
(Disproportionation)
B
C
3a
D
4a
B
E
3b
F
A
4b
Toluene
α-Methylstyrene
Back-biting
Scission at a
A
Styrene
Styrene Dimer

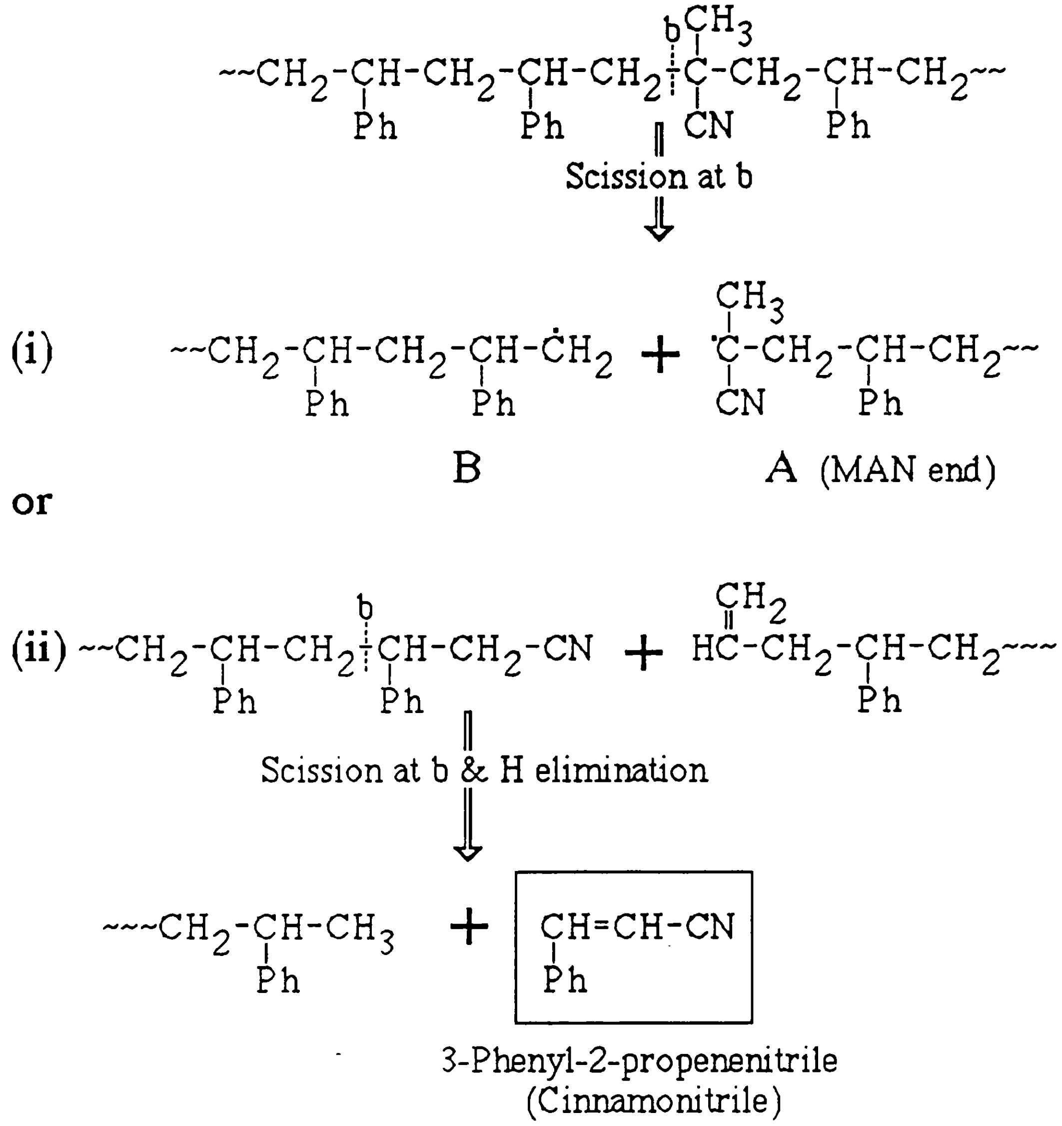
SCHEME 7.2.


(a)
a
b
G
A
Scission at b & rearrngement
Scission at a & rearrngement
B +
or
β-Methylstyrene
Allylbenzene
4-Phenyl-1-butene
(b)
a
Scission at a & CH_3 Transfer
b
a
H
J
Scission at a & $-\dot{H}$
2-Phenyl-1-butene
Scission at b & $-\dot{H}$
B +
or
β-Methylstyrene
Allylbenzene

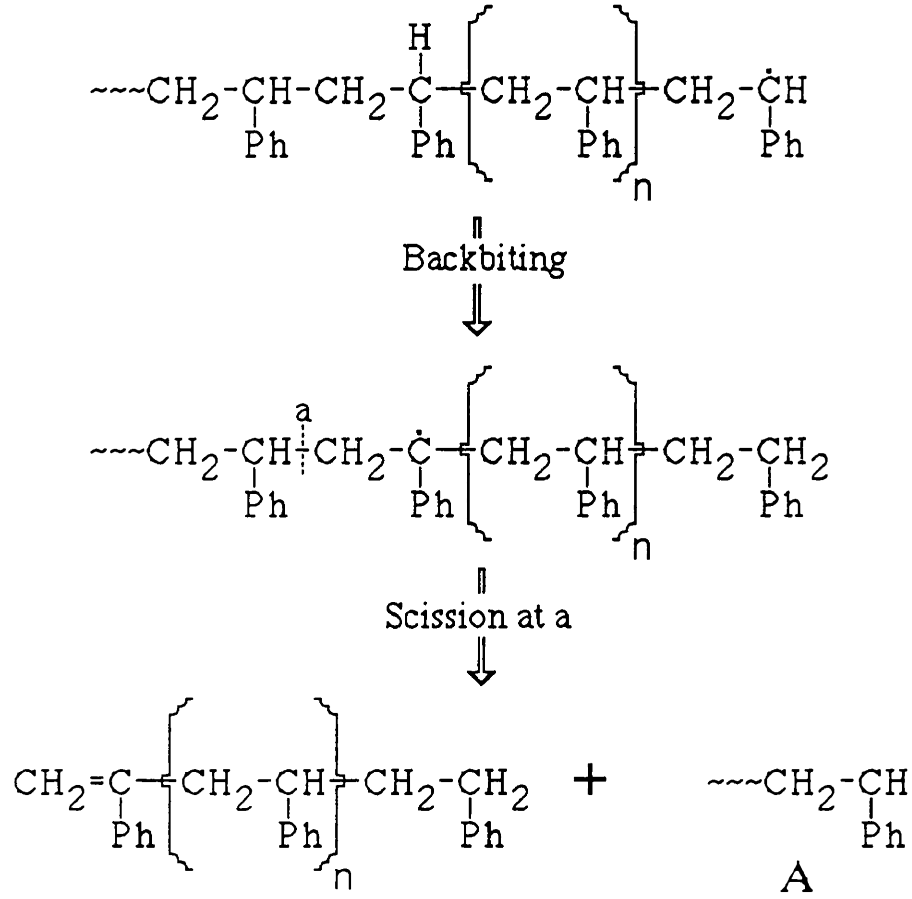
SCHEME 7.3


Scission at a
K
A
H abstraction
H CN
L
Scission at a
& H abstraction
Scission at b
& H abstraction
+ A
B +
Isobutene
4-Phenyl-2-methylbutene

SCHEME 7.4

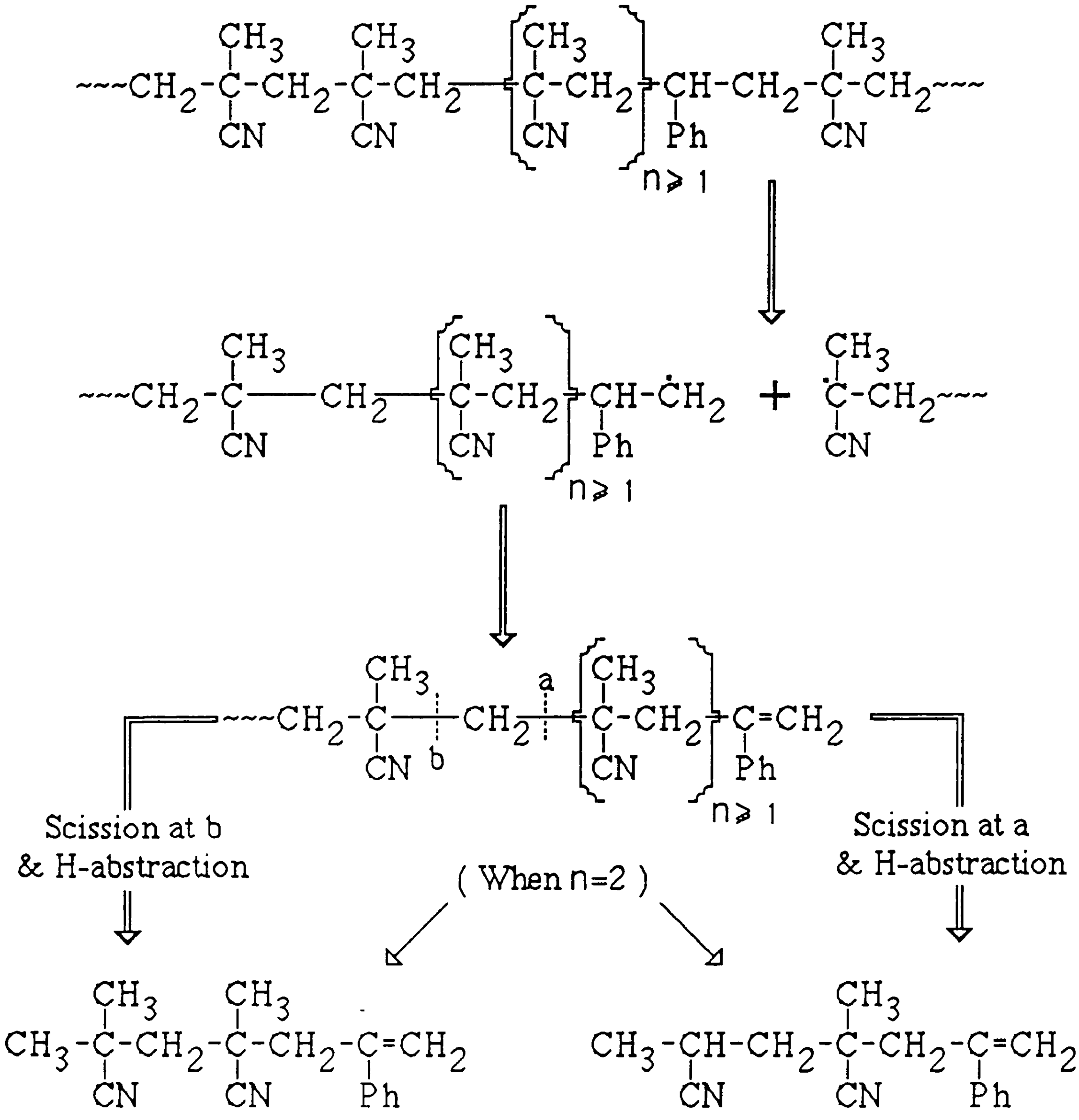

Scission at b
(i)
B
A (MAN end)
or
(ii)
Scission at b & H elimination
3-Phenyl-2-propenenitrile
(Cinnamonitrile)

