A THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

THE THERMAL DEGRADATION OF POLYMER BLENDS OF POLYACRYLONITRILE

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SUMMARY

The introductory chapter reviews both general aspects of polymer degradation and, in more detail, the relationships between the chemical structure and thermal stability of vinyl polymers. A brief description of polymer blends and their usage is given together with a survey of recent work upon the thermal behaviour of such systems.

Chapter 2 summarizes the experimental aspects of the work. The first section deals with the preparation and purification of polymers used in subsequent chapters. The second part described the thermal analysis techniques and procedures which were used in examination of both polymers and polymer blends.

The thermal degradation of polyacrylonitrile and of blends of polyacrylonitrile and polymethylmethacrylate is studied in detail in Chapter 3. The decomposition of polymethylmethacrylate is shown to undergo significant changes upon blending. The effect has been found to vary with blend composition and has been attributed to reaction with gaseous volatiles evolved from polyacrylonitrile decomposition.

The rate of coloration and thermal degradation of nitrile polymers has been previously shown to be influenced by both the nature and amount of initiating structures either within the polymer chain or present as additives. In Chapter 4 the degradation of polyacrylonitrile in the presence of chlorinated polymers is found to be similarly influenced and in each system examined separation of the exothermic nitrile oligomerization process from chain scission reactions is evident.

In Chapter 5 polyacrylonitrile blends containing polystyrene and polymethylacrylate are studied. Molecular mass results obtained after isothermal degradation of the blends reveal a reduction in chain scission which is consistent with a reduction in intermolecular chain transfer reactions between degrading polystyrene and polymethylacrylate.

The thermal behaviour of both polymethacrylonitrile and blends of polyacrylonitrile and polymethacrylonitrile is examined in Chapter 6. The results of blend degradation indicate nitrile oligomerization to occur in polymethacrylonitrile accompanied by a reduction in the evolution of methacrylonitrile.

A range of methylmethacrylate-methacrylamide copolymer compositions is discussed in Chapter 7. Thermal decomposition is shown to result in cyclization reactions between adjacent comonomer units which effectively reduces the methacrylate monomer yield. Similarities are drawn between copolymer behaviour and polymethylmethacrylate degradation in the presence of polyacrylonitrile.

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CONTENTS

PAGE

CHAPTER 1 INTRODUCTION 1

1.1 GENERAL ASPECTS OF POLYMER DEGRADATION 1

1.2 THERMAL DECOMPOSITION OF VINYL POLYMERS 2

1.3 POLYMER BLENDS 9

1.4 THERMAL DEGRADATION OF POLYMER BLENDS 10

CHAPTER 2 EXPERIMENTAL PROCEDURE AND TECHNIQUES OF THERMAL ANALYSIS 12

2.1 PREPARATIVE METHODS 12

2.2 TECHNIQUES OF THERMAL ANALYSIS 17

2.3 COMPARISON OF UNMIXED AND MIXED SYSTEMS 26

2.4 ANALYSIS OF DECOMPOSITION PRODUCTS 30

CHAPTER 3 THE THERMAL DEGRADATION OF POLYACRYLINITRILE-POLYMETHYL METHACRYLATE BLENDS 33

3.1 INTRODUCTION 33

3.2 THE THERMAL DECOMPOSITION OF POLYACRYLONITRILE 35

3.3 POLYMER SAMPLE HISTORY 38

3.4 THERMAL VOLATILIZATION ANALYSIS OF POLYACRYLONITRILE 40

3.5 THERMAL VOLATILIZATION ANALYSIS OF POLYMETHYL-METHACRYLATE 46

3.6 ANALYSIS OF BLEND DECOMPOSITION BY TVA 47

3.7 THERMOGRAVIMETRY 56

3.8 DIFFERENTIAL THERMAL ANALYSIS 63

3.9 INFRA RED ANALYSIS OF VOLATILE PRODUCTS 64

3.10 INFRA RED ANALYSIS OF COLD RING FRACTION AND RESIDUE 70

3.11 ANALYSIS OF LIQUID PRODUCTS BY GLC 78

PAGE

3.12 STRUCTURAL CHANGES IN THE POLYMER BLEND 81

3.13 THE EFFECT OF NH_3 AND HCN UPON PMMA DECOMPOSITION 85

3.14 DISCUSSION 88

CHAPTER 4 THE THERMAL DEGRADATION OF BLENDS OF POLYACRYLONITRILE WITH CHLORINATED POLYMERS 92

4.1 INTRODUCTION 92

4.2 THERMAL DECOMPOSITION OF PVC 92

4.3 THERMAL DECOMPOSITION OF COPOLYMERS OF ACRYLONITRILE WITH CHLORINATED COMONOMERS 96

4.4 POLYMER SAMPLE HISTORY 97

4.5 RESULTS 98

4.6 DISCUSSION 127

CHAPTER 5 THE THERMAL DEGRADATION OF POLYACRYLONITRILE BLENDS CONTAINING (A) POLYSTYRENE (B) POLYMETHYLACRYLATE 130

5.1 INTRODUCTION 130

5.2 POLYMER SAMPLE HISTORY 130

5.3 POLYACRYLONITRILE–POLYSTYRENE BLENDS 131

5.4 RESULTS 132

5.5 DISCUSSION 138

5.6 POLYACRYLONITRILE–POLYMETHACRYLATE BLENDS 142

5.7 RESULTS 143

5.8 DISCUSSION 150

CHAPTER 6 THE THERMAL DEGRADATION OF (A) POLY-METHACRYLONITRILE (B) POLYMETHACRYLONITRILE POLYMER BLENDS 151

6.1 INTRODUCTION 151

6.2 POLYMER SAMPLE HISTORY 152

PAGE

6.3 THE THERMAL DEGRADATION OF POLYMETHACRYLONITRILE 152

6.4 DISCUSSION 162

6.5 THE THERMAL DEGRADATION OF POLYMETHACRYLONITRILE BLENDS:- POLYACRYLONITRILE-POLYMETHACRYLONITRILE BLENDS 165

6.6 THE THERMAL DEGRADATION OF POLYMETHACRYLONITRILE-POLYVINYLCHLORIDE BLENDS 171

6.7 DISCUSSION 173

CHAPTER 7 THE THERMAL DEGRADATION OF METHYLMETHACRYLATE-METHACRYLAMIDE COPOLYMERS 176

7.1 INTRODUCTION 176

7.2 POLYMER SAMPLE HISTORY 177

7.3 RESULTS 179

7.4 DISCUSSION 196

CHAPTER 8 GENERAL CONCLUSIONS 198

APPENDIX 200

REFERENCES 202

CHAPTER 1

INTRODUCTION

1.1 GENERAL ASPECTS OF POLYMER DEGRADATION

The term 'degradation', when applied to polymers, is normally associated with a deterioration in the physical or chemical properties of the polymer. This may arise through interaction with a number of possible agencies and can be generally classified as primarily thermal, oxidative, solvolytic, radiation or mechanical degradation. Polymer degradation is often the result of the combined influence of several of these agencies, particularly during processing and also in later commercial use. Qualitative or quantitative determination of the contribution of each, when acting together, is an almost impossible task and has, therefore, resulted in studies of the effect of a single agency under carefully controlled conditions.

Of the various modes of degradation, thermal decomposition has been the most extensively studied due mainly to its occurrence during processing and also to the useful relationships which can be derived between the thermal stability of a polymer and detailed aspects of its chemical structure[1,2]. In addition, the demands of modern technology have stimulated considerable research effort into the development of materials with good retention of physical properties at temperatures in excess of 300°C which has further helped to define the criteria governing molecular structure and stability[3].

It is not possible to generalize the variations in thermal stability observed throughout the wide range of both natural and synthetic polymers at present in use and discussion in this chapter will, therefore, concentrate on vinyl polymers of the general structure - $(CH_2-CXY)-_m$, where X and Y can be hydrogen or a functional group, which form the basis of the present study.

1.2 THERMAL DECOMPOSITION OF VINYL POLYMERS

The chemical structure of the repeating unit is clearly of importance in determining the thermal stability and mode of decomposition of any polymer yet comparative studies of the decomposition of model compounds often reveal polymeric materials to be considerably less stable than one might predict[4]. The products of decomposition may often be similar to those expected yet the temperature at which the polymer degrades may well be as much as 200°C lower than estimated as can be found in PVC decomposition[4]. This behaviour typifies polymer decomposition and arises principally through the incorporation of labile defect structures within the molecule and because chain processes can often occur in the polymer chain environment.

The thermal degradation of polymers may be divided into two broad groups - (A) reactions involving chain scission, and (B) substituent or non chain scission reactions. The former result in monomer or chain fragment formation while the latter often result in the elimination of small molecules from the chain leaving a chemically modified residue. Examples of both types of behaviour are included in this study and it is, therefore, appropriate to examine briefly their principal features:

CHAIN SCISSION REACTIONS

Chain scission is the predominant process during the decomposition of poly-methyl methacrylate (PMMA), polypropylene (PP) and polyethylene(PE) and occurs to varying extents in a number of other addition polymers.

It is found, however, that whereas PMMA decomposition results in almost quantitative monomer formation, both PP and PE give little monomer, the products being mainly olefinic chain fragments. These two extremes of behaviour may be interpreted in terms of a single free radical reaction mechanism which may be represented as follows:[5]

RANDOM INITIATION $M_n \xrightarrow{Ki} M_j^{\bullet} + M_{n-j}^{\bullet}$

TERMINAL INITIATION $M_n \xrightarrow{Ki} M_{n-1}^{\bullet} + M^{\bullet}$

DEPROPAGATION $M_i \xrightarrow{Kd} M_{i-1}^{\bullet} + M$

TRANSFER $M_i^{\cdot} + M_n \xrightarrow{Kf} M_i + M_n^{\bullet}$

SCISSION $M_n \xrightarrow{Ks} M_j^{\bullet} + M_{n-j}$

TERMINATIONS $M_i + M_j \xrightarrow{Kt} M_i + M_j$ or M_{i+j}

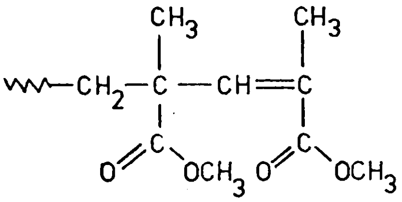
where n is the chain length of the starting material and M_i, M_j and $M_i^{\bullet}$, $M_j^{\cdot}$ represent respectively 'dead' polymer molecules and long chain radicals.

Thus PMMA exhibits depropagation to monomer in the absence of transfer reactions while both PE and PP decomposition, transfer reactions will predominate. The absence of the depropagation step in the latter is shown by its low yields of monomer obtained. In this way Simha and Wall[5] have shown that both modes of decomposition and those lying between the two extremes may be interpreted as dependent upon the relative importance of the depropagation and transfer steps occurring in the polymer. Depropagation will lead to a gradual reduction in molecular weight accompanied by high yields of monomer, whereas transfer reactions, which normally involve H abstration, result in a rapid reduction in molecular weight and the formation of chain fragments containing a number of monomer unit.

EFFECT OF POLYMER STRUCTURE UPON DEPOLYMERIZATION

The importance of labile structures within the polymer molecule has already been mentioned with respect to PVC decomposition in which initiation may occur at a number of chemically different structures which include chain end groups, random unsaturation and branching within the polymer[6]. The relative stability of each of these is examined in Chapter 4.

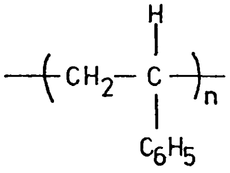
The depolymerization of PMMA is similarly influenced by labile structures whose concentration is dependent upon the polymerization conditions employed[7]. Thus, where termination of free radical propagation occurs through disproportionation reactions, the chain end so formed is unstable relative to the remainder of the chain. The unsaturated chain end is illustrated below:-



The strength of bonds in the position with respect to the unsaturation is reduced by the resonance energy of the allylic radical formed by their scission. In this way the rate of depolymerization will be dependent upon chain end concentration and hence inversely proportional to molecular weight.

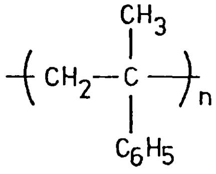
A clear relationship has been shown to exist between the chemical structure of a polymer and the proportion of monomer in the degradation products. This may be ascribed to the balance between unzipping of the initially formed macroradical and fragmentation since the extent of the latter process is dependent upon chain transfer reactions. Increasing the substitution in the polymer chain reduces the potential number of transfer sites by shielding the chain from radical attack.

This behaviour is best exemplified by comparison of polystyrene (PS) (a) and poly α methyl styrene (PαMS) (b):-



$$-\!\left(CH_2-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle C_6H_5}{|}}{C}}-\right)_n$$

(a)



$$-\!\left(CH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle C_6H_5}{|}}{C}}-\right)_n$$

(b)

Chain transfer reactions are reduced by replacement of the tertiary hydrogen atom in PS by an additional methyl group with the result that monomer yield can be increased from around 40% in PS at 300-400°C to almost 100% in PαMS.

In general, highly substituted radicals are more stable electronically and thus less likely to attach C-H bonds. Steric hindrance to the approach between radical and polymer chain must also increase with both substitution and the bulk of the substituent. Therefore tertiary radicals may be expected to be least active in transfer reactions, while primary radicals are most active and therefore tend to reduce the monomer yield.

SUBSTITUENT REACTIONS

Substituent reactions will occur in any given system only if they can be initiated at temperatures lower than that at which chain scission takes place. Thus such reactions are normally observed at relatively low temperature since thermal depolymerization seldom takes place below 200°C. Substituent reactions may be classified into three main types -

(a) Elimination reactions

(b) Ester decomposition

(c) Cyclization reactions

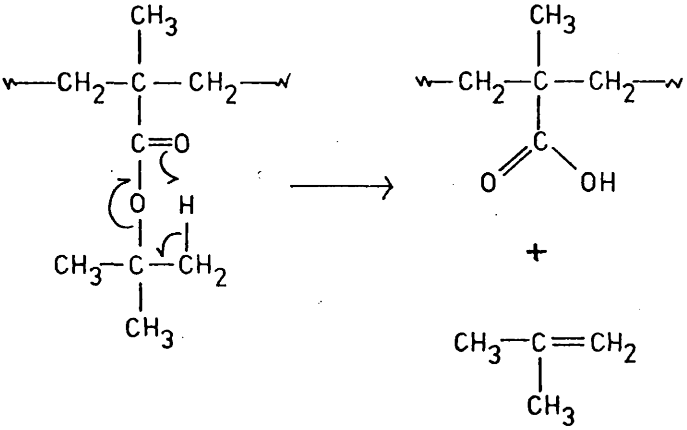
Type (a), as illustrated by PVC, involves the elimination of HCl producing a conjugated polyene chain[6] -

$$-CH_2-CHX-CH_2-CHX- \longrightarrow -CH{=}CH-CH{=}CH- \quad +HX$$

This can also be found to occur where X = OH, Br or $-O-\underset{\underset{O}{\|}}{C}-CH_3$ respectively.[8]

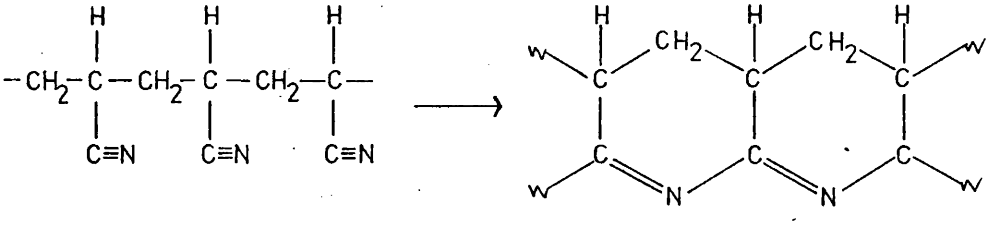
Most detailed studies of this type have been concerned with PVC decomposition and yet the mechanism remains very much in doubt. It has been variously suggested that the reaction is radical, molecular and ionic with evidence to support each [6,9]. The radical mechanism appears to be favoured by most workers but neither autocatalysis by HCl nor the interactions of stabilizers can be satisfactorily explained by it.

Ester decomposition reactions, involving the production of parent acid together with an olefin, have been found to occur in ester polymers, as in short chain ester pyrolysis. The process is exemplified by the pyrolysis of poly (t-butyl methacrylate) which involves the formation of a poly (methacrylic acid) residue with the evolution of butene[10] -



Ester decomposition is typical of other polymethacrylates containing a β H atom in the alcohol residue. This reaction is also found to occur during polhmerization of n-butyl methacrylate effectively producing copolymers containing small amount of methacrylic acid.[11]

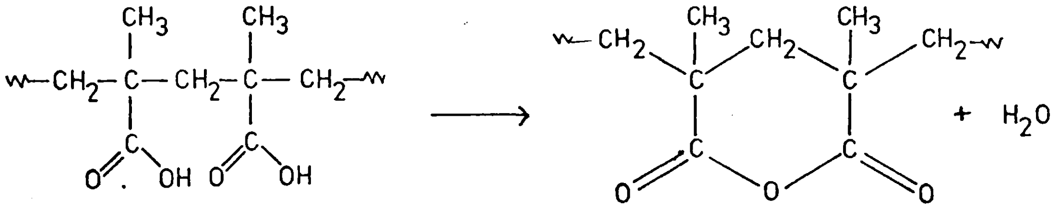
Cyclization reactions between adjacent pendant groups in the polymer chain are a significant feature of the present study since they form the predominant mode of decomposition in polyacrylonitrile (PAN) itself^{12} -



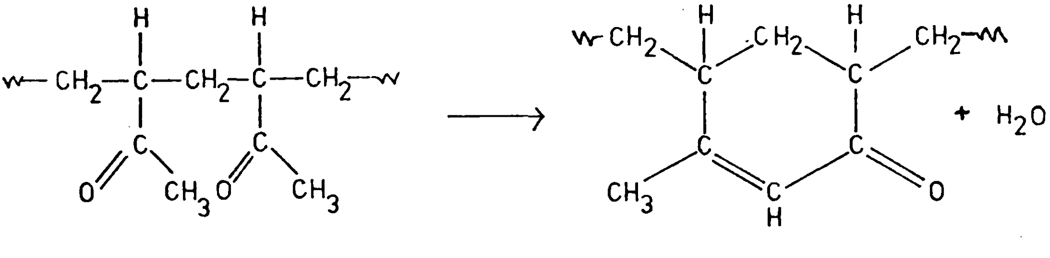
As in the previous examples of elimination reactions, this too results in a conjugated structure, chemically different from the initial polymer although the evolution of small molecules does not occur.

Other examples illustrating cyclization accompanied by elimination are found in both poly (methacrylic acid) decomposition (A) and also that of poly (methyl vinyl ketone) where H_2O is the eliminated product^{13,14} -

(A)



(B)



Thus the result of substituent reactions, of all three types, is a structurally different polymer containing cyclic or conjugated sequences or both as in PAN. In both elimination and cyclization reactions, extensive cross linking may also occur resulting in decreased solubility of the product. Although most substituent reactions drastically alter the solubility of the polymer, it is not an unavoidable consequence of this type of reaction as shown by the behaviour of methacrylonitrile-methacrylic acid copolymers of low acid content which remain soluble although intensely coloured as a result of extensive intra molecular cyclization[15]. The decomposition of methacrylonitrile-methacrylic acid copolymers also exemplifies the effect of combined substituent and depolymerization processes. Methacrylonitrile is a 1:1 disubstituted monomer for which the predominant mode of decomposition of the pure polymer is depolymerization. The incorporation of relatively small amounts of methacrylic acid, which result in low temperature cyclization reactions, has been shown to be very effective in reducing the monomer yield by blocking the depropagation process.

The ultimate aim of studies of degradation is the prediction of the thermal stability of a polymer, given its chemical constitution. It is evident from the foregoing considerations that this stability is dependent on a number of structural factors beyond simple extrapolation of the behaviour of model compounds. Structural abnormalities can arise during the polymerization process or through incorporation of trace amounts of impurities. The conditions of polymerization and the monomer history may, therefore, have a profound influence upon thermal stability.

It is also generally true that extrapolation of the behaviour of homopolymers is unsatisfactory in trying to predict the behaviour of the corresponding copolymers or polymer blends. Copolymer decomposition studies have demonstrated that degradation of a polymer molecule can be modified considerably by the presence of quite a small proportion of a second monomer unit in the chain and in a similar manner mixing of homopolymers can give rise to further differences[16,17,18]. It is clearly of interest, therefore, to attempt to rationalize the differences betwen each system.

1.3 POLYMER BLENDS

Polymer blends are physical mixtures of structurally different homopolymers or copolymers. The commercial use of such blends allows their classification into two principal types - homogeneous systems where one of the polymers acts as a plasticizer, and heterogeneous, where one acts as a toughening agent.

The commercial significance of polymer blends is the way in which a physical property may be improved with a minimum sacrifice of other properties. Among the best examples of homogeneous blends are those of polymeric oils with PVC, which allow processing of the blend at lower temperatures, thereby minimising the risk of PVC decomposition. This system does not suffer the disadvantages associated with low molecular weight plasticisers which are both volatile and have a more pronounced effect upon the Tg of the blend.

High impact plastics probably form the majority of commercially available blends. Heterogeneous blends of polystyrene with natural or synthetic rubbers have resulted in 'engineering plastics' which combine both oughness and stiffness with the ease of fabrication characteristic of thermoplastics. It is evident that the physical properties of polymer blends have been of greatest interest in developing their applications. Comparatively little research has involved the effect of mixing of polymers upon thermal stability.

Copolymer decomposition studies have shown that the degradation of a polymer molecule can be modified by the presence of a second foreign monomer unit in the chain and it is therefore of interest to establish the effect, if any, which the presence of a second polymer may have upon the degradation of a polymer molecule.

1.4 THERMAL DEGRADATION OF POLYMER BLENDS

Much of the previous work upon the thermal decomposition of polymer blends has concentrated on PVC compositions. Thus Barlow, Lehrle and Robb[19] in comparisons between PVC/PMMA blends and the corresponding copolymers have shown the former to be more stable. In addition, Zutty and Welch[16] have found methyl chloride as an additional product of decomposition to those from the two homopolymers, thus providing further evidence of interactions between the two degrading polymers.

A detailed study of PVC/PMMA blends by McNeill & Neil[17,18] has further shown that PVC decomposition is responsible for an initial acceleration in PMMA 'unzipping'. The evidence obtained from this system has been used by the same authors as support for the free radical scheme of PVC decomposition which will be outlined in a later chapter.

Other blends which have been examined include those of polypropylene. Mucha and Kryszewski[20] have examined polypropylene-polyethylene blends by thermogravimetry demonstrating their increased stability relative to pure polypropylene. Mizutani[21], however, has shown polypropylene decomposition to be accelerated in the presence of vinyl polymers such as polystyrene or poly(methyl methacrylate), while the formation of graft or block copolymers could also be detected.

Richards and Salter[22] have demonstrated that initiation of polystyrene decomposition can be induced at lower temperatures by blending with poly methyl styrene. The latter decomposes at a lower temperature than polystyrene with the resultant radical activity believed to be responsible for initiation of polystyrene decomposition through intermolecular transfer reactions.

POLYACRYLONITRILE BLENDS

There are few recorded studies of polyacrylonitrile blends. The oxidative thermal degradation of PAN-acetyl cellulose mixtures was studied by Vasile[23]. It was found that the energy of activation for the decomposition of the polymer blends was a function of their composition, and differed considerably from the results obtained by extrapolation of the values for the two components, indicating that some form of interaction was occurring.

Mucha and Kryszewski[20] have examined polyacrylonitrile-polyvinylidene chloride mixtures by thermogravimetry. The blends were found to be less stable than the respective homopolymers, both activation energy and reaction order again varying with blend composition.

It is thus evident that the mixing of polymers can give rise to significant differences in polymer stability. The primary object of this study is, therefore, an investigation of the thermal decomposition of polymer blends, and in particular those containing polyacrylonitrile. It is hoped that any interactions which occur may also provide useful information about the mechanisms of degradation of the constituent homopolymers.

CHAPTER 2

EXPERIMENTAL PROCEDURE AND TECHNIQUES OF THERMAL ANALYSIS

2.1 PREPARATIVE METHODS

PURIFICATION OF MONOMERS

Acrylonitrile monomer (Hopkin and Williams Ltd.) contained no inhibitor as dissolved oxygen is an effective inhibitor of polymerization. The monomer was dried over calcium hydride before distillation twice under vacuum, the first and last fractions being discarded in each case.

Methyl methacrylate (Hopkin and Williams Ltd.) and styrene (BP Chemicals International Ltd.) were purified by washing with dilute alkali, to remove inhibitor, then with distilled water before drying over calcium chloride. The monomers were distilled under vacuum before polymerization.

Methylacrylate was obtained stabilized by inhibitors of the hydroquinone type. It was dried over calcium hydride for twentyfour hours to remove any water present. The inhibitor was removed by twice distilling in vacuo.

Methacrylonitrile (Eastman Kodak) was washed with dilute alkali to remove inhibitor (0.01% hydroquinone), followed by distilled water. After drying over calcium chloride for one day it was then dried over calcium hydride before vacuum distillation.

Methacrylamide (Aldrich Chemical Co.) was recrystallized twice from hot toluene before drying under vacuum.

PURIFICATION OF INITIATORS

Azobisisobutyronitrile (Eastman Kodak) was purified by twice recrystallizing from ethanol, the solution being filtered hot to remove insolubles which are polymeric materials derived from decomposition of the initiator.[24] The crystals were filtered off and dried under vacuum.

Benzoyl peroxide (BDH) was supplied stabilized by 30% by weight of water. The initiator was dissolved in the minimum volume of chloroform and the aqueous layer removed before pouring the solution into methanol. The fine crystals which separated were then dried under vacuum.

Sodium napthalene A sample of PMMA was prepared by anionic polymerization at -78°C using a sodium napthalene solution as initiator. The method of preparation was substantially that used by Scott.[25] Redistilled tetrahydrofuran was stoved over calcium hydride for twentyfour hours before final distillation under dry nitrogen into a reaction vessel containing a weighed amount of napthalene. An excess of sodium was then added to the mixture which was stirred under dry nitrogen for two hours during which a deep green solution of the sodium napthalene complex formed. The solution was stoved under dry nitrogen in a light proofed flask. The initiator was standardized by titration against a standard HCl solution using methyl red indicator.

POLYMERIZATION TECHNIQUES

With the exception of the anionic sample of PMMA all polymers were prepared by free radical initiation. These polymerizations were carried out in Pyrex glass dilatometers, with calibrated stems. A weighed amount of solid initiator was added and washed into the tube with Analar acetone. The acetone was then removed under vacuum. The liquid monomers were degassed three times under vacuum using standard procedure before distillation from a graduated reservoir into the dilatometer. The dilatometer was then sealed under a vacuum of better than 10^{-5}m.m. Hg. Polymerizations were carried out in a thermostat tank controlled to ± 0.01°C. The volume contraction during polymerization was followed in order to restrict conversion to around 10% in homopolymers and 5% in copolymer systems.

Several samples of polymethacrylonitrile were prepared by photosensitized polymerization at 25°C using an Osram 125 watt mercury vapour lamp. Both azobisisobutyronitrile and benzoyl peroxide were used as initiators while a silica glass dilatometer was used to ensure more efficient UV transmission.

For the anionic polymerization of methyl methacrylate, 2 ml. of a 0.1M solution of sodium napthalene was added to 150 ml. of THF freshly distilled after drying for twentyfour hours over CaH_2. The mixture was stirred continuously under a dynamic nitrogen atmosphere and cooled to -78°C. Purified methyl methacrylate monomer was added over a period of a few minutes discharging the green colouration of the initiator solution. After stirring for one hour approximately 5 ml. of MeOH was added to the solution and the mixture allowed to warm to room temperature. The polymer was then precipitated by adding the solution to a large volume of methanol.

COPOLYMERIZATION: MONOMER FEED RATIOS

The molar ratios of monomers necessary to produce copolymers of the desired composition were calculated using the copolymer composition equation[26,27,28,29]

$$\frac{P_1}{P_2} = \frac{M_1}{M_2}\left(\frac{r_1 M_1 + M_2}{M_1 + r_2 M_2}\right)$$

where P1/P2 is the ratio of the molar concentration of the two monomers in the polymer and M1/M2 is the ratio of the molar concentrations of the monomers in the feed. This relationship applies if the conversion to polymer is sufficiently low for the monomer concentrations to remain unchanged; r_1 and r_2 are the reactivity ratios of the two monomers.

ISOLATION AND PURIFICATION OF POLYMERS

With the exception of polyacrylonitrile, polymers prepared as above which were soluble were isolated by precipitation in a miscible non-solvent, while polymers which precipitated during the course of polymerization were filtered from the reaction mixture before being reprecipitated and dried in vacuo.

Polyacrylonitrile is insoluble in the monomer and in most common organic solvents. N,N dimethyl formamide (DMF) is most often used as solvent. The polymer was isolated by filtering free of monomer and washing thoroughly with methanol before drying in vacuo. No attempt was made to purify the polymer further by reprecipitation from DMF as this solvent has been found to be an efficient colour initiating agent[30]. Polyacrylonitrile does not melt below coloration temperatures thus making solvent removal difficult and reducing the colour stability of the polymer.

Details of polymer sample history are given in the appropriate chapter.

PREPARATION OF POLYMER MIXTURES

Polymer blends are obtained by the mixing of two or more polymers. The mixing process is generally aided by high temperatures and by diluents or a suspending medium. Commercially melt mixing, solution blending and latex mixing are the principal methods employed[31].

In studying the properties of blends the techniques used in mixing the polymers plays an important role and is often governed by the solubility of the component polymers. The thermal stability of polypropylene blends was examined by Mizutani[21,32] after preparation as a slurry of polypropylene in a solution of the second polymer. Richards and Salter[22] in studies of poly methyl styrene-polystyrene blends prepared them by freeze drying from benzene solution. Vasile[23] investigating the oxidative thermal degradation of polyacrylonitrile-acetyle cellulose mixtures, coprecipitated the two polymers from DMF solution.

Mucha and Kryszewski[20] also utilised coprecipitation to prepare polyacrylonitrile-polyvinylidene chloride blends. McNeill and Neil[33], in studies of polymethyl methacrylate-polyvinyl chloride blends, employed both powder mixtures and also films prepared from mixed solutions in a common solvent.

In the present study polymer mixtures were studied both as fine powder mixtures capable of passing through a 0.0049"(125μ) sieve and also as cast films prepared in the same manner as that outlined by McNeill and Neil. Solvent removal from the cast films was achieved by heating the sample tube and sample in a vacuum oven at 35°C for fortyeight hours. Powder mixtures, although producing a less uniform dispersion of the two polymers, were examined particularly for comparison with the corresponding blend in film form. In this way one might determine differences which may arise not only from sample form but from residual solvent in the film samples. The latter effect, viz. that of solvents and other additives upon the thermal degradation of nitrile polymers, has been studied by a number of workers[30,34,35].

The solvent effect upon the thermal stability of PAN must always be considered when studying film samples or samples precipitated from solution because of the difficulty of solvent removal from the polymer which does not melt before degradation.

Binary mixtures of chemically dissimilar polymers generally are incompatible. The frequent occurrence of polymer incompatibility is attributed to the small entropy of mixing for large polymer molecules and a general tendency for polymers to have endothermic heats of mixing. Polymer pairs incompatible in one solvent usually are incompatible in a range of solvents consistent with the prediction that the solvent should play a secondary role in determining compatibility.

An exception to this behaviour is found in the work of Bank, Leffingwell and Thies[36] into studies of mixtures of PS and polyvinyl methyl ether. In solvents such as toluene and benzene the polymers are usually compatible while in $CHCl_3$ and CH_2Cl_2 they are incompatible. This difference persisted upon solvent evaporation. The conformation of the polymer molecule in solution, therefore, has some effect on determining compatibility.

Incompatibility in the solid state is often identified by the opaque or hazy appearance of the composite. Where a clear mixed system is obtained, on evaporation to dryness of a solution of the two components or by melt mixing, it is usually taken as a sign that the polymer pair is compatible[37]. In the present study films of polyacrylonitrile polymer mixtures cast either from DMF or DMS did not appear transparent, the opacity varying in appearance according to mixture composition.

2.2 TECHNIQUES OF THERMAL ANALYSIS

THERMAL VOLATILIZATION ANALYSIS

Thermal volatilization analysis (TVA) has been developed by McNeill[38,39] primarily for the study of the thermal degradation of polymeric systems although it is equally applicable to other materials from which volatile products are formed during thermal decomposition[40]. The technique, its development and application to a number of polymer degradations have been the subject of recent publications[33,41,42,43].

In view of the extensive use made of this technique during the course of the present study, and in particular during the investigation of the thermal stability of polymer mixtures, it is therefore appropriate to give an account of the apparatus construction and its operation.

PRINCIPLE OF TVA

Degradation of polymers under high vacuum conditions generally results in the formation of three easily separable product fractions, namely:-

A. Gaseous products

B. Products volatile at the temperature of degradation but involatile at ambient temperature

C. Polymeric residue

Thermogravimetric studies record the total weight loss due to the formation of A + B thus defining the reaction in terms of volatile and involatile products. By combining this approach with gas effluent analysis[44] one can obtain a more detailed account of the degradation processes.

TVA, allied with commonly used spectroscopic techniques, provides further information by defining the rates and pattern of evolution of the gaseous products (A) specifically, while at the same time separating the products in a way that makes subsequent examination of the volatiles, chain fragments and residue easy to carry out.

The TVA thermogram is obtained by monitoring continuously the pressure of gaseous products produced during thermal degradation under high vacuum using either isothermal or linear temperature programmed conditions. In the latter case the resultant plot is, therefore, one or rate of volatilization vs temperature. The essential features of the technique are illustrated in Fig. 2.1. The system allows measurement of the total pressure of gaseous products distilling under vacuum from the hot sample zone into the cold trap. The pirani response is directly related to the rate of volatilization of the heated sample.

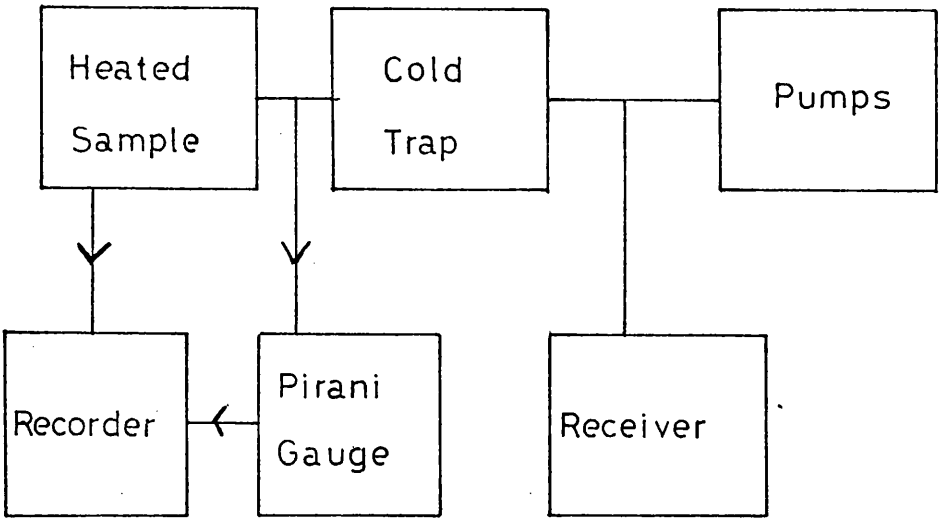


FIG. 2.1 SCHEMATIC DIAGRAM OF BASIC TVA APPARATUS

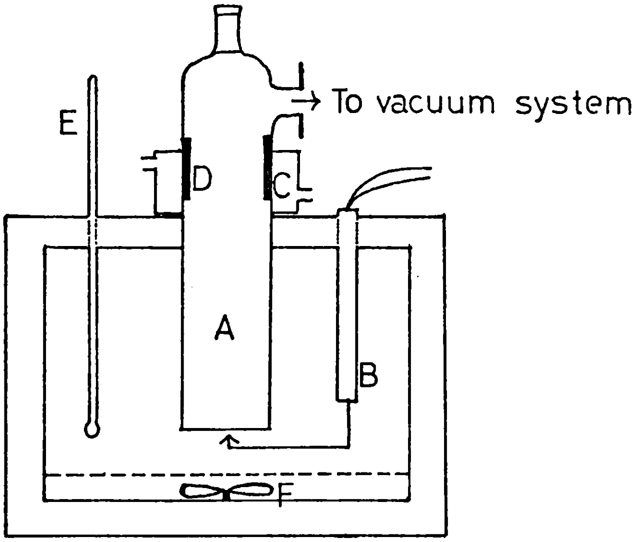


FIG. 2.2 OVEN CONSTRUCTION

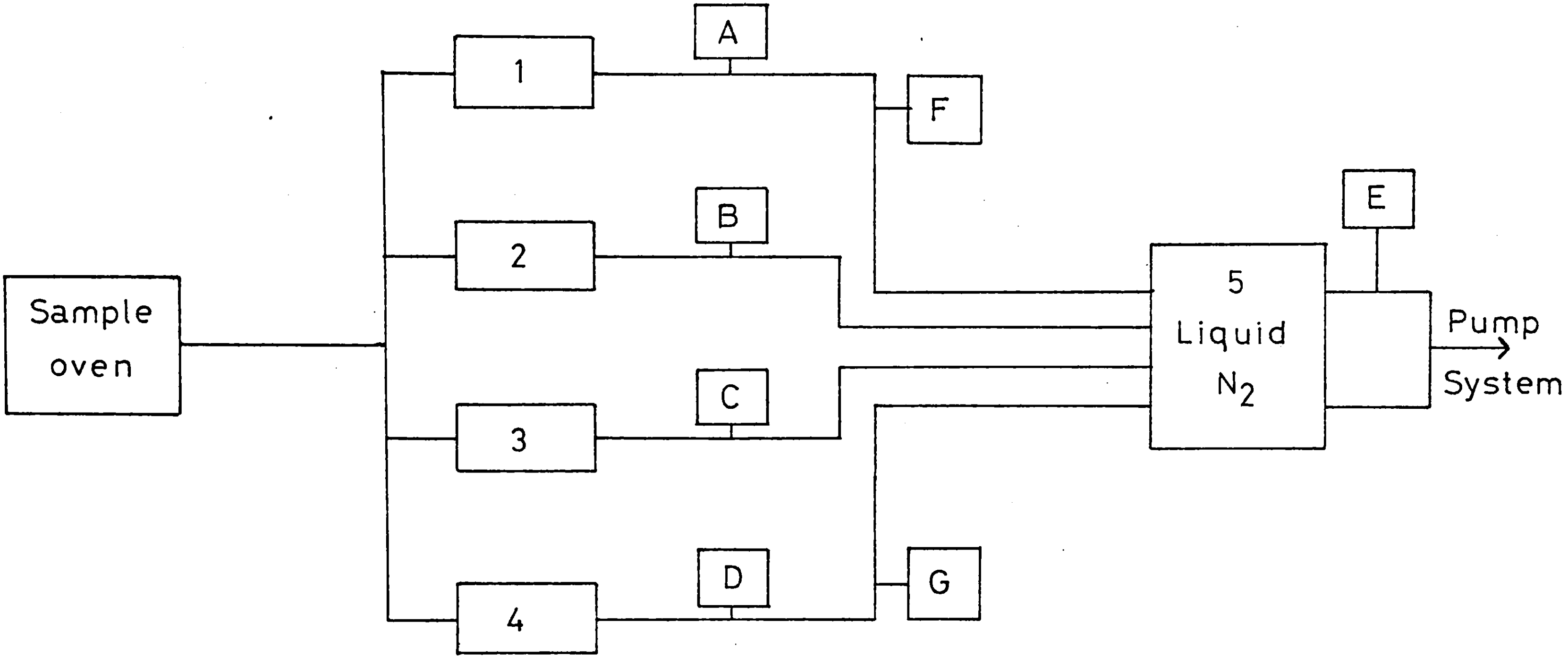
A - Degradation tube
B - Chromel alumel thermocouple
C - Cooling jacket
D - Greased quickfit joint
E - 500°C thermometer
F - Oven fan

The construction of the oven and sample container are illustrated in Fig. 2.2. The oven is an adapted Perkin Elmer F11 which can be used isothermally in conjunction with a programmer allowing linear rates of heating between 1-40°C/min. from ambient temperature of 500°C. The degradation tube is 20 cm. in length and has a cross sectional area of approximately 12 cm^2. The relatively large area of the base of the tube allowed considerable variation in sample size which may be used without alteration in sample thickness. The upper portion of the tube consists of a Quickfit 40/38 joint which is cooled by means of a water jacket. The temperature is measured in the region of the base of the tube by the chromel alumel thermocouple.

In this, the simplest form of TVA, no further information can be gained of the chemical nature of the gaseous material without recourse to spectroscopic techniques. Further refinement of the system to enable differential condensation of the products by inclusion of a series of secondary cold traps can, however, provide additional information[40,41] about the nature of the volatile products.

A schematic drawing of the Differential Condensation TVA is shown in Fig. 2.3. During the course of an experiment the gases evolved from the heated polymer sample distil to the liquid nitrogen main trap. The gases are allowed to pass along four equivalent routes, each with a secondary cold trap, usually at four different temperatures, 0, -45, -75 and -100°C respectively. Pirani gauges are used to monitor the pressure in each of the four product streams between the secondary cold trap and the common liquid N_2 trap while a fifth pirani monitors the pressure of gases beyond this trap. The responses from the five pirani gauges are transmitted via a multi gauge head unit to a Leeds Northrup twelve channel recorder where they are recorded with the output from the over thermocouple.

FIG. 2.3 TVA 4 LINE DIFFERENTIAL CONDENSATION SYSTEM



1,2,3,4	SECONDARY COLD TRAPS AT -100°C, -75°C, -45°C, 0°C
5	MAIN LIQUID N_2 TRAP, -196°C
A,B,C,D,E	PIRANI GAUGES
F,G	SAMPLE COLLECTION ADAPTORS

The resultant thermogram then illustrated the pattern of evolution of gaseous products and demonstrates the condensabilities at the five trap temperatures.

SAMPLE FORM IN TVA EXPERIMENTS

The effect of sample form on the shape of TVA thermogram was examined by McNeill and Neil[17] for samples of polystyrene, polymethyl methacrylate and polyvinyl chloride. Comparison was made of PS and PMMA samples degraded in the form of a film cast from benzene, a powder obtained by freeze drying from benzine solution, and a fine powder capable of passing through a 0.0049" mesh. It was shown that sample form was not a crucial factor in determining the shape of the TVA thermogram for either PS or PMMA. However, comparison of degradation of PVC as a film and a fine powder did show a marked change in behaviour which was interpreted as reflecting differences in the rate of diffusion of HCl in the two sample forms.

It was observed by the same workers in studies of PS degradation that the value of the maximum rate of volatilization (T max) was independent of initial sample weight over a range 1-100 mg. It was concluded that in the absence of diffusion controlled volatilization the value of T max should be independent of initial sample weight.

In many studies of polymer degradation film thickness is an important factor in determining the rate of volatilization of the heated sample. A plot of film thickness against rate of degradation by Barlow, Lehrle and Robb[45] was used to test for diffusion controlled decomposition. It was found that the rate of decomposition of PMMA and PS were diffusion controlled above a film thickness of 400 and 250Å respectively. McNeill & Neil found this effect absent in their studies using TVA, even in samples above 10^6Å thickness, ascribing the differences as due to the lower heating rates normally employed in TVA experiments and to the continuous evacuation of the system which ensures efficient product removal.

However, in TVA studies of ultra thin films McNeill & Mohammed[46] found that the T max for PS samples of less than 1 mg was displaced to higher temperatures and were led to suggest that the mechanism of degradation was a function of sample thickness. This has also been proposed in the work of Jones & Moyles[47] where it was shown that in PS degradation the yield of monomer as a percentage of total volatiles increased when extremely small samples were studied.

CALIBRATION OF OVEN THERMOCOUPLE

The oven thermocouple, since it is outwith the relatively large glass degradation tube which has a correspondingly large thermal capacity, records a higher temperature at any particular time during the degradation reaction, than the true temperature of the polymer sample. The difference between the recorded temperature and true sample temperature will, therefore, be particularly dependent upon the mass of the degradation tube and the heating rate employed. The heating rate of the tube is always lower than that of the oven.

The internal base temperature can be obtained by calibration with a second chromel alumel thermocouple whose junction is surrounded at the point of contact with the glass base by a small head of Apiezon L grease, to improve thermal contact and to simulate molten polymer[38]. The calibration plot for a heating rate of 10°C/min. is shown in Fig. 2.4 McNeill[38] found that for a particular heating rate the temperature lag was reproducible, increasing with increased rate of heating. It can be seen that the correction required decreases with increasing temperature.

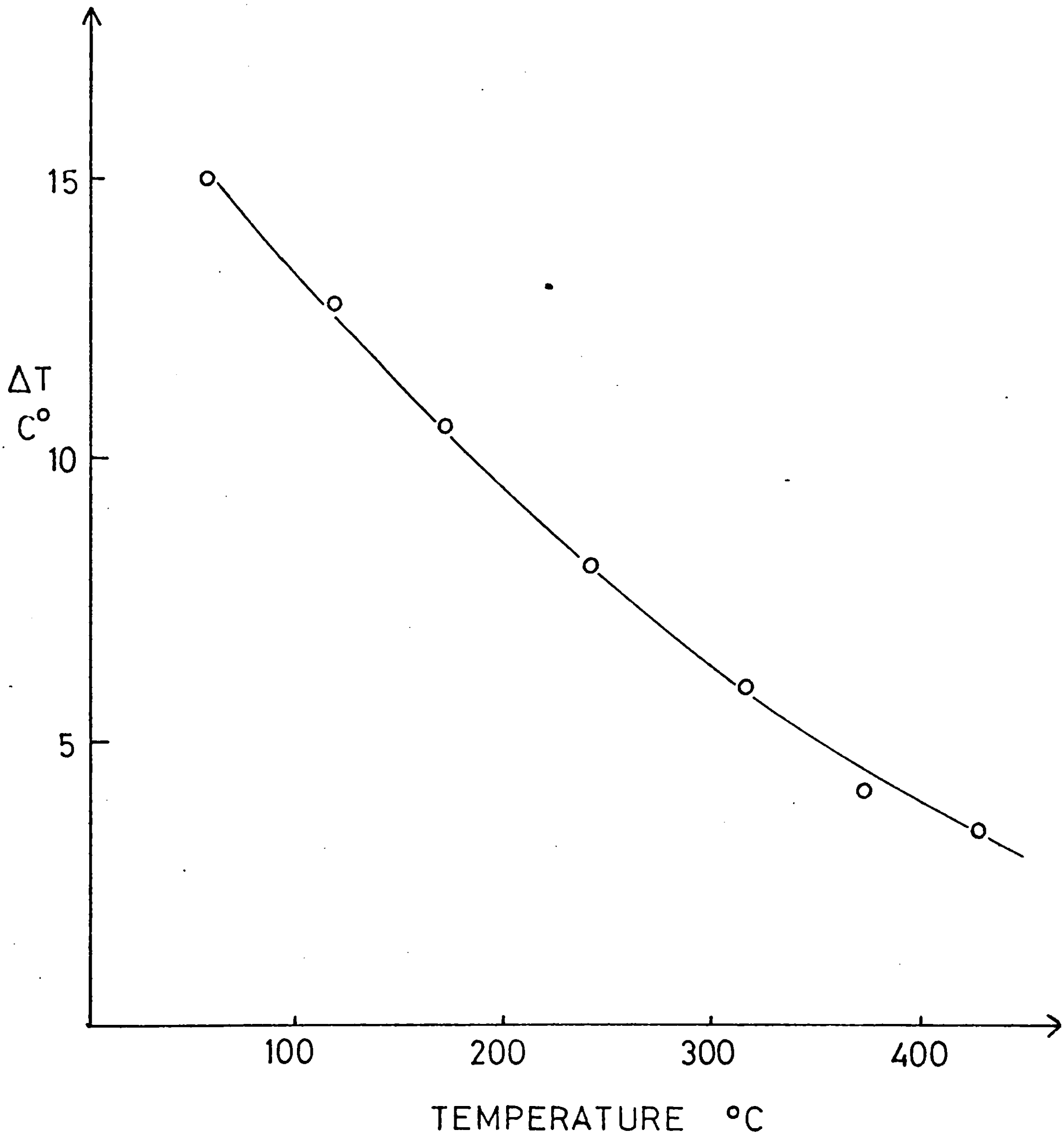


FIG. 2.4 TVA OVEN THERMOCOUPLE CALIBRATION
(HEATING RATE 10C°/min.)

In using this calibration it is assumed that the polymer sample temperature is equal to that of the base of the tube, which is reasonable considering the large mass of the tube (140 g).

PRODUCT ANALYSIS FROM TVA

Gaseous products These can be further divided into products condensed at liquid N_2 temperature (-196°C) and those volatile at this temperature. The former can be isolated in the cold traps during degradation and then distilled into a suitable receiver for subsequent analysis e.g. a combined cold trap and gas cell as described by McNeill & Neil.[48] Products which are non condensible cannot be collected under the continuous pumping conditions employed in TVA and must be collected in a closed system employing similar techniques and apparatus.

Molecular chain fragments Products of this nature collect on the upper region of the TVA tube, cooled by the water jacket, and generally consist of low molecular weight fragments which are involatile at ambient temperature and which are derived from fracture of the polymer chain. These products are often waxy, facilitating removel for infra red spectroscopy either in the form of a smear on a halide disc or by using a tissue moistened by an appropriate solvent which can then be extracted enabling a solution spectrum to be run.

Polymer residue Infra red analysis may be carried out by incorporation into a KBr pellet when the residue is insoluble. Spectra may be obtained from soluble residues either from solutions or as films cast on an NaCl disc. Molecular weight determination and UV analysis are also feasible in the case of soluble residues.

2.3 COMPARISON OF UNMIXED AND MIXED SYSTEMS

Comparison of the thermal stability of polymer blends with the unmixed homopolymers by thermogravimetry was achieved by obtaining TG curves for known weights of the homopolymers and the mixture to determine whether the result was consistent with that expected from sample 'addition' of the curves for the two homopolymers.

A similar approach was employed by Grassie, McNeill and Cooke[51] in TVA studies of polymethyl methacrylate-polystyrene blends. Difficulties encountered by this method arise from the non linearity of the pirani gauge response and differences in gauge response to similar amounts of chemically different substances. This resulted in the adoption of the technique described by McNeill & Neil which allows simultaneous degradation of unmixed polymer systems.

The modified TVA degradation tube is illustrated in Fig. 2.5 The base of the tube consists of two limbs of equal volume in which measured amounts of polymer can be added either in solution or in the form of a powder. Comparison between mixed and unmixed degradation can then be made using the same total weight of polymers, the mixture being equally divided between the two limbs of the degradation tube. The same tube was used in both mixed and unmixed samples and could be calibrated in a similar manner to that previously described.

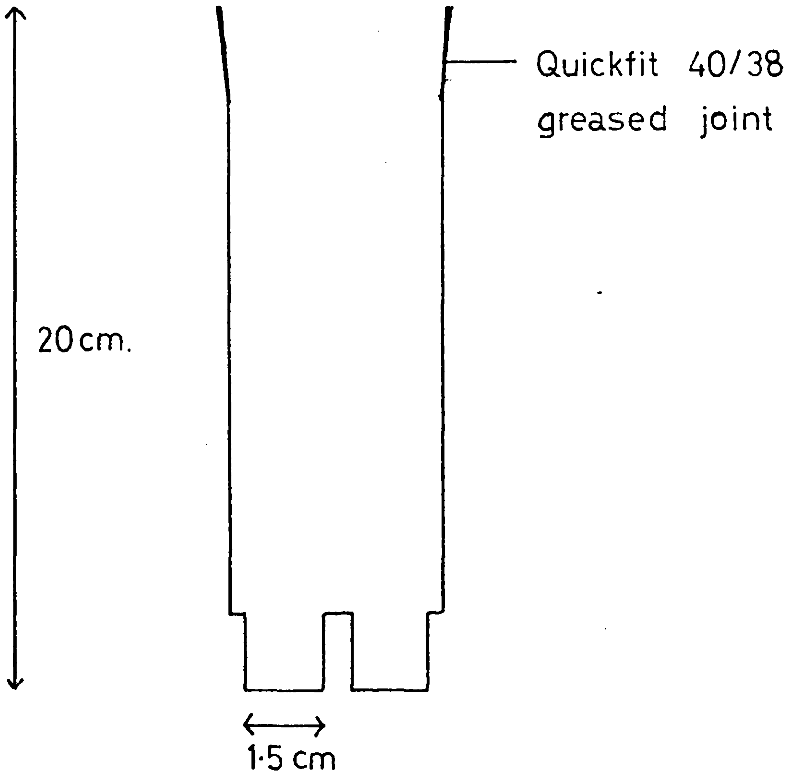


FIG. 2.5 TWIN LIMBED DEGRADATION TUBE FOR COMPARISON OF MIXED AND UNMIXED POLYMER SAMPLES

THERMOGRAVIMETRY

Thermograms of both homopolymers and polymer mixtures were obtained using a Du Pont 950 Thermobalance. The design of this instrument and in particular the dimensions of the platinum sample boat (1x0.5x0.25 cm) restricts sample analysis mainly to powder samples.

Sample sizes of up to 10 mg were degraded to 500°C in a dynamic nitrogen atmosphere (80 ml/min.). A standard heating rate of 10°C/min. was adopted in this and the other techniques of thermal analysis.

DIFFERENTIAL THERMAL ANALYSIS AND DIFFERENTIAL SCANNING CALORIMETRY

A Du Pont 900 Thermal Analyzer was used with the appropriate modules for DTA and DSC.

DTA Finely ground polymer samples were weighed accurately into a small glass sample tube (25 mm x 4 mm) and a chromed alumel thermocouple positioned centrally within the packed polymer mass by means of a ceramic sleeve. The reference junction was similarly incorporated in an equivalent mass of fine glass beads. Both sample and reference tubes were contained in a heater assembly through which nitrogen was passed at a flow rate of 0.5 litre/min. A standard heating rate of 10°C/min. was employed.

DSC DSC is related to DTA measuring the differential energy required to maintain a sample and inert reference at the same temperature throughout programmed heating of the sample. The area under the curve so produced can, therefore, be equated to the heat of reaction by suitable calibration of the DSC cell.

Calibration of the DSC cell in the temperature range of primary interest was achieved using the known heats of fusion of the metals In, Sn, Bi and Zn. The calibration coefficient is given by the equation :-

$$E = \frac{\Delta H\, Wa}{A \Delta Ts\, Ts}$$

where E - calibration coefficient

ΔH - latent heat of fusion

A - area under curve

ΔTs - Y axis scale $^{\circ}$C/inch

Ts - X axis scale $^{\circ}$C/inch

The results of this calibration are given below:-

TABLE 2.1 DSC CELL CALIBRATION

Metal	M.Pt. $^{\circ}$C*	ΔH cal/g*	E
In	156	6.8	146
Sn	232	14.4	153
Bi	271	12.0	165
Zn	419	24.4	178

* Handbook of Chemistry & Physics 54th Edition, 1973-74.

The dimensions of the aluminium sample pans used in DCS experiments limited the amount of sample studied to 5 mg or less. A dynamic nitrogen atmosphere (100 ml/min) was used and the samples studied in uncrimped or open pans to ensure adequate atmosphere exchange.

Thus in each method of thermal analysis there is a significant variation in sample form due to the physical constraints of the equipment used. In TGA the powder sample is loosely packed in a platinum boat ensuring free access of purge gas while in DTA experiments the polymer sample is firmly packed into a glass tube ensuring good contact between thermocouple and sample but reducing the accessibility of the purge gas. The sample form in DSC is intermediate between that in the other techniques while the maximum sample size is also severely restricted.

By comparison TVA allows a wide variation in both sample size and form to be used thus facilitating thermal analysis under high vacuum conditions. Although the sample size normally employed in this technique is greater than in the previous system, the base area of the tube is also large so that the sample is actually more dispersed in this technique.

2.4 ANALYSIS OF DECOMPOSITION PRODUCTS

GAS LIQUID CHROMATOGRAPHY

Two instruments were used in the course of this work: the Perkin Elmer F11 G.C, equipped with a hot wire analyzer and the Microtek (GC) 2000R with a flame ionization detector.

Quantitative measurement of liquid products was obtained by the addition of a known weight of a suitable material as internal standard to a weighed quantity of liquid products. A series of pure samples of each of the products were mixed with known amounts of the internal standard and run on the chromatograph to determine the sensitivities of the product relative to the standard. Measurement of the peak areas on glc traces was carried out by weighing Xerox "cut outs" since the peak area for a particular substance is proportional to the weight present.

If the sensitivity factor, K, for any product Y is defined as the ratio of the peak areas of product to standard when equal weights of both are considered then the percentage by weight of Y in G grame of sample is given by:

$$\% \text{ Y} = \frac{(\text{Peak area of Y})}{(\text{Peak area of standard})} \left(\frac{100}{\text{G/weight of standard}}\right) 1/\text{K}$$

The calibration plots and details of the column temperatures and conditions are given in the appropriate chapter.

MASS SPECTROMETRIC ANALYSIS

This was carried out on volatile degradation products using an AEI MS12 mass spectrometer. Products collected from TVA experiments were either directly expanded into the spectrometer or fractionated using a liquid N_2 trap to separate condensible and non condensible products.

INFRA RED SPECTROSCOPY

Spectra were recorded on a Perkin Elmer 257 instrument. Polymer samples and residues were examined as KBr discs (approximately 3-5 mgs polymer per 300 mg KBr) or as films cast from solution on NaCl plates. Products from TVA experiments were examined as thin films or in the gaseous phase according to their volatility.

Quantitative measurements were made on gaseous products by prior calibration of a 10 cm path length gas cell using known pressures of the product in the pressure range of interest. The gases were distilled into the previously evacuated gas cell using standard vacuum techniques and the resultant pressure measured using a mercury manometer.

MEASUREMENT OF MOLECULAR WEIGHT

Number average molecular weights were determined osmotically using a Mechrolab Model 501 High Speed Membrane Osmometer fitted with a Sylvania 300 grade cellophane membrane and using toluene as solvent. Osmotic pressure measurements were made at a series of polymer concentrations applying the equation -

$$\frac{\pi}{C} = \frac{RT}{Mn} + bC$$

A plot of π/C vs C was drawn. By linear extrapolation of the graph to infinite dilution, the number average molecular weight was determined from the relationship

$$\left(\frac{\pi}{C}\right)_{C\to 0} = \frac{RT}{Mn}$$

A number of polymers whose molecular weights fell below the lower limit of operation of the membrane osmometer were determined by vapour pressure osmometry using a Hewlett Packard Model 301A V.P.O. In this instrument measurements are made of the resistance change (DR) necessary to balance the temperature differential between droplets of sample solution and solvent resultant from the differences in rates of volatilization of solvent in an equilibrated solvent atmosphere. Molecular weights could then be determined using the relationship -

$$\left(\frac{\Delta R}{C}\right)_{C\to 0} = \frac{K}{Mn}$$

where K is a calibration constant dependent on temperature, solvent and the particular instrument. A temperature of 37°C was employed with acetone as solvent. Instrument calibration data are given in Appendix 1. Gel permeation chromatography was employed for examination of molecular mass changes in both PMMA and PS in the presence of PAN. The measurements were provided by the Polymer Supply & Characterization Centre (RAPRA) using a Waters G.P.C. The operating conditions and calibration constants are given in Appendix 2.

Viscosity measurements using an Ubberlohde viscometer were employed for the determination of the molecular weight of polyacrylonitrile in DMF solution at 25°C using the relationship[49,50] -

$$[\eta] = 3{\cdot}92 \times 10^{-4}\, Mn^{0{\cdot}75}$$

CHAPTER 3

THE THERMAL DEGRADATION OF POLYACRYLONITRILE-POLY METHYL METHACRYLATE BLENDS

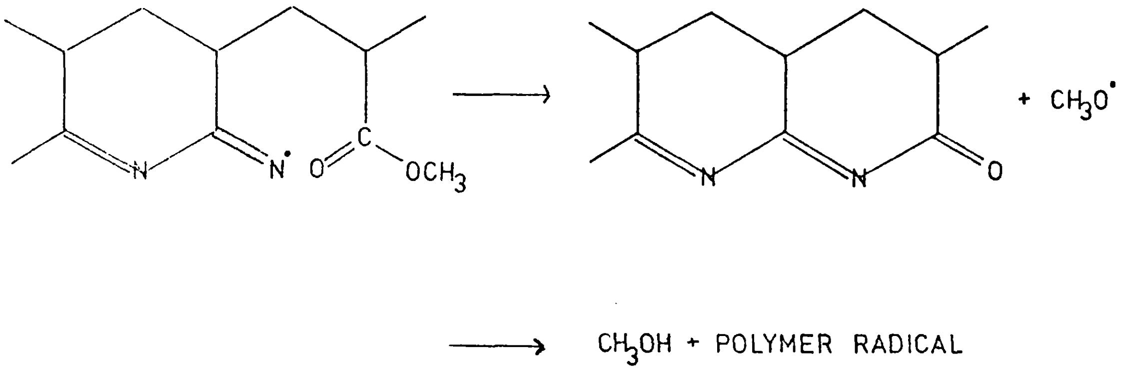
3.1 INTRODUCTION

It has long been established that the thermal decomposition of a polymer may be modified considerably by the incorporation of relatively small amounts of comonomers either deliberately introduced or present as trace impurities often derived from the monomer itself. This behaviour has been particularly evident in studies of both poly (methyl methacrylate) (PMMA) and of nitrile polymers.

In studies of the thermal decomposition of methyl methacrylate-acrylonitrile copolymers containing 0.2-10 mole % acrylonitrile, Grassie and Farish [52] found significant differences from the behaviour of PMMA itself. These included an induction period during decomposition which varied with acrylonitrile content and also with the temperature of decomposition. Copolymer degradation was found to proceed both by chain end initiation and by random scission of the polymer backbone followed by 'unzipping' of the polymer to yield MMA monomer in a similar manner to PMMA as outlined in Chapter 1. It was found, however, that unlike PMMA, a rapid drop in molecular weight occurred during the induction period and this was attributed to acrylonitrile units in the polymer chain effectively blocking the 'unzipping' process.

Investigation of the thermal stability of acrylonitrile copolymers containing small amounts of methyl methacrylate as comonomer by Grassie & McGuchan[53] has demonstrated that copolymerization has little effect upon the nitrile rearrangement reactions which are the primary decomposition processes involved in the thermal decomposition of polyacrylonitrile (PAN). As a result of TVA studies it was concluded that the incorporation of the methyl methacrylate monomer leads to participation in ring forming oligomerizations resulting in degradation products not normally associated with methacrylate decomposition.

The comonomer was envisaged as participating in the following process:-



The effect of comonomers upon the thermal decomposition of PAN and, in particular, upon the nitrile group oligomerization has formed the basis of a number of papers by the same authors.[54, 55]

In view of the marked variation in the thermal stability of the homopolymers through copolymerization it is, therefore, clearly of interest to determine whether there exists a similar correlation between composition and thermal stability in the degradation of mixtures of the two homopolymers.

The thermal decomposition of polymer mixtures containing PMMA has been studied by a number of workers. Thus, in the work of Barlow, Lehrle and Robb[19] it was noted that the thermal stability of mixtures of PMMA and poly(vinyl chloride) (PVC) was greater than the corresponding random copolymer. Further work on PMMA-PVC mixtures by McNeill & Neil [17,18,56] employing the technique of TVA demonstrated increased monomer evolution from PMMA during the early stages of degradation accompanied by a delay in hydrogen chloride production from the PVC present in the blend.

An analogous study of blends of poly(vinyl acetate) and PMMA by Jamieson[57] again exhibited an increased rate of evolution of methyl methacrylate during thermal decomposition and was used to provide support for the free radical mechanism of decomposition of poly(vinyl acetate).

Mizutani[21] has found that the presence of vinyl polymers including PMMA causes acceleration of the decomposition of polypropylene. In the same study the formation of graft or block copolymers was also detected and considered to result from the interaction of vinyl polymer radicals formed during decomposition with the polypropylene chain.

All these results indicate that the behaviour of a polymer can be influenced by the presence of a second polymer or more specifically by the decomposition products of the second polymer, although this does not occur in every mixed system. Thus in PMMA-polystyrene blends it has been demonstrated by Grassie, McNeill and Cooke[51] that no interaction occurs between the two homopolymers during degradation.

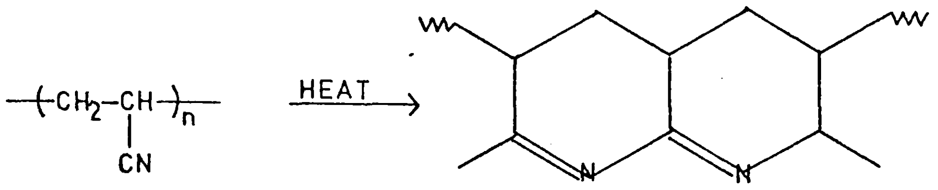
The mechanisms involved in the decomposition of PMMA appear well established. This simplifies to some extent the difficulties in interpretation of the overall patterns of degradation presented by polymer mixtures and can therefore provide, in favourable systems as outlined earlier, an insight into the mechanisms predominant in decomposition of the other polymer present in the blend.

3.2 THE THERMAL DECOMPOSITION OF POLYACRYLONITRILE

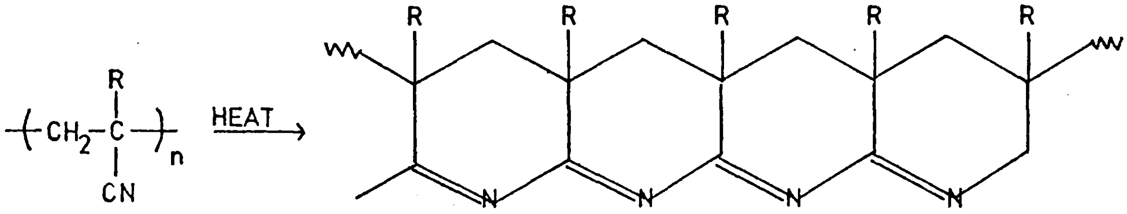
Under linear temperature programmed heating in vacuo or in an inert atmosphere, pure PAN exhibits one outstanding feature during decomposition, namely a rapid exothermic reaction accompanied by the evolution of both gaseous products and the extensive formation of molecular chain fragments.

The discolouration of the polymer which occurs during the course of the exotherm has received considerable attention in order to establish the structure of the chromophore responsible and in so doing to formulate a mechanism by which the process may be more clearly understood.[58,59,60,61,62] A number of possible chromophores have been suggested and are reviewed by Peebles.[63]

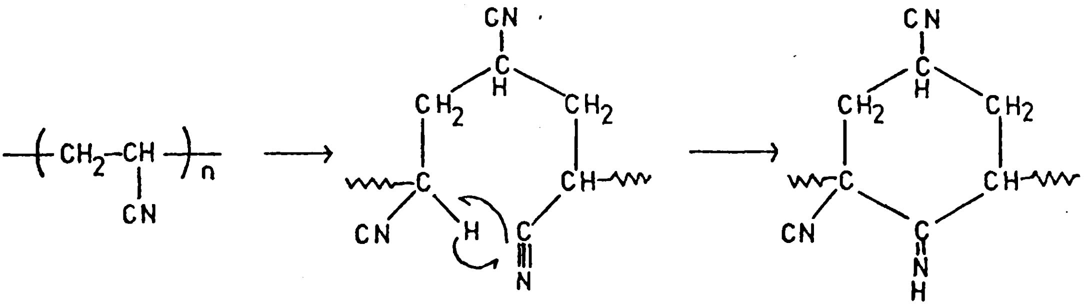
Studies of PAN degradation in inert atmospheres by Burlant and Parsons[64] enabled them to conclude that a cyclized structure was formed by polymerization of adjacent nitrile groups to give partly hydrogenated napthyridene rings:-



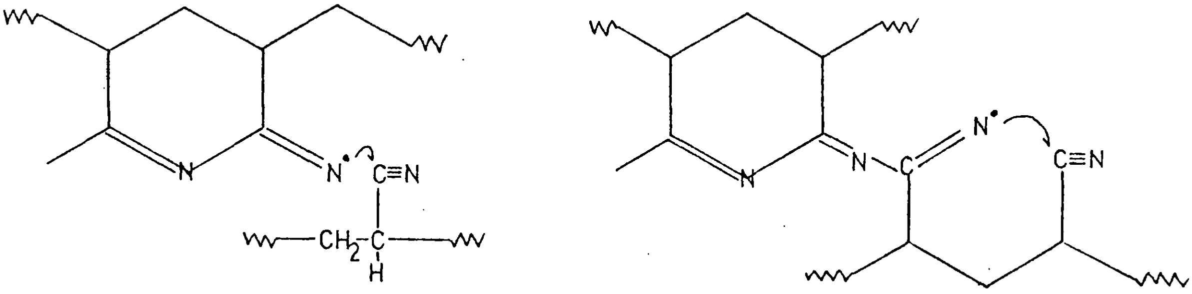
Further studies of the discolouration of nitrile polymers by Grassie and McNeill[59] and by Grassie and Hay[34] also led to the conclusion that the chromophore consists of conjugated -C=N- structures and that an extended ladder structure is formed with no restriction upon the zip length of nitrile polymerization:-



It was proposed that in polymethacrylonitrile (R=CH$_3$) initiation of coloration is due to trace amounts of acidic groups in the polymer chain and it was further demonstrated that the addition of acidic derivatives accelerated discoloration. It was concluded, however, that initiation of the nitrile reaction in PAN is due to the labile tertiary hydrogen atom in the polymer chain. A process of self initiation was envisaged:-

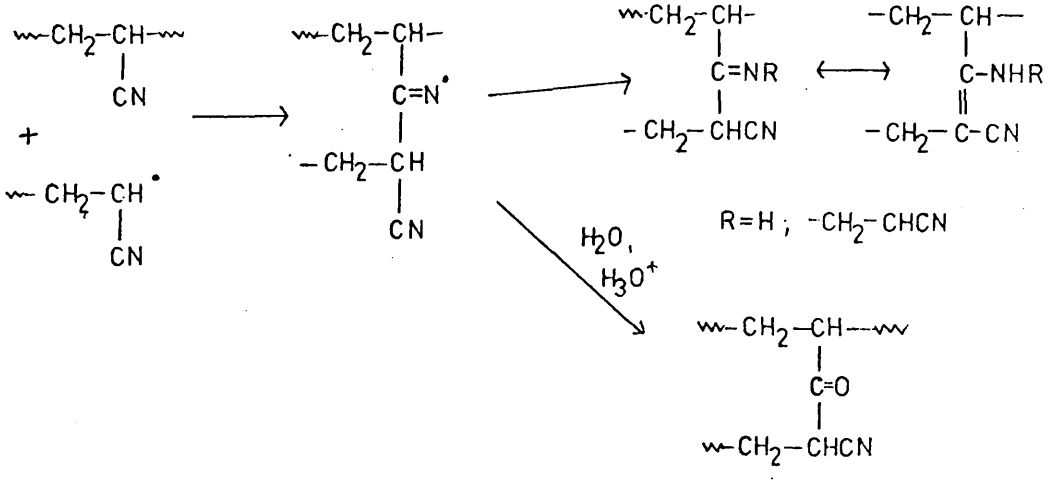


The development of colour during the decomposition of PAN is accompanied by decreasing solubility of the polymer. This was interpreted by the same workers as due to propagation cross linking through the pendant nitrile group:-



Confirmation of the chromophore proposed by Grassie and co-workers has been provided by spectral studies by Takata[65] employing both ultra violet and i.r. spectroscopy to examine the absorptions of low molecular weight model compounds.

Peebles[63] and co-workers, although confirming the proposed chromophore suggest that initiation of coloration in PAN is caused by defect structures formed in the polymer during polymerization. The exact structure responsible is dependent upon polymerization conditions and may be an enamine or a ketenitrile. The same workers showed that the U.V. spectrum of PAN is consistent with the presence of these structures:-



A number of recent publications by Grassie & McGuchan[12, 66] in which the pyrolysis of PAN and related polymers is described, review the decomposition of the polymer. Much of the previous work is confirmed but an additional modification to the mechanism proposed by Grassie is suggested, which restricts the zip length of the nitrile reaction to three to five monomer units, while at the same time accounting for the nitrile group disappearance by the maintenance of radical activity through transfer reactions. The overall decomposition process and the structure of the resultant polymer is thus summarized in Fig. 3.1.

3.3 POLYMER SAMPLE HISTORY

Polymer samples representative of the range of thermal stability observed in PMMA decomposition were examined to investigate the role this might play in determining overall blend stability. Both PMMA and PAN samples are listed together with preparative details in Table 3.1.

