

THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

THERMAL DEGRADATION OF SOME VINYL CHLORIDE COPOLYMERS

By

Thomas Straiton, B.Sc., (Glasgow)

Supervisor:

Dr. I.C. McNeill

Chemistry Department

University of Glasgow

February, 1974

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P R E F A C E

The work described in this thesis was carried out during the period October 1970 to September 1973 at the University of Glasgow in the Department of Physical Chemistry, which is under the supervision of Professor G.A. Sim.

I am indebted primarily to the Science Research Council for the award of a Research Studentship and to my supervisor Dr. I.C. McNeill, for his advice and constant encouragement. In addition, my thanks are due to Dr. B. Dodson, notably for his co-operation in the chlorine - 36 labelling studies and to Dr. A. Scotney for his helpful advice.

Finally, I would like to thank Messrs. J. Gorman and R. Ferrie for their technical assistance and all members of the Polymer Group for their tolerance and good humour.

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CHAPTER ONE

POLYMER DEGRADATION

Polymers in everyday use are subjected to a variety of modifying influences, some or all of which may be in operation at any time, depending on the particular environment and application of the material. These influences include the action of heat, light (and other high energy radiation), mechanical stresses, atmosphere, chemicals and bacteria.

In classical chemical usage, the term "degradation" implies a breaking down in chemical structure and in polymer chemistry this would be equivalent to a fall in molecular weight. However, polymer degradation is now generally regarded as any deterioration of those properties which make the material commercially useful as a plastic, rubber or fibre. A decrease in molecular weight is not always involved.

Quite often, the loss of one useful property may lead to the development of another, so that degradation can be used to extend the applications of the polymer. Because of this, the term "degradation" will be used in its broadest sense to cover all chemical reactions of polymers.

The usual approach to the understanding of polymer degradation is to study each modifying agency separately and then try to deduce their combined effect. Clearly this approach has many shortcomings and is only adopted for ease of study.

This work deals with the thermal degradation of vinyl-type polymers of general structure $(\text{CH}_2 - \text{CXY})_n$, where \underline{X} and \underline{Y} are either \underline{H} or some functional group.

THE REASONS FOR STUDYING THERMAL DEGRADATION

From a scientific point of view, thermal degradation studies help to elucidate macromolecular structure, such as the sequence and arrangement of the repeat units and side-groups in the polymer or copolymer chain, as well as the nature of the chain-ends and of the crosslinks between chains. Such studies also throw light on the strengths of the various bonds within the macromolecule, on the kinetics of degradation reactions, on the effects of time, temperature, pressure, and other variables on rates and products of degradation.

From a practical point of view, thermal degradation studies are important in that they can explain the behaviour of polymers under conditions of high temperature and, after a precise knowledge of the degradation mechanism has been obtained, existing polymers can be stabilised in a logical way and new polymers "tailored" to meet new or existing requirements.

THE MECHANISMS OF THERMAL DEGRADATION

The thermal degradation mechanisms of polymers fall into 2 distinct categories:

- (1) Chain-scission reactions.
- (2) Substituent reactions.

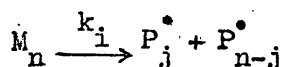
Chain-scission reactions involve rupture of the main backbone of the polymer molecule. The products at any intermediate stage of the reaction are similar to the parent material in the sense that the monomer units are still distinguishable in the chains. New types of end-groups may or may not appear, depending upon the nature of the chain-scission process.

Substituent reactions involve modification or total elimination of the substituents attached to the polymer backbone. The latter is not broken, but the chemical nature of the repeating unit in the macromolecule is changed. Any volatile products are chemically unlike monomer.

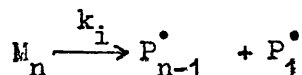
CHAIN SCISSION REACTIONS

These proceed by a free radical chain process. Initiation, which is the splitting of the chain to form radicals, may occur at chain-ends, at impurities in the chain structure, or at random along the length of the chain. Monomer may then be produced in a depropagation process, which is simply the reverse of propagation in the polymerisation reaction. Transfer reactions may occur in competition with depropagation and these involve attack by a long-chain radical on another polymer chain (intermolecular) or on itself (intramolecular); they give rise to fragments larger than monomer and to chain scission. Free radicals are finally removed from the system in a termination step which may involve combination or disproportionation. Simha, Wall and Blatz⁽¹⁻⁴⁾ showed that the total mechanism may be represented as follows:-

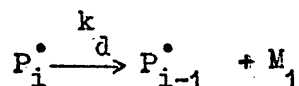
Random Initiation:



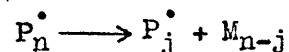
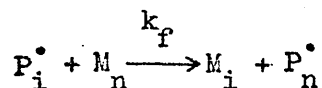
Chain-end Initiation:



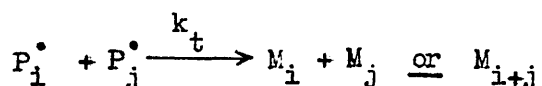
Depropagation:



Transfer:



Termination:



where n is the chain length of the starting material and M_i, M_j , etc. and P_i^\bullet, P_j^\bullet etc. represent, respectively, dead polymer molecules and long-chain radicals, i/j etc. monomer units in length.

It was also shown that although chain-scission reactions can generally be accounted for in terms of this single mechanism, distinct behaviours are observed in different polymers due to variations in the relative importance of depropagation and transfer. When depropagation predominates, the molecular weight tends to be maintained, since whole molecules are being rapidly removed from the system. High yields of monomer are produced and the rate of volatilization decreases throughout the reaction when the polymer is heated isothermally under vacuum. Poly(methyl methacrylate), PMMA, behaves in this fashion, giving a 100% yield of monomer. (5)

If intermolecular transfer is the predominant reaction, the outcome will be a rapid decrease in molecular weight. The overall process approximates closely to the situation in which the polymer chains are being randomly broken and the rate of volatilization now passes through a maximum. A continuous spectrum of products of various chain-lengths is produced, the shorter fragments being volatile at the reaction temperature. The yield of monomer is very low.

Intramolecular transfer, on the other hand, has no drastic effect on molecular weight, since only very short chain fragments are produced. In degradations where intramolecular transfer is predominant, no rate maximum is observed. Linear polyethylene exhibits behaviour typical of intermolecular transfer during degradation, while branched polyethylene appears to undergo intramolecular transfer. (6)

Clearly, the mode of chain-scission is determined by the chemical structure of the polymer molecule.

THE EFFECT OF POLYMER STRUCTURE ON CHAIN SCISSION

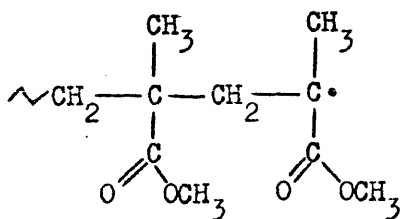
The relative importance of depropagation and transfer depends basically on the two following factors:-

- (i) The reactivity of the degrading polymer radical.
- (ii) The availability of reactive atoms (usually H atoms) in the polymer molecule.

Both factors are clearly dependent upon polymer structure.

If a polymer radical is relatively unreactive or if the free electron is shielded by bulky substituents, the radical will tend to depropagate rather than abstract neighbouring atoms, especially when the latter are relatively unreactive and sterically hindered themselves.

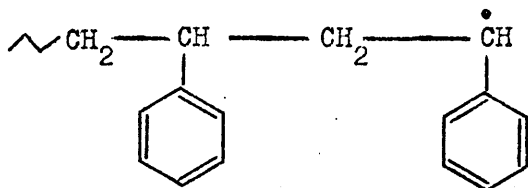
Unreactive radicals are generally those which are stabilized by resonance or by a high degree of substitution. A typical example is PMMA:-



Here the degrading radical is tri-substituted and additional stabilization results from delocalization of the free electron into the double bond of the α -carbonyl group. In addition, none of the H atoms in the polymer molecule are particularly reactive — the secondary H atoms, which are the most likely candidates for abstraction, are sterically unavailable.

Consequently, PMMA depropagates to the complete exclusion of transfer and this behaviour is typical generally of the polymers of 1,1-disubstituted vinyl monomers.

In polystyrene degradation, (7) transfer and depropagation are equally important, since although the polymer radicals are resonance-stabilized by the adjacent benzene rings, they are only disubstituted and can easily abstract the highly reactive (and relatively unhindered) α H atoms of the polymer molecules:-



Replacement of these atoms with deuterium results in an increase in the yield of monomer from 42 to 70% at the expense of the larger fragments.

SUBSTITUENT REACTIONS

For chain-scission reactions, it has been noted how the nature of the substituents can greatly influence the preferred course of the reaction, without actually changing the basic free-radical mechanism. Substituent reactions differ in that the basic mechanism of degradation depends largely on the chemical nature of the pendant functional groups. Free-radical, molecular or ionic processes may be involved.

Substituent reactions can only occur when their initiation temperature is below that required for backbone scission. Even the

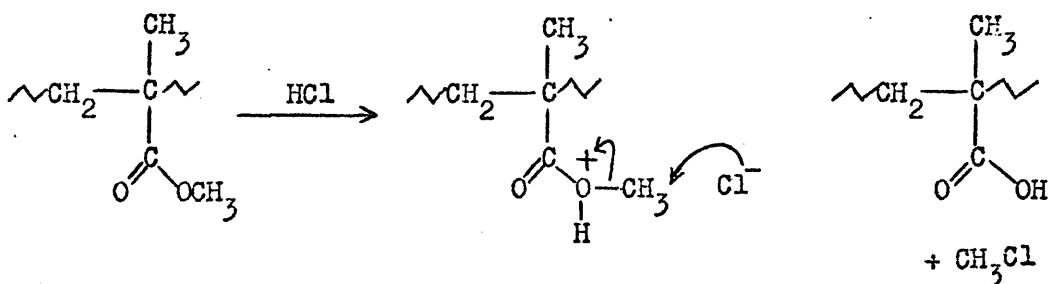
most structurally favoured chain-scission processes seldom occur below 200°C and substituent reactions, if they can occur at all, are often well advanced at this temperature.

The most unifying feature of substituent reactions is the modification of the repeat unit in the polymer chain and the type of substituent reaction involved is determined by the way in which this change comes about:-

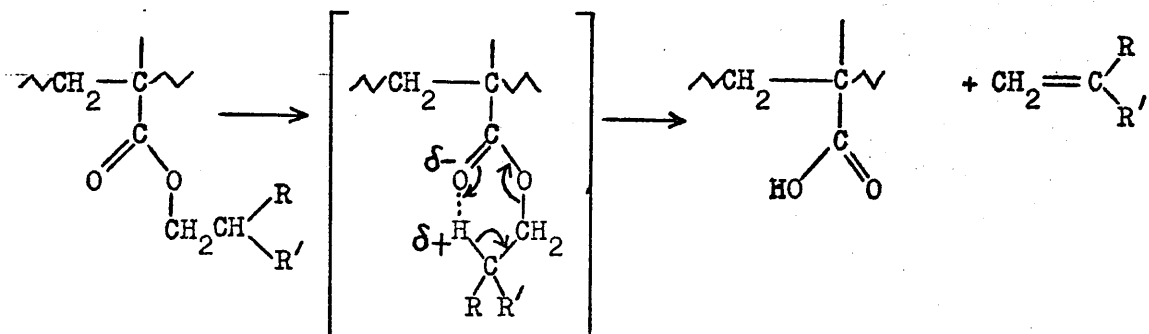
TYPE A: The repeat unit is changed as a result of product-modification or self-modification of the substituents.

TYPE B: The repeat unit is changed by chemical reaction between neighbouring functional groups or atoms.

An example of modification of the substituents by the degradation products is the reaction of gaseous HCl (from the degradation of vinyl chloride, VC, sequences) with the pendant ester groups in PVC-PMMA blends (8) and VC-MMA copolymers. (9) The mechanism is probably ionic. Methyl chloride is produced and carboxylic acid units are left in the residue:-



Self-modification of a substituent is typified by ester decomposition reactions of the type:-

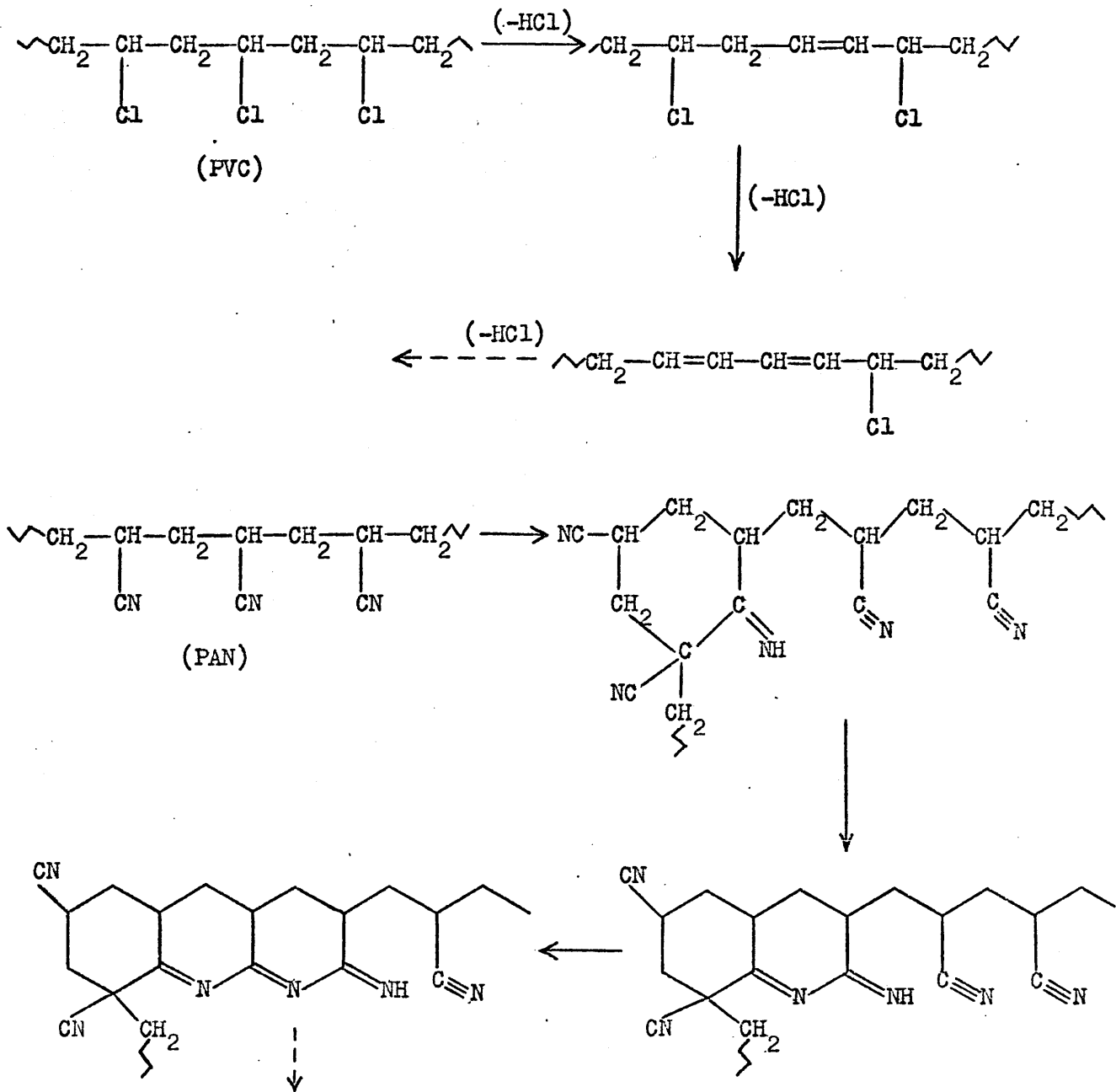


(-R, -R' \equiv -ALKYL, -H)

One example of this is the thermal degradation of poly(t-butyl methacrylate) ⁽¹⁰⁾ which gives rise to isobutene and poly(methacrylic acid). A concerted molecular mechanism, proceeding via a 6 - membered cyclic transition-state is believed to be involved.

TYPE B reactions are much more common and are particularly significant in the present work. The neighbouring functional groups or atoms, between which reaction takes place, may be vicinal or separated by three or more carbon atoms. In the latter instance, the interaction leads to the formation of cyclic structures in the polymer chain.

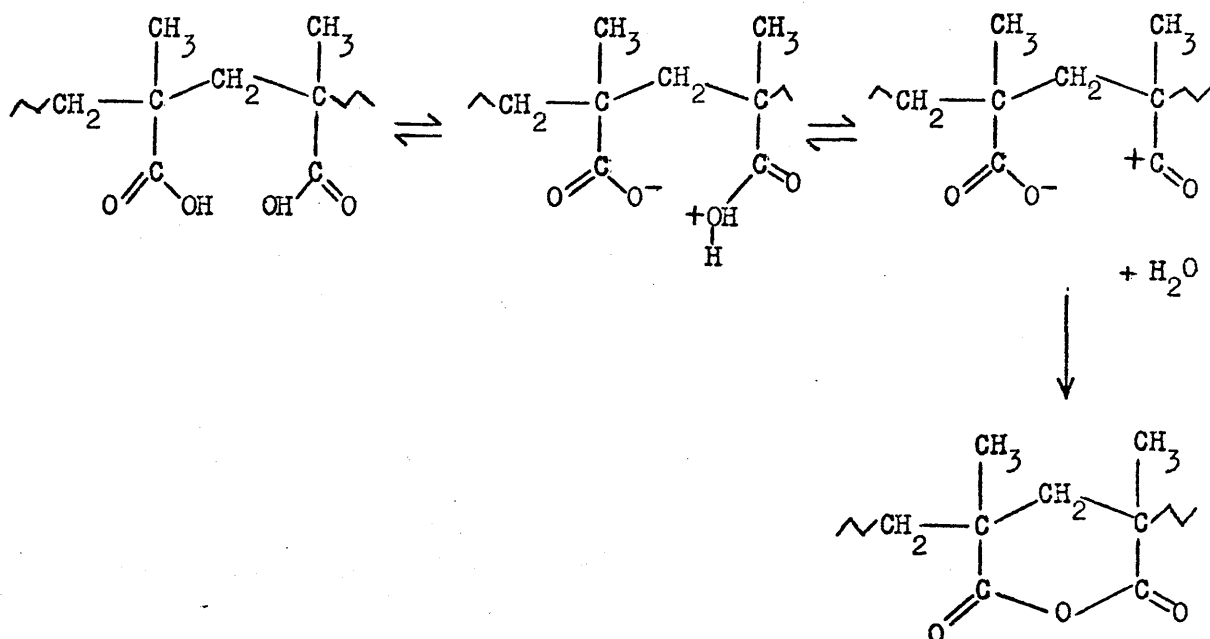
In some cases, type B reactions are chain-like in character, with several pairs of substituents being involved in succession along particular segments of the polymer chain. Common examples of this are the thermal colouration reactions of PVC ⁽⁴⁹⁾ and poly(acrylonitrile) ^(11, 12) :-



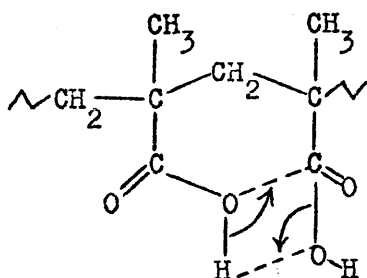
In PVC, colouration of the polymer arises by a progressive build-up in polyene sequences along the backbone, due to elimination of HCl. This reaction will be discussed in greater depth later. Colouration in PAN is probably due to stepwise polymerisation of the nitrile groups as shown; no elimination is involved.