SCHEME 7.5



If n=1 Trimer, n=2 Tetramer & etc

SCHEME 7.6



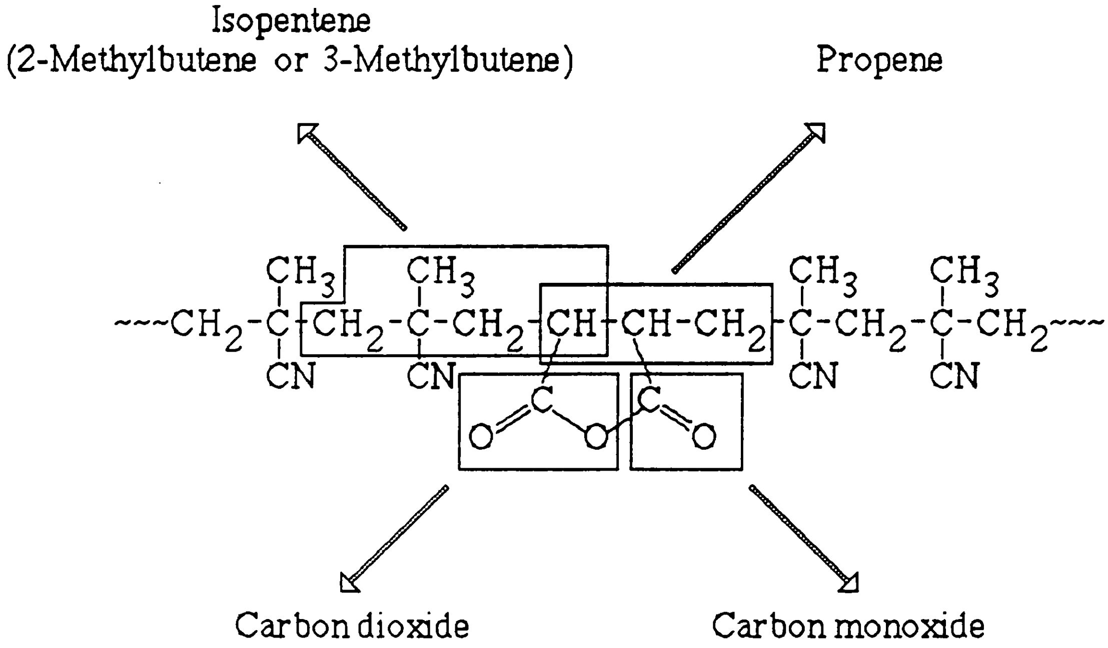
MAN dimer with extra methyl group containing one styrene unit.

MAN dimer containing one styrene unit

And other oligomers of the type

And other oligomers of the type

SCHEME 7.7

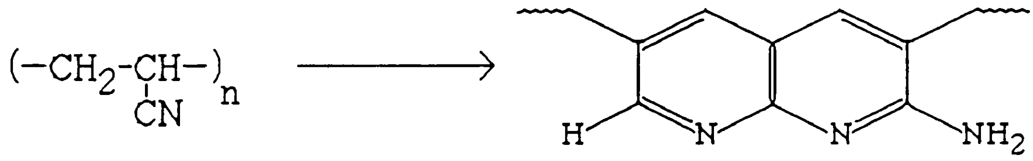

Isopentene
(2-Methylbutene or 3-Methylbutene)
Propene
Carbon dioxide
Carbon monoxide

CHAPTER EIGHT

THERMAL COLOURATION IN METHACRYLONITRILE HOMO AND COPOLYMERS

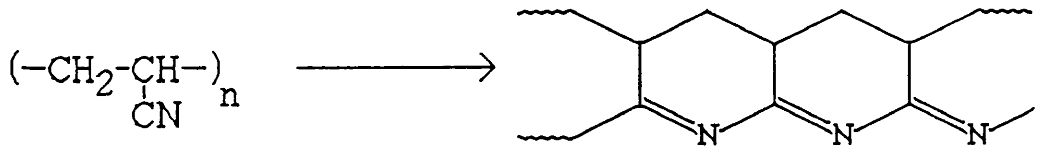
8.1 A REVIEW OF EARLIER THERMALCOLOURATION STUDIES OF NITRILE POLYMERS.

Thermal colouration in nitrile polymers has been studied for not more than half a century. Houtz[85] was the first to report this in his early studies of the thermal behaviour of polyacrylonitrile in 1950. It was noted that a flame proof material is obtained by prolonged heating in air and it was suggested that acrylonitrile units were converted to aromatic heterocyclic structures like naphthyridine type rings:



$(-CH_2-\underset{CN}{CH}-)_n \longrightarrow$

McCartney[61] observed colouration when PAN was degraded by addition of alkali. Burlant and Parsons[86] studied colouration during pyrolysis of PAN by using infrared absorption measurements. It was found that nitrile group absorption disappears as heating progress and absorption for the -C=N- linkage appears, under inert (nitrogen) conditions. These studies[61,86] concluded that cyclised structures formed under these conditions were not fully aromatic.

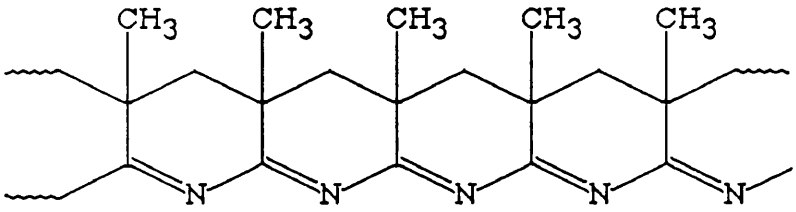


E. L. Lacombe[87] also observed that colouration could be induced at very low temperatures by the action of base. Again the colouration was attributed to the rearrangement of pendant nitrile group.

An extensive study of thermal colouration in PMAN was carried out by Grassie and McNeill. These authors found[24] that the colouration which develops above 120 °C in methacrylonitrile polymer is due to a reaction initiated at some kind of impurities already present in the polymer chain and colouration can be eliminated by suitable purification of monomer, and by polymerising in presence of azo catalyst in vacuum. It was also suggested that colouration can most conveniently be studied in copolymers of methacrylonitrile with traces of methacrylic acid units which act as centres of initiation for colouration.

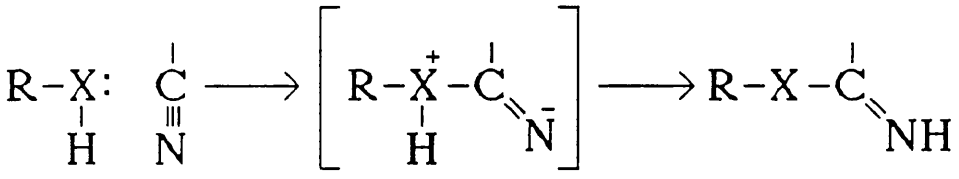
The same authors carried out a systematic study[25-27] of the thermal colouration which occurs in these copolymers. It was observed[25] that the IR spectra of coloured polymers show a decrease in the nitrile absorption (which was followed quantitatively) and new absorption was observed to appear at 1693-1490 cm^{-1}, and assigned to C=N absorption. During these isothermal colouration studies[26] no volatile material was lost, and molecular weight measurements showed that neither chain scission nor crosslinking is involved. A structure was proposed (I) for coloured PMAN and reported to be the result of the linking up of adjacent nitrile group to form extended conjugated carbon-nitrogen sequences

I



It was also suggested that the formation of this structure (I) is through a non-radical chain process initiated at methacrylic acid units and propagated through adjacent nitrile units. The decrease in the solubility was attributed to the rigidity of the modified polymer structure rather than to crosslinking.

Furthermore, it was also observed[27] that colouration can also be initiated by heating with a variety of other substances containing a suitable reactive hydrogen atom (usually Lewis acid), and not necessarily incorporated to the polymer chain, and hence a generalised initiation mechanism may be written:



These authors established[27] that impurity may either be present in the polymer chain, or physically mixed with polymer.

In later studies[88] it was also observed that colouration in PAN and PMAN may be induced by organotin compounds. These studies supported the theory of linking up of adjacent nitrile groups in thermally or base induce colouration. Meanwhile Schurz[89] expressed some doubts about the cyclised structure proposed for coloured polymer, and crosslinking through the tertiary hydrogen in PAN was suggested to be the reason for decrease in solubility in coloured polymer. These doubts were answered by Grassie et al.[90] who insisted that coloured polymer contained the conjugated -C=N- ladder structure.

Overberger et al.[91] also suggested a conjugated -C=N- structure for coloured PMAN during their studies with anionically prepared polymethacrylonitrile. It was emphasised that linking up of adjacent nitrile group occurred through an ionic mechanism. Though the cyclisation theory for colouration seemed to accepted widely, Fester[92] and Berlin[93] contested it and suggested that polymer was dehydrogenated by the heat to form a polyene type of polymer with pendant nitrile group.

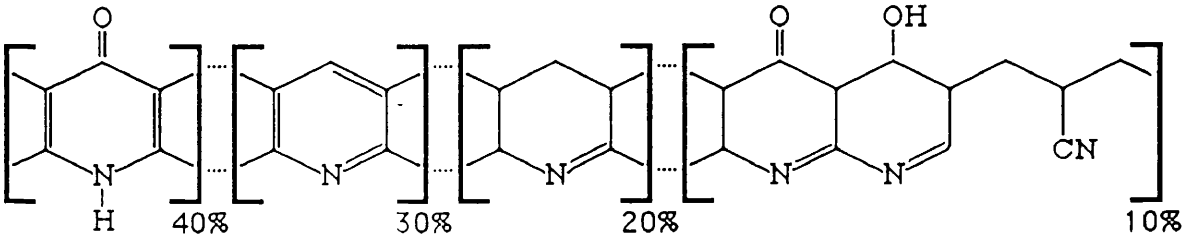
In a later investigation,[94] it was suggested that nitrile group cyclisation depends upon the tacticity of the polymer, and the isotactic structure creates the most favourable conditions for the interaction of nitrile groups in adjacent units of PAN chain. On the other hand, Chen et al.[95] found evidence which suggested that the thermal cyclisation was not stereospecific.

Grassie and McGuchan made a comparative study[64] of thermal behaviour of PAN with its α–substituted analogues, and concluded that α–hydrogen atom in PAN plays an important role in the chain process involved in the oligomerisation of nitrile groups, whereas the preferred degradation process in a α–substituted polymers is depolymerisation to monomer, but some nitrile rearrangement can be induced through using suitable additives or comonomers.

Coleman et al.[96] carried out FT-IR studies of the isothermal degradation of polyacrylonitrile under reduced pressure. A nitrile group cyclisation mechanism (ionic in nature) was advanced and infrared bands occurring in the spectrum of degraded PAN were assigned. A crucial step in the proposed mechanism involved the transfer of tertiary hydrogen to the nitrogen atom contained in the heterocyclic ring system. These conclusions were later substantiated[97] by isothermal degradative studies of poly-α-deuteracrylonitrile under reduced pressure.

Coleman et al. also studied the degradation of an acrylonitrile copolymer containing a small amount (~4 %) of methacrylic acid at 130°C under reduced pressure, and a mechanism was put forward[98] for the degradation supported with the IR spectral evidence.