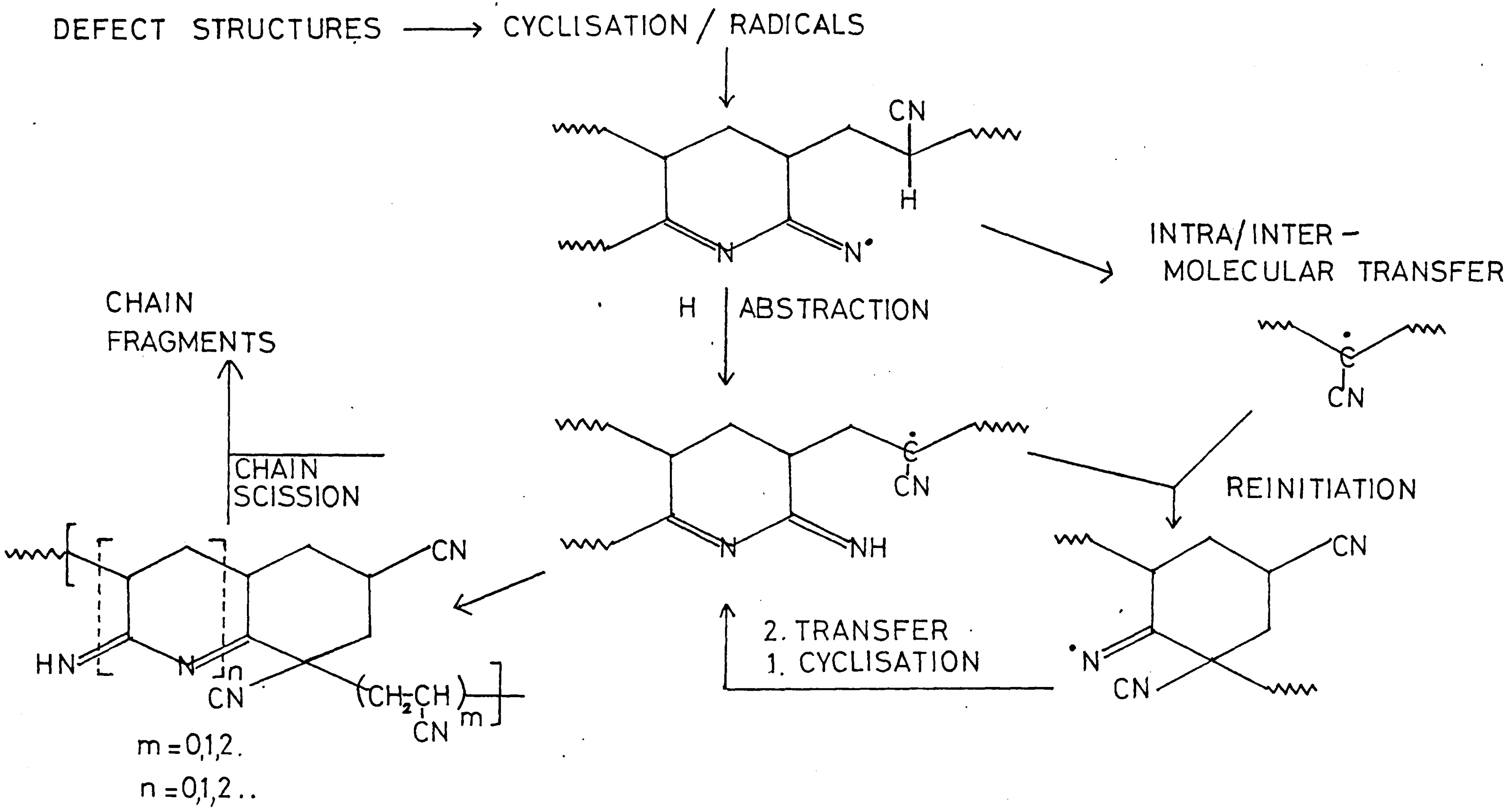
TABLE 3.1 POLYMER SAMPLE HISTORY

POLYMER	Mn	POLYMERIZATION CONDITIONS
PMMA I	30,000	Bulk polymerization, 3% w/v AIBN, 75°C
PMMA II	590,000	Bulk polymerization, 0.1% s/v AIBN, 60°C
PMMA An	150,000	Anionic polymerization, using sodium napthalene, -75°C
PAN I	$1\text{-}2\times10^{6}$ *	Bulk polymerization, 0.05% w/v AIBN, 40°C
PAN II	35,000 *	Solution polymerization, 20% AN:DMF, 1% AIBN, 60°C

* Determined by viscometry using the relationship given in Chapter 2.

Two samples of PAN were examined although the study concentrates on the behaviour of the higher molecular weight sample. It has been found previously that variation of initiator concentration has little effect in determining the molecular weight of the polymer formed in bulk polymerization, due probably to the suppression of the bimolecular termination reaction when polymer precipitates from the reaction mixture.

FIG 31 THERMAL DECOMPOSITION OF POLYACRYLONITRILE



To obtain a low molecular weight sample a solution polymerization in DMF was employed. Differences in the thermal stability of the two polymers cannot, therefore, be attributed simply to molecular weight since DMF has been shown to be an effective initiator of nitrile polymerization.

RESULTS AND DISCUSSION

3.4 THERMAL VOLATILIZATION ANALYSIS OF POLYACRYLONITRILE

The evolution of gaseous products from PAN I during linear temperature programmed heating in vacuo is illustrated by the TVA curve in Fig. 3.2. The same diagram also incorporates the key to the traces for different trap temperatures used throughout the present study.

The trace reveals the rapid evolution of volatile products as a definite peak with a maximum rate of evolution (T max.) at 265°C. I.r analysis of the products show only ammonia and hydrogen cyanide to be present. Ammonia has been reported by Monahan[67] to be evolved during PAN decomposition only in the presence of water. Grassie & McGuchan, however, found by preheating the polymer prior to degradation, that ammonia is a true decomposition product.[66]

The TVA curve shows a plateau in the region between 300-400°C in which ammonia and hydrogen cyanide can be identified by i.r. Between 350-400°C the pirani response in the gauge beyond the -196°C trap is evident. Both ammonia and hydrogen cyanide are completely condensed at -196°C and by a combination of mass spectrometric analysis and i.r. both hydrogen and methane were identified. The sensitivity of the pirani gauge to such gases exaggerates the relative amount of non condensible material present.

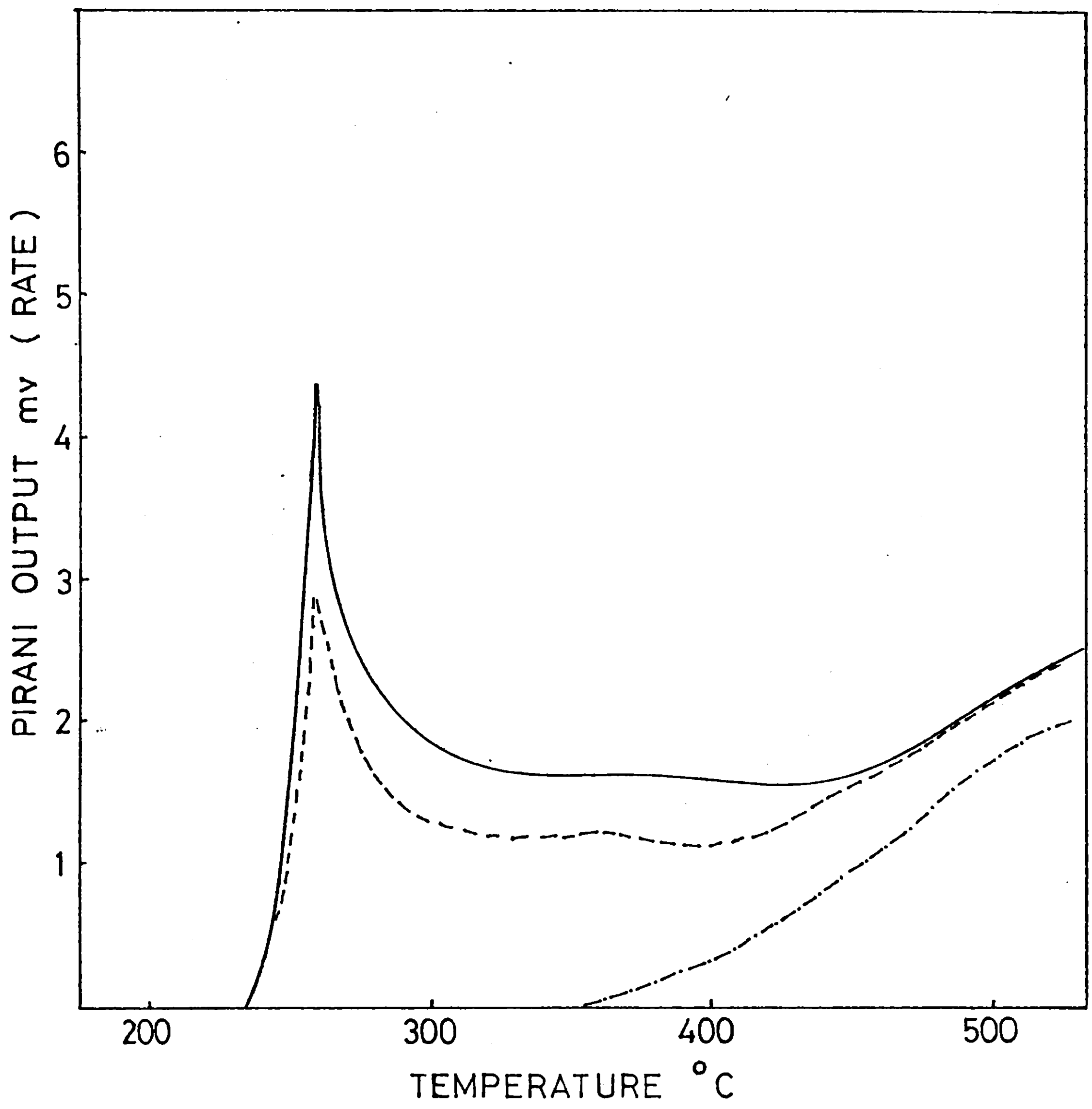


FIG. 3.2 TVA CURVE FOR PAN-I

50 mg POWDER SAMPLE

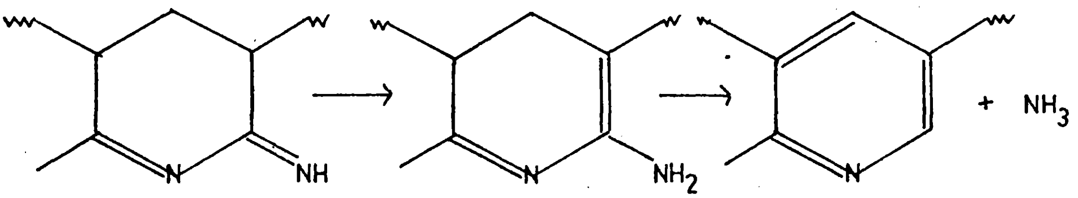
A standard heating rate of 10C°/min has been employed in this and subsequent TVA results

KEY
——— 0°C TRACE
·········· −45° "
------- −75° "
— — — — −100° "
—·—·— −196° "

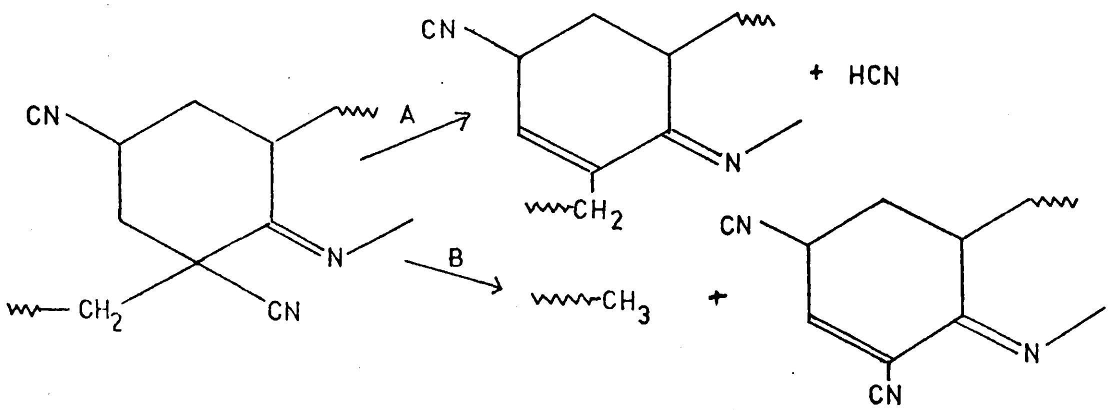
TVA studies by Grassie & McGuchan[66] revealed a sample size dependence of the trace in the 300-400°C region, the plateau being replaced by a broad peak on increasing sample size from 50 to 200 mg. while the product composition remained unchanged. This was confirmed in the present study, but was not observed within the sample sizes employed during investigation of polymer mixtures (100 mg. maximum amount of PAN).

Between 450 and 500°C the pirani response indicates the formation of an increasing amount of non condensible gases. In TVA studies performed by Grassie & McGuchan, employing a heating oven capable of achieving a maximum temperature of 900°C it was observed that the curve continues to form a broad peak almost solely consisting of non condensible gases. These were again confirmed as hydrogen with a trace amount of methane.

Ammonia and hydrogen cyanide are thus the major gaseous products of decomposition to a temperature of 500°C. The elimination of both gases is consistent with the mechanisms previously proposed by Grassie & McGuchan. Thus ammonia is eliminated by the aromaticization of amino substituted rings formed by the oligomerization of nitrile groups:-



Elimination of hydrogen cyanide may occur both from residual acrylonitrile units trapped in the polymer chain between cyclised segments and also from the carboxyclic structures in the chain which result from radical transfer reactions.



Route B illustrates a competing chain scission reaction postulated by Grassie & McGuchan which results in the formation of a relatively stable nitrile group which may further decompose at higher temperatures to evolve hydrogen cyanide.

Quantitative estimation of both ammonia and hydrogen cyanide evolved during the decomposition of a 50 mg sample of PAN I was obtained from optical density measurements of i.r. absorptions at 969 and 714 cm^{-1} respectively. Prior calibration of the 10 cm path length gas cell using known pressures of each gas gave the results illustrated in Fig. 3.3.

By use of the gas equation -

$$PV = nRT$$

the number of moles, n, can then be calculated with a knowledge of the gas cell volume V.

In this manner ammonia and hydrogen cyanide evolution was estimated as 0.6 and 1.7% of initial polymer weight respectively.

A number of minor degradation products have been reported by previous workers. These include monomer and other nitrile containing species. The mass spectrum obtained from the gaseous products collected after degradation of a 50 mg. sample to 500°C in a closed system is illustrated in Fig. 3.4. Table 3.2 lists major peaks and their assignment.

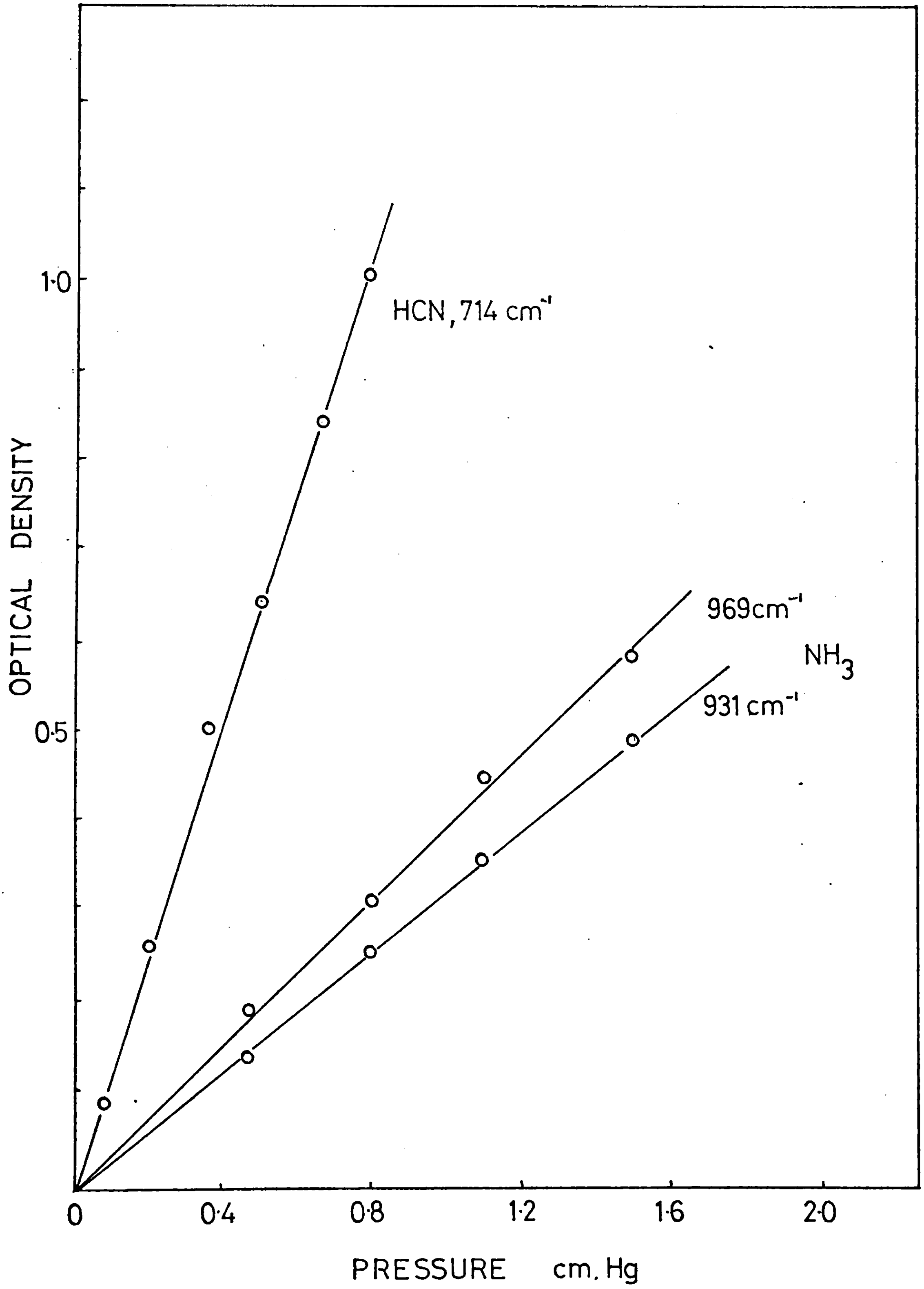


FIG. 3.3 I.R. CALIBRATION PLOTS OF OPTICAL DENSITY VS GAS PRESSURE FOR NH_3 AND HCN (10 cm PATH LENGTH)

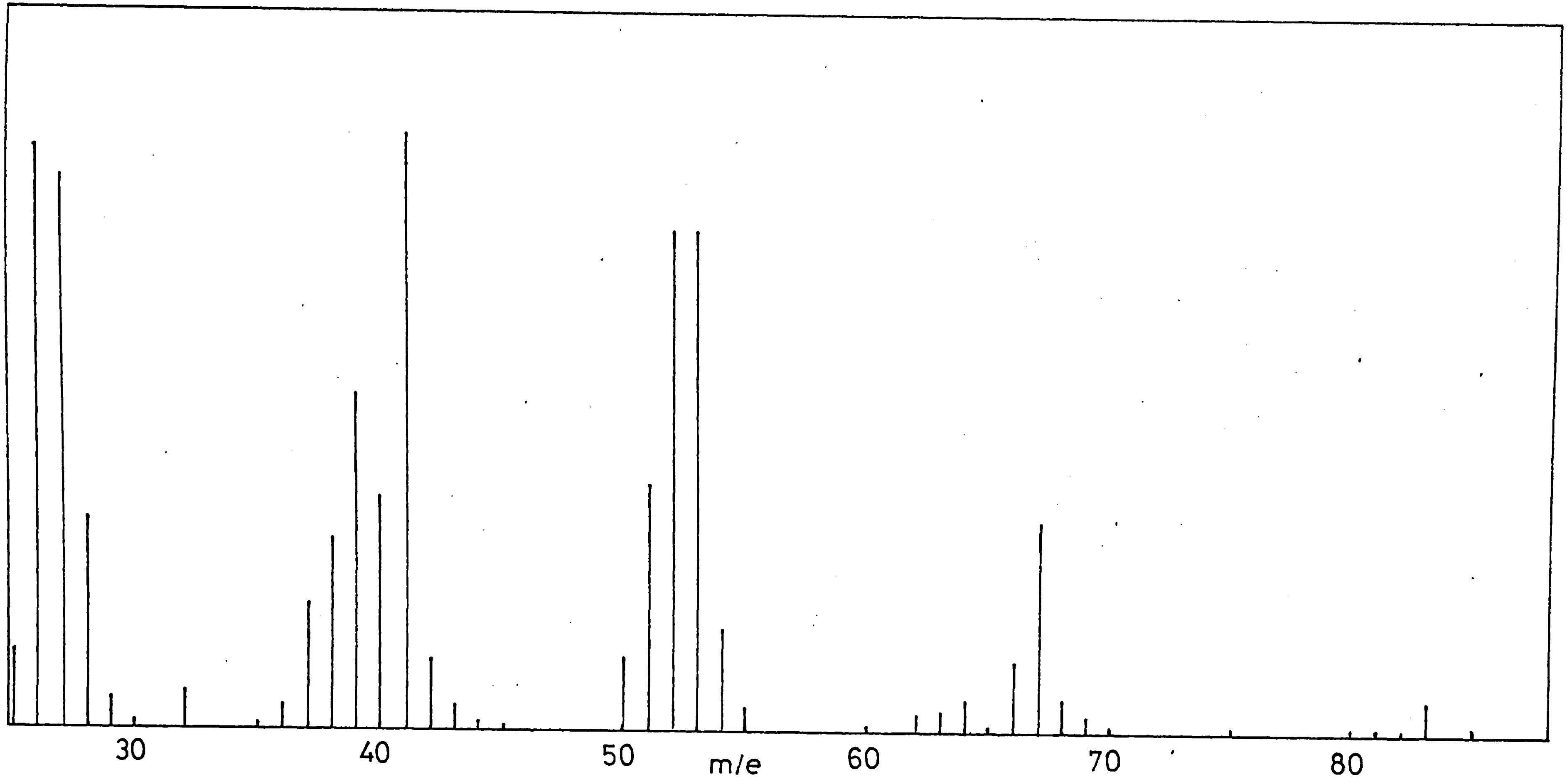


FIG. 3.4 MASS SPECTRUM OF GASEOUS VOLATILES FROM PAN DECOMPOSITION TO 500°C

TABLE 3.2 MASS SPECTROMETRIC ANALYSIS OF POLYACRYLONITRILE DECOMPOSITION PRODUCTS

m/e	Assignment
83	$CH_3CH(CH_3)CM_2$ C≡N
67	$CH_2{=}CH{-}CH_2{-}C{\equiv}N$
53	$CH_2{=}CHCN$
41	CH_3CN
27	HCN
2	H_2^+

Monahan[67], in vacuum pyrolysis studies of PAN, identified vinylacetonitrile, acetonitrile and acrylonitrile as minor decomposition products in agreement with the assignments made in the present work. The appearance of these nitrile species may arise from chain scission reactions at elevated temperatures allowing the splitting out of trapped nitrile residues in the polymer chain.

The spectral evidence may be summarized as follows:-
The decomposition of PAN under linear temperature programmed heating to 500°C is accompanied by the evolution of a relatively small proportion by weight of gaseous products, the major components of which are ammonia and hydrogen cyanide, with further trace amounts of hydrogen, methane and several nitrile species including monomer.

3.5 THERMAL VOLATILIZATION ANALYSIS OF POLYMETHYL METHACRYLATE

By comparison with the observed complexity of the processes occurring during the decomposition of PAN, the degradation of PMMA appears to be well understood, resulting in almost quantitative yields of monomer.

TVA curves for PMMA samples prepared by both free radical and anionic polymerization are illustrated in Fig. 3.5. The pirani response in each trace is typical of that of a single substance, methyl methacrylate, passing through the trap system. The monomer is non-condensible in both the 0° and -45° traps and partially condensed in the -75° trap. The continued response from the -75° trap after the maximum rate of monomer evolution is due to condensed methyl methacrylate distilling into the common liquid nitrogen trap at a steady rate and is referred to as Limiting Rate behaviour in the TVA system.[41]

Two distinct rate maxima are evident in Fig. 3.5(a). The lower temperature peak results from monomer evolved by depolymerization initiated at unsaturated chain ends formed by disproportionation reactions during polymerization. The high temperature peak is then due to the 'unzipping' of macroradicals formed by random chain scission. The ratio of the amount of monomer produced by each mode of decomposition will depend upon the proportion of unsaturated chain ends present in the polymer which is, in turn, dependent upon both the molecular weight of the polymer and the polymerization technique employed. TVA studies by McNeill have demonstrated the molecular weight dependence of the monomer evolution pattern in PMMA.[68]

Fig. 3.5(b) illustrates the TVA curve for PMMA An. This sample contains no unsaturated chain ends and thus shows only the rate maximum corresponding to random chain scission. Thus the trace for PMMA prepared by this technique is independent of molecular weight.

3.6 ANALYSIS OF BLEND DECOMPOSITION BY TVA

In Chapter 2 the effect which the most commonly used solvents for PAN, namely DMF and DMS, have in determing the stability of the polymer, was mentioned in relation to polymer purification. The solvents are highly polar and together with the infusible nature of PAN make impossible

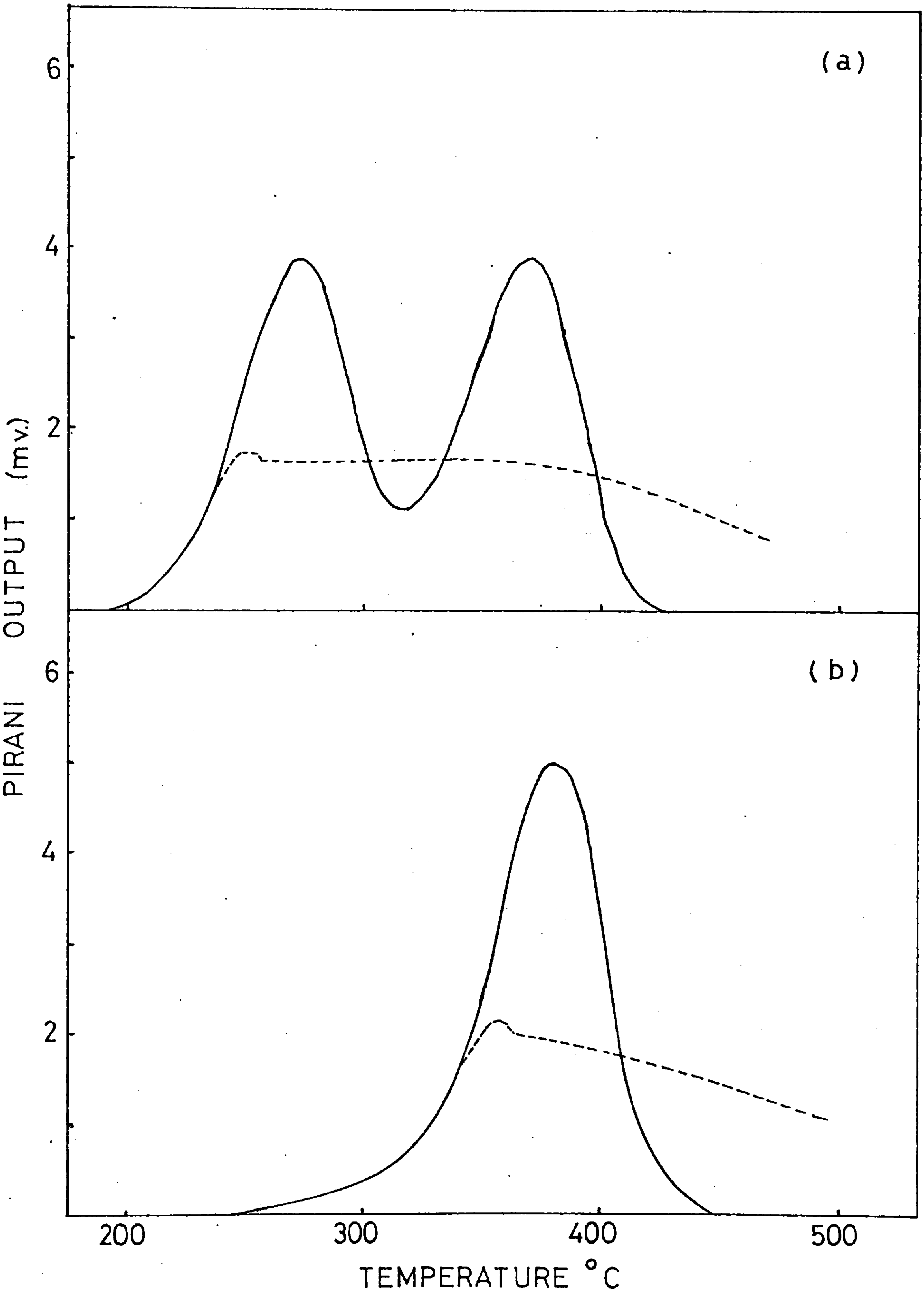


FIG. 3.5 TVA CURVES FOR PMMA (a) PMMA-I (b) PMMA-An
50 mg POWDER SAMPLES

complete solvent removal from cast films or precipitated samples. It was, therefore, considered desirable to study the polymer mixtures both as mixed powder and as films cast from a common solvent.

In degradation studies the most serious consequence of the heterogeneity of polymer mixtures is the difficulty of achieving a reproducible sample form. One would expect that reproducibility must inevitably be more easily accomplished in blends prepared by mixing of polymer solutions than by mixing of fine powders. However the ultimate test for any procedure of blend preparation is the reproducibility of the subsequent degradation experiment which was found to be satisfactory when both methods were applied. An important advantage of studying the blends as fine powders is the fact that the same sample form may be used in the three principal analysis techniques, namely TVA, TGA and DTA.

The results of degradation of equal amounts of PAN I and PMMA II in the form of fine powders, both mixed and unmixed, are illustrated in Fig. 3.6. The evolution of MMA, with the resultant L.R. in the -75° trace, is clearly distinguishable in the unmixed system as an almost symmetrical peak, T max 363°C. A small shoulder upon the low temperature portion of the peak is indicative of the small proportion of monomer evolved by chain end initiated depolymerization. The presence of PAN is indicated by the rapid evolution of gaseous products at 265°C which is then followed by the gradual evolution of non-condensible gases. Thus the total curve is that which one would predict from the separate degradation of the two homopolymers. This is further confirmed by i.r. analysis of the gaseous products.

A number of significant differences are apparent in the mixed system. These include a displacement of the T max associated with MMA to around 405°C; the evolution of non-condensible gases in the region of PMMA breakdown; and a reduction in the initial rate of volatilization of the methacrylate peak.

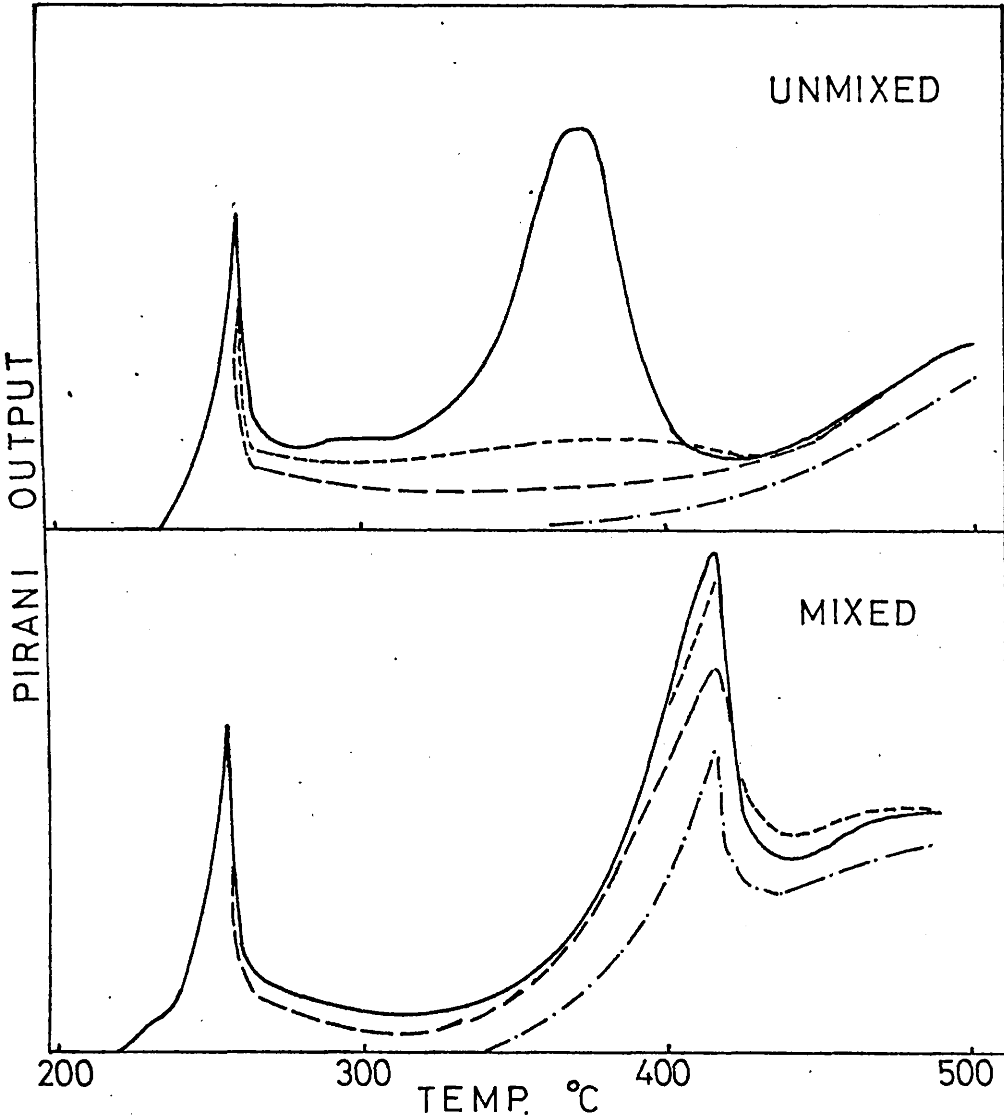


FIG. 3.6 TVA CURVES FOR SIMULTANEOUS DEGRADATION OF PAN I AND PMMA II, 1:1 BY WEIGHT. POWDER SAMPLES, TOTAL WEIGHT 100 mg.

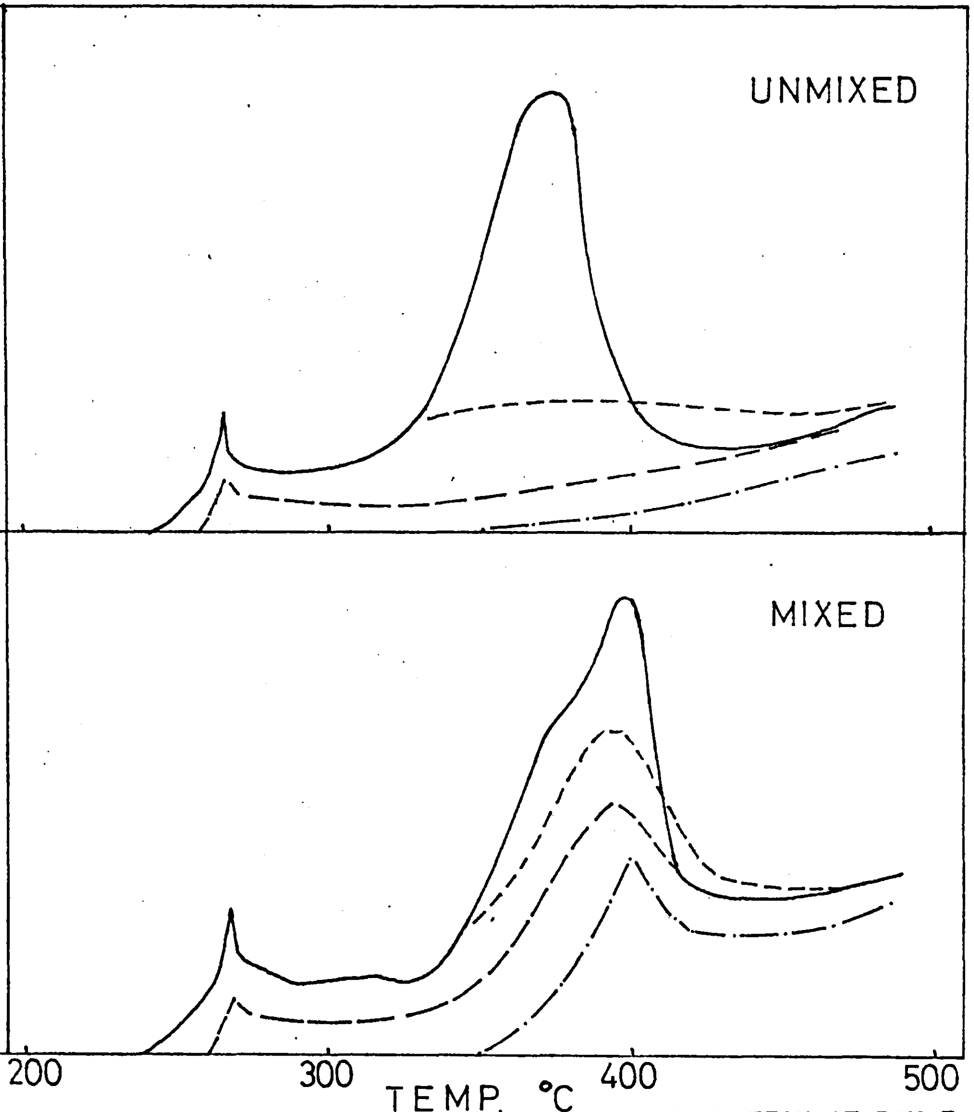


FIG. 3.7 TVA CURVES FOR SIMULTANEOUS DEGRADATION OF PAN I AND PMMA II, 1:4 BY WEIGHT. POWDER SAMPLES, TOTAL WEIGHT 100 mg.

The production of gases non-condensible at -196°C can be seen to occur at a lower temperature than is associated with decomposition of PAN while the altered rate of decomposition of the blend has resulted in a pronounced asymmetry of the peak associated with evolution of MMA. This may imply one or more competing modes of decomposition at this stage of degradation in addition to depolymerization. The Limiting Rate effect is still observed in the -75° trap indicating that MMA is still a major decomposition product, while the evolution of gases associated with PAN remains unchanged in both form and temperature of occurrence (T max 263°C).

Figs. 3.7 and 3.8 illustrate the effect of varying the ratio of PMMA to PAN (4:1 and 9:1 by weight of PMMA to PAN respectively). The general observations made upon the 50:50 mixture are again evident, namely the evolution of increased amounts of non-condensible gases and an increased T max associated with PMMA breakdown.

A blend containing only 5% by weight of PAN I demonstrates similar behaviour and also shows that relatively small amounts of PAN are required to effect the observed change. This blend also shows separation of the reactions occurring during PMMA breakdown which resulted in asymmetry of the peaks observed in blends of higher PMMA content. The TVA curve is illustrated in Fig. 3.9.

The TVA results for a series of blend compositions are summarised in Table 3.3.

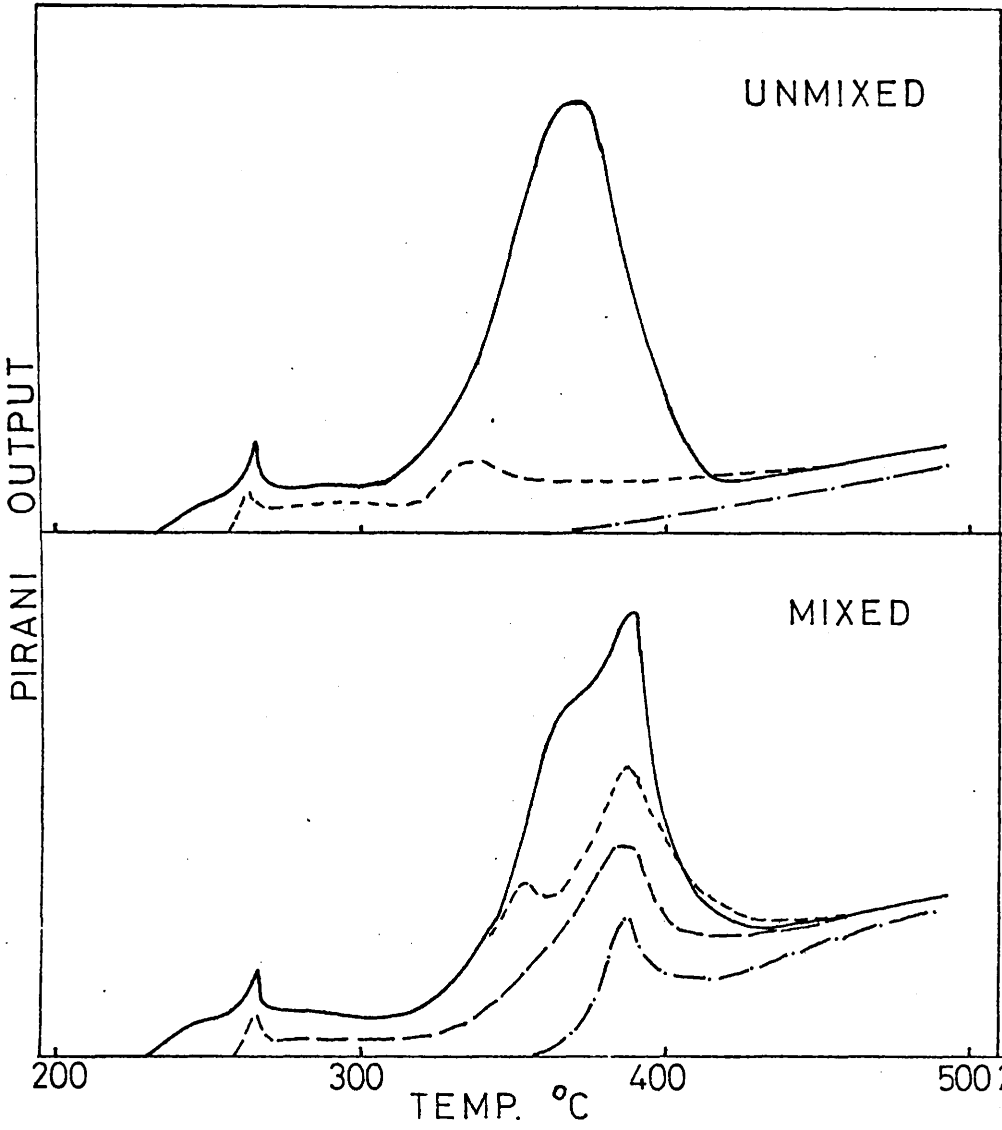


FIG. 3.8 TVA CURVES FOR SIMULTANEOUS DEGRADATION OF PAN I AND PMMA II, 1:9 BY WEIGHT. POWDER SAMPLES, TOTAL WEIGHT 100 mg.

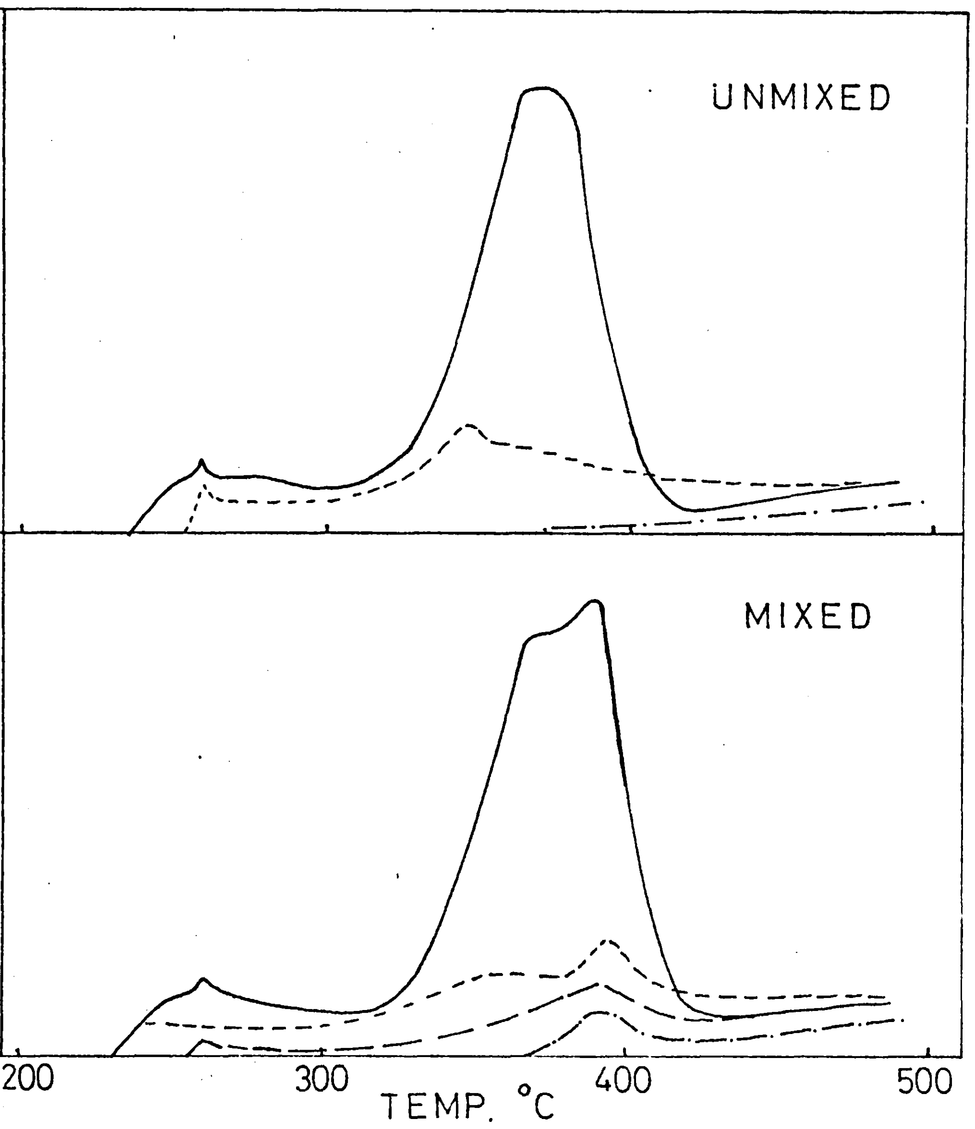


FIG. 3.9 TVA CURVES FOR SIMULTANEOUS DEGRADATION OF PAN I AND PMMA II, 1:19 BY WEIGHT. POWDER SAMPLES, TOTAL WEIGHT 100 mg.

TABLE 3.3 VARIATION OF T MAX WITH BLEND COMPOSITION IN PAN I:PMMA II BLENDS

BLEND COMPOSITION % PMMA BY WEIGHT	T MAX PAN DECOMPOSITION °C	T MAX PMMA DECOMPOSITION °C
PMMA	-	360
95	267	378
90	262	385
80	270	395
50	263	404
20	258	400
PAN	265	-

Comparison of mixed and unmixed systems containing both PMMA I and PAN An give qualitatively similar results. Additional differences observed in examination of blends containing PMMA I (Mn 30,000) are illustrated by the behaviour of a 50% PMMA I blend as in Fig. 3.10.

The peak arising from MMA evolution by random scission of the polymer chain is again displaced to a higher temperature with the concurrent evolution of non-condensible gases. A significant reduction in the evolution of volatiles occurs upon blending in the temperature region associated with unzipping of terminally unsaturated PMMA and it is further found that the extent of this reduction is a function of the proportion of PAN present in the mixture (Fig. 3.11).

The TVA results obtained from a series of blend compositions are summarised in Table 3.4.

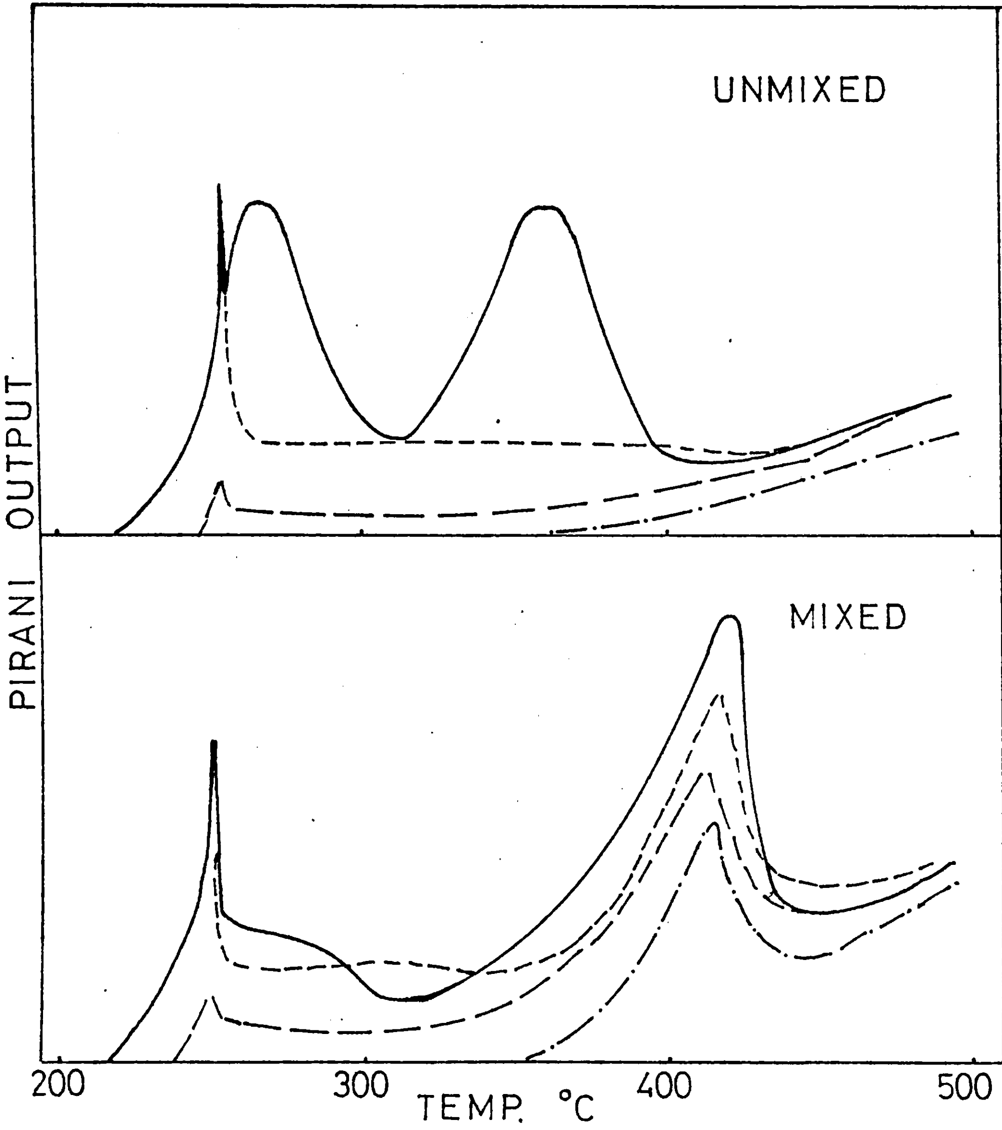


FIG. 3.10 TVA CURVES FOR SIMULTANEOUS DEGRADATION OF PAN I AND PMMA I, 1:1 BY WEIGHT. POWDER SAMPLES, TOTAL WEIGHT 100 mg.

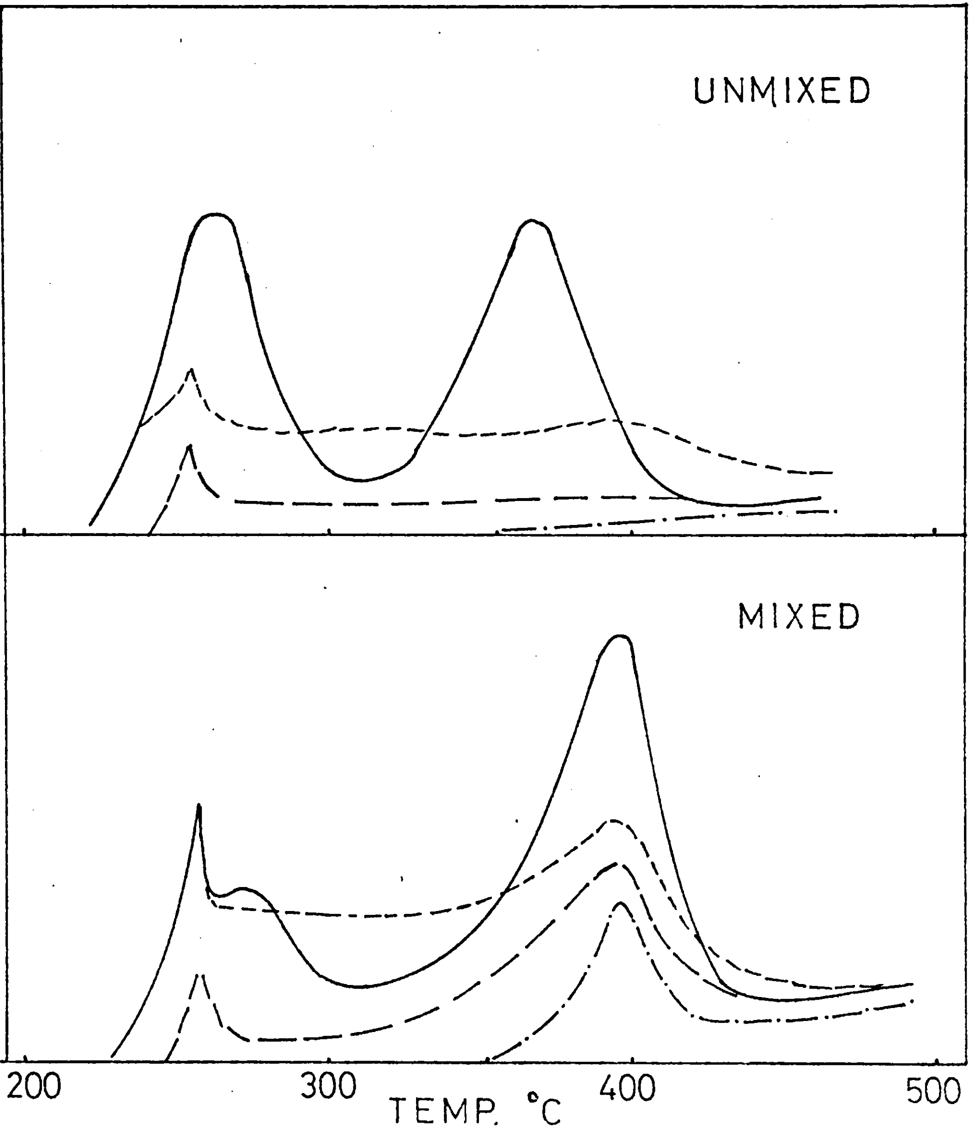


FIG. 3.11 TVA CURVES FOR SIMULTANEOUS DEGRADATION OF PAN I AND PMMA I, 1:5 BY WEIGHT. POWDER SAMPLES, TOTAL WEIGHT 100 mg.

TABLE 3.4 VARIATION OF T MAX WITH BLEND COMPOSITION IN PAN I:PMMA I BLENDS

BLEND COMPOSITION % PMMA BY WEIGHT	T MAX PAN DECOMPOSITION °C	T MAX MMA-TERMINAL UNSATURATION °C	T MAX MMA-RANDOM CHAIN SCISSION °C
PMMA I	-	283	373
95	-	276	387
90	283	283	388
83	263	283	393
50	257	286	403
PAN I	265	-	-

TVA experiments on blends prepared as films from DMF solution showed qualitatively similar results as did a blend prepared by stirring a chloroform slurry of PAN in PMMA solution to dryness.

TVA results may, therefore, be summarized as follows:-

1. Both low and high molecular weight PMMA show a reduced rate of volatilization during the early stages of decomposition of PAN blends, the effect being more pronounced in mixtures containing low molecular weight PMMA.
2. The composition of the degradation products is a tered in each of the systems studied, the magnitude of this change dependent upon the PAN content of the blend.
3. T max for the later stage of blend decomposition is displaced to higher temperatures and is accompanied by the evolution of non-condensible gases.
4. The interaction is independent of the molecular weight of PAN and is qualitatively similar for each method of blend preparation.

3.7 THERMOGRAVIMETRY

Sample size dependence of TG curves of PAN has been reported by Grassie & McGuchan[66]. It was observed that within the range 1-10 mg smaller samples were associated with greater stability in the temperature region between 300-400°C. It was also noted that reproducibility of TG curves for large samples was lower than for small samples.

The TG curves obtained for PAN I as a fine powder (0.0049" mesh) are illustrated in Fig. 3.12. The effect of sample size is less than that found by the above authors although this will depend upon the polymer sample. It is noted, however, that the difference in stability between 10 mg. and 5 mg. samples is greater than for smaller samples.

Each TG curve illustrates a sudden 10-14% weight loss around 265°C. This is concurrent with the evolution of gaseous volatiles observed in TVA studies and is due both to the loss of NH_3 and HCN through elimination reactions and to the production of chain fragments volatile at the temperature of degradation. This weight loss is reproducible whereas the slow loss of weight associated with the programmed decomposition of the residual polymer at higher temperatures is more dependent upon sample size.

The TG curves for 5 mg. samples of PAN I and PMMA I are illustrated in Fig. 3.13(a). The curve for PMMA was found to be independent of sample size in the range considered. The two stage weight loss of PMMA corresponds to the evolution pattern observed from TVA, each stage resulting in approximately 50% weight loss, the exact amount being difficult to determine due to overlap between the two modes of degradation.

Comparison of mixed and unmixed samples by TG was achieved by simple 'addition' of the curves for the constituent homopolymers. The curve so obtained was compared with the experimentally determined curve for a 50:50 mixture, shown in Fig. 3.13(b). A sample size of 5 mg. was employed in

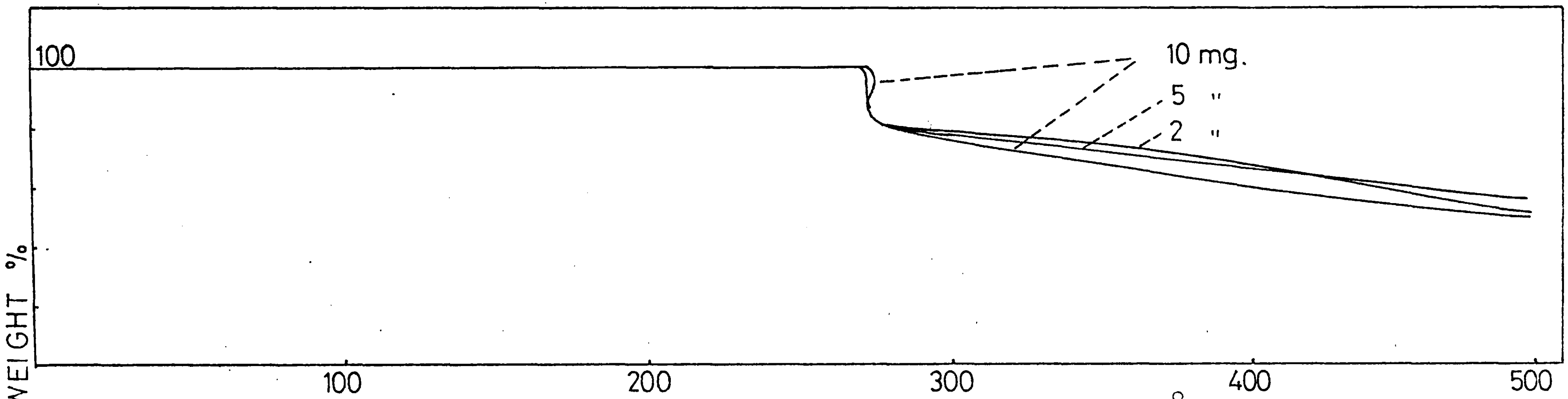


FIG. 3.12 SAMPLE SIZE DEPENDENCE OF TG CURVES FOR PAN I POWDER SAMPLES, HEATING RATE 10C°/min, DYNAMIC N_2 ATMOSPHERE

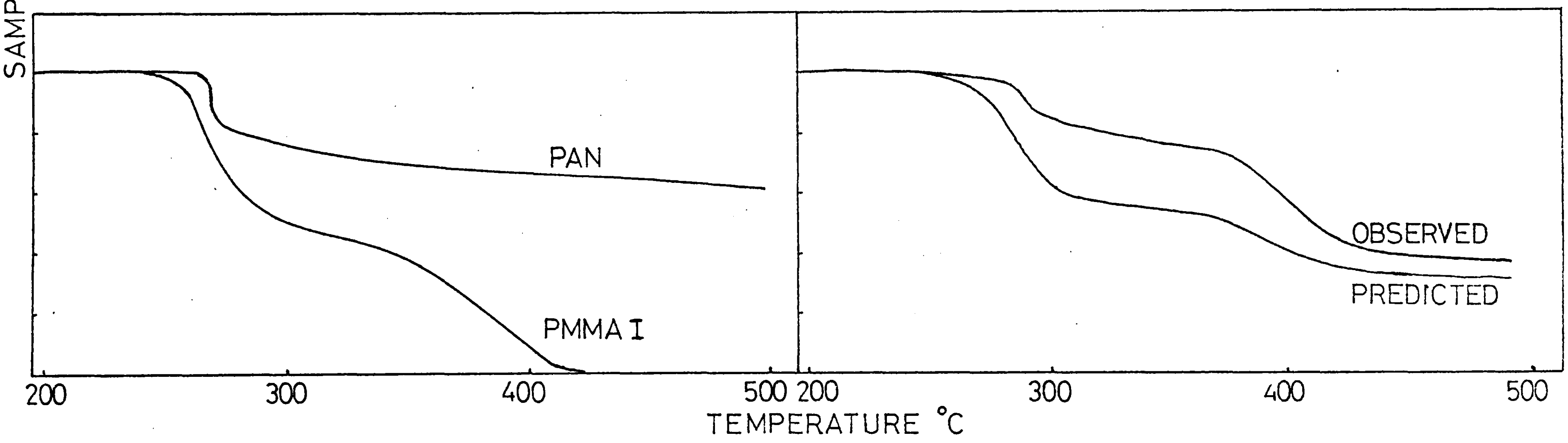


FIG. 3.13 (a) TG CURVES FOR PAN I AND PMMA I

(b) OBSERVED AND PREDICTED TG CURVES FOR A 1:1 BY WEIGHT PAN I-PMMA I BLEND, 5 mg POWDER SAMPLES, HEATING RATE 10C°/min. DYNAMIC N_2 ATMOSPHERE order to minimize the variation in TG behaviour previously described for PAN. The differences between the TVA behaviour of mixed and unmixed polymer is clearly reflected in the TG curves. Thus the weight loss in the blend at 300°C is approximately 50% of that expected from prediction of the behaviour of the unmixed system if no interaction takes place.

It can also be noted that the stabilized blend undergoes a rapid rate of decomposition in the region 375-425°C corresponding to the decomposition associated with non-condensible production in TVA. The amount of residue remaining at 500°C does not differ significantly from that predicted.

To evaluate the effect of blend composition upon the stability of the system a series of polymer mixtures containing 10, 20, 40, 50, 60 and 80% by weight of PMMA I were examined. The TG curves obtained from degradation of 5 mg. samples of each are illustrated in Fig. 3.14.

The enhanced stability associated with the introduction of comparatively small amounts of PAN is evident. It is also noted that the pattern of degradation on heating to a temperature around 375°C is similar for each blend, the stability of each composition within this range being similar within the limits of reproducibility of the experimental procedure. The blend composition is, however, reflected in the residue yield at 500°C, increasing from 16 to 48% as the PAN content varies between 10 to 80% by weight. The major weight loss process is thus associated with the temperature range between 375 and 425°C, increasing with PMMA content.

Fig. 3.15 illustrates the TG curves for PMMA An together with that of predicted and experimental results for a 50% PMMA An:PanI blend. This system does not reveal any significant increase in stability during the early stage of degradation but again exhibits greater stability in the temperature region 350-400°C. As in the mixtures containing low molecular weight PMMA I, the residue yield at 500°C does not differ considerably from the values produced from decomposition of the two

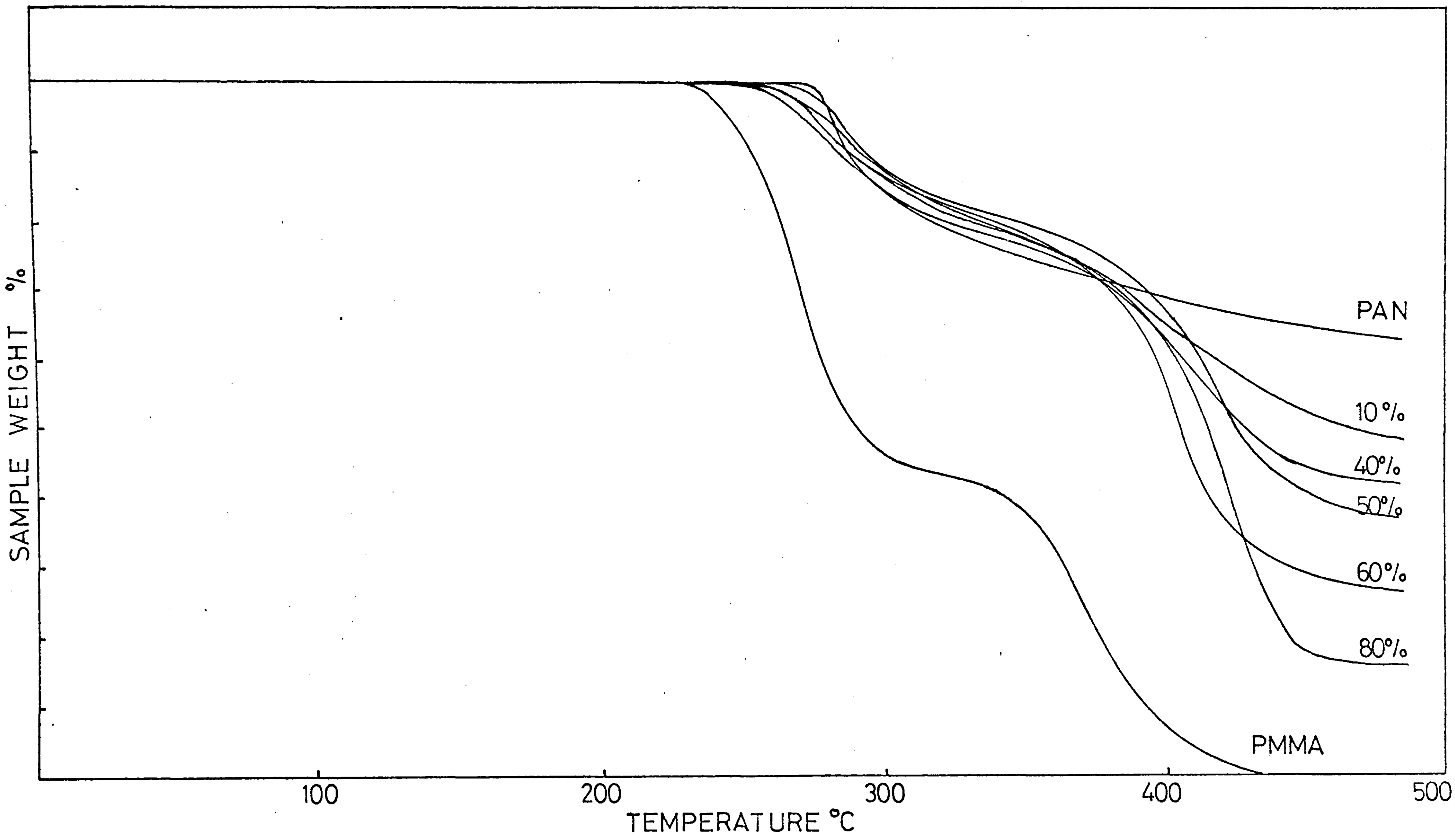


FIG. 3.14 TG CURVES FOR PAN I-PMMA I BLENDS (WEIGHT % PMMA) 5 mg POWDER SAMPLES, HEATING RATE 10C°/min, DYNAMIC N_2 ATMOSPHERE

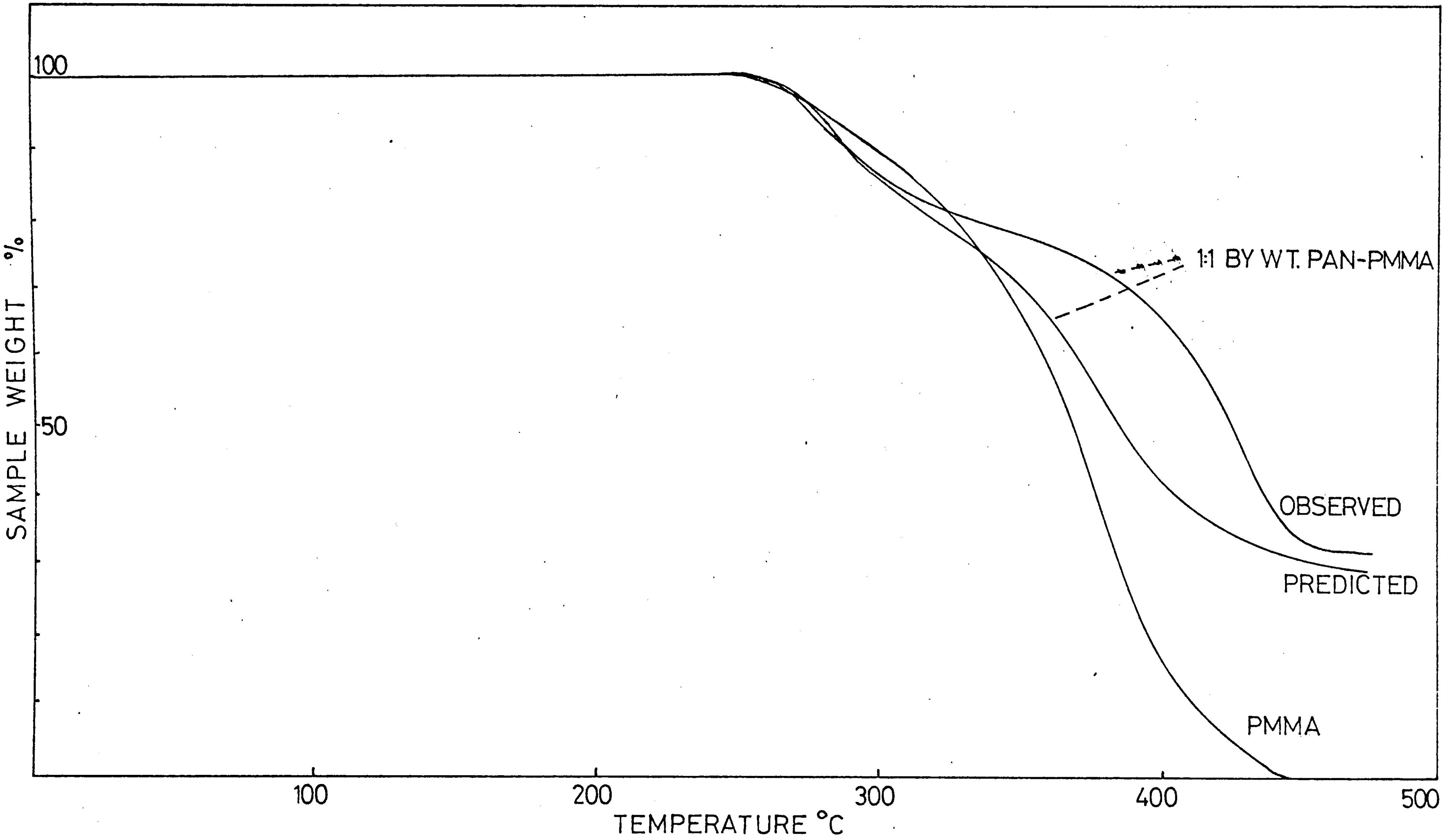


FIG. 3.15 OBSERVED AND PREDICTED TG CURVES FOR A 1:1 BY WEIGHT PAN I-PMMA-An BLEND, 5 mg POWDER SAMPLES, HEATING RATE 10C°/min, DYNAMIC N_2 ATMOSPHERE

homopolymers.

The weight loss during isothermal degradation in a dynamic N_2 atmosphere of a polymer blend containing 80% by weight of PMMA I together with with those for the homopolymers are illustrated in Fig. 3.16. It is apparent that the increased stability of the polymer blends observed during programmed heating is reflected in the initial rates of volatilization found from isothermal weight loss measurements. Thus the initial rates found for PMMA I at 250°C is around 4% per minute while the blend studied shows an initial rate of less than 1% per minute at the same temperature.

It is convenient at this point to summarize the information derived from both TGA and TVA experiments.

TG results confirm the observations made from TVA viz. a reduction in the rate of volatilization of polymer blends containing low molecular weight PMMA I observed during both programmed temperature decomposition and isothermal degradation. Programmed TGA indicates that the rate of volatilization during the early stages of degradation of such blends is little influenced by blend composition while TVA reveals a reduction in gaseous products which appears to be determined by the PAN content.

The two techniques however measure different processes - TVA recording only the gaseous volatiles while TG records the total weight loss due to both gases and chain fragments volatile at the degradation temperature. Thus the similar weight losses observed in TG during the initial processes may result from both a decrease in MMA monomer production and a reduction in the amount of formation of chain fragments from the PAN which would vary according to the amount of PAN in the blend.