It is still uncertain whether these processes are molecular, ionic or free-radical in character.

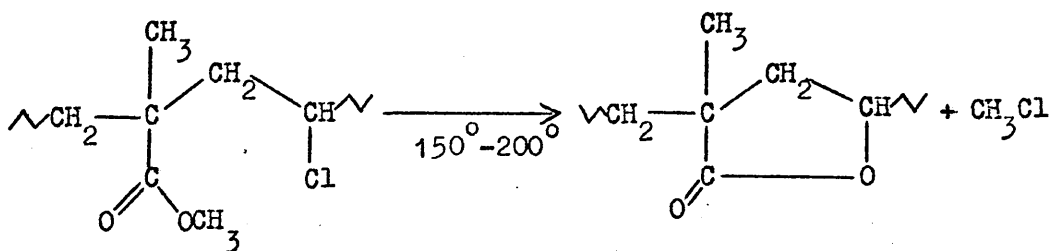
Other type B substituent reactions involve interaction between randomly selected pairs of neighbouring substituents on the polymer molecule. If cyclization occurs, its extent can be predicted by statistical considerations, both for homopolymers and copolymers. One example of this is the thermal dehydration of poly(methacrylic acid) ⁽¹³⁾ which is believed to be mechanistically similar to an acid-catalysed esterification:-



i.e., the reaction passes through the following transition-state:-



Another reaction in this category is the thermal lactonization which occurs in copolymers of vinyl halides with esters of methacrylic and acrylic acids. A typical reaction occurs during the thermal degradation of vinyl chloride-methyl methacrylate copolymers:- (14)



Methyl chloride elimination accompanies the cyclization and the amount evolved can be predicted statistically if the copolymer composition is known.⁽¹⁵⁾ However, the exact nature of the mechanism involved is uncertain. This particular system will be discussed more fully in Chapter III.

GENERAL ASPECTS OF THE THERMAL DEGRADATION MECHANISMS OF POLYMERS

Attempts to correlate the thermal breakdown of polymers with low molecular weight model compounds have been largely unsuccessful. The unique nature of macromolecular structure allows intimate contact between reactive sites and potentially reactive ones, so that the possibilities for reactions involving chain mechanisms are much enhanced. The "reactive sites" in polymers are usually chain impurity structures such as unsaturation, chain branches, head-to-head or tail-to-tail units, initiator fragments or oxygenated structures. These will be absent in the low molecular weight counterparts, which consequently show higher thermal stability.

More sophisticated models, incorporating one or other of these abnormal structures, have provided some information on their relative importance in initiating degradation. Samples of the same polymer prepared under different conditions will generally show somewhat different thermal behaviours due to variations in the relative abundance of the important impurities.

The physical properties of a copolymer are generally quite distinct from those of the corresponding homopolymers and this is also true of degradation behaviour. In random copolymers, sequences of like units in the polymer chain will often degrade to give the same products as they would generate in the homopolymer. However, the method of initiation may be quite different, leading to breakdown at temperatures lower or higher than those found in the homopolymers. In addition, other reactions, which are absent from the homopolymer degradations, may occur, these being mainly substituent reactions between chemically-unlike units, product-product or product-copolymer interactions.

The difficulty in assigning a particular mechanistic type (i.e. molecular, ionic or free-radical) to substituent reactions has already been mentioned. Organic reactions which proceed by an ionic mechanism are generally influenced by the polarity of the solvent and are often catalysed by acids and bases. Consequently, the thermal dehydrochlorination of PVC in dimethylformamide,⁽¹⁶⁾ for example, which is greatly accelerated by the presence of organic bases, is believed to proceed via charged intermediates. Ionic reactions, however, are difficult to envisage during bulk degradation unless the polymer melt is substantially polar.

Under these conditions, molecular or free-radical mechanisms seem much more plausible, but even for these, the evidence is often indirect. It is possible to detect short-lived free-radical intermediates using E.S.R. spectroscopy but the method is not easily adapted to study polymer degradation. In addition, it is possible that radicals observed by E.S.R. spectroscopy may not be true intermediates in the degradation process, e.g. the polyene sequences in partially degraded PVC can give rise to paramagnetic behaviour due to thermal excitation of electrons in the π orbitals.⁽¹⁷⁾ More often, the possibility of a radical process is deduced from the influence of free-radical initiators and inhibitors on the reaction rate or from kinetic data.

Failure to detect the existence of ionic or free-radical intermediates usually results in the mechanism being termed "molecular".

METHODS USED FOR STUDYING THERMAL DEGRADATION

In order to be able to assign a specific mechanism to a degradation process, a number of experimental results have to be obtained and correlated. These include:-

- (i) The chemical nature, quantity and rate of formation of each of the volatile products of degradation.
- (ii) The chemical nature, extent and rate of production of any new chemical structures formed within the polymer molecule.
- (iii) The rate of change of molecular weight of the residue.

Clearly the acquisition of kinetic data is of fundamental importance.

The main difficulty lies in finding a method which allows continuous monitoring of as many as possible of the above factors as the polymer degrades, while minimising complicating practical factors which obscure the true thermal behaviour of the polymer (i.e. behaviour on a molecular scale). It is impracticable to monitor concurrently all of these changes and it is therefore necessary to study each factor in turn using a range of experimental methods, some of which will inevitably entail interruption of the degradation process to allow retrieval of data.

This work involves application of methods in categories (i) and (ii) above. It should be noted that the formation of a new chemical structure in the polymer can often be studied indirectly by monitoring the volatiles evolved (e.g. many type B substituent reactions).

The method chosen for the study of volatile evolution will depend upon whether the components of the gas effluent stream are already known, whether high-vacuum conditions are required and whether the gases must be monitored continuously or collected first and analysed later. The most commonly used techniques may be listed as follows:-

Gas-phase chromatography

Mass spectrometry

Infrared spectrophotometry (including rapid-scan techniques for continuous monitoring)

Thermoparticulate analysis

Titration and other methods of chemical analysis

Selective absorption/condensation of one or more
of the components.

Torsion effusion analysis

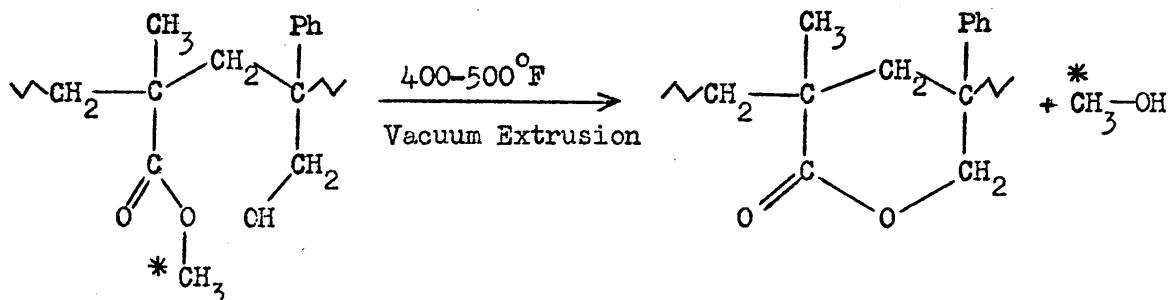
Pressure measurement, using a manometer, spoon
gauge or Pirani gauge

Most of these methods are now so generally applied as to merit no special description and they have been well reviewed by Carroll⁽¹⁸⁾ and by Lodding⁽¹⁹⁾. Thermoparticulate analysis (TPA) is a comparatively new technique for the thermal analysis of polymeric materials and is based on the photodetection of moisture condensation nuclei evolved from a polymer sample that is temperature programmed. Torsion effusion analysis has been described by Rosen and Melveger⁽²⁰⁾ in a study of the rate of volatilisation of a poly(tetrafluoroethylene) sample. When it is known that only one reaction involving the release of volatiles occurs within a specified temperature range, then other techniques such as thermogravimetric analysis (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) may be useful for obtaining further quantitative kinetic and calorimetric information about the reaction. These methods are also well reviewed by the above authors.

RADIOTRACER TECHNIQUES

The use of radiotracers in polymer chemistry has been reviewed by Bevington⁽²¹⁾. Their application to monomer reactivity ratio determination in copolymer systems will be discussed in Chapter II. In the thermal degradation field, Powell et al⁽²²⁾ have studied the thermally-induced lactonization which occurs in MMA/ α -hydroxymethylstyrene

copolymers using ^{14}C ester - labelled MMA.



The loss of activity from the polymer was studied using liquid scintillation counting of polymer solutions.

In fact, most radiotracer studies in polymer chemistry involve the monitoring of changes in the specific activity of the polymer itself, either by solution counting or occasionally (where ^{14}C is used) by oxidation to CO_2 and gas counting.⁽²³⁾ The direct monitoring of volatile evolution using radioactively-labelled polymers has not been widely used. McGuchan and McNeill used ^{36}Cl to study the isothermal degradation of chlorinated poly (isobutenes) by measuring the amounts of chlorinated volatiles (mainly HCl) evolved with time, using gas-phase Geiger-Müller counting. The specific activity of chlorine in the apparatus could be found⁽²⁵⁾ by counting a sample of chlorine gas, condensing it into a solution of potassium iodide and titrating the liberated iodine against standard sodium thiosulphate solution.

In general, radiotracer techniques can provide accurate, quantitative analysis of samples of polymer or degradation products, with the accuracy of the results limited only by the counting time available. (see Chapter II, page 25)

This must be balanced against the disadvantages of preparing labelled monomer, measuring its specific activity and observing additional safety precautions.

THERMAL VOLATILIZATION ANALYSIS (TVA)^(26,27)

Unlike the monitoring of volatiles using radiotracers, this is essentially a "physical" technique involving continuous measurement of the pressure exerted by the volatile products as they are released from the heated polymer. Degradation is conducted under high-vacuum conditions and the volatiles are continuously pumped from the sample past a Pirani gauge to a cold trap. Pirani response is recorded continuously as a function of oven temperature and gives a measure of the rate of volatilization of the sample. Discrete reactions which produce volatiles give rise to "peaks" on the TVA trace.

Unfortunately, TVA is only a semi-quantitative technique, since Pirani response is only linear with the rate of volatilization for responses up to about 1mv. At higher flow-rates, the Pirani becomes progressively less sensitive, although calibration is possible using a flow-meter. It is also found that Pirani response per unit mole is dependent on the substance distilling, so that a direct comparison of amounts of different volatile materials, even at low Pirani responses, is not possible. In addition, the peaks on a TVA trace often merge and this may obscure discrete reactions occurring in the polymer.

A useful development of the technique has been the introduction of differential condensation of products⁽²⁸⁾, based on the principle that the condensability of a substance in traps at various temperatures is

characteristic of that substance. By simple inspection of the TVA traces corresponding to traps at various temperatures, it is often possible to make useful deductions about the volatile products which are contributing to each peak, assuming that no two show the same condensability characteristics. A more comprehensive account of the practical and theoretical aspects of TVA will be given in Chapter IV.

THE AIM OF THIS WORK

The primary aim of this work is to study the thermal degradation mechanisms of random copolymers of VC with comonomers bearing pendant acid, ester, amide and carboxylate anion substituents and to compare their thermal behaviour with those of the parent homopolymers.

Although the basic technique employed in these studies has been Differential Condensation TVA, a large part of the work is devoted to the assessment of a radiochemical method using ^{36}Cl for the quantitative study of volatile evolution from VC-MMA copolymers. Radioactive assay of the copolymers has been used to calculate monomer reactivity ratios for the system, while the copolymer compositions have also been related to the relative quantities of degradation products evolved and comparison made with those predicted by statistical considerations.

Using information supplied by TVA and degradation product analysis, an attempt has been made to deduce more fully the nature of the 1,3-interactions which occur in the various copolymer systems outlined above and to establish the effect of these interactions on the general degradation characteristics of the polymers.

C H A P T E R T W O

PREPARATION AND ANALYSIS OF ³⁶Cl - LABELLED VINYL

CHLORIDE — METHYL METHACRYLATE COPOLYMERS

INTRODUCTION

In order to account for the thermal (and other) properties of a random copolymer system, a precise knowledge of copolymer compositions is first of all required. Comparison of these with the composition of the monomer mixture used to make each copolymer enables reactivity ratios to be determined for the system and these in turn can be used in statistical calculations to find the arrangement of monomer sequences in the copolymer.

If intersequence cyclization (e.g., lactonization) is possible in the copolymer, it will be most prevalent where there is a tendency towards alternation of monomer units in the chain, so that the composition of the degradation products can often be related to sequence distribution in the polymer. Thus a sequence distribution of the type —ABABBABAAAABABAAA— will give a high proportion of A - B cyclization products, whereas a copolymer having long sequences of like units, say of type A, and short sequences of type B, will show a degradation pattern more akin to that of the corresponding homopolymer, poly(A).

In the present work, an attempt has been made to relate volatile composition (obtained experimentally) to the theoretical sequence distribution predicted from empirically - determined reactivity ratios. The calculation of sequence distribution and its quantitative relation

to reaction mechanism will be more fully discussed in Chapter IV.

The most common method of determining copolymer composition is by elemental analysis. This can often be applied with a minimum of difficulty, since the procedures usually involve destruction of the polymer and solubility problems are not encountered. When attempts are made to apply chemical methods other than elemental analysis (e.g., the determination of carboxylic acid groups by titration), solubility problems are frequently serious, although suitable solvent mixtures can often be found.

Many copolymer systems lend themselves to analysis by I.R. or U.V. spectrophotometric techniques, but a major problem here is the need for standard copolymers of known composition for calibration purposes — absorptivities based on the absorbance of individual homopolymers are not always identical with those obtained from copolymers.

All the above methods of analysis are made especially difficult if the monomers are very similar or if one monomer is present in very small amounts. Use of a labelled monomer overcomes these problems since the copolymer composition can be readily determined by radioactive assay. Most of the tracer studies on copolymerization have involved ^{14}C , but ^3H and ^{36}Cl have also been used. In suitable cases, comparisons of the results from the tracer method with those from other analytical techniques have shown good agreement⁽²⁹⁾.

The use of very weak β -emitters like ^{14}C or ^3H is convenient only when liquid scintillation or proportional counting is available. ^{36}Cl has a long half-life ($t_{1/2} = 3.0 \times 10^5$ years), is a pure β -emitter with $E_{\text{max}} = 0.72$ MeV and is comparatively non-hazardous. Radiochlorine (Cl_2)

has been used by McNeill to study unsaturation in butyl rubbers⁽³⁰⁾ and by McGuchan and McNeill to estimate the much lower concentrations of unsaturated end-groups in polyisobutene prepared by cationic polymerization⁽²⁵⁾. The latter workers subsequently studied the thermal stability of chlorinated polyisobutenes containing various concentrations of chlorine labelled with ³⁶Cl. In all cases, material labelled with the isotope was found to respond well to Geiger - Muller counting in both liquid and gas phases.

Bevington and Johnson used ³⁶Cl in a study of the copolymerization of methyl methacrylate with methyl α -chloroacrylate⁽³¹⁾ and found scintillation counting in solution to be suitable for assay of ³⁶Cl in the copolymers, by comparison with results obtained using ¹⁴C-labelled methacrylate. Quenching was found to be important and varied with copolymer composition. A comparison was also made of scintillation counting and Geiger - Muller counting using a liquid-sleeve counter for ³⁶Cl. The two methods gave results in good agreement. It should be noted, however, that Geiger - Muller counting of ³⁶Cl using a liquid-sleeve counter is only about 1% efficient, while liquid scintillation counting gives about 60% efficiency, so that for measuring very low concentrations of the isotope, the latter method (if available) is to be preferred.

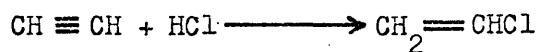
Taking these factors into account, reactivity ratios, for subsequent use in the sequence distribution calculations, could feasibly be determined for the vinyl chloride - methyl methacrylate system by the incorporation of ³⁶Cl-labelled vinyl chloride into the polymers. Equally important, the label would allow a precise analysis of chlorine-containing volatile products, by gas-phase Geiger - Muller counting, in the subsequent degradation studies.

Geiger - Muller solution counting was adopted as the method of copolymer analysis. Comparison of results obtained with labelled poly(vinyl chloride), after correction for the specific activity of the monomer used in each case, would yield copolymer compositions.

THE PREPARATION OF ^{36}Cl - LABELLED VINYL CHLORIDE (with B. Dodson)

The most convenient labelled starting material available was hydrochloric acid and two possible synthetic routes based on this were considered:-

- (1) The direct combination of acetylene with hydrogen chloride in the gas phase:-



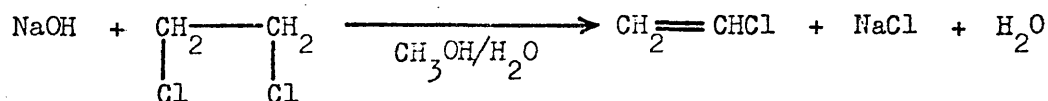
This method is used industrially and has the advantage of being a single-step process with no products other than vinyl chloride, so that there would be no loss of activity. On a laboratory scale, there remained the difficulties of generating gaseous HCl from its aqueous solution and of arranging suitable gaseous flow-rates, catalyst and temperature to give a good yield of the monomer.

- (2) The reaction of chlorine with ethylene to give 1,2-dichloroethane and subsequent dehydrochlorination of this to vinyl chloride.

Chlorine can be prepared easily from hydrochloric acid, using the method of Brown, Gillies and Stevens⁽³²⁾:-

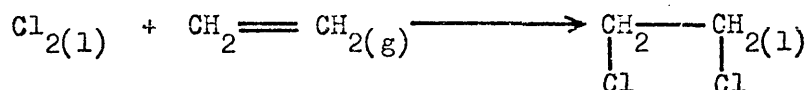


while the dehydrochlorination of 1,2-dichloroethane can be achieved by the method of Baxter⁽³³⁾:-



The controlled reaction of chlorine and ethylene in dichloroethane and in presence of a catalyst is used industrially in the manufacture of vinyl chloride. On a laboratory scale, chlorination of alkenes can often be carried out by passing the alkene through a solution of chlorine in carbon tetrachloride. However, this method was unsuitable for the preparation of 1,2-dichloroethane, due to the difficulty of separating product from solvent (boiling points 83.7°C and 76.7°C respectively). Several other solvents (e.g. ether) were tried, but none was found satisfactory. A major problem was the displacement of dissolved chlorine by ethylene.

The best method was found to be the passage of ethylene gas through liquid chlorine. At -80°C , 1,2-dichloroethane of high purity (boiling point and I.R. analysis) was obtained in good yield and this method was adopted as the middle step in the synthesis. i.e.,



Experimental Procedure

2 M aqueous hydrochloric acid with specific activity 42 $\mu\text{Ci/ml}$. (Radiochemical Centre, Amersham) was diluted with inactive hydrochloric acid to 0.5 M and specific activity 2 $\mu\text{Ci/ml}$. Potassium persulphate (35g.) was then heated with the 0.5 M acid (200ml.) to $75-80^{\circ}\text{C}$ in a stream of nitrogen. The chlorine produced was first bubbled through water to remove unreacted acid, then dried by passage through concentrated H_2SO_4 . The gas was finally passed through cotton wool to remove any acid spray and collected by condensation at -90°C , the collection vessel being protected by a calcium chloride drying tube.