Takahagi et al.[99] studied the mechanism of the colouration reaction in air PAN and the structure of the coloured PAN was fully elucidated. It was reported that the ladder polymer consists of 40% acredone, 30% pyridine and 20% hydronaphthyridine rings with 10 % of other structures and it is represeted by formula shown below



Recently, during a critical study of the nitrile cyclisation concept, Bashir et al. investigated base induced colouration in PAN[100] and PMAN.[65] It was reported that 10 % of a homogeneous solution of PAN or PMAN turns to red gel when strong base was added and hence colouration was concluded to be due to some kind of intermolecular reaction (crosslinking). It was claimed that colouration due to addition of base in PMAN is not due to cyclisation, but rather is due to an unidentified chromophore which is very intense. It was suggested that the polymer chains in a 10 % solution are close enough for crosslinking.

8.2 ISOTHERMAL DEGRADATION.

In the present investigation several homopolymers and copolymers of methacrylonitrile have been utilised. End-initiated MAN homopolymers ranging from average molecular weight ($\overline{Mn}$. 28000) to low molecular weight ($\overline{Mn}$.4500) were used for isothermal degradation. Three MAN/MAA copolymers with different methacrylonitrile/methacrylic acid ratios (45/1, 25/1 and 10/1) were chosen for colouration studies. The choice of these five MAN end-initiated polymers and three copolymers were made mainly for two reasons.

(i) To study the colouration initiated from polymer chain ends (in case of end-initiated MAN polymers) and from inside the polymer chain (in case of methacrylonitrile polymers containing methacrylic acid units).

(ii) To examine the effect of decreasing chain length per initiating site (in case of end-initiating polymers) and by increasing initiating centres inside the polymer chains (in case of copolymers containing MAA units) on the extent of colouration.

8.2.1 SAMPLING

Systematic colouration studies by infrared spectroscopy were carried out utilising mainly two sampling procedures.

(i) By preparing potassium bromide (KBr) discs.

(ii) By casting polymer sample film from a suitable solvent (mainly acetone or dichloromethane) on a stainless steel plate.

These two sampling procedures were employed intentionally to see the effect of environment, which is ionic in case of KBr discs and non-ionic in case of cast films.

Potassium bromide discs were prepared containing 5 mg of polymer (EIPMAN or COMAN/MAA) sample in each case and the IR spectra of the undegraded materials were obtained.

Films of the polymer samples were cast on the stainless plates as follows. Firstly a saturated solution of 10 mg of polymer sample in acetone was poured and uniformly spread on the steel plate, and the acetone was allowed to evaporate. The apparently dried film was then kept in a vacuum oven at 40 ^{o}C for 48 hours and finally heated at 100^{o}C for 20 min. to evaporate any trace of acetone remaining. IR spectra of these cast films (undegraded polymer sample) were obtained, prior to starting isothermal studies by total internal reflectance spectroscopy.

The undegraded polymer samples (KBr discs or cast films) were then heated isothermally under a reduced pressure of 10^{-3} torr. The temperatures chosen for isothermal treatments were 140, 160 and 180^{o}C. Isothermal heating was interrupted at intervals for measurements of the IR spectrum. Temperature control was attained (±2 ^{o}C) using a Specac automatic temperature controller.

8.3 RESULTS AND DISCUSSION

Room temperature IR spectra of undegraded end-initiated methacrylonitrile polymer (EIPMAN 1, 3 and 5) and three MAN/MAA copolymers (COMAN/MAA 1, 2, and 3) are presented in Figs. 8.1a, 8.2a, 8.3a, 8.4a, 8.5a and 8.6a respectively. All the six original spectra are almost similar except in the relative intensities of the bands at 1734 and 3280 cm^{-1} corresponding to the carbonyl (C=O) and hydroxyl (OH) of methacrylic acid units or ACVA initiator. The principal peaks occurring in undegraded end-initiated methacrylonitrile polymers and copolymers of methacrylonitrile and methacrylic acid are summarised in Table 8.1.

Most of the CH_3 and CH_2 modes can readily be assigned on the basis of the spectra of other polymers. The bands at 2993, 2945, 1468, 1454, and 1395 cm^{-1} are undoubtedly to be assigned to $\nu_a(CH_3)$, $\nu_a(CH_2)$, $\delta(CH_2)$, $\delta_a(CH_3)$ and $\delta_s(CH_3)$ respectively. In case of polyacrylonitrile,[105] the band at 1359 cm^{-1} has been assigned as $\gamma_\omega(CH_2)$. CH_2 wagging (or out of plane rocking) usually does not exhibit significant intensity absorption but in the case of PAN[102] and PMAN, the $\gamma_\omega(CH_2)$ mode is much stronger which may be due to the influence of the neighbouring CN group on the electronic structure, and thereby the dipole of the CH_2 group. A small shoulder at 1170 cm^{-1} has been tentatively assigned as CH_2 twisting and the reason could be the same as described above for CH_2 wagging. In this connection further details will be discussed later.

Figs. 8.1, 8.2, 8.3, 8.4, 8.5, and 8.6 show the changes occurring during isothermal treatments at 160 ^{o}C for various lengths of time in the IR spectra of EIPMAN 1, EIPMAN 3, EIPMAN 5, COMAN/MAA 1, COMAN/MAA 2 and COMAN/MAA 3 respectively.

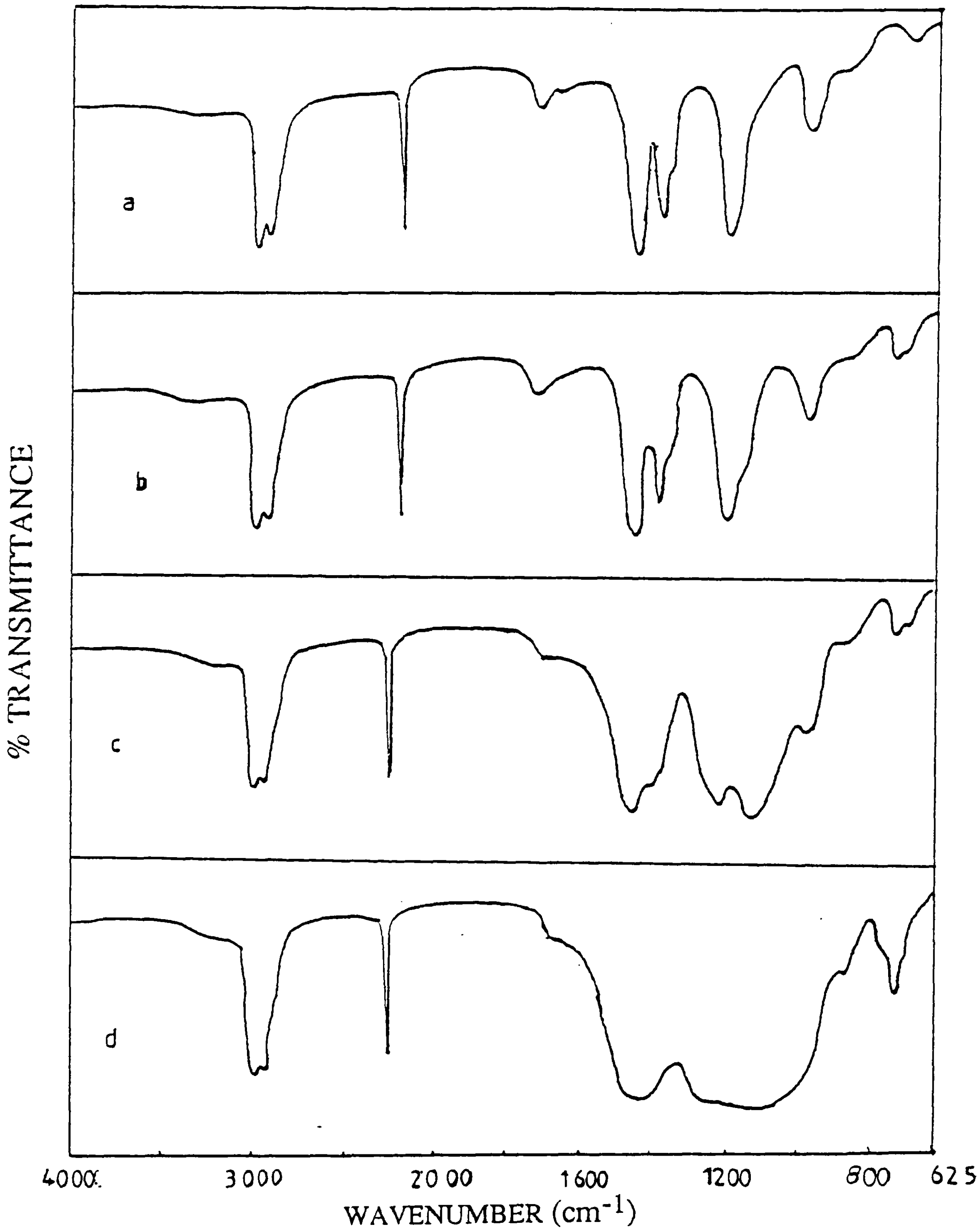


Fig. 8.1. IR Spectra of the EIPMAN 1 as a Function of Time at 160 ^{o}C.

(a) Undegraded.(b) Degraded for 2 hours.

(c) Degraded for 8 hours. (d) Degraded for 24 hours.

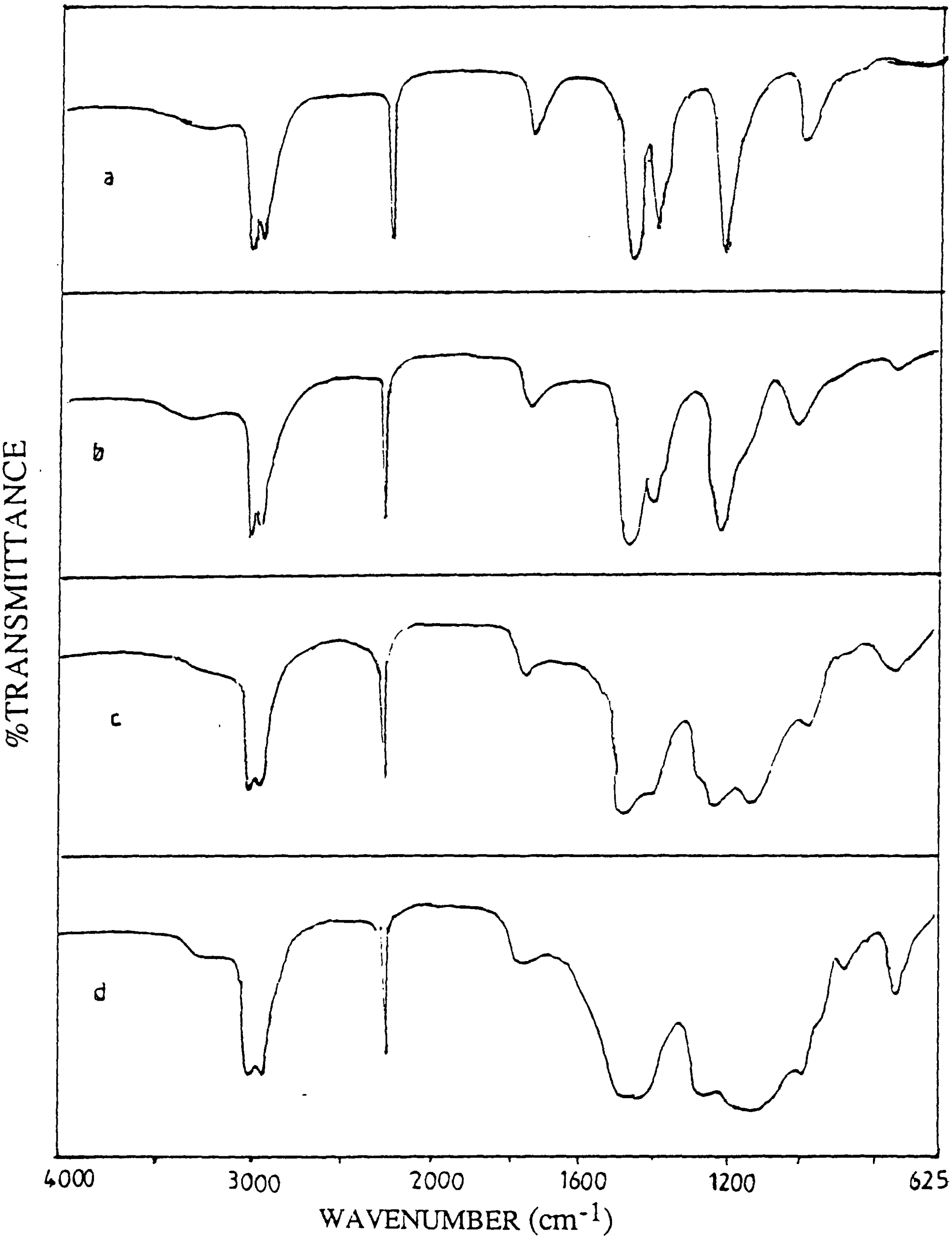


Fig. 8.2. IR Spectra of the EIPMAN 3 as a Function of Time at 160 ^{o}C.