TVA has shown that non-condensible gases are evolved in the region 375-400°C, which may be associated with an additional mode of decomposition. It is at this same temperature that the TG curves demonstrate a maximum weight loss in the blends. Since the percentage

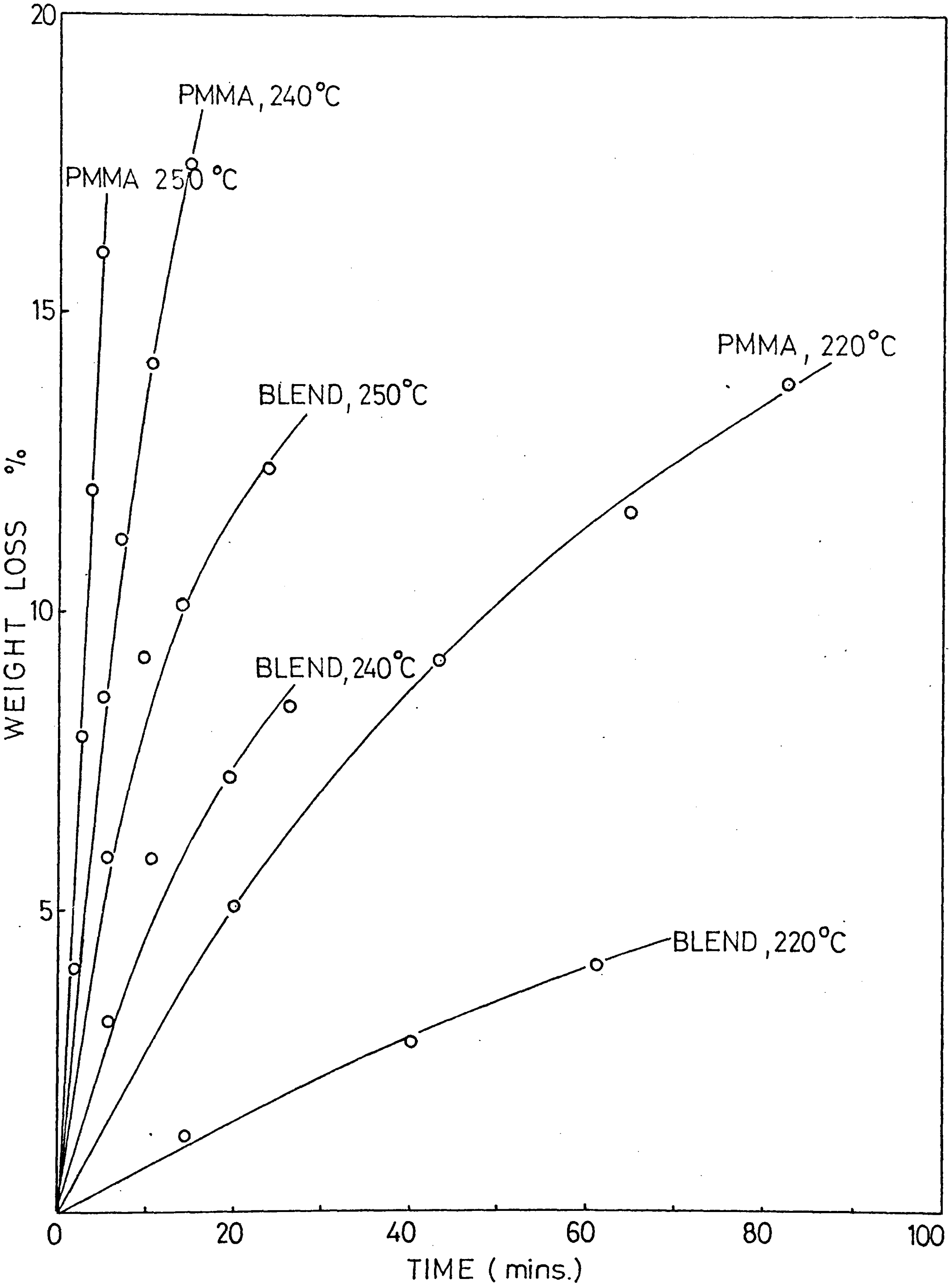


FIG. 3.16 ISOTHERMAL WEIGHT LOSS CURVES FOR
(a) PMMA I (b) 4:1 BY WEIGHT PMMA I:PAN I
5 mg. POWDER SAMPLES, DYNAMIC N_2 ATMOSPHERE

weight loss corresponding to non-condensible gases such as CO or CH_4 must invariably be small, it is reasonable therefore to postulate that molecular fragmentation is occurring at this temperature in addition to unzipping of the PMMA.

Comparison of both film and mixed powder samples by TVA shows qualitatively the same behaviour. It has also been found that a further variation sample form obtained by pressing the mixed powder samples into discs, using a Perkin Elmer die normally employed for the formation of KBr discs for IR spectroscopy, gives a similar degradation pattern.

It has been shown that a significant variation in blend stability is achieved by altering the molecular weight of the PMMA but varying the molecular weight of PAN does not alter the overall pattern. The result is not unexpected in view of the absence of molecular weight dependence in PAN decomposition.

3.8 DIFFERENTIAL THERMAL ANALYSIS

The results of DTA for sample weights in the range 2–10 mg PAN I, are illustrated in Fig. 3.17. The trace exhibits one outstanding feature, a sharp exotherm, which at the standard heating rate of 10^{o}C/minute, starts around 250^{o}C and peaks at the reference temperature of 268^{o}C (Reference temperature T_R = sample temperature (T_S) – Differential temperature (ΔT)).

A 10 mg sample thus gives a $\Delta T = 35^{o}C$, whereas 5 mg and 2 mg give 11^{o}C and 2.5^{o}C, while T ref. values for the same samples are 268, 273 and 281^{o}C respectively.

It has been found that the detailed characteristics of the DTA exotherm, that is the differential temperature, the temperature at which ΔT occurs and the temperature of initiation of the exotherm are all extremely sensitive to environmental factors and to structural changes in the polymer such as small amounts of additives or comonomers.

Fig. 3.18 illustrates the DTA traces for 10 mg and 5 mg samples of PAN II. ΔT values were found as 30 and 85°C while T ref. was 254 and 256.5°C respectively. The temperature of initiation in both was between 220-225°C.

It is evident that the initiation temperatures in the solution polymer are lower than those in the bulk sample. This is thought to be associated with the solvent NN dimethyl-formamide, which may become incorporated into the polymer structure through transfer reactions occurring during polymerization or may be present as residual solvent in the polymer.

DTA curves for both PMMA I and II are illustrated in Fig. 3.19. Both traces reveal the endothermic nature of the depolymerization processes corresponding to the peak maximum observed in the TV thermograms of the same polymers.

Fig. 3.20 illustrates the typical DTA behaviour of polymer mixtures. The differential temperature found for a 50:50 mixture is approximately that expected for the PAN content although the reference temperature is slightly displaced to a higher temperature. The trace also shows a similar displacement of the PMMA endotherm. The results found for PMMA I were again similar to these.

No additional information about the nature of the exotherm can, therefore, be gained from this technique but it serves to confirm the previous observations about the delay in MMA evolution at higher temperatures.

3.9 INFRA RED ANALYSIS OF THE VOLATILE PRODUCTS

The major gaseous products of decomposition of PAN to 500°C+ which can be identified by i.r. were previously described as NH_3 and HCN. The products from mixed and unmixed samples throughout the composition range were examined in a similar manner.

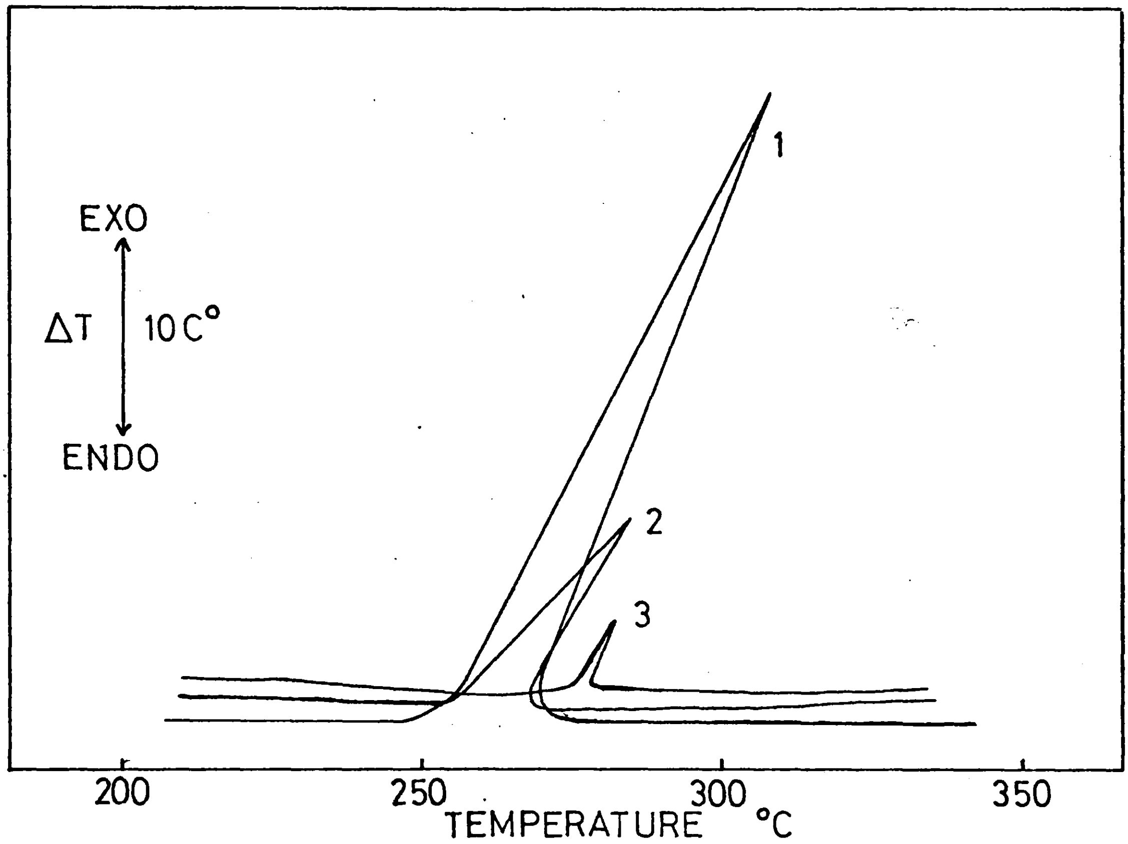


FIG. 3.17 DTA CURVES FOR PAN I POWDER SAMPLES
(1) 10 mg (2) 5 mg (3) 2 mg HEATING RATE 10C°/min
DYNAMIC N_2 ATMOSPHERE

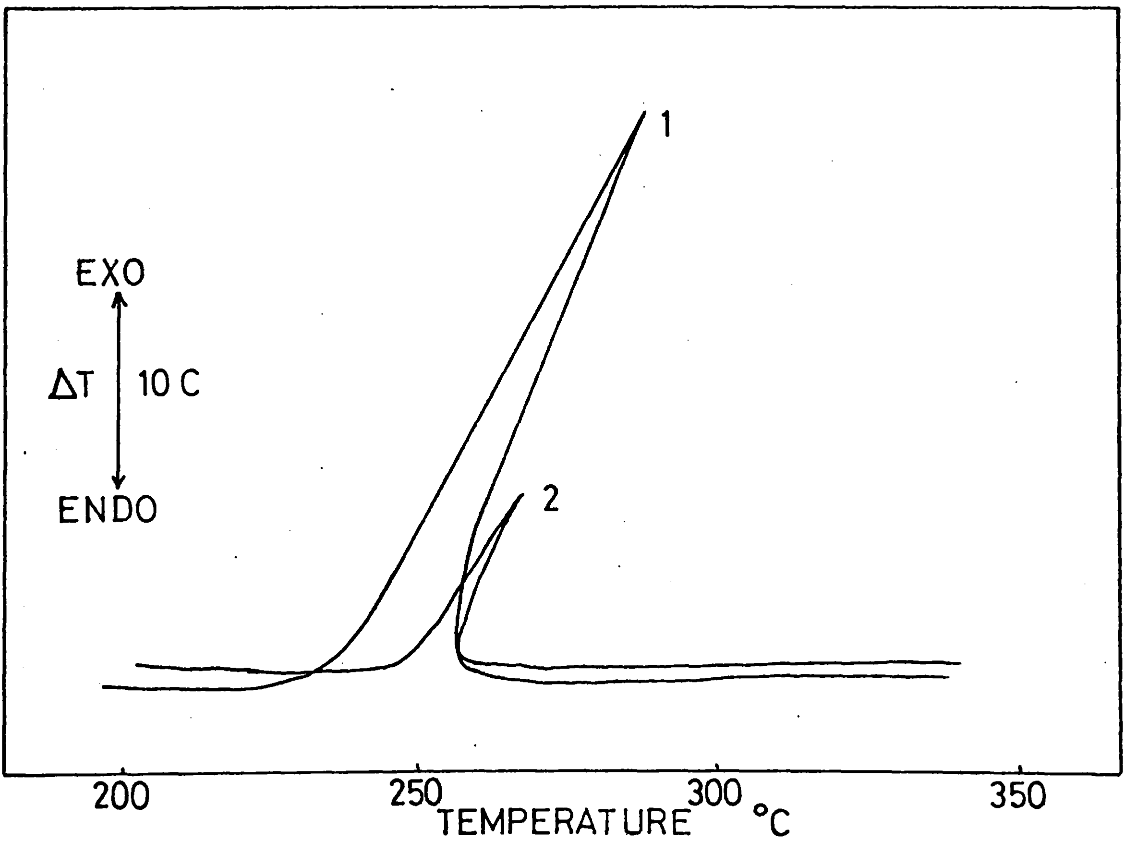


FIG. 3.18 DTA CURVES FOR PAN II POWDER SAMPLES
(1) 10 mg (2) 5 mg HEATING RATE 10C°/min.
DYNAMIC N_2 ATMOSPHERE

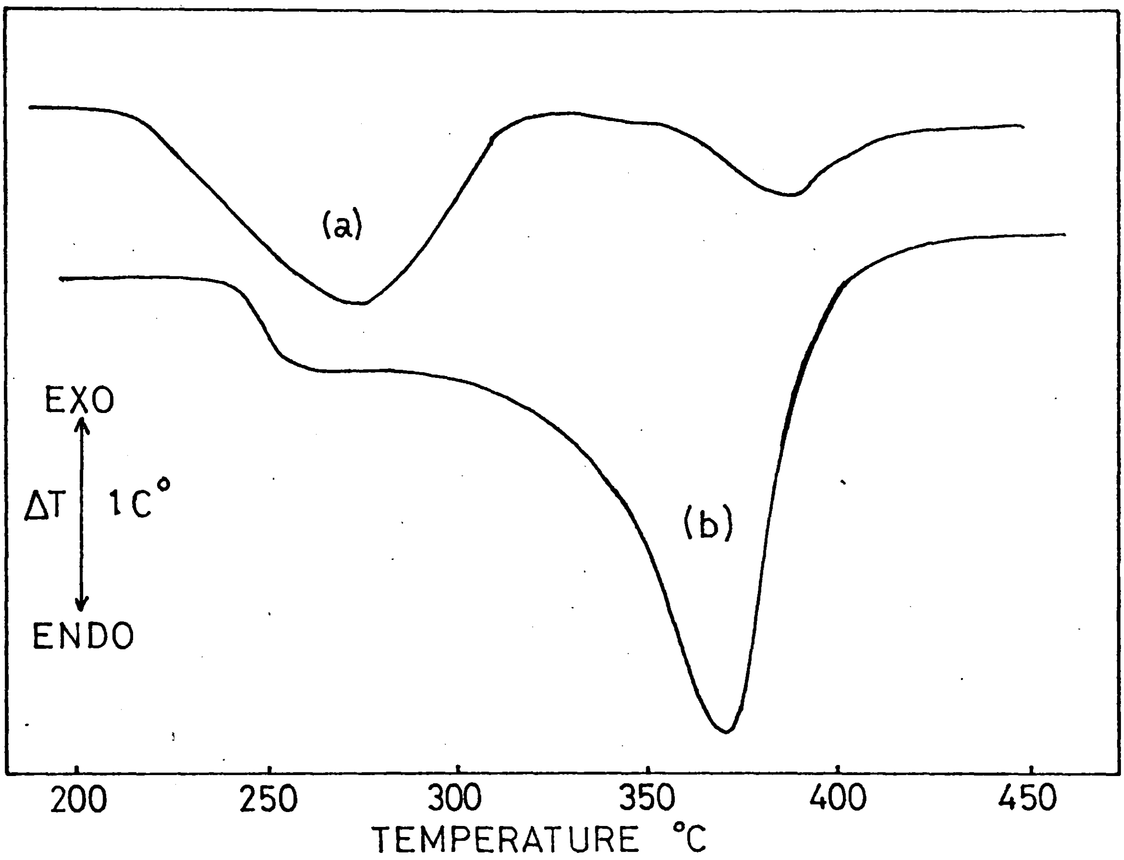


FIG. 3.19 DTA CURVES FOR (a) PMMA I (b) PMMA II 10 mg POWDER SAMPLES HEATING RATE 10C^{o}/min, DYNAMIC N_2 ATMOSPHERE

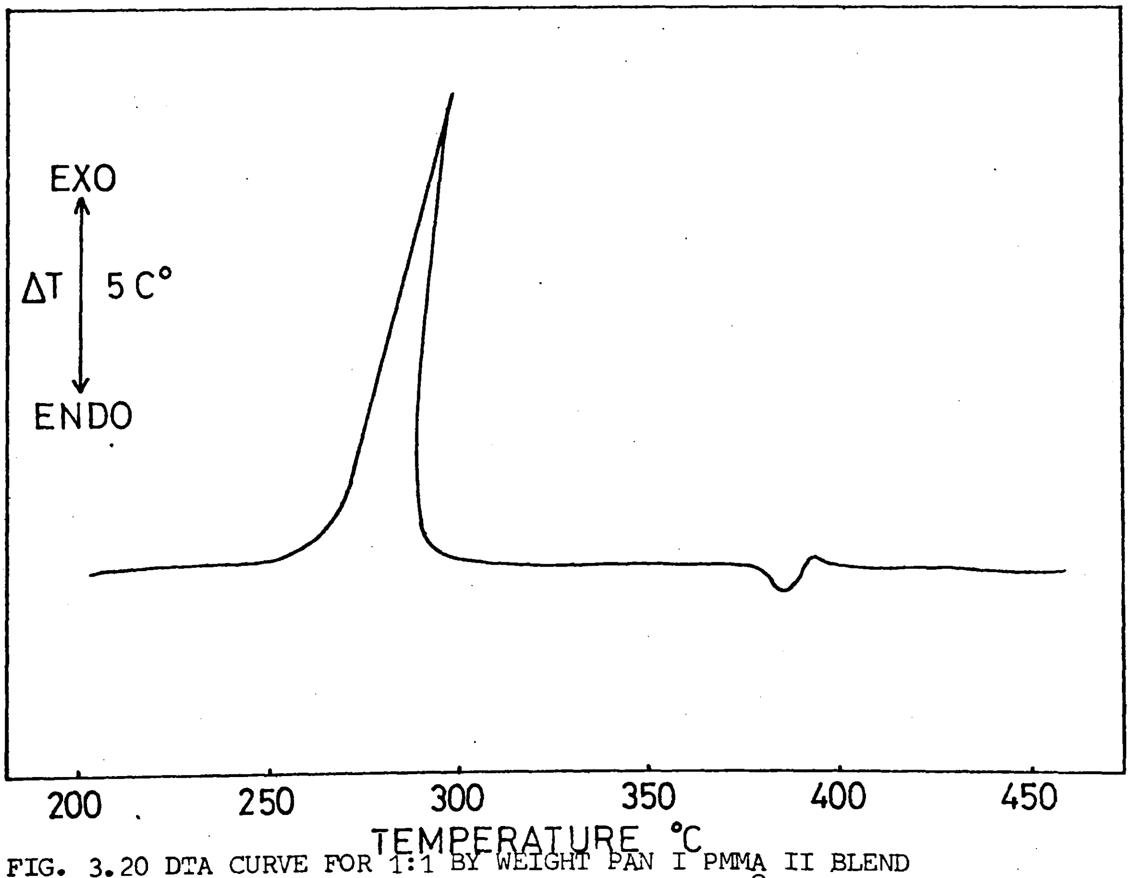


FIG. 3.20 DTA CURVE FOR 1:1 BY WEIGHT PAN I PMMA II BLEND 10 mg POWDER SAMPLE, HEATING RATE 10C^{o}/min, DYNAMIC N_2 ATMOSPHERE

The condensible gases evolved during temperature programmed degradation at 10°C/minute to 500°C were distilled from the system into an I.R. cell (path length 10 cm) using the product collection adaptor described in Chapter 2.

Gases non-condensible at -196°C cannot be collected under the continuous evacuation conditions employed in TVA and were, therefore, examined after degradation in a closed system.

The i.r. spectrum obtained from degradation of a 1:1 PAN I:PMMA I mixture to 500°C in a closed system, is illustrated in Fig. 3.21.

The major absorptions due to NH_3 are identifiable as twin peaks occurring at 933 and 969cm^{-1} of approximately equal intensity while the absorption at 713 cm^{-1} with associated fine structure is due to HCN.

The dominant absorptions throughout the spectrum arise from MMA monomer, the only product observed in decomposition of the homopolymer. The MMA carbonyl peak occurs as a double at 1740 and 1750cm^{-1} and is the strongest absorption in the MMA spectrum. The intense peak at 1032cm^{-1} has been assigned to methanol by comparison with standard spectra of gaseous alcohols. Additional weak absorptions throughout the spectrum have also been assigned to methanol. The absorptions and relative intensities of both MMA and methanol are listed in Appendix 3.

Carbon dioxide can be identified by the broad absorption at 2300-2400cm^{-1} and also by a weak absorption at 671cm^{-1}. Carbon monoxide exhibits fine structure at 2110 and 2180cm^{-1}.

Methane cannot be positively assigned from this spectrum due both to the small amount present and to overlap with more intense MMA absorptions. It can, however, be identified by condensation of the remaining gases using a -196° trap after which bonds at 3015cm^{-1} and 1300cm^{-1} may be observed.

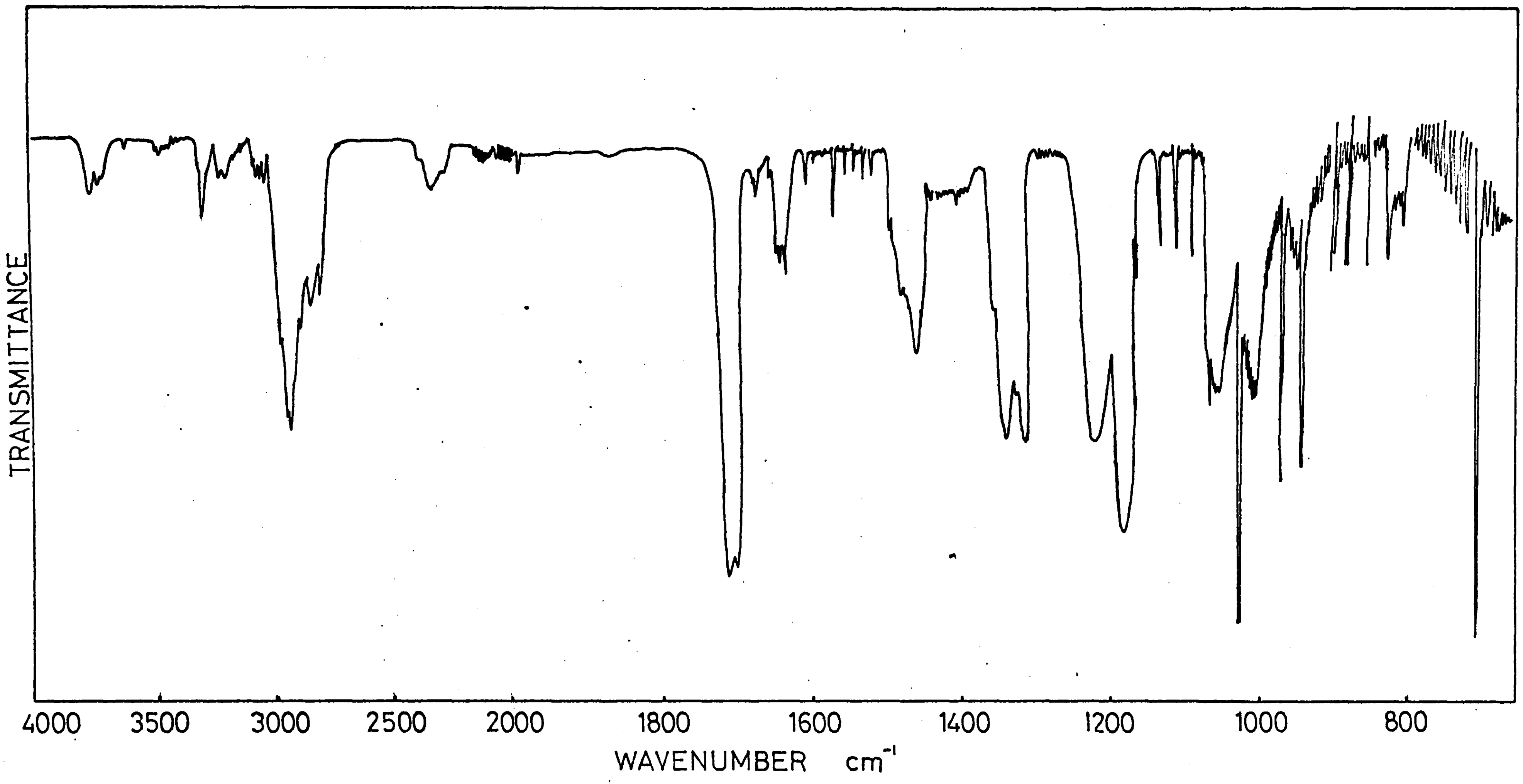


FIG. 3.21 I.R. SPECTRUM OF GASEOUS VOLATILES EVOLVED BY DECOMPOSITION TO 500°C OF A 1:1 BY WEIGHT PAN I:PMMA I MIXED POWDER BLEND IN A CLOSED SYSTEM

The total gaseous products identified by i.r. are listed in Table 3.5.

TABLE 3.5 GASEOUS DEGRADATION PRODUCTS IDENTIFIED BY I.R. SPECTROSCOPY IN PMMA-PAN BLENDS

Products condensible at −196°C	Products non-condensible at −196°C
Methyl methacrylate Ammonia Hydrogen cyanide Carbon dioxide Methanol	Carbon monoxide Methane

Comparison with the products of decomposition of the two homopolymers shows CO_1, CO_2 and methanol in addition to those expected. The absorption due to methane is also slightly greater than that observed from pure PAN.

With the exception of methane, the products are clearly derived from modified PMMA degradation. The increased evolution of methane cannot be assigned definitely to either homopolymer. As a consequence the yield of MMA from degradation of PMMA in the presence of PAN must be reduced.

Examination of i.r. spectra of products from a number of blend compositions shows that the absorbance in the regions associated with methanol, carbon dioxide and carbon monoxide increases with PAN content. Blends containing as little as 5% by weight PAN could be shown to evolve methanol as a decomposition product.

These observations were true of the different sample forms examined.

The temperatures at which the gases are evolved, in particular those not normally associated with the decomposition of PMMA, can be defined more closely by interrupting the temperature programmed degradation of the blend at various temperatures during a normal TVA experiment. Thus it was found in studying a 1:1 PAN:PMMA I mixture, that at 300-320°C only trace amounts of methanol could be detected in addition to the expected products. Further degradation to 500°C produced increased amounts of methanol in addition to CO_2, CO and CH_4.

3.10 INFRA RED ANALYSIS OF COLD RING FRACTION AND RESIDUE

The major proportion of the degradation products of PAN formed in TVA to 500°C (approximately 50-60% by weight of the original polymer) consist of a waxing cold ring fraction (CRF) which collects in the region of the cooled water jacket described in Chapter 2.

This fraction is much greater than that observed in TG employing a dynamic N_2 atmosphere, principally due to the high vacuum conditions employed in TVA allowing a greater proportion of material involatile at ambient temperatures and pressures to be volatilised.

The amount of CRF formed concurrently with the evolution of HCN and NH_3 around 300°C is largely dependent upon the magnitude of the exothermic nitrile polymerization - the more heat evolved in this process the greater the extent of chain fragmentation. The CRF rapidly colours from an initial pale yellow through to amber-red at 500°C. In relatively large samples of PAN (100 mg or greater) the further decomposition of this CRF can influence the overall appearance of the TVA trace.

In Fig. 3.22 is shown the i.r. spectrum of the initial polymer and that of the CRF obtained from degradation to 500°C. A review of PAN and its copolymers by Beevers[69] contains an examination of the relatively small number of papers concerned with i.r. analysis of PAN and also tabulates the frequencies commonly observed. It is interesting to note among them the absorption at 1620-30cm^{-1}. All polyacrylonitriles show several absorptions in the region 1500-1800cm^{-1} which can vary in intensity relative to the nitrile bond depending on the conditions of polymerization. Liang and Krimm[70] ascribed absorption in this region to impurities. It has, however, been found that absorption in this region arises from both conjugated and non-conjugated -C=C- and C=N groups. Study of these absorptions is made difficult by the apparent random variations in both frequency and intensity[71]. The absorption, however, does indicate initial defect structures in the polymer.

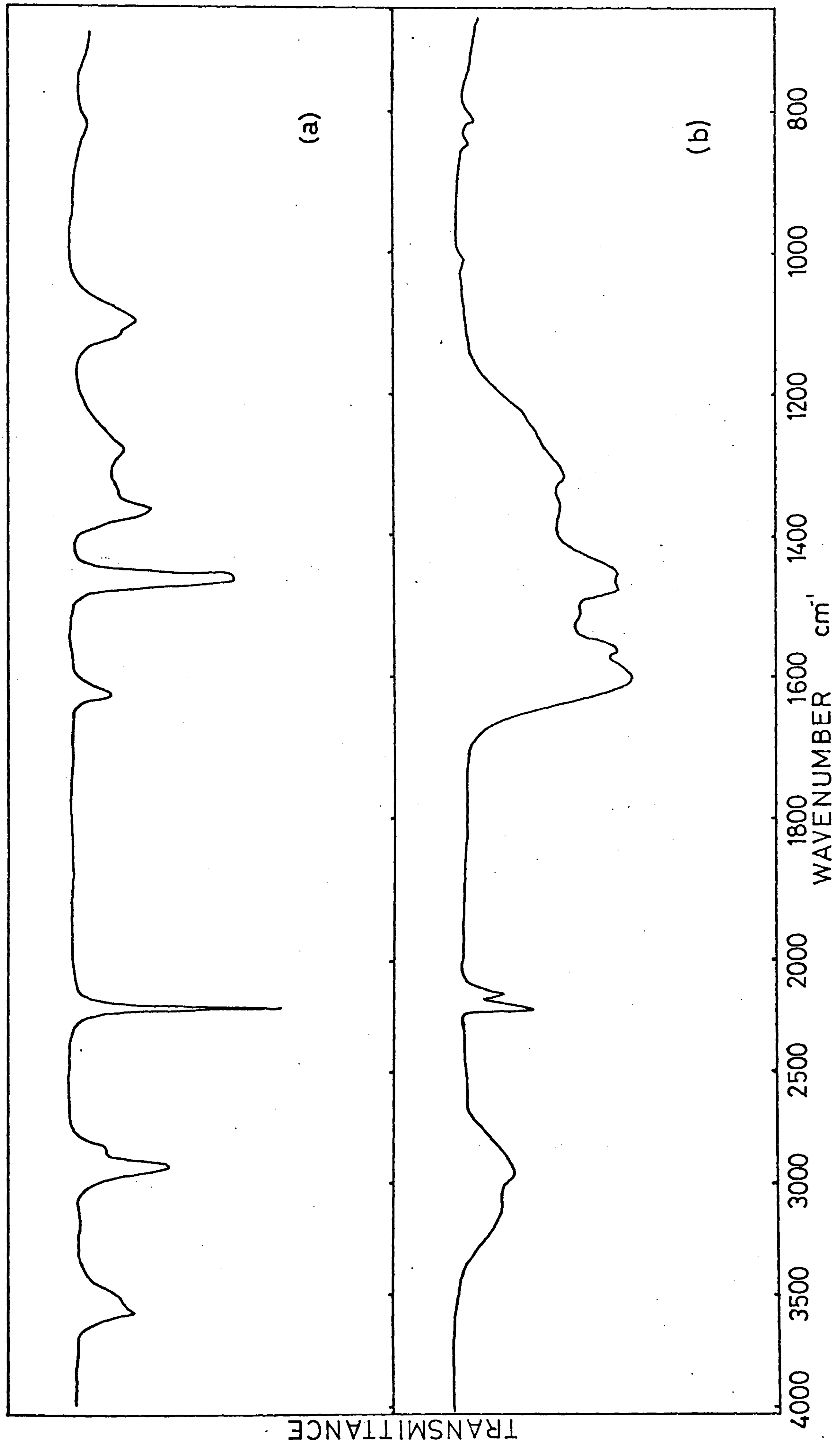


FIG. 3.22 I.R. SPECTRUM OF (a) PAN I (b) CRF AFTER DECOMPOSITION OF PAN I TO 500°C

I.R. analysis of the CRF reveals a number of new absorptions. Peaks which may be assigned to N-H structures are evident above 3000cm^{-1} while the original C=N absorption at 2240 is considerably reduced (an additional peak can be seen around 2185cm^{-1}). The development of this absorption has been concluded by other workers to arise from a new nitrile structure. Hay[72] assigned it to unsaturated nitrile groups although they commonly occur above this frequency (2240-2210).

Spectral studies of nitrile compounds by Long and George[73] show amino substituted unsaturated nitriles to have an abnormally low nitrile frequency and it has been concluded that structures similar to these must exist in the degraded polymer.

The other significant differences arise from the development of intense bonds around 1600cm^{-1} and in the 1400-1000cm^{-1} region. The former arises from conjugation in the degraded polymer but also must include N-H modes associated with the structures identified above 3000cm^{-1}.

In contrast to PAN, PMMA depolymerizes quantitatively to monomer with no chain fragment formation. It has been shown by TVA of the polymer mixtures that the decomposition products from the mixed system are considerably altered. Furthermore the TG behaviour was earlier ascribed to possible molecular chain fragment formation during the latter stages of degradation. It is of interest, therefore, to examine the CRF from the mixed systems for evidence of methacrylate fragmentation.

Fig. 3.23 shows the i.r. spectrum of the CRF obtained by degradation of a 100 mg mixed powder sample of a 1:1 PAN:PMMA blend. The spectrum reveals the peaks already mentioned in the examination of the PAN cold ring fraction but a number of peaks in the carbonyl region in addition to a strong -C-O- stretching absorption are also present. The major carbon-oxygen absorptions and their assignments are listed in Table 3.6.

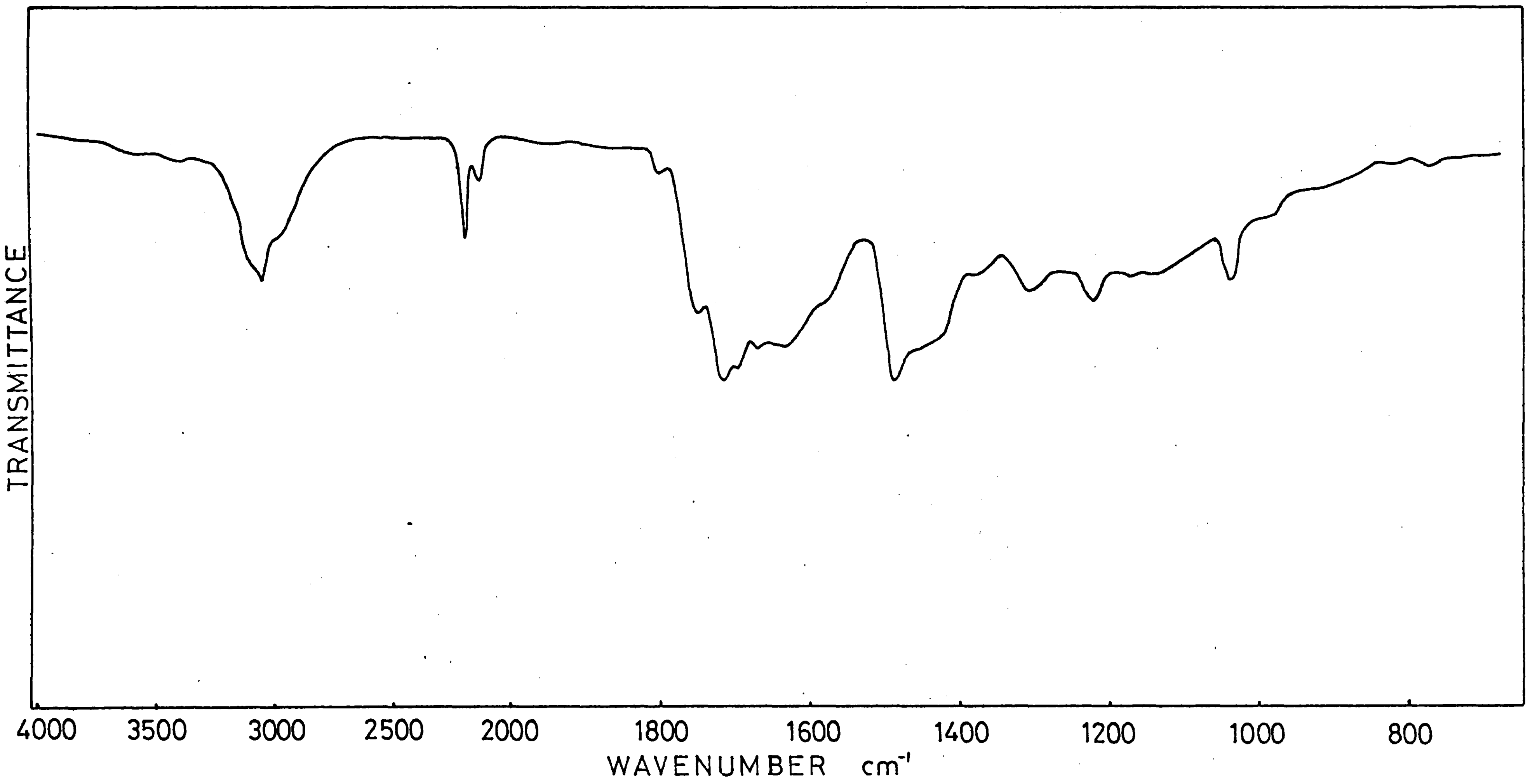
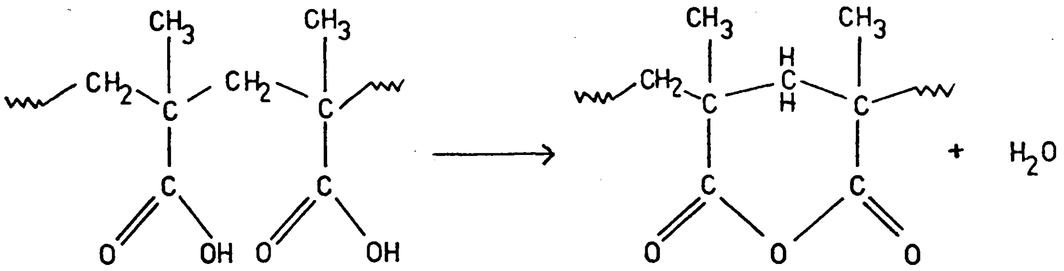


FIG. 3.23 I.R. SPECTRUM OF THE C.R.F. AFTER DECOMPOSITION OF A 1:1 PAN I:PMMA I BLEND TO 500°C

The twin carbonyl absorptions at 1795cm^{-1} and 1753cm^{-1} are similar to those found in anhydro polymethacrylic acid found during pyrolysis of PMMA.

TABLE 3.6 I.R. ANALYSIS OF COLD RING FRACTION IN PAN-PMMA BLENDS

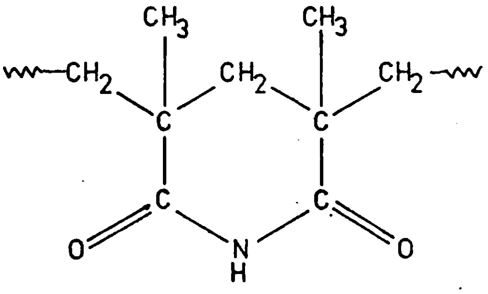
Absorption		Assignment
1795cm^{-1} 1753cm^{-1}	C=0;	cyclic anhydride, 6-membered ring
1725cm^{-1}	C=0;	ester
1695-1705cm^{-1}	C=0;	carboxylic acid, cyclicamide-acyclic or 6-membered ring
1665cm^{-1}	C=0;	primary amide
1022cm^{-1}	C-0-C,	anhydride



In studies of the decomposition of PMMA, Grant and Grassie[31] investigated both the frequency of the carbonyl absorption and the separation and relative intensities of the twin peaks. Comparison with low molecular weight model anhydrides confirmed the structure illustrated. The strong absorption at 1022cm^{-1} was also identified as the -C-0-C- stretch frequency in anhydride structures.

The absorption at 1665cm^{-1} has been assigned to an amide. It may be compared with the primary amide absorption in poly methacrylamide (1670cm^{-1}) although considerable overlapping of primary and secondary amide bands occurs in this region.

Carbonyl absorptions around $1695\text{-}1705\text{cm}^{-1}$ are not well resolved in any of the spectra examined, appearing as a shoulder upon the main absorption. Both carboxylic acid (PMMA 1700cm^{-1}) and cyclic imide units occur in this region -



1700,1710 cm⁻¹

The absorptions found in the examination of the pyrolysis of polymethacrylamide, described in Chapter 7, lend support to this assignment.

I.r. analysis of the CRF obtained from a range of blend compositions confirm the absorption pattern found in the 1:1 blend.Fig. 3.24 illustrates th ratio of the optical densities associated with the three major carbonyl absorptions to that of the nitrile peak (2240cm^{-1}) in the CRF of blends containing between 25 and 90% PMMA. The relevant data is listed in Table 3.7. It is evident that extensive fragmentation of the PMMA chain must occur in blends containing as little as 10% PAN, the products consisting of a complex mixture of carbonyl derivatives.

TABLE 3.7 CARBONYL-NITRILE INFRA RED ABSORPTION DATA FOR CRF COLLECTED FROM DECOMPOSITION TO 500°C OF PAN I PMMA I BLENDS

BLEND COMPOSITION % BY WEIGHT PMMA	OPTICAL DENSITY RATIO CARBONYL/NITRILE ν C = 0		
	1720cm^{-1}	1760 cm^{-1}	1790 cm^{-1}
25	1.45	0.47	0.05
50	2.43	1.80	0.47
67	2.65	2.78	0.91
80	5.0	2.74	1.05
90	11.7	6.86	2.25

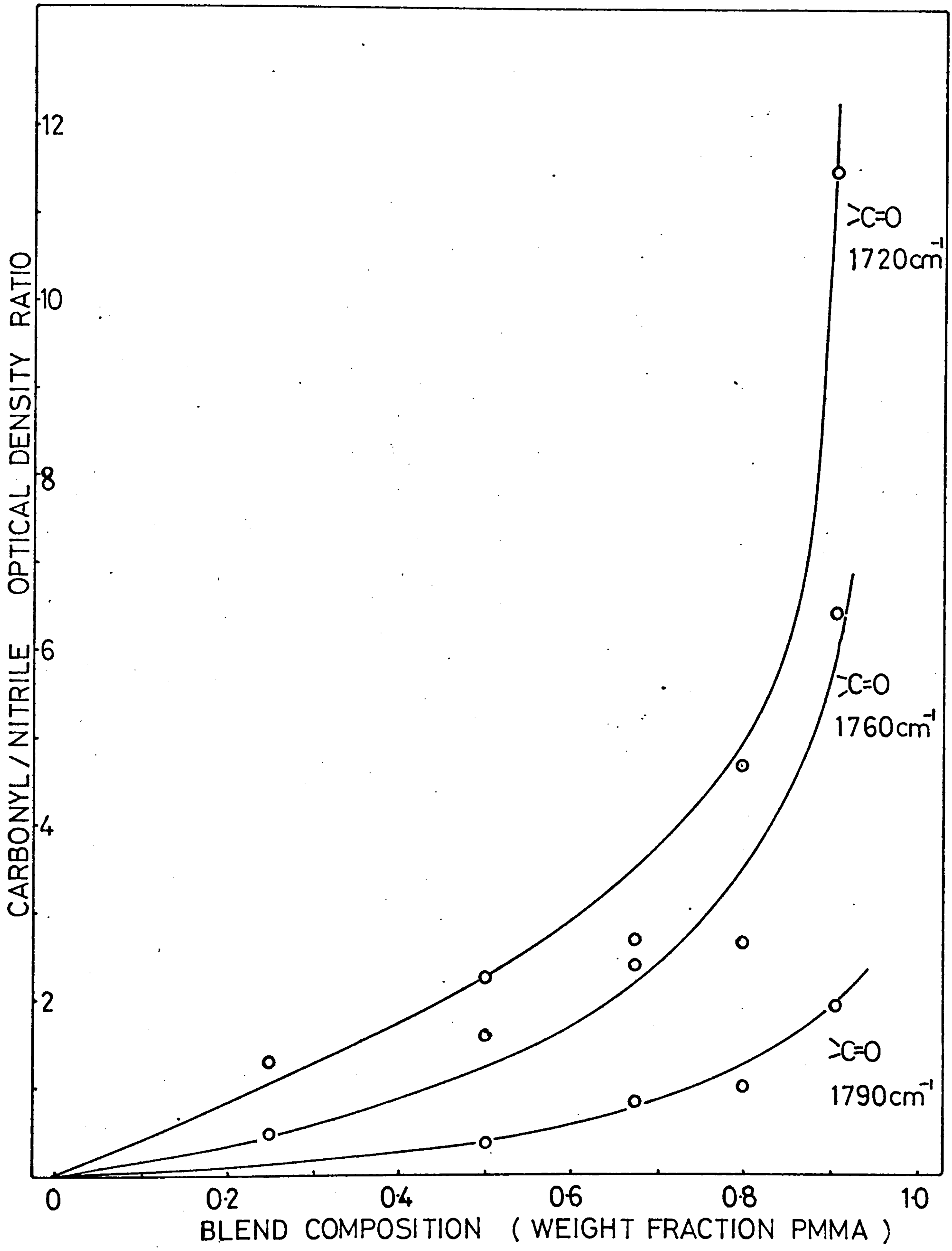


FIG. 3.24 CARBONYL-NITRILE I.R. ABSORPTION DATA FOR THE C.R.F. COLLECTED FROM DECOMPOSITION TO 500°C OF PAN I-PMMA I BLENDS

The residue remaining in both degradation of PAN and of the blends is black and insoluble. The i.r. absorption contains the broad peaks associated with conjugation similar to those found in the CRF (Fig. 3.25) No nitrile absorption is observed in either system nor is there any residual carbonyl absorption in the blend. Comparison between the spectra of the blend and the PAN residues shows no significant difference between the two.

3.11 ANALYSIS OF LIQUID PRODUCTS BY GAS LIQUID CHROMATOGRAPHY

It has been shown that the behaviour of the blends is qualitatively similar in both film and mixed powder systems. In this section the liquid products from the blends, cast as films from DMF, and heated at 10°C/minute to 500°C, were analysed qualitatively and quantitatively for the PAN I:PMMA I system.

A Perkin Elmer F11 Gas Liquid Chromatograph equipped with a hot wire detector was employed. The columns and packing were as follows:-
2 metre, ⅛" o.d., 13½% M.E.A. + 6½% Di-2 Ethyl hexyl sebacate on Chromosorb P80-100 mesh as supplied by Perkin Elmer.

It was observed by TG that production of volatiles during the early stages of degradation of PAN/PMMA I mixtures was reduced. This feature was also revealed by TVA and therefore since the major production in this region is MMA, it is reasonable to assume that depolymerization from unsaturated chain ends is influenced by blending.

A typical glc trace of the liquid degradation products at 500°C is illustrated in Fig. 3.26, together with the retention time for propan-2-ol the internal standard employed in quantitative measurements. The falibration plots for CH_3OH and MMA are given in Fig. 3.27.

The evolution of MMA and CH_3OH was estimated at two different extents of reaction during temperature programmed degradation, at 320°C and 500°C. In this manner it is possible to evaluate the extent to which the evolution of MMA by the two distinct modes of decomposition varies with blend composition.

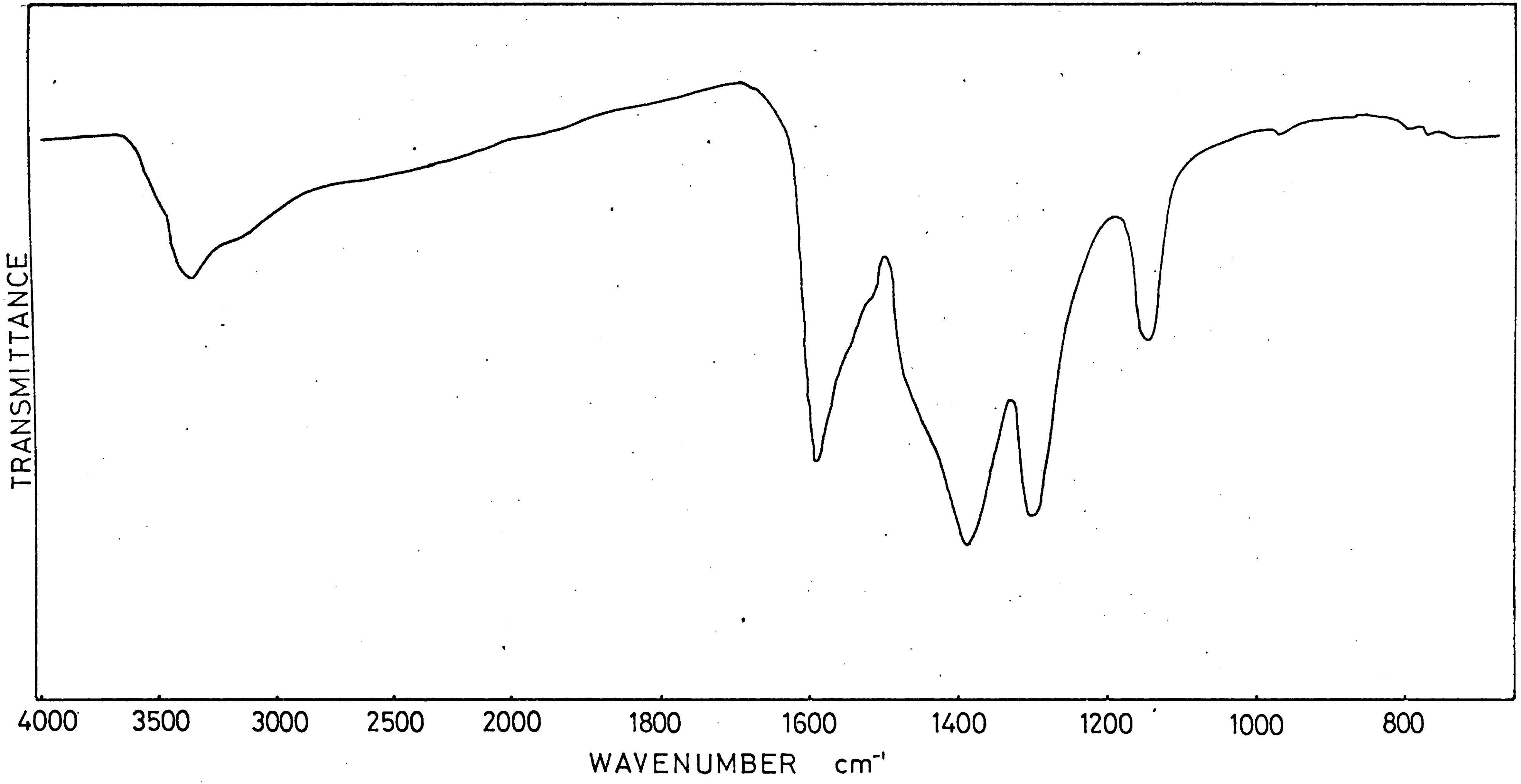


FIG. 3.25 I.R. SPECTRUM OF PAN-I RESIDUE AFTER DEGRADATION TO 500°C

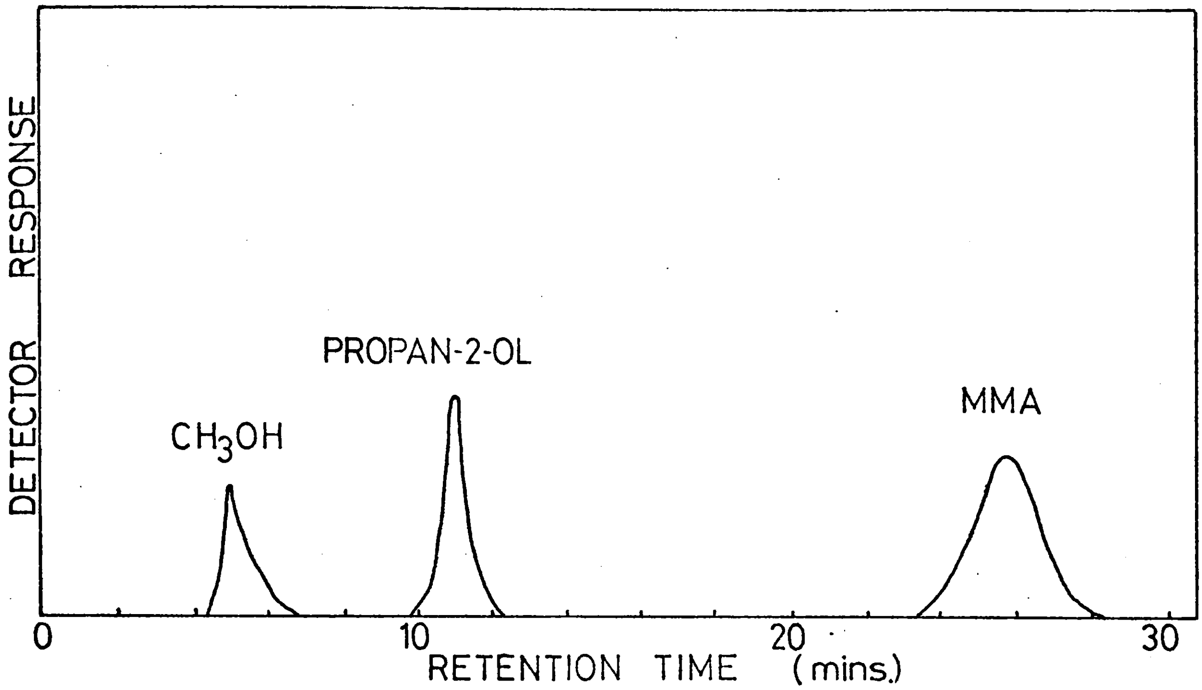


FIG. 3.26 GLC ANALYSIS OF LIQUID DEGRADATION PRODUCTS
OF PAN:PMMA BLENDS
COLUMN TEMPERATURE 60°C; HELIUM CARRIER GAS, 35 ml/min.

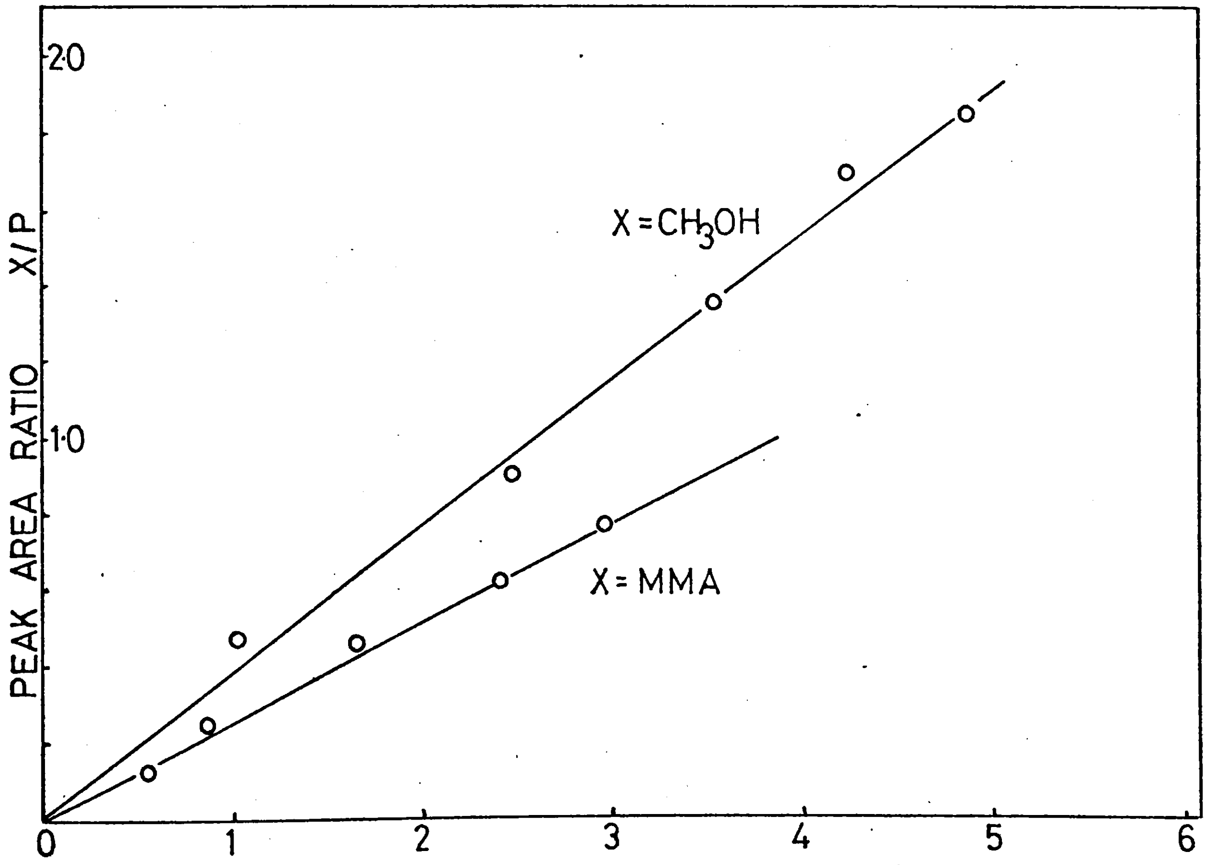


FIG. 3.27 GLC CALIBRATION PLOTS FOR METHYLMETHACRYLATE AND METHANOL
VERSUS PROPAN-2-OL
COLUMN TEMPERATURE 60°C; HELIUM CARRIER GAS, 35 ml/min.

The results for a series of blend compositions between 50–100% PMMA, each containing 50 mg PMMA, are illustrated in Fig. 3.28. It is evident that the total evolution of MMA is reduced by blending, this phenomena being greater during the initial stage of monomer evolution.

Fig. 3.29 compares both CH_3OH and MMA yield at 500°C. CH_3OH evolution is associated with reactions occurring between 320 and 500°C, only trace amounts being detected below 320°C. The amount of CH_3OH evolved from a 1:1 PAN:PMMA I blend comprises more than 50% by weight of the total liquid products.

3.12 STRUCTURAL CHANGES IN THE POLYMER BLEND

MOLECULAR WEIGHT OF PMMA

Comparison of molecular weight changes in PMMA II degraded alone and in a blend containing 80% by weight PMMA II, was achieved by isothermal degradation at temperatures betwen 244°C and 320°C for varying time intervals in a TVA system. In this temperature region it has been shown earlier that MMA was the only liquid product detected in GLC studies.

The molecular weight of the degraded PMMA was determined by GPC after Sohxlet extraction of the blend (acetone, 15 hrs) PAN is completely insoluble under the conditions. The operational variables employed in GPC analysis are given in Appendix 2.

The results are illustrated in Fig. 3.30. It is evident that for a given extent of volatilization the molecular weight of the polymer incorporated in the blend is lower than in the homopolymer alone.

The behaviour of PMMA varies according to its molecular weight, the limiting behaviour in accordance with the mechanisms previously outlined being represented by the diagonal shown in Fig. 3.30. The experimental results of Grassie and Melville[74] have shown that for low molecular weight polymers the curves fall above the diagonal, while the theoretical limit, as represented by the diagonal, approximates to the behaviour of high molecular weight polymers.

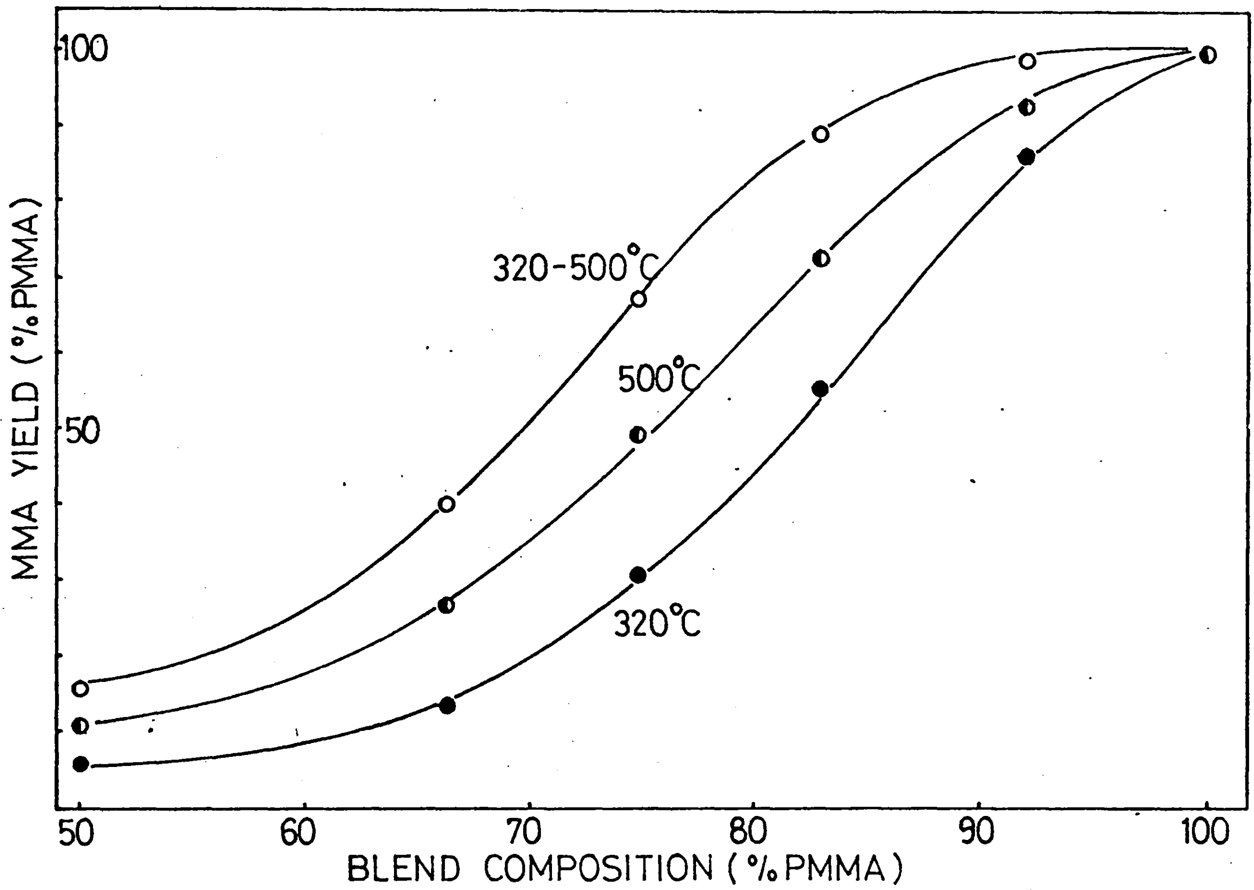


FIG. 3.28 EVOLUTION OF MMA MONOMER AT 320°C, 320-500°C, 500°C AS A FUNCTION OF BLEND COMPOSITION

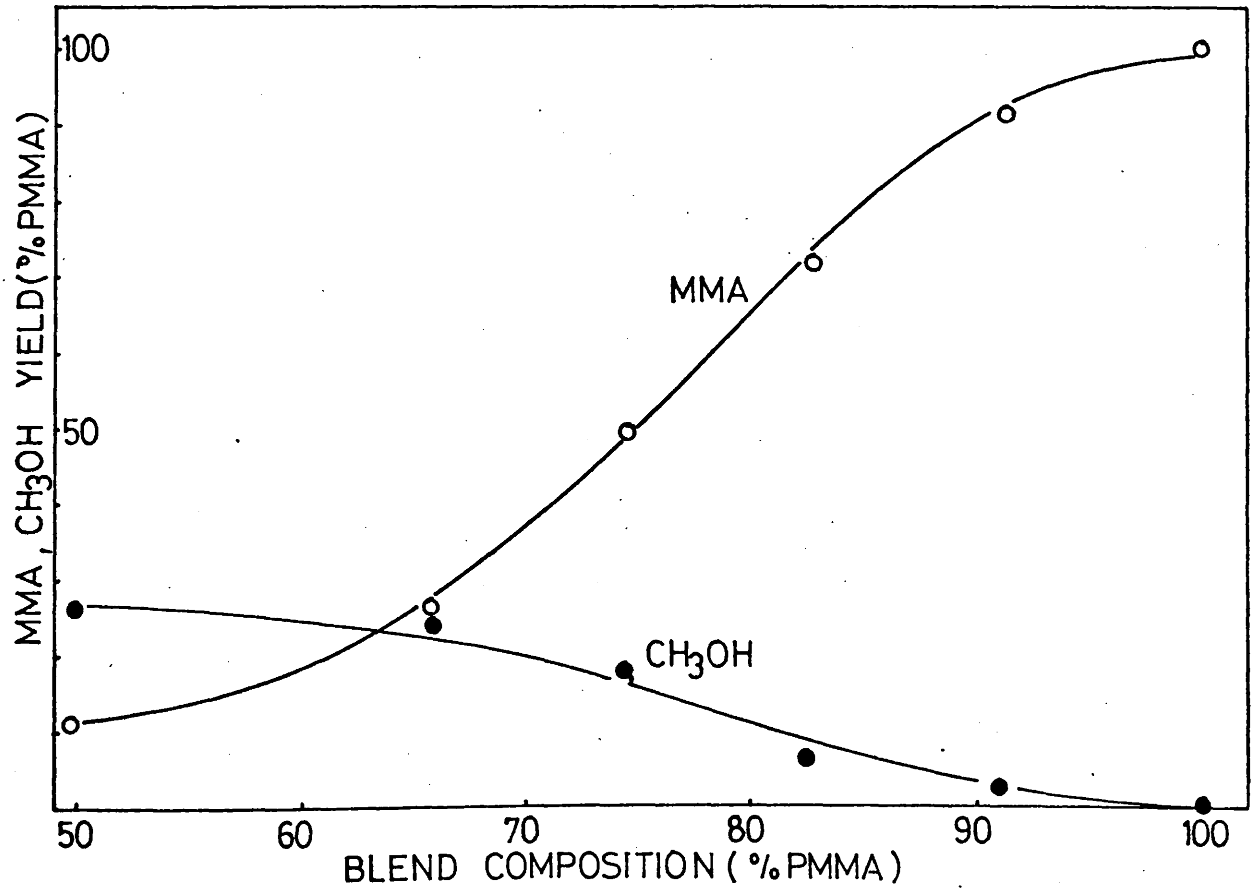


FIG. 3.29 EVOLUTION OF MMA MONOMER AND CH_3OH AT 500°C AS A FUNCTION OF BLEND COMPOSITION

In order that the curve may fall below the diagonal as in Fig. 3.30, it is necessary that more than one fragment per molecule of degraded PMMA remains in the residue. This is commonly observed in decompositions accompanied by chain transfer reactions as found in polystyrene and polymethyl acrylate which will be illustrated in Chapter 5. It has also been demonstrated in acrylonitrile-methyl methacrylate copolymers by Grassie and Melville [74] and by Grassie and Farish[52] the effect being ascribed to the blocking of depolymerization of the PMMA macroradical by acrylonitrile units in the polymer chain.

The results of this study are made more complex by the presence of a carbonyl absorption identified in i.r. analysis of the PAN residue after the Soxhlet extraction procedure. It appears that a small proportion of the degraded PMMA remains insoluble and may be associated with the development of the carbonyl ring structures observed in i.r. analysis of the molecular chain fragments. The insolubility resultant on incorporation of relatively small amounts of such structures has been demonstrated in studies of MMA-methacrylamide copolymers in Chapter 7.

THE EFFECT OF PARTIALLY DEGRADED PAN UPON PMMA DECOMPOSITION

The major process in PAN decomposition is the free radical cyclization of nitrile groups occurring around 270°C, accompanied by chain fragmentation and the evolution of NH_3 and HCN. In an attempt to evaluate the effect of the PAN residue in isolation from the gaseous decomposition products, a blend containing PAN degraded under normal TVA conditions to 400°C was examined. In this manner the majority of the NH_3 and HCN evolution is removed, although further amounts of both gases are evolved between 400-500°C indicating further radical rearrangements to be occurring.

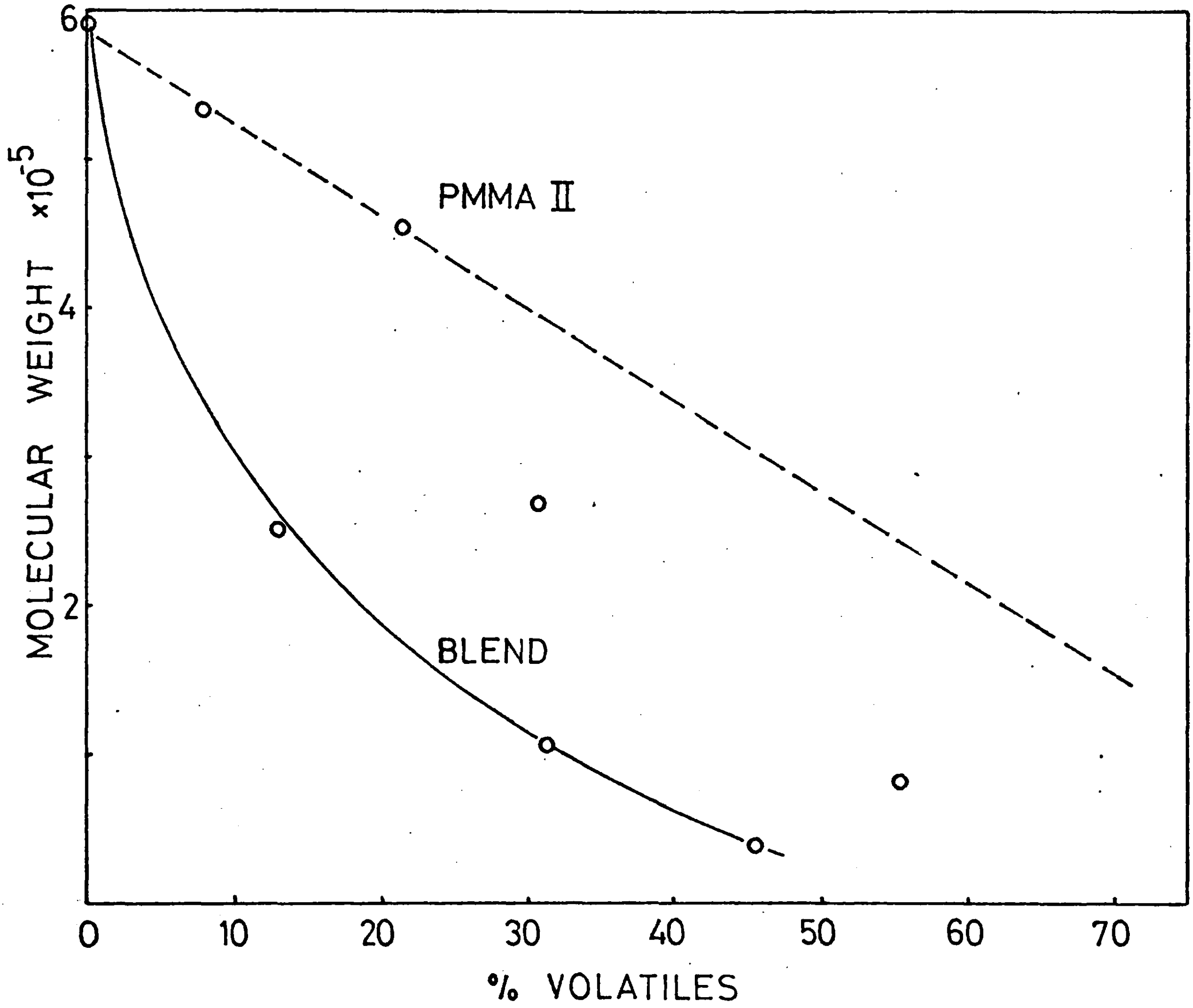


FIG. 3.30 PMMA MOLECULAR WEIGHT VERSUS % VOLATILES IN DEGRADATION OF (1) PMMA II (2) 4:1 BY WEIGHT PMMA II:PAN I BLEND FILM SAMPLES FROM DMF SOLUTION

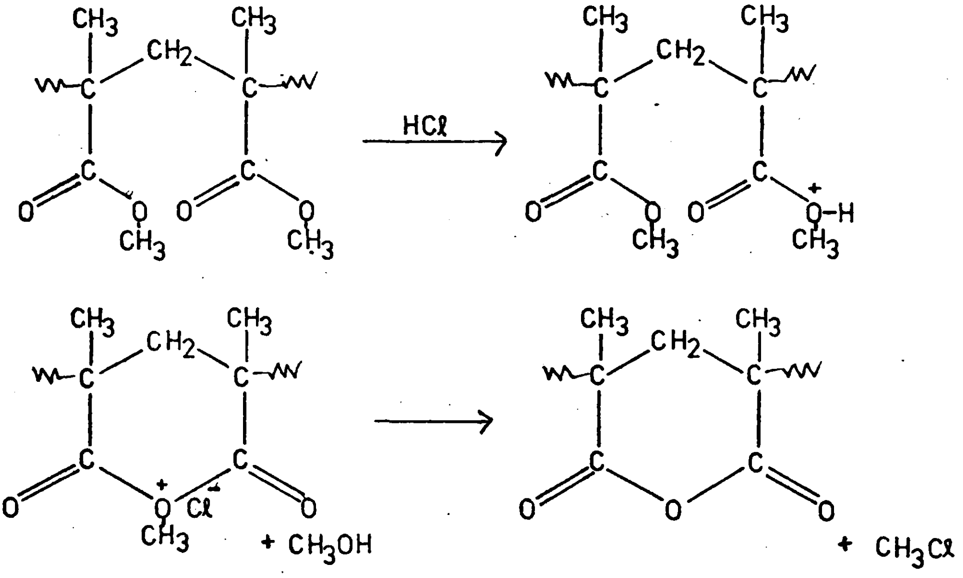
SAMPLE	TEMP °C	TIME(hrs)	% VOL.	MOL. WT.
PMMA II	244	3	9·1	541,000
"	280	3	21	479,000
"	280	5	30·5	271,000
"	300	4	55	91,000
4:1 BY WT. PMMA II	280	3	13	255,000
- PAN I	300	4	31	105,000
"	320	4	45·5	32,400
PMMA II	—	—	—	590,000

The TVA curve for a 1:1 blend containing PAN heated to 400°C and PMMA I is illustrated in Fig. 3.31. It is evident that substantially similar reactions are occurring and this is confirmed by i.r. analysis of both the CRF and the gaseous products. In the early stages of decomposition the evolution of MMA monomer appears reduced although to a lesser extent than in previous blends. The experiment, therefore, does not make a clear differentiation between the effect of the residue and that of the gaseous products in determining blend behaviour although the result may indicate that radical activity in the PAN residue may play a role in determining the evolution of MMA during the early stages of decomposition.