When chlorine evolution had ceased, ethylene (B.O.C., Ltd.) was gently bubbled through the liquid chlorine at -80°C to produce 1,2-dichloroethane (3.5g; 70%). When the yellow colour had disappeared, the coolant was removed to prevent freezing of the dichloroethane and the ethylene flow was continued for a short time to ensure complete reaction of any dissolved chlorine.

The addition of inactive dichloroethane at this stage can be conveniently used to control the specific activity of the vinyl chloride ultimately obtained. In the present case, a forty-fold dilution with inactive material was made and the dichloroethane was then purified by washing with dilute, aqueous KOH, then with water, drying over calcium chloride and distilling. The fraction with boiling point 84°C . was retained.

This was used to prepare vinyl chloride by the method outlined on p. 22. 1,2-dichloroethane (100g.) was added dropwise to a stirred 1:1 mixture of methanol and 50% W/W aqueous NaOH at 60°C . Water and methanol were removed from the vinyl chloride by passing the gas up through a water condenser and then through a trap cooled to -12°C . Vinyl chloride (50g; 80%) was collected at -70°C in a double-walled glass vessel, the latter being used to minimise the risk of any radioactive hazard/contamination by insulating the inner tube from thermal shock.

The collection vessel was transferred to the vacuum line and the vinyl chloride degassed by successive freezing and thawing. The monomer was then distilled into a stainless steel bomb (Hoke Ltd.) for storage.

Radioactive sodium chloride by-product, which contained half of

the original activity used in the last part of the synthesis, was retained for subsequent treatment.

THE ALLOCATION OF AVAILABLE RADIOACTIVITY TO HOMOPOLYMER AND COPOLYMERS

If a series of activity readings is taken from a "fixed mass" of radioactive sample and these take the values $n_1, n_2, n_3, \dots, n_N$ counts/minute, then the average count-rate is clearly given by $\frac{n_1 + n_2 + n_3 + \dots + n_N}{N}$ counts/minute. From the frequency distribution curve obtained when $N \rightarrow \infty$, it can be shown⁽³⁴⁾ that there is a 68% chance that any measured count rate, \underline{n} , will lie within the limits $\pm \sqrt{n}$ of the true average value, a 95% chance that it will lie within $\pm 2\sqrt{n}$ of this value, and so on, where $\sqrt{n} = \sigma$ is the standard deviation on any given measurement.

This can be extended to the case where only one measurement is recorded for each sample. For example, if a sample gives a measured activity of 10,000 counts/minute, then there is a 95% chance that the true average value will lie within ± 200 counts/minute of this figure — that is, we must quote a possible error of $\pm 2\%$ on a count rate of the order of 10,000 c.p.m. Less active samples will require to be counted until 10,000 counts are registered to give an error on the count rate of $\pm 2\%$.

Thus for a reasonable level of accuracy at practicable counting times in the subsequent assay of samples of polymer or degradation products, copolymers having low chlorine contents will clearly have to incorporate the highest possible specific activity.

A range of copolymer compositions, which would allow a good

graphical determination of monomer reactivity ratios by the Fineman - Ross method and also provide the most useful data in thermal degradation studies, was chosen, ranging from 10 to 90% (molar) VC*. The weight of VC required to prepare 2 g. of 10% VC* copolymer was calculated from monomer reactivity ratios obtained by Tkachenko et al.⁽³⁵⁾ for the solution polymerization at 45°C. and the crude, labelled 1,2-dichloroethane, obtained in the second stage of the VC* synthesis, was diluted to the appropriate extent before dehydrochlorination, allowing for losses incurred during purification and the percentage yield of VC obtained with inactive material. Copolymers of increasing VC* content, and finally PVC*, were made by successively diluting the monomer retrieved from the previous polymerization with inactive material.

ALTERNATIVE METHOD FOR ALLOCATION OF AVAILABLE RADIOACTIVITY

The total available radioactivity can be divided up at the dichloroethane stage, followed by separate syntheses of VC* for use in each copolymer and this method has the advantage of allowing easy and accurate determination of the specific activity of each batch of vinyl chloride by liquid counting of the dichloroethane. Unfortunately, the method does not allow incorporation of the highest possible activity into the low VC content copolymers where it is most needed. Consequently, it was necessary to devise a procedure for the direct measurement of the specific activity of vinyl chloride.

DETERMINATION OF THE SPECIFIC ACTIVITY OF GASEOUS VINYL CHLORIDE

The method adopted was to transfer a known fixed volume of gas at a measured temperature and pressure into a Geiger - Muller counter and monitor the activity of the sample. Quantitative transfer of the vinyl

chloride was achieved by distillation from a manometer into the counter under conditions of high vacuum and the resulting pressure in the counting volume was of the order of half an atmosphere.

The method assumes that vinyl chloride behaves as an ideal gas under the experimental conditions used. i.e., $n = PV/RT$, where n is the number of moles of gas, P the pressure, V the volume, T the absolute temperature and R is the General Gas Constant. The following experiment showed that this was a reasonable approximation to the true behaviour:-

Different pressures of VC* of a fixed specific activity and at a fixed volume and temperature were transferred to the counter and a relationship between counts/minute and gas pressure was obtained graphically (see Fig. 1 ,p. 28). A good approximation to linearity is obtained and, assuming that the number of counts observed is proportional to the number of moles of gas present, then the specific activity of the VC* can be expressed as follows:-

$$\text{specific activity} = \frac{\text{counts/min. (corrected)}}{PV/RT}$$

(c.p.m./mole)

The layout of the manometer and gas counting system is shown in Fig. 2 ,p. 29. The exact volume of the bulb, V , had been determined previously and the temperature of the gas being transferred to the counter was measured by the thermometer, T . The counting zone comprised the volume enclosed by S_1 and S_3 , with S_2 open and a "vacuostat" pressure gauge was connected to the counting zone via S_1 . The Geiger - Muller tube was a modified halogen-quenched liquid-sleeve

COUNTS/MIN.

Fig.1

ACTIVITY OF VC* IN COUNTER
VERSUS PRESSURE OF GAS
TRANSFERRED FROM MANOMER

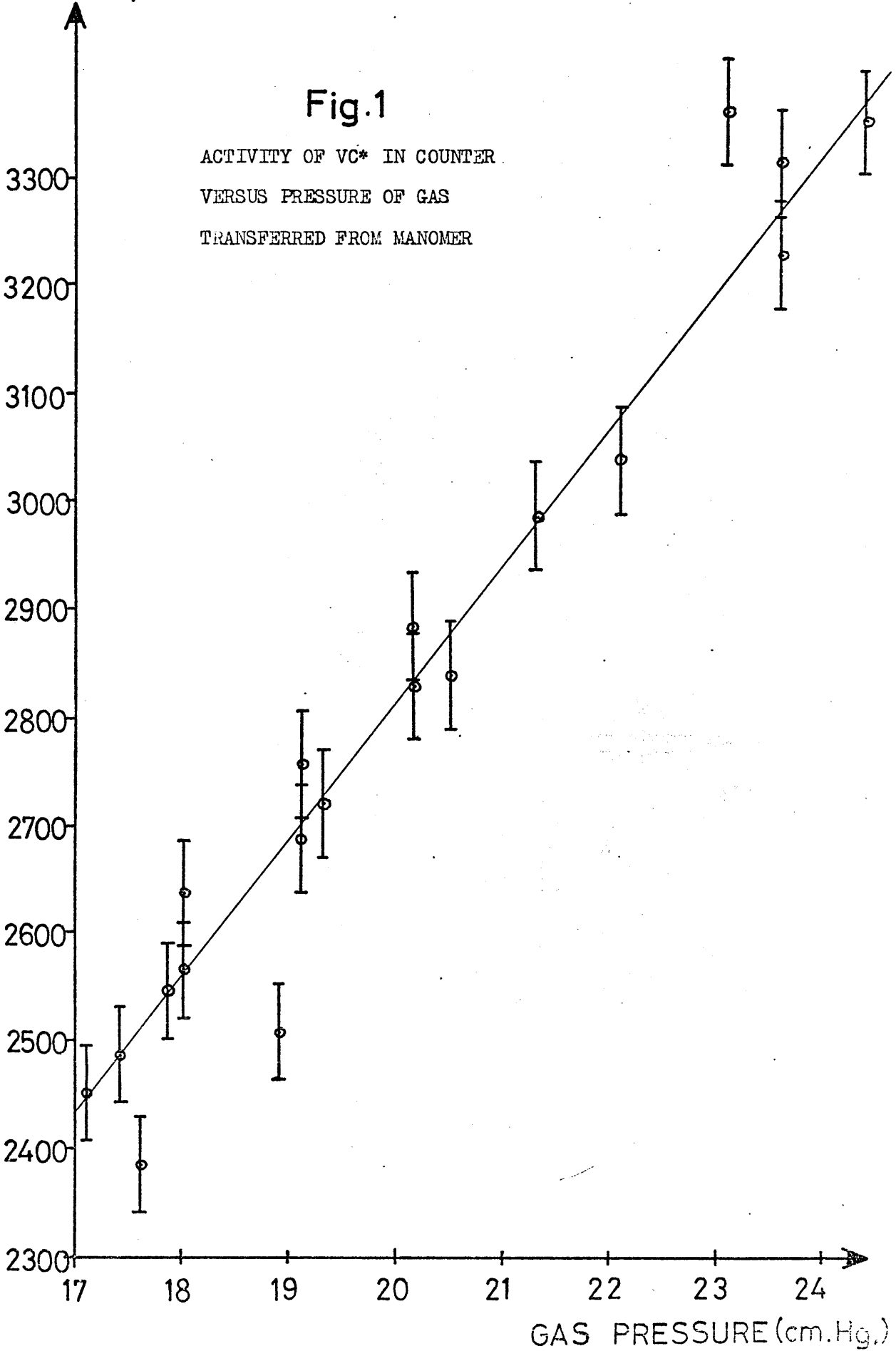
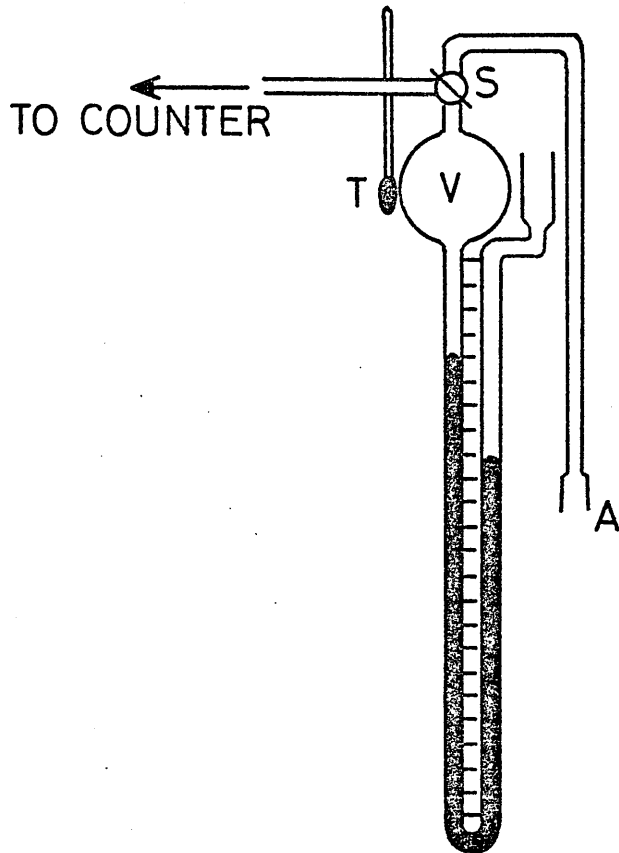
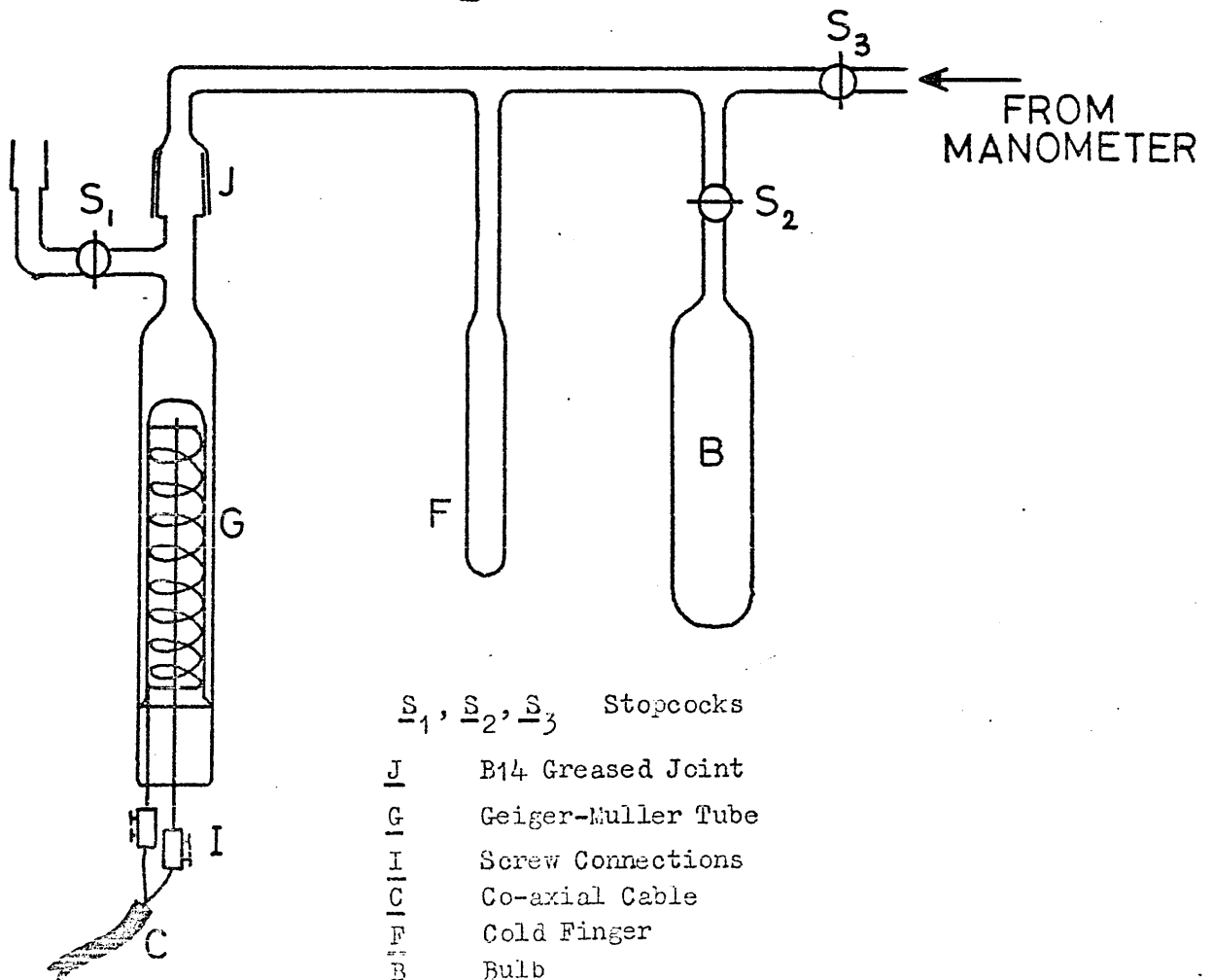


Fig.2

MEASUREMENT OF SPECIFIC ACTIVITY OF VINYL CHLORIDE



- S Three-way Stopcock
- T Thermometer
- V Bulb, Volume = 572.5 CM³
- A VC* Reservoir attached here



- S₁, S₂, S₃ Stopcocks
- J B14 Greased Joint
- G Geiger-Muller Tube
- I Screw Connections
- C Co-axial Cable
- F Cold Finger
- B Bulb

type (Mullard Ltd., type MX 124/01) operating at 375 volts and used in conjunction with a Bendix - Ericsson Ltd. type 110A probe unit and Ekco Electronics Ltd. type N529D scaler.

After the VC* had been thoroughly degassed, the double-walled tube (which was closed by a stopcock) was attached to the manometer at A and the whole system was pumped down to give a "sticky" vacuum on the vacuostat. A background count was taken for one hour and atmospheric pressure was then read from the manometer. S was closed to the pumps and opened to A and V and about 20cm. Hg of VC* was fed into the manometer. After the gas pressure and temperature had been noted, the manometer-counter connection was isolated from the pumps and S was closed to A and opened to V and the counter, enabling a known amount of gas to be transferred to the counting zone by cooling F to -196°C . The pressure reading on the manometer returned to "atmospheric". S₁ and S₃ were then closed and the gas was allowed to warm to ambient temperature before counting. The gas was counted for 15 minutes (correction being made for counter dead-time and background) and subsequently distilled back into its container.

POLYMERIZATION PROCEDURE

Methyl methacrylate (Hopkin and Williams, Ltd.) was freed from inhibitor by washing with dilute aqueous alkali, followed by distilled water, separated and dried over anhydrous calcium chloride. Benzoyl peroxide initiator was purified by recrystallization — a saturated solution in chloroform was filtered and added dropwise to a small volume of methanol. Crystals of benzoyl peroxide separated out, were filtered off and dried under vacuum.

0.35% (W/V) of benzoyl peroxide was introduced in acetone solution into a 100ml. dilatometer, fitted with a Quickfit Teflon TF2/18 tap and B14 cone, and the solvent was pumped off on the vacuum line. With the tap closed, the dilatometer was then weighed on an analytical balance. ^{36}Cl vinyl chloride of known specific activity was degassed six times in the double-walled reservoir and the appropriate volume distilled at -75°C . into the dilatometer, which was then reweighed. A calculated volume of methyl methacrylate (MMA) was then distilled at ambient temperature into the dilatometer after thorough degassing. (The volumes of VC* and MMA monomer used for a given copolymer composition allowed for thermal expansion to 45°C . and measured coefficients of cubical expansion of 0.00238 and 0.000160 $(^{\circ}\text{C})^{-1}$ were used for VC and MMA respectively). The dilatometer was reweighed and then immersed in a thermostat bath at $45(\pm 0.005)^{\circ}\text{C}$. All of the copolymers were taken to about 2% conversion, while PVC* homopolymer was taken to about 8%. Polymerization was stopped by cooling in liquid nitrogen.

Vinyl chloride monomer was recovered after each polymerization by distillation from the dilatometer at -75°C — MMA is a solid at this temperature. The residual mixture was dissolved in redistilled tetrahydrofuran and the polymer precipitated in Analar methanol. The polymers were filtered off, dried and weighed and then twice reprecipitated. They were dried in a vacuum oven at 50°C . for several days and finally stored in a dessicator.

Labelled vinyl chloride for subsequent polymerizations was diluted with inactive material (B.D.H. Ltd.), which was first degassed then distilled into a reservoir of active material at -75°C to give the required volume.

MOLECULAR WEIGHT DETERMINATIONS

Solutions of the polymers in cyclohexanone were run on a Hewlett-Packard model 501 membrane osmometer. The results are shown in Table II, P. 34.

ASSAY OF POLYMER SOLUTIONS

A Mullard MX 124/01 liquid-sleeve Geiger - Muller tube was fitted with a Quickfit B19 socket and ground glass stopper. Operating at 390 volts and enclosed in a lead castle, the counter was used in conjunction with the same probe unit and scaler as before. Solutions were made up with redistilled tetrahydrofuran and these contained 0.01g. of polymer/ml. After a solvent background had been taken, 10.0ml. of polymer solution was assayed and the mean of six consecutive readings taken, correction being made for counter dead-time and background. The counting tube was decontaminated after each experiment by washing with tetrahydrofuran and chromic acid.