Keys: (a) Undegraded.(b) Degraded for 2 hours.

(c) Degraded for 8 hours. (d) Degraded for 24 hours.

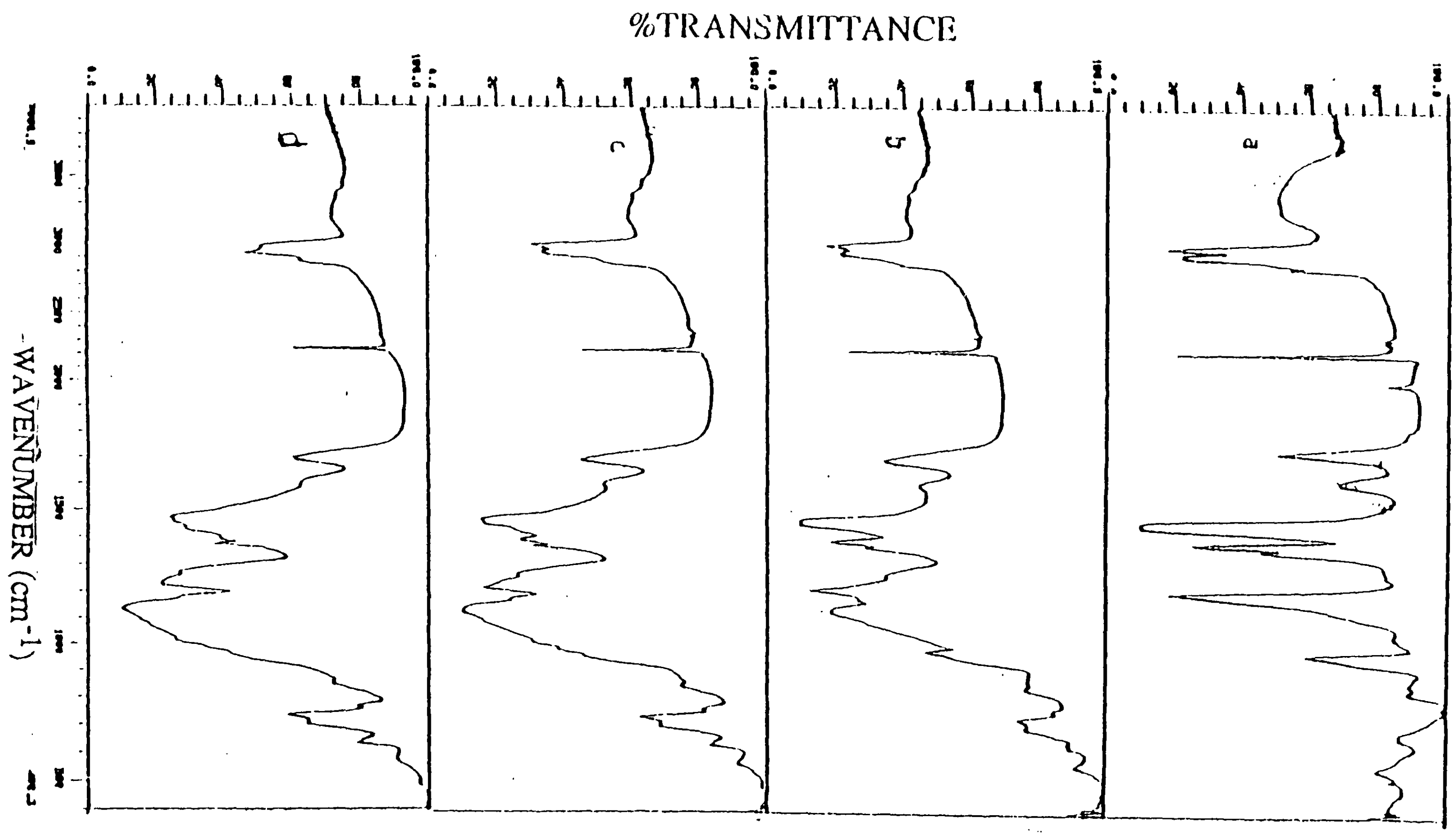


Fig. 8.3. IR Spectra of the EIPMAN 5 as a Function of Time at 160 ^{o}C

Keys: (a) Undegraded.(b) Degraded for 2 hours.
(c) Degraded for 8 hours. (d) Degraded for 24 hours.

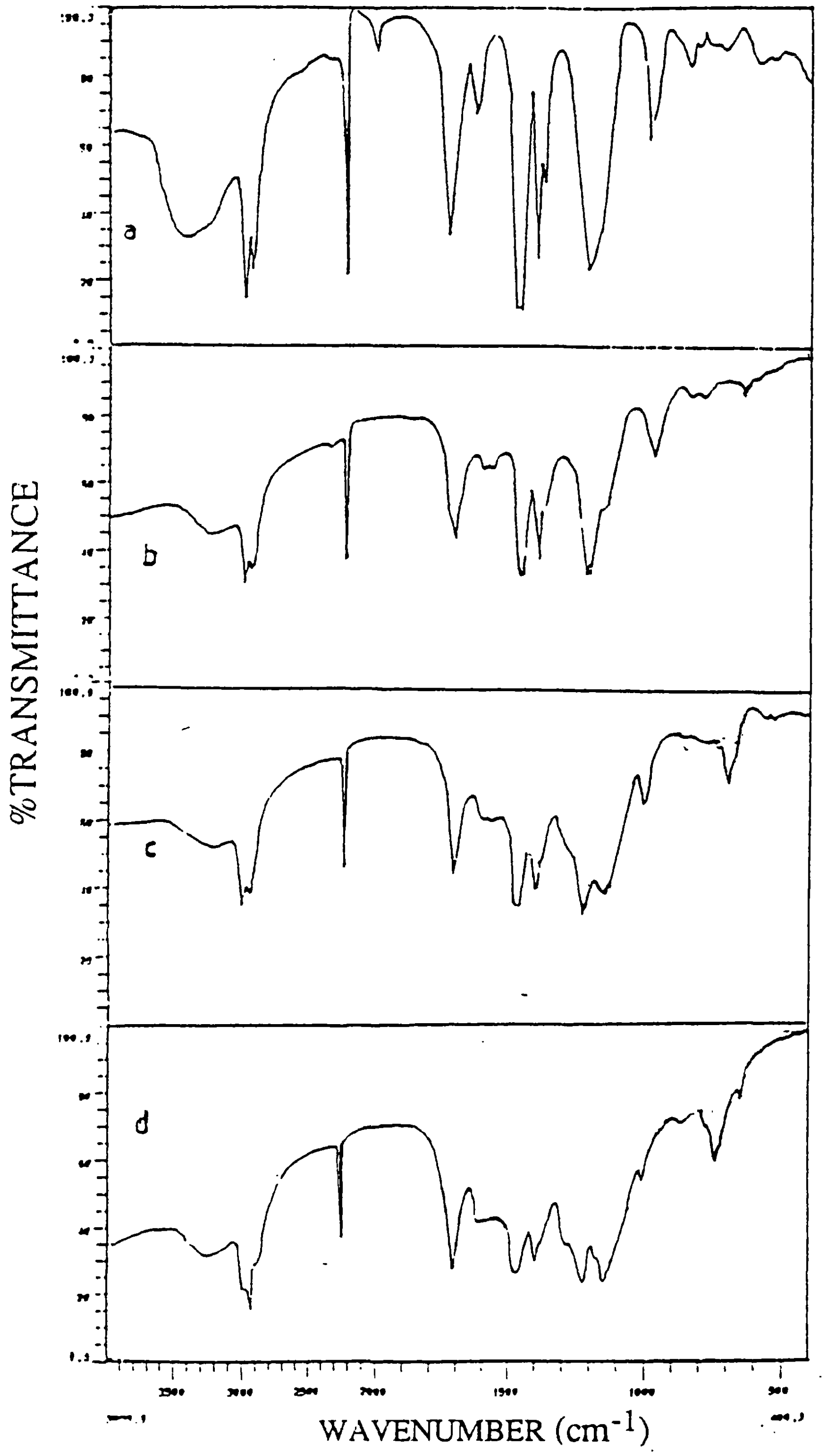


Fig. 8.4. IR Spectra of the COMAN/MAA 1 as a Function of Time at 160 °C

Keys: (a) Undegraded.(b) Degraded for 2 hours.
(c) Degraded for 8 hours. (d) Degraded for 24 hours.