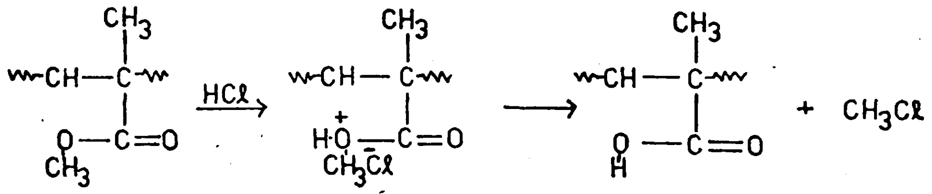
3.13 THE EFFECT OF NH_3 and HCN UPON PMMA DECOMPOSITION

Evidence for the hydrolysis of the ester group in PMMA by acids such as HCl and CH_3COOH has been found in studies of PMMA/PVC and PMMA/PVAc blends respectively. Thus it was found by McNeil & Neil[56,17,18] that anhydride formation in the PMMA/PVC system was accompanied by the evolution of methyl chloride for which two possible mechanisms were postulated.

(1)



(2)



The failure to detect methanol as a product favoured the second mechanism. Studies of polychloroprene-poly(methyl-methacrylate) blends, however, indicate both CH_3OH and CH_3Cl formation, suggesting the first mechanism[74].

In studies of PMMA/PVAc, Jamieson[57] has demonstrated similar behaviour arising from acetic acid, the primary product of decomposition of PVAc.

By analogy, the result of a similar interaction with HCN would result in CH_3CN and CH_3OH formation. Methanol has been detected in significant amounts but acetonitrile which was detected in PAN decomposition was not found in increased amounts compared with the 1:1 ratio of CH_3OH:CH_3CN proposed by mechanism 1. The evidence of blend decomposition obtained fails to differentiate between the two mechanisms but suggests that anhydride formation, if occurring by this mechanism, is not a major process.

The effect of NH_3 upon PMMA I was determined by heating a powder sample under an atmosphere of ammonia previously distilled from sodium dried solution at -40°C.

The result of heating at 165°C for 10 hours is illustrated in Fig. 3.32 together with the TVA curve for the same polymer after heating in vacuo for a similar period.

It is evident that the PMMA heated in vacuo is unaffected having undergone little decomposition. The sample heated in NH_3 shows two effects - a reduction in the peak height associated with low temperature decomposition; the presence of small amounts of non-condensible gases at higher temperature. Ir analysis of the gaseous products shows small amounts of CO_2, CH_3OH and HCN present in addition to MMA monomer. A small amount of CRF also formed exhibits similar absorptions to those observed in the blends indicating the absorption assigned to anhydride formation.

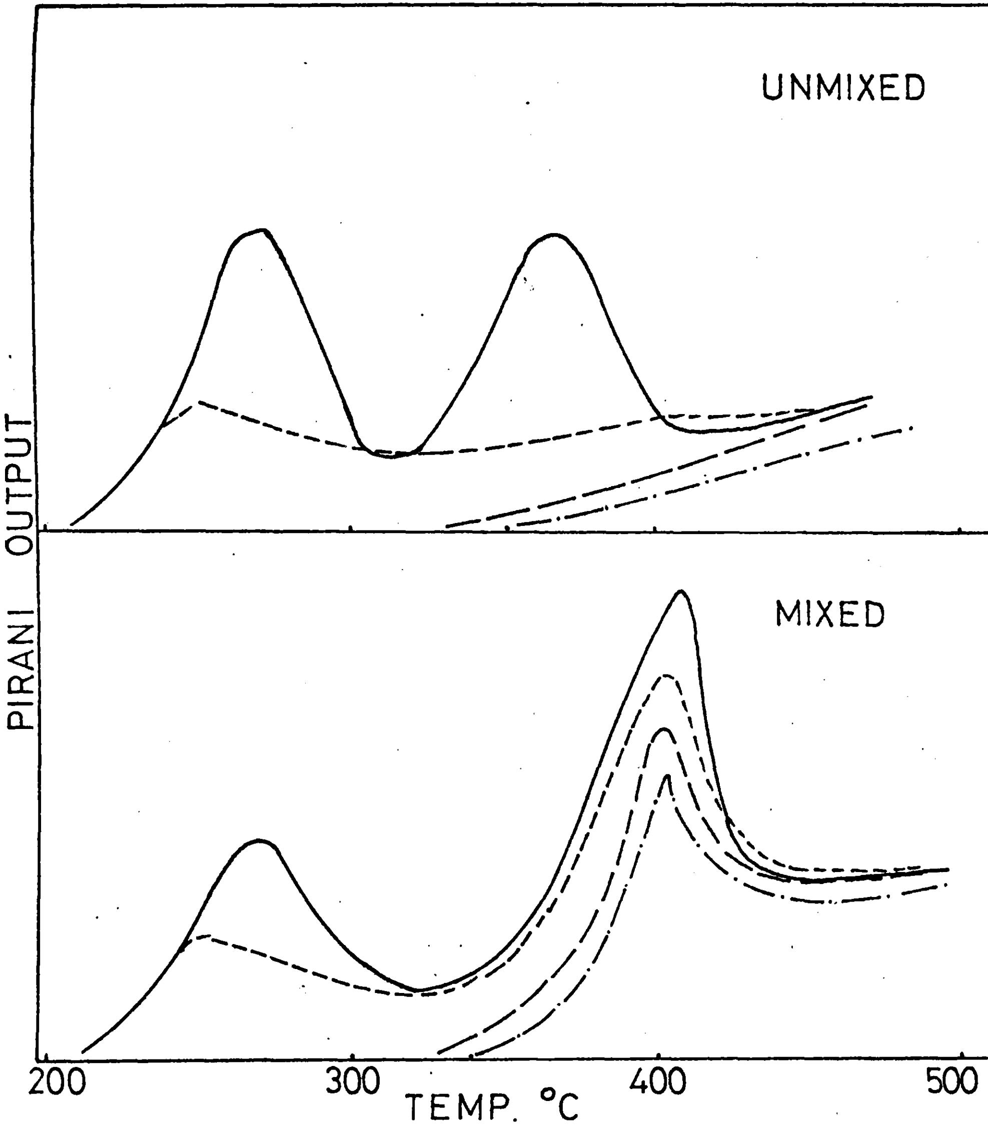


FIG. 3.31 TVA CURVES FOR SIMULTANEOUS DEGRADATION OF PAN I (PREHEATED TO 400°C) AND PMMA I, 1:1 BY WEIGHT POWDER SAMPLES, TOTAL WEIGHT 100 mg.

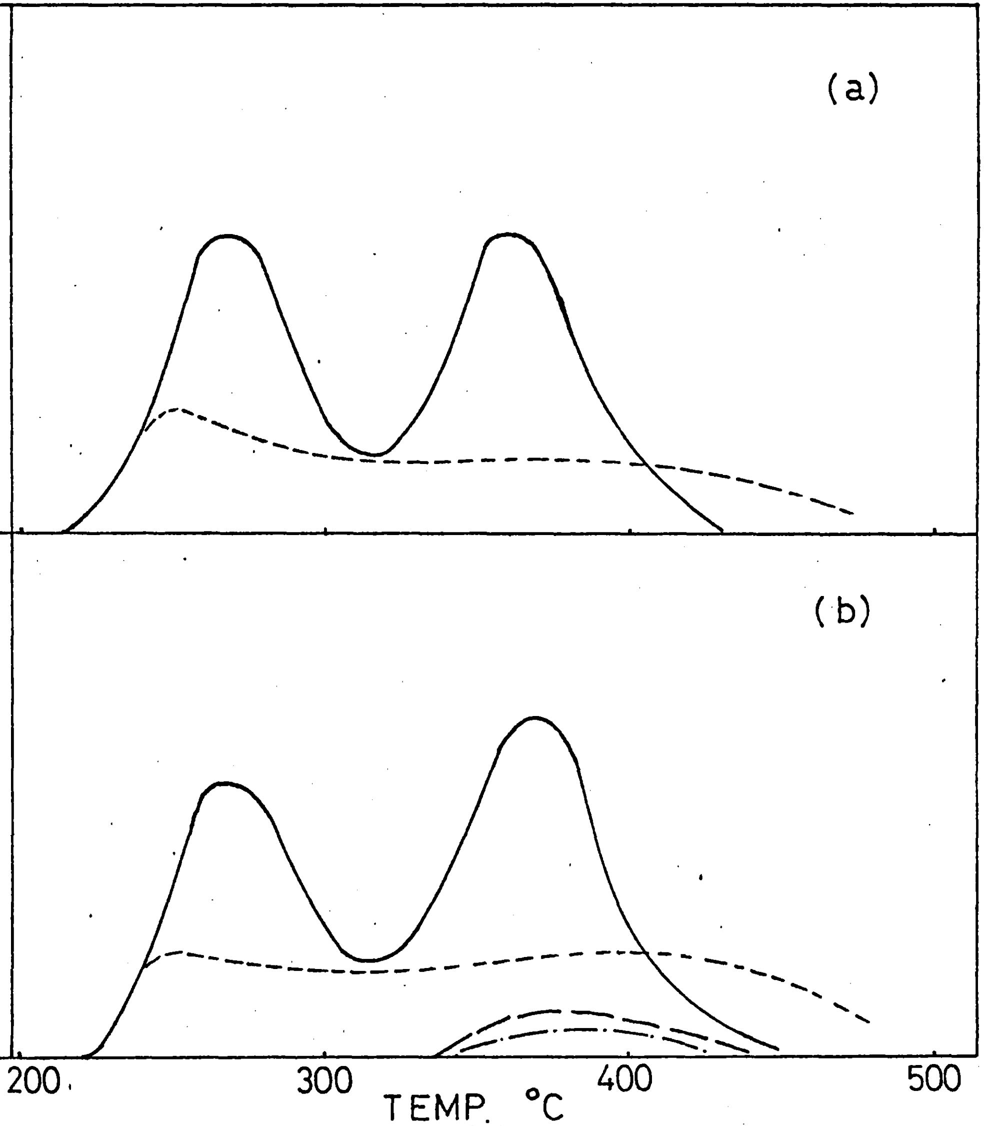
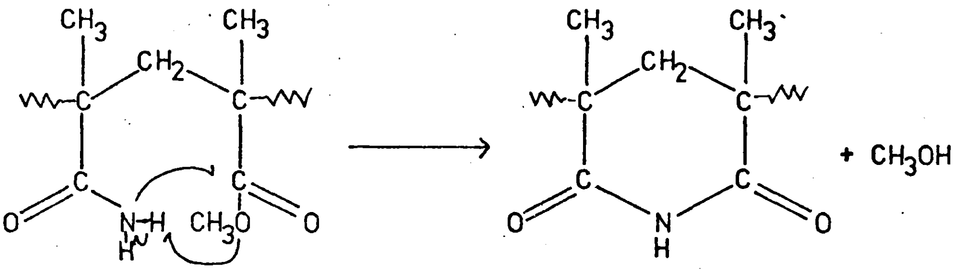


FIG. 3.32 TVA CURVES FOR (a) PMMA I, AFTER ISOTHERMAL DEGRADATION AT 165°C FOR 10 HOURS IN VALUE (b) PMMA I, AFTER ISOTHERMAL DEGRADATION AT 165°C IN NH_3 FOR 10 HOURS

The reduction of volatilization during the early stages of PMMA decomposition has been noted in low molecular weight methylacrylamide-methyl methacrylate copolymers as examined in Chapter 7. This has been associated with the formation of cyclic amide ring structures accompanied by elimination of CH_3OH as follows:-



Decomposition of this structure has also been shown to result in the formation of gaseous CO, CO_2 and HCN.

The presence of anhydride structures is more difficult to explain but may be due to trace amounts of water which would result in hydrolysis of the ester groups to form a methacrylic acid-methyl methacrylate copolymer which may in turn undergo similar cyclisation reactions to those outlined.

3.14 DISCUSSION

The interactions possible in any polymer blend can generally be divided into two groups:- those reactions occurring between macro radicals derived from one or both of the decomposing polymers; reactions between small molecules or radical species formed during degradation with the polymer chain or its substituents.

The former is illustrated by the work of Mitzutani[10] in studies of polypropylene blends with vinyl polymers where the formation of graft copolymers by reaction of the vinyl polymer macroradical with the polypropylene chain was observed.

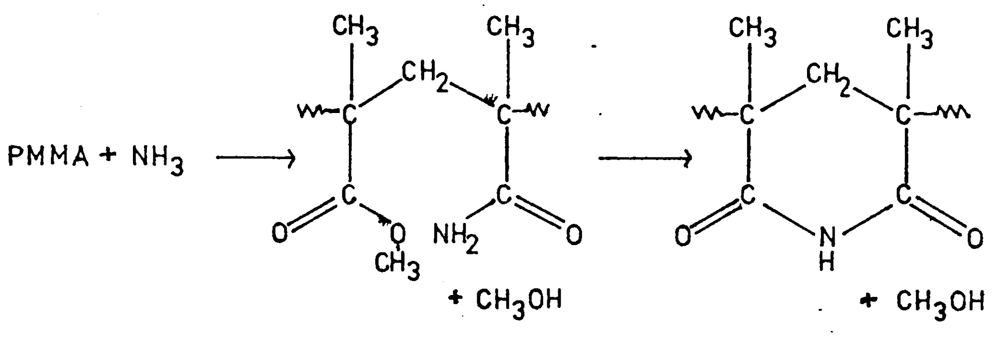
Processes involving both a radical chain carrier and a gaseous decomposition product are found in PVC/PMMA blends. This McNeill & Neil[17,18,56] accounted for the observed increased initial rate of PMMA decomposition through the attack of $Cl^{\bullet}$ radicals upon PMMA. It was proposed that subsequent stabilisation of the residual PMMA results from anhydride structures in the polymer chain derived from the reaction of HCl with the ester group during diffusion through the molten polymer.

In the present study the majority of the observations made upon the thermal stability of the blends, relate to the behaviour of PMMA in the blend. Little evidence can be found of any alteration in PAN decomposition. It is proposed therefore that the predominant processes occur through the interactions arising from the diffusion of small molecules through the molten polymer. The non-compatibility of the polymer mixture together with the rapid development of crosslinks in PAN must further minimise the opportunity for interactions between macroradicals formed during decomposition.

It is apparent that both the stabilization of PMMA and of gaseous decomposition products can arise as a result of ring structures formed by cyclization of adjacent functionalities in the polymer chain. This has already been outlined for methacrylic acid-methyl methacrylate copolymers and is also a feature of the decomposition of methacrylamide-methyl methacrylate copolymers (Chapter 7). The primary product of cyclization in both systems is methanol.

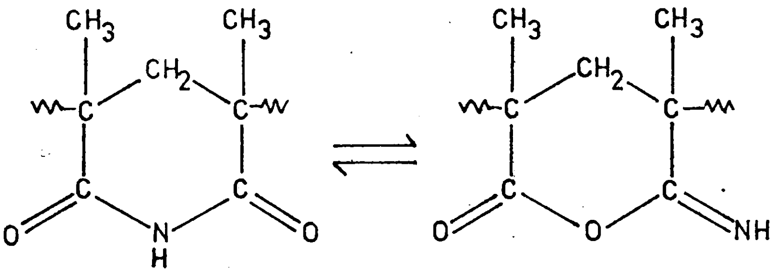
The absence of significant amounts of acetonitrile, in view of the mechanisms outlined previously to account for the absorptions at $1760cm^{-1}$ and $1795cm^{-1}$ complicates both positive assignment to these structures and also the role played by HCN.

An alternative mechanism which does not involve acetonitrile formation may, however, be postulated as follows:-

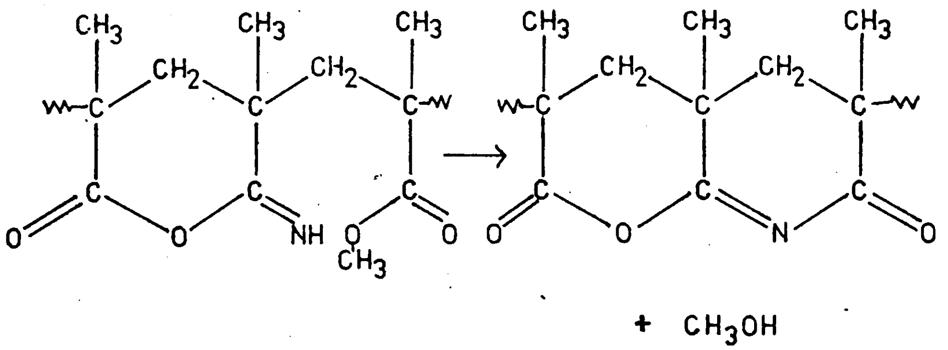


The presence of cyclic imides has been shown by comparison with the decomposition of polymethacrylamide (Chapter 7) and with the i.r. spectrum of glutarimide[75].

It has been established[76,77] that during amide pyrolysis the isoimide structure exists in equilibrium with the cyclic imide as illustrated:-



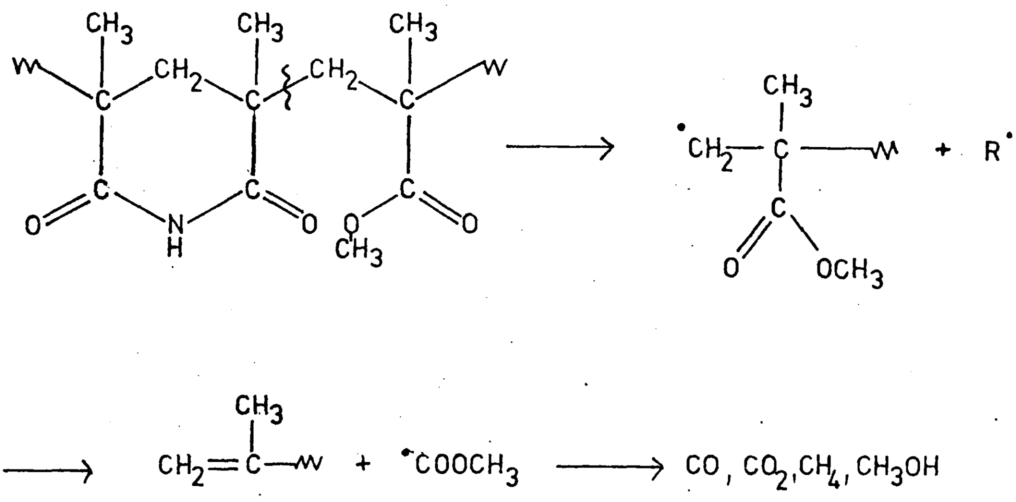
It is, therefore, proposed that further cyclization may occur through this isomer:-



The ring structure so formed may thus be responsible for i.r. absorptions similar to those observed although spectral evidence could not be found to confirm this.

In this manner one can account for the formation of both chain fragments and the gaseous products arising from their subsequent decomposition.

The evolution of methanol during degradation at temperatures above 350°C may also indicate another significant departure from normal PMMA decomposition. This can be derived from decomposition of ester sequences trapped by cyclized structures in the polymer chain as follows:-



Thus stabilized PMMA may be expected to result in the evolution of CH_3OH and other gaseous products through random scission of C-C bonds at elevated temperatures.

The thermal behaviour of the blends examined can, therefore, be summarized in terms of interactions occurring between the decomposition products of PAN with PMMA. The results of this investigation, however, do not allow any further information to be inferred about the decomposition of PAN.

CHAPTER 4

THE THERMAL DEGRADATION OF BLENDS OF POLYACRYLONITRILE WITH CHLORINATED POLYMERS

4.1 INTRODUCTION

The greater part of this chapter describes an investigation of the thermal stability of polyacrylonitrile (PAN) polymer blends containing polyvinyl chloride (PVC), polyvinylidene chloride (PVDC), alloprene and poly- α chloroacrylonitrile (PαCAN).

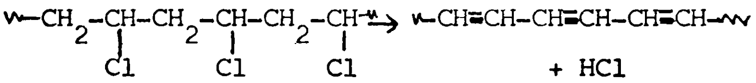
The thermal decomposition of nitrile polymers has been shown to be extremely susceptible to the presence of acids or nucleophiles present either as additives or incorporated through copolymerization[15,30,34,78]. It has been shown that additives such as carboxylic acids will initiate coloration of PAN at temperatures as low as 130°C while strong inorganic bases colour the polymer at ambient temperatures.

In each of the chlorinated homopolymers considered, initial decomposition results in the elimination of HCl to yield an unsaturated polyene residue although both the rate of evolution of HCl and the temperature at which it occurs differ considerably. The modified decomposition of PAN in the presence of acidic additives may, therefore, be predicted to have some influence in determining the overall stability of such polymer mixtures.

PVC is by far the most commercially important of the chlorinated homopolymers and as a result has been the subject of detailed study, particularly in relation to its thermal properties. It is appropriate, therefore, to examine briefly its behaviour during thermal decomposition which, to some extent, is representative of the remaining polymers.

4.2 THERMAL DECOMPOSITION OF PVC

Dehydrochlorination of PVC results in a coloured residue containing conjugated polyene sequences:-



$$\sim CH_2-\underset{Cl}{CH}-CH_2-\underset{Cl}{CH}-CH_2-\underset{Cl}{CH}\sim \xrightarrow{\Delta} \sim CH=CH-CH=CH-CH=CH\sim + HCl$$

The reaction proceeds through allylic activation of carbon-chlorine bonds adjacent to the unsaturation initially formed in the polymer chain. HCl is the major product although trace amounts of other materials, notably benzene, can also be detected and have been reported to occur at temperatures as low as 180°C[79].

The more detailed aspects of the decomposition of PVC have been comprehensively reviewed by Geddes[6] and by Braun[9] and can be divided into three categories, namely - sites for initiation of dehydrochlorination; mechanistic interpretation of the propagation processes; the effect of HCl upon the rate of dehydrochlorination.

INITIATION OF DEHYDROCHLORINATION

Comparison of the thermal stability of model compounds (2,4 dichloroalkanes) has shown PVC to be considerably less stable than would be predicted and suggests that initiation of dehydrochlorination occurs at defect structures within the polymer molecule[4]. A number of such structures have been proposed and include chain end unsaturation or chain end residues arising from initiator decomposition; branch points in the polymer chain with tertiary carbon chlorine bonds; and random chain unsaturation resulting in chloroallylic groups.

Investigation of the thermal decomposition of model compounds by Braun has shown that chloroallylic groups randomly distributed throughout the polymer chain should constitute the least stable of the defect structures considered. The amount of double bonds present in the polymer has been estimated at around 1.6 per 1000 monomer units[80]. Braun and Thallmaier[81] have shown by absorption spectra of decomposed PVC that the average sequence of conjugated bonds is between 5–10. One can, therefore, estimate the degree of PVC degradation which may be initiated by chloroallylic groups to be a maximum of not more than 1.6% below 200°C. It is known, however, that the extent of decomposition at this temperature is considerably greater and, therefore, this mechanism can only be one of several competitive at this temperature.

Chain branching in PVC has been assumed to result in the formation of labile tertiary carbon chlorine bonds which might act as possible sites of initiation. Although branching has been identified spectroscopically[82], recent work has shown the existence of tertiary carbon–chlorine bonds to be unlikely at branch points[80].

If dehydrochlorination was initiated at chain ends it would be anticipated that the rate of HCl evolution should be inversely proportional to molecular weight. It has been observed by Palma et al[83] that whereas an inverse relationship is observed for low molecular weight polymers, the rate of dehydrochlorination is independent of molecular weight above a limiting value. For valid comparisons to be made between different polymers, it is essential that the content of defect structures in each polymer is similar and this has prevented any firm conclusions upon this aspect of decomposition.

Recent work by Valko and Tvaroska[84] has suggested that the activation energy required for unimolecular elimination of HCl from unsaturated chain ends is such that they may be more stable than previously assumed.

Although most attention has been devoted to the detection of weak points in the polymer chain, recent work by Millan et al[85] has concluded that the tacticity of the polymer is also of importance and that the presence of syndiotactic sequences increases the rate of decomposition.

THE MECHANISM OF DEHYDROCHLORINATION

Consideration of the pyrolysis of simple alkyl halides led Stromberg[86] to propose the free radical chain process shown below:–

Initiation $PVC \longrightarrow Cl^{\cdot}$

Propagation
$$Cl^{\cdot} + \sim CH_2-CHCl-CH_2-CHCl-CH_2-CHCl-\sim$$
$$HCl + \sim\dot{C}H-CHCl-CH_2-CHCl-CH_2-CHCl-\sim$$
$$Cl^{\cdot} + \sim CH{=}CH-CH_2-CHCl-CH_2-CHCl-\sim$$
$$HCl + \sim CH{=}CH-\dot{C}H-CHCl-CH_2-CHCl-\sim$$
$$Cl^{\cdot} + \sim CH{=}CH-CH{=}CH-CH_2-CHCl-\sim$$

Termination
$$Cl^{\cdot} + Cl^{\cdot} \longrightarrow Cl_2$$
$$R_1^{\cdot} + R_2^{\cdot} \longrightarrow R_1 + R_2 \text{ or } R_1R_2$$
$$R^{\cdot} + Cl^{\cdot} \longrightarrow RCl$$

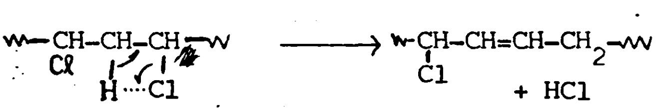
where $R^{\cdot}$ and R = polymer radical and molecule respectively.

By assuming that terminating is principally due to combination of Cl$^{\cdot}$, Stromberg was able to account for the 3/2 order dependence of the reaction.

Evidence supporting the free radical mechanism is claimed by the detection of free radicals by E.S.R. in degrading PVC[79] although the validity of this approach has been questioned[87]. PVC has been found to initiate radical reactions in studies of the decomposition of polymer mixtures, the effects being explained in terms of diffusion of Cl radicals in the polymer melt[18,88].

The ionic mechanism of decomposition involving heterolytic C-Cl bond scission has found support from a number of workers including Marks et al[89]. The latter have proposed that the dielectric constant of PVC during decomposition may be sufficient to support the charge separation requirements. Furthermore it has been postulated that the autoacceleration of decomposition may result from the ability of HCl to catalyse carbonium ion reactions.

Unmolecular decomposition has been found in studies of simple alkyl halides and may also occur during PVC decomposition. The mechanism involves a cyclic transition state and, therefore, differs from the previous mechanisms in that no free radical or ionic species capable of migration in the polymer melt are formed:-

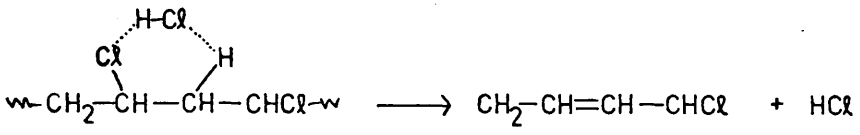


$$\sim \underset{Cl}{CH}-CH-CH-\sim \longrightarrow \sim\underset{Cl}{CH}-CH{=}CH-CH_2-\sim + HCl$$

INFLUENCE OF HCl UPON DEHYDROCHLORINATION

In contrast to the uncertain nature of much of the evidence relating to the mechanism and sites for initiation of dehydrochlorination it has been firmly established that HCl is responsible for autoacceleration of PVC decomposition[90].

Braun & Bender have proposed a non radical interaction to account for this phenomenon -



Autocatalysis, however, has also been cited as evidence in support of the ionic mode of decomposition. Decomposition of HCl to give basic Cl ions can be postulated to react in a similar manner to that proposed in the free radical process[91]. Thus, although the agent responsible for autoacceleration is known, the mechanism by which it acts has not been well defined.

4.3 THERMAL DECOMPOSITION OF COPOLYMERS OF ACRYLONITRILE WITH CHLORINATED COMONOMERS

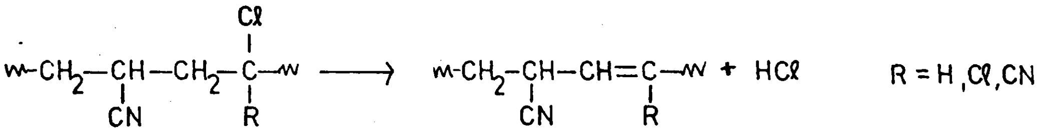
Studies of the thermal stability of copolymers of acrylonitrile with vinyl chloride, vinylidene chloride and α-chloroacrylonitrile have shown dehydrochlorination to occur readily and to precede the exothermic oligomerization of the nitrile groups[92]. The presence of the comonomer units reduces the intensity of the exotherm but does not effectively block the reaction since the total enthalpy change remains constant.

Vinyl chloride copolymers were found to evolve HCl more readily than PVC itself while the major weight loss process associated with fragmentation of the nitrile residue was found to occur at higher temperatures than in pure PAN. It was also observed using TGA that the exothermic reaction corresponded to a region of minimum weight loss, between HCl evolution and chain fragmentation. In this way it was concluded that the exothermic process did not necessarily involve weight loss.

Vinylidene chloride and α chloroacrylonitrile copolymers showed similar patterns of decomposition, although HCl evolution occurred earlier than in VC copolymers.

Infra red analysis of the polymers during decomposition showed an initial unsaturation assigned to elimination of HCl. On heating to around 300°C, however, the i.r. spectra were similar to that of PAN residues.

Each of the chlorinated comonomers degrades at a lower temperature than PAN. The initial reaction in the copolymer is, therefore, dehydrochlorination resulting in acrylonitrile sequences separated by chain unsaturation -



$$\sim CH_2-\underset{CN}{CH}-CH_2-\overset{Cl}{\underset{R}{C}}-\sim \longrightarrow \sim CH_2-\underset{CN}{CH}-CH=\underset{R}{C}-\sim + HCl \qquad R = H, Cl, CN$$

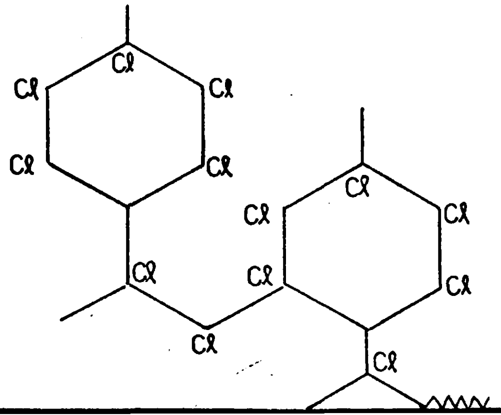
It has been postulated by Grassie and McGuchan[92] that the formation of such structures may block subsequent nitrile oligomerization although not eliminating it completely.

4.4 POLYMER SAMPLE HISTORY

The polyacrylonitrile samples employed were as in Chapter 3. Polyvinyl chloride was an additive free, British Geon 101 sample, and had a number average molecular weight of 16,000.

Polyvinylidene chloride (Bulk polymerization, 40°C, 0.05% AIBN) and poly α chloroacrylonitrile (Bulk polymerization 50°C, 0.04% AIBN) were prepared by Dr. R. McGuchan.

Alloprene is a chlorinated natural rubber containing 64.5% by weight fixed chlorine and was donated by I.C.I. Ltd. Recent studies of the thermal decomposition of alloprene have suggested the structure shown below[93] -



The sample used had a number average molecular weight of 65,000.

4.5 RESULTS

THERMAL VOLATILIZATION ANALYSIS

Blends of PAN with PVC were examined both as fine powders and as films cast from dimethyl sulphoxide (DMS) solution. A total sample weight of 100 mg was employed in powder studies while a maximum of 40 mg. was found necessary in film samples due to the low solubility of PAN (approximately 5 mg/ml) restricting the volume of solution which could be conveniently handled. Films were cast from a mixed solution of the two polymers in DMS (Spectroscopic grade). Residual solvent was removed by heating at 30°C for a period of 24 hours under vacuum.

The behaviour of PVC both as a powder and as a film is illustrated by the TVA curves in Fig. 4.1. The overall pattern in both is similar with HCl as the major volatile during the initial stage of decomposition which can be seen to be non condensible in all but the -196°C trap. The peak occurring at higher temperatures in both traces results from decomposition of the conjugated polymer sequences remaining after dehydrochlorination and contains a significant amount of non condensible products.

Differences observed in the initial stage of decomposition between the two sample forms have been attributed to the effect of catalysis by HCl diffusion through the sample. McNeill and Neil[17] have in this manner shown enhanced stability of thin film samples relative to powders.

Fig. 4.2 shows the TVA curves obtained by decomposition of equal amounts of PAN I and PVC both mixed and unmixed in the form of fine powders. The rate maxima associated with both PVC and PAN decomposition are evident in both samples. This is particularly surprising since degradation of the two homopolymers suggests considerable overlapping of the two reactions. It is also evident that the maxima associated with PAN decomposition are in both systems at a higher temperature than

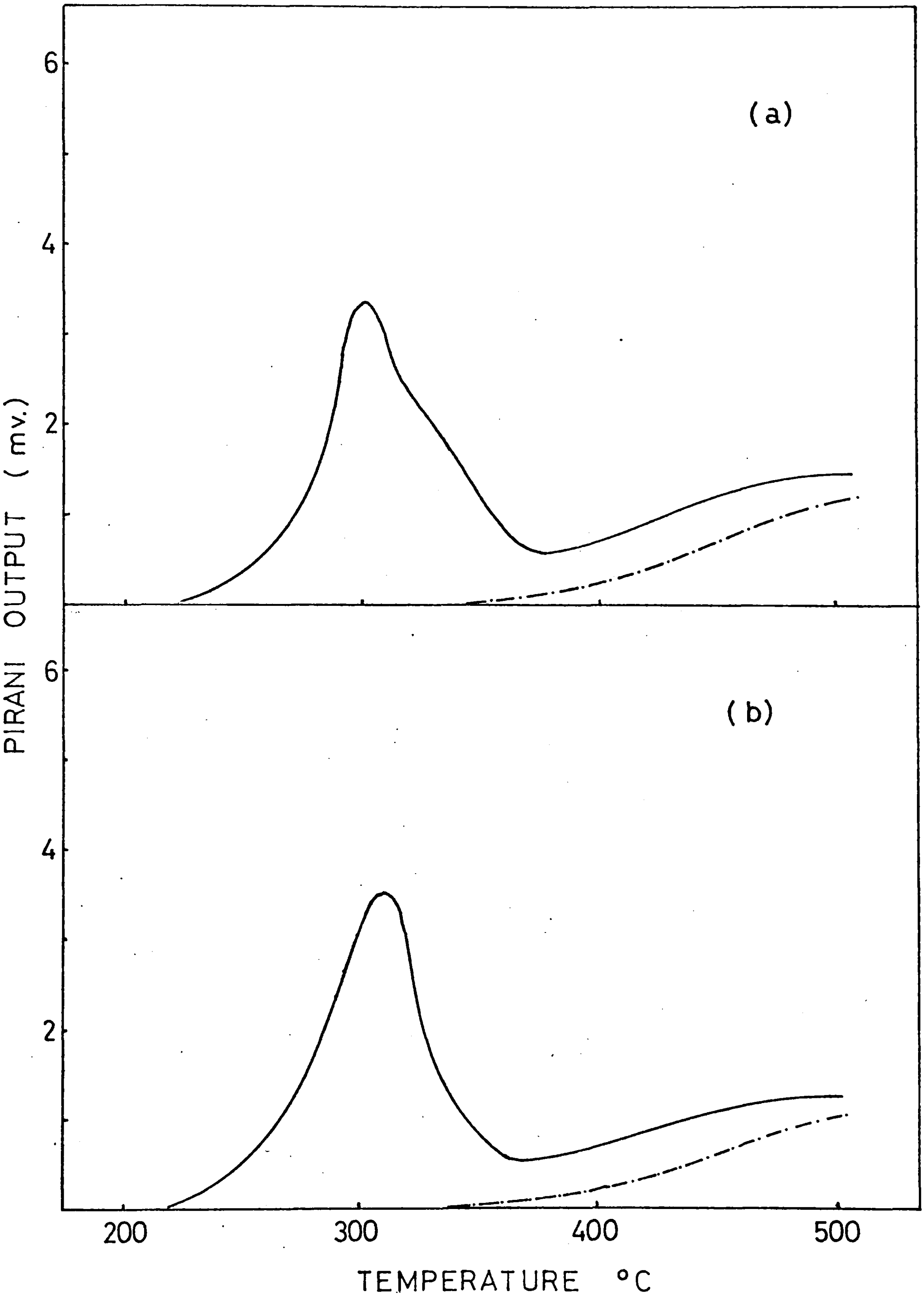


FIG. 4.1 TVA CURVES FOR PVC, (a) POWDER, (b) FILM SAMPLE
FROM DMS SOLUTION, 40 mg SAMPLES

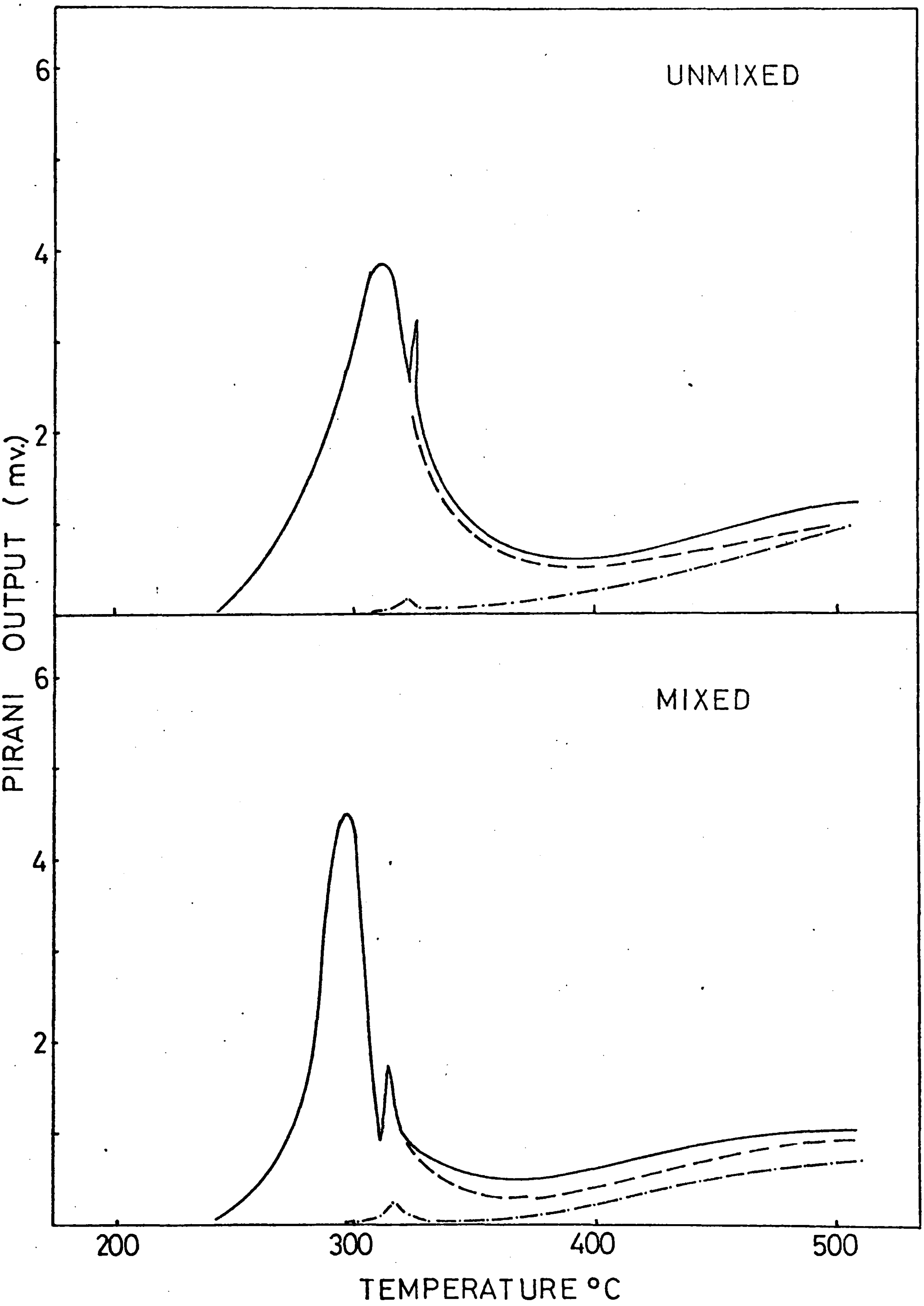


FIG. 4.2 TVA CURVES FOR SIMULTANEOUS DEGRADATION OF PAN I AND PVC, 1:1 BY WEIGHT, POWDER SAMPLES, TOTAL WEIGHT 100 mg.

observed in the decomposition of pure PAN.

The mixed system displays destabilization of the PVC as shown by both the lower temperature at which the maximum rate of evolution of HCl is occurring (295°C as opposed to 305°C) and by the increased peak height relative to the unmixed system. While the separation of the two rate maxima in the mixed system is reduced, so also is the peak height corresponding to decomposition of the PAN present. Although destabilization of the PVC in the mixed system is apparent, the initial decomposition temperature does not differ significantly from that observed in the unmixed system.

The effect of varying blend composition is illustrated in Fig. 4.3 for a 4:1 by weight mixture of PVC:PAN. The decomposition of the PAN present in both mixed and unmixed samples is obscured by the dehydrochlorination of the PVC. Again an increased rate of volatilization can be observed for the mixed system resulting in a lower T max. Blends containing a greater proportion of PVC did not reveal any further differences in behaviour due to overlapping of the two principal modes of decomposition.

It was found that the pattern of evolution of volatiles for a PAN film, cast from DMS, was similar to the TVA curve illustrated in Chapter 3. Only small differences were observed between the two traces, namely a broadening of the initial sharp peak associated with nitrile oligomerization accompanied by a shift of approximately 10°C in the T max. The differences observed in TVA experiments were less evident than those found in both DTA and TGA which will be discussed later in this chapter.

Fig. 4.4 illustrates the TVA curves for a 1:1 PAN:PVC blend examined as a film. The features observed are qualitatively similar to those of the mixed powders, although overlap between dehydrochlorination is again lowered, although no significant differences in peak heights could be identified. An additional observation is the appearance of a plateau in the mixed film TVA not apparent in the unmixed sample.

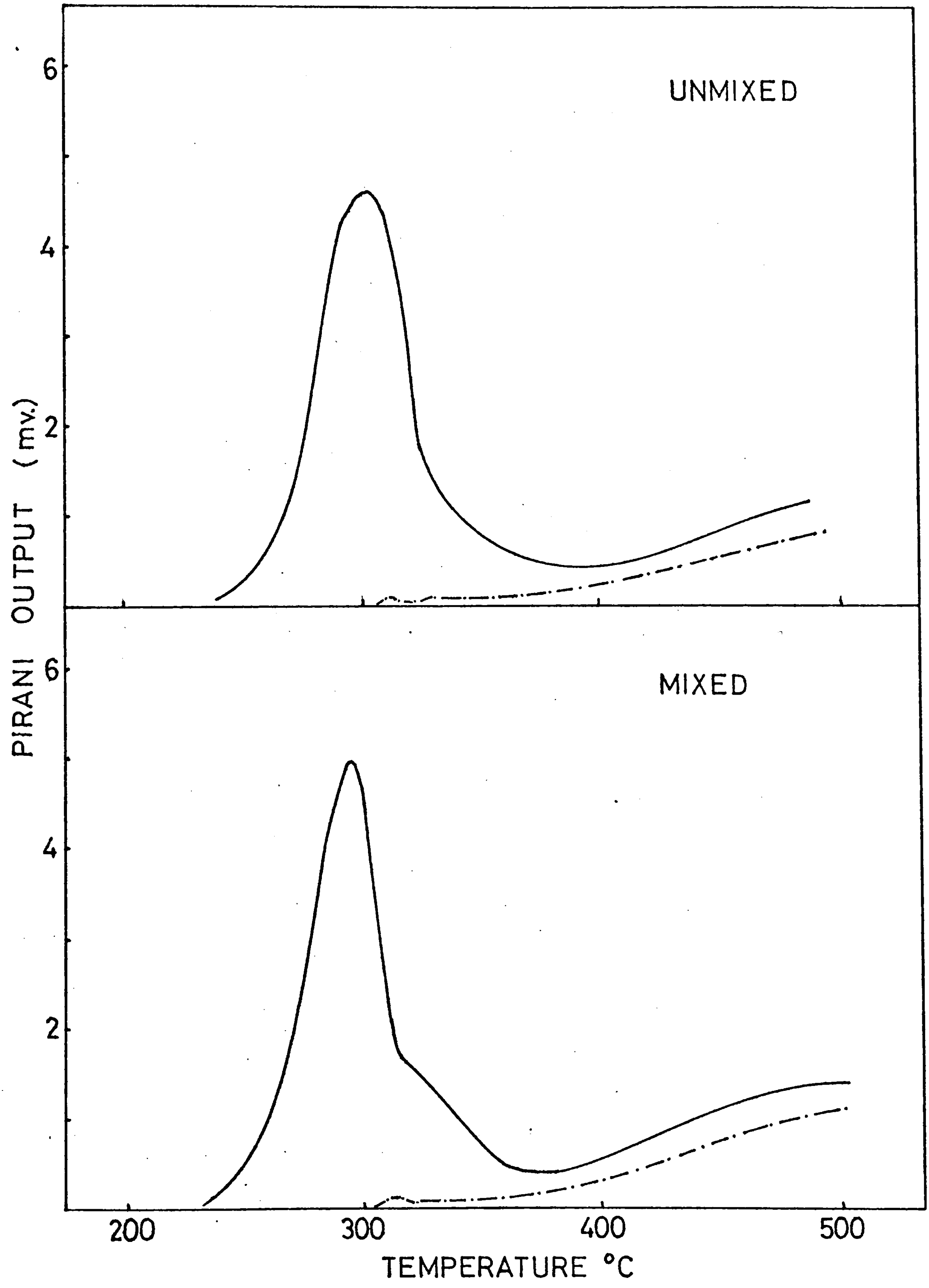


FIG. 4.3 TVA CURVES FOR SIMULTANEOUS DEGRADATION OF PAN I AND PVC, 1:4 BY WEIGHT, POWDER SAMPLES, TOTAL WEIGHT 100 mg.

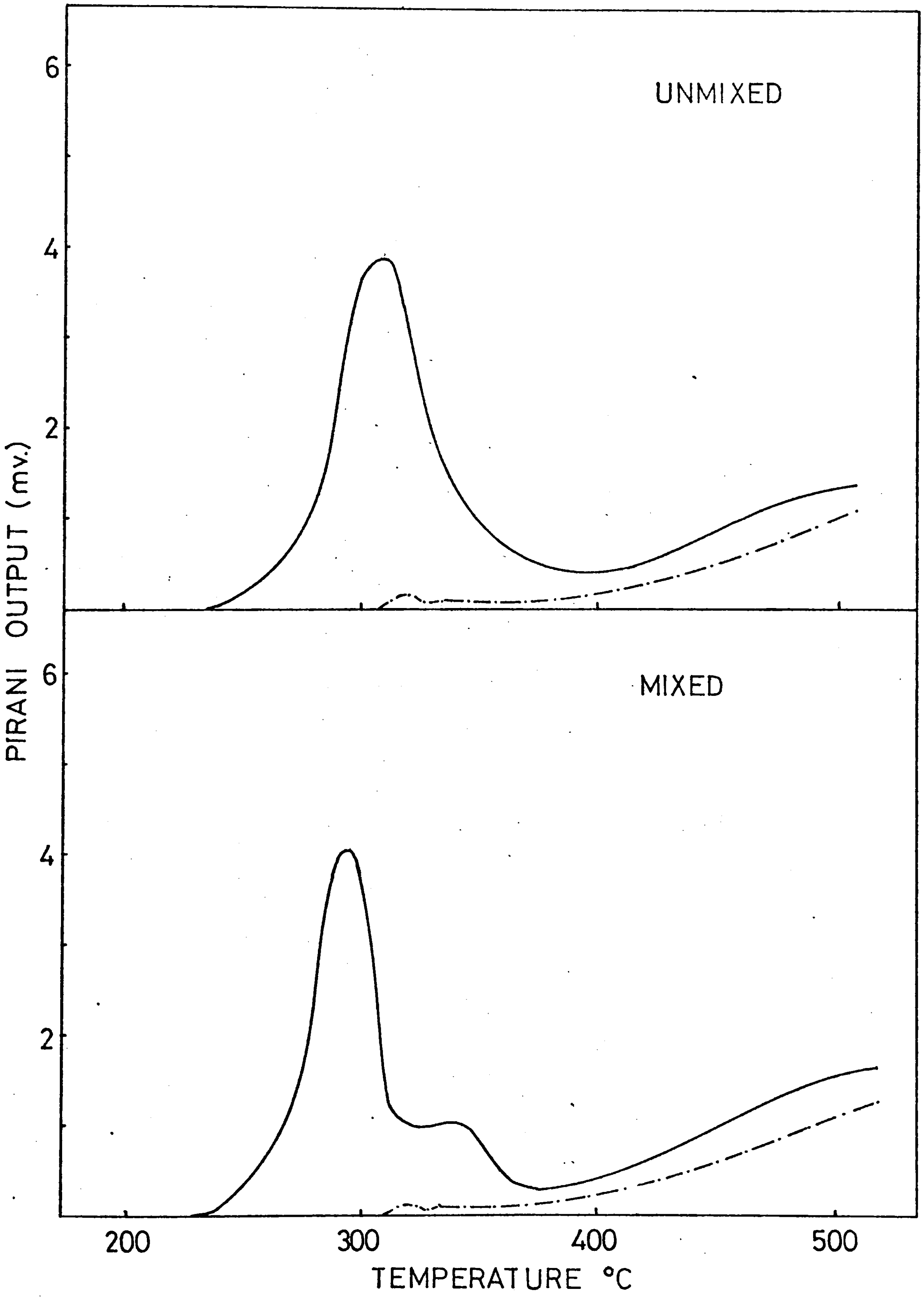


FIG. 4.4 TVA CURVES FOR SIMULTANEOUS DEGRADATION OF PAN I AND PVC, 1:1 BY WEIGHT. FILM SAMPLES CAST FROM DMS SOLUTION, TOTAL WEIGHT 80 mg.

The reaction between gaseous NH_3 and HCl to form solid NH_4Cl can occur in the trap system and could, therefore, be expected to influence the appearance of the TVA curve when significant amounts of the gases are evolved simultaneously. This will occur to some extent in both mixed and unmixed systems but cannot be responsible for the differences observed between the two systems if no other interaction takes place. The net result any interaction occurring in the blend, however, may be to increase the overlap between the reactions giving rise to HCl and NH_3 and in this way influence the pattern of evolution observed.

On the basis of the information derived from the TVA curves alone it may be postulated that PVC decomposition is accelerated by the presence of PAN although the initial temperature of decomposition is unaltered. PAN itself appears to be stabilized although simultaneous decomposition of unmixed polymers shows a similar phenomenon occurring to a lesser extent.

ISOTHERMAL TVA

The evolution of HCl from 1:1 and 2:1 by weight PVC:PAN powder blends, each containing 50 mg PVC was examined during isothermal decomposition at 285°C using identical trap temperatures to those in normal TVA experiments. Linear temperature programming at 10°C/min. was employed to achieve the desired temperature which was then maintained for a period of 1 hour.

The results are illustrated in Fig. 4.5 showing both mixed and unmixed systems. The unmixed samples in both compositions show similar peak maxima due to dehydrochlorination. Mixing of the two polymers results in an accelerated rate of dehydrochlorination the effect being more pronounced for the 1:1 mixture.

INFRA RED ANALYSIS OF DECOMPOSITION PRODUCTS

Ir analyses of the gaseous products collected after TVA of PVC to 500°C reveal only HCl and a small amount of benzene. Similar decomposition employing a closed system showed trace amounts of methane in addition to

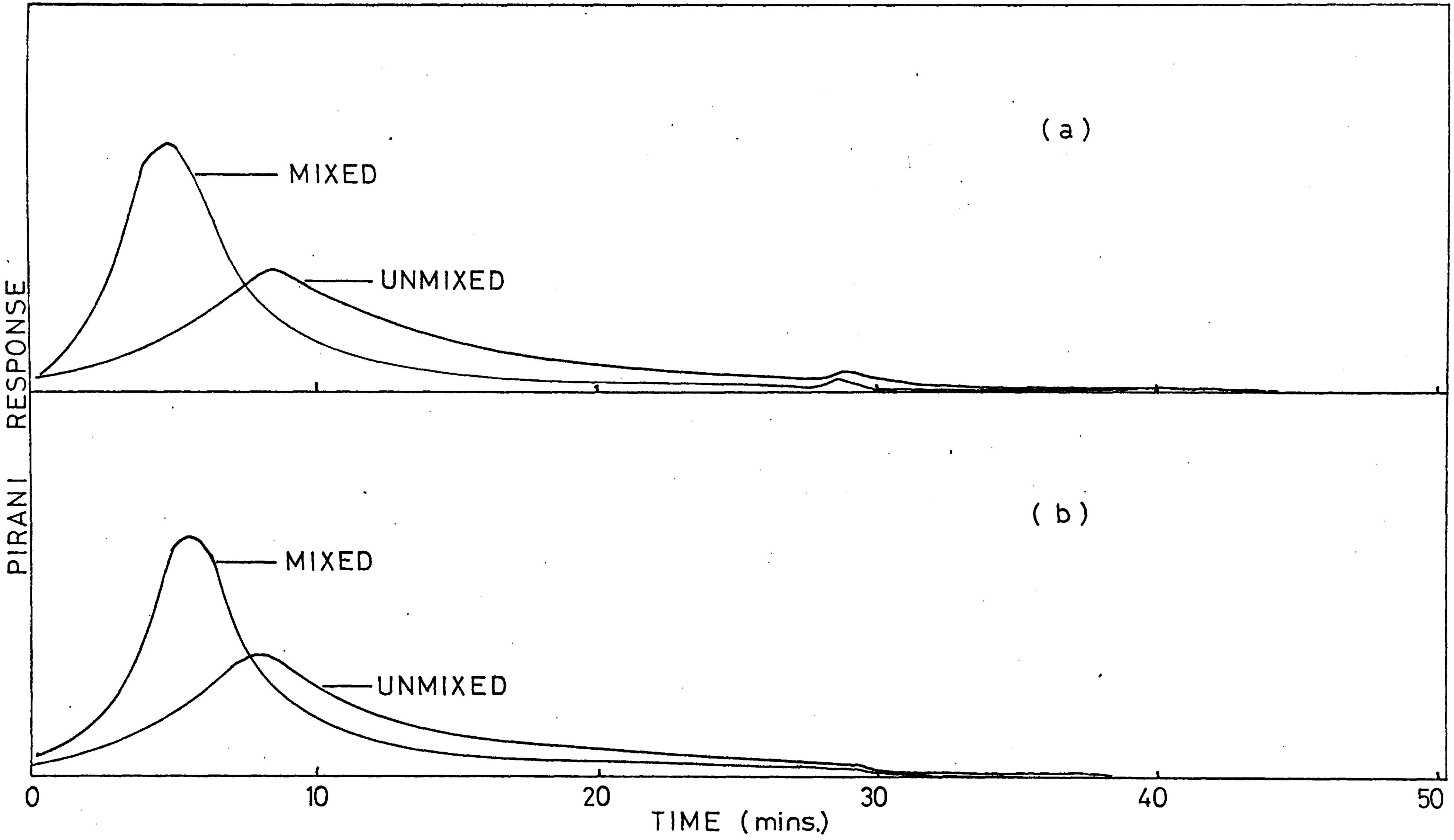


FIG. 4.5 ISOTHERMAL TVA CURVES FOR (a) 1:1 BY WEIGHT PAN I:PVC (b) 1:2 BY WEIGHT PAN I:PVC TEMPERATURE 285°C, 50 mg. PVC

those already mentioned. This product must arise from decomposition of the conjugated polyene residue between 400-500°C. It is probable that trace amounts of short chain alkenes may also be present although they could not be positively identified in the present study.

Similar analyses of the gaseous products throughout the blend compositions examined revealed no products other than those previously identified from homopolymer decomposition. The i.r. absorptions due to NH_3 formed through PAN decomposition are reduced or eliminated through the formation of NH_4Cl during product collection, while the absorption intensities of the remaining products are unchanged in comparisons of mixed and unmixed systems.

Typical i.r. spectra of the cold ring fractions collected during TVA experiments are illustrated in Fig. 4.6 for both a 1:1 mixed and unmixed PAN:PVC powder blend. The spectra in both systems are similar to that found in PAN alone, indicating that the majority of chain fragmentation still arises from PAN present in the blend.

Qualitative examination of the two spectra shows a relative reduction in $C{\equiv}N$ absorption occurring at 2180 cm^{-1} and 2240 cm^{-1} upon mixing accompanied by a similar decrease in intensity of absorption around 1600 cm^{-1} associated with unsaturation and N-H bending frequencies. In addition a shoulder upon the nitrile absorption at 2220 cm^{-1} which may be attributed to nitrile groups adjacent to unsaturation can be seen in both spectra.

The coloration of the cold ring fraction is unchanged upon mixing, appearing red-amber as in PAN decomposition. The residue remaining at 500°C is also unchanged both in coloration and spectroscopically.

Quantitative examination of the spectral changes occurring in the cold ring fraction could not be pursued for two main reasons - the limited solubility of the fragments which are in part further pyrolysed upon the hotter regions of the degradation tube; the intense coloration and waxlike consistency of the material which allows i.r. examination only in the form

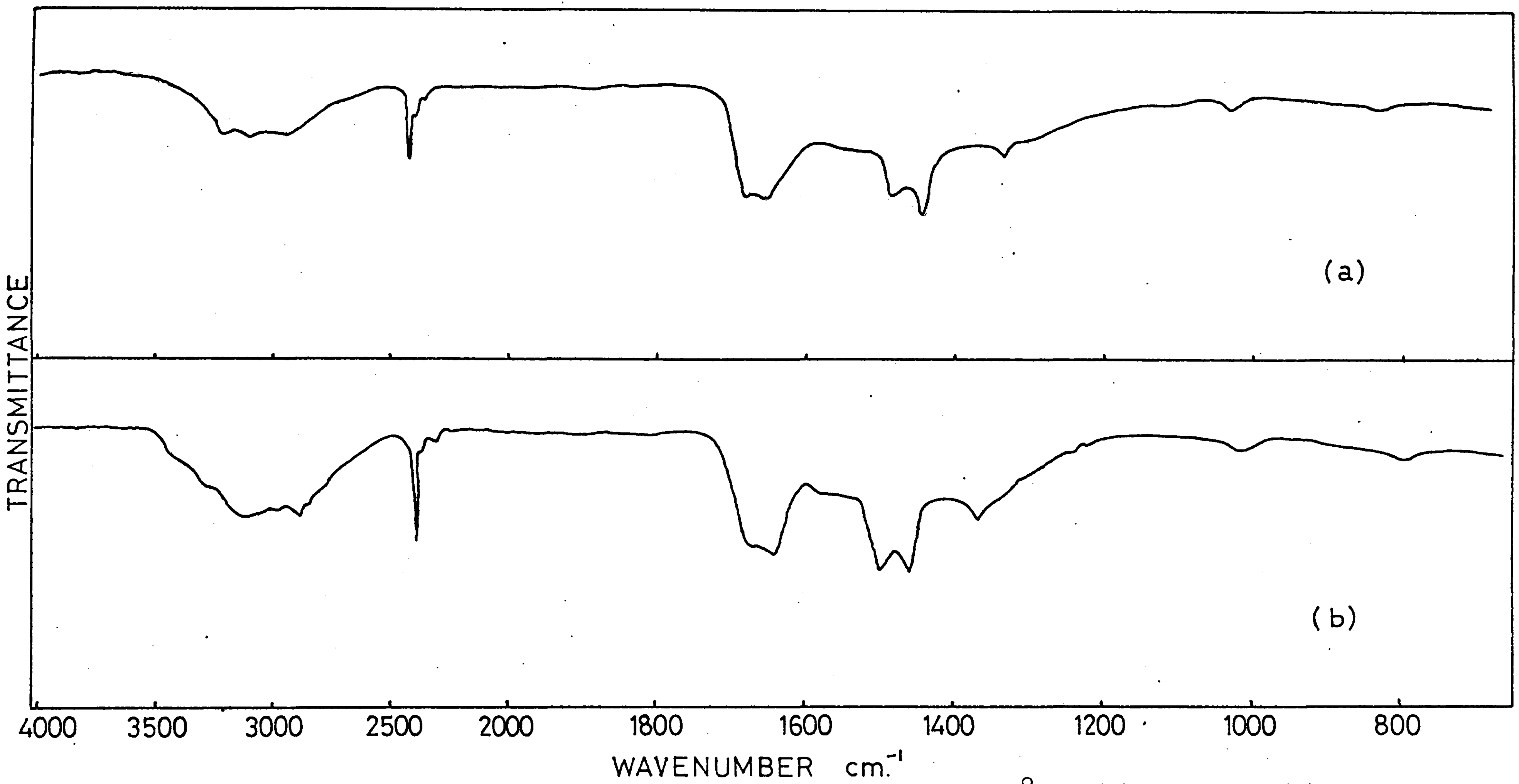
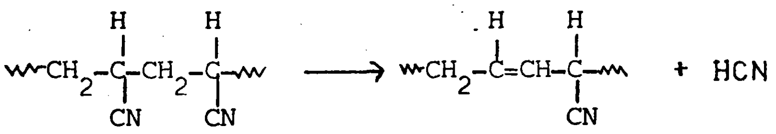


FIG. 4.6 I.R. SPECTRA OF COLD RING FRACTIONS ANALYSED AFTER DECOMPOSITION TO 500°C OF (a) 1:1 MIXED, (b) 1:1 BY WEIGHT UNMIXED PAN I:PVC POWDER BLENDS

of a smear upon a halide disc and, therefore, is subject to considerable scattering of the i.r. beam.

A reduction in nitrile intensity in the chain fragments may arise from two possible routes - more extensive nitrile oligomerization; an increase in HCN elimination reactions. The former explanation would involve an increase in the exothermicity of the cyclization processes which would lead to increased fragmentation of the polymer since in general the weight loss during the cyclization process reflects the exothermicity. This possibility is examined by D.T.A. in a later section.

The stabilization of the PAN residue upon blending may result in HCN elimination reactions being more competitive with concurrent nitrile oligomerization and chain scission at higher temperatures. The small C≡N absorption at 2220 cm^{-1} might then arise from C≡N groups adjacent to unsaturation in the polymer chain similar to those observed in copolymers of acrylonitrile with chlorinated monomers -



$$\sim CH_2-\underset{CN}{\overset{H}{C}}-CH_2-\underset{CN}{\overset{H}{C}}\sim \longrightarrow \sim CH_2-\overset{H}{C}=CH-\underset{CN}{\overset{H}{C}}\sim + HCN$$

THERMOGRAVIMETRIC ANALYSIS

T.G. curves for a series of blend compositions containing between 20-90% by weight PVC are illustrated in Fig. 4.7, together with those of the two homopolymers. The samples were examined as 5 mg. samples in an inert N_2 atmosphere.

The PVC curve shows the two stage weight loss associated with initial dehydrochlorination and subsequent decomposition of the conjugated polyene. Dehydrochlorination is virtually quantitative as measured by the weight loss during the first stage.

Two main observations can be made of the stability shown by the blends - (a) the initial weight loss is greater than occurring in PVC alone, and (b)the second stage of decomposition due to PAN fragmentation is displaced

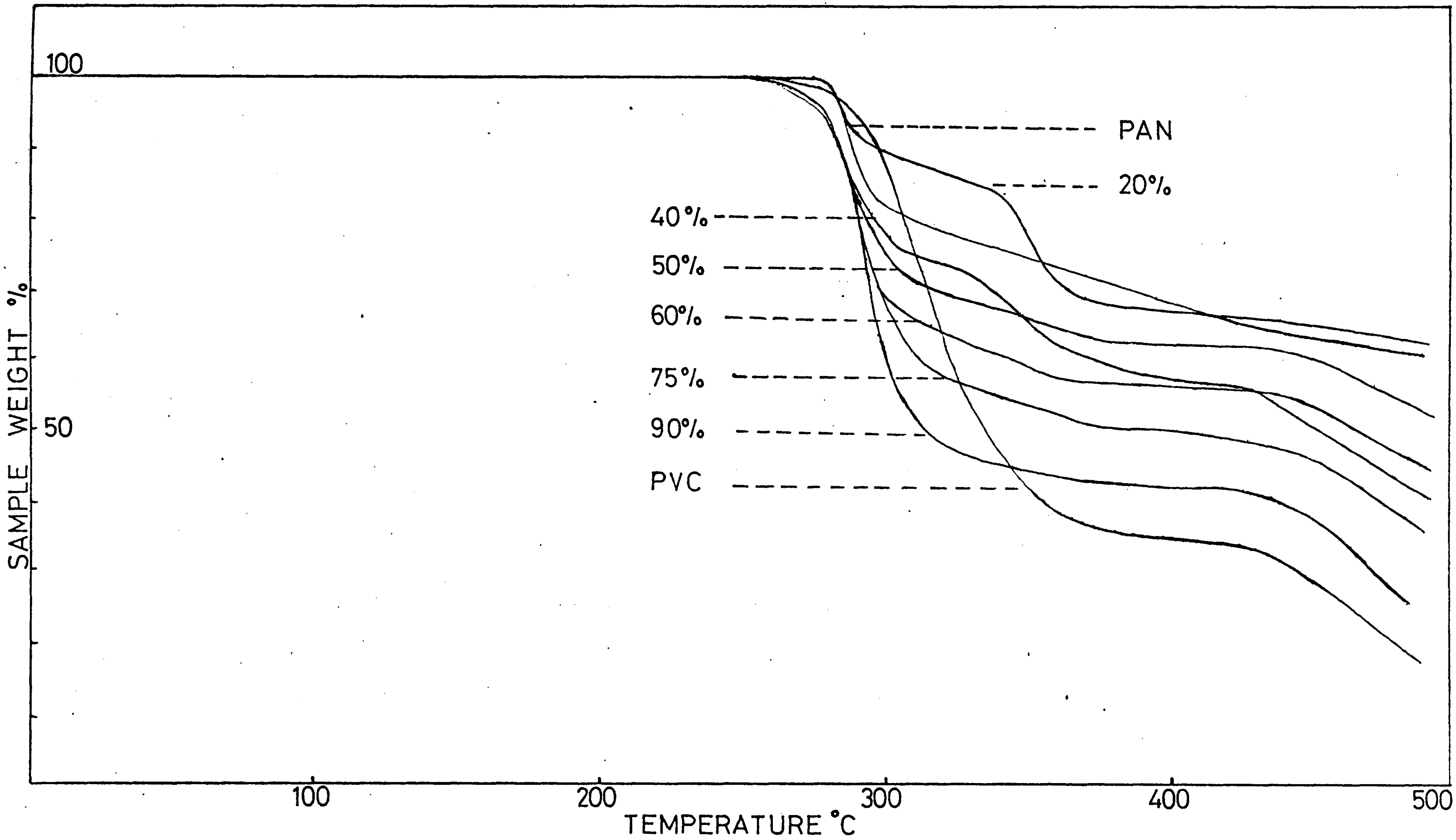


FIG. 4.7 TG CURVES FOR PAN I:PVC BLENDS (WEIGHT % PVC) 5 mg POWDER SAMPLES, HEATING RATE 10C°/min.
DYNAMIC N_2 ATMOSPHERE

to a higher temperature in each of the blends (80°C in a 20% by weight PAN blend). Chain fragmentation, which has been shown to be the main process responsible for weight loss in PAN, has been separated from the dehydrochlorination of the PVC present. The increased weight loss during initial decomposition may, therefore, be reasoned to result from an increased rate of dehydrochlorination as proposed earlier from TVA.

Using the curves in Fig. 4.7, the maximum rates of volatilization were estimated by measurement of the average rate at 5C° intervals. This was achieved by measurement of the residual weight fraction both 10C° before and after the temperature at which the rate was to be determined i.e. at two minute intervals when employing at 10C°/minute heating rate. The results are given in Table 4.1.

It is evident that incorporation of only 10% by weight PAN is sufficient to give a singificant increase in rate of dehydrochlorination while in blends containing greater amounts of PAN a second rate maximum can be identified due to fragmentation of the PAN residue.

TABLE 4.1 TG ANALYSES OF PAN:PVC MIXED POWDERS *

Blend Composition % PVC by weight	Maximum rate of wt.loss (% per min.) R max.	Conversion at R max C Max (%)	T_{max} °C
100	13	21	300
90	18	32	295
75	14.5	24	295
60	13	22	290
50	11	12	285
40	8.5, 5.0	11	285,340
20	5.0, 6.0	6	290,350

* 5 mg samples, dynamic N_2 atmosphere, heating rate 10C°/min.

Fig. 4.8 illustrates the observed TG behaviour for a 50% by weight PAN/PVC blend together with that predicted by simple addition of the curves obtained for the two homopolymers. The trace again confirms the two major observations namely an initial acceleration in the rate of decomposition which is followed by increased stability at higher temperatures prior to chain fragmentation associated with nitrile oligomerization.

A number of PAN:PVC compositions were also examined after blend preparation through coprecipitation of a dimethyl sulphoxide (DMS) solution containing the two polymers into MeOH. This technique has been used in TG studies of PAN/PVDC blends by Mucha and Kryszewski. There are, however, a number of disadvantages in this process. These include efficient solvent removal from the blend which makes difficult the identification of the initial decomposition temperature. Another more serious feature is the drastic alteration in the thermal behaviour of PAN in the presence of trace amounts of residual solvent. This effect together with those arising from several other additives will be demonstrated later in this chapter. In this system the changes which may be observed in decomposition of the blends cannot be unambiguously assigned to interactions between the two homopolymers since the solvent effect upon PAN may outweigh the other processes occurring.

Fig. 4.9 illustrates the TG curves for PAN, PVC and a 90% by weight PVC blend, all of which have been prepared by coprecipitation from dimethyl sulphoxide into methanol and then vacuum dried at 35°C over a period of two days. There is an obvious stabilization in the weight loss processes during PAN decomposition. The initial weight loss occurs slightly earlier than in the pure polymer but proceeds more slowly to a similar residue yield at 500°C. The PVC blend shows destabilization as was found in the powder studies but both this composition and those containing increased amounts of PAN failed to show the second stage of weight loss. This may result from the combined interaction of the decomposing polymers and that due to solvent effects upon the initial decomposition of PAN.