Unlike the quenching effect observed in liquid scintillation counting, which varies not only with sample weight but with copolymer composition⁽³¹⁾, self-absorption by a dilute polymer solution assayed by the Geiger - Muller method does not appear to vary significantly from polymer to polymer. A simple model system was studied in which the assay of a 1:1 (W/W) mixture of ³⁶Cl PVC and inactive PVC in tetrahydrofuran solution was compared with that of a 1:1 (W/W) mixture of ³⁶Cl PVC and PMMA in the same solvent, the same weight of ³⁶Cl PVC being used each time. The specific activities (corrected counts/min./ml.) of the solutions were equal within the limits of experimental error for solutions of the same concentration as were used in assay of the copolymers.

ESTIMATION OF THE CHLORINE CONTENT OF THE COPOLYMERS

From the results obtained for labelled PVC, the following relationship was worked out:-

$$\frac{\text{molar specific activity of } ^{36}\text{Cl in polymer solution (counter I)}}{\text{molar specific activity of } ^{36}\text{Cl in gas phase (counter II)}}$$

Counters I and II refer to those used for solution and gas-phase counting respectively.

If the specific activity of ^{36}Cl vinyl chloride used to make a copolymer is measured in the gas phase, then the activity/mole of Cl in the copolymer can be predicted using the above conversion factor. By measurement of the specific activity of the copolymer solution, the number of moles of Cl in a known weight of polymer can be determined.

RESULTS AND DISCUSSION

Details of the polymerization conditions and polymer analyses are given in Tables I and II. Errors have been estimated for all measurements involved in determination of the reactivity ratios (including a 2σ limit on all activity readings) and the uncertainties quoted were found by the standard methods for combination of errors. Percentage conversion data (Table II) are based on weights of polymer precipitated for the copolymers and on the measured volume contraction for PVC*.

TABLE I : Polymerization Conditions

Polymer	Molar Monomer Feed Ratio: $F = \frac{[VC]}{[MMA]}$	Specific Activity of ^{36}Cl Vinyl Chloride used. (cpm/mole)	Initiator Concentration (% W/V)	Polymerization time at 45°C. (Min.)
Copolymer 1	1.733	933,383(+8452)	0.366	165
" 2	5.262	595,013(+6380)	0.365	295
" 3	25.73(+0.01)	457,378(+5749)	0.365	423
" 4	70.53(+0.05)	371,755(+4507)	0.365	367
" 5	115.8 (+0.1)	421,985(+5287)	0.366	322
PVC*	—	412,553(+5036)	0.366	218

TABLE II : Polymer Properties

Polymer	% Conversion to polymer	Molecular weight	Specific Activity of polymer in THF Solution (cpm/g. of polymer)	Molar Monomer Ratio in copolymer: $f = \frac{d [VC]}{d [MMA]}$
Copolymer 1	2.39	208,000	5170(+100)	0.1079(+0.0018)
" 2	1.90	111,000	8700(+130)	0.3202(+0.0038)
" 3	> 1.37	36,600	20570(+200)	1.685(+0.074)
" 4	1.68	32,800	25440(+230)	5.678(+0.536)
" 5	1.72	37,000	31130(+250)	8.464(+1.103)
PVC*	8.17	84,900	36190(+270)	—

The equations of Fineman and Ross⁽³⁶⁾ have been used to obtain values for the monomer reactivity ratios:-

$$\frac{F}{f} (f-1) = \frac{F^2}{f} r_1 - r_2 \quad \text{-----} \textcircled{1}$$

$$\frac{f-1}{F} = r_1 - r_2 \frac{f}{F^2} \quad \text{-----} \textcircled{2}$$

where \underline{F} = $\frac{\text{molar concentration of VC in monomer feed}}{\text{molar concentration of MMA in monomer feed}}$

\underline{f} = $\frac{\text{molar concentration of VC in copolymer}}{\text{molar concentration of MMA in copolymer}}$

and \underline{r}_1 and \underline{r}_2 are the monomer reactivity ratios for VC and MMA respectively.

Equation $\textcircled{2}$ is obtained by rearrangement of the standard form $\textcircled{1}$ and its application gives better separation of points on the graph corresponding to the low VC content copolymers.

The data corresponding to equations $\textcircled{1}$ and $\textcircled{2}$ are contained in Table III and the corresponding graphs appear on pages 36 and 37.

TABLE III : Fineman - Ross Data

Copolymer	$\frac{F}{f} (f-1)$	$\frac{F^2}{f}$	$\frac{f-1}{F}$	$\frac{f}{F^2}$
1	-14.33(+0.27)	27.83(+0.46)	-0.5148(+0.0010)	0.03593(+0.00059)
2	-11.17(+0.45)	86.47(+2.38)	-0.1292(+0.0017)	0.01156(+0.00032)
3	10.46(+0.67)	392.9(+17.3)	0.02662(+0.00288)	0.002545(+0.000112)
4	58.11(+1.17)	876.1(+82.7)	0.06633(+0.00760)	0.001141(+0.000103)
5	102.1(+1.78)	1584(+206)	0.06446(+0.00952)	0.0006311(+0.0000522)

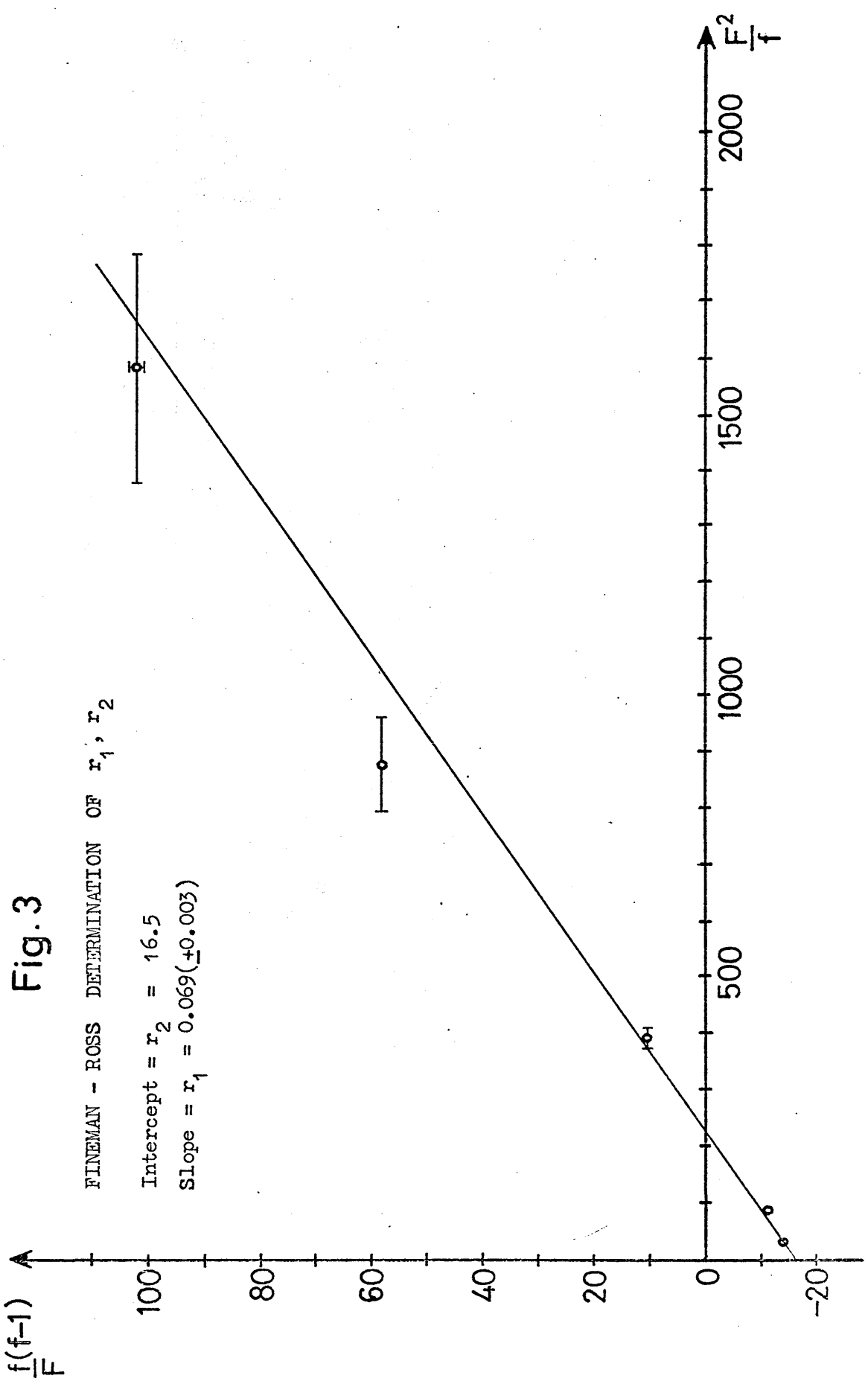


Fig. 3

FINEMAN - ROSS DETERMINATION OF r_1, r_2

Intercept = $r_2 = 16.5$

Slope = $r_1 = 0.069 (\pm 0.003)$

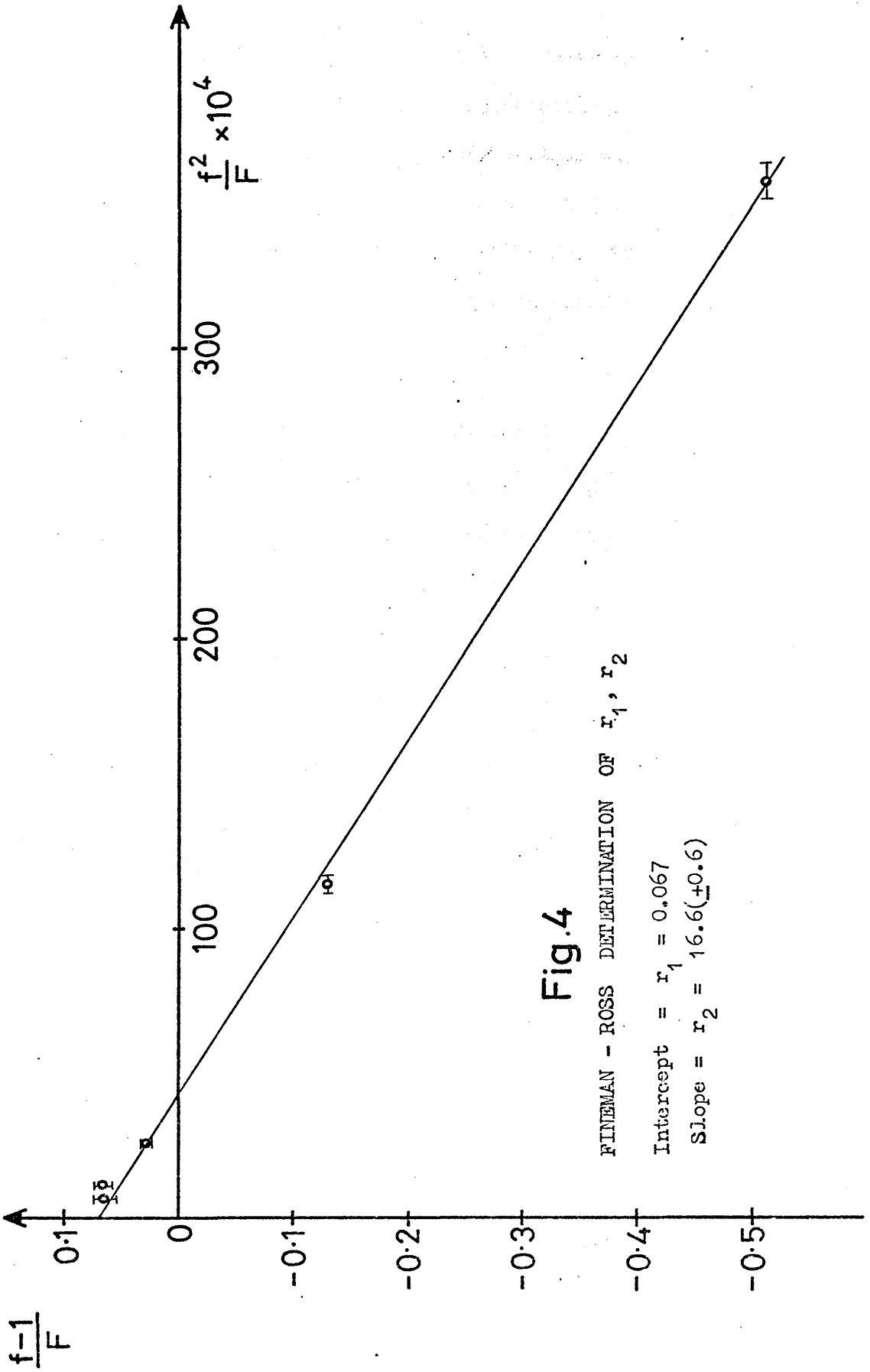


Fig.4

FINEMAN - ROSS DETERMINATION OF r_1, r_2

Intercept = $r_1 = 0.067$

Slope = $r_2 = 16.6(\pm 0.6)$

Reactivity ratios have also been estimated using the graphical method of Mayo and Lewis⁽³⁷⁾ (Fig. 5, p.39). These results, together with the ones obtained by the Fineman - Ross plots are given in Table IV, where they are compared with data obtained by other workers.

Finally, a copolymer composition curve has been drawn for the system (Fig. 6, p.39). The large, negative deviation from the diagonal corresponding to $f = F$ is typical of systems in which r_1 is much smaller than r_2 .

"PENULTIMATE" EFFECTS DURING COPOLYMERIZATION

The effect of penultimate units in determining the reactivity of the growing polymer radicals has been shown by Guyot and coworkers⁽³⁷⁾ to be unimportant in the VC - MMA system, so that only two reactivity ratios need be considered.

TABLE IV : Reactivity Ratios

r_1 (VC)	r_2 (MMA)	Remarks	Reference
0.1	10.0	Bulk Polymerization ; 68°C.	(38)
0.044(±0.005)	11.2(±1.0)	Bulk Polymerization ; 68°C.	(15)
0	12.5	Bulk Polymerization ; 60°C.	(39)
0.02	15	Solution Polymerization ; 45°C.	(35)
0.069(±0.003)	16.5	Fineman - Ross } This work: Bulk Polymer- ization at 45°C. Mayo - Lewis }	
0.067	16.6(±0.6)		
0.072	17.0		

Fig. 5

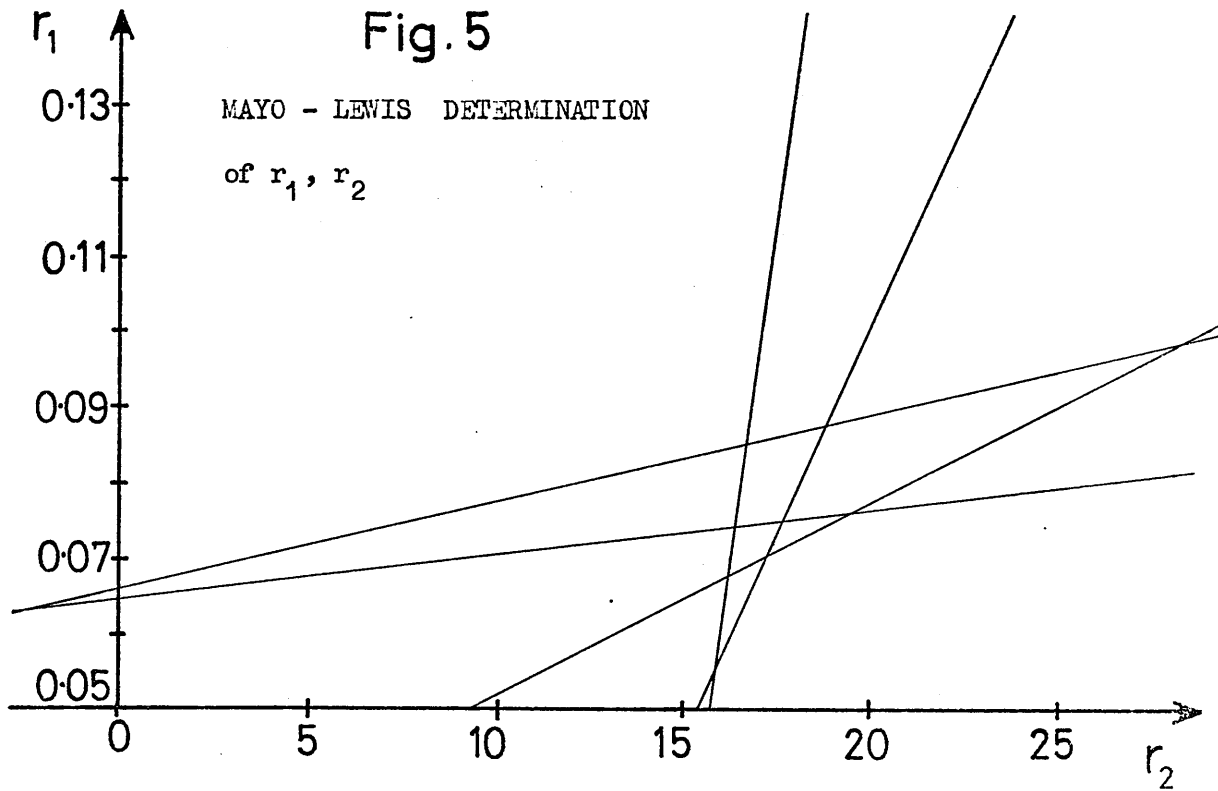
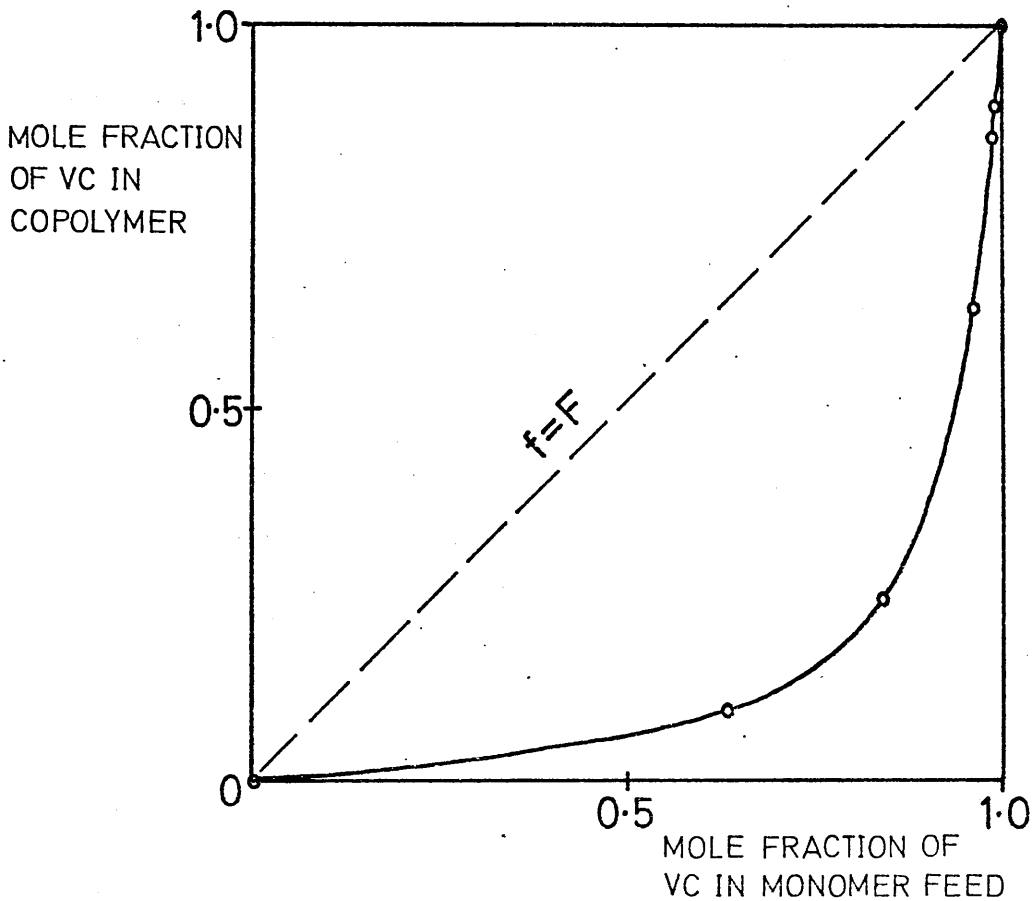


Fig. 6

COPOLYMER COMPOSITION CURVE FOR VC - MMA SYSTEM.