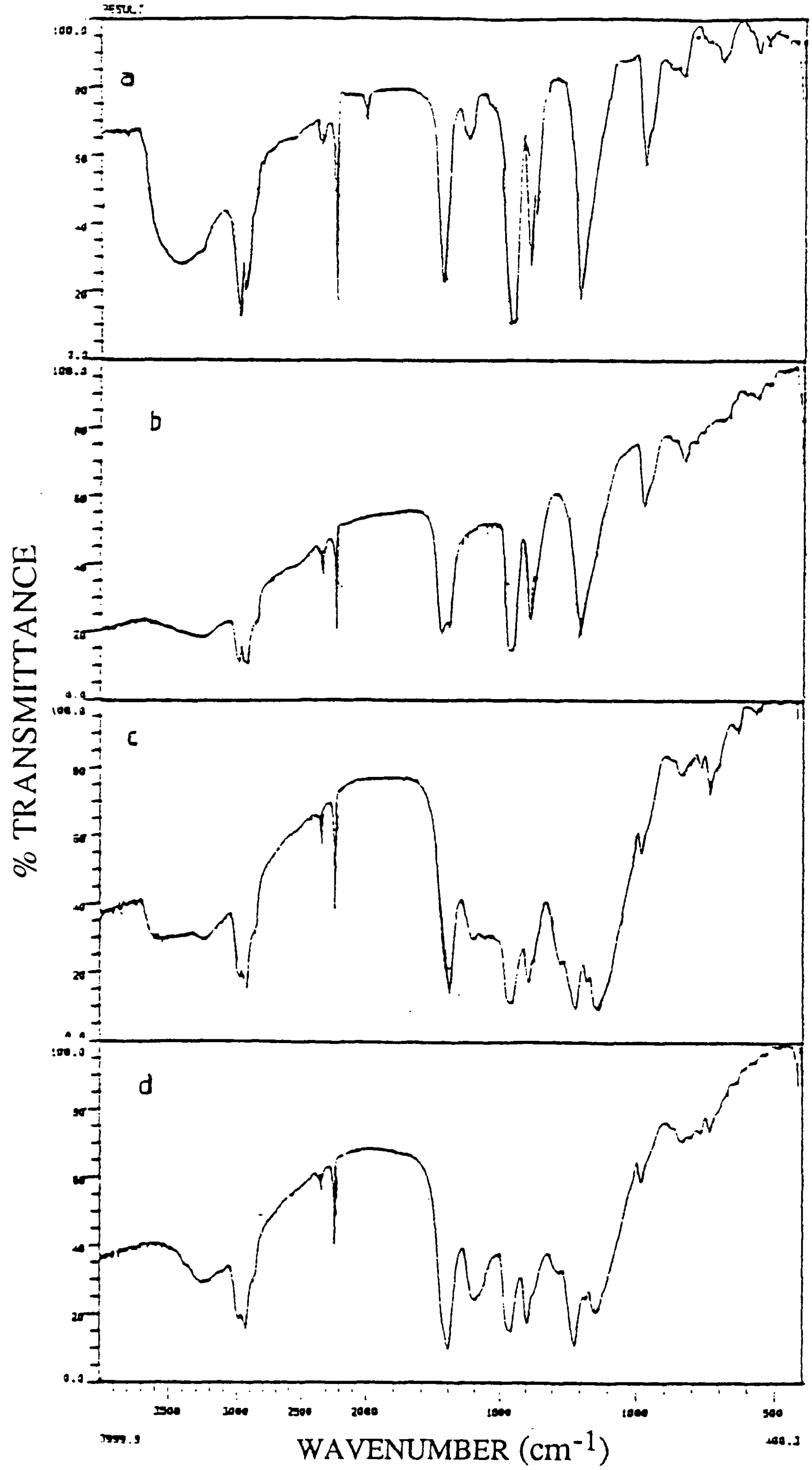


Fig. 8.5. IR Spectra of the COMAN/MAA 2 as a Function of Time at 160 ^{o}C

Keys: (a) Undegraded.(b) Degraded for 2 hours.
(c) Degraded for 8 hours. (d) Degraded fo 24 hours.

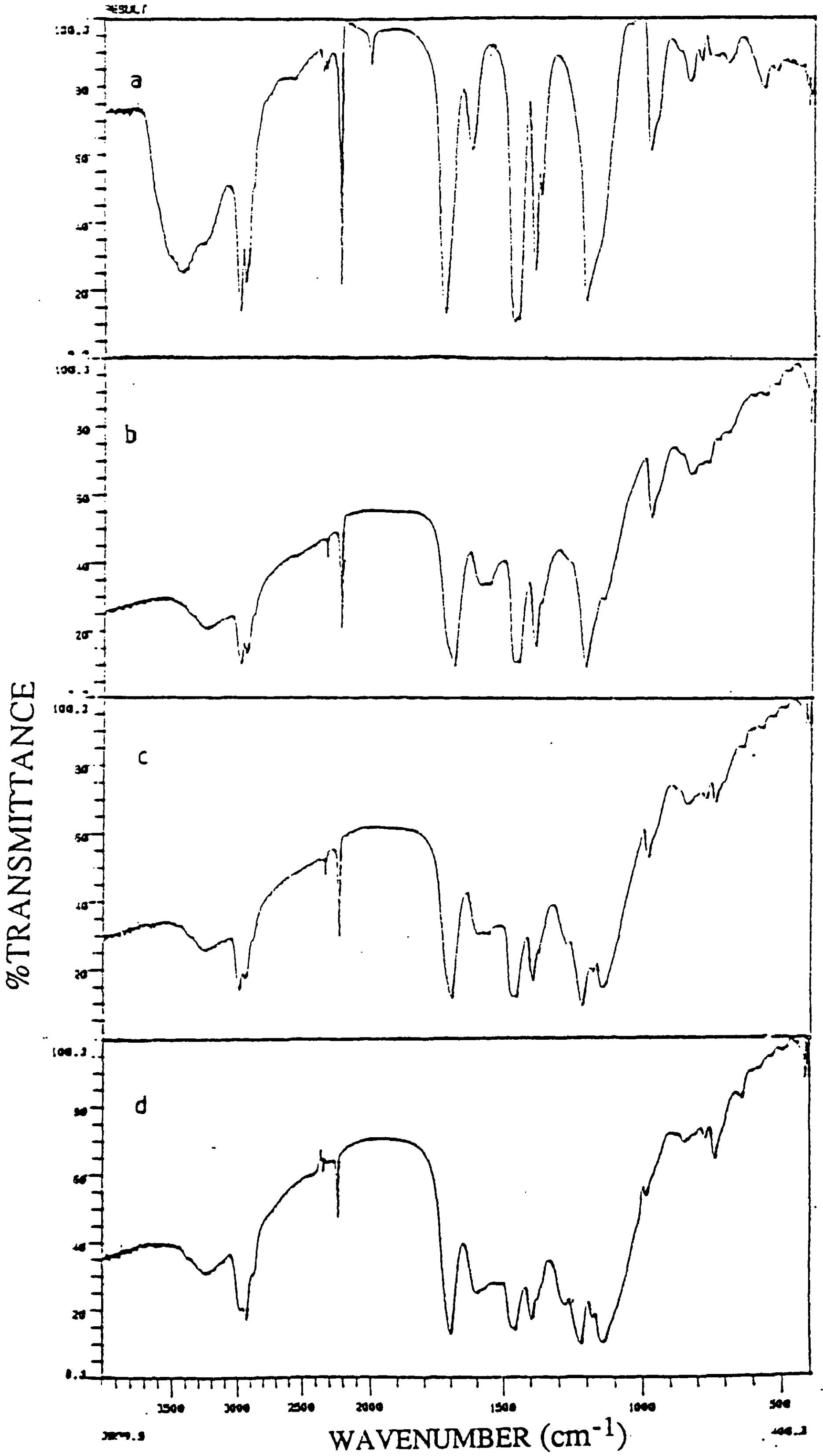


Fig. 8.6. IR Spectra of the COMAN/MAA 3 as a Function of Time at 160 ^{o}C

Keys: (a) Undegraded.(b) Degraded for 2 hours.
(c) Degraded for 8 hours. (d) Degraded for 24 hours.

TABLE 8.1 Assignments of the Principal Peaks Present in the IR Spectra of Various Undegraded End-initiated Methacrylonitrile Polymers and Methacrylonitrile/Methacrylic Acid Copolymers.

Infrared band (cm^{-1})	Assignment
3280–2500 Br	(OH) O-H Stretching
2993 s	(CH_3) C-H Asymmetric stretching
2945 m	(CH_2) C-H Asymmetric stretching
2855 w	Saturated C-H symmetric stretching
2235 s	($C\equiv N$) Nitrile $C\equiv N$ Stretching
2021 w	(C=C=N) Ketene-imine stretching
1735 s	(>C=O) Carbonyl C=O stretching
1468 s	(CH_2) C-H Bending or scissoring
1454 s	(CH_3) C-H Asymmetric deformation
1395 s	(CH_3) C-H symmetric deformation
1371 m	(CH_2) C-H Wagging or out of plane rocking
1215 s	Quaternary carbon distortion or backbone skeletal.
1175 sh	(CH_2) C-H twisting
980 m	(CH_3) Rocking

m = medium, s = strong, sh = shoulder w = weak

During the isothermal studies of various end-initiated and copolymers of methacrylonitrile, the major variations observable in the infrared spectra are generally at 3400–3200, 2236, 1808, 1735, 1700,1600, 1156. , 1375, 1275, 1180 and 740 cm^{-1}. The IR spectral changes mentioned above have been further categorised in to smaller groups, in order to explain the behaviour of each polymer conveniently.

(i) Decrease in the intensity of the nitrile band at 2236 cm^{-1}.

(ii) Growth of new bands at 3220, 1600, 1565 and 1275 cm^{-1}.

(iii) Complete disappearance of carbonyl band at 1735 cm^{-1} and appearance of corresponding carbonyl band of same intensity at 1699 cm^{-1}.

(iv) Gradual shift of the infrared bands at 2993 $\nu_a(CH_3)$ and 2945 cm^{-1} $\nu_a(CH_2)$ to 2986 and 2938 cm^{-1} respectively.

(v) Appearance of a strong broadening at 1155 cm^{-1}, a ωm intensity band at 736 cm^{-1} and increase in the intensity of the $\gamma_{\omega}(CH_2)$ band at 1375 cm^{-1}.

(vi) Appearance of a weak band at 1808 cm^{-1} [this IR spectral band was only observed during isothermal degradation of copolymers as a cast film, especialy in case of COMAN/MAA 3 (Fig. 8.10)].

ν_a= Asymmetric stretching, δ = Deformation or bending, δ_a = Asymmetric deformation
δ_s = Symmetric deformation. γ_{ω} = wagging

Using the categories described above, it is easy to explain the changes occurring in various end-initiated MAN polymers and MAN copolymers containing MAA units degraded isothermally.

All polymers and copolymers studied in these investigations commonly show the changes described in (v). End-initiated methacrylonitrile polymers EIPMAN 1 & EIPMAN3 (Figs. 8.1 and 8.2) show only those changes listed under (iii), (iv) and in particular (v). There is no detectable decrease in the nitrile absorption or growth of new peaks at 1600 and 1568 cm^{-1} in these cases.

EIPMAN 5 (Fig. 8.3) does show a clear decrease in the nitrile band at 2236 cm^{-1} and the appearance of new bands at 1600–1568 cm^{-1}, together with the changes mentioned under (iii)-(v). The changes described in (i) and (ii) becomes more and more significant as we go from end-initiated polymers to MAN / MAA copolymers, and among the MAN/MAA copolymer, these changes [(i) & (ii)] become more pronounced with increasing numbers of MAA units inside the polymer chain (i.e., COMAN/MAA 3.> COMAN/MAA 2 > COMAN/MAA 1) as shown in Figs. 8.4–8.6. In the case of COMAN / MAA 3, the band at 2236 cm^{-1} reduces to about half of its intensity compared to the original sample (Fig. 8.6). just after 16 hours of heating at 160 ^{o}C.

The growth of a new band at 3220 cm^{-1} has also been reported in the case of isothermal colouration in PMAN[25] and PAN,[64,96–98] and has been assigned to an NH structure, possibly an imine. Gradual disappearance of the band at 1735 cm^{-1} and the appearance of a new band of the same intensity at 1700 cm^{-1}, both attributed to carbonyl group (C=O), have also been observed during isothermal studies of acrylonitrile/methacrylic acid copolymer.[98] The former was assigned to the unreacted MAA comonomer while the later was suggested to be due to reacted material, and same assignments could be given in the present case.