Kinetic parameters characterising the thermal stability of PAN:PVDC blends were estimated by Mucha and Kryszewski[20], from thermogravimetric curves employing the method outlined by Freeman and Carroll[94]. They found that both activation energy and the order of reaction varied with composition. The use of this method in the present study did not provide consistent results, its application being limited to a small portion of

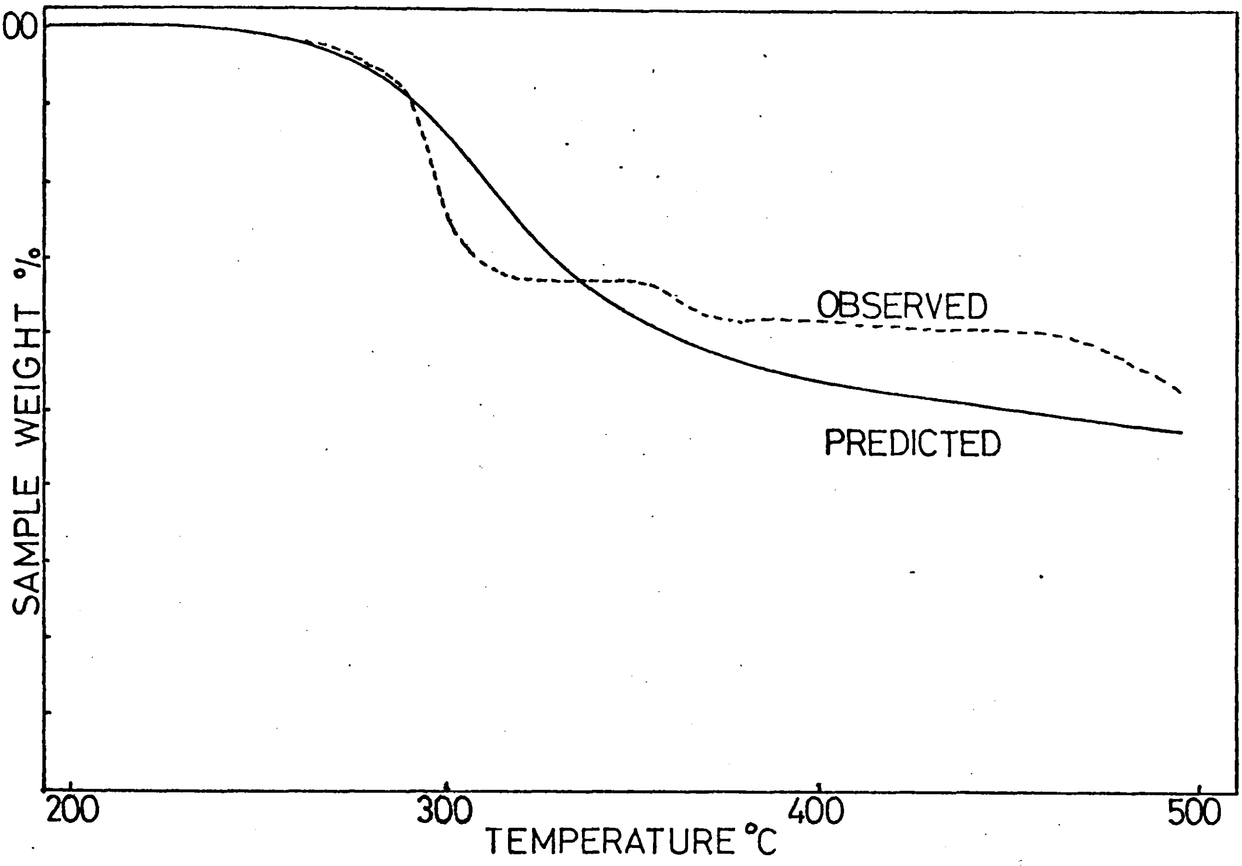


FIG. 4.8 TG CURVES ILLUSTRATING OBSERVED AND PREDICTED RESULTS FOR A 1:1 BY WEIGHT PAN I:PVC BLEND

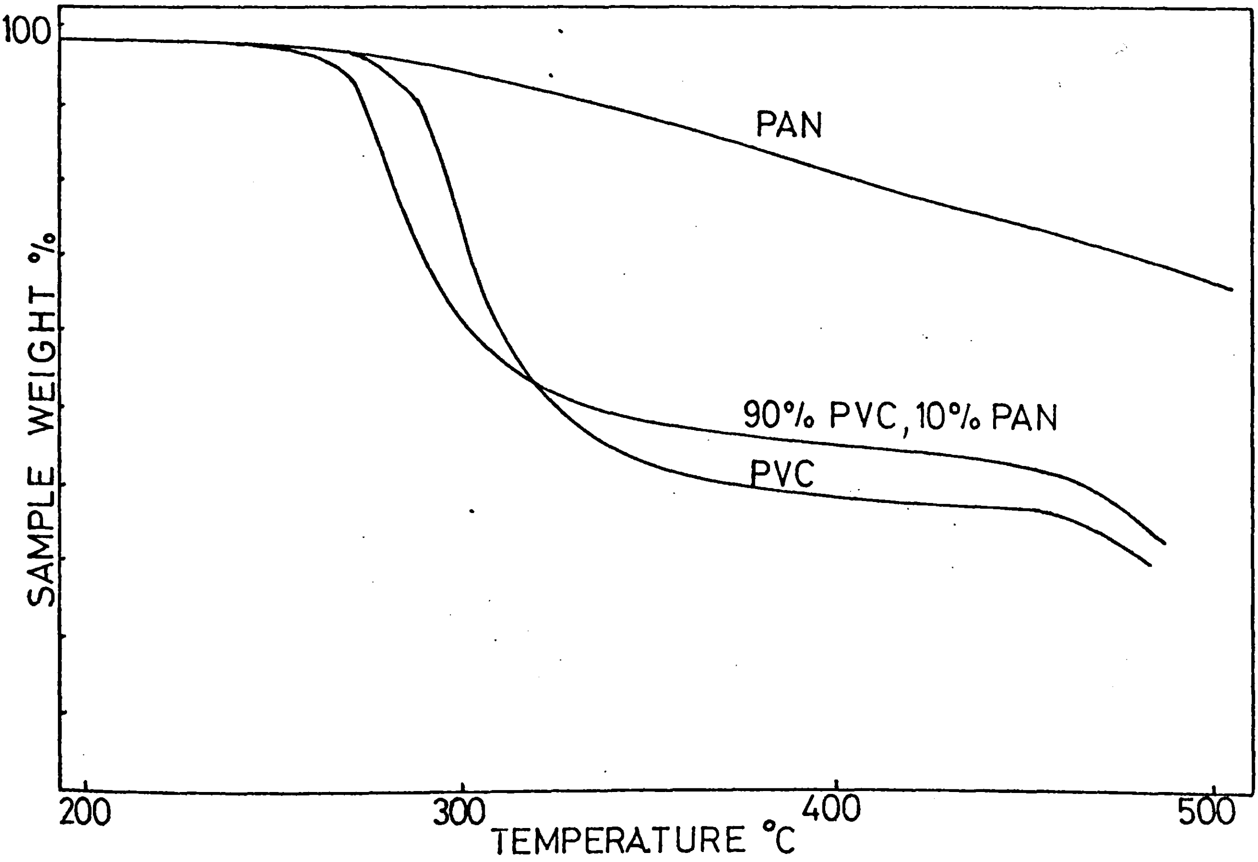


FIG. 4.9 TG CURVES FOR PAN, PVC AND A 90% BY WEIGHT PVC BLEND SAMPLES PREPARED BY COPRECIPITATION FROM DIMETHYL SULPHOXIDE

the TG curve. Other methods, such as those of Doyle[95] require a prior knowledge of the reaction order or determination of the order by trial and error to provide best fitting curves. Since the reaction order can be found to vary with composition, it was therefore considered inappropriate to attempt to evaluate such parameters which seldom have any mechanistic significance and can provide no further information other than that already evident in the TG curve.

DIFFERENTIAL THERMAL ANALYSIS AND DIFFERENTIAL SCANNING CALORIMETRY

Typical DTA curves for PAN have been illustrated in Chapter 3 (Fig. 3.17). Curves representative of 10 mg. powder samples of PVC and both a 50% and 80% by weight PAN blend are shown in Fig. 4.10.

The principal feature of the PVC trace is a small endotherm corresponding to dehydrochlorination which overlaps with the temperature region in which nitrile oligomerization occurs in PAN. The average values of peak and differential temperatures were found as $300^\circ C \pm 5C^\circ$ and $6.8 \pm 1C^\circ$ for 10 mg. samples of a blend containing 50% by weight PAN while the corresponding values for 80% by weight PAN were $T_{pk.}=303 \pm 5C^\circ$, ΔT $6.2 \pm 1C^\circ$.

The magnitude of the exotherm, its shape and the temperature at which it occurs are altered by mixing with PVC. Although some overlap occurs with the small PVC endotherm the breadth of the exotherm is now approximately $80C^\circ$ as opposed to $10C^\circ$ in the pure polymer. It can also be noted that although the exotherm peak temperature has been displaced by around $30C^\circ$, this is less than the displacement of the maximum rate of weight loss observed by thermogravimetry. The exotherm has in this way been separated from the chain scission processes which result in weight loss. Similar observations were noted by Grassie and McGuchan[92] in studies of copolymers of acrylonitrile with chlorinated comonomers.

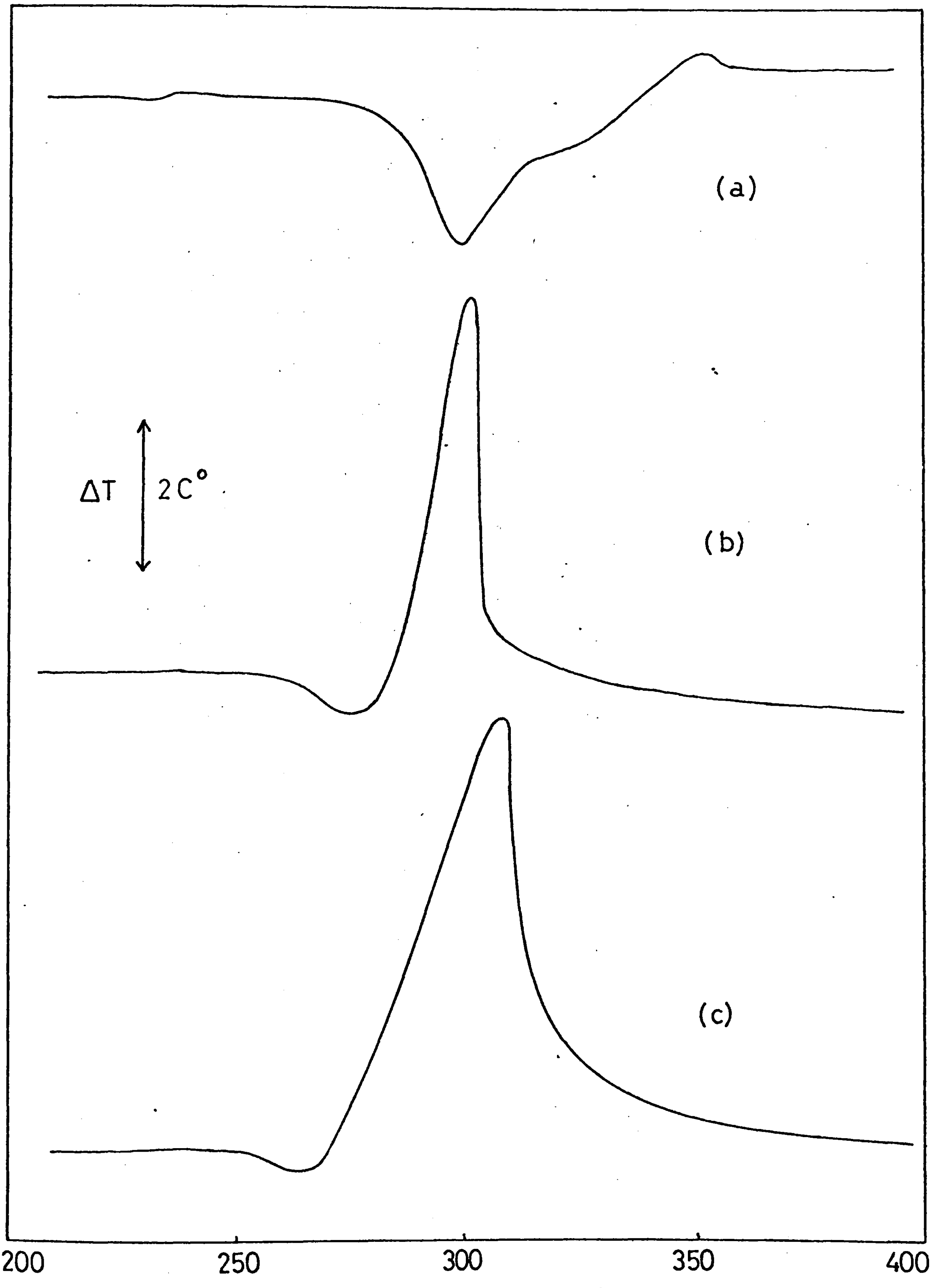


FIG. 4.10 DTA CURVES FOR
(a) PVC (b) 1:1 BY WEIGHT PAN:PVC (c) 4:1 BY WEIGHT PAN:PVC
10 mg POWDER SAMPLES, HEATING RATE 10C°/min, DYNAMIC N_2 ATMOSPHERE

The altered shape of the exotherm does not necessarily imply variation in the total enthalpy change during nitrile oligomerization. Differential scanning calorimetry was performed using a DuPont 900 Thermal Analyzer equipped with D.S.C. module which was calibrated as given in Chapter 2.

ΔH values for both PAN and a 1:1 by weight PAN:PVC mixture were found as 139 cal/g (7.4 K cal mole^{-1}AN) and 214 cal/g (11.3 K cal mole^{-1}AN).

A deviation of ± 10% was estimated in these values due both to the small sample size employed and the overlap of the exotherm w th the PVC endotherm making accurate area measurements difficult. It is reasonable however to infer that the exotherm is increased upon mixing.

It is convenient at this point to examine briefly the behaviour of the remaining blends before summarizing the results of all four systems.

BLENDS CONTAINING PVDC, ALLOPRENE AND PαCAN

THERMAL VOLATILIZATION ANALYSIS

TVA curves for 50 mg. powder samples of each of the polymers are given in Fig. 4.11. The primary decomposition product in each is HCl while the maximum rates of evolution and initial temperature of decomposition differ.

The thermal decomposition of PVDC is a two stage process involving initial formation of a conjugated chlorinated polyene through elimination of one mole of HCl per monomer unit -

$$-(CH_2-CCl_2)_m- \longrightarrow -(CH=CCl)_m- + mHCl$$

Elimination of further quantities of HCl can only be accomplished by heating to temperatures in excess of 700°C.

The initial decomposition is generally believed to be a radical chain process occurring largely by a zip reaction along the polymer chain, although the structures responsible for initiation are disputed[96,97].

The TVA curve shows the initial rate of dehydrochlorination to be greater than in PVC, T max being around 255°C.

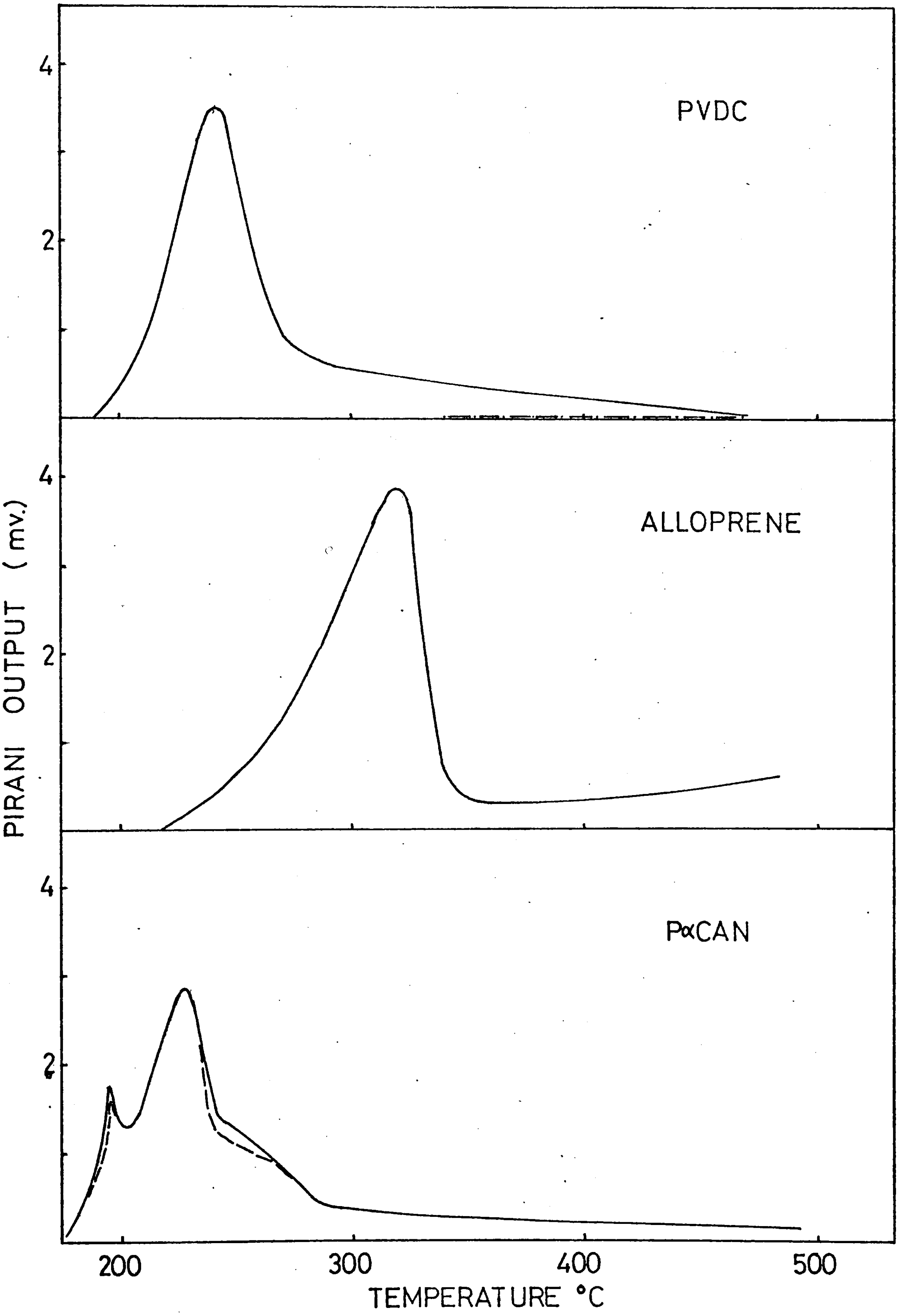
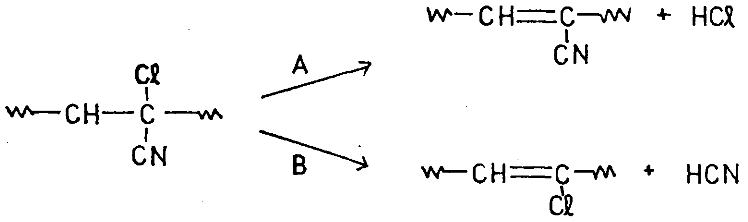


FIG. 4.11 TVA CURVES FOR
(a) PVDC (b) ALLOPRENE (c) PαCAN
50 mg. POWDER SAMPLES

Poly(α chloroacrylonitrile) is the least stable of the polymers examined, measurable evolution of gaseous products occurring as low as 170°C. The elimination of HCl is accompanied by competing HCN elimination-



Route A is the predominant process during initial decomposition[98] although cyclization of the nitrile groups may also occur to a limited extent[99].

Alloprene has been found to lose 95% of the total chlorine content below 400°C as HCl during temperature programmed heating. Degradation products which have been identified above 400°C include methane, ethylene and hydrogen, resulting from fragmentation of the conjugated residue. The TVA curve shows initial decomposition to occur below 200°C with T max around 300°C.

TVA curves illustrating the behaviour of 1:1 by weight mixed and unmixed samples of PAN:PVDC, PAN:Alloprene and PAN:PαCAN are given in Figs. 4.12 and 4.13. In each trace the increased temperature at which PAN decomposition occurs can be observed although a lesser effect again occurs in unmixed samples. The rate of HCl evolution does not appear to be altered on mixing in any of the blends examined contrary to the behaviour of PVC blends.

Infra red examination of each system shows similar results to those outlined for PVC.

DIFFERENTIAL THERMAL ANALYSIS

Fig. 4.14 illustrates the DTA curves obtained for 10 mg. samples of the same 1:1 blends. It is again evident that there is a reduction and broadening of the exotherm. Using 5 mg. samples D.S.C. gave the following results -

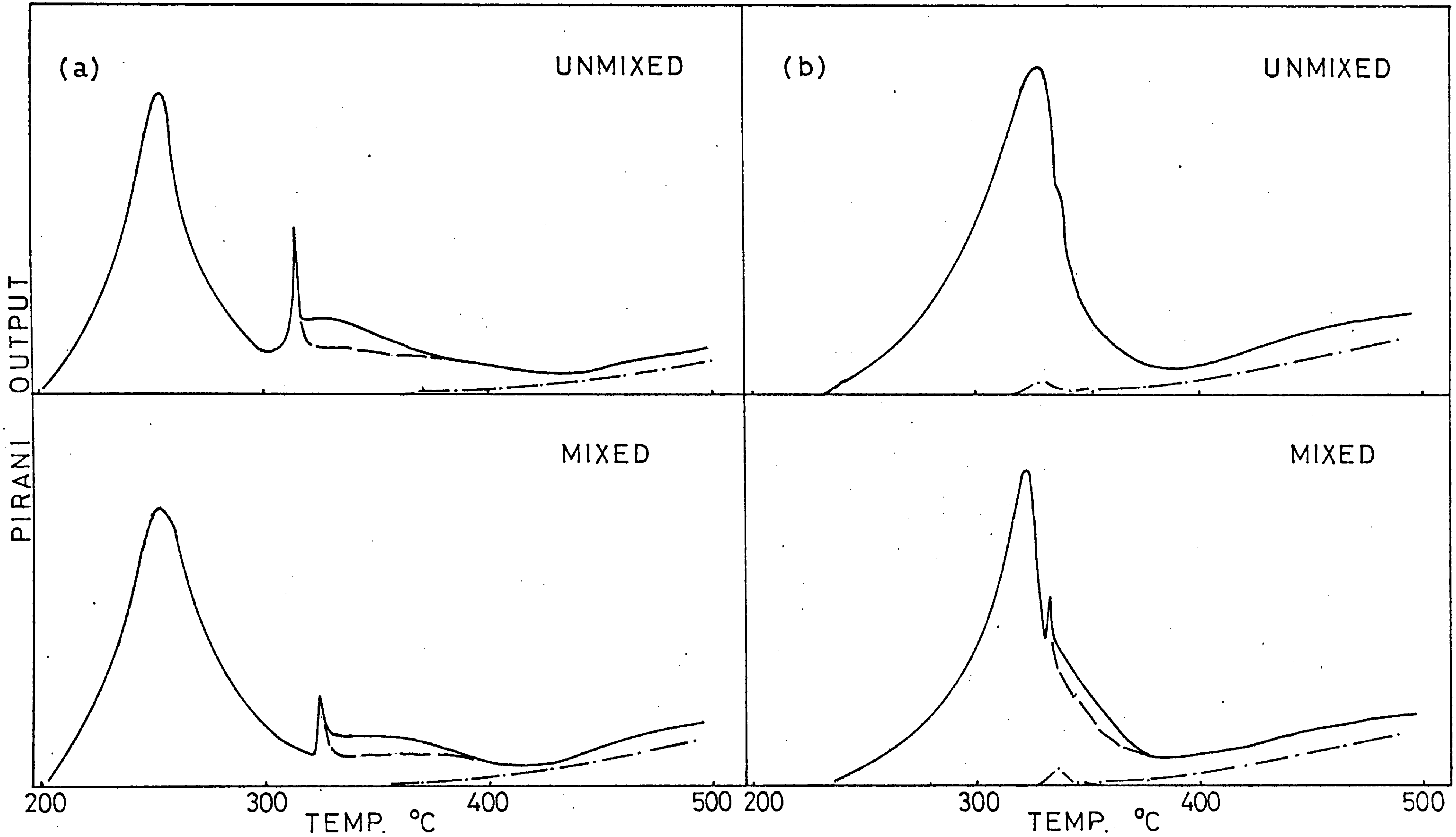


FIG. 4.12 (a) TVA CURVES FOR SIMULTANEOUS DEGRADATION OF PAN I AND PVDC, 1:1 BY WEIGHT POWDER SAMPLES, 100 mg TOTAL WEIGHT

(b) TVA CURVES FOR SIMULTANEOUS DEGRADATION OF PAN I AND ALLOPRENE, 1:1 BY WEIGHT POWDER SAMPLES 100 mg TOTAL WEIGHT

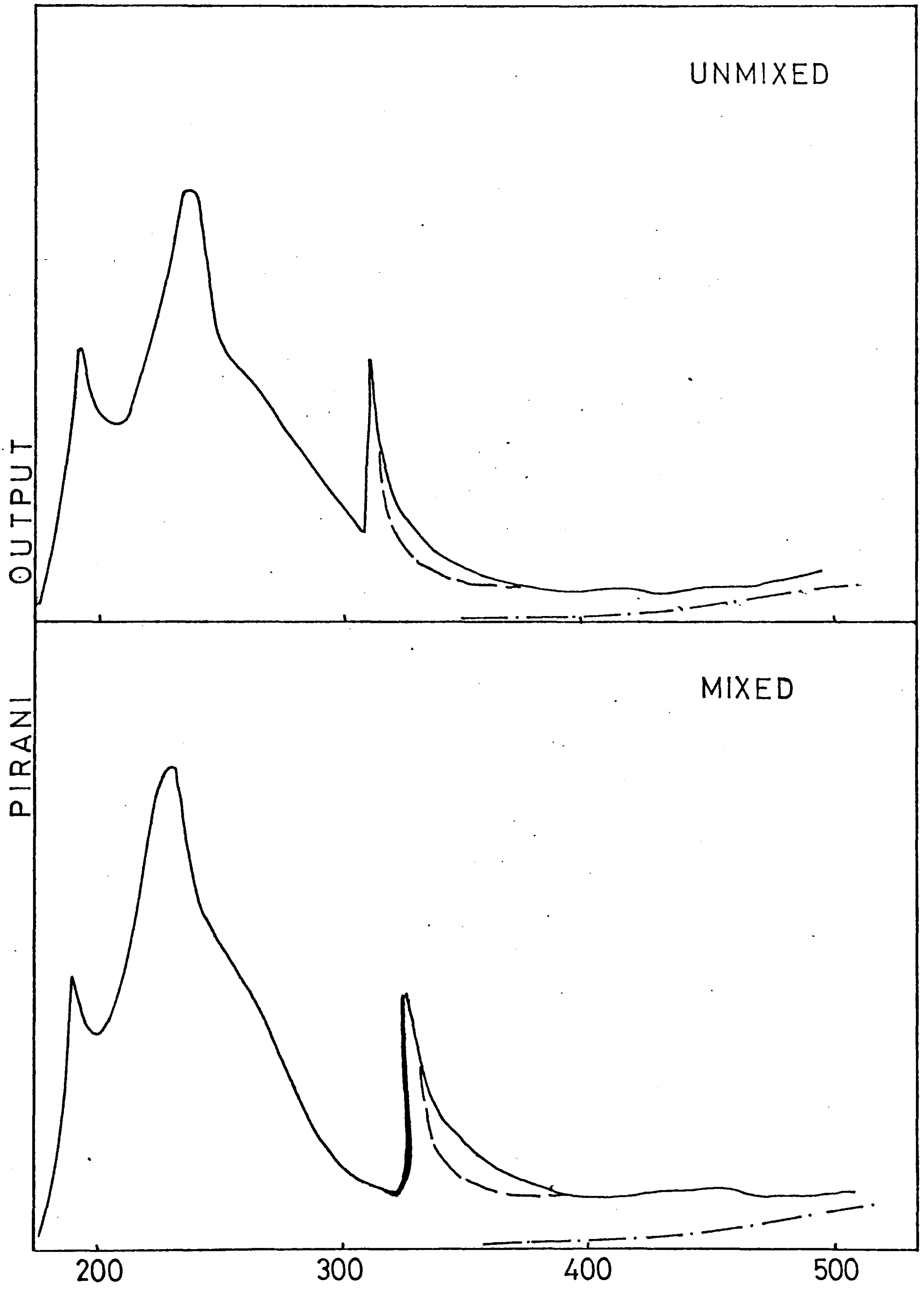


FIG. 4.13 TVA CURVES FOR SIMULTANEOUS DEGRADATION OF PAN I AND PαCAN
POWDER SAMPLES, 100 mg TOTAL WEIGHT

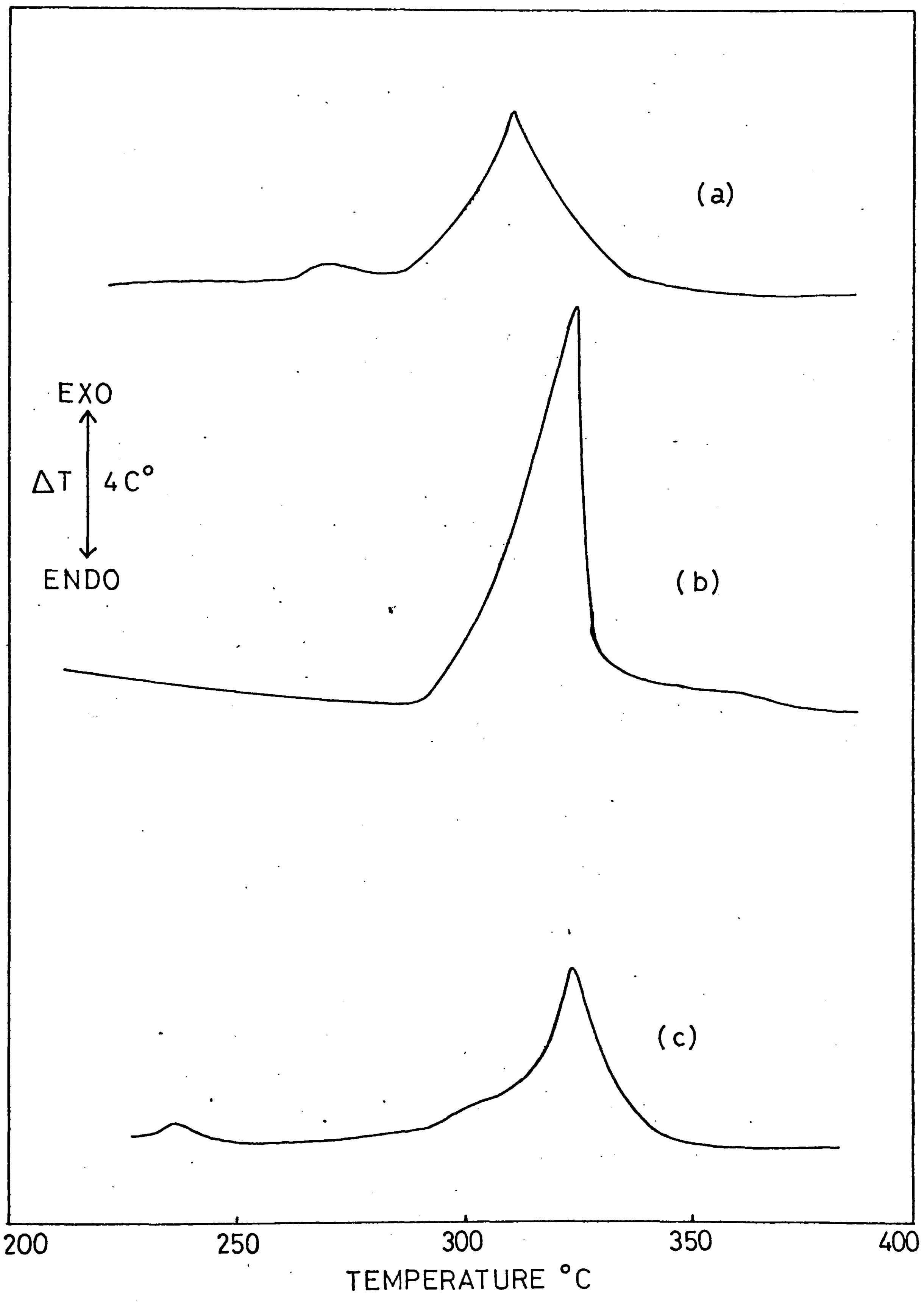


FIG. 4.14 DTA CURVES FOR (a) 1:1 BY WEIGHT PAN I:PVDC (b) 1:1 BY WEIGHT PAN I:ALLOPRENE (c) 1:1 BY WEIGHT PAN I:PαCAN 10 mg POWDER SAMPLES, HEATING RATE 10C°/min, DYNAMIC N_2 ATMOSPHERE

1:1 PAN/PVDC	171 cal/g	9.1 K cal/mole AN
1:1 PAN/Alloprene	190 cal/g	10.1 K cal/mole AN
1:1 PAN/PαCAN	179 cal/g	9.5 K cal/mole AN

The values obtained are significantly higher than for PAN and similar to that obtained for PAN/PVC blend samples.

THERMOGRAVIMETRIC ANALYSIS

A series of blend compositions was examined in each of the three systems, as 5 mg. mixed powder samples. The results are shown in Figs. 4.15 - 4.17.

The curves in all three systems exhibit similar stabilization of PAN decomposition to that observed in the PVC blends, the magnitude of this shift is almost independent of the chlorinated polymer. No tendency to decompose at temperature lower than that of the least stable component - the chlorinated polymer - can be detected, and in addition the accelerated rate of dehydrochlorination observed in PVC studies is absent in all three systems.

The information derived from the TG curves is summarized in Table 4.2.

EFFECT OF ADDITIVES UPON PAN DECOMPOSITION

The similarity between all four blend systems in their effect upon PAN decomposition suggests HCL, common to the decomposition of each, may be responsible. The effect of HCl and other additives upon both TG and DTA behaviour was, therefore, examined.

Fig. 4.18 shows both the TG and DTA curves for (a) PAN after addition of concentrated HCl to a powder sample, followed by vacuum oven drying of the contaminated sample at 30°C (b) PAN containing 10% by weight NH_4Cl.

It is evident that HCl can stabilize the weight loss during PAN decomposition, this being more apparent in the HCl rinsed sample presumably due to the open sampling conditions employed in TG experiments allowing the majority of the NH_4Cl to sublime readily, thus reducing the possibility of HCl reacting with the polymer. In DTA however, where the sample is

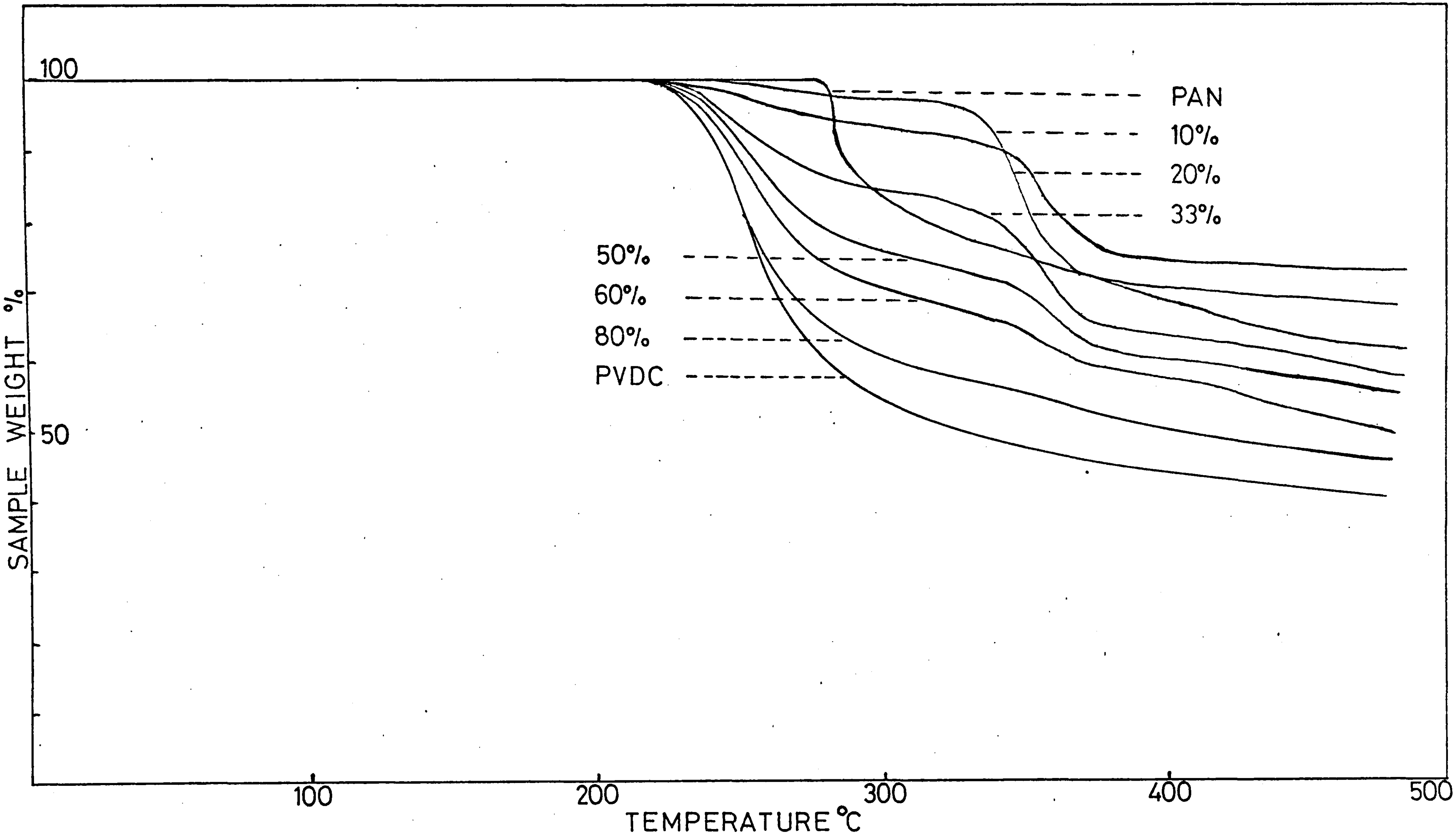


FIG. 4.15 TG CURVES FOR PAN-PVDC BLENDS (WEIGHT % PVDC) 5 mg POWDER SAMPLES, HEATING RATE 10C°/min. DYNAMIC N_2 ATMOSPHERE

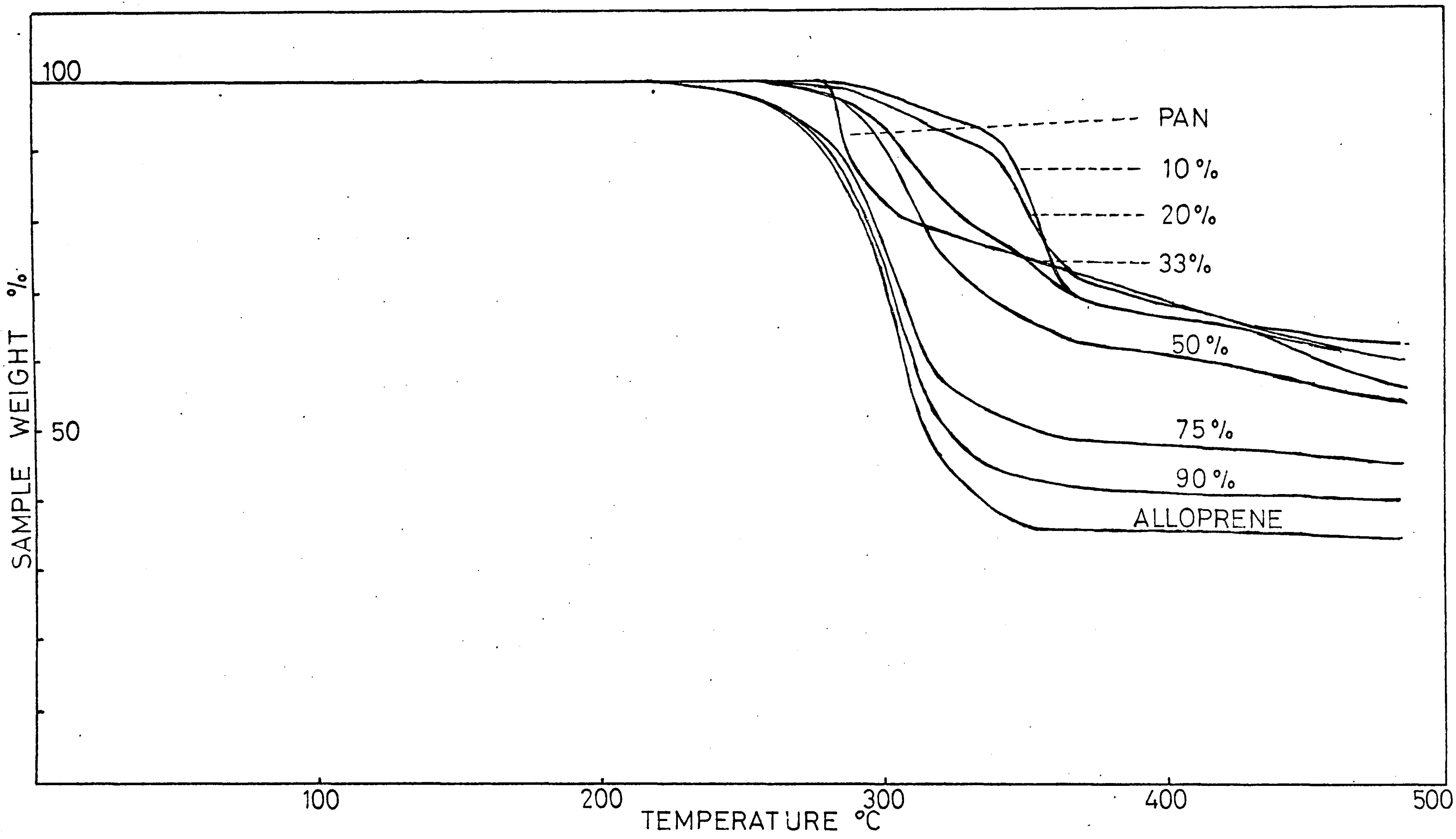


FIG. 4.16 TG CURVES FOR PAN-ALLOPRENE BLENDS (WEIGHT % ALLOPRENE) 5 mg POWDER SAMPLES, HEATING RATE 10C^{o}/min, DYNAMIC N_2 ATMOSPHERE

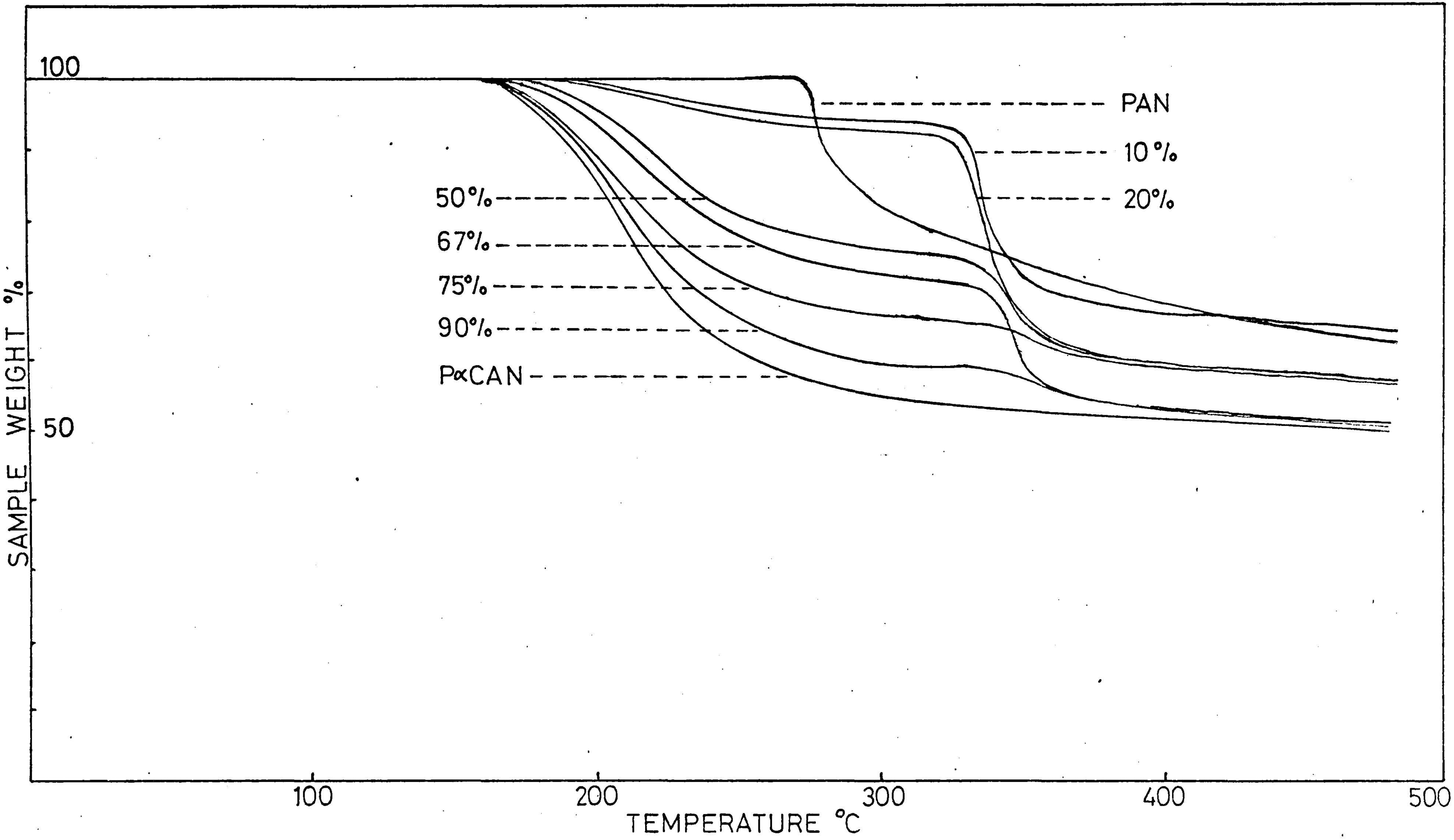


FIG. 4.17 TG CURVES FOR PAN:P CAN BLENDS (WEIGHT % PαCAN) 5 mg POWDER SAMPLES
HEATING RATE 10C°/min, DYNAMIC N_2 ATMOSPHERE

TABLE 4.2 TG ANALYSES OF MIXED POWDERS *

Blend Composition % by weight		Maximum rate of weight loss (% per min) R max	Conversion at R max(%) C max	T max (^{o}C)
PVDC	100	10	22	260
	80	8	20	260
	60	6	19	260
	50	5.5,3.5	14,35	260,355
	33	3.0,5.0	9,28	255,350
	20	1.5,5.0	4,20	255,350
	10	-,12.0	-,14	-,345
ALLOPRENE	100	14	-	305
	90	13.5	32	305
	75	11	30	305
	50	8,1.5	14,33	310,345
	33	5,2	12,24	310,345
	20	2,7	5,17	310,345
	10	-,9	-,15	-,340
POLY(α	100	7	24	215
CHLORO-	90	6.5,1.5	20,43	215,355
ACRYLO-	75	5.5,1.5	17,37	215,355
NITRILE)	67	4.5,6.0	13,39	215,350
	50	4.0,5.5	10,33	220,350
	20	1.0,11.5	4,23	220,345
	10	-, 6.0	-,19	-,335

*5 mg. samples, Dynamic N_2 Atmos. heating rate 10C^{O}Min.$^{-1}$

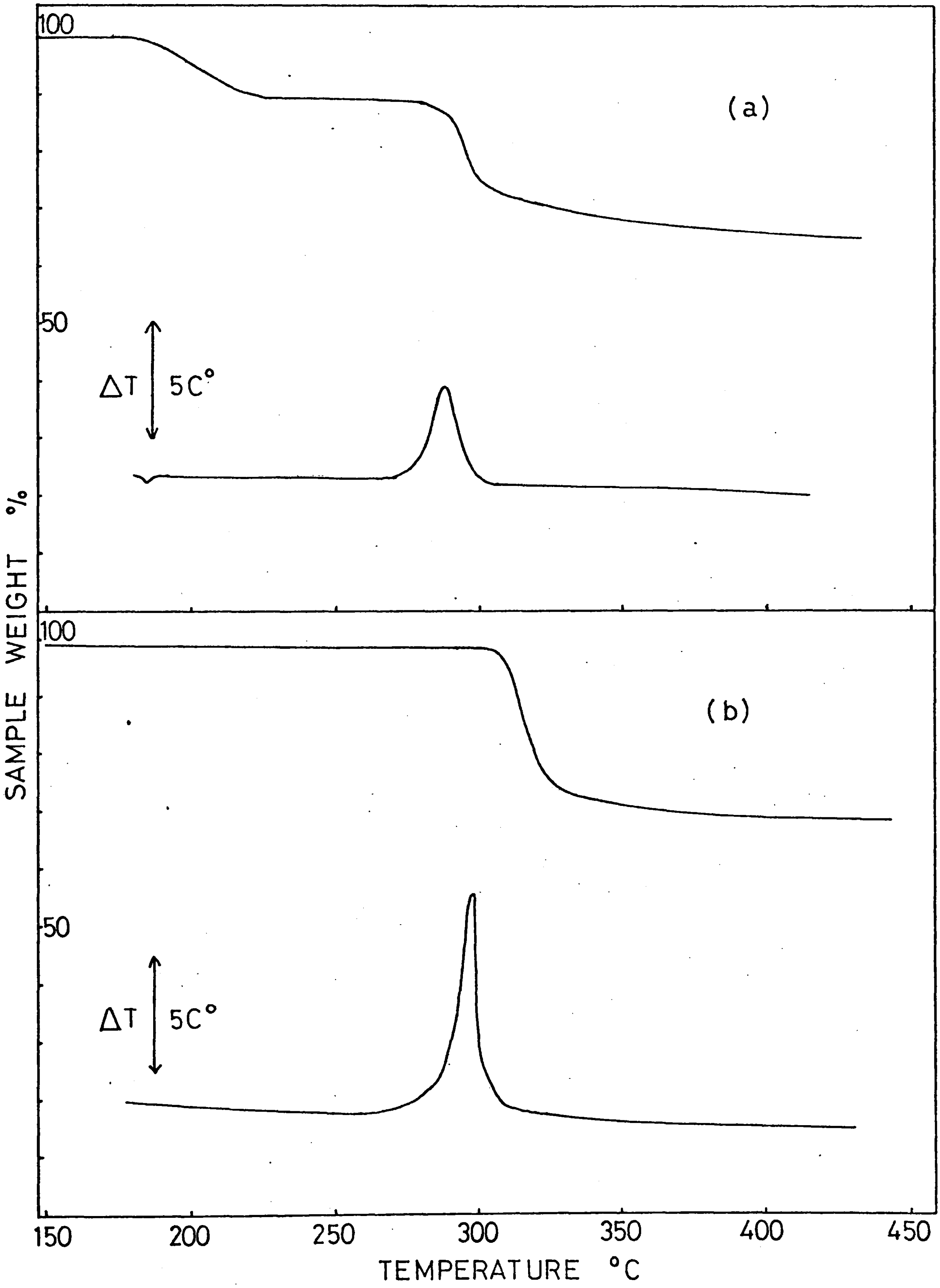


FIG. 4.18 TG AND DTA CURVES FOR
(a) PAN CONTAINING 10% BY WEIGHT NH_4Cl
(b) PAN CONTAINING 7% BY WEIGHT HCl
5 mg POWDER SAMPLES, HEATING RATE 10C°/min,
DHNAMIC N_2 ATMOSPHERE

more tightly packed, shows the efficiency of the large concentration of NH_4Cl, relative to the small amount of HCl incorporated through rinsing in HCl, to reduce the intensity of the exotherm.

Nitric acid, a solvent for PAN, was found to have a more drastic effect upon both TG and DTA resulting in a smooth weight loss curve and a similarly reduced exotherm.

Qualitatively it can be argued that the effects observed during blend decomposition may be at least in part due to the interaction between HCl diffusing through the blend with the PAN.

It is also interesting to note the behaviour of PAN after precipitation or film casting from DMS or DMF. The TG curve for PAN precipitated from DMS was shown earlier. It was found that precipitation from DMF had a similar effect, removing the rapid weight loss process and giving a smooth TG curve, while the DTA trace also shows a reduction in the intensity of the exotherm.

4.6 DISCUSSION

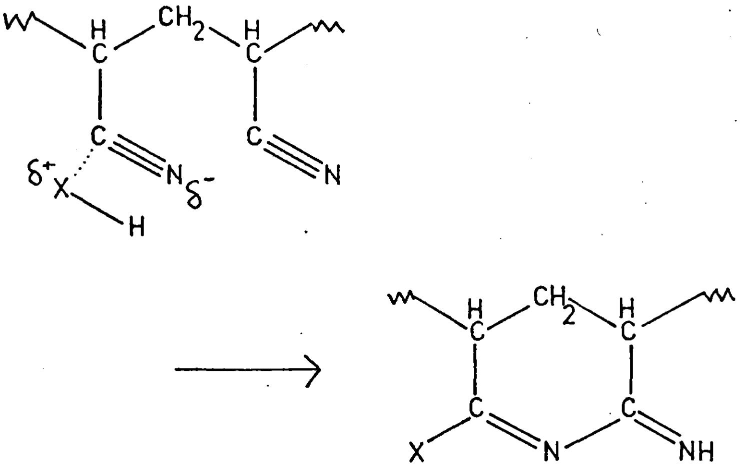
Two phenomena are common to the decomposition of each of the blends -

1. A reduction in the rate of nitrile oligomerization in PAN shown by the broadening of the temperature range through which it occurs.
2. Retardation of the weight loss due to chain scission in PAN which results in separation of the exotherm from weight loss.

Thermal decomposition of pure PAN involves the simultaneous occurrence of both the exotherm and weight loss - the latter arising primarily from chain scission which is an endothermic process. The exotherm observed is, therefore, the sum total of both exothermic and endothermic reactions and separation of the two would be expected to result in an exotherm which more closely reflects nitrile condensation.

The exotherms obtained from the blends were in fact found to be greater than in pure PAN but will be influenced by the reaction of HCl with the polymer which has been shown to result in a reduced rate of nitrile polymerization.

In pure PAN initiation of decomposition involves the formation of radical activity from breakdown of defect structures within the polymer. Initiation is the slow step while propagation is rapid as shown by the sharp exotherm. Grassie and McNeill[15,30,78], in studies of the coloration of nitrile polymers by the presence of additives, have concluded that initiation then arises through nucleophilic attack upon the unsaturated nitrile -



It may be thus expected that propagation will be the slow process by this mechanism since it is now ionic in character and involves charge separation. The role of HCl during decomposition of the blends can be adequately explained by this mechanism.

Decomposition of the PVC blends has shown acceleration in HCl evolution not apparent in the remainder. In view of the physical nature of the system interaction between the two polymers is unlikely as is reaction of the gaseous products of PAN with PVC since their evolution has been shown to be retarded.

A plausible explanation must take into account the sample form which has been shown to be important in PVC decomposition[17, 100]. Thus powder samples and thick films exhibit a faster attainment of the maximum rate of

HCl evolution which may be interpreted as the catalytic effect of HCl during diffusion controlled evolution. The role of PAN may, therefore, be simply to enhance the catalytic effect of HCl by effectively reducing the rate of diffusion of HCl from the blend.

CHAPTER 5

THE THERMAL DEGRADATION OF POLYACRYLONITRILE BLENDS CONTAINING (A) POLYSTYRENE (B) POLYMETHYLACRYLATE

5.1 INTRODUCTION

In contrast to PMMA, chain transfer reactions are a predominant feature of the thermal decomposition of both polystyrene (PS) and polymethylacrylate (PMA). Chain fragmentation is extensive in each, the monomer yield from PS being approximately 45% by weight of total volatiles while monomer evolution is virtually eliminated during PMA decomposition.

The pronounced effect of PAN upon the thermal decomposition of PMMA, in which depropagation of the initially formed macroradical is the exclusive mode of degradation, was examined in the previous chapter. It is of interest therefore to compare the results from analagous PMA blends in particular.

In addition to examination of polymer blends containing PS and PMA, a brief investigation of PAN blends with poly α methyl styrene is also reported.

5.2 POLYMER SAMPLE HISTORY

POLYMER	Mn	POLYMERIZATION CONDITIONS
PAN I	$1.2\text{x}10^6$	Bulk Polym^n., 0.05% w/v AIBN, 40°C
PS I	590,000	Bulk Polym^n., 0.02% w/v AIBN, 60°C
PS II	73,000	Bulk Polym^n., 0.11% s/v B_zO_2, 100°C
PαMS	97,500	Laboratory sample, cationic polym^n., -75°C
PMA I	* $1.92\text{x}10^6$	Solution polym^n., 50% v/v Methyl acetate, 0.05% w/v AIBN, 60°C
PMA II	* 430,000	Solution polym^n., 50% v/v Ethyl benzene, 0.01% w/v B_zO_2, 45°C

* Determined by viscometry using the relationship[109] -

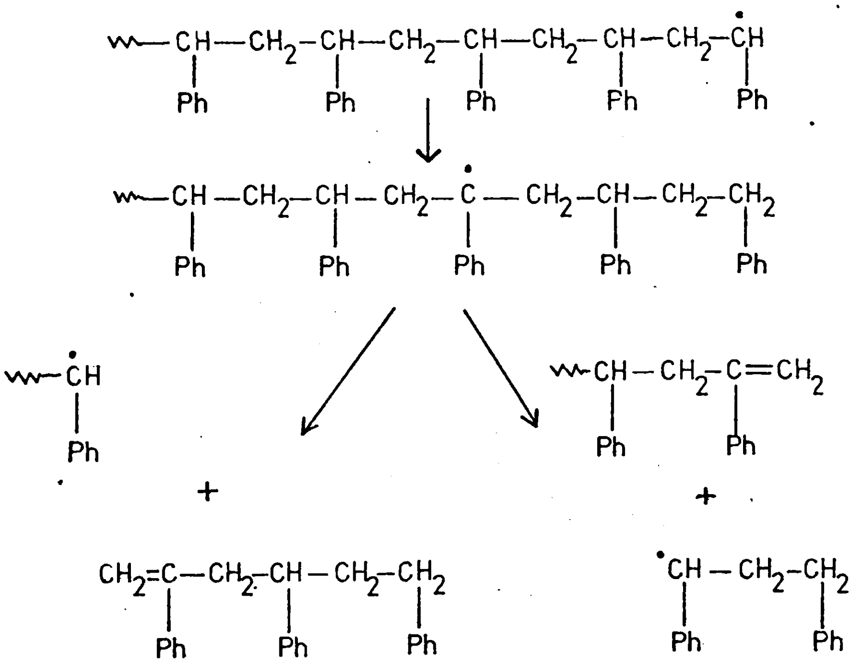
$$[\eta] = 1.28\text{x}10^{-4}\ M^{0\text{-}7143}$$

5.3 POLYACRYLONITRILE-POLYSTYRENE BLENDS

The detailed mechanism of PS degradation has been the subject of much controversy and confusion for a number of years and has recently been reviewed by Cameron and MacCallum[101].

The products of vacuum pyrolysis of PS are monomer in approximately 45% yield together with progressively decreasing amounts of dimer, trimer, tetramer and pentamer[102]. On the basis of such a product distribution, interpretation of the radical chain process necessitates the occurrence of both intra- and intermolecular transfer reactions in addition to depropagation. Grassie & Kerr[10] have shown that the constancy of product distribution during decomposition, namely the monomer-non monomer ratio in the volatiles, can only be explained in terms of depropagation of the initially formed macroradical accompanied by intra molecular chain transfer.

Intermolecular transfer reactions produce a comparatively small amount of volatile products but will have a profound effect upon the molecular weight of the remaining polymer. Intra molecular transfer is thus believed to be the main source of volatile low polymer as shown below[104]:-



Thus intra molecular transfer restricted mainly to chain ends has a much smaller effect upon molecular weight.

The initial rapid decrease in molecular weight may, therefore, be explained by a combination of random chain scission reactions accompanied by intermolecular chain transfer[22], although another plausible interpretation may be found in the concept of "weak links" randomly distributed throughout the polymer chain[105].

5.4 RESULTS

THERMAL VOLATILIZATION ANALYSIS

Fig. 5.1 illustrates the TVA curve for a 50 mg sample of PS I degraded as a film sample cast from DMF solution. A single stage reaction can be discerned with the product exhibiting a low L.R. effect in the -75° trace and completely condensed at -100°C. T max occurs around 410°C. Similar behaviour was found for the lower molecular weight sample. The condensibility of the gaseous products is consistent with the observed behaviour of styrene monomer in the trap system[41]. The higher molecular weight oligomers, with the possible exception of dimer, are relatively involatile and are collected as a cold ring fraction on the cooled zone of the degradation tube.

The behaviour of powder samples was found identical confirming the absence of either sample form or molecular weight dependence. Mohammed and McNeill[46] have shown this behaviour to be general for PS prepared by a number of techniques. It was found, however, by the same authors, that the decomposition of ultra thin films of around 100Å average thickness showed increased stability while the general peak shape remains unchanged.

Fig. 5.2 shows the TVA curves for 1:1 by weight mixed and unmixed film samples of PAN I and PS I. The two traces illustrate the products to be qualitatively similar, their condensibility being unchanged. The principal difference is a delay in the T max for styrene evolution which now occurs at 443°C in the mixed system cf 410°C in the unmixed sample.

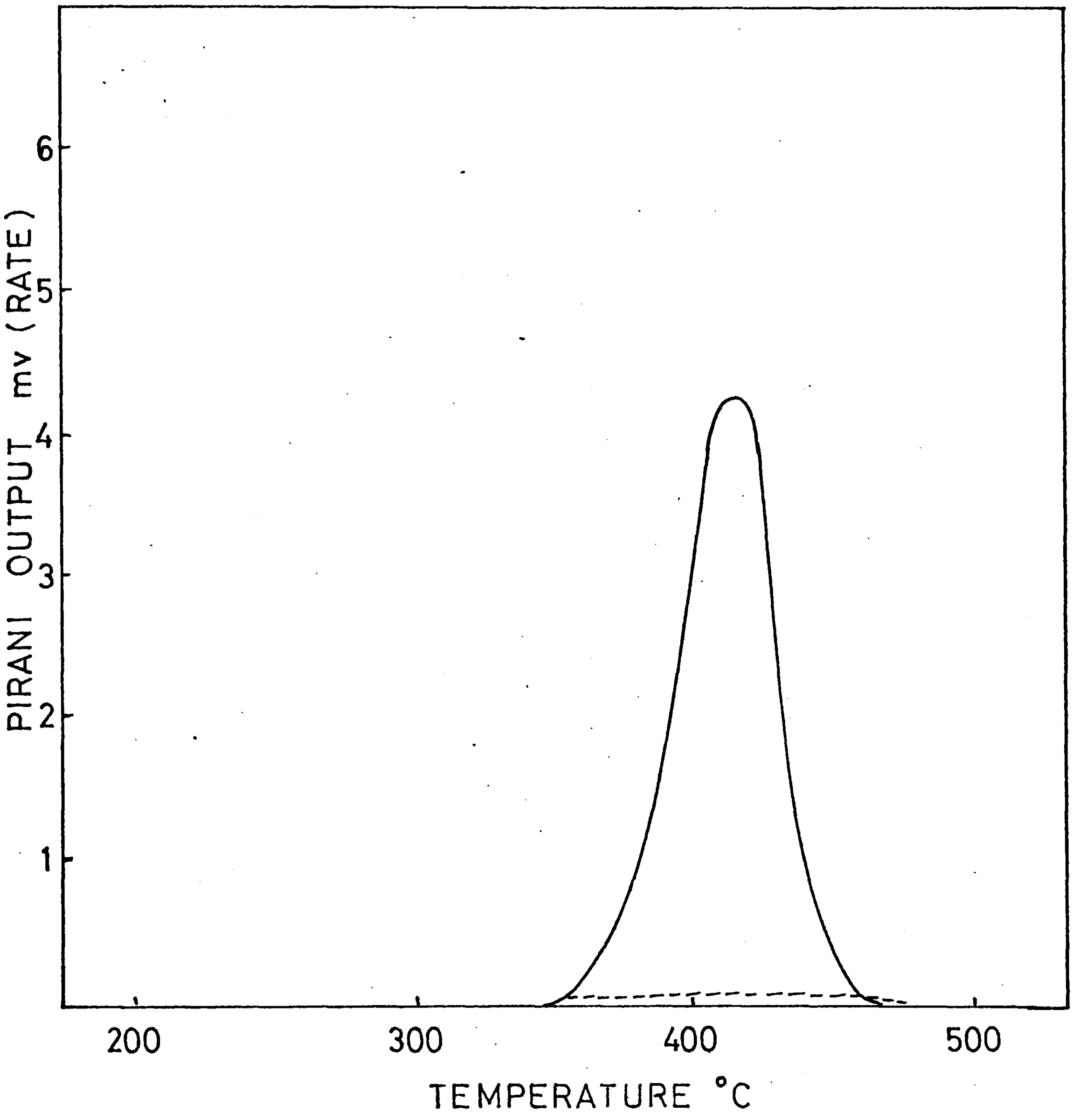


FIG. 5.1 TVA CURVE FOR PS-I 50 mg FILM SAMPLE CAST FROM DMF SOLUTION

The overlap with PAN decomposition makes difficult the accurate determination of the initial temperature of decomposition of the PS component but it appears unaltered at around 350°C.

A similar result was obtained by examination of mixed powder samples. Small differences between this system and the previous film samples were primarily the effect of residual solvent upon PAN decomposition. The overall features were qualitatively unaltered.

The effect of varying the ratio of the two polymers is illustrated in Fig. 5.3 for a 5:1 by weight PS I-PAN I mixed and unmixed film sample. T max for PS in this blend was found as 440°C.

The results for a series of film samples are summarised in Table 5.1. With the exception of the blend containing 25% by weight of PS, each system contained 50 mg. PS, the former being 10 mg:

TABLE 5.1 VARIATION OF T MAX FOR STYRENE EVOLUTION IN THERMAL VOLATILIZATION ANALYSIS OF PAN I:PS I BLENDS

Blend composition (% PS by weight)	25	50	83	90	100
T Max (°C)	446	443	440	435	410

It is evident that incorporation of as little as 10% by weight of PAN induces stabilization of the PS present. Subsequent addition of PAN has only a slight effect, the maximum extent of stabilization being 36C°.

PRODUCT ANALYSIS

The major volatile products were found unchanged, namely NH_3, HCN and styrene.

GLC analysis was employed using a Microtek GC2000R chromatograph, equipped with a flame ionization detector and 1% SE30 columns. Styrene was confirmed as the major liquid product with trace amounts of both toluene and benzene. It was found, within the limits of the technique, that the percentage by weight of liquid products in relation to PS content was unchanged in comparison with PS alone, namely around 40-45%.

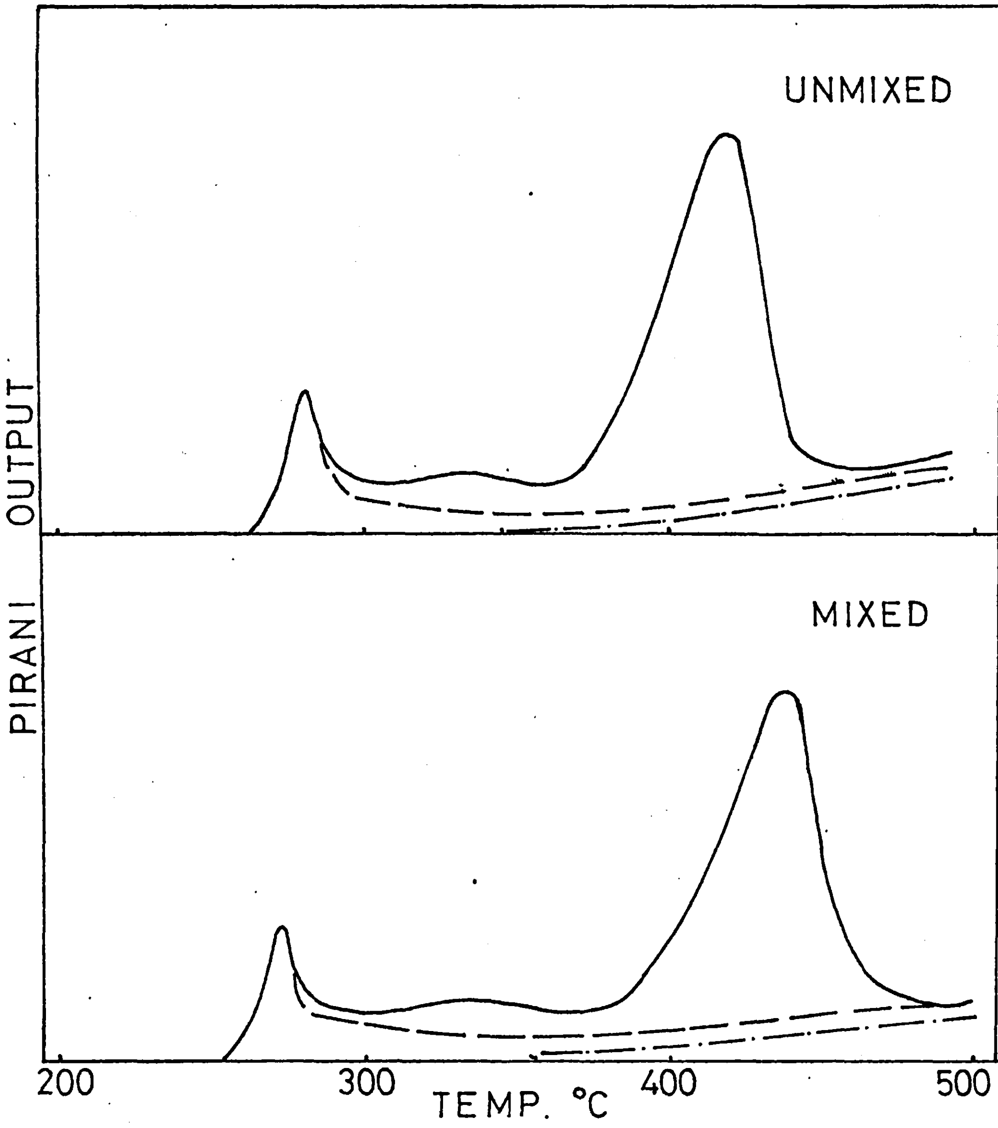


FIG. 5.2 TVA CURVES FOR SIMULTANEOUS DEGRADATION OF PAN I AND PS-I, 1:1 BY WEIGHT. FILM SAMPLE FROM DMF SOLUTION, 50 mg PS

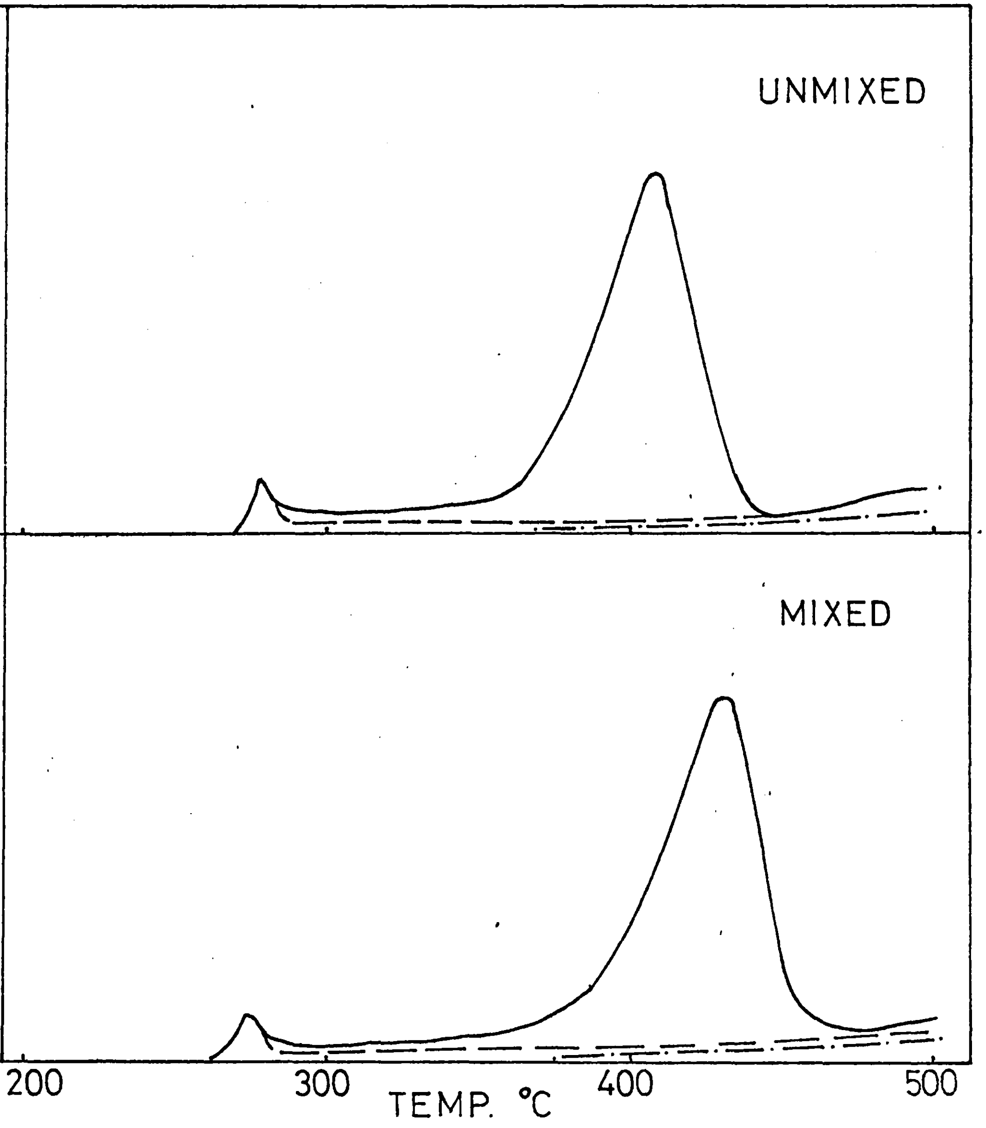


FIG. 5.3 TVA CURVES FOR SIMULTANEOUS DEGRADATION OF PAN I AND PS-I, 1:5 BY WEIGHT. FILM SAMPLES FROM DMF SOLUTION, 50 mg PS

Fig. 5.4 illustrates the i.r. spectra of the chain fragments collected from degradation of (A) Polystyrene and (B) a 1:1 by weight PAN:PS blend. Both the position and absorption intensities observed in the PS chain fragment spectrum are similar to PS itself, confirming their assignment as low molecular weight polymers. The blend spectrum is unaltered from that which one would predict from simple addition of the spectra obtained from decomposition of the two homopolymers.