CHAPTER THREE

INTRODUCTION

Thermal degradation studies on the ^{36}Cl -labelled polymers will be described fully in Chapter IV. At this stage, it will be useful to review the facts already known about the thermal properties of random VC - MMA copolymers. As a prerequisite to this, the thermal degradation mechanisms of PMMA and PVC must be discussed in some depth.

THE THERMAL DEGRADATION OF POLY(METHYL METHACRYLATE)

First studied by Grassie and Melville⁽⁵⁾, PMMA degradation has been well reviewed by MacCallum⁽⁴⁰⁾. It is one of the few homopolymers from which quantitative yields of monomer are obtainable on heating and it has been shown that the degradation can be accounted for in terms of a free radical chain mechanism which follows the general scheme postulated by Simha, Wall and Blatz (see page 3), except that transfer processes are known to be unimportant.

It has been firmly established for some considerable time that the mechanism is a two-stage process. In polymer samples prepared by a free-radical mechanism, initiation occurs at unsaturated chain-end structures at 200°C while at temperatures between 250°C and 300°C , initiation is predominantly by random scission of the backbone. In either case, the radicals formed "unzip" to give quantitative yields of monomer.

More recent work⁽⁴¹⁻⁴⁷⁾ has confirmed this picture and shown also that termination is bimolecular at low temperatures and changes

to unimolecular at high temperatures. The most obvious interpretation of this is that pairs of radicals mutually destroy each other at low temperatures, while the ultimate small radical from complete unzipping escapes from the system at high temperatures.

McNeill has used thermal volatilization analysis to study the thermal degradation of PMMA^(43,28) and this method shows clearly the two stages of monomer production as two peaks on the TVA traces. (see p.138) The effects of variables such as molecular weight, polymerisation method, unsaturation and comonomers are also clearly demonstrated and may be summarized as follows:-

The effect of polymer preparation method

Unsaturated chain ends, present in polymer made by the free-radical process cause instability. Polymers prepared by an anionic mechanism have no such ends and are stable to much higher temperatures.

The effect of molecular weight

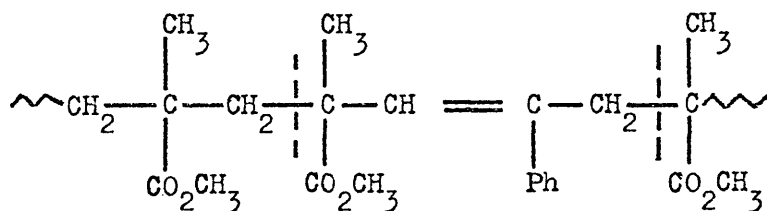
The amount of monomer produced by chain-end initiation is highest for low molecular weight polymer, due to the higher concentration of unsaturated terminal units. For the same reason, the maximum rate of monomer production for the low-temperature process occurs at progressively lower temperatures as the molecular weight is reduced.

For the high-temperature random scission process, on the other hand, McNeill has shown that the rate of monomer production increases with the initial molecular weight and that the maximum rate of volatilization occurs at progressively lower temperatures as the molecular weight is raised.

This agrees with the earlier isothermal results of Grant and Bywater⁽⁴⁸⁾ and of MacCallum⁽⁴⁰⁾ and is consistent only with random scission of the polymer backbone.

The effect of backbone unsaturation

When MMA is copolymerised with phenyl acetylene, two interesting effects are noticed. Firstly, there is very little end-initiated reaction, but what little there is gives rise to a rate maximum at the same temperature as for a homopolymer of similar molecular weight. This is presumably due to a "blocking" action by the comonomer units which reduces the zip length of the depropagation. Secondly, the maximum rate of monomer production associated with the random scission process occurs about 30°C earlier than in the homopolymer. This is probably due to the ease of scission at the unsaturated units along the backbone:-



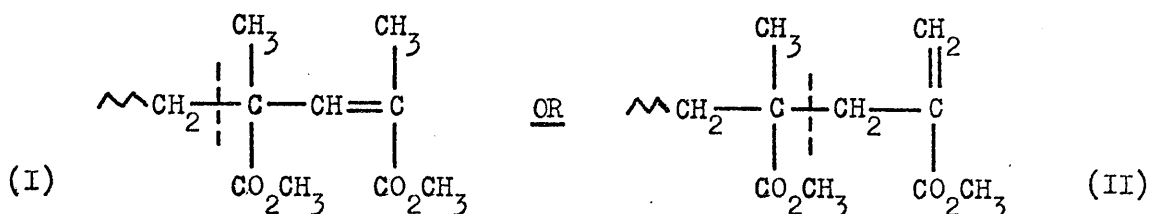
The bonds indicated probably constitute weak points.

The effect of other foreign units in the backbone

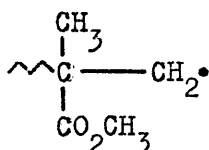
Assuming that they do not depolymerise readily themselves or interfere with the formation of terminal unsaturated structures during polymerization, other comonomers can stabilize polymer made by the free radical method against breakdown at low temperatures. Methyl, ethyl, propyl and butyl acrylates show this behaviour, as

does styrene. Copolymerization with the structurally similar monomer, ethyl methacrylate, however, has a negligible effect on the degradation pattern, due to its ability to depropagate.

Some attention should finally be given to the nature of the unsaturated end units. Formed by disproportionation of macroradicals during the termination step of polymerization, two possible structures can be envisaged:-



Bond rupture will occur as shown. Structure (II) will generate a macroradical identical to that formed during polymerization, while (I) will give rise to the radical



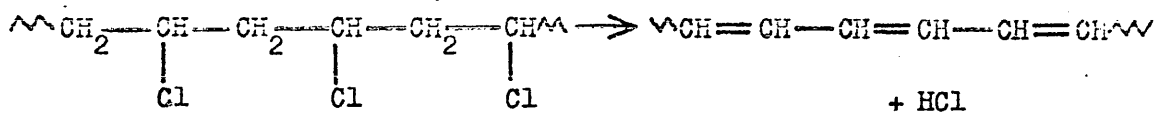
On the basis of empirical activation energy values for the initiation process, MacCallum has suggested⁽⁴⁰⁾ that this form may also be able to depropagate.

THE THERMAL DEGRADATION MECHANISM OF PVC

Due to its ever-increasing importance as a commercial polymer, PVC has been the subject of a vast amount of industrial and academic research, with its thermal degradation behaviour being of particular importance. As will be seen, the mechanism of degradation is still a matter of some controversy.

PVC suffers from the disadvantage of undergoing considerable thermal degradation near to its melting point (ca. 180°C). In the absence of suitable stabilizers, the temperatures required for fabrication of the polymer are often sufficient to induce colouration and deterioration of mechanical and electrical properties. Over the years, several classes of materials (e.g. metal soaps, organotin compounds and epoxides) have been used successfully to combat degradation and open the way to new applications of PVC products, but such stabilizers have been evolved empirically and are often relatively expensive and sometimes toxic. A complete understanding of the mechanism of stabilization is clearly important if such factors are to be minimised and this will follow only when the degradation mechanism itself can be fully interpreted. In the present work, the effect of various comonomers as potential "internal" stabilizers is investigated.

The thermal degradation of PVC has been well reviewed by Braun⁽⁴⁹⁾ and by Geddes⁽⁵⁰⁾. Basically, the reaction involves the stepwise ("zipper") removal of HCl from the polymer to leave a coloured residue which contains conjugated polyene sequences. Once double bonds have been formed, they are able to activate atoms in the allylic position and so promote further reaction:-



In unstabilized polymer, colouration is apparent long before any of the other effects of degradation and becomes more intense as the degradation proceeds.

It will be convenient to discuss the dehydrochlorination in four parts:-

- (1) Sites for initiation
- (2) Colouration
- (3) Mechanism of HCl loss
- (4) The influence of hydrogen chloride

INITIATION SITES

The initiation step is very important as it demands a relatively high activation energy (25-35 kcal/mole). Model investigations with 2,4-dichloroalkanes (e.g. 2,4-dichloropentane) have shown that pure PVC should, in theory, be rather stable, with dehydrochlorination of the model compounds at 350^o-400^oC requiring an activation energy of about 50 kcal/mole⁽⁵¹⁾. It follows that initiation must occur at "impurity" structures in the chain and these have been described in the literature as follows:-

- (i) Chain end groups with initiator residues or unsaturated structures
- (ii) Branch points with tertiary chlorine atoms
- (iii) Random unsaturation with allylic chlorine atoms
- (iv) Oxygen-bearing structures
- (v) Head-to-head units

Studies of small molecule models incorporating unsaturation and branch-points have revealed that unsaturated chain ends should be relatively unimportant, whereas random isolated double bonds with allylic chlorine atoms and also branches with tertiary chlorine atoms should constitute points of weakness.

The amount of chain branching in PVC can be determined fairly accurately by comparing infrared spectra of linear polymethylene against PVC reduced with LiAlH_4 (52). Depending on the method of preparation of the polymer, about 5 to 15 CH_3 - groups per 1000 C - atoms are found. Although branching definitely exists, however, it is now considered unlikely that tertiary chlorine atoms exist at these structures. (53,54)

End-groups in PVC can be formed from initiator residues or by chain-transfer termination, but many of the experiments used to study their effect on degradation have been inconclusive. Unsaturated end-groups in PVC have been identified and estimated qualitatively by Bengough (55) but their suggested role as initiation sites in the degradation is not confirmed by experiments with low molecular weight models. Baum and Wartman (56) found only a 10% difference in intrinsic viscosity between a solution of undegraded PVC and a solution of polymer which had first been thermally degraded and then subsequently ozonized. They suggested that initiation occurs mostly at unsaturated chain-ends and that the formation of polyene sequences from random double bonds in the polymer chain is relatively unimportant. Their results conflict sharply with those of Braun and Quarg (57) who claim to have observed a rapid decrease in molecular weight when thermally-degraded PVC is oxidatively cleaved.

In a recent study by Valko and Tvaroška (58), semi-empirical calculations have been made of the activation energy required for the unimolecular elimination of HCl (see page 52) from unsaturated

end units and these have predicted that such structures should, in fact, be relatively stable.

Random unsaturation with allylic chlorine atoms was noted earlier to produce thermal lability in low molecular weight models and the experimental evidence for the existence of these structures in PVC is probably more conclusive.

In a study of vinyl chloride - vinyl bromide copolymers, it was noted that below 200°C, dehydrochlorination was initiated at allylic chlorine sites, formed by the prior elimination of HBr.⁽⁵⁹⁾ Recently, Braun and Quarg have observed a direct correlation of random unsaturation with the rate of dehydrochlorination⁽⁵⁷⁾ in a study involving the oxidative cleavage of various PVC samples using KMnO_4 in dimethylacetamide. During the oxidation at 20°C, the molecular weight fell to a constant final value, allowing the number of cleavages per 1000 C-atoms to be calculated. For fractions of bulk PVC, the number of cleavages was found to be independent of molecular weight (\bar{M}_v), as was the rate of dehydrochlorination. However, when technical suspension PVC samples from various sources were used, both the number of cleavages/1000 C and the rate of HCl loss were observed to decrease smoothly with increasing molecular weight and a correlation of the two effects showed that the rate of dehydrochlorination increases regularly with the number of cleavable sites.

It could be shown that in the early stages of dehydrochlorination, one polyene sequence was formed from each isolated double bond. In addition, careful chlorination of the double bonds led to increased thermal stability and a reduction of the number of double bonds found by cleavage with KMnO_4 .

Degradation for one hour at 180°C, followed by oxidation in solution, gave the same molecular weight decrease as with direct oxidation of undegraded PVC, suggesting that the polyene sequences formed were initiated at the original unsaturated structures and were relatively short. The average length of the polyene sequences could be calculated from the amount of HCl evolved and the number of cleavages. The results obtained were in good agreement with the spectroscopic findings (see page 49).

The importance of random unsaturation is also supported by the calculations of Valko and Tvaroška⁽⁵⁸⁾, which have already been mentioned (see page 46).

Carbonyl absorptions have been observed in the infrared spectra of PVC⁽⁶⁰⁾ and these are thought to arise by subsequent decomposition of peroxide or hydroperoxide structures, formed by oxidation of the polymer. Popova⁽⁶¹⁾ has shown that an increase in the oxygen content of the polymer is associated with an increase in the rate of dehydrochlorination and it is possible that the radicals formed during the decomposition of the peroxide structures may initiate a radical dehydrochlorination.

Head-to-head units, although not yet identified in PVC, have been studied using chlorinated trans-1,4-polybutadiene⁽⁶²⁾ and the vicinal chlorine atoms shown to be more thermally labile than their 1,3-counterparts. HCl loss begins sooner than in pure PVC, but the rate of elimination is slower, probably due to the relative stability of the $\sim\text{CH}_2 - \text{CH} = \underset{\text{Cl}}{\text{C}} - \text{CH}_2\sim$ structures initially formed, compared with allylic units (based on low molecular weight model comparisons).

In conclusion, it must be noted that the stereoregularity of PVC also appears to affect its thermal stability⁽⁶³⁾. Little information has been collected so far, with the obvious difficulty being the differentiation from crystallinity and melting point effects.

COLOURATION DURING DEHYDROCHLORINATION

The development of colouration is firmly established as a consequence of polyene formation but, as yet, no quantitative relation between colour and the amount of HCl evolved has been formulated. However, U.V. and visible spectroscopy has revealed several interesting factors concerning the lengths and frequency distribution of the various lengths of polyene sequence.

Using the Beer-Lambert Law and the fact that the extinction coefficient of the main electronic absorption band of a polyene is directly proportional to the number of double bonds (n), Thallmaier and Braun⁽⁶⁴⁾ derived the expression:-

$$H_n = \frac{\log I_o/I}{\ln x C_p}$$

where H_n is a relative measure of the frequency of polyene sequences with n double bonds in degraded PVC.

$\log I_o/I$ is the absorbance

l is the cell path length

x is the conversion (i.e. moles Cl removed: moles Cl in undegraded polymer)

C_p is the concentration of polymer in solution (g/l)

By plotting H_n against n for PVC degraded to 0.17% at 180°C, it was found that polyene sequences comprising 5 double bonds were most

common, while the longest sequences had about 25 to 30 double bonds.

Furthermore, with increasing conversion (or temperature), it was found that the frequency distribution underwent a small shift to shorter sequences and also the concentration of polyene (measured spectroscopically) decreased. This can be explained by the onset of cyclization and crosslinking reactions. Aromatic hydrocarbons (e.g. benzene and toluene) are formed and the I.R. spectra of the polymers show aromatic structures⁽⁶⁵⁾. Presumably, this process occurs mostly at the expense of the longer sequences.

The observations of Thallmaier and Braun suggest that HCl elimination begins simultaneously at many sites. With increasing conversion, the number of polyene sequences increases, but not their length, and after the formation of sequences with 20-25 double bonds, the "zipper" type mechanism is finally arrested (see page 54).

THE MECHANISM OF DEHYDROCHLORINATION

Like the mode of initiation, the mechanism of dehydrochlorination itself is still in dispute. Radical, ionic and unimolecular mechanisms have been discussed widely in the literature and it is not inconceivable that different mechanisms may operate together within certain temperature ranges.

(i) Radical Mechanism:

Many early workers postulated a free-radical dehydrochlorination, with the mechanism of Stromberg et al.⁽⁶⁵⁾ receiving most support. Experiments by Bengough and Sharpe⁽⁶⁶⁾, however, have shown that free-radical inhibitors have no effect on the thermal degradation of PVC in an inert solvent, which appears to discount a radical process (at least under these conditions).

In addition, the E.S.R. spectrum of strongly-degraded PVC has not offered unambiguous proof of free-radical intermediates (see page 13).

However, Bamford and Fenton⁽⁶⁷⁾, in a study of the thermal degradation of PVC in tritium-labelled toluene, found incorporation of tritium into the polymer chain and there was a linear relation between the extents of tritium incorporation and dehydrochlorination. Using this, together with other evidence, a free-radical mechanism was postulated.

McNeill and Neil⁽⁶⁸⁾ have offered the degradation behaviour of PVC blends with other polymers (e.g. PMMA) as evidence for a free-radical process during bulk degradation. PMMA is found to be initially less stable and gives monomer at temperatures corresponding to PVC dehydrochlorination, while some initial retardation of the dehydrochlorination itself is also observed. These effects can be explained in terms of diffusion into the PMMA phase of chlorine radicals which can there abstract hydrogen atoms and produce early radical depropagation.

The fact that Cl_2 has not been detected during PVC degradation does not support a radical mechanism, but this could easily be due to the high reactivity of the species.

(ii) Ionic Mechanism:

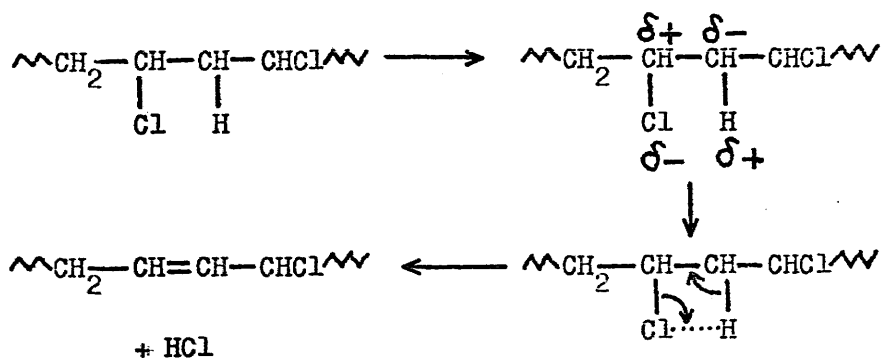
The dehydrochlorination of PVC at $80^{\circ}C$ by bases such as lithium chloride in dimethylformamide follows an ionic mechanism⁽¹⁶⁾. Sulphuric acid⁽⁶⁹⁾ and some heavy metal salts, (especially iron salts), together with additives bearing mobile protons, such as organic acids, alcohols and phenols⁽⁷⁰⁾, are found to accelerate the dehydrochlorination

of bulk PVC, while Marks et al.⁽⁷¹⁾ have found a relationship between the rate of degradation in solution and the dielectric constant of the solvent.

There thus exists strong evidence for a dehydrochlorination mechanism involving charged intermediates under certain conditions, but the fact that certain additives of an ionic character accelerate the degradation does not prove conclusively that the mechanism is ionic in their absence. Probably the greatest support for an ionic process during bulk degradation stems from the ability to explain autocatalysis by HCl (see page 53).