During colouration of the PAN under reduced pressure, the appearance of new bands at 1610 and 1575 cm^{-1} has been observed,[64,96-99,101] which can be related,in the present case, to the growth of new bands at 1600 and 1568 cm^{-1} respectively. Petcavich et al.[97] had assigned the above mentioned bands to ketone and the ladder structures of degraded PAN fiber under reduce pressure, whereas Shemida et al.[99] considered these bands to come from the ladder structure only. In the present investigations, the bands at 1600 and 1568 cm^{-1} are assigned to the C=N stretching of cyclised structure, and the =N-H bending of imine and amino groups (present in the nitrile cyclised coloured polymer), respectively, and the reasons for these assignments are as follows.

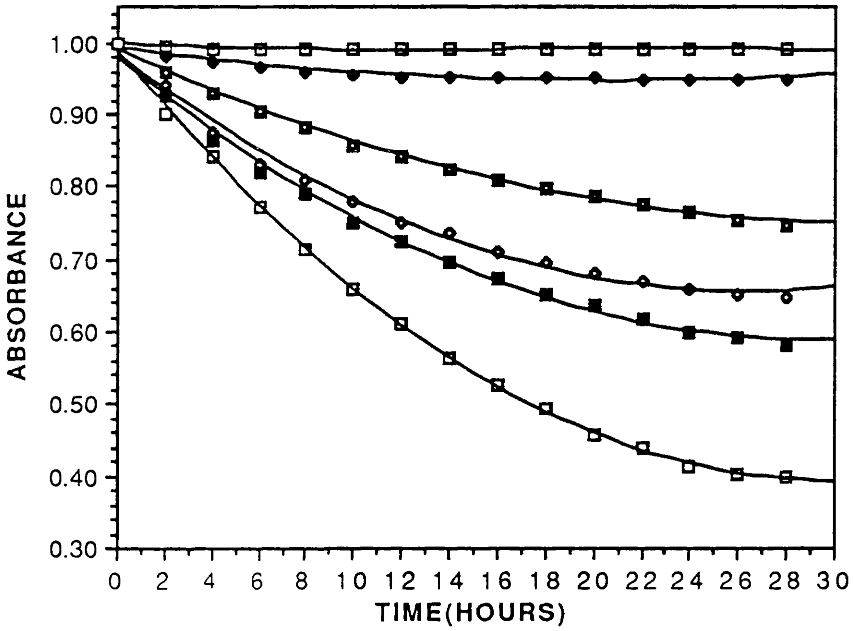
During a comparative infrared spectroscopic study [98,99] (in the IR region from 1500-1800 cm^{-1}), between a film of PAN degraded isothermally for 24 hours at 200 °C under reduced pressure, showing strong bands at 1610 and 1580 cm^{-1} (which can be tentatively related to bands observed at 1600 and 1568cm^{-1} respectively, in the present work), and the same film , exposed to D_2O for 24 hours, it was observed that band at 1580 cm^{-1} significantly reduced whereas the intensity of the band at 1610 cm^{-1} was not affected at all. Previously[97] the bands at 1610 and 1568 cm^{-1} were considered to come from ketone (pyridone) and ladder structure, respectively whereas in the present work, firstly, the presence of methyl group (CH_3) instead of tertiary hydrogen (present in case of PAN) does not favour the reaction mechanism which leads to pyridone type of structure,[97] and secondly it is reasonable to assume that working under vacuum conditions (1.0 X 10^{-3} torr) limits the chances of oxygen uptake.

The assignments for the new bands in the fingerprint region (at 1275, 1148 and 736 cm^{-1}) and other changes listed under (V) (shift of bands attributed to asymmetric and symmetric stretching of CH_3 and CH_2 groups) will be discussed later.

A graph of relative intensity of the absorbance of C≡N stretching frequency as a function of time for various MAN homo and copolymers (capable of colouration during isothermal treatments) is given in Fig.8.7. The Fig.8.7 shows the extent of nitrile group oligomerisation in terms of decrease in the intensity of the nitrile band for the various polymer samples studied under isothermal conditions, and it is quite evident that the decrease in the nitrile group is in the order as COMAN/MAA 3 > COMAN/MAA 2 > COMAN/MAA 1 > EIPMAN 5 > EIPMAN 3 > EIPMAN 1.

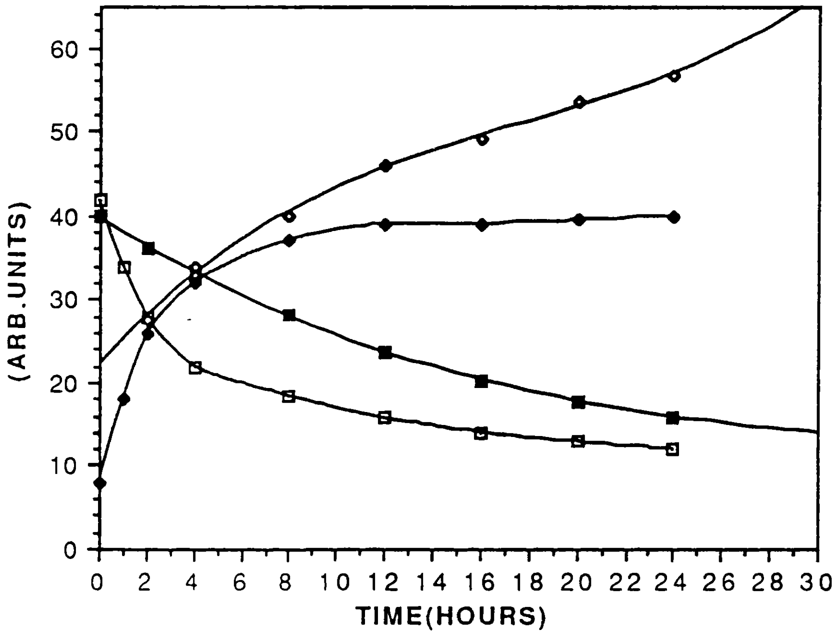
The measurements of the relative intensities of important IR bands at 2236, 1735, 1700, and 1150 cm^{-1} for EIPMAN 5 and COMAN/MAA 3 as a function of time are revealing, and these measurements are displayed in Figs 8.8. and 8.9 respectively. These results can only be considered approximate due to the assumption inherent in assuming a reasonable base line, nevertheless they do indicate trends. The decrease in the relative intensity of the bands at 2236 and 1735 cm^{-1} and parallel increase in the relative intensities of bands at 1700, and 1150 cm^{-1} are particularly noticeable. From these observations of decreasing and increasing trends of various IR bands, it is reasonable to assume that the original polymers containing nitrile groups and acidic units represented by bands at 2236 and 1735 cm^{-1}, respectively, are being converted into degraded products characterised by the major IR bands at 1700, and 1150 cm^{-1}.

Figure 8.7. Plot of the Relative Intensities (in Absorbance) of the Nitrile Group as a Function of Time for Various Homo and Copolymers Methacrylonitrile Heated Isothermally at 160 °C.



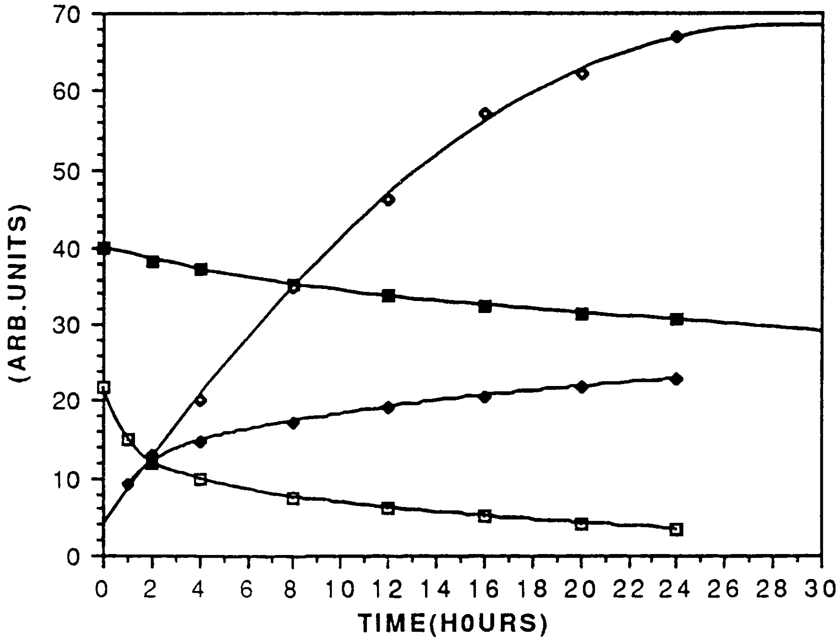
Keys ⊡ EIPMAN 1, ◆ EIPMAN 3, ▪ EIPMAN 5,
◇ COMAN/MAA 1, ■ COMAN/MAA 2,
□ COMAN/MAA3

Figure. 8.8 Graph of Relative Intensities (in Arbitrary Units) Plotted vs Time For Four IR Bands Occurring in the Spectra of MAN/MAA 3 Copolymers at 160 ^{o}C under Vacuum conditions.



Keys ■ 2235 cm^{-1}, ▣ 1737 cm^{-1}, ◆ 1700 cm^{-1}, ◇ 1140 cm^{-1}

Figure. 8.9 Graph of Relative Intensities (in Arbitrary Units) Plotted vs Time For Four IR Bands Occurring in the Spectra of EIPMAN 5 Sample at 160 °C under Vacuum conditions



Keys ■ 2235 cm^{-1}, ▣ 1737 cm^{-1}, ◆ 1700 cm^{-1}, ◇ 1140 cm^{-1}

Fig. 8.10 shows the changes occurring in the IR spectrum as a result of isothermal treatment at 160 °C for various lengths of time for COMAN/MAA 3 cast as a film as described previously. The comparison of the IR results obtained from isothermal degradation of a polymer sample (for example COMAN/MAA 3) in KBr disc (Fig. 8.5) and as a cast film (Fig. 8.10) is revealing. It may be worth mentioning here that during isothermal investigation of various homo and copolymers, most of the polymer samples have shown apparently more colouration when degraded as cast film, but the decrease in the nitrile band and other complementary changes mainly listed under (i)-(iv) which correspond to the proposed nitrile group cyclisation are found to be relatively more significant, when these sample were isothermally degraded in KBr discs for the same period of time and at the same temperature. This shows the positive effect of ionic environment on the nitrile group cyclisation mechanism, which is itself ionic in nature. The mechanism of colouration (next section) involves a crucial step of nitrile group propagation through proton transfer from iminol tautomers which can be more facilitated by ionic environment.

Comparison of the isothermal degradation studies of COMAN/MAA 3 in a KBr disc and as a cast film (Figs. 8.6 and 8.10 respectively) indicated an additional reaction occurring when polymer sample is degraded as a cast film. The presence of a new weak band at 1808 cm^{-1} (which is characteristic of acid anhydride absorption) in the IR spectrum in the initial stage for COMAN/MAA 3 degraded isothermally as a cast film (Fig.8.10) and the absence of the same band when the same copolymer sample was studied isothermally in a KBr disc, suggested the possible dehydration of adjacent methacrylic units in the polymer chain, resulting into the formation of anhydride structures.