The residue remaining after blend decomposition to 500°C was similar to that of PAN. It was also found that interrupting temperature programmed degradation of the blends at various temperatures, and isothermal degradation at 320°C produced no alteration in the i.r. spectra of the PS which was extracted using benzene.

THERMOGRAVIMETRY

Fig. 5.5 illustrates the TG curves for two PS I blends containing 20 and 50% by weight PAN, together with the curve for PS I.

The blends were examined as powder samples prepared by coprecipitation from DMF solution into methanol and as a result the weight loss associated with PAN decomposition has been modified through solvent interactions. The principal feature, however, is the retardation of weight loss associated with styrene evolution. This confirms the observations made in TVA experiments and further illustrates the independence of the phenomena from both sample form and geometry.

MOLECULAR WEIGHT DETERMINATION

80 mg samples of PS I, cast from DMF solution, were degraded isothermally at 320°C in vacuo for various time intervals up to a maximum of three hours. Parallel experiments were performed using 100 mg film samples of a PS I:PAN I blend containing 80% by weight PS. After degradation the remaining PS was extracted by stirring the residue in benzene over a period of 24 hours. PAN is insoluble under similar conditions. The molecular weight of the extracted polymer was determined

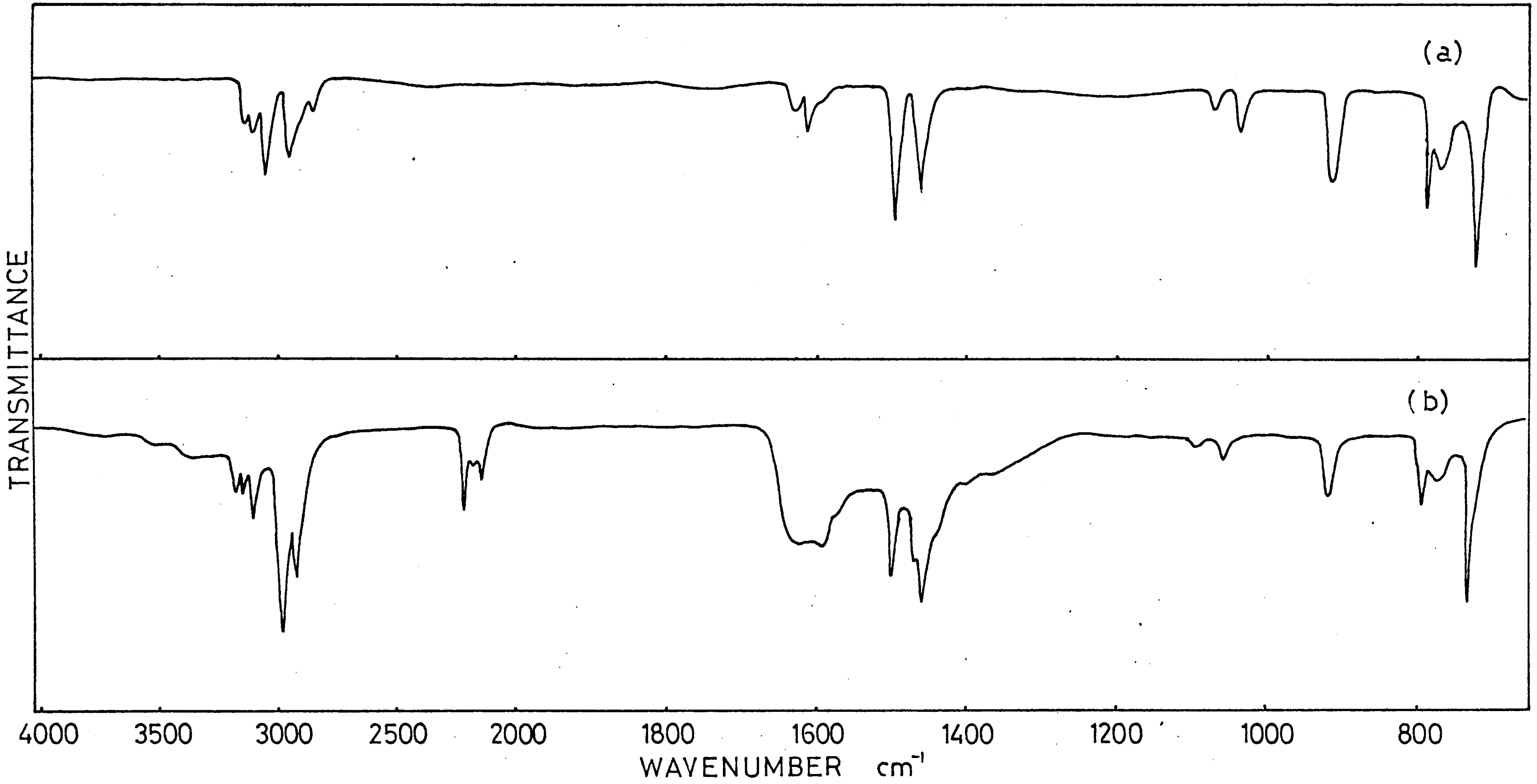


FIG. 5.4 I.R. SPECTRUM OF CRF OBTAINED AFTER DECOMPOSITION TO 500°C OF (a) PS-I (b) 1:1 BY WEIGHT PAN-I:PS-I

by GPC, with the results given in Table 5.2:

TABLE 5.2 MOLECULAR MASS CHANGES AFTER ISOTHERMAL DEGRADATION AT 320°C OF (a) POLYSTYRENE (b) PS I:PAN I BLEND (80% PS)

TIME (mins)	PS Mn	PS BLEND * Mn
0	559,000	559,000
45	167,000	349,000
90	154,000	295,000
120	153,000	349,000
180	89,000	280,000

*SOLUBLE PS

The results indicate a significant reduction in the rate of chain scission of degrading PS in the presence of PAN. Examination of the extracted PS by both i.r. and TVA, however, does not reveal differences in either structure or stability.

It is appropriate to mention briefly at this point the results of degradation of PAN:PαMS blends. Both α methyl styrene and methyl methacrylate are 1,1 disubstituted monomers, which to some extent is reflected in the thermal decomposition of the polymers in which depropagation of the initially formed macroradical occurs in the absence of chain transfer reactions. Initiation of decomposition in PαMS is believed to involve random chain scission with a large kinetic chain length[106].

Fig. 5.6(a) illustrates the TVA curve for both PαMS and a 1:1 by weight PAN:PαMS mixed sample. The polymer is considerably less stable than PS with T max occurring at 320°C. The low volatility of the monomer is evident in the L.R. effect in the -45°C trace. Fig. 5.6(b) gives the results for a 1:1 by weight PAN:PαMS blend. The pattern of evolution of volatiles is unaffected by mixing of the polymers. I.r. analysis confirmed the products to be unchanged. TG analysis gave a similar result.

5.5 DISCUSSION

The experimental evidence of the interactions occurring may be summarized as follows -

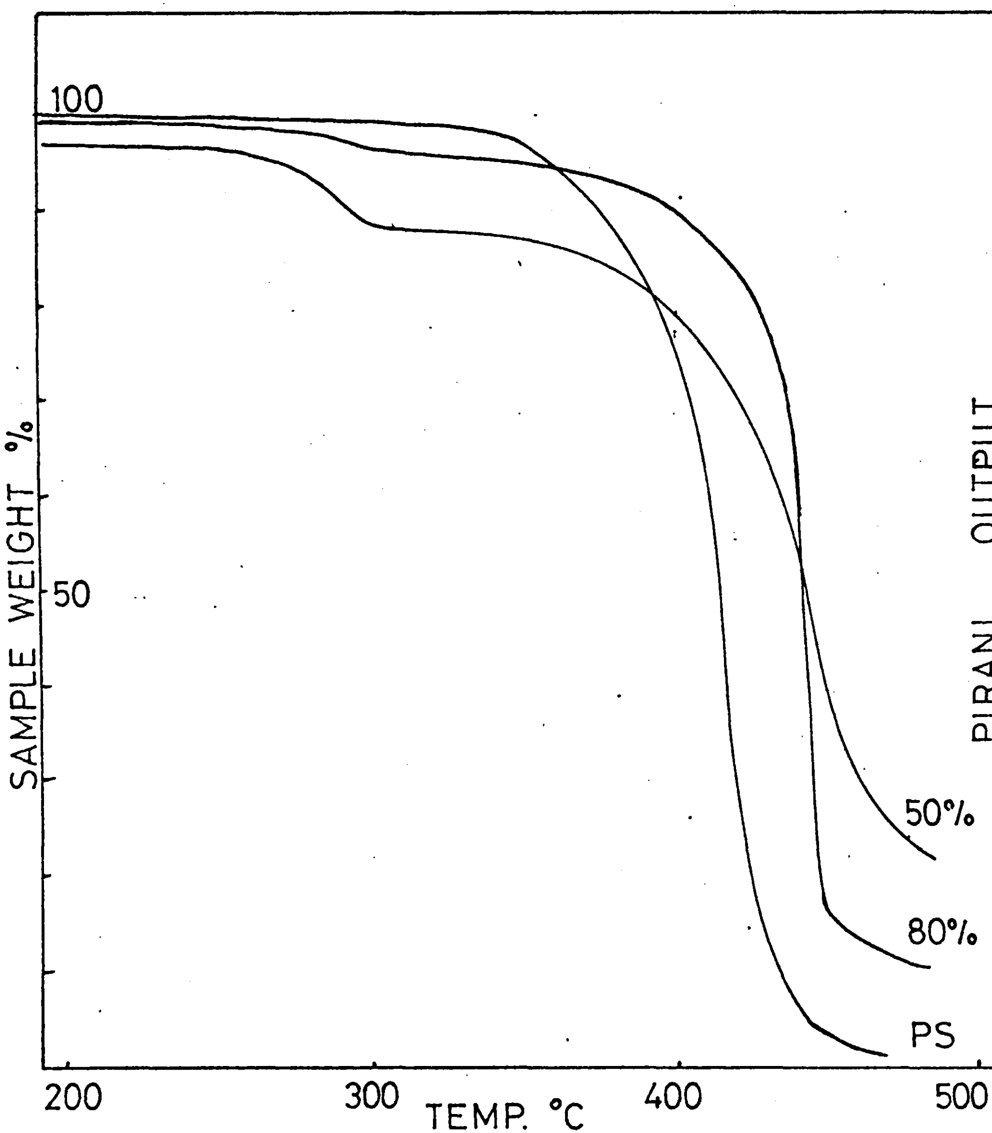


FIG. 5.5 TG CURVES FOR PAN-I:PS-I BLENDS PREPARED BY COPRECIPITATION FROM DMF SOLUTION, 5 mg SAMPLES HEATING RATE 10C^{O}/min, DYNAMIC N_2 ATMOSPHERE

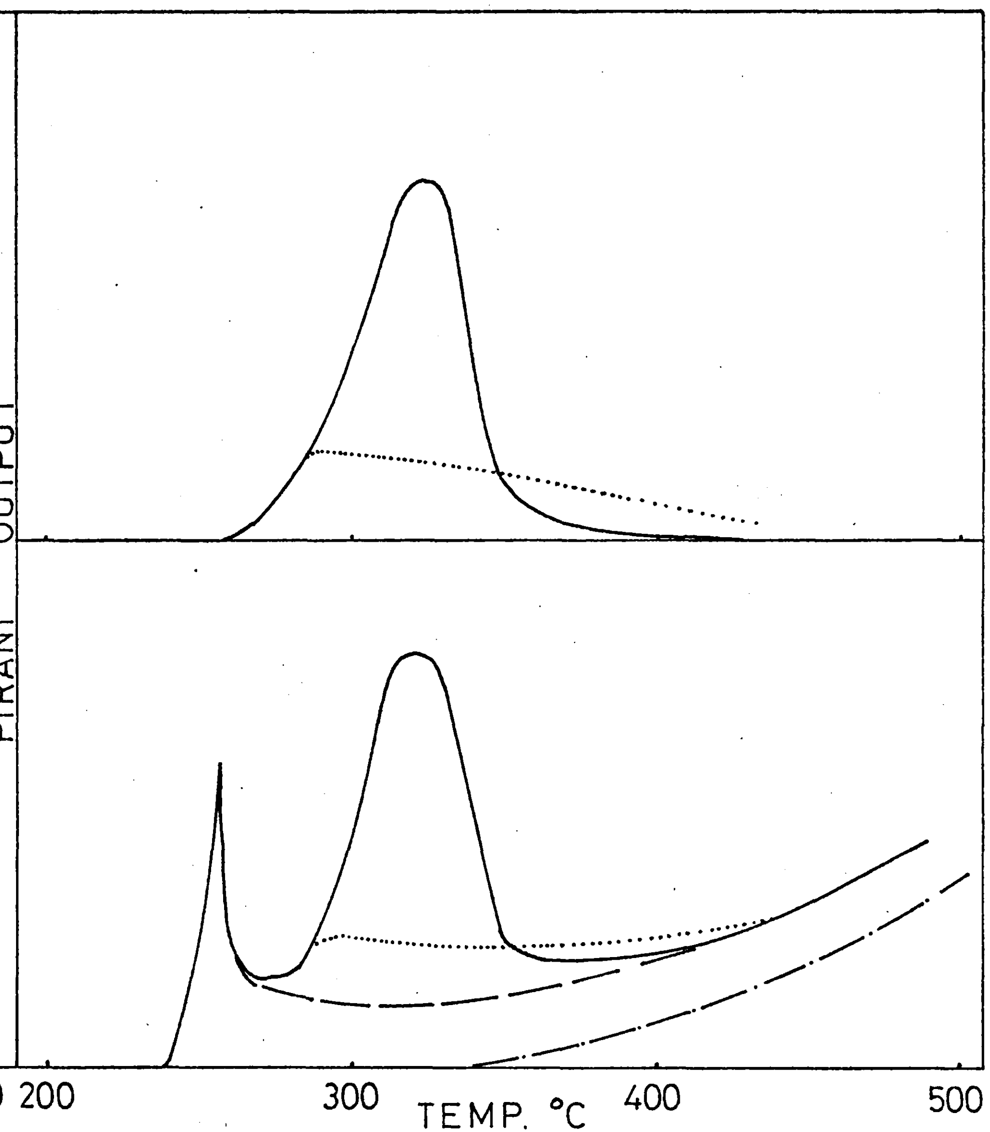


FIG. 5.6 (a) TVA CURVE FOR P MS, 50 mg POWDER SAMPLE
(b) TVA CURVE FOR A 1:1 BY WEIGHT PAN-I:P MS BLEND 100 mg POWDER SAMPLE

1. Mixing of PAN with PS results in stabilization of PS. T max for styrene evolution is increased by 25-35C° under the programmed heating conditions employed in TVA and varies little with blend composition.
2. Sample size and form are not significant within the range examined. The stabilization occurs in samples as mixed powders, films and as powders prepared by coprecipitation from a common solvent.
3. The rate of chain scission during isothermal decomposition of PS is reduced upon blending with PAN.
4. Mixtures of PAN with PαMS show no interaction.

Stabilization of PS degradation has been reported in blends containing PVC. Thus McNeill et al[33], by TVA, were able to demonstrate a maximum stabilization of 40C° accompanied by retardation of PVC dehydrochlorination. It was postulated that chlorine radical attack upon PS could give rise to structural changes within the polymer through crosslinking or chain scission reactions resulting in molecules containing stable end structures.

Jamieson[57], in analagous studies involving polyvinyl acetate, observed a similar result and postulated that interaction of the PS macroradical with the polyvinyl acetate residue remaining after deacetylation could result in the formation of graft copolymers

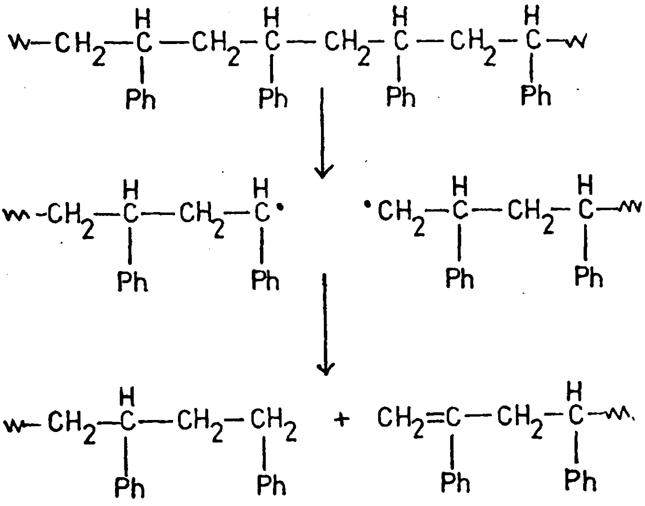
Perhaps the most significant result, however, is that of McNeill and Mohammed[46], in which it was observed that degradation of ultra thin films of PS (100Å average thickness) gives similar results to those outlined earlier. It was also established, by the same authors, that ease of styrene volatilization from the polymer surface during TVA was not a factor contributing to the observed increased stability of the polymer.

Whereas chlorine radicals have been postulated to have some effect in PVC blends, diffusion of small radical species is unlikely in either PVAc or PAN mixtures. In each of the mixed polymer systems, however, a common factor is the presence of a highly unsaturated residue resulting from the initial decomposition of the second polymer. It might, therefore, be considered that this would act as a physical barrier to styrene diffusion. This seems unlikely for three reasons:-

1. A similar stabilization occurs in ultra thin films where diffusion would be expected to occur more readily.
2. The presence of as little as 10% by weight PAN induces enhanced stability.
3. The rate of volatilization of PαMS is unaffected by blending.

It is, therefore, more probable that a chemical interaction is responsible.

Evolution of volatile products occurs by depropagation initiated by allylic activation through the presence of unsaturated chain ends in the polymer molecule[104, 105]. Unlike PMMA, however, terminal unsaturation is not present in PS initially since the principal mode of radical termination during polymerization is by combination of macroradicals. Monomer evolution is thus dependent on the formation of such labile structures through chain scission -



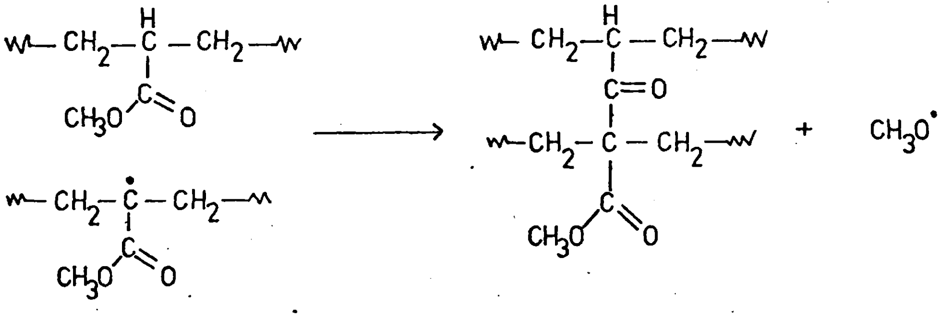
The relative amounts of monomer and chain fragments formed is then determined by competing depropagation and intramolecular chain transfer reactions.

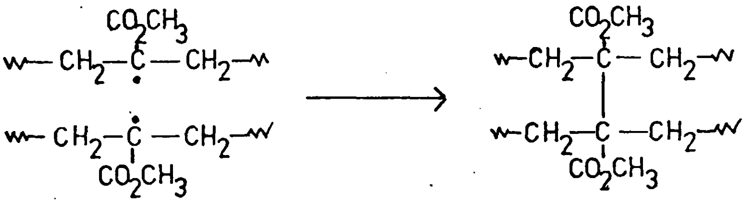
The contribution of intermolecular chain transfer to chain scission reactions and hence the formation of unsaturated chain ends may, therefore, be reduced in degradation of polymer blends either simply by dilution of the PS radical concentration or by intermolecular transfer now occurring between the PS macroradical and the unsaturated polyene residue of the other polymer. Thus the observed increase in stability may indicate the contribution of intermolecular transfer reactions to the overall mode of degradation.

5.6 POLYACRYLONITRILE-POLYMETHYL ACRYLATE BLENDS

The thermal decomposition of PMA has been shown to proceed through random homolytic scission of the polymer chain, followed by a chain of free radical transfer reactions both inter- and intra-molecular. This, as in PS, the molecular weight of the polymer falls rapidly during the initial stages of decomposition[107].

In contrast to PS, however, depropagation does not occur and cross-linking reactions result in the formation of insoluble gel at an early stage of decomposition presumably through the processes such as those illustrated below -





Low polymer from degradation of PMA is found to constitute approximately 90% of the total weight loss with additional small amounts of carbon dioxide and methanol also formed by ester decomposition[108].

5.7 RESULTS

Fig. 5.7 illustrates the TVA curve for a PMA I film sample cast from DMF solution. The decomposition process is a single stage reaction with T max at 390°C. Differential condensation of the products is observed with a L.R. effect in the -100° trace. The products identified by i.r. were found to be CH_3OH and CO_2, both minor products. CH_3OH was estimated quantitatively by i.r. employing the calibration plot in Fig. 5.8. A result of 5.9% of initial polymer weight was found. Carbon dioxide has been estimated by Cameron and Kane to be of similar magnitude.

The TVA curve also shows the presence of gases non-condensible at -196°C. but exaggerates the relative amount through the sensitivity of the Pirani gauge to such materials. The identity of the gases could not be proven conclusively but Straus[108] has found both CO and CH_4, which together constitute $<$ 0.1% by weight of the products.

Fig. 5.9 and 5.10 illustrate the effect of mixing with PAN I for both 1:1 and 4:1 by weight PMA:PAN blends. In both systems the increased evolution of noncondensible gases is apparent although the pattern of evolution remains unchanged. I.r. analysis of the gaseous products employing a closed system technique, now enabled identification of both CO and CH_4 as products. Quantitative estimation of CH_3OH by the same technique showed no alteration within the limits of the technique as did qualitative comparison of CO_2 production.

I.r. analysis of both the polymer residue and cold ring fraction from the blends have shown no significant differences. PMA itself is found to colour upon degradation while spectroscopic analysis gives no indication of structural changes[107]. Thus the i.r. absorptions of the C.R.F. are almost identical to that of PMA, only a slight broadening in the carbonyl region being apparent. (Fig. 5.11).

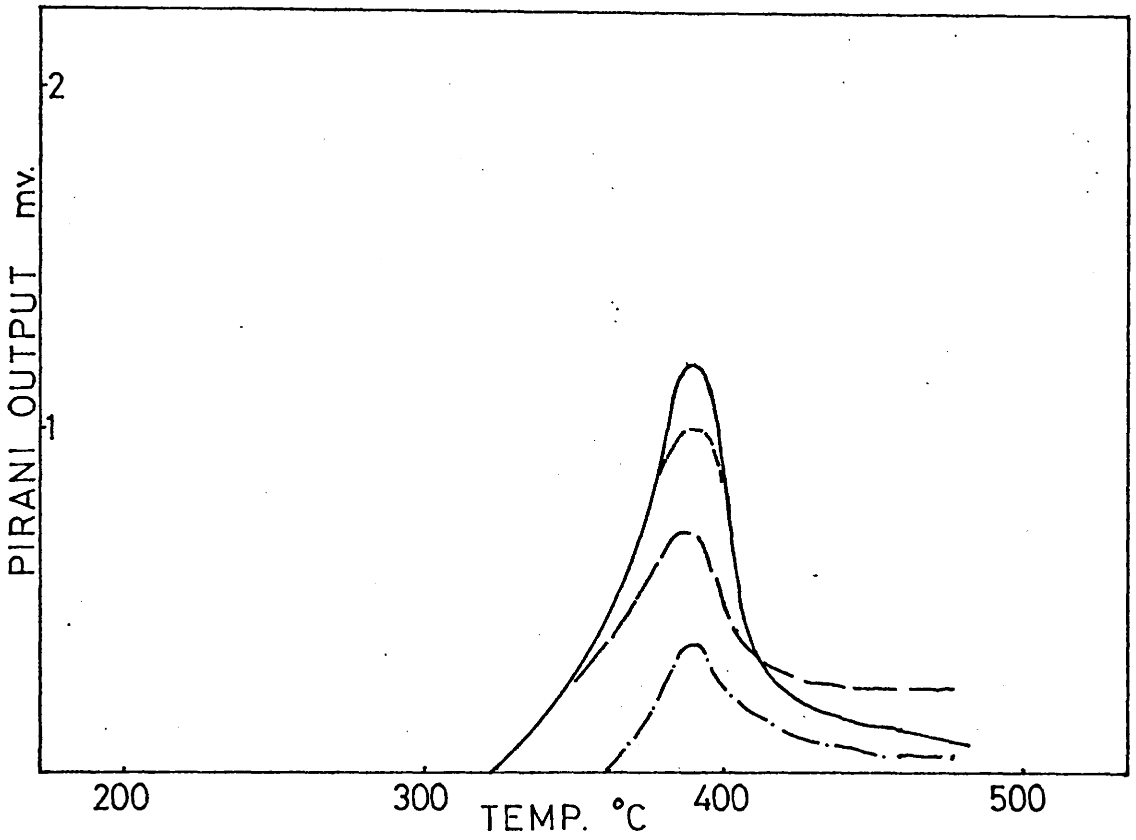


FIG. 5.7 TVA CURVE FOR PMA I, 20 mg FILM SAMPLE FROM DMF SOLUTION

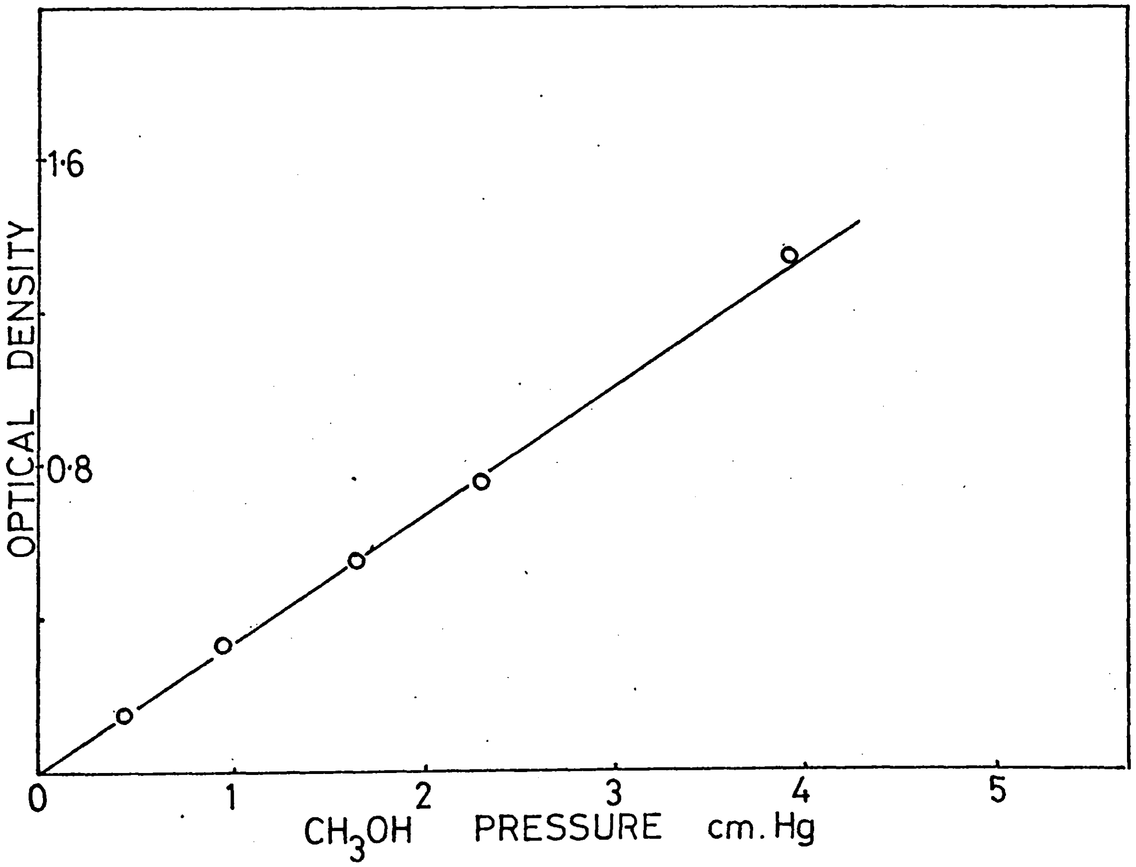


FIG. 5.8 I.R. CALIBRATION PLOT OF OPTICAL DENSITY VS GAS PRESSURE FOR METHANOL (10 cm PATH LENGTH)

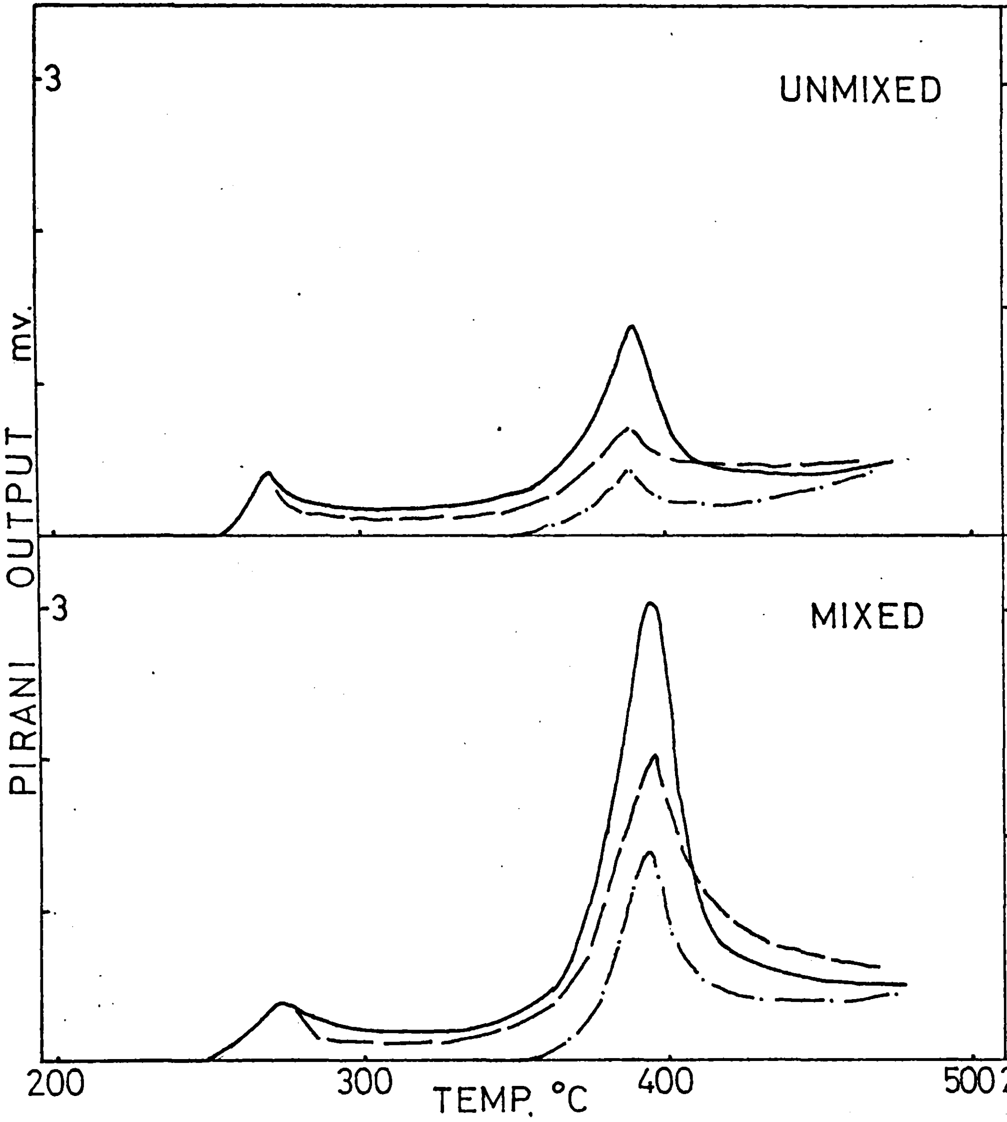


FIG. 5.9 TVA CURVE FOR SIMULTANEOUS DEGRADATION OF PAN I AND PMA, 1:1 BY WEIGHT, 20 mg PMA, FILM SAMPLES FROM DMF SOLUTION

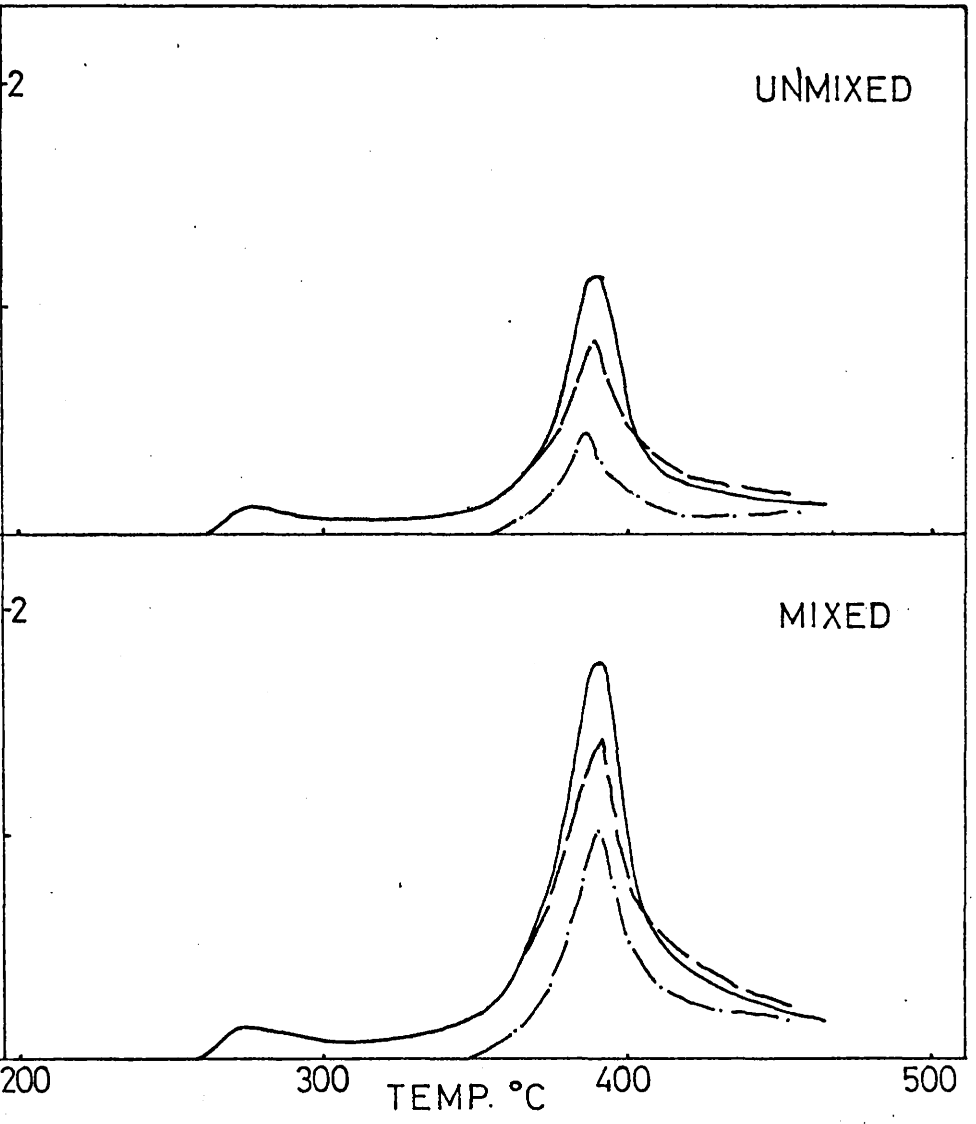


FIG. 5.10 TVA CURVE FOR SIMULTANEOUS DEGRADATION OF PAN I AND PMA, 1:4 BY WEIGHT, 20 mg PMA, FILM SAMPLES FROM DMF SOLUTION

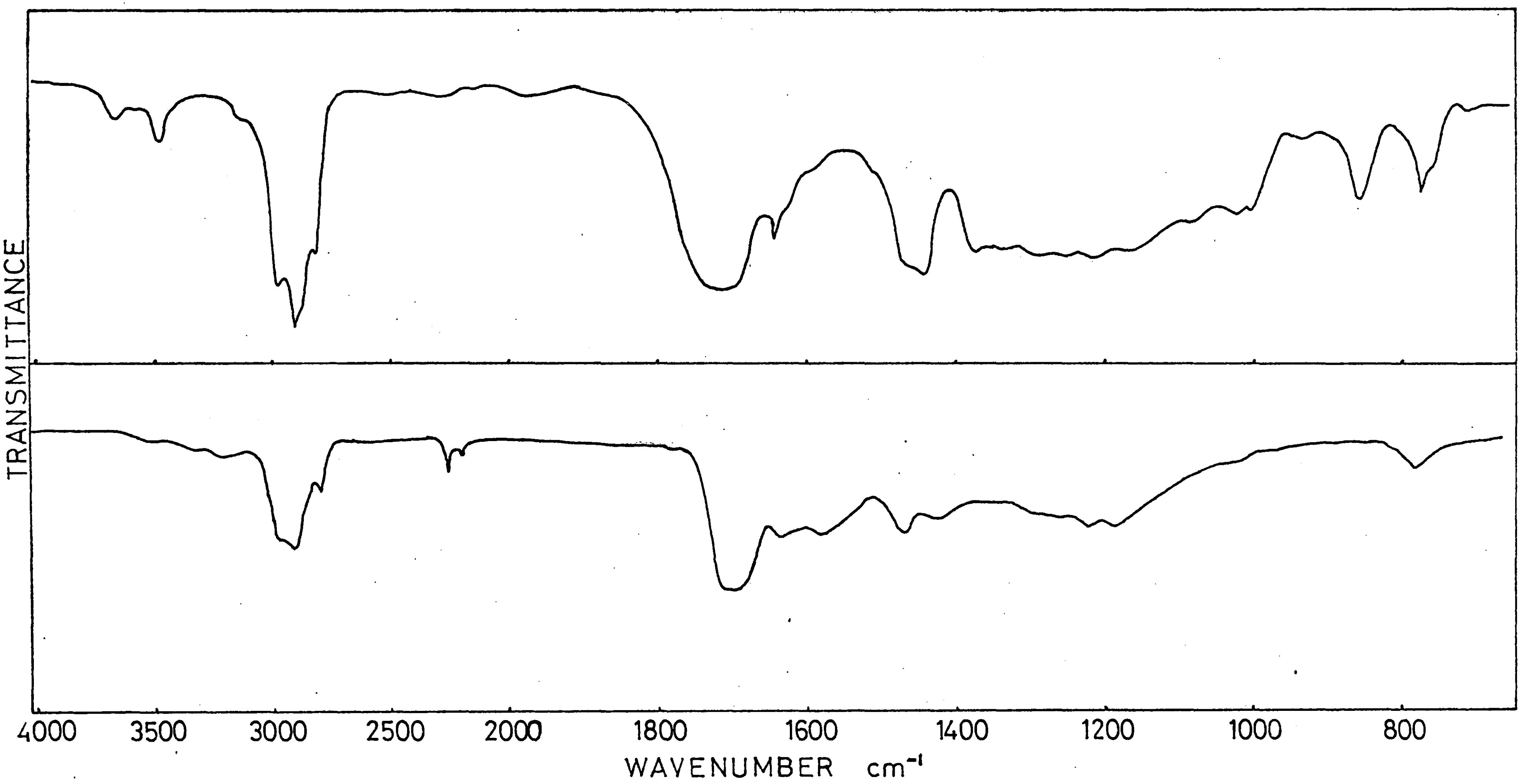


FIG. 5.11 I.R. SPECTRUM OF CRF OBTAINED AFTER DECOMPOSITION TO 500°C OF (a) PMA (b) 1:1 BY WEIGHT PAN I-PMA

Similar results were obtained in blends containing PMA 2.

THERMOGRAVIMETRIC ANALYSIS

The results of degradation of 5 mg samples prepared by coprecipitation from D.M.F. solution into methanol are illustrated in Fig. 5.12(a).

Comparison of expected and experimental results for a 1:1 by weight blend is given in Fig. 5.12(b). It is apparent that the observed TVA results correspond to minor changes in weight loss which is consistent with increased evolution of small noncondensible gases such as CO and CH_4.

MOLECULAR WEIGHT DETERMINATION

80 mg film samples of PMA 2 were degraded isothermally in vacuo for various time intervals at a temperature of 280^{o}C. Soluble polymer remaining in the residue was extracted by stirring in benzene solution over a period of 24 hours. The solution was then filtered through a fine glass sinter before making viscosity measurements using an Ubbelohde viscometer at 30^{o}C. Yhe concentration of polymer in the solutions used for viscometry were estimated by evaporation to constant weight of a known volume of solution.

A series of experiments employing 100 mg film samples of 4:1 by weight PMA 2:PAN I blend were similarly treated. Control experiments upon PAN alone confirmed the degraded polymer to be insoluble in benzene. Furthermore, no nitrile peaks could be detected in the i.r. spectra of polymer extracted in the manner outlined.

The results are illustrated in Fig. 5.13 and Table 5.3 Solution viscosity could not be accurately measured after 2 hours degradation in PMA alone since the amount of soluble polymer was only around 15% of initial weight of polymer with a corresponding large error in the estimation of concentration. It was found, however, that blend degradation resulted in a reduction in gel formation enabling approximately 25% by weight of PMA to be extracted after 5 hours isothermal degradation at 280^{o}C.

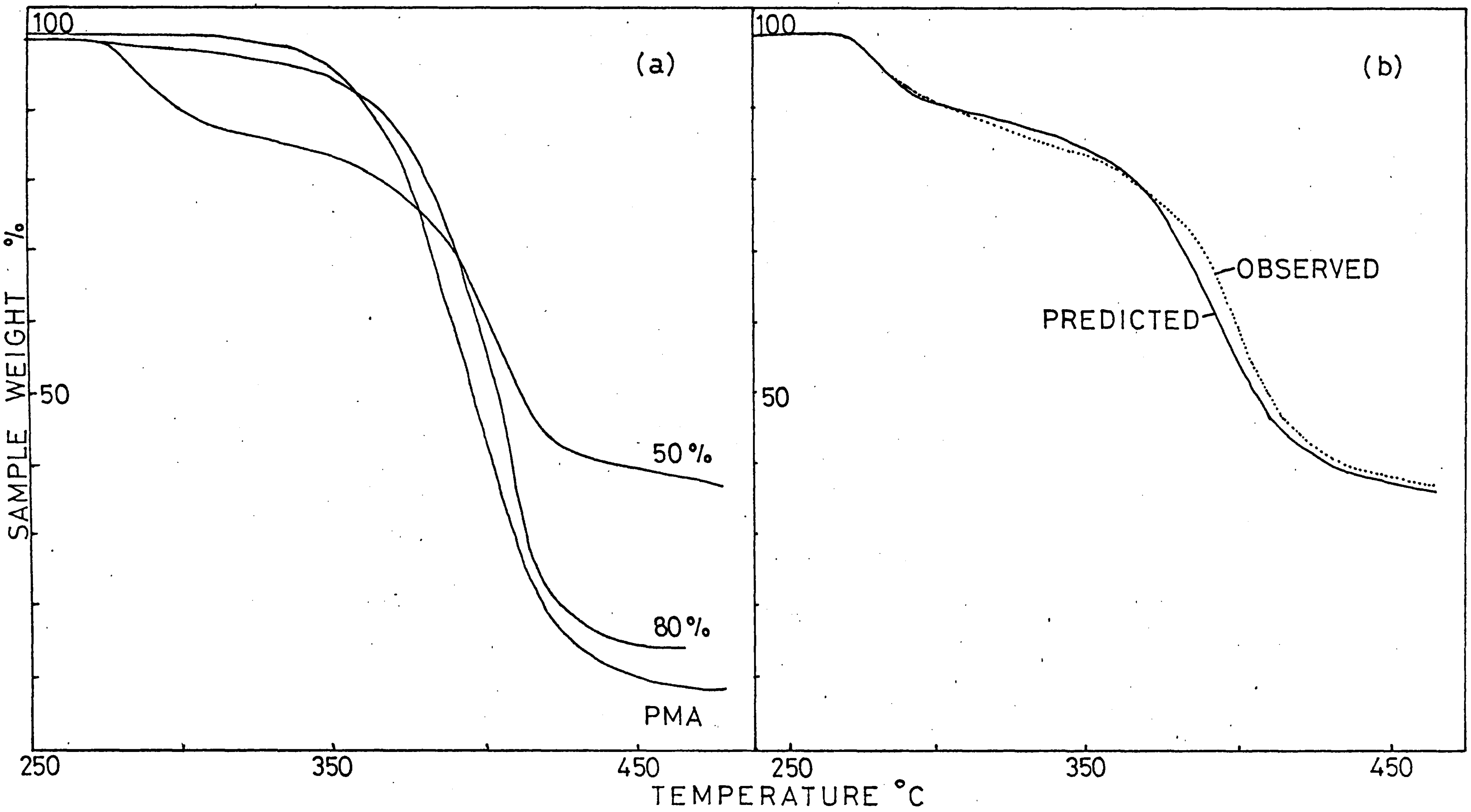


FIG. 5.12 (a) TG CURVES FOR PAN I:PMA BLENDS (WEIGHT % PMA) 5 mg POWDER SAMPLES PREPARED BY COPRECIPITATION FROM DMF SOLUTION

(b) OBSERVED AND PREDICTED TG CURVES FOR A 1:1 BY WEIGHT PAN I:PMA BLEND, 5 mg POWDER SAMPLES

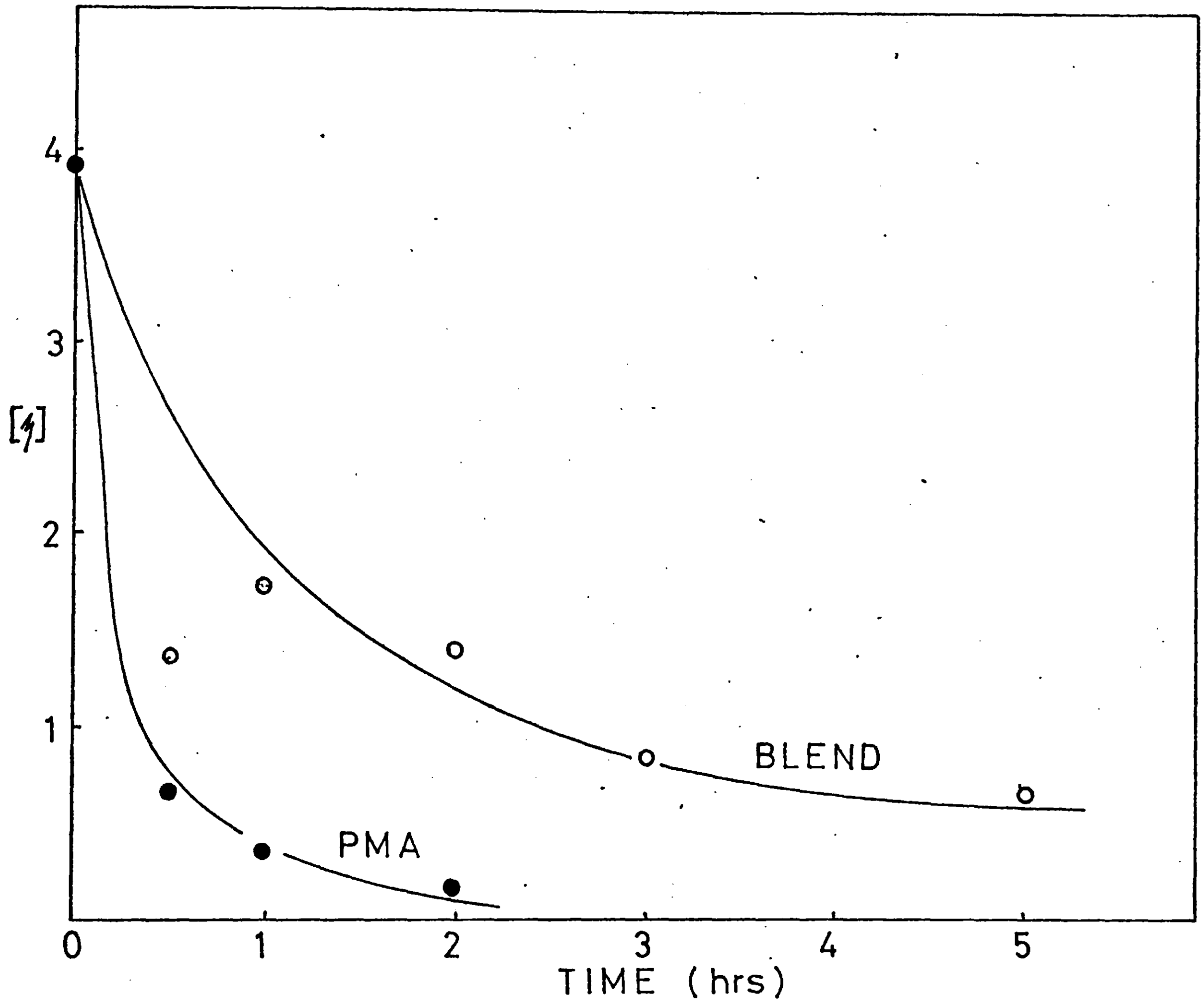


FIG. 5.13 INTRINSIC VISCOSITY OF BENZENE SOLUBLE PMA EXTRACTED AFTER ISOTHERMAL DEGRADATION AT 280°C, OF (1) PMA II (2) 4:1 BY WEIGHT PMA II:PAN I BLEND

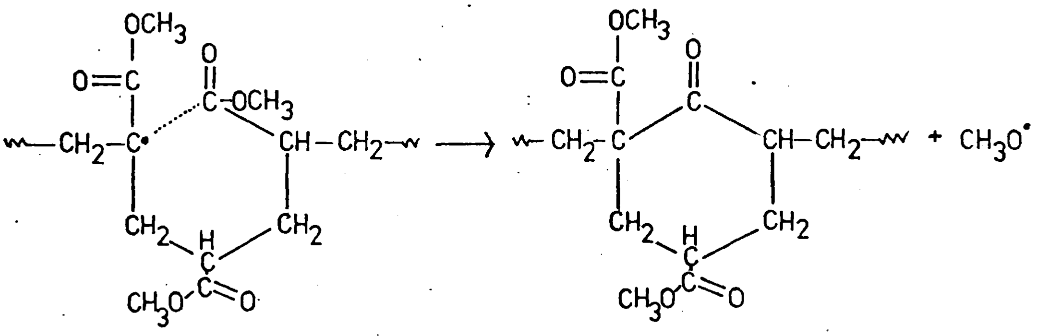
TIME hrs.	PMA [η] dl/g	4:1 BY WT. PMA:PAN [η] dl/g
0	3·95	3·95
0·5	0·65	1·21
1·0	0·27	1·73
2	0·15	1·62
3	—	0·93
5	—	0·90

TABLE 5.3 (η) PMA AFTER ISOTHERMAL DEGRADATION AT 280°C OF (1) PMA II (2) 4:1 BY WEIGHT PMA II:PAN I BLEND

The results are presented as intrinsic viscosities. Degradation of PMA induces coloration associated with structural changes and invalidates the use of viscosity-molecular weight relationships such as that of Palir[109] which can only apply to undegraded polymer.

5.8 DISCUSSION

Little information can be derived from comparison of the gaseous volatiles from blend degradation with those of PMA. Perhaps the most significant factor is the unaltered evolution of methanol since this was earlier postulated to be in part due to crosslinking reactions. Since blend degradation appears to involve a reduction in PMA crosslinking reactions one would anticipate a corresponding decrease in CH_3OH evolved if this was the predominant mode of evolution. An alternative explanation may be found in an intramolecular reaction of the following type:-



Thus one might anticipate an intramolecular reaction to be less influenced by blending than intermolecular reactions. Methanol could also arise from interactions such as those postulated to occur in PMMA blends involving the gaseous degradation products of PAN. The broad carbonyl absorption in PMA does not, however, allow identification of anhydride peaks.

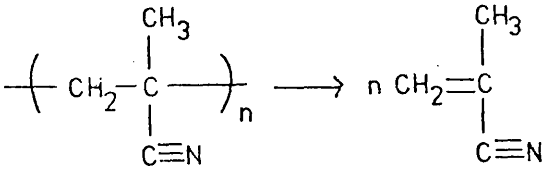
It is evident that much of the interpretation applied to the previous PAN-PS system is also relevant to PMA blends. The similarity may be a measure of the importance of intermolecular transfer reactions in each system.

CHAPTER 6

THE THERMAL DEGRADATION OF (A) POLYMETHACRYLONITRILE (B) POLYMETHACRYLONITRILE POLYMER BLENDS

6.1 INTRODUCTION

Polymethacrylonitrile (PMAN) is derived from a 1,1 di-substituted monomer and may, therefore, be expected to undergo quantitative decomposition to monomer, as occurs in both PMMA and PαMS -



$$\left(CH_2 - \underset{C\equiv N}{\overset{CH_3}{C}} \right)_n \longrightarrow n\, CH_2 = \underset{C\equiv N}{\overset{CH_3}{C}}$$

It is found, however, that PMAN can undergo several distinct modes of decomposition and, as in PAN, these may include coloration of the residual polymer although the extent of the latter reaction varies widely from sample to sample being dependent upon both monomer source and purification and also the method of polymerization.[15] PMAN is found to differ from PAN in that coloration is not an inherent property of the polymer but results from trace amounts of carboxylic acid derivatives within the polymer chain.

In carefully prepared samples, thermal decomposition of PMAN can result in monomer yields in excess of 90%. In such polymers two principal modes of decomposition may be distinguished, viz. (a) radical depolymerization initiated both by allylic activation due to the presence of unsaturated chain ends within the polymer and also by random chain scission, (b) the decomposition of unstable keteneimine structures, $-\underset{|}{C}=C=N-$, which are formed during polymerization by reaction of the growing radical in the configuration $-CH_2-\underset{CH_3}{\underset{|}{C}}=C=N^{\bullet}$.

The similarity in thermal stability between PMMA and PMAN allows comparison with respective blends containing PAN. In addition a brief examination of PMAN:PVC mixtures has been included.

6.2 POLYMER SAMPLE HISTORY

TABLE 6.1 POLYMER SAMPLE HISTORY

POLYMER	Mn	POLYMERIZATION CONDITIONS
PMAN 1	5,700	Bulk Polym^n., 1% w/v AIBN, 70°C
PMAN 2	7,500	" 1% w/v B_zO_2, 70°C
PMAN 3	2,500	" 1% w/v AIBN, 20°C, U.V.
PMAN 4	3,600	" 1% w/v, B_zO_2, 20°C, U.V.
PMAN 5	8,700	" 0.1% w/v, AIBN, 60°C
PMAN 6	4,800	" 0.3% w/v, AIBN, 60°C
PMAN 7	7,800	" 0.5% w/v,AIBN, 60°C
PMAN 8	6,900	" 1.0% w/v,AIBN, 60°C
80:20 MAN:MMA *	7,200	" 1.0% w/v,AIBN, 60°C
50:50 MAN:MMA *	13,700	" 1.0% w/v,AIBN, 60°C

*Prepared using r_1(MMA) = 0.67, r_2(MAN) = 0.65[110]

Polymers were purified by reprecipitation from acetone solution into 40-60° per. ether before drying in vacuo at 30°C. The molecular weights of the homopolymers were determined by GPC, and those of the copolymers by vapour phase osmometry (Appendix 1).

6.3 THERMAL DEGRADATION OF POLYMETHACRYLONITRILE

RESULTS

THERMAL VOLATILIZATION ANALYSIS

The two stage decomposition, previously illustrated in PMMA breakdown (Chapter 3), is again observed in Figs. 6.1(a) and (b) representing the TVA curves for 50 mg powder samples of PMAN-1 and 2. Differential condensation of MAN results in LR effects in both -75° and -100° traps. The evolution of small amounts of noncondensible gases occurs above 350°C in both polymers. I.r. analysis of the total gaseous products revealed trace amounts of HCN and CH_4 in addition to MAN.

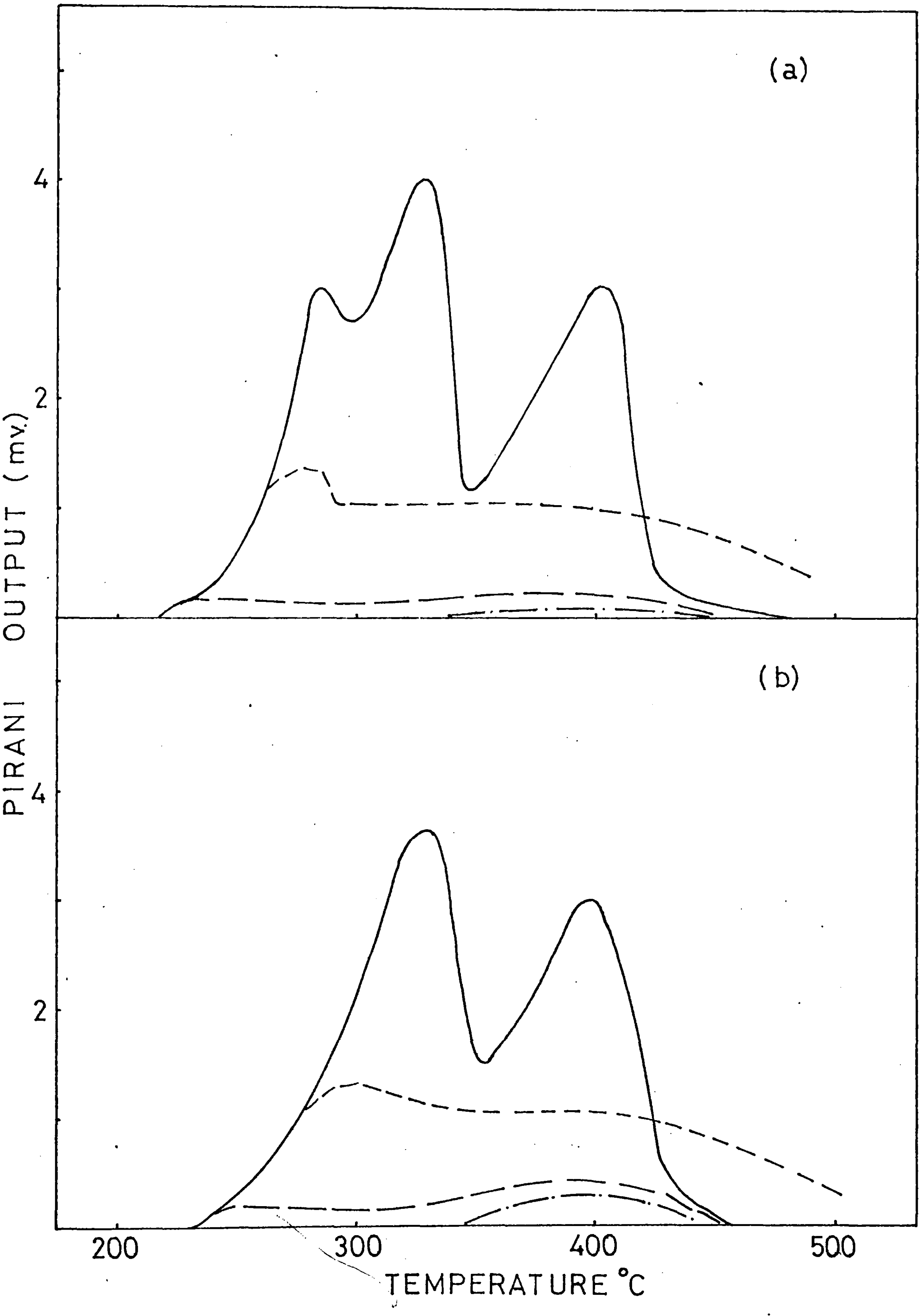


FIG. 6.1 TVA CURVES FOR (a) PMAN-1 (b) PMAN-2
50 kg. POWDER SAMPLES

There are two prominent features of the TVA curves which differ from PMMA. These are (a) the height of the initial peak in each polymer is greater than that of the high temperature peak (b) an additional low temperature mode of decomposition in PMAN 1. Thus rate maxima occur at 295, 327 and 397°C in PMAN 1 and at 320 and 392°C in PMAN 2.

Figs. 6.2 (a), (b), (c) and (d) illustrate TVA curves for 50 mg samples of PMAN 5-8. Each curve indicates that two major degradation processes occur. The additional low temperature process cannot, however, be discerned in PMAN 5 and only results in slight asymmetry of the initial peak in PMAN 6. Both PMAN 7 and 8 more closely resemble PMAN 1. It is evident that whereas the molecular weight of the polymers does not show a clear relationship with initiator concentration, the extent of the initial mode of decomposition is found to increase with initiator concentration. Figs. 6.3 (a) and (b) illustrate the TVA curves for PMAN 3 and 4, both of which were polymerized at 20°C and thus have a higher initial content of thermally labile keteneimine structures within the polymer chain. The relative defect content can be readily determined by their characteristic i.r. absorption at 2012 cm^{-1}. Thus the optical density ratio of keteneimine/nitrile was found to be 1.04 and 0.55 for PMAN 3 and 4 respectively. (Solution spectrum 4% w/w cyclohexanone).

It is apparent by comparison of the TVA curves in Fig. 6.3 that increased keteneimine content does not reveal any further differences between the two initiator systems.

The results of TVA experiments may thus be summarized as follows -

1. The initial stage of decomposition of low molecular weight PMAN accounts for greater than 50% of total monomer evolution as measured by the corresponding TVA peak areas.

2. An additional reaction occurs concurrent with chain end initiated 'unzipping' of PMAN in polymers prepared using AIBN as catalyst. The extent of this reaction varies according to AIBN concentration but is absent in

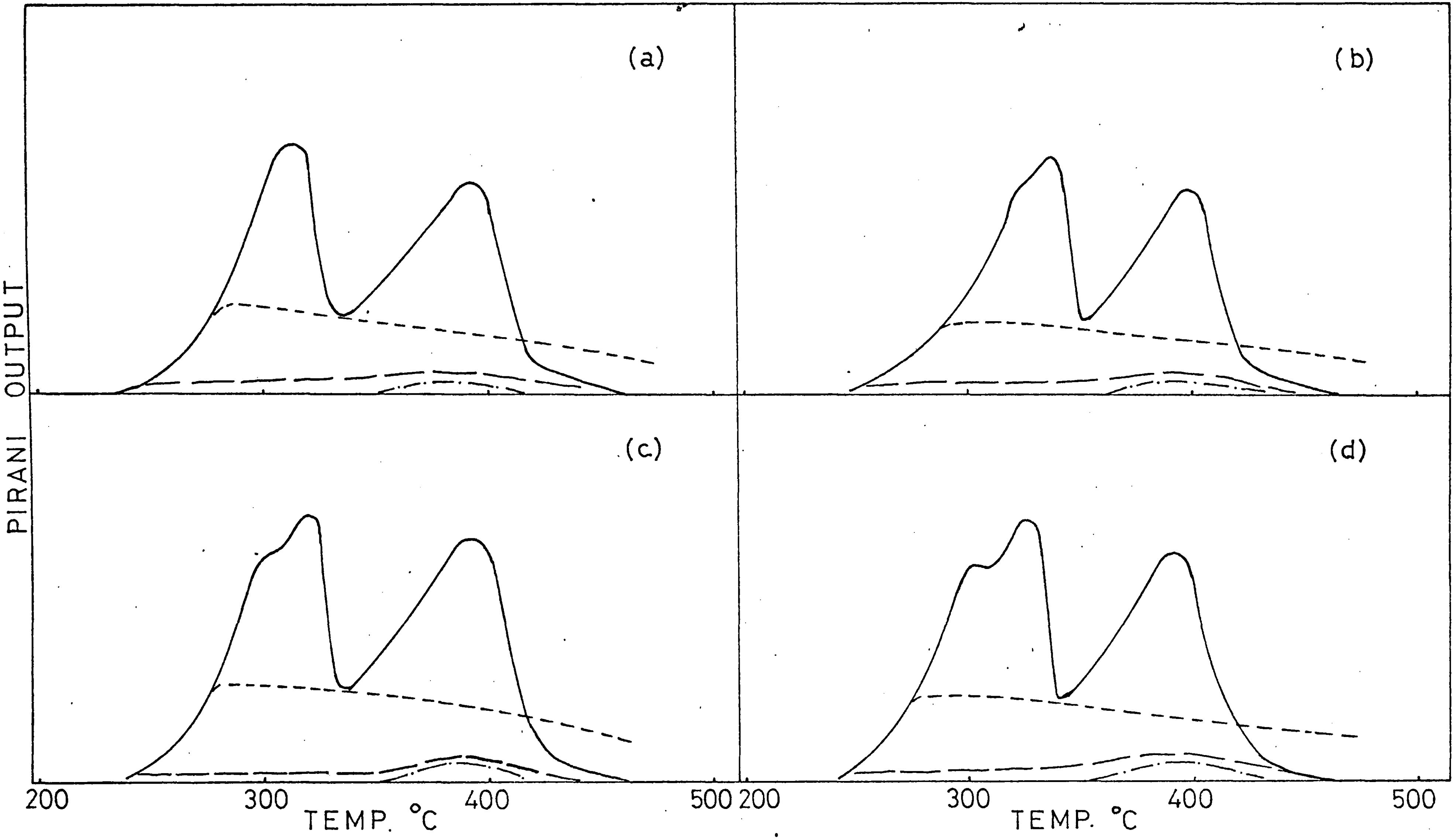


FIG. 6.2 TVA CURVES FOR (a) PMAN 5 (b) PMAN-6 (c) PMAN 7 (d) PMAN 8, 50 mg. POWDER SAMPLES

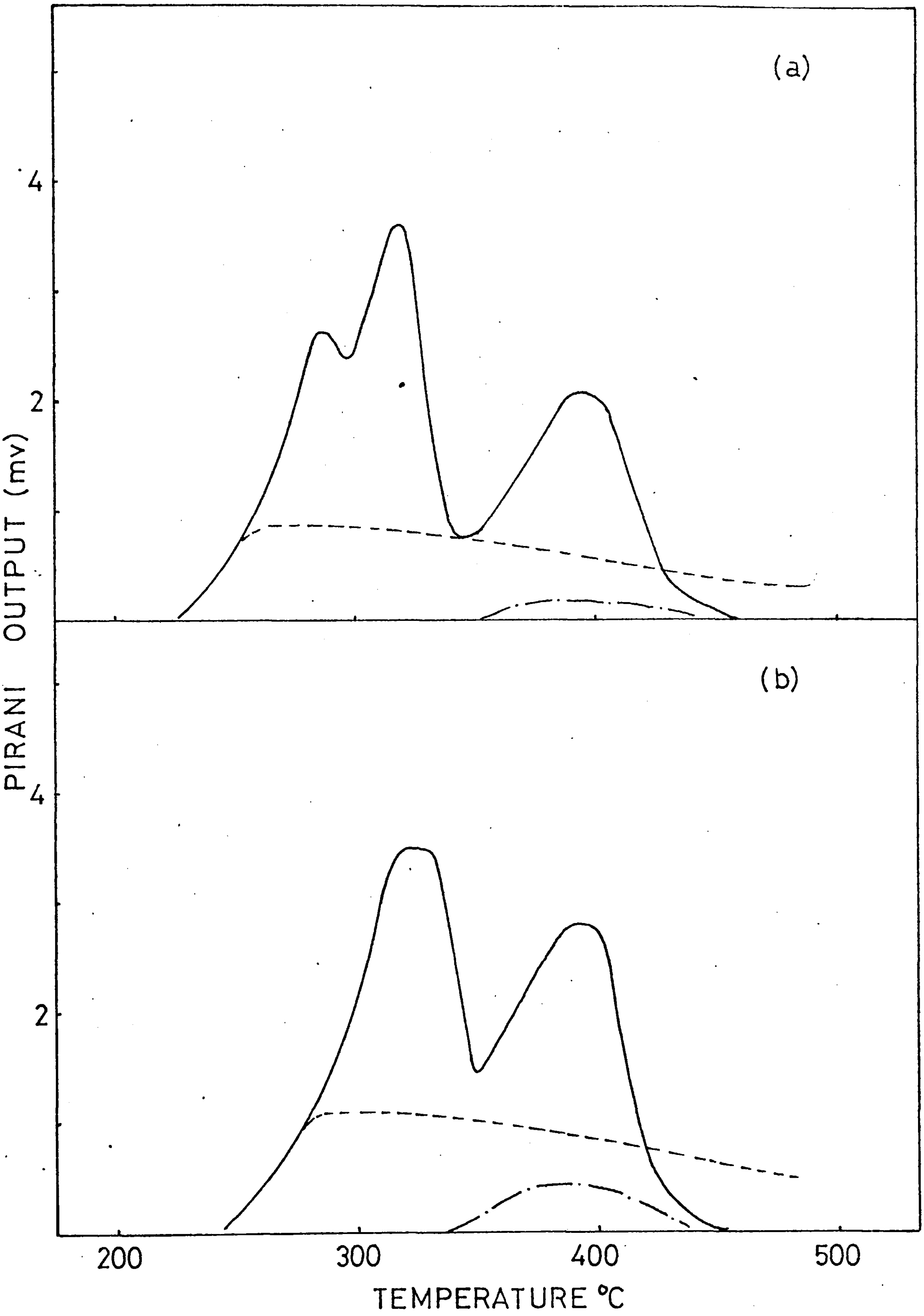
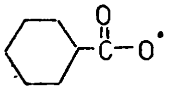


FIG. 6.3 TVA CURVES FOR (a) PMAN 3 (b) PMAN 4, 50 mg POWDER SAMPLES

polymers prepared using B_zO_2.

INFRA RED ANALYSIS

The i.r. spectra of PMAN 3 and 4 are illustrated in Fig. 6.4. In each the strong absorption at 2012 cm^{-1} may be assigned to the presence of keteneimine linkages within the polymer chain. Grassie and McNeill[15] have demonstrated complete removal of such defect structures by heating the polymer to its softening point. This was confirmed in the samples examined while further heating to temperatures in excess of 300°C produced a faint pink coloration in the residual polymer.

In studies of the thermal decomposition of methacrylic acid-methacrylonitrile copolymers, it has been shown that the increased intensity of the absorption at 1620-1640 cm^{-1} which accompanies polymer coloration may be attributed to -C=N- stretch arising by cyclization of adjacent comonomer units. It is more difficult to assign this absorption in the original polymer, however, since -C=C, -C=N- stretching frequencies and -N-H- bending modes all occur within this region. Absorptions around 3500 cm^{-1}, however, suggest the presence of -C=N in the undegraded polymer. Differences observed between PMAN 3 and 4 are primarily those associated with aromatic ester absorptions occurring at 1720 cm^{-1}, 1270 cm^{-1} and 720 cm^{-1} respectively, and may be attributed to the incorporation of  fragments in the polymer chain.

The kinetics of the disappearance of keteneimine units upon heating were investigated in order to establish that the difference in thermal analysis of PMAN 3 and 4 was independent of keteneimine concentration. This was achieved by i.r. analysis of cyclohexanone solutions (4% w/w) after isothermal degradation at 70°C using the optical density of the absorption at 2012 cm^{-1} as a measure of keteneimine concentration. The results are given in Table 6.2 and are illustrated as both first and second order plots in Figs. 6.5 and 6.6.