(iii) Unimolecular Elimination:

Braun and Bender⁽⁷²⁾ found that the dehydrochlorination of PVC between 160°C and 200°C, in an inert solvent (ethyl benzoate) and under an inert atmosphere, follows a first order rate law and they postulated a unimolecular mechanism which proceeds via a cyclic transition state:-



Once initiated, the mechanism continues in the usual "zipper" fashion along the chain, with allylic activation of the chlorine atoms.

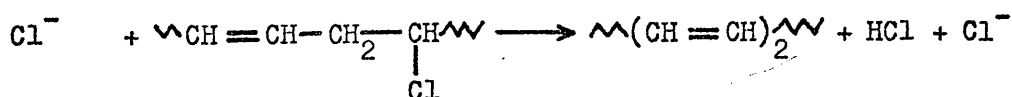
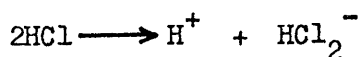
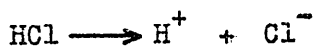
The autocatalytic effect of HCl can also be explained in terms of a molecular process (see below), but once again the best evidence does not refer to degradation of the bulk polymer.

In conclusion, it would appear that the only practicable solution of the mechanism enigma lies in the refinement of the E.S.R. techniques.

THE INFLUENCE OF HYDROGEN CHLORIDE

In the more recent literature, definite evidence is cited for catalysis of the dehydrochlorination by HCl. Talamini et al. observed auto-catalysis during the thermal degradation of solid PVC⁽⁷³⁾, while Braun and Bender observed a higher rate of dehydrochlorination in ethyl benzoate in presence of free HCl⁽⁷²⁾. At temperatures below 200°C, autocatalytic features only appear if HCl is allowed to accumulate in the system and activation energies of 21 and 28 kcal/mole respectively for the catalysed and uncatalysed systems have been reported⁽⁷⁰⁾.

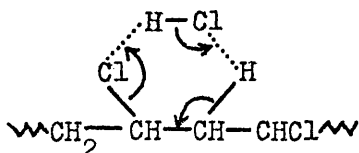
The precise nature of the interaction between HCl and the degrading PVC is not yet clear, but below 200°C any dissociation of HCl into free radicals seems unlikely. Van der Ven and de Wit⁽⁷⁴⁾ have proposed the participation of basic species Cl⁻ or HCl₂⁻, formed by dissociation of HCl:-



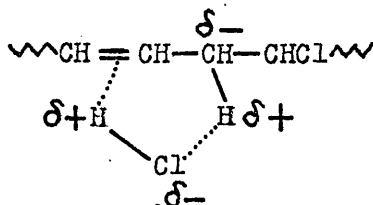
(or HCl₂⁻)

Evidence for the formation of Cl^- or HCl_2^- is, however, indirect, being based on the influence of complexing agents such as FeCl_3 on the autocatalysis.

Braun and Bender⁽⁷²⁾ have suggested a molecular reaction of the type:-



while Morikawa⁽⁷⁵⁾ has proposed an interaction between HCl and the double bonds:-



Regardless of the mechanism involved, the presence of HCl during commercial processing of PVC poses a definite threat to the heat stability of the polymer. Commercial PVC stabilizers (all of which are able to react with HCl) help to alleviate autocatalysis.

It still remains to be explained why the "unzipping" process terminates after the formation of only 5-10 double bonds (on average) per sequence. Above 200°C , termination of the unzipping can be explained by the onset of cyclization and crosslinking (see page 50), but for the termination at low conversion, another reason must be sought.

If a free radical elimination is involved, this will presumably involve chain termination or transfer reactions, in which the chlorine atom or the polymer radical is deactivated in some way.

The ratio of transfer or termination to propagation is probably temperature-dependent, so that average polyene sequence lengths, and hence the colour of the degrading polymer, may well be a function of degradation temperature.

For a non-radical process, a different explanation is required. Possibly, the growth of polyene sequences is blocked by structural irregularities in the polymer chain, but these only appear to be present in very low concentration. A more plausible explanation is that after the first few eliminations in a sequence, the additional energy gained by the system by further extension of the conjugation begins to diminish, so that a point is reached where the thermodynamic driving force is insufficient to justify elimination of another HCl molecule. Since the C-Br bond is weaker than the C-Cl bond, this could explain the formation of longer polyene sequences in poly(vinyl bromide) under the same conditions⁽⁶⁴⁾.

THE THERMAL DEGRADATION OF VINYL CHLORIDE - METHYL METHACRYLATE COPOLYMERS.

The anomalous thermal behaviour of vinyl halide - MMA copolymers puzzled several early workers. Blauer and Goldstein⁽⁷⁶⁾ noted that poly(vinyl bromide), PVB, was more stable than a copolymer of VB with MMA, while Alfrey and coworkers⁽⁷⁷⁾ showed that VC-MMA copolymers evolved abnormally large amounts of chlorinated products upon reaction with zinc.

Lehrle and Robb⁽⁷⁸⁾ used pyrolysis - gas chromatography to compare the thermal degradation of VC-MMA block and random copolymers with the behaviour of a blend of the two homopolymers.

The degradation at various temperatures between 150°C and 950°C was studied. PMMA gave monomer and acetylene as the principal degradation products, while PVC gave HCl and acetylene. The copolymers and also the blend yielded a mixture of MMA and HCl. The random copolymer contained 70% (molar) VC and appeared to be stabilised with respect to loss of MMA but strongly destabilised with respect to dehydrochlorination. The block copolymer and blend (which were both of similar composition to the random copolymer) showed similar behaviour, but HCl loss did not occur at such low temperatures.

Zutty and Welch⁽¹⁴⁾ studied the thermal degradation of random VC-MMA copolymers of different composition and compared their behaviour with the degradation of a homopolymer blend. The gaseous products were analysed by mass spectrometry. They found that pyrolysis of the copolymers at temperatures around 150°C induced a purely intramolecular lactonization reaction which formed α -methyl- γ -butyrolactone groups in the polymer backbone, concomitant with the quantitative elimination of methyl chloride. The following copolymer and terpolymer systems underwent analogous reactions:-

VC - ethyl methacrylate

VC - ethyl acrylate

VC - dimethylitaconate

VC - MMA - tetrahydrofurfuryl methacrylate

vinylidene chloride - MMA

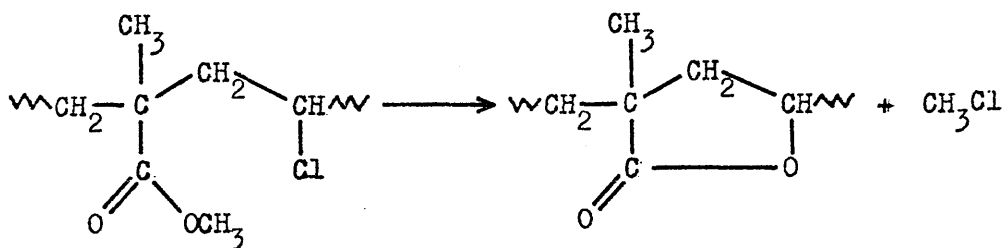
vinyl bromide - MMA

The formation of methyl chloride was only seen to a small extent in the case of the PMMA - PVC blend, the major products being those associated with the homopolymer degradations. HCl was the only other major volatile product observed below 200°C during degradation of the VC - MMA copolymers.

In general, the formation of lactone groups was found to lead to increased chain rigidity and higher polymer softening points. The evolution of gaseous alkyl chloride above the softening point of the polymers allowed rigid foams of good compressive strength to be formed. In this instance, however, no study was made of the part played by lactonization in the complete degradation process.

THE MECHANISM OF LACTONIZATION

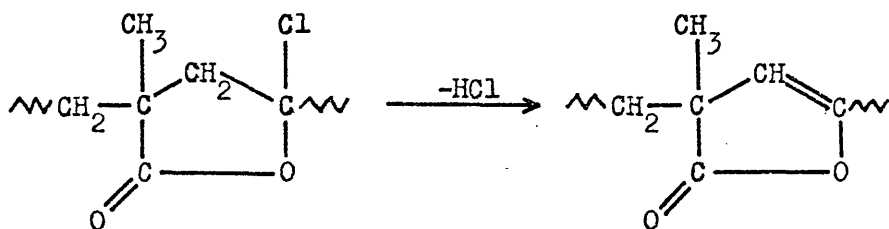
For the lactonization occurring in random VC - MMA copolymers, Zutty and Welch proposed the following overall process:-



Their deductions, gleaned from studies of the other copolymer systems listed above, together with the observations made by other workers, will now be discussed:-

- (1) Replacing Cl with Br leads to an enhancement of the rate of lactonization in accordance with the lower bond strength of C-Br.

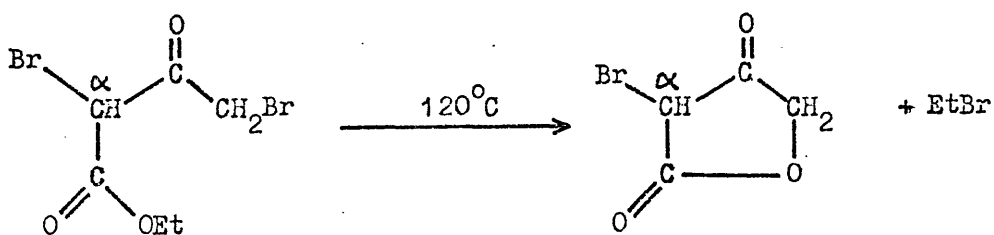
(2) Increasing the positive charge on the C - atom bearing the halogen (as in a vinylidene chloride copolymer) also enhances the rate of substitution. Burnett et al.⁽⁷⁹⁾ have shown that the reaction in fact proceeds a step further in the case of vinylidene chloride, giving a γ -unsaturated γ -lactone by elimination of HCl:-



(3) Varying the ester group in the methacrylate series has apparently no effect on the rate or efficiency of lactonization.

(4) Ester comonomers containing no α -substituent form little, if any, lactone upon pyrolysis. (e.g. ethyl acrylate copolymers). The significance of electron withdrawal/repulsion by the α -substituent has not been fully revealed, due to confusion with steric effects. For example, the slower rate of lactonization of poly(methyl α -chloroacrylate) versus the VC - MMA copolymers could be due to steric hindrance by the ester group on the halogen-bearing C - atom, rather than the positive and negative inductive effects of the α -substituent.

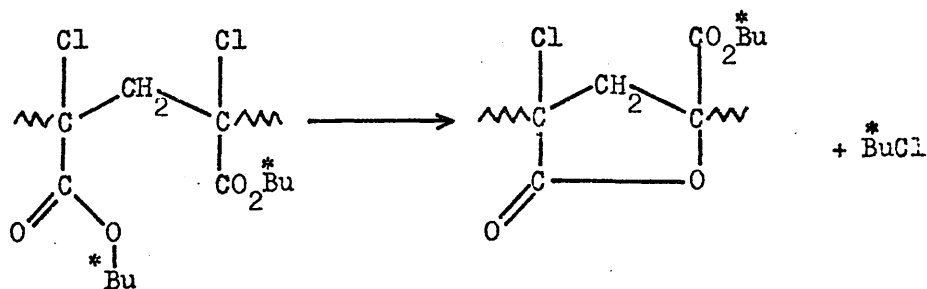
A similar situation was encountered by Perkin and Stone⁽⁸⁰⁾ who performed the synthesis shown below:-



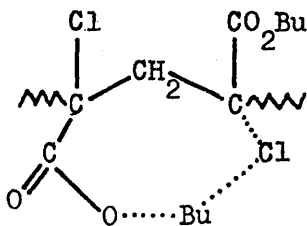
The reaction proceeded normally when the α -Br was replaced by $-\text{CH}_3$, but failed to take place when $-\text{Cl}$ was substituted. Possibly the smaller size of the Cl atom is responsible, rather than its very strong electron-withdrawing properties.

(5) Studies on the VC - dimethylitaconate system showed that formation of a 6-membered lactone in the degrading polymer occurs more readily than formation of a 5-membered one. (the respective reaction temperatures were $110-130^\circ\text{C}$ and $150-170^\circ\text{C}$). This is in accordance with classical cyclization in small molecules.

Probably the most informative study of the mechanism of thermal lactonization to date is the one carried out by Crawford and Plant⁽⁸¹⁾, who studied the pyrolysis of poly[(+)-sec-butyl α -chloroacrylate]. By heating the polymer at 190°C in vacuo, sec-butyl chloride was evolved and its configuration found to be inverted, with about 40% racemization:-

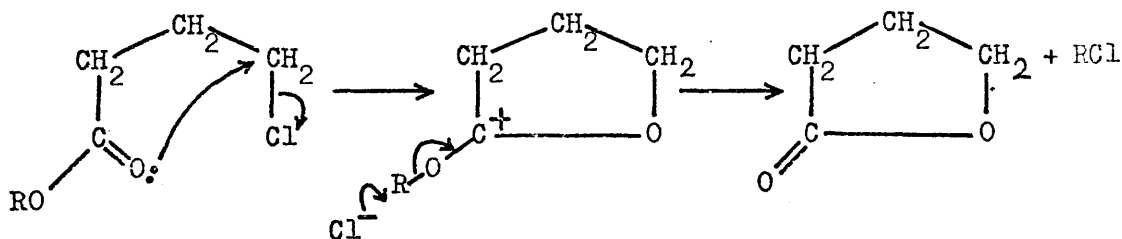


If lactonization proceeds solely by a bimolecular mechanism, through the transition state shown below, then the butyl group should have undergone complete inversion of configuration to yield fully active BuCl.



The fact that racemization occurs suggests some participation of a unimolecular process, involving first formation of a discrete butyl cation, followed by reaction of the ion with chlorine. This must occur at least to the extent of racemization. Screening of the butyl ion by the carboxylate ion could possibly lead to some inversion.

Johnston and Harwood⁽¹⁵⁾, on the other hand, consider that the mechanism of lactonization is analogous to that involved in the thermal cyclization of cetyl γ -chlorobutyrate. This reaction has been studied by Denney and Giacini⁽⁸²⁾ using ^{18}O - labelled carbonyl and it was found that only the carbonyl oxygen participates in ring formation. The mechanism postulated is shown below:-



It is interesting to note that the experimental results of Crawford and Plant could also be explained by this mechanism.

In a recent study of the kinetics of lactonization in VC - MMA copolymers, Johnston and Joesten⁽⁸³⁾ have obtained a value of 31 kcal/mole for the activation energy for pyrolysis in vacuo between 170°C and 190°C. Thermogravimetric analysis was used to monitor the loss of methyl chloride and rate constants found indicated that the evolution of the gas is first order with respect to the number of cyclizable A - B groups.

THE EFFECT OF LACTONIZATION ON COPOLYMER STABILITY

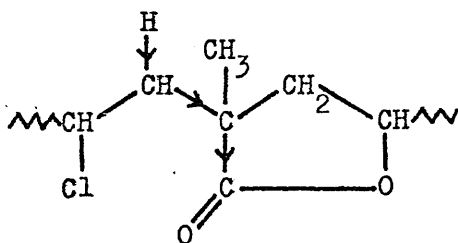
The effect on dehydrochlorination

At first sight, it might be expected that the presence of lactone units in the polymer backbone will reduce the kinetic zip-length of dehydrochlorination and so increase stability. In a recent study of VC - MMA copolymers, however, Guillot et al.⁽⁹⁾ have shown that for copolymers rich in VC, the presence of lactone structures appears to induce dehydrochlorination at lower temperatures than in pure PVC. This is in accordance with the early results of Lehrle and Robb (see page 55). Presumably, some interaction occurs between lactone groups and adjacent VC units which lowers the high activation energy normally required to initiate unzipping.

In copolymers of low VC content (< 20% molar), most of the VC units are isolated between lactone structures and consequently cannot unzip in the normal way. Guillot et al. have shown that the dehydrochlorination of these units occurs at temperatures above those required by pure PVC and this is also supported by the findings of Neil⁽⁸⁴⁾, who has studied low-VC-content MMA copolymers using TVA.

In these isolated VC units, the activation energy for dehydrochlorination should still be lowered by the lactone - VC interaction, but the energy normally acquired by the system through polyene formation will no longer be available.

The tendency for comonomer units in the polymer chain to destabilise VC sequences has also been observed in VC - styrene copolymers⁽⁸⁵⁾ and in VC - vinyl acetate copolymers⁽⁸⁶⁾. In the latter case, it has been suggested that dehydrochlorination is initiated by neighbouring group participation by the acetate groups. However, a similar interaction in VC - MMA copolymers is difficult to envisage, since any labilisation of the chlorine atoms adjacent to a lactone group is sterically unfavoured. It is possible, that in this case, it is the methylenic C - H bonds which are weakened by the inductive effect of the lactone carbonyl as shown below:-



It is also conceivable that reactive intermediates formed during the lactonization process can initiate degradation of the VC sequences. This possibility has been investigated in the present work and will be discussed later.

The effect on methyl methacrylate production

It has already been noted (page 42) how the presence of comonomer units in the polymer chain can stabilise PMMA.

Lactonization in VC-MMA copolymers occurs at temperatures well below those required for depropagation and Neil⁽⁸⁴⁾ has found that the lactone units "block" depropagation in a similar way. (The maximum rate of monomer production in the copolymers was found to occur as much as 50°C above that found in PMMA).

In their study of the complete range of copolymer compositions, Guillot et al.⁽⁹⁾ have confirmed this effect and noted that depropagation is only significant in copolymers with greater than about 50% (molar) MMA content. As expected, two stages of MMA production were observed, with the high temperature one being more important in the high-MMA-content copolymers. The high-temperature (random initiation) process will clearly be less inhibited by "blocking", while the low-temperature one (chain-end initiation) is badly affected. It has also been suggested that the low-temperature production of monomer may also comprise MMA released from isolated units, thus explaining the greater relative importance of the first step in the most alternating copolymer.

Apart from their function as "blocking" agents, Neil has also suggested that the lactone units may induce competitive transfer reactions, because of the ease of removal of their tertiary or secondary H - atoms by a depropagating radical⁽⁸⁴⁾.

OTHER PRODUCTS OF DEGRADATION

Guillot et al.⁽⁹⁾ have observed a second production of methyl chloride between 200 and 300°C, which is most conspicuous in copolymers

of alternating structure and they have explained this in terms of a reaction of dry HCl with unreacted ester groups to give CH_3Cl and a polyacid residue. The mechanism has already been discussed under type A substituent reactions on page 7, Chapter I.

Benzene production in the copolymers is reduced because of participation of some of the VC units in lactonization, but Guillot et al.⁽⁹⁾ have found that evolution of this product by cyclization of the remaining VC sequences is not perturbed by the comonomer units. Benzene is a minor product and has only been observed in the volatiles from VC - rich (> 40% molar) copolymers.

At higher temperatures, toluene and other hydrocarbons have been detected, but these too are only minor products.

Breakdown of the lactone rings commences within approximately the same temperature range as the second phase of MMA formation and Neil has identified CO_2 as a major product⁽⁸⁴⁾. An appreciable amount of more volatile material is also produced in this temperature range, but has not yet been characterized.

The degradation pattern of VC - MMA copolymers, based on the results of Guillot et al.⁽⁹⁾ and of Neil⁽⁸⁴⁾, is summarized below. It is important to note that the data covers the entire composition range and is based on experiments using different conditions of sample atmosphere and heating rate.

TVA curves obtained in the present work for a 43% VC - MMA copolymer are shown in Fig. 29, p.122, together with the volatile products identified by Gas-Phase I.R. analysis. The characteristic absorption bands of benzene and methane may be obscured by other absorptions.