The presence and absence of the band at 1808 cm^{-1} in the IR spectrum

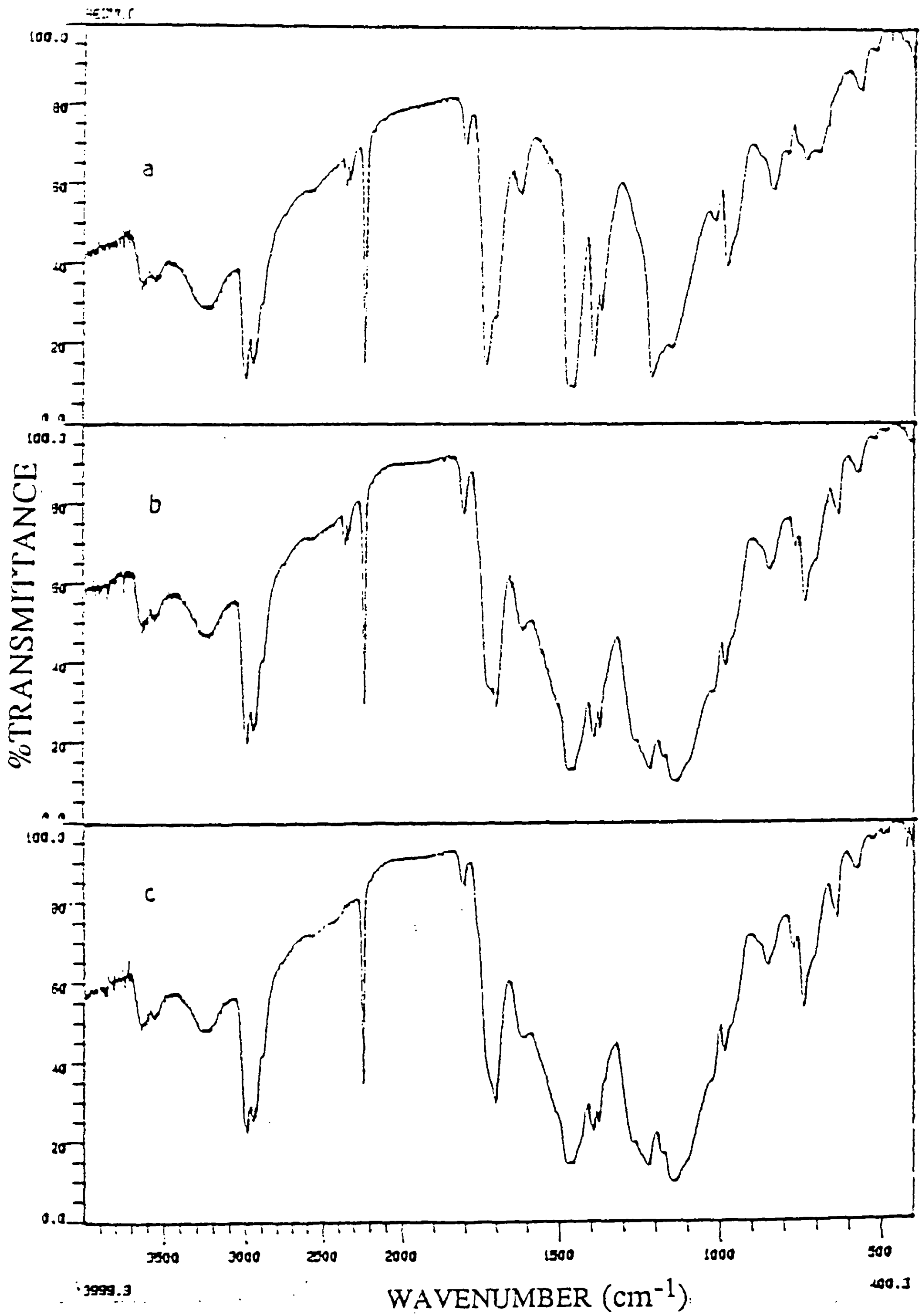


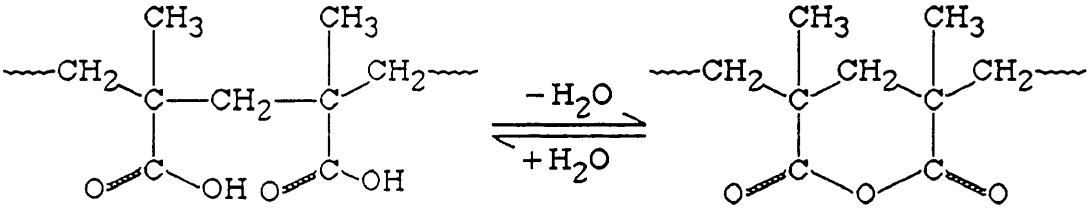
Fig. 8.10. IR Spectrum of COMAN/MAA 3 as a Function of Time at 160 °C as a Cast Film.

Keys: (a) Degraded for 2 hours. (b) Degraded for 8 hours.

(c) Degraded for 24 hours.

of COMAN/MAA 3 when degraded isothermally as a cast film or in a KBr disc, respectively, may be explained as follows:

The dehydration from acids leading to anhydride structures is reversible in presence of water in the environment (if water of dehydration is not removed efficiently) and reaction could be presented as

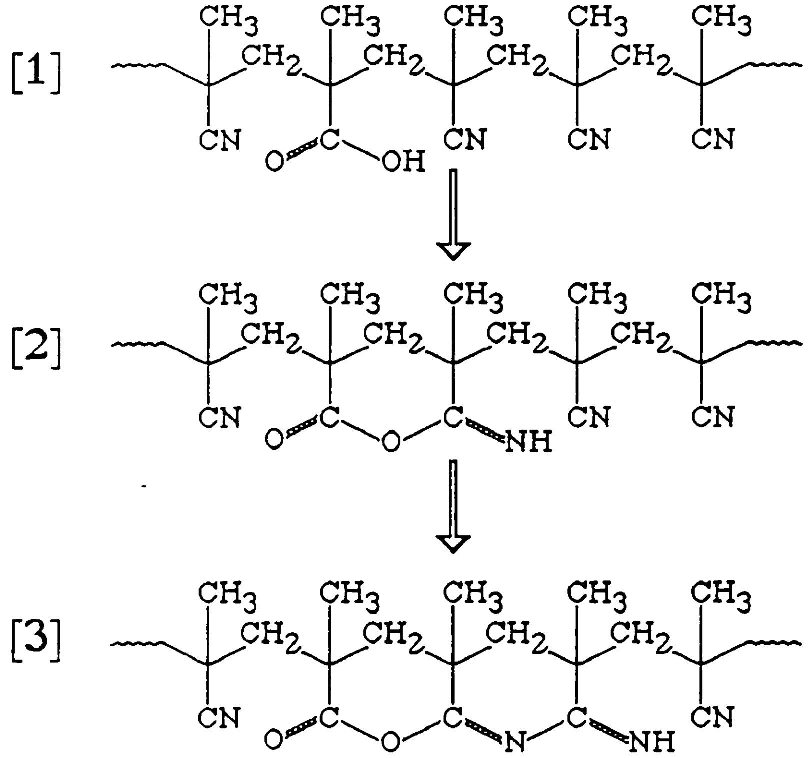


When the sample of copolymer MAN/MAA 3 is degraded isothermally as a cast film, the water from acid dehydration possibly escapes easily under high vacuum conditions and forces the above mentioned equilibrium in the forward direction, resulting int the formation of anhydride structures responsible for band at 1808 cm^{-1}. On the other hand, when the copolymer sample is studied in a KBr disc, the water from the dehydration may be trapped in the ionic atmosphere of the KBr disc and hence favours the backward direction in the equilibrium resulting in the absence of any band in the 1808 cm^{-1} region.

The other copolymers (COMAN/MAA 2 & 1) also showed this type of behaviour (IR band at 1808 cm^{-1} in case of degradation as a film), although the effect was found to be much less significant, probably as a result of the much lower probability of the presence of adjacent MAA units.

8.4 MECHANISM FOR THERMAL COLOURATION

In order to understand the involvement of acidic units (terminal acidic group of ACVA initiator in case of end-initiated methacrylonitrile polymers (EIMANPs) and MAA units in case of various MAN/MAA copolymers) in the cyclisation process, an intuitive and already proposed mechanism[6] is initially considered in which the hydroxyl group of the acid simply attacks the nitrile, accompanied by subsequent proton transfer, as shown in structure 2. Continued propagation through iminic hydrogen transfer leads to the formation of the cyclised structure [3].

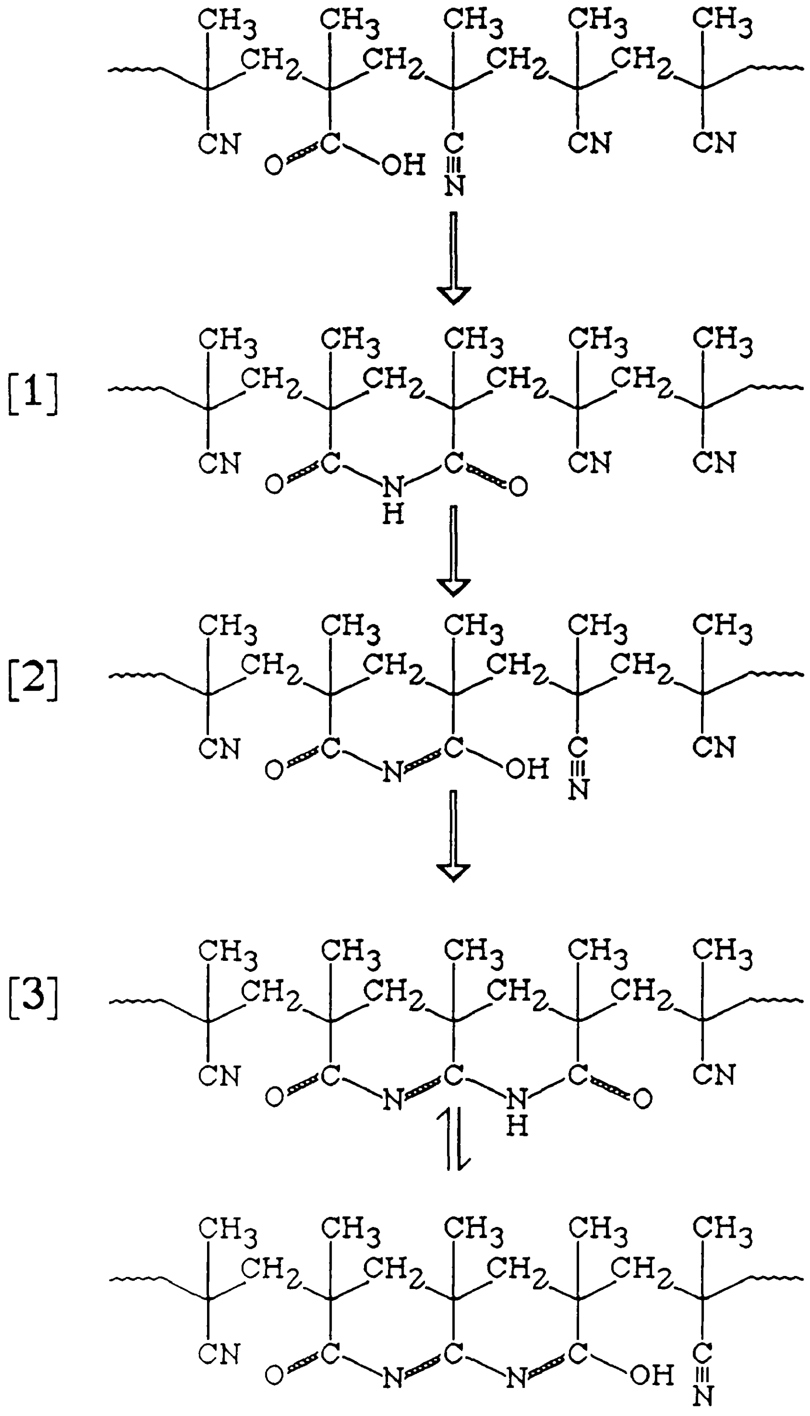


The first cyclisation product structure [3] does not appear to be consistent with the IR spectral results. In the structure [3], the pendant acidic group becomes an ester but the carbonyl is not in conjugation with >C=N- structure. The carbonyl frequency for such structures (unconjugated cyclised esters) should occur at higher wavenumber than for the free acid and would be expected at about 1750 cm^{-1}, while the new major carbonyl band is observed at 1700 cm^{-1}. Furthermore, this type of reaction is inconsistent with known acid-nitrile reactions at elevated temperatures which yield predominantly imides.[102, 103]

A mechanism for the initial degradation for various EIMANPs and MAN/MAA copolymers consistent with the IR spectral studies is given in Scheme 8.1. A similar mechanism for colouration initiated by acidic additives in PAN was proposed by Grassie and McGuchan[103] involving initial formation of an imide, and later Sivy and Coleman[98] expressed doubts regarding the subsequent reaction of further monomer (acrylonitrile) units along the chain, and suggested an oxidised (4H-pyran-4-one) structure as the final product.