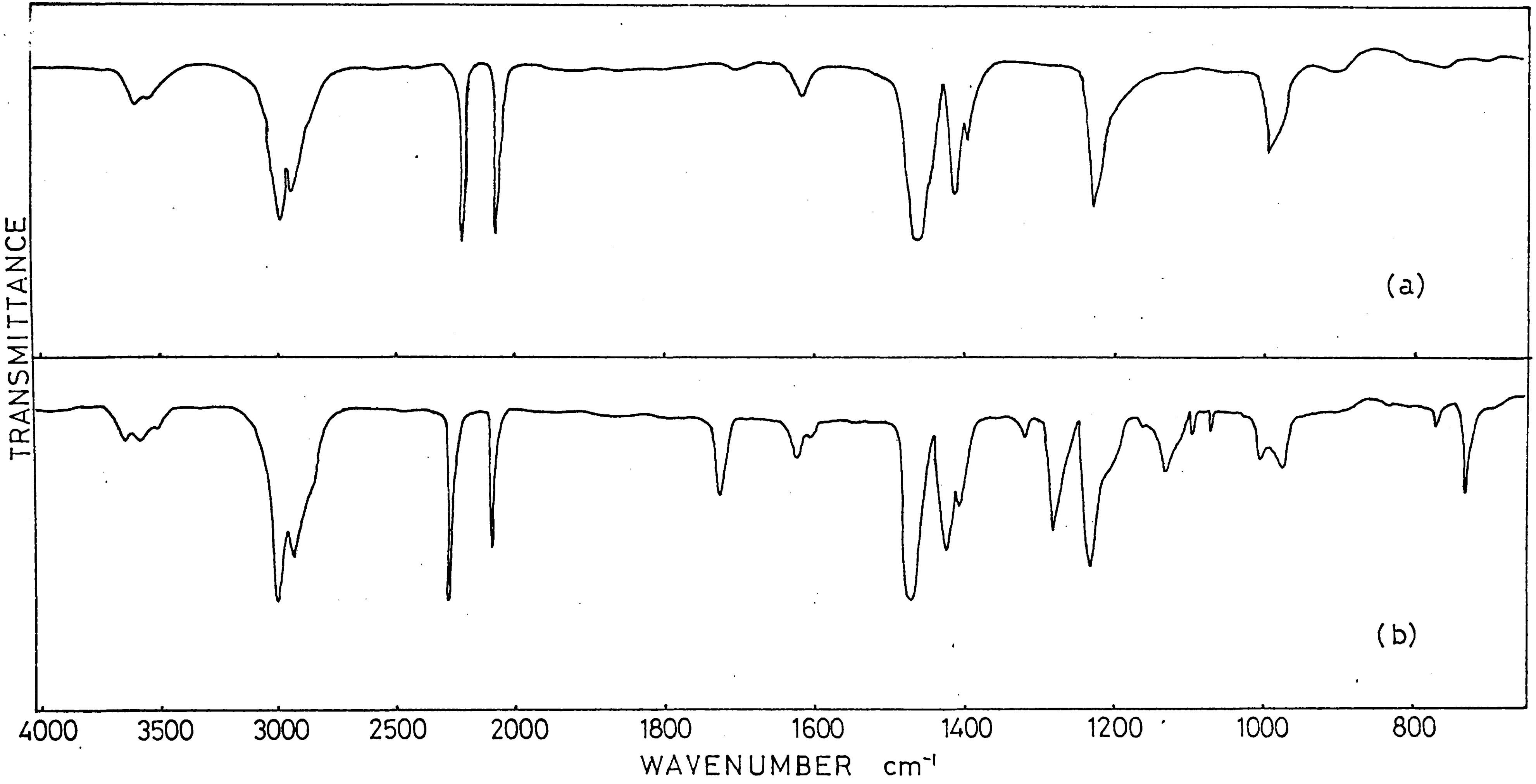


FIG. 6.4 INFRA RED SPECTRUM OF (a) PMAN 3 (b) PMAN 4

TABLE 6.2 I.R. ANALYSIS OF KETENEIMINE DECOMPOSITION IN 4% W/W CYCLOHEXANONE SOLUTIONS OF PMAN 3 AND PMAN 4 AT 70°C

TIME (hrs)	$\log {}^{Io}/_{I} = X(2012cm^{-1})$	$-\log {}^{X}/_{X0}$	${}^{1}/_{X} - {}^{1}/_{X0}$
(a) PMAN 3			
0	0.361	0	0
1	0.260	0.143	1.01
2	0.171	0.325	3.01
3	0.127	0.454	7.87
4	0.084	0.633	11.91
5	0.054	0.825	18.52
(b) PMAN 4			
0	0.161	0	0
1	0.107	0.177	3.13
2	0.072	0.350	7.68
3	0.046	0.544	15.53
4	0.023	0.845	37.27
5	0.015	1.03	60.46
6	0.013	1.09	70.72

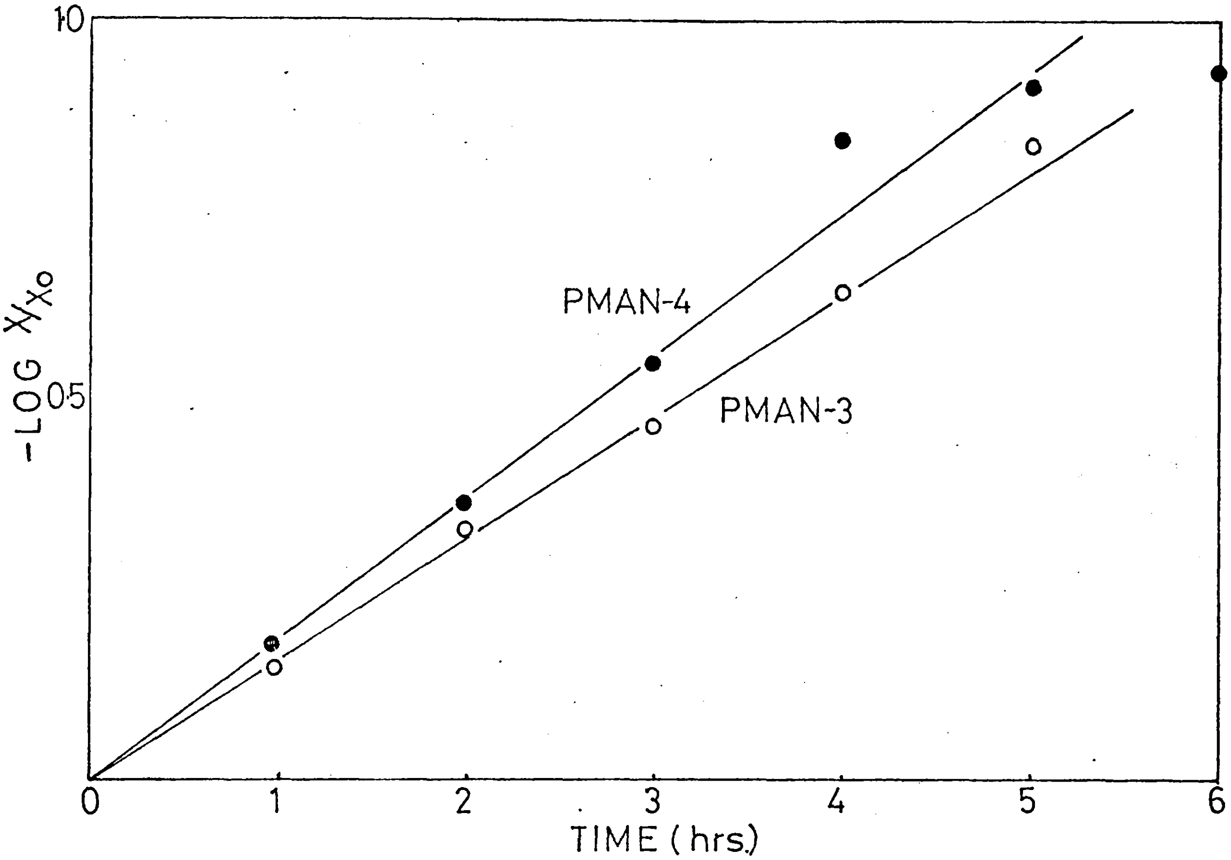


FIG. 6.5 I.R. ANALYSIS OF KETENEIMINE DECOMPOSITION IN 4% W/W CYCLOHEXANONE SOLUTIONS OF PMAN 3 AND PMAN 4 AT 70°C FIRST ORDER KINETICS

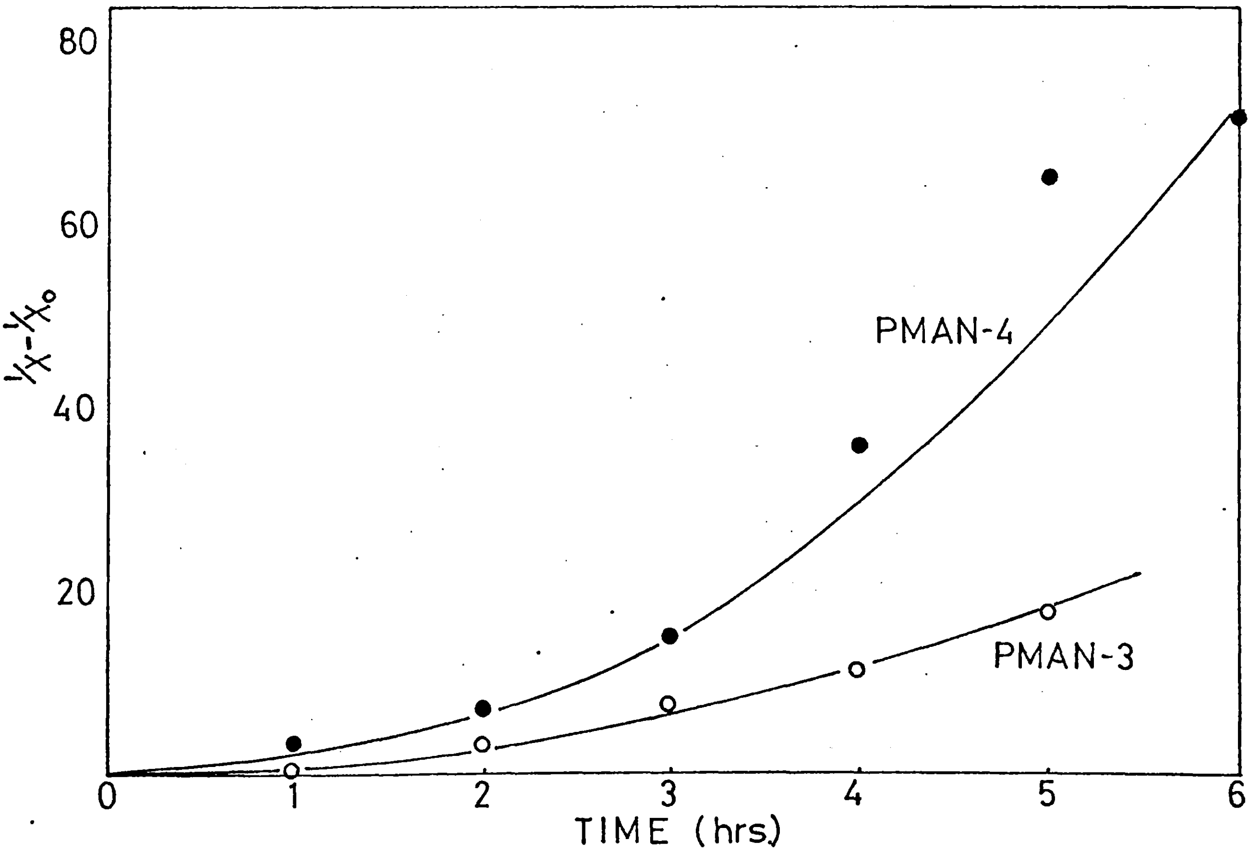
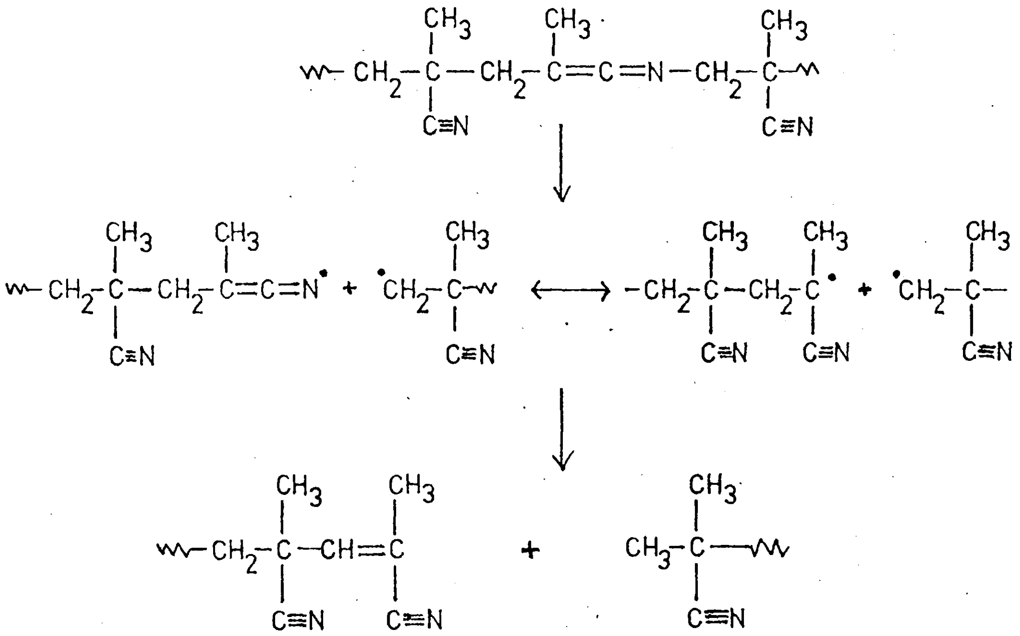


FIG. 6.6 I.R. ANALYSIS OF KETENEIMINE DECOMPOSITION IN 4% W/W CYCLOHEXANONE SOLUTIONS OF PMAN 3 AND PMAN 4 AT 70°C SECOND ORDER KINETICS

It is evident from Fig. 6.5 and 6.6 that ketenimine decomposition obeys first order kinetics with $t_{\frac{1}{2}}$ equal to 4.25 and 3.96 hours for PMAN 3 and 4 respectively. Previous workers have found good agreement with 2nd order kinetics and have proposed an initial dimerization of keteneimine linkages to account for this phenomenon[15,78]. The present findings, however, suggest that this step is unnecessary and that the process can be described by the mechanism below–



Thus, the reaction results in an increased proportion of terminal unsaturation in the polymer which results in higher monomer yields arising from chain end initiated 'unzipping'. Furthermore, the proposed mechanism is independent of the initiator system employed.

THERMOGRAVIMETRIC ANALYSIS

Fig. 6.7 illustrates the TG curves obtained for 5 mg powder samples of PMAN 1, PMAN 2 and PMAN 3. In each polymer the weight loss associated with allylic activation of terminal bonds is > 50% as predicted from TVA experiments. Both PMAN 1 and PMAN 3 exhibit an additional point of inflection upon the cumulative weight loss curve at around 300°C, corresponding to the completion or overlap of the additional mode of decomposition observed in differential TVA curves. All three polymers have similar residue yields of $< 5\%$ at 500°C.

Fig. 6.8 illustrates the isothermal weight loss data corresponding to temperatures of 247, 258, 267 and 273°C for PMAN 1 and 2. From the Arrhenius plots in Fig. 6.9 E_A for MAN evolution is found to be 59.5 K cal/mole ± 4 K cal and 63.1 ± 5 K cal/mole for PMAN 1 and 2 respectively. It is evident that although accompanied by a process with a lower E_A, allylic activation of terminal bonds remains the predominent mechanism of decomposition in PMAN 1.

THERMAL VOLATILIZATION ANALYSIS OF METHYL METHACRYLATE-METHACRYLONITRILE COPOLYMERS

A brief examination of the thermal stability of low molecular weight MMA:MAN copolymers prepared using 1% w/v AIBN has revealed a similar additional rate maximum to that observed in PMAN. The TVA curves for copolymers containing 20 and 50 mole% MMA are illustrated in Fig. 6.10 and again demonstrate 750% weight loss during the initial stage.

6.4 DISCUSSION

In the absence of acidic impurities the initial decomposition of PMAN prepared using B_z0_2 may be adequately interpreted in terms of free radical depolymerization initiated at unsaturated chain ends formed both by disproportionation reactions during polymerization and also by thermal decomposition of labile keteneimine groups.

It is evident that this reaction scheme applies also to PMAN prepared using AIBN but that additional labile structures are incorporated within the polymer which are responsible for monomer evolution concurrent with that observed from terminal unsaturation.

A plausible explanation may involve the existence of chain branching. Kinetic studies of MAN polymerization have also suggested this possibility[111]. Thus, the reaction may be envisaged as follows -

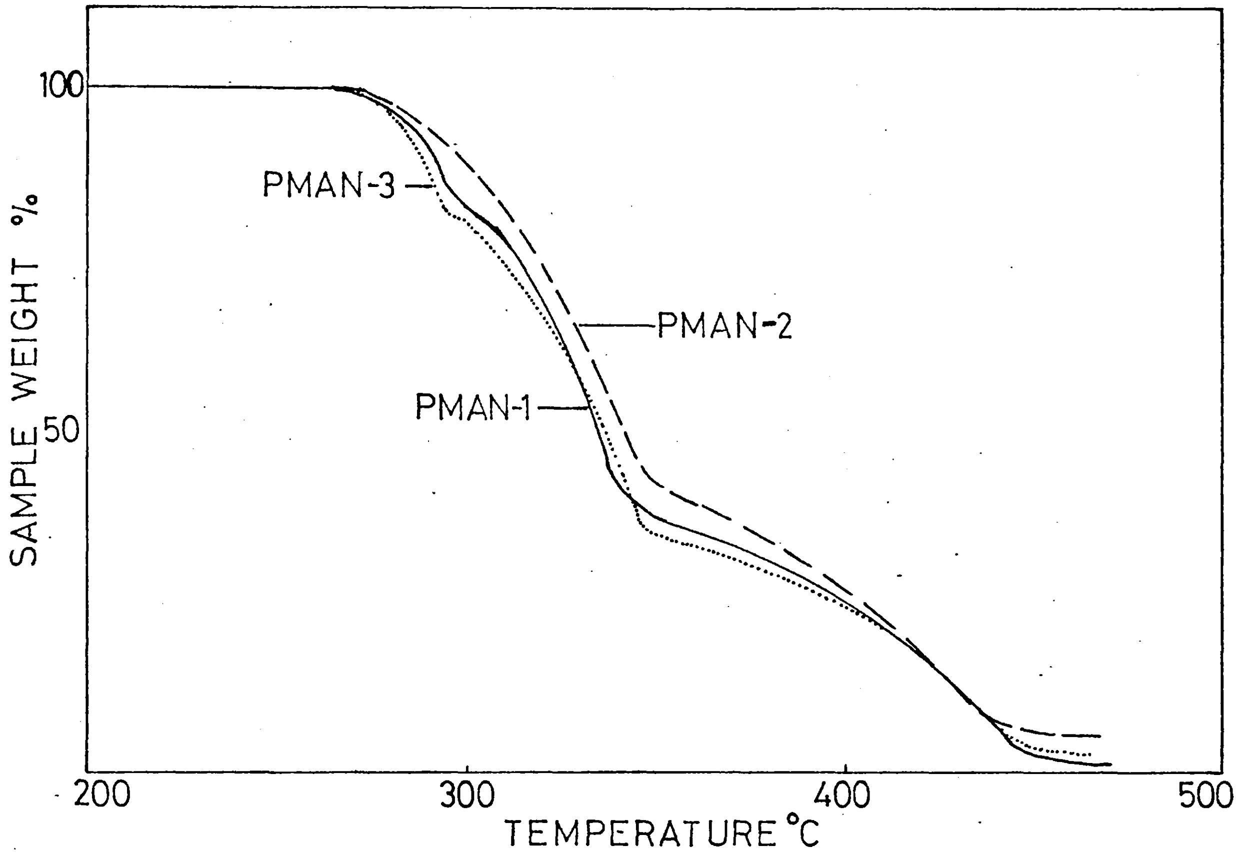


FIG. 6.7 TG CURVES FOR PMAN 1, PMAN 2 AND PMAN 3, 5 mg. POWDER SAMPLES, HEATING RATE 10C°/min, DYNAMIC N_2 ATMOSPHERE

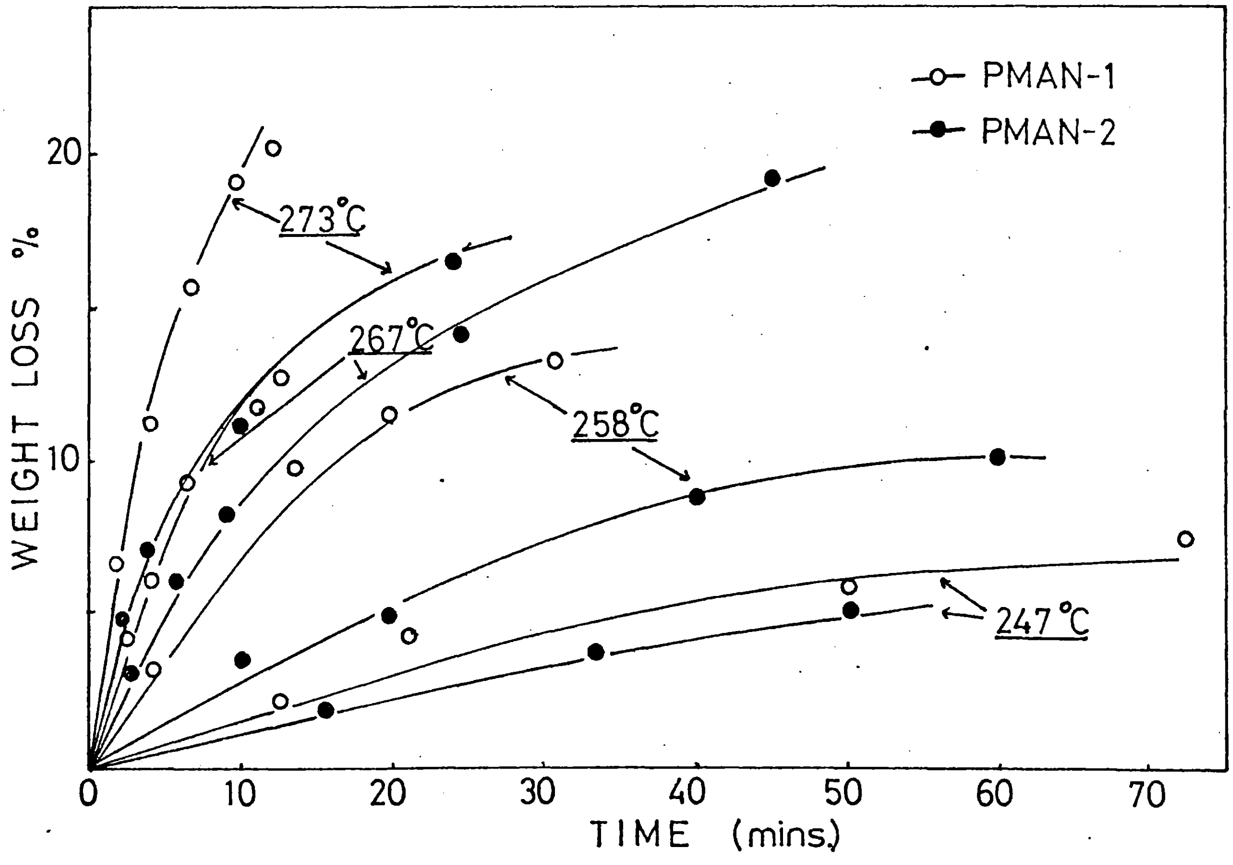


FIG. 6.8 ISOTHERMAL WEIGHT LOSS CURVES FOR PMAN 1 AND PMAN 2 5 mg. POWDER SAMPLES, DYNAMIC N_2 ATMOSPHERE

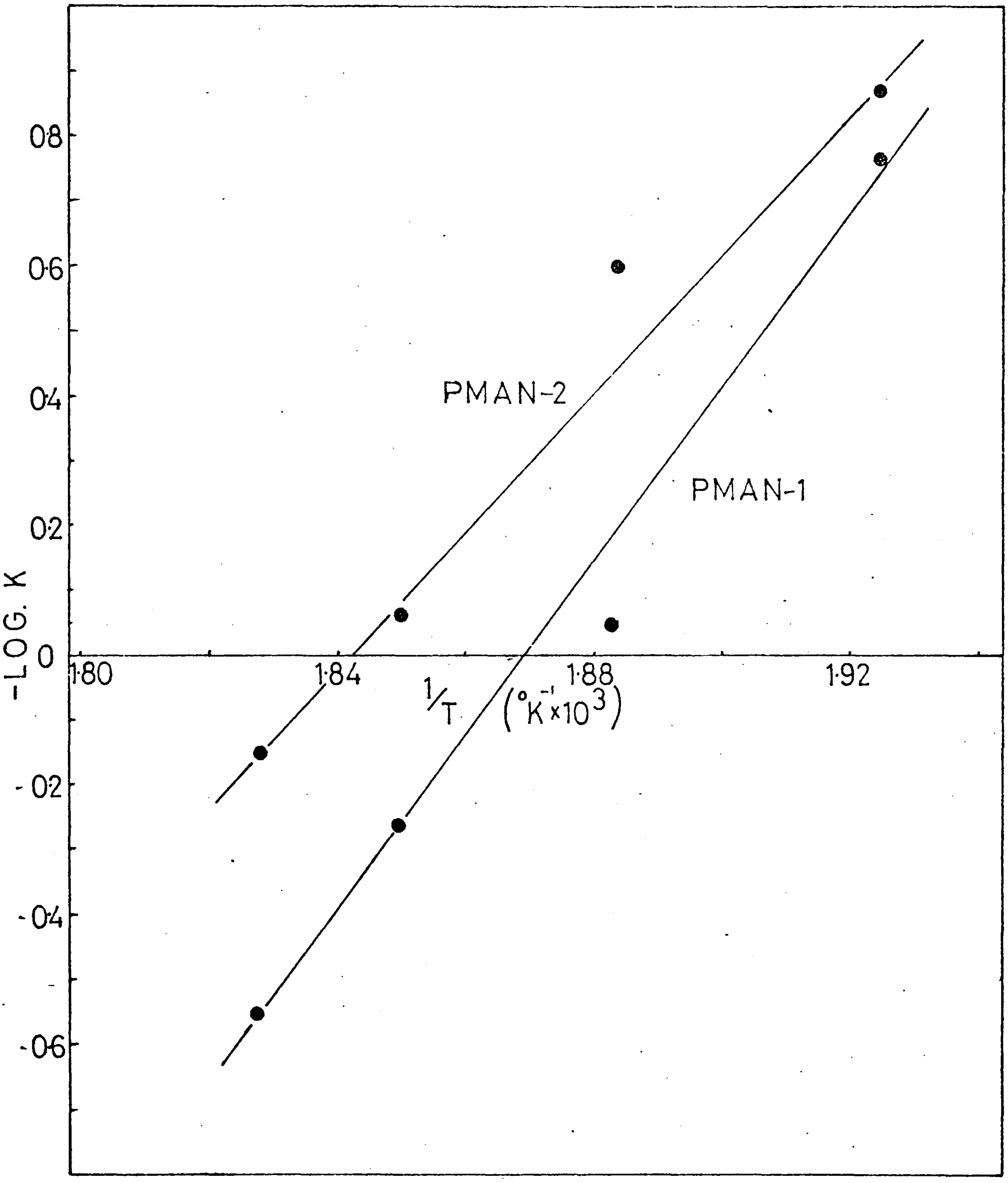
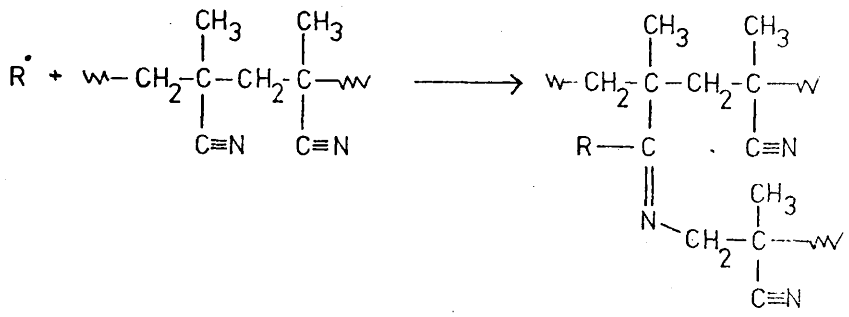
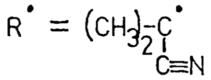


FIG. 6.9 ARRHENIUS PLOTS FROM ISOTHERMAL WEIGHT LOSS DATA FOR DEGRADATION OF PMAN 1 AND PMAN 2 AT 247, 258, 267 AND 273°C



where



$R^{\bullet} = (CH_3)_2\underset{C\equiv N}{C^{\bullet}}$

Thus the existence of chain branching may depend upon the steric requirements of R• which may, therefore, exclude such reactions occurring with B_zO_2 residues or macroradicals.

6.5 THERMAL DEGRADATION OF POLYMETHACRYLONITRILE BLENDS

POLYACRYLONITRILE-POLYMETHACRYLONITRILE BLENDS

RESULTS

THERMAL VOLATILIZATION ANALYSIS

The thermal decomposition of PMAN has been shown to be extremely susceptible to the presence of nucleophilic derivatives and this is reflected in the TVA curve illustrating the behaviour of a 50 mg film sample of PMAN 1 cast from N,N dimethyl formamide solution (Fig. 6.11) I.r. analysis of the gaseous decomposition products reveals increased evolution of CH_4 which can result from the initiation of nitrile oligomerization by trace residual solvent. A similar sample cast from acetone solution, however, shows PMAN decomposition to be independent of sample form.

In order to minimise the difficulties of interpretation of blend degradation the present study has been restricted to mixed powder samples.

Fig. 6.12 illustrates the TVA curves for 100 mg unmixed and mixed powder samples of a 1:1 by weight PAN I:PMAN 1 blend. No interaction is observed in the unmixed sample, but a number of significant differences occur upon mixing, viz (a) a reduction in the exothermic evolution of

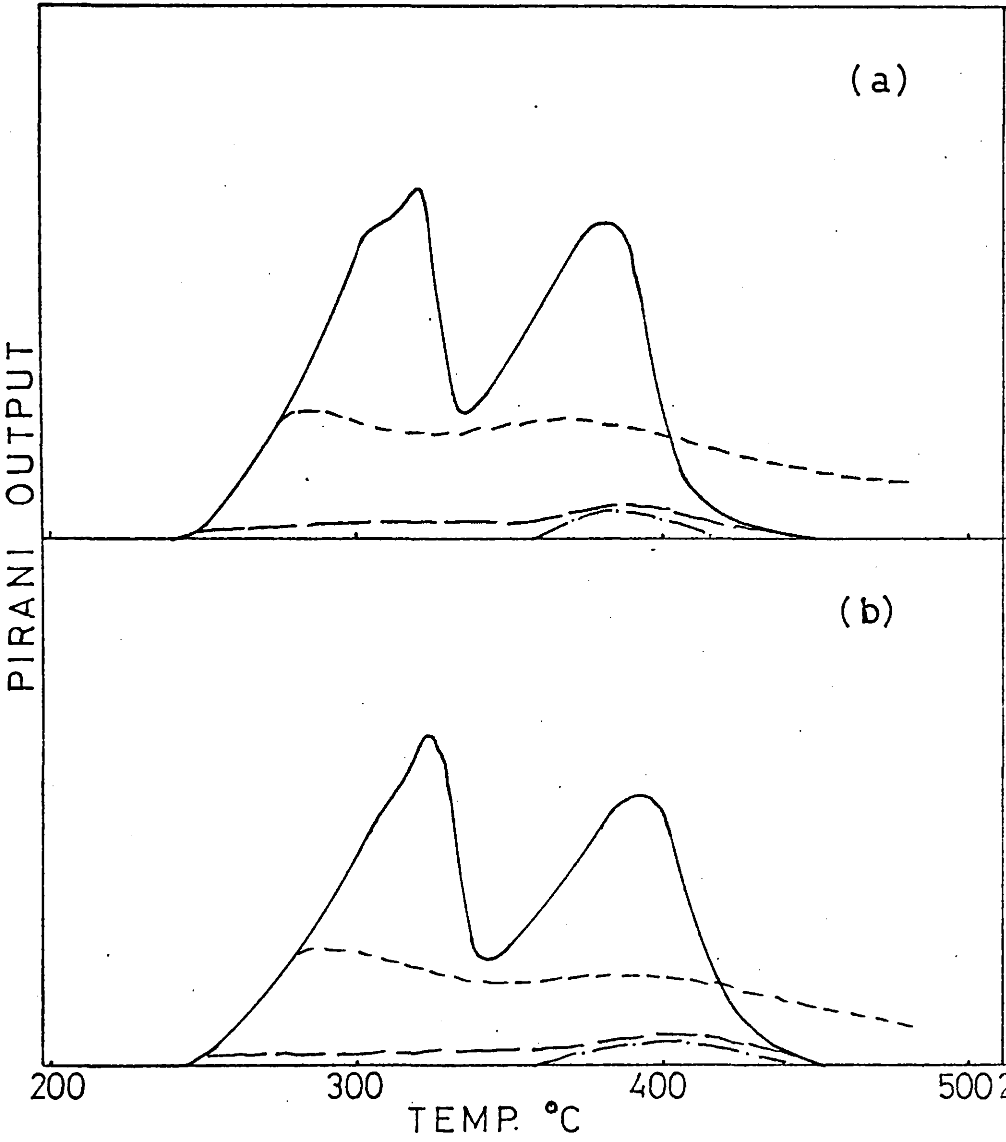


FIG. 6.10 TVA CURVES FOR (a) 20:80 MMA:MAN COPOLYMER
(b) 50:50 MMA:MAN COPOLYMER,
50 mg. POWDER SAMPLES

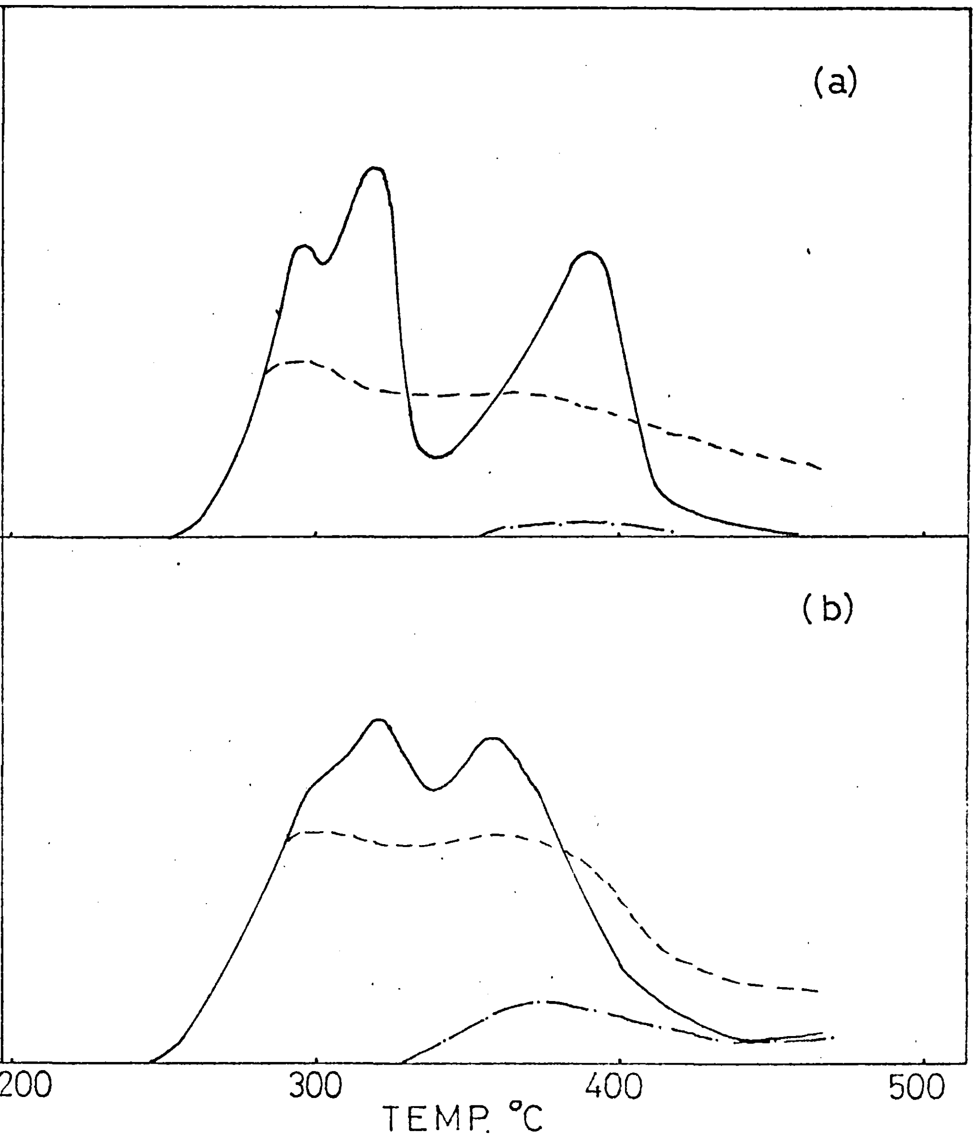


FIG. 6.11 TVA CURVES FOR PMAN-1; (a) 50 mg. FILM SAMPLE FROM ACETONE; (b) 50 mg. FILM SAMPLE FROM DMF

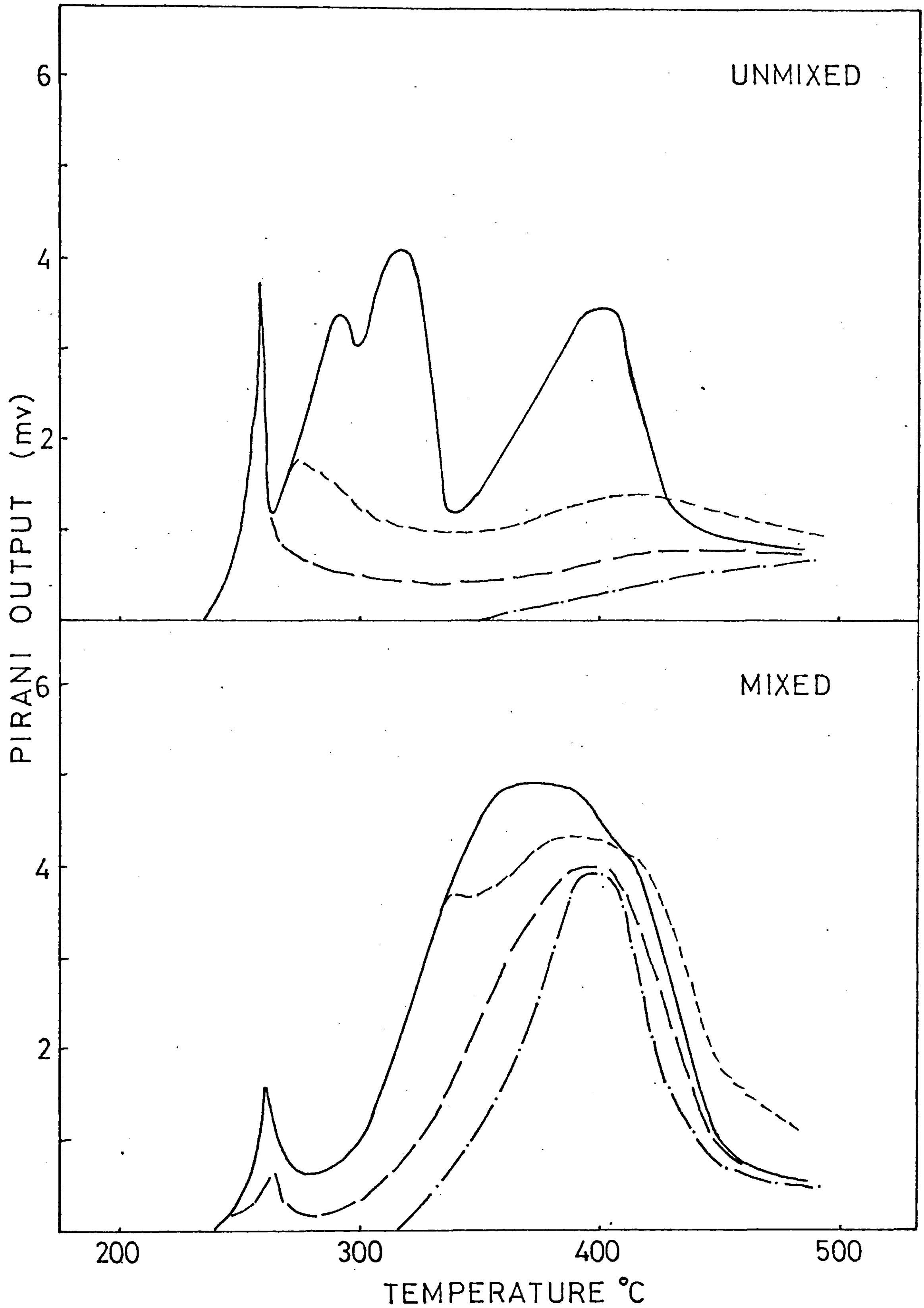


FIG. 6.12 TVA CURVES FOR SIMULTANEOUS DEGRADATION OF PAN I AND PMAN I, 1:1 BY WEIGHT
POWDER SAMPLES, 100 mg. TOTAL WEIGHT

NH_3 and HCN associated with PAN decomposition, (b) replacement of the three distinct modes of PMAN decomposition by one broad complex peak and (c) increased evolution of non-condensible products.

Similar observations have been made using 2:1 and 5:1 blends (Fig. 6.13).

INFRA RED ANALYSIS

Examination of the i.r. spectra of the total gaseous products collected after closed system degradation of 100 mg samples of the polymer blends reveals little alteration in the distribution of constituents. The evolution of CH_4, however, could be shown to vary with blend composition by measurement of the intensity of the absorption occurring at 1302 cm^{-1}. The results for a series of blends, each containing 50 mg PMAN, are summarized in Table 6.3.

TABLE 6.3 METHANE EVOLUTION FROM PAN I:PMAN I BLENDS

Blend Composition (% PMAN)	50	67	81.5	91	100
Optical density (1302 cm^{-1}) *	0.14	0.127	0.082	0.062	Trace

* 50 mg PAN, O.D. (1302 cm^{-1}) = 0.02

THERMOGRAVIMETRIC ANALYSIS

Fig. 6.14 illustrates the TG curves obtained (a) by experiment and (b) by sample addition of component curves, for a 1:1 PMAN I:PAN I blend.

A similarity exists between the results illustrated and those obtained from low molecular weight PMMA:PAN blends (Chapter 3). Thus the initial weight loss is less than that predicted, the experimental result being 16% weight loss at 320°C while the predicted result is 30% at the same temperature. Good correlation exists between the experimental and predicted results for the residual yield at 500°C however, and indicates that the maximum rate of weight loss is displaced to higher temperatures as in PMMA blends.

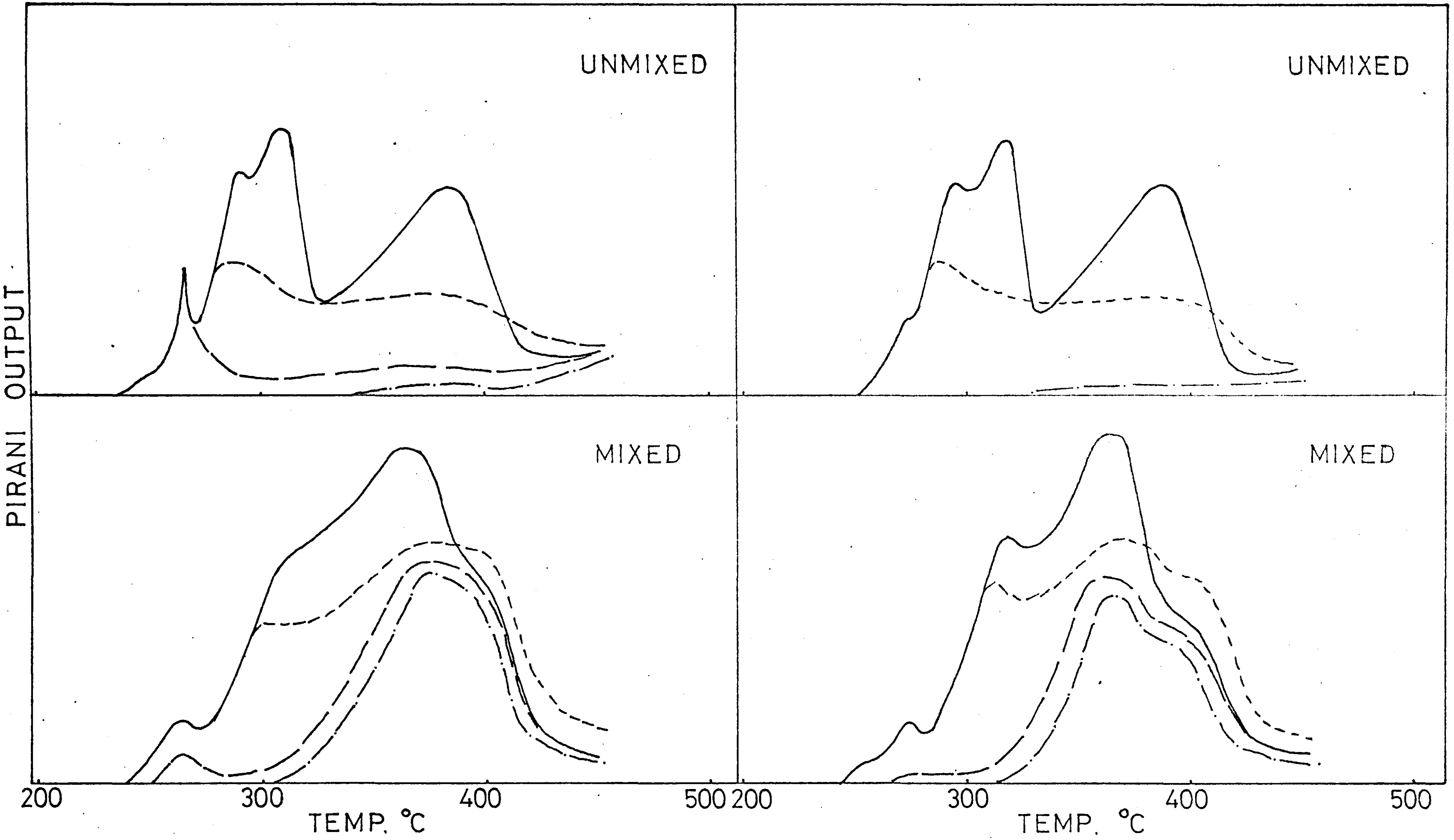


FIG. 6.13 TVA CURVES FOR SIMULTANEOUS DEGRADATION OF PAN I AND PMAN I (a) 2:1 BY WEIGHT (b) 5:1 BY WEIGHT POWDER SAMPLES, TOTAL WEIGHT 100 mg.

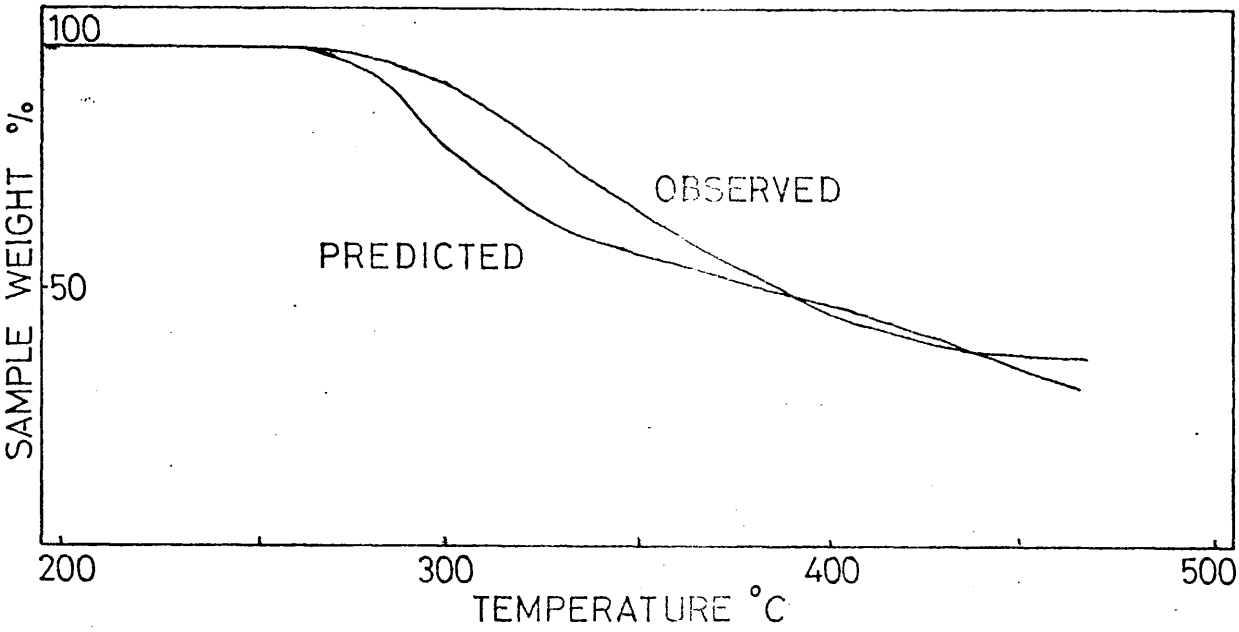


FIG. 6.14 OBSERVED AND PREDICTED TG CURVES FOR A 1:1 BY WEIGHT PAN I:PMAN I BLEND

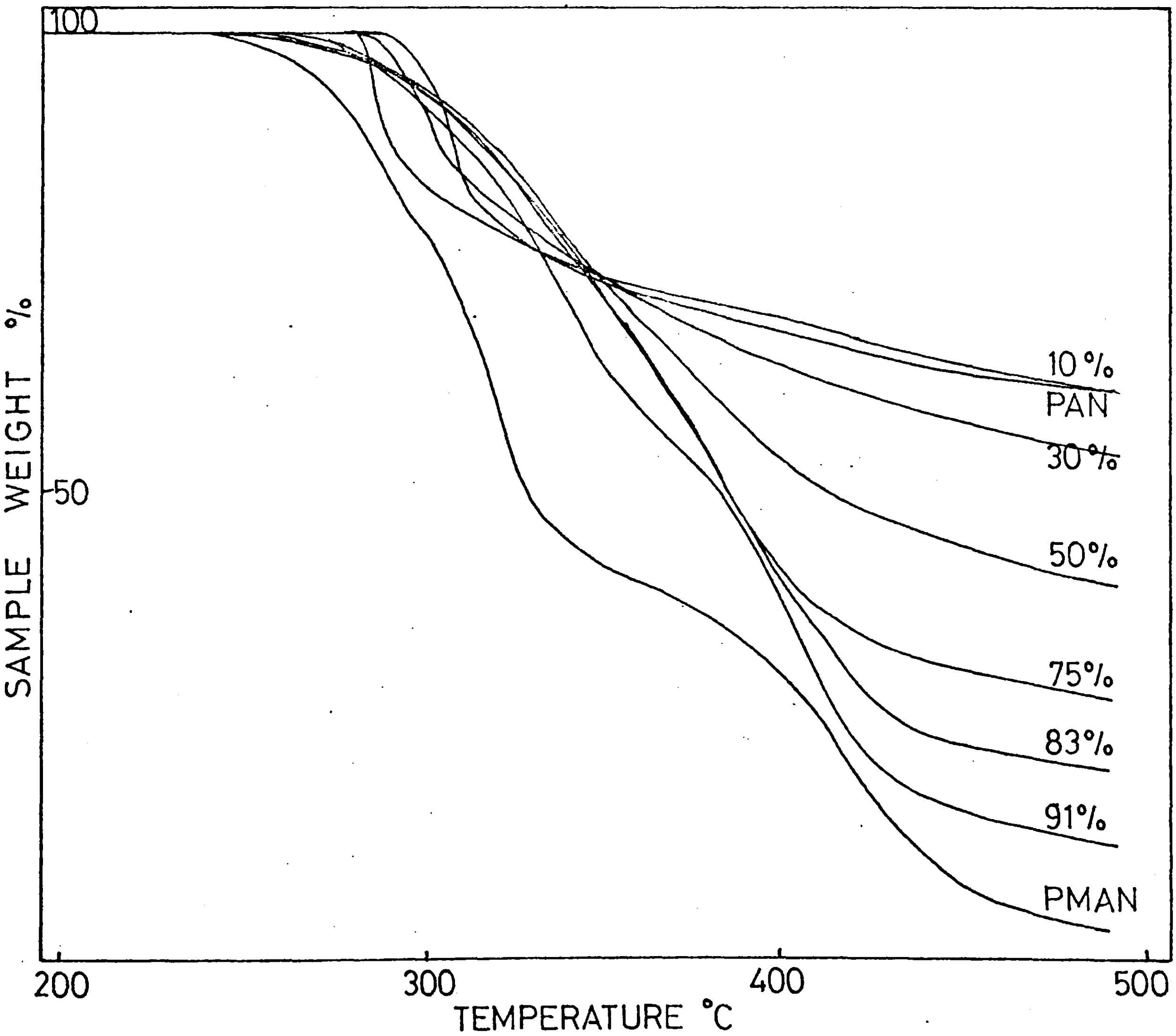


FIG. 6.15 TG CURVES FOR PAN I PMAN I BLENDS (% BY WEIGHT PMAN I) 5 mg. POWDER SAMPLES, HEATING RATE 10C°/min, DYNAMIC N_2 ATMOSPHERE

Fig. 6.15 illustrates the TG curves for a series of blend compositions together with those of the two homopolymers. The initial weight loss is similar in each composition, with low PMAN content blends showing a marked increase in stability presumably due to retardation of the evolution of PAN derived chain fragments. The residue yields at $500^{\circ}C$ in each blend reflects closely the initial PMAN content.

EFFECT OF BLEND COMPOSITION UPON MAN MONOMER YIELD

The yield of MAN for a series of blend compositions was determined by g.l.c. analysis of the condensible liquid products after degradation of blend samples containing 50 mg PMAN to $500^{\circ}C$. Propan-2-ol was used as internal reference (Fig. 6.16). The results are given in Table 6.4 below:-

Table 6.4 METHACRYLONITRILE EVOLUTION FROM PAN I-PMAN I BLENDS

Blend Composition (% PMAN by weight)	100	91	84.5	67	50	33	0
MAN yield (% PMAN)	95	86.6	84	83.2	80	78	0

It is evident that the results obtained from TVA experiments emphasize the extent to which PMAN breakdown is modified due to the sensitivity of the Pirani gauge to non-condensible gases such as CH_4. The decrease in monomer yield is considerably less than that observed upon copolymerization of MAN with small amounts of acidic derivatives.

6.6 THERMAL DEGRADATION OF POLYMETHACRYLONITRILE-POLYVINYLCHLORIDE BLENDS

The thermal decomposition of PMAN:PVC mixtures is of interest for two main reasons - (a) in order to evaluate the effect of concurrent evolution of acidic biproducts upon PMAN decomposition, in this instance HCl; and (b) for comparison with the observed interactions in PAN/PVC blends (Chapter 4).

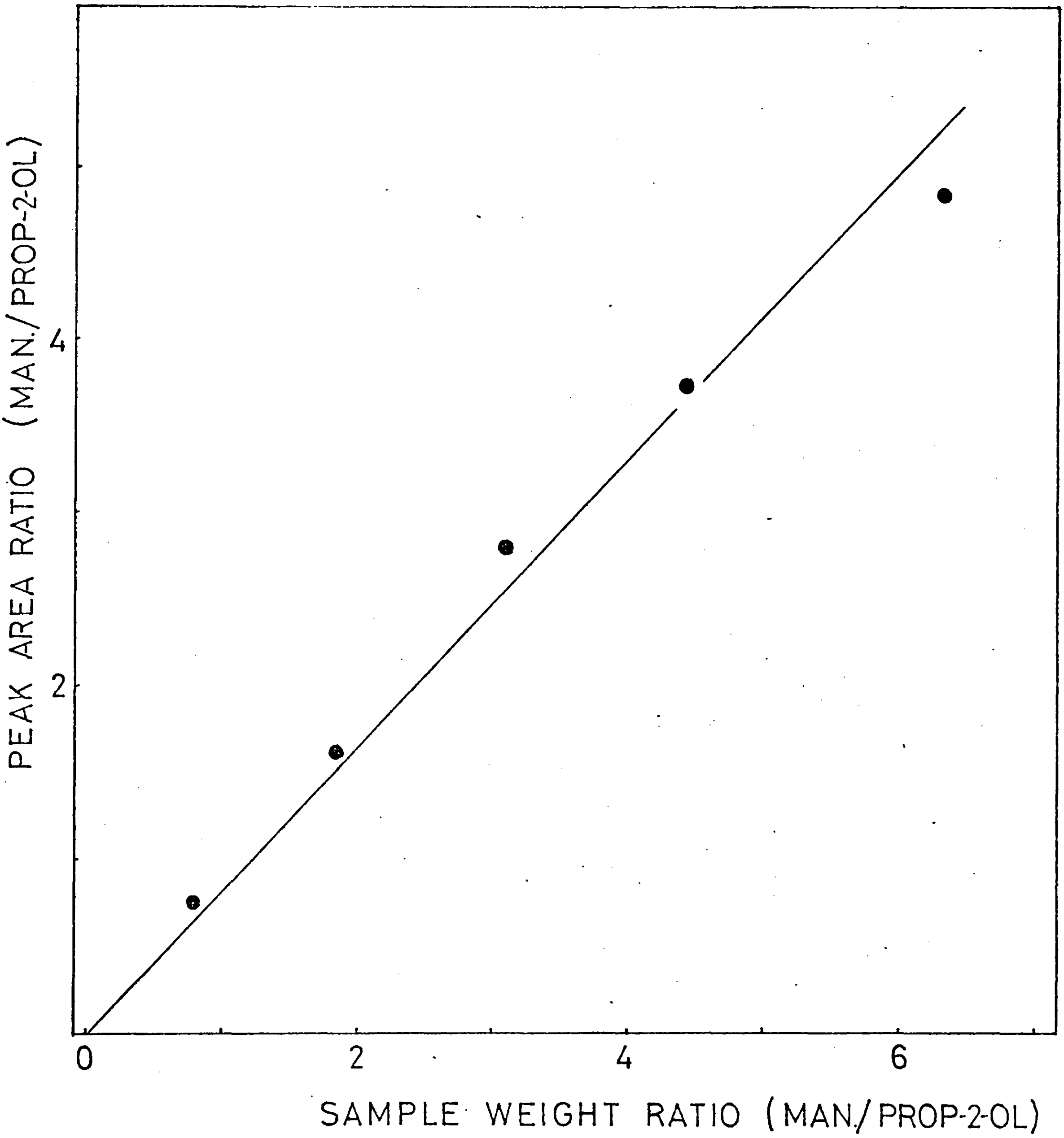


FIG. 6.16 GLC CALIBRATION PLOT - METHACRYLONITRILE VERSUS PROPAN-2-ol
COLUMNS - 13½% MEA + 6½% Di-2 ETHYL HEXYL SEBACATE
ON CHROMOSORB P80-100 MESH 60°C, HELIUM CARRIER GAS 35 ml/min.

Fig. 6.17 illustrates both mixed and unmixed PMAN I:PVC blends containing 50 and 80% by weight PMAN respectively.

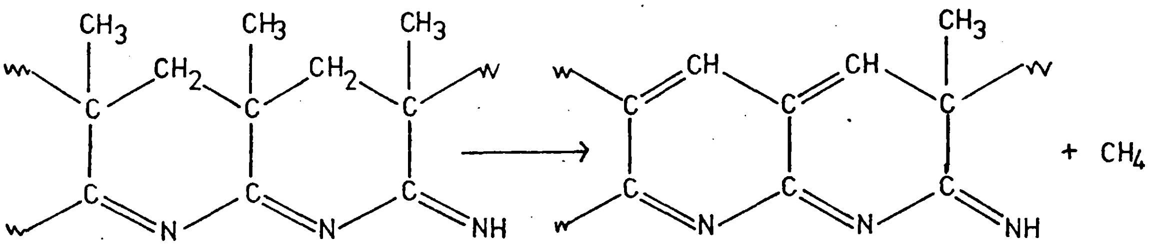
Two principal effects may be observed, namely -

1. The increased evolution of non-condensible gases, identified as CH_4 by i.r. and mass spectroscopy. In addition HCN evolution can also be detected.
2. Accelerated decomposition of PVC. This may be determined by the Pirani trace from the $-100^{\circ}C$ trap representing primarily HCl evolution. Thus in both 1:1 and 4:1 PMAN:PVC samples a destabilization of around $20C^{\circ}$ is observed.

6.7 DISCUSSION

The decomposition of PMAN in blends containing PAN or PVC has been shown to result in increased evolution of CH_4. In addition PAN:PMAN blends are also observed to yield less MAN and to give a reduced initial rate of volatilization.

The interactions observed in both blends are consistent with nitrile oligomerization in competition with PMAN depolymerization. Initiation of the cyclization reaction may occur through nucleophilic attack at the nitrile by either HCN or HCl as previously outlined in Chapter 4. Elimination of methane between 300-500°C is then consistent with the observed evolution of H_2 during PAN decomposition within the same temperature range (Chapter 3).



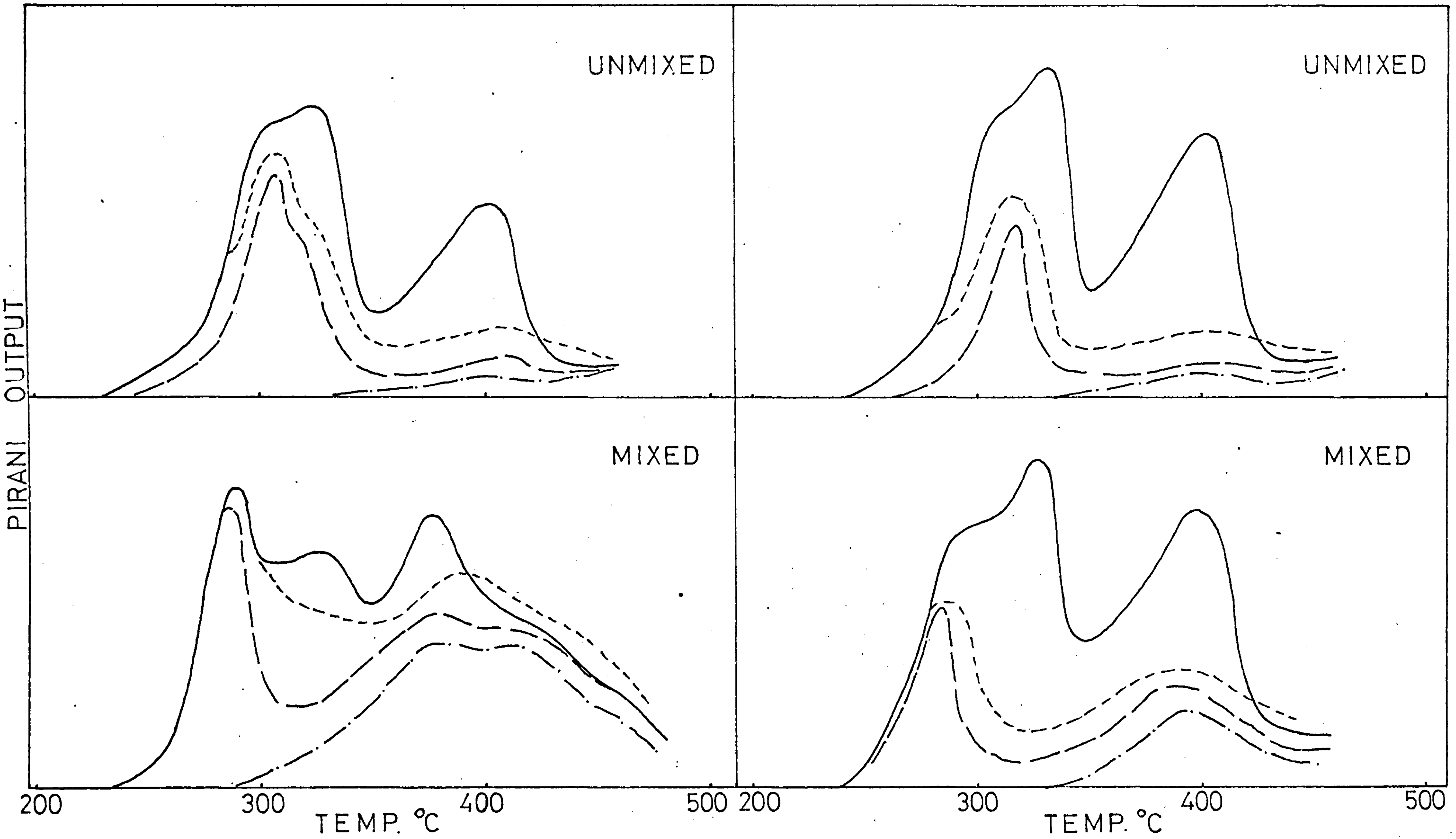


FIG. 6.17 TVA CURVES FOR SIMULTANEOUS DEGRADATION OF PMAN I AND PVC; (a) 1:1 BY WEIGHT (b) 4:1 BY WEIGHT POWDER SAMPLES, 100 mg. TOTAL WEIGHT

The initial formation of napthyridine rings within the PMAN chain can, therefore, effectively block the unzipping of the PMAN macroradical in a similar manner to that observed from incorporation of anhydride or cyclic imide units in PMMA (Chapter 3).

The increased rate of PVC decomposition is similar to that observed in PAN:PVC mixtures and may be the result of the diffusion controlled evolution of HCl from the molten blend, since it has already been demonstrated that PVC decomposition shows sample form dependence.

CHAPTER 7

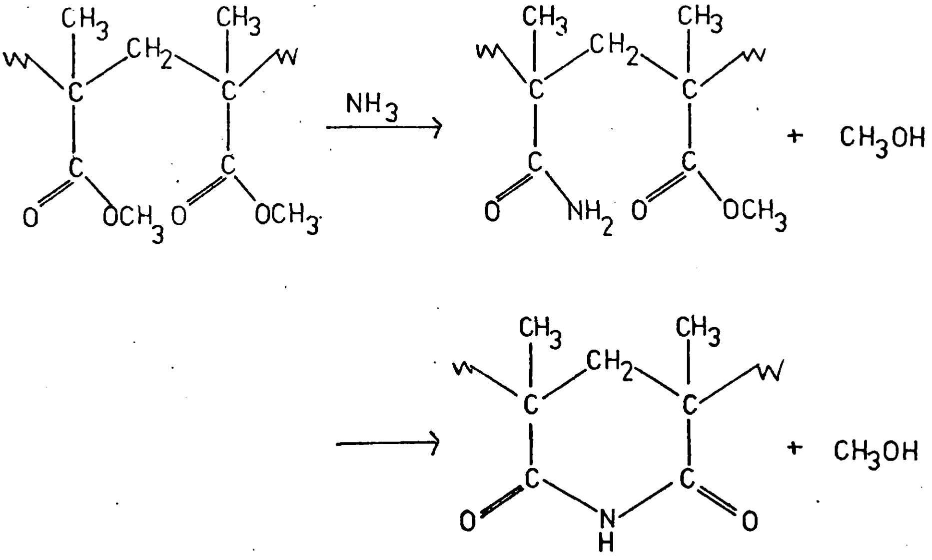
THE THERMAL DEGRADATION OF METHYLMETHACRYLATE-METHACRYLAMIDE COPOLYMERS

7.1 INTRODUCTION

Studies of the thermal decomposition of PAN-PMMA mixtures have shown the occurrence of intramolecular cyclization reactions in the PMMA polymer chain to be a prominent feature. Thus it was possible to identify, by i.r. spectroscopy, the presence of both six membered cyclic anhydride and imide structures both in chain fragments (CRF) and, to a lesser extent, in the residual polymer.

Anhydride structures have previously been observed in thermal decomposition of PMMA blends containing PVC and PVAc[57, 88]. This has been ascribed to the initial formation of acid units by simple ester decomposition involving HCl and CH_3COOH respectively. It may, therefore, be considered that an analogous reaction occurs with HCN during the decomposition of PAN-PMMA blends, although deficiencies in this assumption have been outlined (Chapter 3).

Cyclic imide units may occur in the methacrylate chain in the same blend system in the following manner -



It is evident that support for the proposed mechanisms may be gained from a study of methyl methacrylate-methacrylamide copolymers which are effectively an intermediate stage of the decomposition scheme outlined.

Thermal imidization has been examined by a number of workers[112,113,114]. Haas and McDonald[114] have shown imidization to occur both during the polymerization and subsequently during thermal degradation of polyacrylamide and polymethacrylamide. Imide formation during polymerization will result in nitrogen deficiency in polymer analysis arising through escape of NH_3 from the system. The extent of this reaction is found to vary according to polymerization conditions.

The decomposition of methylmethacrylate-methacrylic acid and MMA-MAM copolymers was studied by Kalinushkin and Ryabow[115] employing C^{14} labelling of the ester functionality. Analysis of activity in both the polymer residue and the liquid products was used to show methanol as the major degradation product in both systems. Furthermore it was found that the depolymerization reaction was of little significance in either copolymer system.

7.2 POLYMER SAMPLE HISTORY

Monomer purification was as outlined in Chapter 2. Polymerization was carried out in vacuum in sealed glass dilatometers using absolute ethanol (Burroughs Ltd.) as solvent with a total monomer concentration of 3M. Monomer feed ratios were computed on the basis of the reactivity ratios published by Crauwels and Smets[113].

methacrylamide $r = 0.49 \pm 0.02$; methyl methacrylate $r = 1.65 \pm 0.02$

Copolymers containing 10% MAM were soluble in chloroform but insoluble in toluene. Accordingly they were reprecipitated from chloroform into 40-60° per ether. Higher MAM content resulted in copolymers which were insoluble in common organic solvents. Such polymers were ground to a fine powder and thoroughly washed with hot ethanol before drying in vacuo at 40°C.

TABLE 7.1 POLYMER SAMPLE HISTORY

POLYMER	% MAM	$f = {}^{m1}/_{m2}$	$F = {}^{M1}/_{M2}$	ANALYSIS RESULTS % MAM
CO	100	-	-	97
*C1	80	4	7.84	77
*C2	65	1.86	3.51	62
*C3	50	1.0	1.84	46
C4	35	0.537	0.96	33
C5	10	0.11	0.13	12
C6	5	0.05	0.088	-
C7	2	0.02	0.034	-
C8	0	-	-	0
C9	0	-	-	0

Co, C_4-C_8 Polymerization temperature 65°C, C_1-C_3 50°C

Initiator - AIBN; Co-C_4, C_6, C_8 - 0.05% w/w monomers

C_5, C_7, C_9 - 2 % w/w monomers

f - mole ratio in polymer, F - molar ratio in feed

*Donated by Dr. B. Dodson

7.3 RESULTS

THERMAL VOLATILIZATION ANALYSIS

Two distinct modes of decomposition are evident in the TVA curve obtained for PMAM (Fig. 7.1). The initial stage gives rise to gaseous products volatile at all but -196°C. Volatile chain fragments cannot be detected within the temperature range of the first peak. At higher temperatures products which are non-condensible at -196°C are evolved in addition to material exhibiting differential condensibility in the -75° and -100° traps. In addition, extensive chain scission occurs between 350-450°C resulting in an amber cold ring fraction.

Fig. 7.2 illustrates the TVA curves for 50 mg powder samples of copolymers C_1 - C_4, i.e. 80% - 35% MAM. In each copolymer there are again two quite distinct modes of degradation. After an initial slight increase in peak height for the low temperature reaction observed in the 80% MAM copolymer, the remaining copolymers show a slight reduction in peak height concurrent with an increase in evolution of volatiles during the second stage process. The observed peak maxima remains around 315°C for the first peak but the second peak increases from 421°C to 438°C in going from PMAM to the 35% MAM copolymer. In each of the copolymers, as in PMAM, volatile chain fragments occur only during the latter stage of decomposition.

Fig. 7.3 illustrates the TVA curve for C6. T max occurs at 398°C, lower than that observed for copolymers of higher methacrylamide content and approximating more closely to that of PMMA prepared under similar conditions (Fig. 7.3(b)). Two observations can be made in comparison of the two curves (1) C6 demonstrates LR effects in both -75 and -100°C cold traps. The former effect is consistent with the presence of MMA while the latter was found to arise from CH_3OH evolution and was confirmed by i.r. analysis of the gaseous volatiles. (2) In addition to the presence of non-condensible volatiles, the inclusion of MAM units in the polymer chain results in almost complete elimination of allylic activated depolymerization.