TEMPERATURE RANGE.

VOLATILE PRODUCTS

100° - 200°

{
methyl chloride (lactonization)
hydrogen chloride
benzene (VC-rich copolymers only)

200° - 300°

{
methyl chloride (HCl/ester interaction)
hydrogen chloride
benzene (VC-rich copolymers only)
methyl methacrylate (chain-end
initiation; MMA-rich copolymers only)

300° - 400°

{
hydrogen chloride
toluene and other hydrocarbons
(VC-rich copolymers only)
methyl methacrylate (random-
scission initiation; MMA-rich
copolymers only)
carbon dioxide

CHAPTER FOUR

INTRODUCTION

The experimental methods used to study the degradation of the ^{36}Cl -labelled polymers will shortly be described. Although the degradation studies essentially involve the collection and radioactive assay of chlorinated volatiles, the experimental arrangement is similar to that used in TVA and since the latter technique has been used both to develop the system and also as an additional monitor within the system ultimately used, it will be useful to discuss its theoretical and practical aspects more fully at this point. This description will also form a basis for later chapters where TVA results are presented.

DESCRIPTION OF THE TVA APPARATUS

The TVA technique and its applications have been developed by McNeill and its basic principle has already been described (p. 17). A schematic picture of the general experimental layout is given in Fig. 7, p. 67, while Fig. 8, p. 67 shows details of the sample heating assembly.

The polymer sample, usually in the form of a fine powder or as a film cast from a suitable solvent, is heated on the base of a glass tube, 6" long, constructed from a Pyrex FG35 flange. The top of the tube and the greased flange joint are cooled by a water jacket ("cold ring") during the experiment. The tube is heated using a Perkin Elmer F11 oven and linear temperature programmer, which enables the sample to be heated isothermally or linearly from ambient temperature up to 500°C at heating rates varying from 1 to $40^{\circ}\text{C}/\text{minute}$. Oven

Fig. 7

BASIC TVA APPARATUS

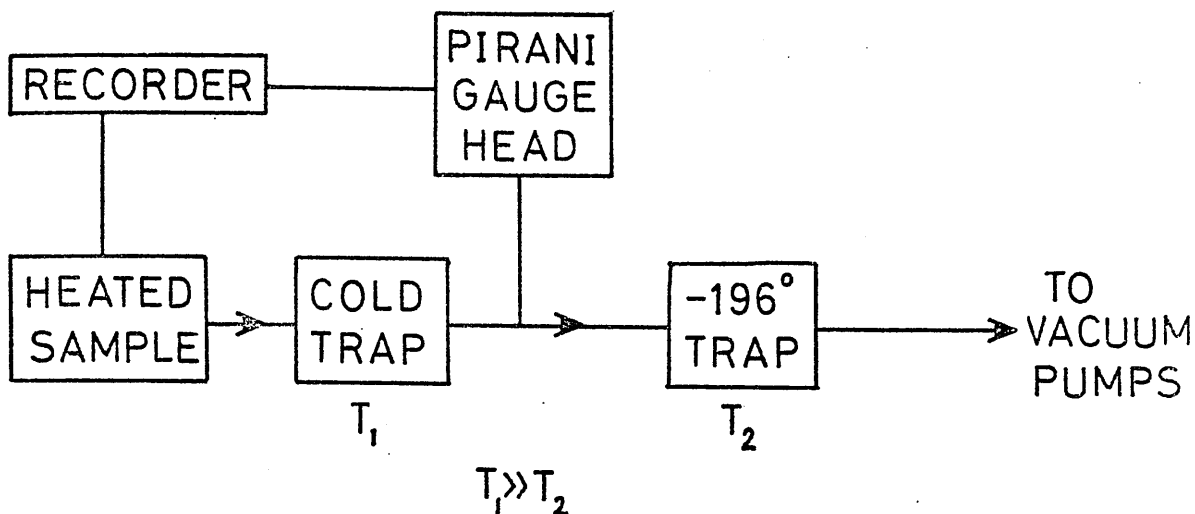
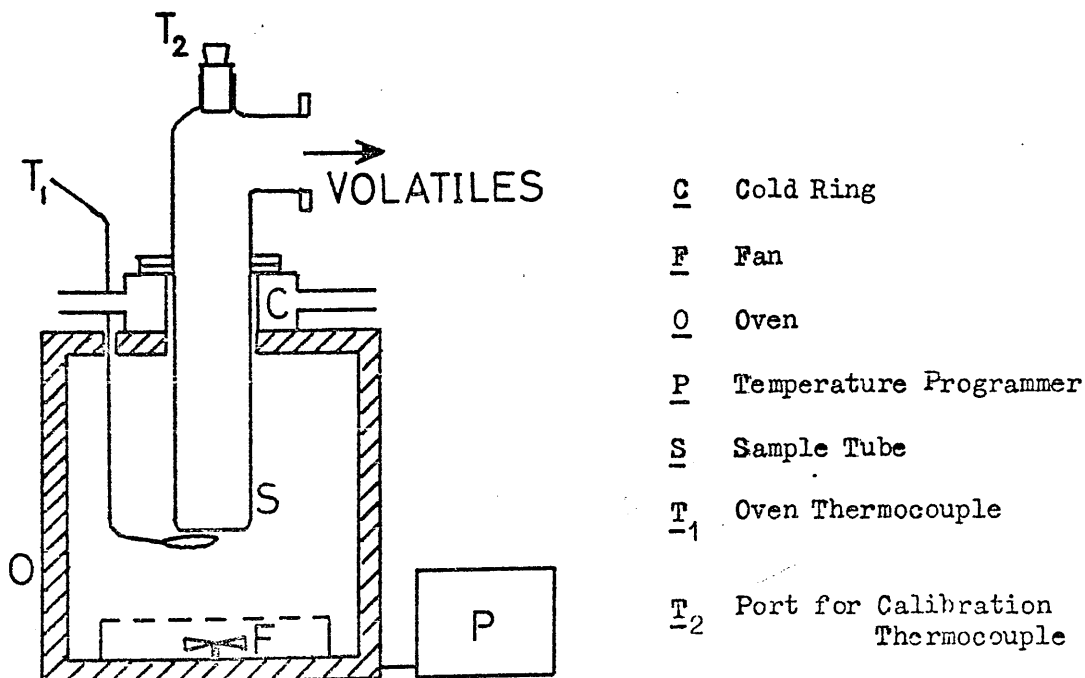


Fig. 8

SAMPLE HEATING ASSEMBLY



temperature is measured using a chromel-alumel thermocouple, fixed near the base of the tube.

Differential Condensation TVA is basically similar, but here the volatiles are pumped along four geometrically-equivalent routes to a common "back-up" trap at -196°C . (see Fig. 9, p. 69). The four routes contain traps at the arbitrarily-chosen temperatures of 0° , -45° , -75° and -100°C respectively. Each trap, including the common trap, is followed by a Pirani gauge and outputs from these are transmitted via a multihead switch unit to a 12-channel recorder, where they are recorded continuously with oven temperature. Products can be collected for analysis at the points indicated.

It can be shown empirically that the same quantity of volatiles passes into each of the four routes, but when a trap is reached, one or more of the components may be condensed out, so that for a mixture of volatiles, the Pirani traces are often non-coincident.

By means of spectroscopic analysis of the products and a prior knowledge of the behaviour of various substances in the different traps, it is often possible to obtain a useful qualitative picture of the degradation pattern at various temperatures. When a product shows "limiting rate" behaviour in one of the traps, this often facilitates its identification. The limiting rate effect occurs when a product condenses in one of the initial traps, but then slowly begins to distil over into the -196°C trap. The Pirani response generated is often seen as a "plateau" and the displacement of this (in millivolts) from the base-line is often characteristic for a particular material.

Fig.9

DIFFERENTIAL CONDENSATION TVA APPARATUS

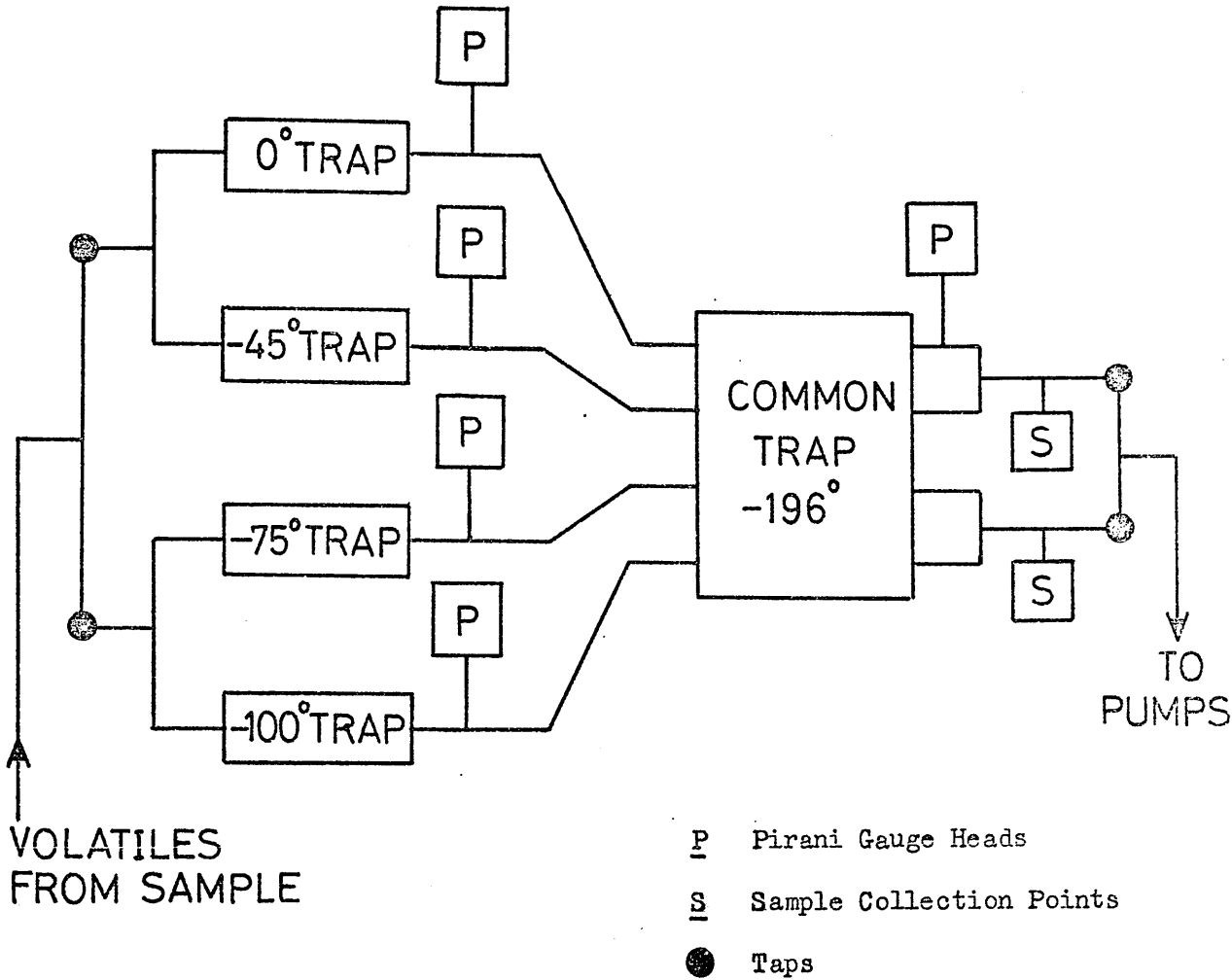
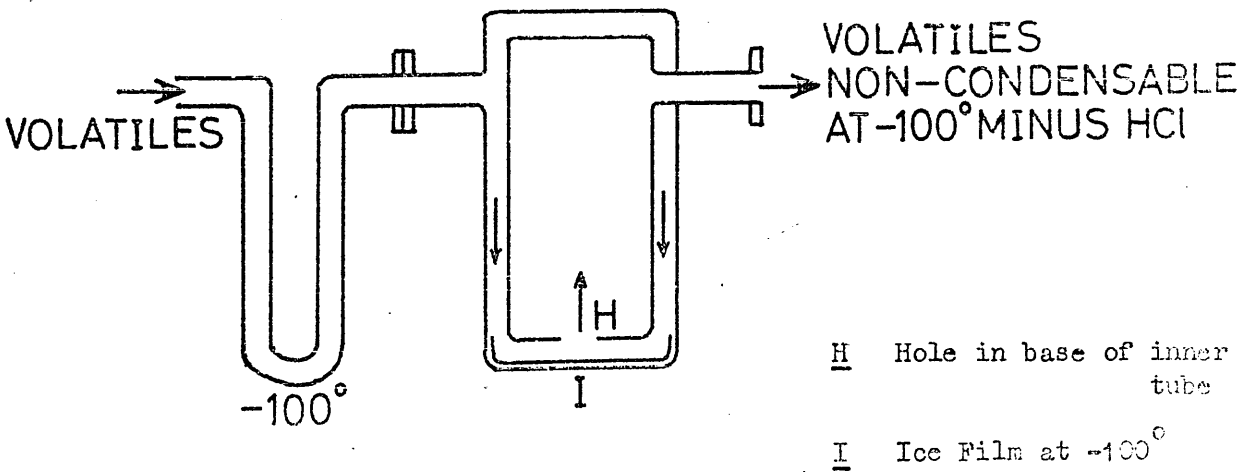


Fig.10

SEPARATION OF HCl FROM VOLATILES



PRODUCT ANALYSIS OF TVA FRACTIONS

The volatiles fall into two categories:-

- (i) "condensables"
- (ii) "non-condensables"

The "condensables" are those materials which condense at -196°C in a continuously-pumped system and they are easily analysed by subsequent distillation into an I.R. gas cell, liquid sample tube, etc. "Non-condensables" are collected by "closed-system" degradation and are analysed, after collection in an I.R. gas cell or gas sample tube, with the -196°C trap in place. Because of the collection method used, the spectra obtained are weaker than for the condensables.

The "cold-ring fraction" comprises those products which are volatile at degradation temperatures, but involatile at ambient temperature, and usually consist of short chain fragments. It is particularly useful for studying the nature of the polymer chain at the intermediate stage of degradation, after the low-temperature substituent reactions have occurred, but before the molecule is grossly fragmented. This fraction may be analysed after removal with a tissue moistened with solvent, followed by extraction from the tissue, or it may be removed as a solid and ground with KBr to form a disc for I.R. analysis.

The involatile residue may be analysed as a solution or as a solid, as for the cold-ring fraction.

DETERMINATION OF SAMPLE TEMPERATURE

For the presentation of consistent and meaningful thermal data, it is clearly the sample temperature which is required and not that

of the oven. Sample temperature lags behind oven temperature and the magnitude of this lag depends not only on temperature and heating rate, but also on the apparatus used and the position of the oven thermocouple. For a particular apparatus and heating rate, the temperature lag is known to be consistent⁽²⁷⁾ and it may be plotted as a function of temperature by simultaneously recording the outputs of the oven thermocouple and that of another resting on the inside base of the sample tube, with a bead of Apiezon "L" grease at its tip to promote good thermal contact and simulate polymer.

Due to the large heat capacity of the sample tube, exothermic or endothermic reactions in the degrading polymer should have little effect on sample temperature.

SAMPLE HEATING RATE

Unless otherwise stated, all TVA data in the present work, including T_{\max} values (i.e. the temperatures at which peak maxima occur) refer to a programmed heating rate of 10°C per minute.

THE DISADVANTAGES OF TVA

The limitations of the Pirani gauge for studying volatile evolution have already been discussed (p.17). The most relevant factor in a study of VC - MMA copolymers is the failure of Differential Condensation TVA to distinguish between products with similar condensability characteristics — in this instance, HCl and methyl chloride. Both of these are non-condensable at -100°C under TVA conditions, but are fully condensed at -196°C .

ADVANTAGES OF RADIOACTIVE ASSAY OF VOLATILES

Radioactive assay of HCl and methyl chloride is suitable not only

for relating their relative proportions to sequence distribution in the copolymers, but also for studying the relation of copolymer composition to thermal stability. The success of the technique hinges on the ability to separate HCl from methyl chloride and it was considered more convenient to separate these products before, rather than after, collection.

THE SEPARATION OF HCl AND METHYL CHLORIDE

A convenient method was sought which would allow continuous separation of HCl and methyl chloride as they were evolved from a copolymer under conditions of high vacuum. There were three basic requirements of the method:-

- (1) Completely selective and quantitative removal of one of the products.
- (2) Non-interruption of the flow of volatiles from the sample, since consistent flow-rates would be required for accurate comparison of the evolution patterns of CH_3Cl or HCl alone and of $(\text{CH}_3\text{Cl} + \text{HCl})$.
- (3) Any method of separation, which involved direct contact of the gases with a solid phase, would require the solid to exert a negligible vapour pressure, in order to maintain the high-vacuum conditions.

The quantitative and totally selective removal of HCl or methyl chloride was investigated by studying changes in the TVA curves of PVC and a VC - MMA copolymer when a physical/chemical separation system was interposed between sample and Pirani gauges. The PVC used was Breon 113, whose first TVA peak ($T_{\text{max}} = 295^\circ\text{C}$) comprised material non-condensable at -100°C (but fully condensed at -196°C) and known to consist essentially of pure HCl. The copolymer used (see Fig. 12, p. 77)

was of intermediate composition and its first TVA peak ($T_{\max} = 220^{\circ}\text{C}$) consisted entirely of material non-condensable at -100°C (but fully condensed at -196°C) and this was assumed to be pure methyl chloride on the evidence of Neil⁽⁸⁴⁾ (later findings supported this). The second peak in the copolymer TVA ($T_{\max} = 300^{\circ}\text{C}$) consisted partially of material non-condensable at -100°C (but fully condensed at -196°C) and this portion was later shown to consist partly of HCl (see Fig. 12, p. 77).

Physical Separation

Both HCl and methyl chloride are condensable under the high-vacuum conditions of TVA. Their normal boiling points at 760mm. Hg are -84.9°C and -23.8°C ., respectively, but there is no simple method for predicting their condensation temperatures in a continuously-pumped system. The difference in their volatility suggested that it might be possible to induce their separation at some temperature between -100°C and -196°C . Cooling the volatiles from the VC - MMA copolymer, by passage through a trap at -130°C , however, gave no visible decrease in the amount of methyl chloride reaching the Pirani gauges and it was decided to abandon this approach due to the difficulty of maintaining accurately the very low trap temperature which would clearly be required for a "clean" separation.

Chemical Separation

Borkowski and Van Venrooy⁽⁸⁷⁾ used ferric oxychloride to remove HCl from a vapour stream and it was found that the HCl could later be desorbed by heating. A U-tube packed with ground ferric oxychloride was inserted between sample tube and Pirani gauges and a TVA was run

of the VC - MMA copolymer. When compared with results obtained with the U-tube empty, there was no apparent selective removal of HCl, although it must be admitted that distortion of the peak shapes, due to the restricted gas flow, made interpretation difficult.

When sodium hydroxide pellets were used in place of ferric oxychloride, there was little distortion of the traces, but the peak with $T_{\max} = 300^{\circ}\text{C}$ on the -100°C trace of the copolymer appeared unaffected. Experiments with PVC confirmed that solid, anhydrous NaOH has little effect on HCl under TVA conditions.