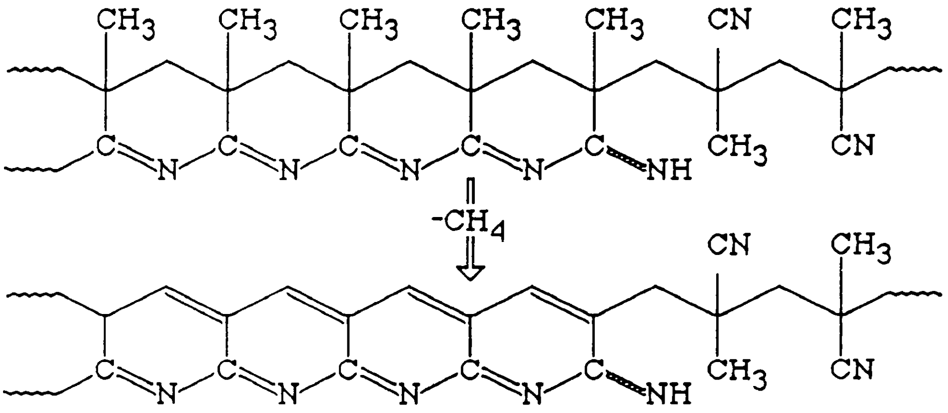
During the isothermal treatment of most of the polymer and copolymer samples studied as cast films, it is observed that the IR spectral changes mentioned as (v) were found to be more pronounced as compared to those studied as KBr discs. It has already been mentioned that the most significant changes observed during isothermal treatment for EIPMAN 1 were also those listed as (v). To ensure that these IR spectral changes (v) are actually attributed to nitrile group cyclisation, a methacrylonitrile polymer made with AIBN initiator (which does not show colouration) was also subjected to prolonged isothermal treatments for confirmatory purpose. It was interesting to find that methacrylonitrile made with AIBN initiator also showed some broadening 1125 cm^{-1} after isothermal treatment of a prolonged period. This observation leads to the understanding that the band at 1145 cm^{-1} may also involve some contribution from a skeletal vibration

SCHEME 8.1



(i.e., CH_2 twisting) of PMAN itself and become more active in the fused state, and be more enhanced in the relatively more rigid cyclised nitrile structures. The position for the CH_2 twisting has already been speculated to 1100–1320 cm^{-1}.[105]

In the present investigation, it has also been observed that most of the MAN polymer and copolymer samples (especially EIMAN polymers with higher molecular weight) have shown a rapid growth of the band at 736 cm^{-1}, for degradation at relatively high temperature (at 180 °C). In these experiments, a small decrease was also observed in the band at 2993 cm^{-1} (which has been assigned to CH_3 stretching), there was no further noticeable decrease in the nitrile band and a new shoulder appeared at 1600–1400 cm^{-1} in the IR spectra (Fig. 8.11). A similar type of behaviour has also been observed during isothermal studies in the IR spectral results of other polymers and copolymers, showing rapid growth of a new band centred at 736 cm^{-1} at the later stage of degradation after extensive colouration. These results suggest the possible aromatisation of rigid structures formed by extensive nitrile cyclisation



The growth of the band at 736 cm^{-1} may be due to the C–H out of plane

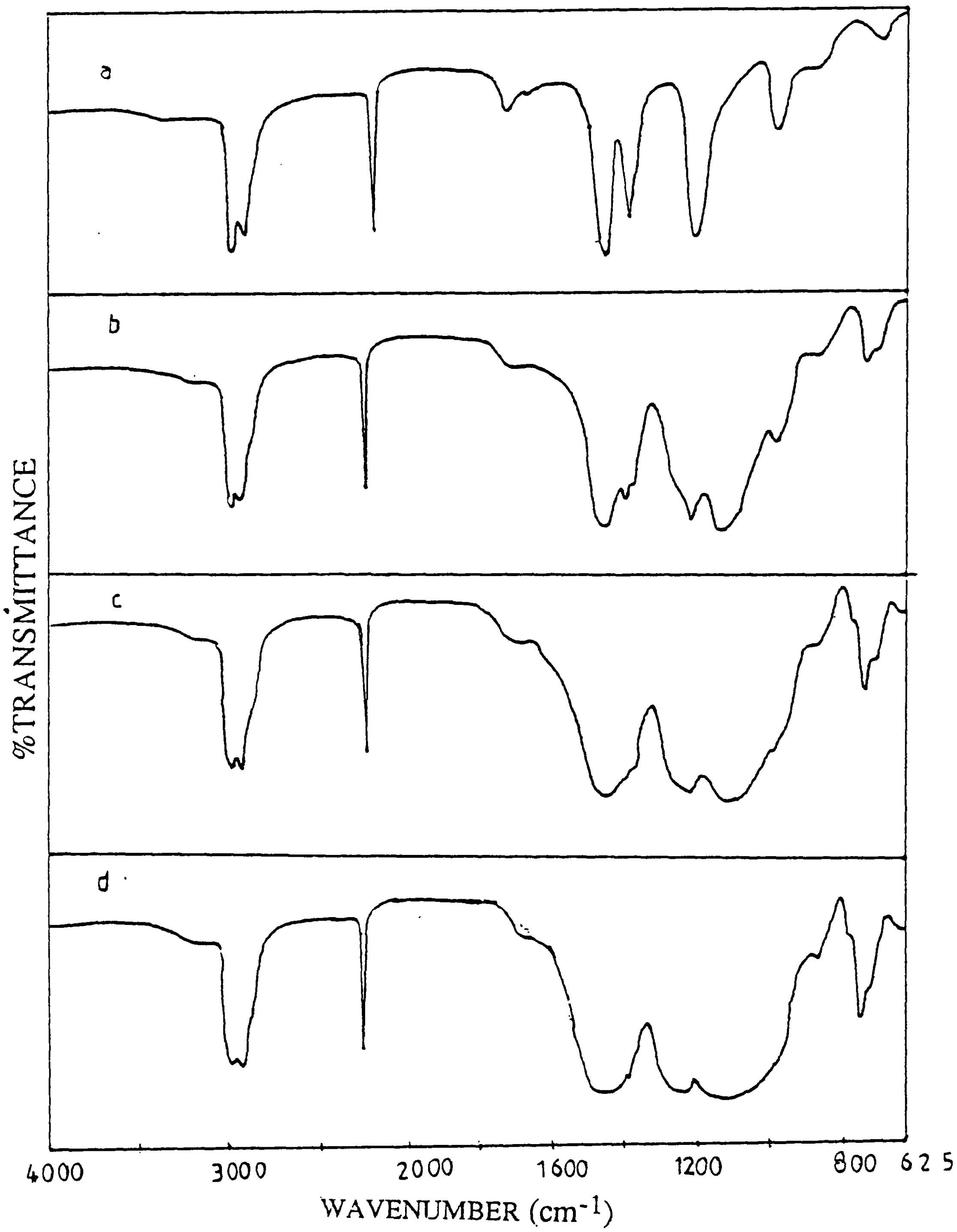


Fig. 8.11. IR Spectrum of EIPMAN 1 as a Function of Time at 180 ^oC.

(a) Undegraded.(b) Degraded fo 1 hours.(c) Degraded fo 2 hours
(d) Degraded fo 3 hours.

deformation for naphthyridine type of extensively aromatised fused ring structures.

The bands centred at 736 and 765 cm^{-1} are also noticeable in some fused ring aromatic compounds (e.g. pentacene[104]) with structure quite comparable with above mentioned structures.

Some of the above mentioned type of aromatised fused ring nitrogen containing structures have also been identified during mass spectrometric studies of the cold ring fractions from various MAN polymers and copolymers capable of colouration (see Chapter Six and Seven), and are also reported[99] to be present in thermally stabilised PAN.

In the present investigations, it has been confirmed that colouration in the methacrylonitrile polymer can only be initiated from some well defined impurity (present inside the polymer chain or at the chain-end), and the colouration is directly proportional to the number of initiating centres. It has been also observed that when the initiating centres (methacrylic acid units) are present in abundance, a side reaction (dehydration of adjacent methacrylic acid units in the chain) also occurs in degradation of film samples, resulting in the formation of anhydride structures.

Table 8.2 summarises the tentative peak assignments for the IR spectra of thermally degraded coloured methacrylonitrile polymers and copolymers

TABLE 8.2. Assignments For The Infrared bands Present in TheIR Spectra of Various Thermally Degraded End-initiated Methacrylonitrile Polymers and Methacrylonitrile/Methacrylic Acid Copolymers.

Freguency IR band (cm^{-1})	Intensity	Tantative Assignment
3250	w	υ(N-H)
2982	m	$\upsilon(CH_3)$
2936	m	$\upsilon(CH_2)$
2235	v	$\upsilon(C \equiv N)$
1808*	w	υ(>C=O) from acid anhydrid
1700	s	υ(>C=O) Structure [3] Scheme 8.2
1600	wm	υ(C=N) ladder structure
1568	wm	$\delta(=N-H) + \delta(N-H_2)$
1510	sh,br	υ(C=C) of polyene + $\delta(N-H_2)$
1468	s	$\delta(CH_2)$
1454	s	$\delta_a(CH_3)$
1395	s	$\delta_s(CH_3)$
1371	s	$\gamma_w(CH_2)$
1273	s	$\gamma_t(CH_2)$?
1215	s	$(CH_2)_2-C(CH_3)(C=N)$ Tertiary carbon distortion or backbone skeletal
1150	vs	$\gamma_t(CH_2)$; or mixed mode $\gamma(C-N) + \gamma(N-H)$?
737 & 763	m s	δ(=C-H) out of plane deformation for proposed naphthyredine type structure

Keys: Relative intesities: m = medium, s = strong, sh = shoulder, w = weak

Modes: υ = Stretching, υ_a = Asymmetric stretching, υ_s = Symmetric stretching, δ = bending, δ_a = Asymmetric bending, δ_s = Symmetric bending, γ_t= twisting, γ_w= wagging

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