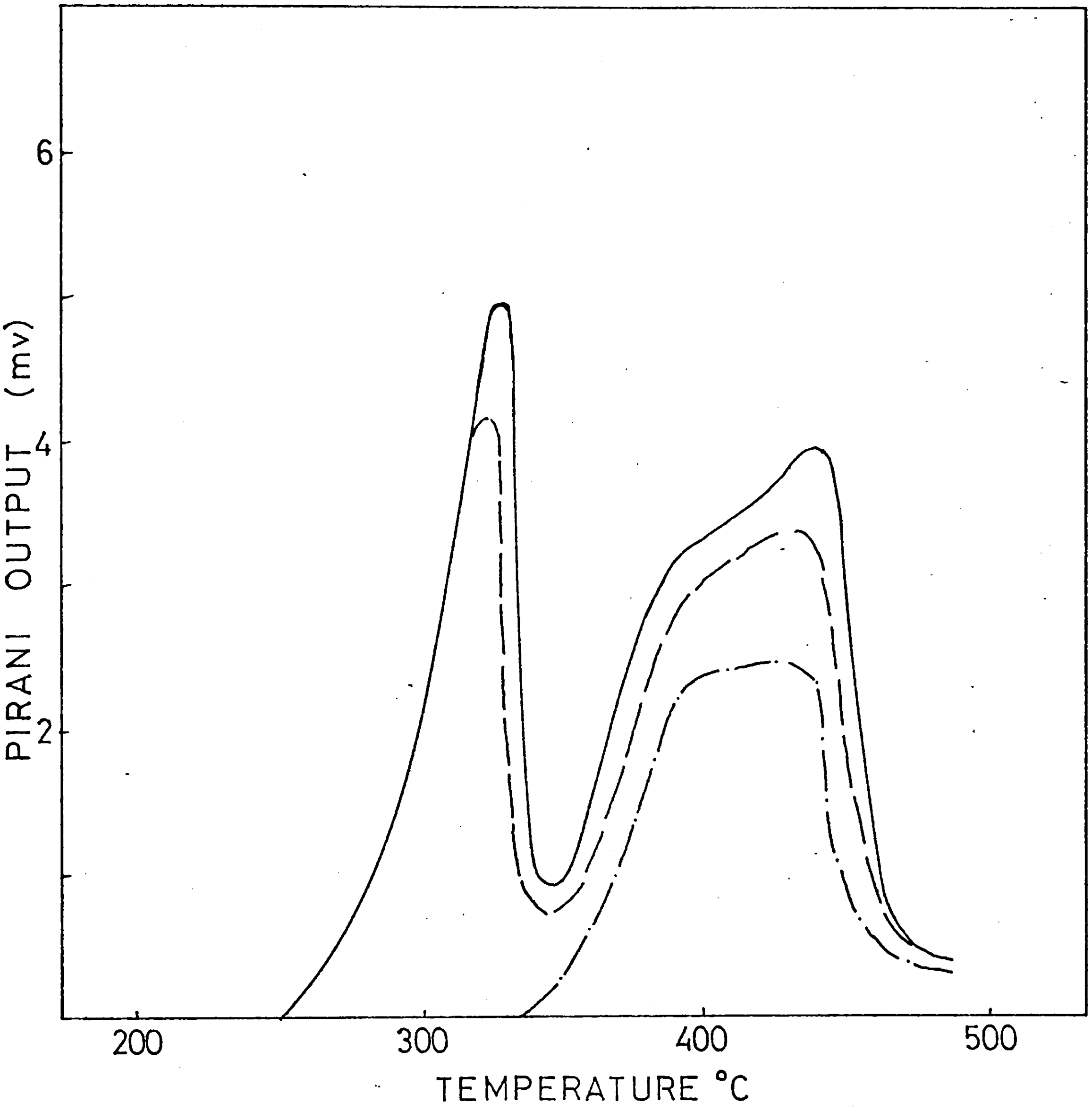


FIG. 7.1 TVA CURVE FOR PMAN (Co) 50 mg. POWDER SAMPLE

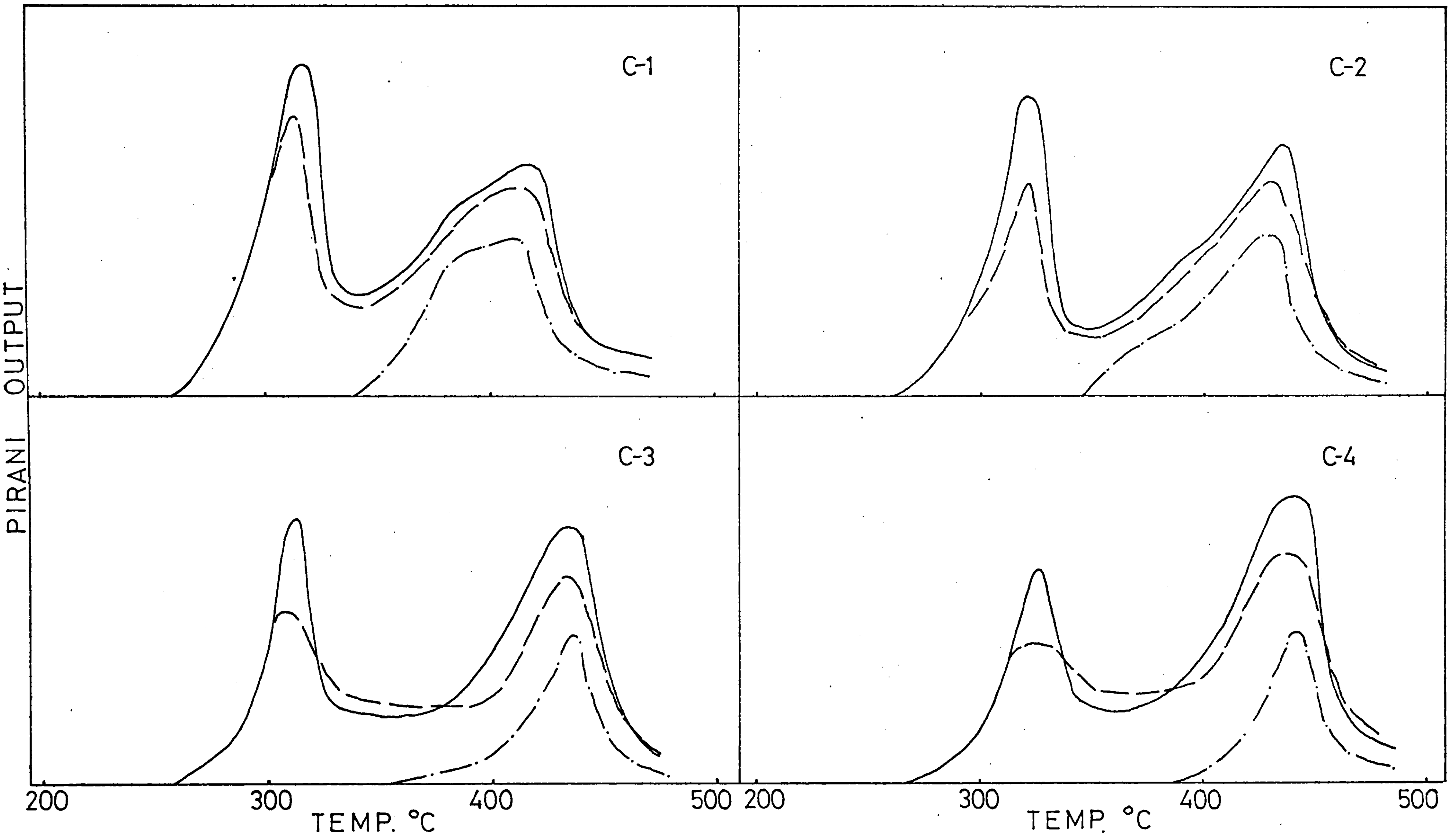


FIG. 7.2 TVA CURVES FOR COPOLYMERS C1, C2, C3 and C4, 50 mg. POWDER SAMPLES

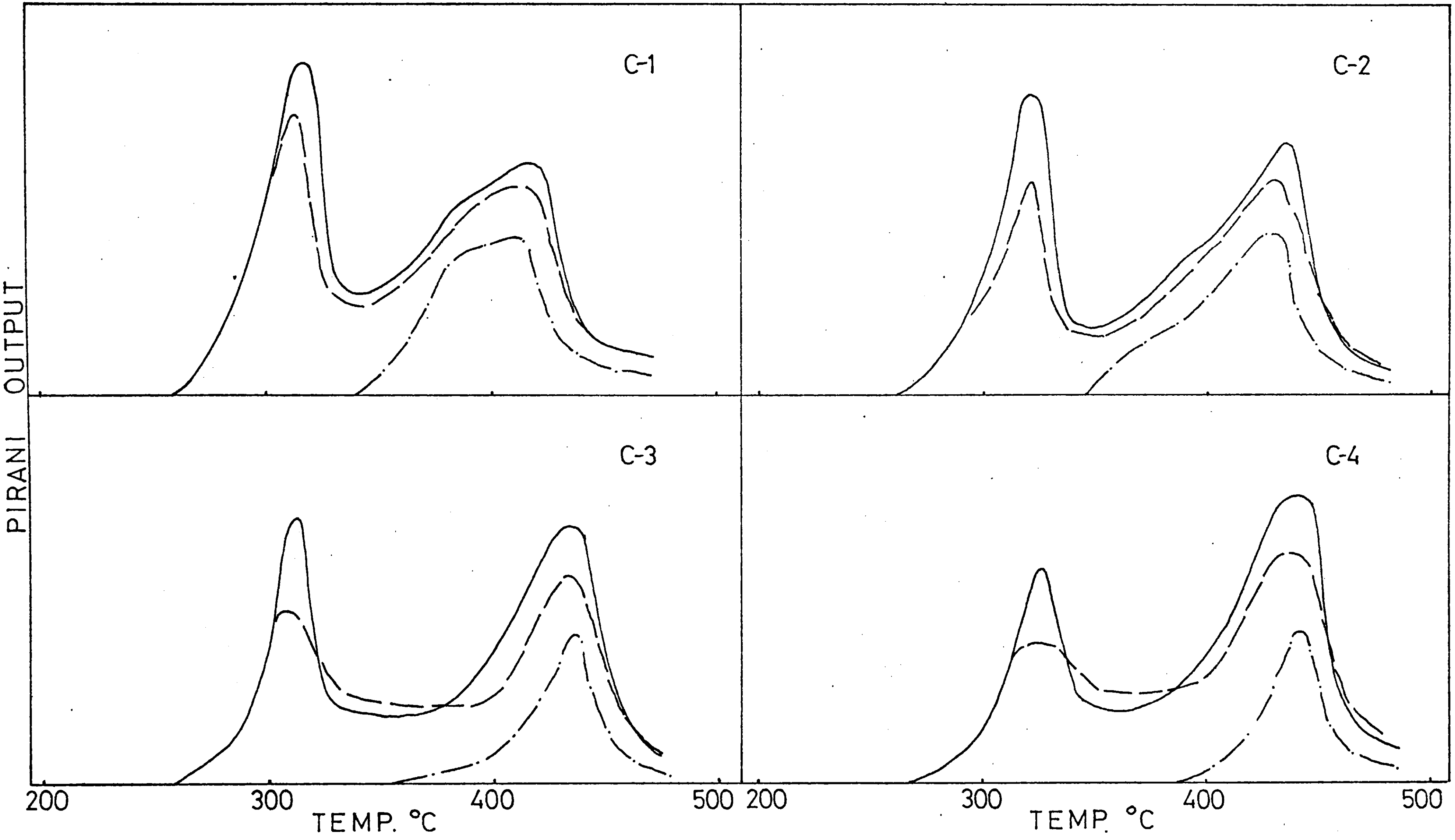


FIG. 7.2 TVA CURVES FOR COPOLYMERS C1, C2, C3 and C4, 50 mg. POWDER SAMPLES

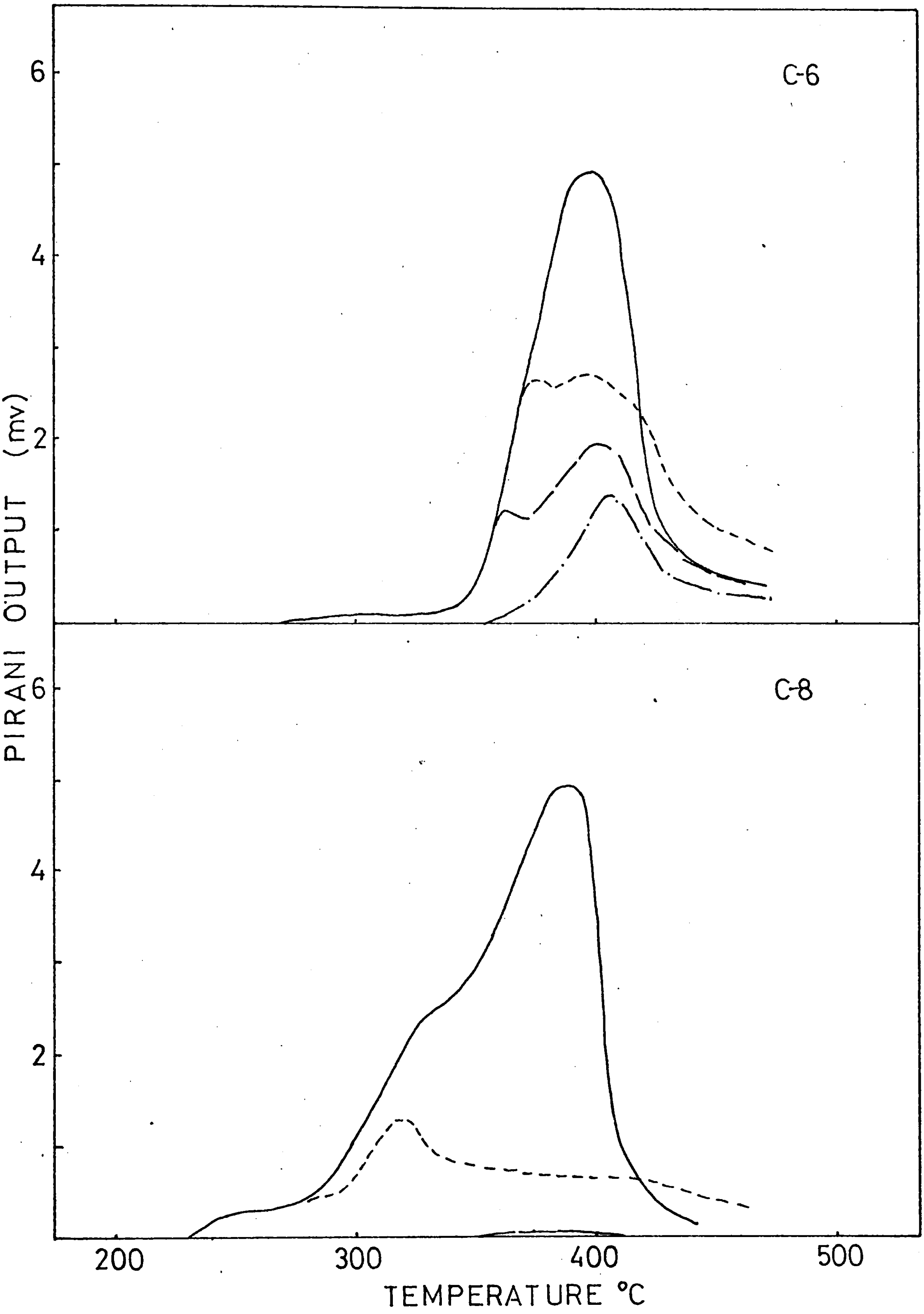


FIG. 7.3 TVA CURVES FOR (a) C6 (b) C8, 50 mg. POWDER SAMPLES

A similar result is obserbed in examination of the TVA curves for C5 and C7 in comparison with the low molecular weight homopolymer C9 (Fig.7.4) Each of the polymers were found by GPC to have molecular masses around 30,000.

TVA results are summarized in Table 7.2 below:

TABLE 7.2 THERMAL VOLATILIZATION ANALYSIS OF METHYLMETHACRYLATE-METHACRYLAMIDE COPOLYMERS

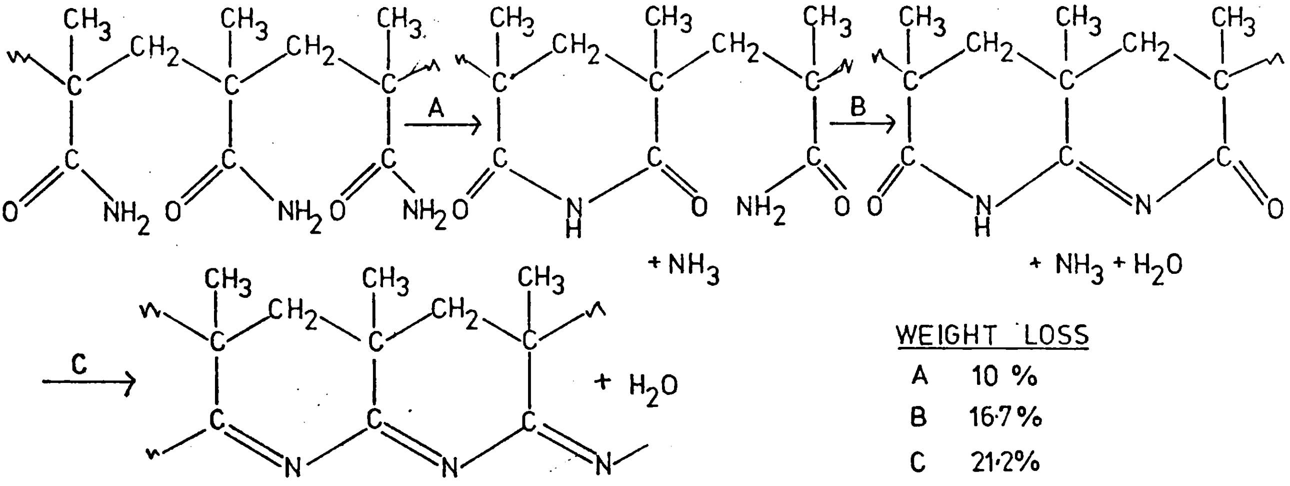
POLYMER	C_0	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9
T Max (I) °C	315	313	315	314	326	309	–	297	–	303
T Max (II) °C	421	422	428	439	439	422	398	398	385	381

THERMOGRAVIMETRIC ANALYSIS

TGA thermograms were obtained using a heating rate of 10°C/min. in a dynamic N_2 atmosphere. Prior to each experiment samples were pre-heated at 50°C under N_2 to remove adsorbed moisture.

Fig. 7.5 illustrates the results for polymers Co–C4. PMAM (Co) exhibits a two stage weight loss concurrent with the evolution of gaseous products observedin TVA experiments. The initial weight loss corresponds to 15.6% original sample weight, while the formation of volatile chain fragments and further gaseous products comprises 66.4%. The remaining 18% of the original sample is a black, involatile and insoluble residue.

Consideration of the proposed intramolecular imidization suggests three possible extents of decomposition which may occur during the initial weight loss in PMAM, namely -



WEIGHT LOSS

A	10 %
B	16·7 %
C	21·2 %

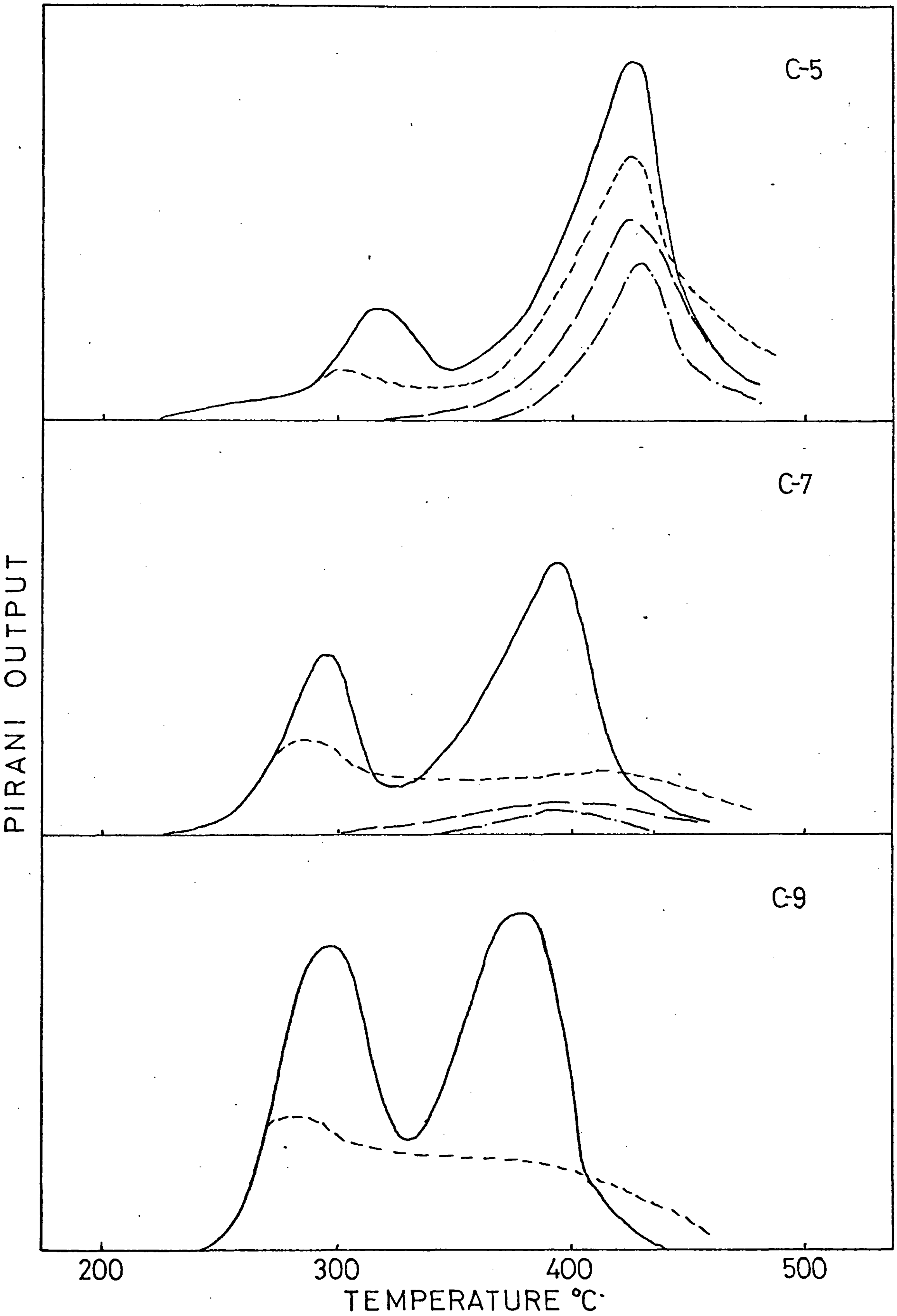


FIG. 7.4 TVA CURVES FOR C5, C7 AND C9, 50 mg. POWDER SAMPLES

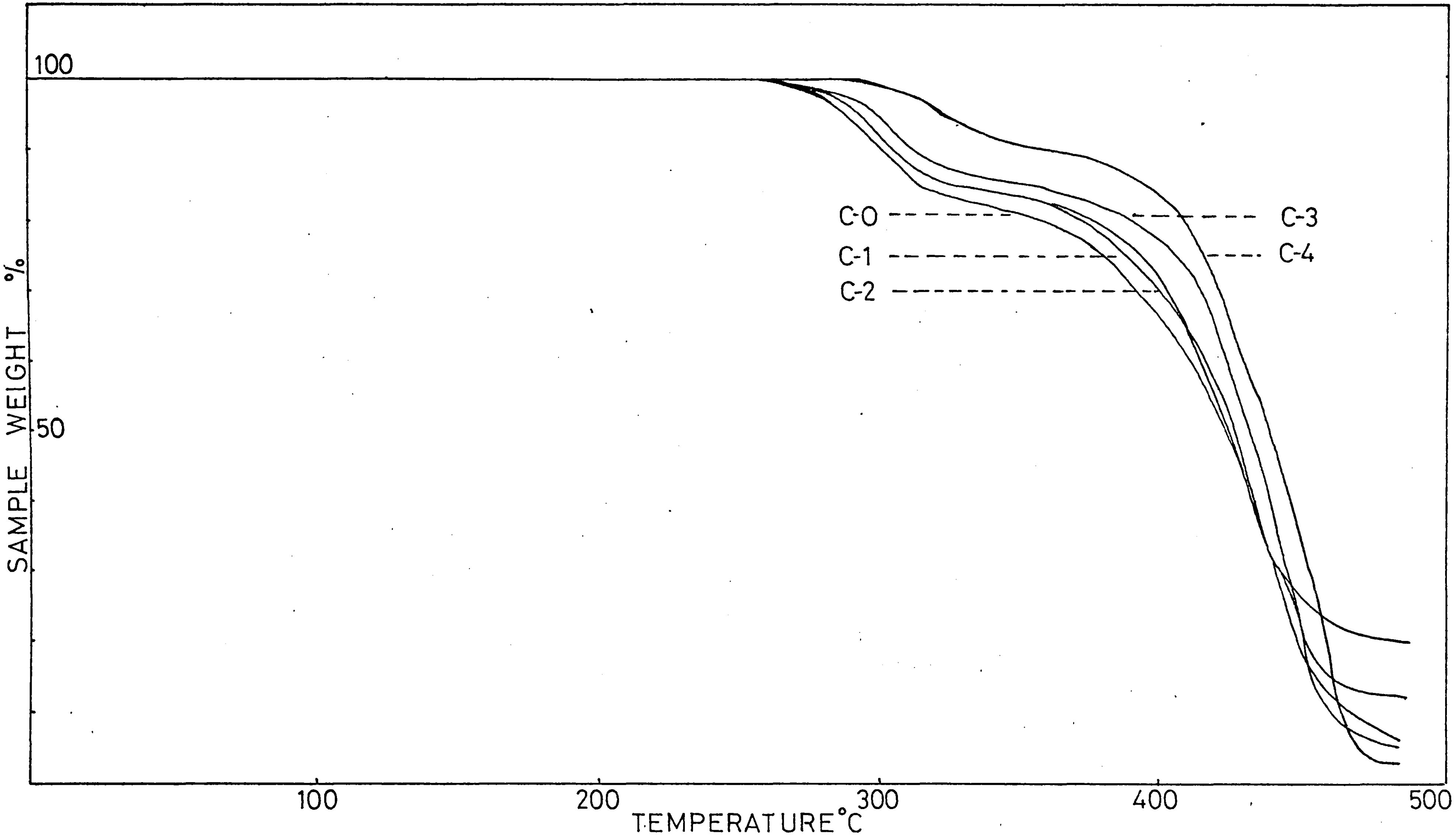


FIG. 7.5 TG CURVES FOR C0, C1, C2, C3 and C4, 5 mg. POWDER SAMPLES, HEATING RATE 10C°/min, DYNAMIC N_2 ATMOSPHERE

The results obtained suggest the contribution by reactions A and B to be most reasonable interpretation of the observed weight loss if only intramolecular cyclization occurs. Thus the residual polymer would consist of short cyclized segments interspaced by unaltered MAM units. Steric considerations render C less probable since this required $\geqslant$ 3 adjacent ring structures in the polymer backbone.

Copolymers C_1-C_4, in order of increasing MMA content, exhibit reduced initial weight loss but a marked increase in volatilization during the latter stage of decomposition in which C_4 has a weight retention of only 6% at 500°C. This behaviour would be predicted from the TG curve of PMMA which undergoes almost 100% weight loss below 450°C.

Fig. 7.6 illustrates the TG curves for copolymers C_5 and C_7 and the low molecular weight PMMA homopolymer C_9. The results confirm those of TVA experiments, namely a reduction in chain end initiated depolymerization. Again during the latter stages of degradation, increase MAM content results in increased weight retention at 500°C.

DIFFERENTIAL SCANNING CALORIMETRY

Fig. 7.7 illustrates the DSC curves of 5 mg powder samples of PMAM and a 50% MAM copolymer. Two endothermic reactions are evident in both samples corresponding to initial cyclization and later fragmentation processes respectively.

A reduction in the sharp endotherm around 300°C from 0.9°C to 0.4°C is observed in the 50% MAM copolymer, indicative of a corresponding reduction in the contribution of the cyclization reaction to the endotherm. The magnitude of the broad exotherm around 420°C, however, remains unchanged at 0.2-0.3°C throughout the polymer composition range examined and will represent the summation of two endothermic processes, namely (1) chain scission and depolymerization which will be the major reaction in high MMA copolymers (2) chain scission and fragmentation to form volatile low polymer which will be the major process in high MAM copolymers.

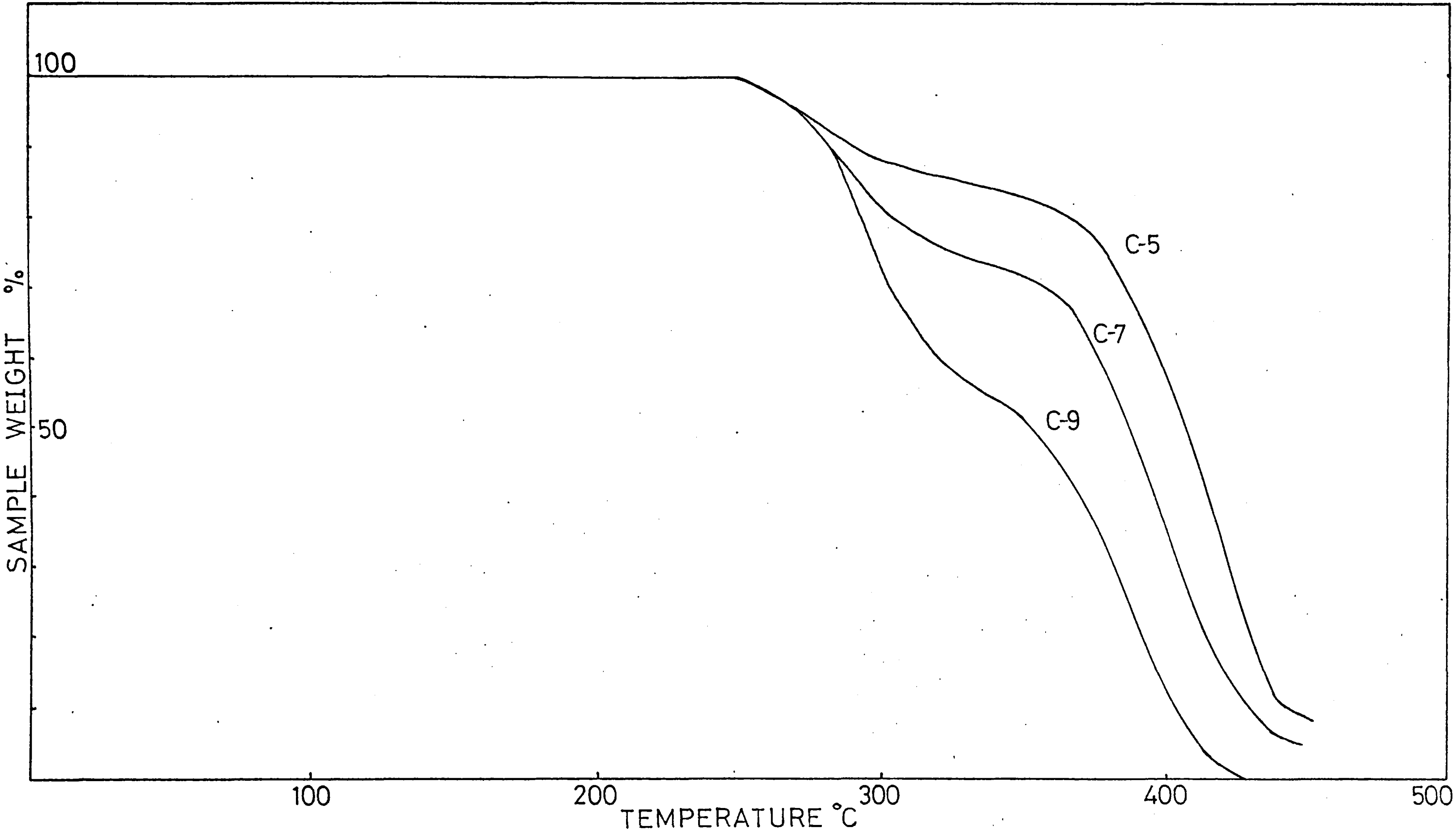


FIG. 7.6 TG CURVES FOR C5, C7 AND C9, 5 mg. POWDER SAMPLES, HEATING RATE 10C°/min, DYNAMIC N_2 ATMOSPHERE

PRODUCT ANALYSIS

The gaseous decomposition products were examined after degradation of 100 mg powder samples in vacuo in a closed system to 500°C. I.r. analysis of the products of PMAM decomposition allows identification of NH_3, HCN and CH_4 as the principal products, together with trace amounts of CO. Peaks attributable to methacrylonitrile and isobutene at 929 cm^{-1} and 891 cm^{-1} respectively were observed in copolymer decomposition, but could not be positively assigned in the homopolymer.

In each of the copolymers examined the additional products identified by i.r. analysis were MMA, CH_3OH and CO_2. G.L.C. results, employing both columns and conditions as described in Chapter 3, confirmed both MMA and CH_3OH as major products from the copolymers and, in addition, allowed identification of H_2O as a product common to both the homopolymer and copolymers.

Quantitative measurement of NH_3 and HCN evolution was obtained by optical density measurement of i.r. absorptions at 931 cm^{-1} and 714 cm^{-1} respectively after collection of the total gaseous products in a 10 cm path length gas cell. The calibration plots of O.D. against pressure as given in Chapter 3 were used to construct Fig. 7.8. It is evident that NH_3 and HCN constitute a small proportion of the total decomposition products and that the ratio of the two products varies with copolymer composition. This may arise if each product results from a different reaction mechanism the contribution of which is dependent upon copolymer composition. This is supported by the two stage decomposition process observed in TVA experiments. Thus, if the decomposition products collected after temperature programmed decomposition of PMAM to completion of the initial reaction are examined, then only NH_3 and H_2O can be detected. Further decomposition to 500°C results in the remaining products together with additional small amounts of NH_3. Thus, NH_3 evolution is associated with the cyclization process while HCN results from decomposition of the structurally modified polymer at higher temperatures.

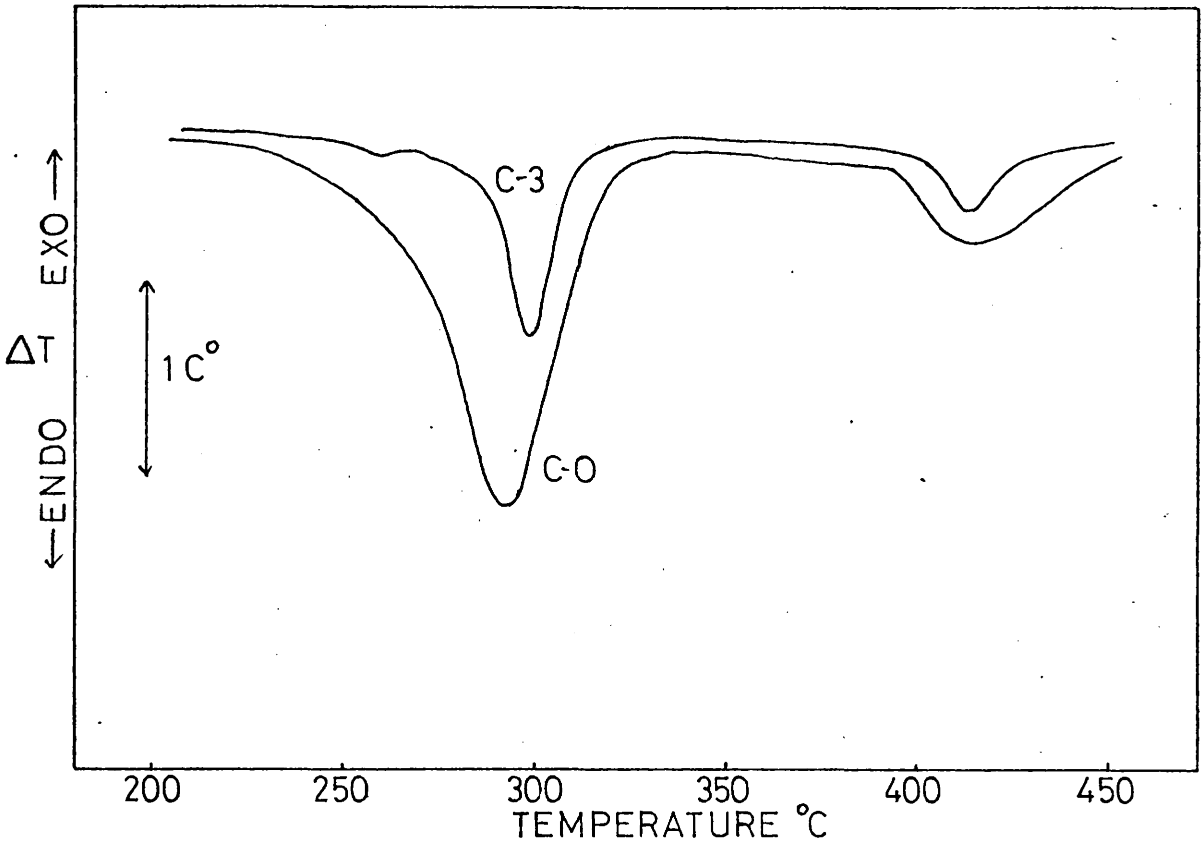


FIG. 7.7 D.S.C. CURVES FOR C0 AND C3, 5 mg. POWDER SAMPLES, HEATING RATE 10C°/min, DYNAMIC N_2 ATMOSPHERE

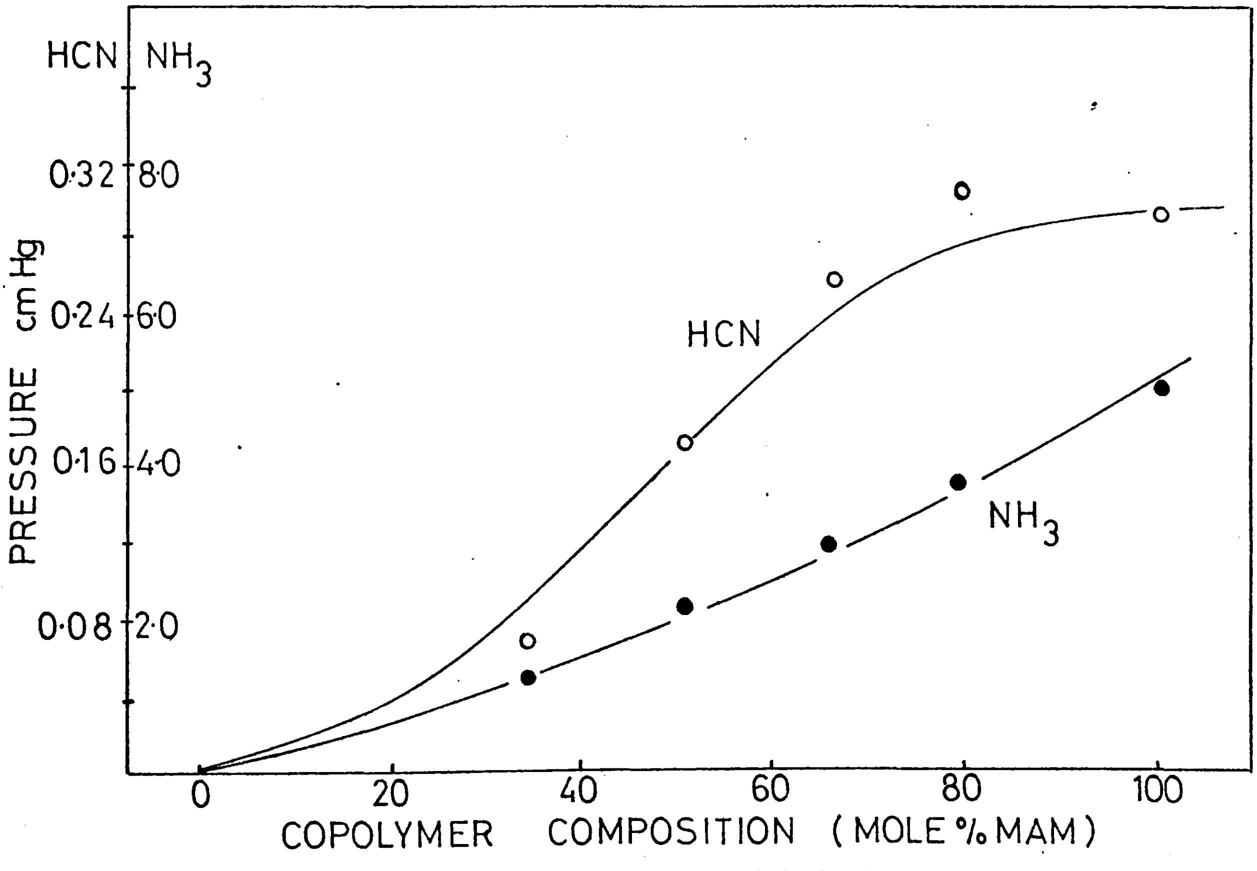


FIG. 7.8 EVOLUTION OF NH_3 AND HCN IN MMA:MAM COPOLYMERS (100 mg. POWDER SAMPLES DEGRADED TO 500°C)

The combined results of TVA, TGA and GLC analyses are summarized in Table 7.3. C.R.F. results were obtained by removal of the amber coloured waxy degradation products from the cooled portion of the TVA tube using a solvent moistened tissue. The residue remaining at 500°C was that obtained from TGA data.

TABLE 7.3 PRODUCT ANALYSES OF METHYLMETHACRYLATE-METHACRYLAMIDE COPOLYMERS*

POLYMER	C_0	C_1	C_2	C_3	C_4
pNH_3 (cm Hg)	5.2	3.74	2.76	2.26	1.2
pHCN (cm Hg)	0.30	0.32	0.25	0.17	0.05
MMA (mg)	-	3.8	2.5	3.4	11.6
CH_3OH (mg)	-	11.6	15.2	30.6	16.6
C.R.F. (mg)	54.7	64.0	50.9	48.9	50.8
Residue (mg)	20.C	14.0	7.0	6.0	4.0

* 100 mg powder samples, temperature programmed degradation, 10C°/min to 500°C.

The remaining products consist largely of water together with small amounts of CO_2, CO, CH_4, isobutene and methacrylonitrile.

It is evident that the evolution of MMA through 'unzipping' of the polymer chain, is a minor process within the composition range examined and that it is replaced by extensive cyclization reactions accompanied by chain fragmentation.

STRUCTURAL CHANGES DURING DECOMPOSITION

I.r. spectra of the CRF obtained from copolymer decomposition provide the best insight into the structural rearrangements which take place, since the relative concentration of 'defect' structures is greater in low molecular weight chain fragments.

Fig. 7.9 illustrates the i.r. region of primary interest in (a) PMAM (b) copolymer C_3 (c) PMAM C.R.F. at 500°C (d) C_3, C.R.F. at 500°C.

Fig. 7.9(a) shows the carbonyl stretching vibration of PMAM, the Amide I bond, to occur at 1650 cm^{-1}, while the Amide II bond, of lesser intensity, is seen at 1600 cm^{-1}. The resultant CRF (b) shows the major carbonyl absorption to occur around 1690 cm^{-1} with both Amide I and Amide II bonds as weak intensity shoulders upon a broad carbonyl absorption. Overlap of residual amide carbonyl absorption thus results in the maximum absorption due to cyclic imide occurring below 1700 cm^{-1} normally associated with such structures, e.g. glutarimide 1700 cm^{-1} [116].

The i.r. spectrum of C_3 is clearly that expected from 'addition' of the two spectra of the corresponding homopolymers. The C.R.F. spectrum, however, differs from that of PMAM, showing the presence of anhydride structures by C=0 absorptions at 1825 cm^{-1}, 1795 cm^{-1} and 1759 cm^{-1} together with C-0-C stretching absorption at 1022 cm^{-1}. Previous work has shown the absorptions at 1795 cm^{-1} and 1759 cm^{-1} to be characteristic of cyclic 6 membered anhydrides[13]. The weaker absorption at 1825 cm^{-1} is less well defined and may arise from the presence of acyclic anhydride structures found by intermolecular reactions. In addition, both ester and Amide I bonds are replaced by a broad carbonyl absorption centred on 1690 cm^{-1} again indicative of cyclic imide formation.

Similar assignments are possible in i.r. analysis of residual copolymer after temperature programmed degradation to 350°C with the exception of the absorption at 1825 cm^{-1} which is too weak to be observed.

ISOTHERMAL DEGRADATION

Temperature programmed degradation of MMA:MAM copolymers to completion of the initial process observed during TVA experiments, allows identification by glc of MMA, CH_3OH and lesser amounts of H_2O as the only condensible products. The evolution of H_2O is ascribed to the cyclization of adjacent MAM units in the polymer chain while CH_3OH may arise from intramolecular condensation of adjacent comonomers. Thus, comparison of CH_3OH and MMA evolution during the initial stage of decomposition may provide some information of the relative rates of cyclization and depolymerization processes.

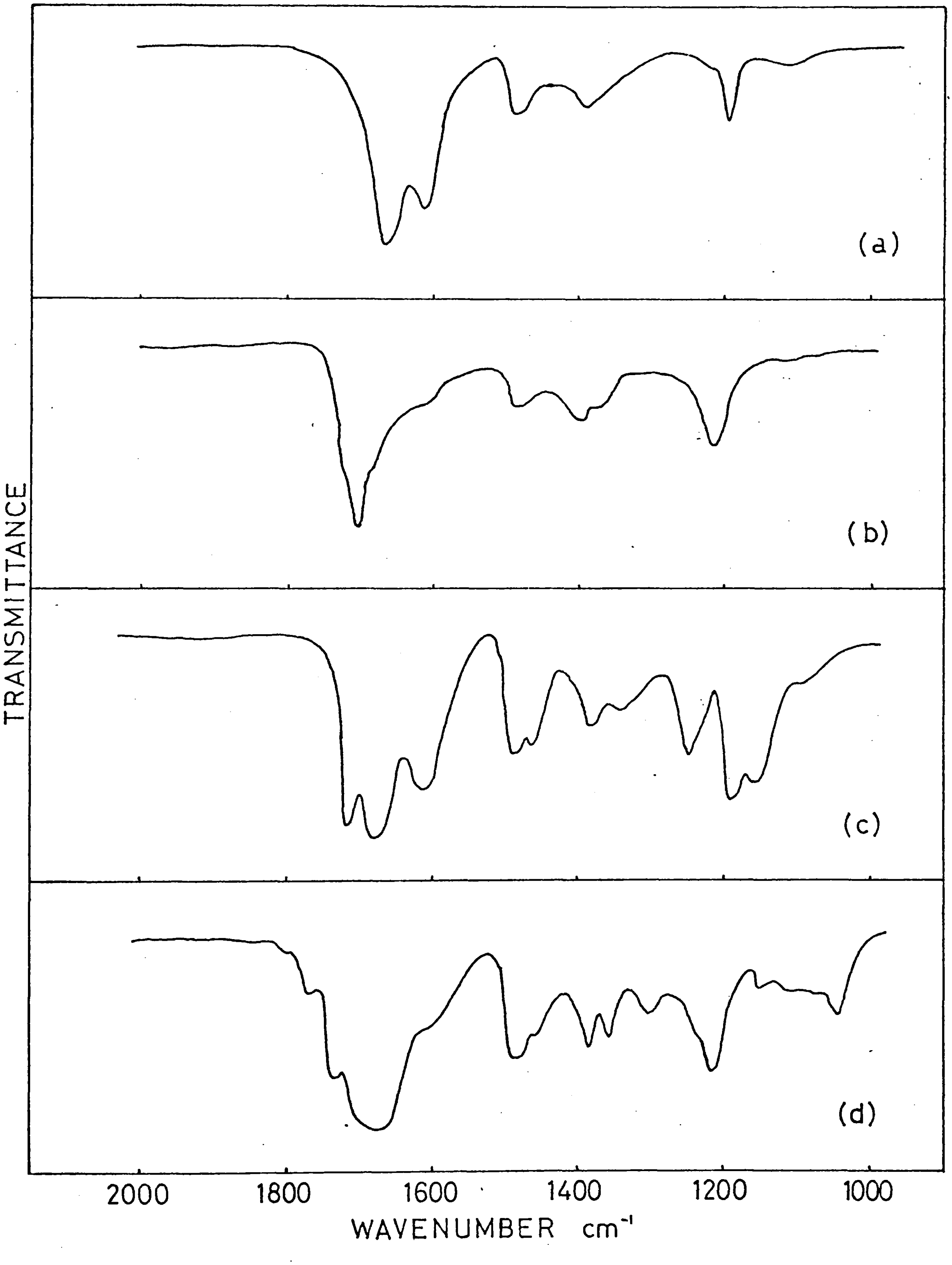


FIG. 7.9 INFRA RED SPECTRA OF (a) PMAM (b) C3 (c) PMAM CRF AT 500°C (d) C3 CRF AT 500°C

Isothermal degradation of 100 mg powder samples of both MMA copolymer C_5 and CH_3OH was examined by glc estimation. Figs. 7.10(a) and (b) illustrate the rates of evolution of MMA and CH_3OH at 260, 270 and 280°C. Measurement of initial rates allows determination of the respective EA's from the Arrhenius plots shown in Fig. 7.11. These were found to be $EAMMA = 35.4$ K cal $mole^{-1}$ and $EACH_3OH = 45$ K cal $mole^{-1} \pm 15\%$ respectively, a relatively large error being incurred in measurement of initial rates.

The results show that the two processes occur at similar rates and, therefore, suggest that the initial formation of cyclized units within the polymer chain, can effectively reduce the MMA yield through blocking of the unzipping of the PMMA macroradical.

MOLECULAR MASS STUDIES

Changes in the molecular mass of copolymer C_5 were examined after isothermal degradation of 100 mg powder samples at 260°C for varying time intervals to a maximum of 150 minutes. Under these conditions the polymer was found to remain soluble in chloroform but insoluble in toluene. Molecular masses were obtained by G.P.C. employing a PMMA calibration (Appendix 2). The results are shown in Table 7.5.

TABLE 7.4 MOLECULAR MASS CHANGES DURING ISOTHERMAL DEGRADATION OF C5 AT 260°C

TIME (mins.)	0	45	90	120	150
Mn	25,000	26,800	27,600	30,700	25,800

The retention of solubility together with unaltered molecular weight is typical of low molecular weight free radical PMMA decomposition and is consistent with the concept of intramolecular imidization rather than intermolecular reaction. Thus, the insolubility of high molecular weight copolymers of low MAM content may result from reduced chain flexibility due to segments of cyclised units within the polymer chain and is less likely to occur through cross-linking of the polymer chain by intermolecular imidization.

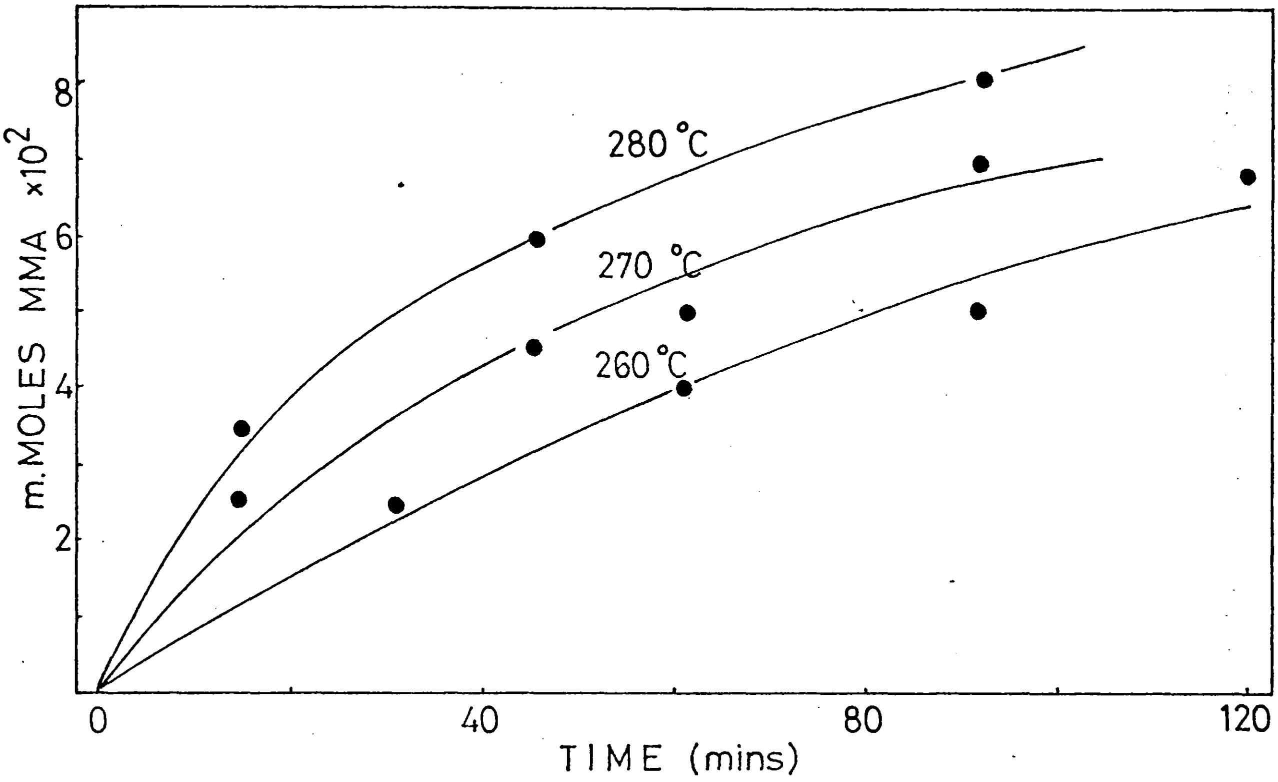


FIG. 7.10 (a) EVOLUTION OF METHYLMETHACRYLATE DURING ISOTHERMAL DEGRADATION OF C5 (100 mg. POWDER SAMPLE)

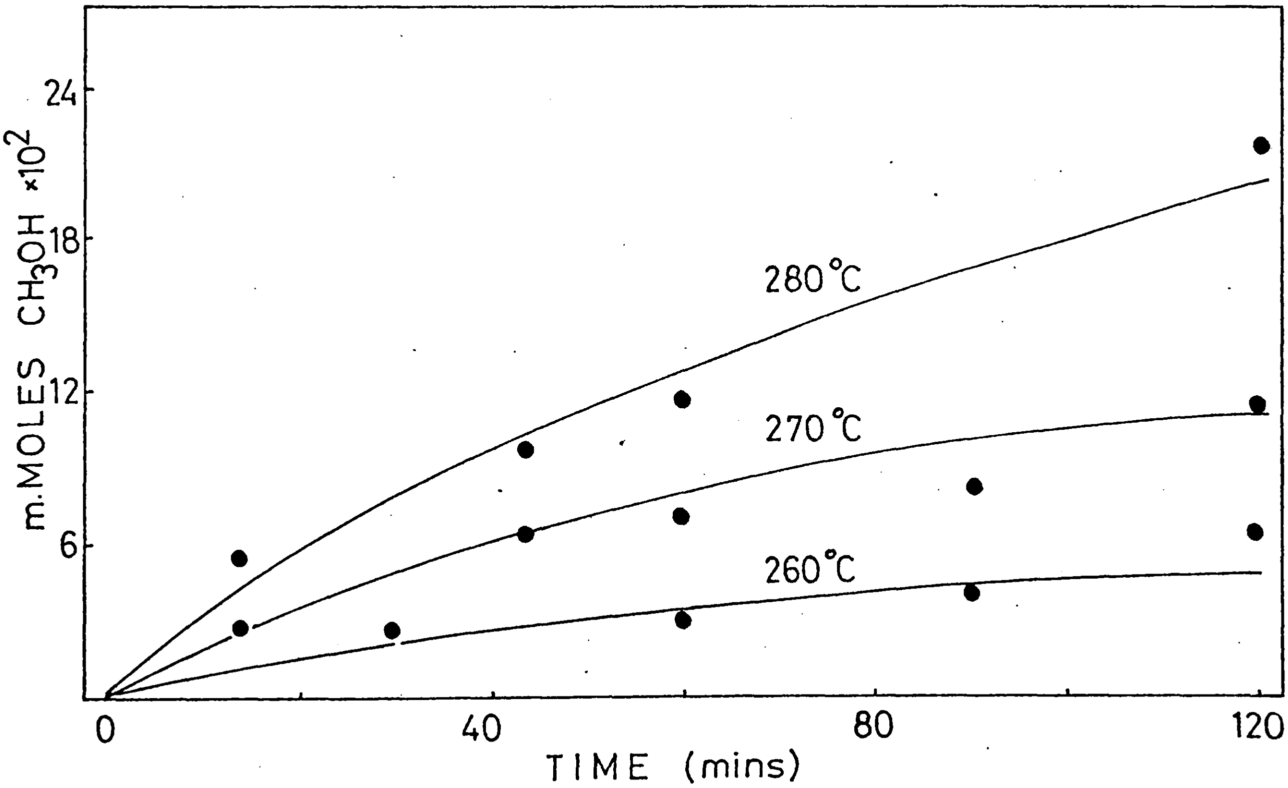


FIG. 7.10 (b) EVOLUTION OF METHANOL DURING ISOTHERMAL DEGRADATION OF C5 (100 mg. POWDER SAMPLE)

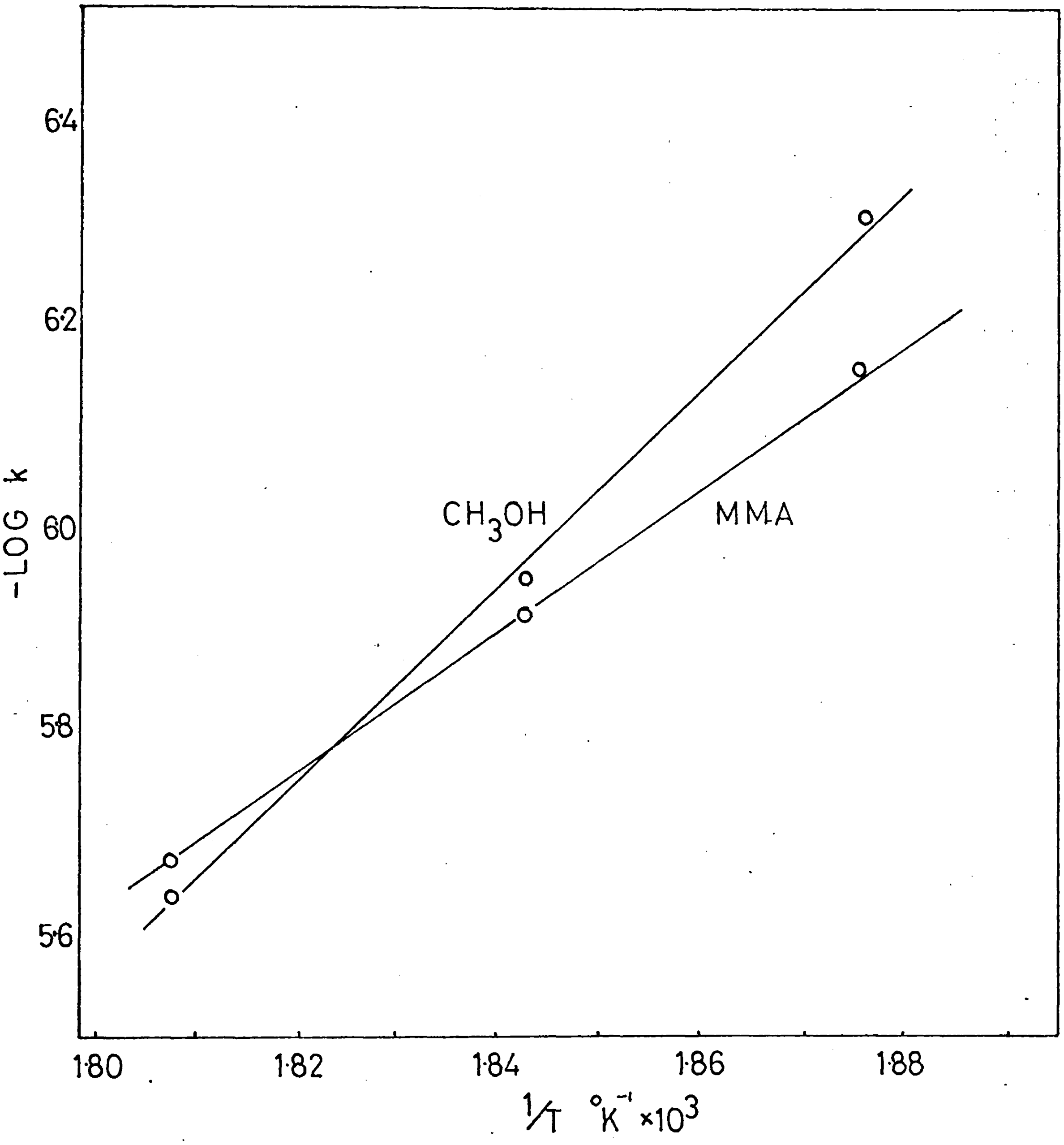
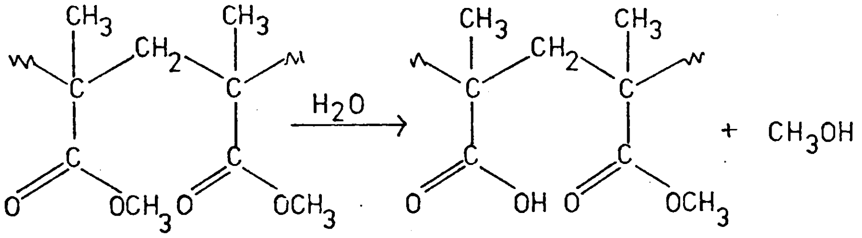


FIG. 7.11 ARRHENIUS PLOTS FOR METHYLMETHACRYLATE AND METHANOL EVOLUTION DURING ISOTHERMAL DEGRADATION OF C5 AT 260, 270 AND 280°C

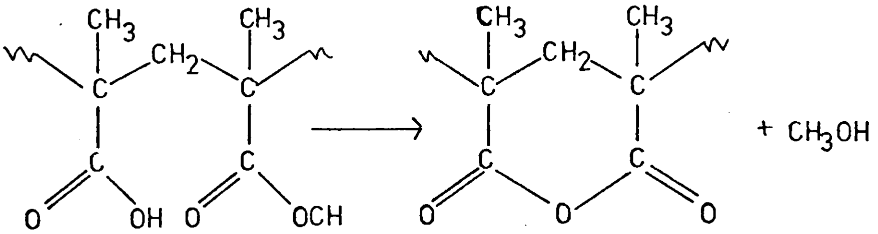
7.4 DISCUSSION

Two distinct processes may be discerned during the thermal decomposition of MMA-MAM copolymers, namely (a) intramolecular cyclization between adjacent monomer units resulting in the elimination of NH_3, CH_3OH and H_2O and (b) the high temperature decomposition of the structurally modified residual polymer.

The low molecular weight copolymers, each stage is accompanied by limited evolution of MMA while in both low and high molecular weight copolymers the high temperature process results predominantly in chain fragments. Analysis of the volatile fragments has shown the presence of anhydride groups in addition to the predicted imide rings. This may arise by the reaction of evolved H_2O with ester or amide groups to give initially acid units in the polymer chain –

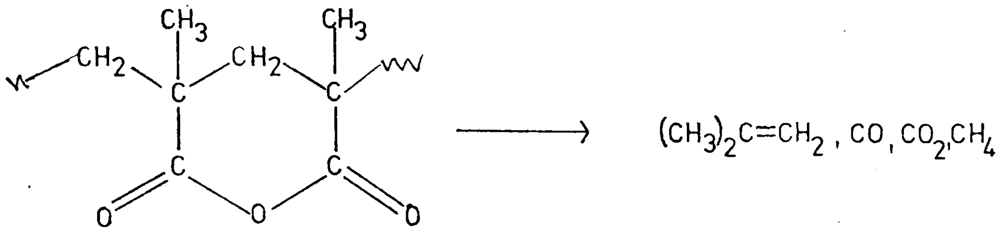


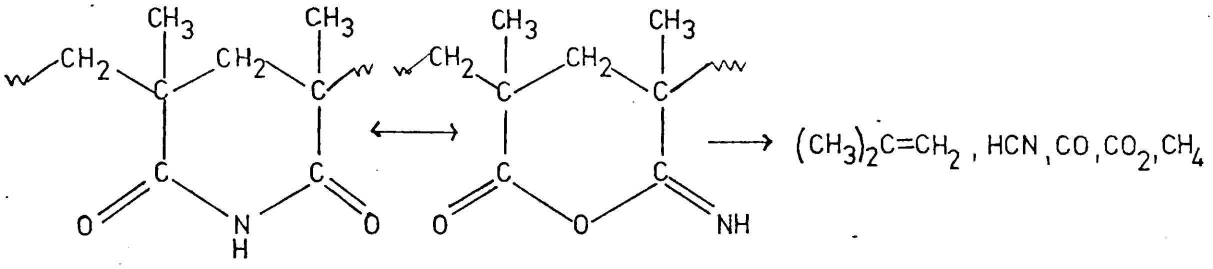
Studies of MMA-MAA copolymers have shown cyclic anhydride units to be readily found between adjacent comonomers [43,115].



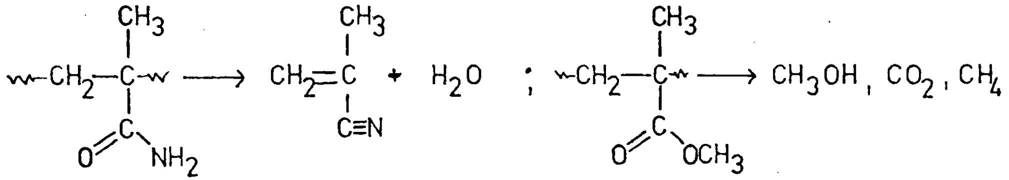
This secondary reaction may occur concurrently with imidization during the initial stage of copolymer decomposition.

The products evolved during high temperature decomposition of the stabilised residue consist mainly of low molecular weight polymer fragments together with gaseous products resulting from decomposition of cyclic structures. Thus isobutene, CO, CO_2, CH_4 and HCN may arise from anhydride and imide units –





In addition, both MAN and CH_3OH can be derived from decomposition of MAM and MMA units trapped between cyclized segments of the polymer chain



The C.R.F. yield in each of the high molecular weight copolymers was similar and may, therefore, explain the observed variation in NH_3 and HCN evolution throughout the composition range. Thus HCN evolution is dependent upon the relative content of cyclised imide groups in the residual copolymer. This is effectively reduced in low MAM copolymers once a higher proportion of the cyclized units are removed in the form of chain fragments and, therefore, do not undergo further decomposition.

The effect of incorporation of small amounts of MAM in PMMA can, therefore, be summarized as -

(1) An enhanced stability of the copolymer as measured by weight loss data.

(2) A reduction in MMA yield.

(3) The evolution of chain fragments and gaseous products which are not normally observed in PMMA decomposition.

CHAPTER 8

GENERAL CONCLUSIONS

The results of the present study may be summarized as follows:-

1. The principal interactions in both polyacrylonitrile and polymethacrylonitrile blends may be attributed to secondary reactions occurring by the diffusion of small molecular decomposition products.

2. Evidence exists for the occurrence of intermolecular hydrogen transfer between the component polymers in polyacrylonitrile blends containing polystyrene and polymethylacrylate.

3. The thermal decomposition of polyacrylonitrile may be modified by blending with chlorinated polymers.

4. The decomposition of polymethacrylon trile is found to be initiator dependent and may be related to the existance of branch points within the polymer molecule.

5. Copolymerization of methacrylamide with methylmethacrylate stabilizes polymethylmethacrylate decomposition and concurrently reduces the methylmethacrylate monomer yield.

SUGGESTIONS FOR FUTURE WORK

A feature common to most polymer blends is the incompatibility of chemically dissimilar polymers. In the present study interpretation of the thermal decomposition of such systems has relied to a great extent upon the diffusion of small molecular species between polymer micelles. It may, therefore, be of interest to examine also the decomposition of polymer systems employing block or graft copolymers as a means of reducing the inherent incompatibility of polymer mixtures.

The anomalous behaviour of polymethacrylonitrile prepared using azo bis isobutyronitrile requires further investigation. This may be best approached by the use of ^{14}C labelled initiator. The existence of chain branching and the extent of its occurrence may then be determined through a knowledge of polymer molecular weight and isotope dilution.

A corollary of the postulated mechanism of polymerization of polymethacrylonitrile is that the addition of azo bis isobutyronitrile to a solution of polymethacrylonitrile in a vinyl monomer may result in the formation of graft copolymers.

APPENDIX 1

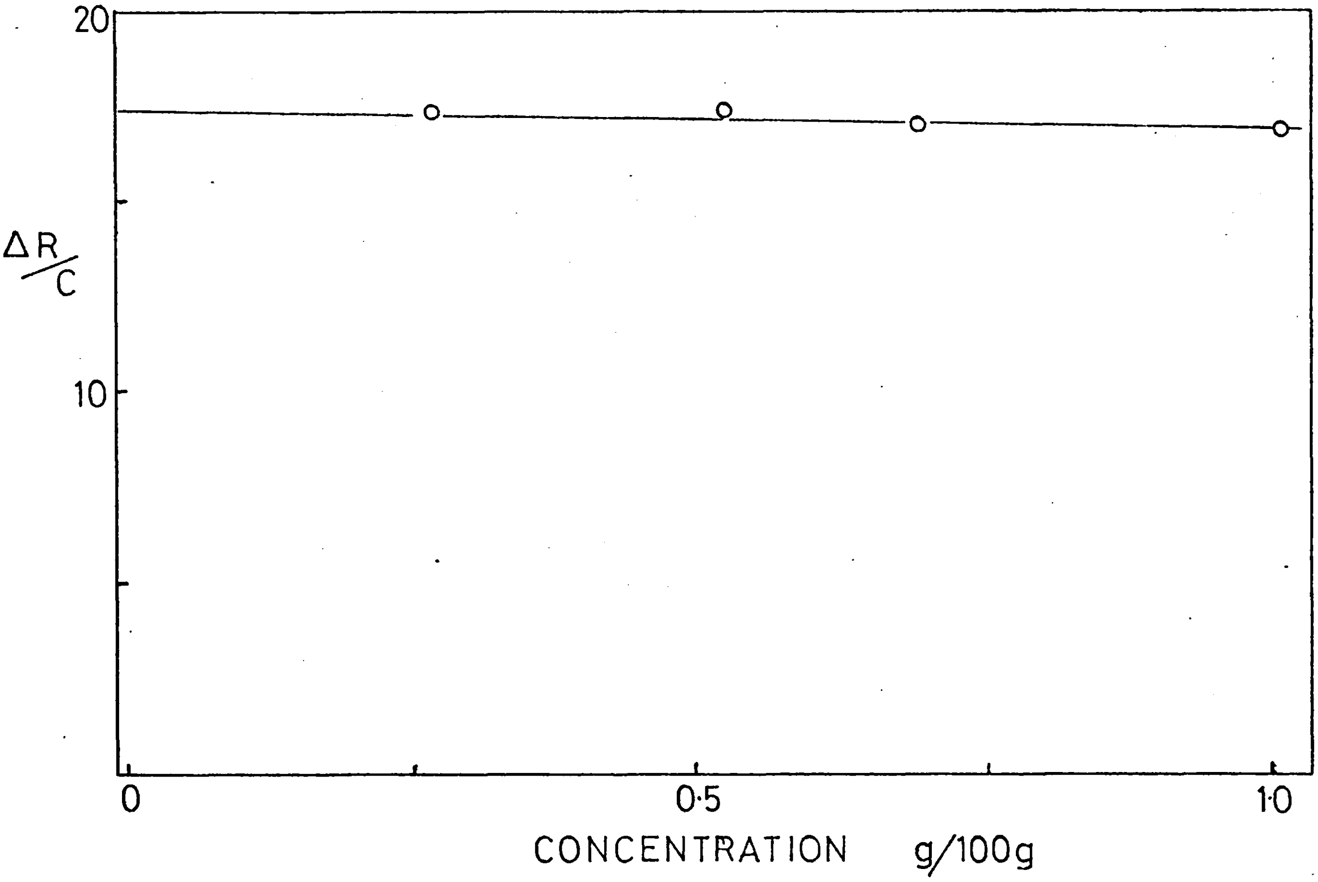
VAPOUR PRESSURE OSMOMETRY

BENZIL CALIBRATION

SOLVENT ACETONE

TEMPERATURE 37°C

TIME INTERVAL 3 minutes



$$\Delta R/C_{(C \to 0)} = 17{\cdot}2$$

$$K = Mn.\Delta R/C_{(C \to 0)} = 3615$$

APPENDIX 2

GPC OPERATING VARIABLES

COLUMNS	4 COLUMNS 100 - 350 Å 700 - 2000 Å $5x10^3-1.5x10^4$ Å $7x10^5-5x10^6$ Å
FLOW RATE	1 ml/minute
SOLVENT	Tetrahydrofuran plus 0.1%, 2.6, di-tert. butyl p cresol as inhibitor
TEMPERATURE	Ambient
CALIBRATION	Mark Houwink constants ($[\eta]=KM^a$) used for conversion of calibration - Polystyrene K = $1.2x10^{-4}$, a = 0.71 Polymethyl methacrylate K = $1.28x10^{-4}$, a = 0.71

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