It was found that quantitative removal of HCl was possible when the U-tube contained large ice crystals at -100°C (ice exerts a vapour pressure of 15×10^{-6} torr at -98°C). This was shown by the effect on the TVA trace for PVC — only the "hydrocarbon" peak ($T_{\max} = 470^{\circ}\text{C}$) remained. In addition, the first peak in the copolymer TVA trace was virtually unchanged, suggesting that there was no interaction of the ice with methyl chloride. Unfortunately, large ice crystals could not give consistent flow-rates and a batch of ice could not be used indefinitely due to saturation with HCl, so that attempts were made to find an ice surface of sufficient area to remove a specified amount of HCl, without interrupting the gas flow.

When a layer of ice was cast on the base of a U-tube by addition of a few ml. of water and cooling to -100°C , the HCl peak from a 100mg. sample of PVC showed one of the following features:-

(1) An "edge effect" (see Fig. 11, p.75), in which all of the HCl being evolved is removed for a time, then suddenly begins to reach the Piranis to give a normal continuation of the TVA traces. This effect occurs when an insufficient area of ice is exposed to the volatiles and

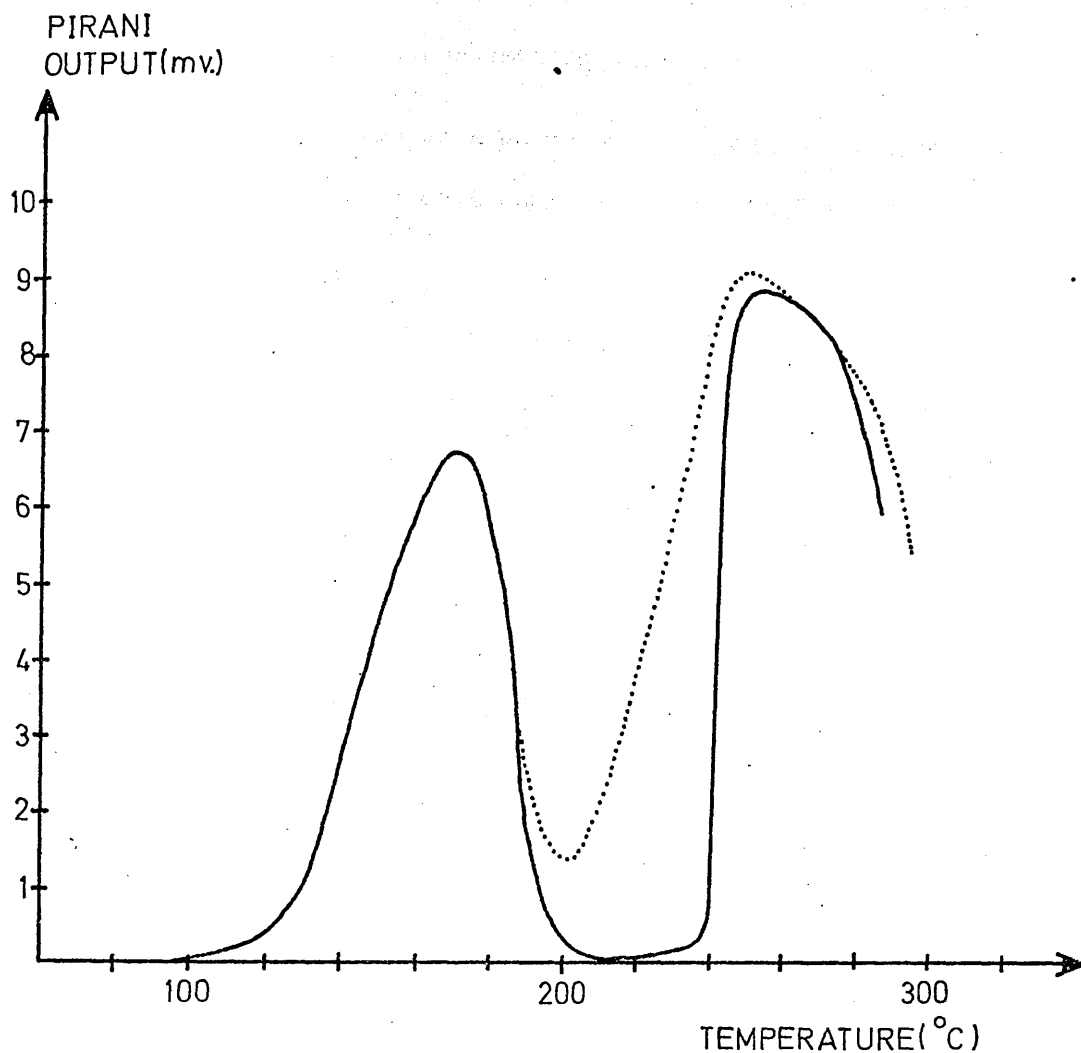


Fig.11

The "edge-effect" as observed in an 88.6% VC-MMA copolymer.

100mg. film cast from cyclohexanone; heating-rate 1.32°C/min.

..... Trace observed with no ice in concentric trap.

———— Trace observed with incomplete HCl adsorption.

is also observed when products or solvents, which are condensable at -100°C , are allowed to contaminate the surface.

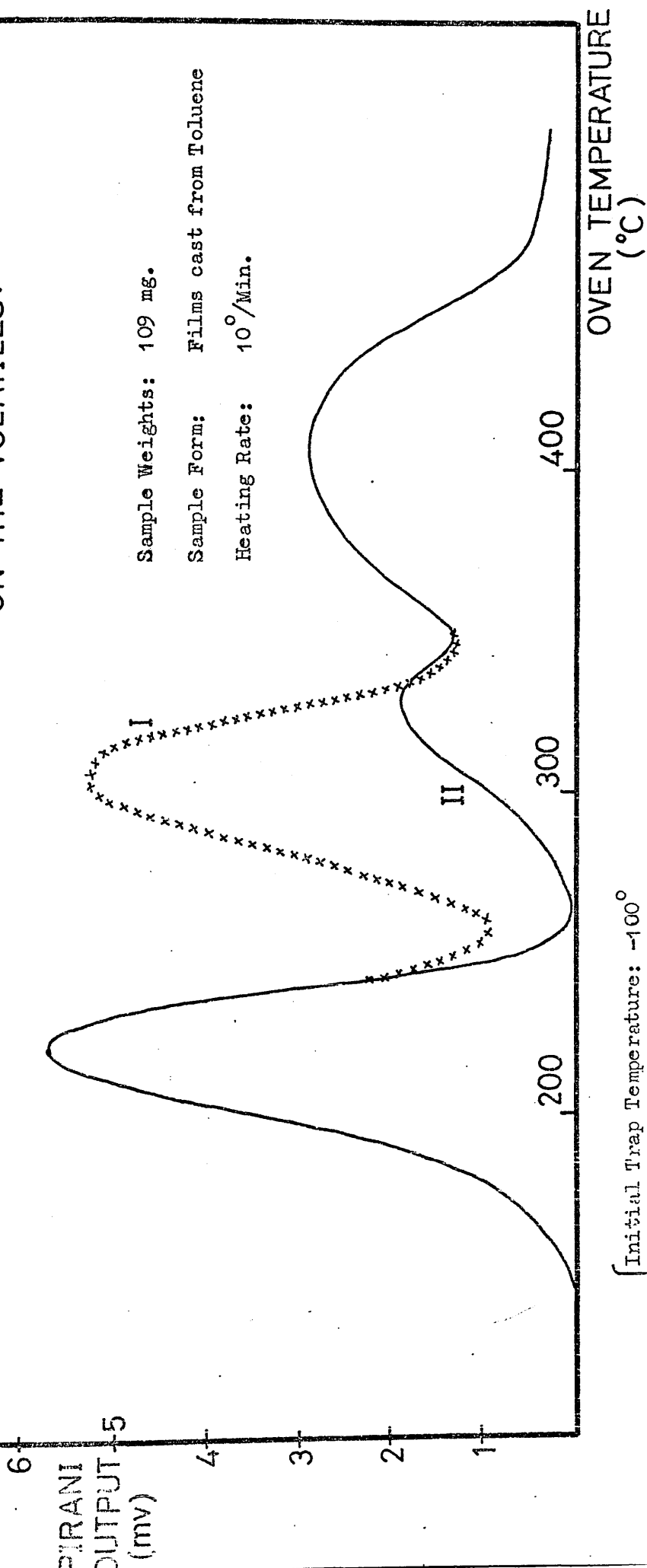
(2) Diminution of the area under the HCl peak. This occurs when only part of the gas stream makes contact with the ice surface, allowing only partial removal of the HCl.

In an effort to overcome these problems, the trap shown in Fig.10,p.69 was tried in conjunction with an initial trap at -100°C to remove potential contaminants (e.g. MMA monomer). The trap consisted of two concentric glass tubes, of respective diameters 4.5 and 6cm., with a 6mm. gap between the bases and a hole of diameter 6mm. on the base of the inner tube. A 4g. ice layer was cast from distilled water on the base of the trap and by using the same weight each time, consistent flow-rates could be obtained. The system was shown to be capable of removing the HCl evolved from 100mg. of PVC by heating the polymer to 500°C at $10^{\circ}/\text{min.}$, thawing the ice layer and titrating the solution against standard 0.1 M NaOH solution, using phenolphthalein as indicator. To prevent any loss of trapped HCl as the ice warmed up, 2ml. of Analar methanol was injected (water caused cracking of the trap), while the ice was still at -100°C — the presence of small amounts of methanol did not affect the end-point. Using reprecipitated Breon 113 and distilled tetrahydrofuran for film-casting, ten degradations were performed and the fraction of total theoretical HCl removed was found to be $100 (\pm 0.7)\%$.

Fig.12,p.77 shows the effect on the approximately 1 : 1 VC - MMA copolymer of inserting the trap with 4g. ice at -100°C between sample and Pirani. 109mg. of copolymer was cast as a film from toluene, the solvent being removed by the initial trap at -100°C . The traces shown

Fig.12 50%(MOLAR)VC-MMA COPOLYMER —EFFECT OF ICE AT -100° ON THE VOLATILES.

Sample Weights: 109 mg.
Sample Form: Films cast from Toluene
Heating Rate: 10°/Min.



TVA I { Initial Trap Temperature: -100°
(xxxxxx) { Ice-trap (Empty) Temperature: Ambient

TVA II { Initial Trap Temperature: -100°
(——) { Ice-trap (5g. Ice) Temperature: -100°

I and II only shown as distinct where non-coincident.

represent material non-condensable at -100°C (but fully condensed at -196°C) and the trace obtained with the same sample weight, the initial trap at -100°C and the concentric trap empty and at ambient temperature, has been superimposed on the original curve. The following features were noted:-

At a heating rate of $10^{\circ}/\text{min.}$, the peaks with $T_{\text{max}} = 220^{\circ}\text{C}$ are coincident, so that:-

- (i) The earlier assumption, that this peak represents CH_3Cl production only, was correct.
- (ii) The ice has no visible effect on methyl chloride.

The peak with $T_{\text{max}} = 300^{\circ}\text{C}$ is greatly reduced in area, indicating a sizable HCl component. (Titration of the ice, after heating the copolymer to 500°C , revealed that 4.25×10^{-5} moles of HCl had been removed). At least one other component which is non-condensable at -100°C clearly contributes to this peak.

The effectiveness of the ice in removing HCl was not reduced when only 2g. of water was used and this was cast as a thin ice film in situ, by cooling the concentric trap to -196°C and pumping water vapour through it. This was verified using labelled PVC, when no activity was registered from the volatiles collected at -196°C beyond the ice trap. It was considered that a film of ice would be more likely to give consistent flow-rates when sample heating rates of $1^{\circ}/\text{min.}$ were employed in the subsequent degradation studies.

The Nature of the HCl-Ice Interaction

One, or both, of the following processes may be occurring on, or above, the ice surface:-

- (i) Association of HCl and H_2O in the gas phase to give a hydrate which is condensable at -100°C .

(ii) Adsorption of HCl on the ice surface.

The adsorption of gases on ice at low temperatures is already documented. Adamson and Dormant⁽⁸⁸⁾ showed that nitrogen could be adsorbed on annealed ice powders at -195°C , the adsorption behaviour being characteristic of a non-polar surface, while Barrer and Ruzicka⁽⁸⁹⁾ have reported spontaneous clathrate formation between ice powders and xenon and krypton at -78°C and spontaneous ethane hydrate formation at -96°C .

In the present work, experiments showed that the HCl/ice interaction is temperature-dependent. When the temperature of either the initial trap or the ice-trap fell below about -110°C , when a 100mg. sample of PVC* was being heated at $1^{\circ}/\text{min.}$, a flow of HCl through the ice-trap was registered on a Pirani gauge and verified by assay of the volatiles which passed through. As the trap temperatures were raised to about -110°C , the Pirani response due to unaffected HCl gradually decreased to zero. Clearly, the degree of interaction is determined by the temperature of the ice and/or by the temperature of the HCl impinging upon it.

An interesting feature of the temperature-dependence was that HCl flow through the ice-trap to the Pirani produced the familiar "edge-effect", characteristic of an insufficient ice surface area. As the ice films were prepared by the same method each time, from the same weight of water, the area of ice exposed to the volatiles must vary with temperature. In fact, it is known that ice undergoes structural changes between -160° and -70°C ⁽⁹⁰⁾ and these will give rise to variations in the total surface area. If the HCl/H₂O interaction is purely a gas-phase process, then no edge-effect should have been observed on lowering the temperature, rather the appearance of an

undistorted, though less intense HCl peak.

EVALUATION OF DEGRADATION APPARATUS AND TECHNIQUE

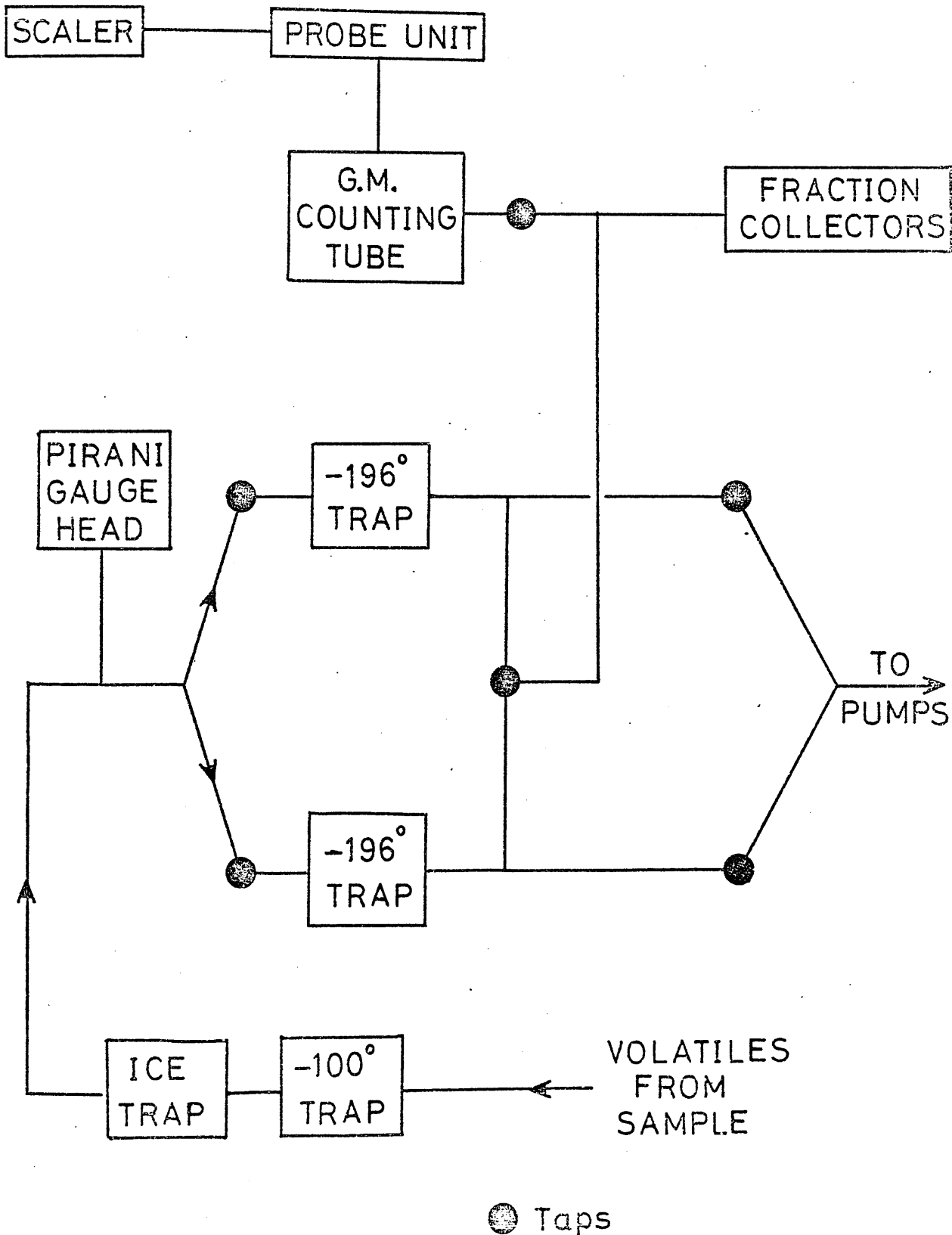
A schematic diagram of the apparatus used for the degradation experiments is shown in Fig. 13, p. 81. The Pirani gauge was added later, being primarily intended as a "trouble-shooting" device (see p. 86) and it should be considered absent at this point in the discussion. The sample-heating assembly was similar to that used in TVA (see Fig. 8, p. 67) and the vacuum line was constructed throughout of 6mm. diameter tubing. Quickfit FG10 flanges on the ice-trap allowed it to be removed at will. Greased stopcocks of 2mm. bore were used throughout and the gas counting assembly was the same as had been used for measuring the specific activity of vinyl chloride (see Fig. 2, p. 29). A vacuum of 10^{-5} torr was obtainable.

Polymer films were cast by pipetting 5ml. of a standard solution in tetrahydrofuran (non-condensable at -100°C) into the sample tube and removing the solvent in a vacuum oven. 100mg. of polymer was degraded using a heating rate of approximately $1^{\circ}\text{C}/\text{min.}$, and the volatiles were passed alternately through the two -196°C traps, during the oven temperature ranges (ambient - 140°C), ($140 - 160^{\circ}\text{C}$), ($160 - 180^{\circ}\text{C}$), -----, ($380 - 400^{\circ}\text{C}$). While one fraction was being condensed in one limb, the previous fraction could be transferred to a collection tube. The fraction-collectors consisted of twelve 20cm. - long tubes, fitted with taps and arranged in clusters of six and the fractions could be stored in liquid nitrogen until required. The two final fractions could be stored in the -196°C traps, but were transferred as soon as collection tubes became vacant.

The fractions were counted cumulatively, in order of increasing

Fig.13

FRACTIONATION AND ASSAY OF CHLORINATED VOLATILES



temperature range, by distilling each one in turn into the counting zone and pumping off any non-condensable material. The volume of the counting zone was arranged so that the pressure exerted by the volatiles from 100 mg. of polymer would not exceed one atmosphere. Output from the counter was transmitted via a probe unit to the scaler, as before.

For each copolymer, two experiments were carried out, the first with a 2g. ice film at -100°C in the trap and the second with an empty ice trap at -100°C . The first curve obtained (corrected counts/min. vs. temperature) showed methyl chloride evolution only, while the second showed the evolution profile for the total chlorinated volatiles ($\text{CH}_3\text{Cl} + \text{HCl}$). Subtraction of the two curves showed the evolution of HCl alone.

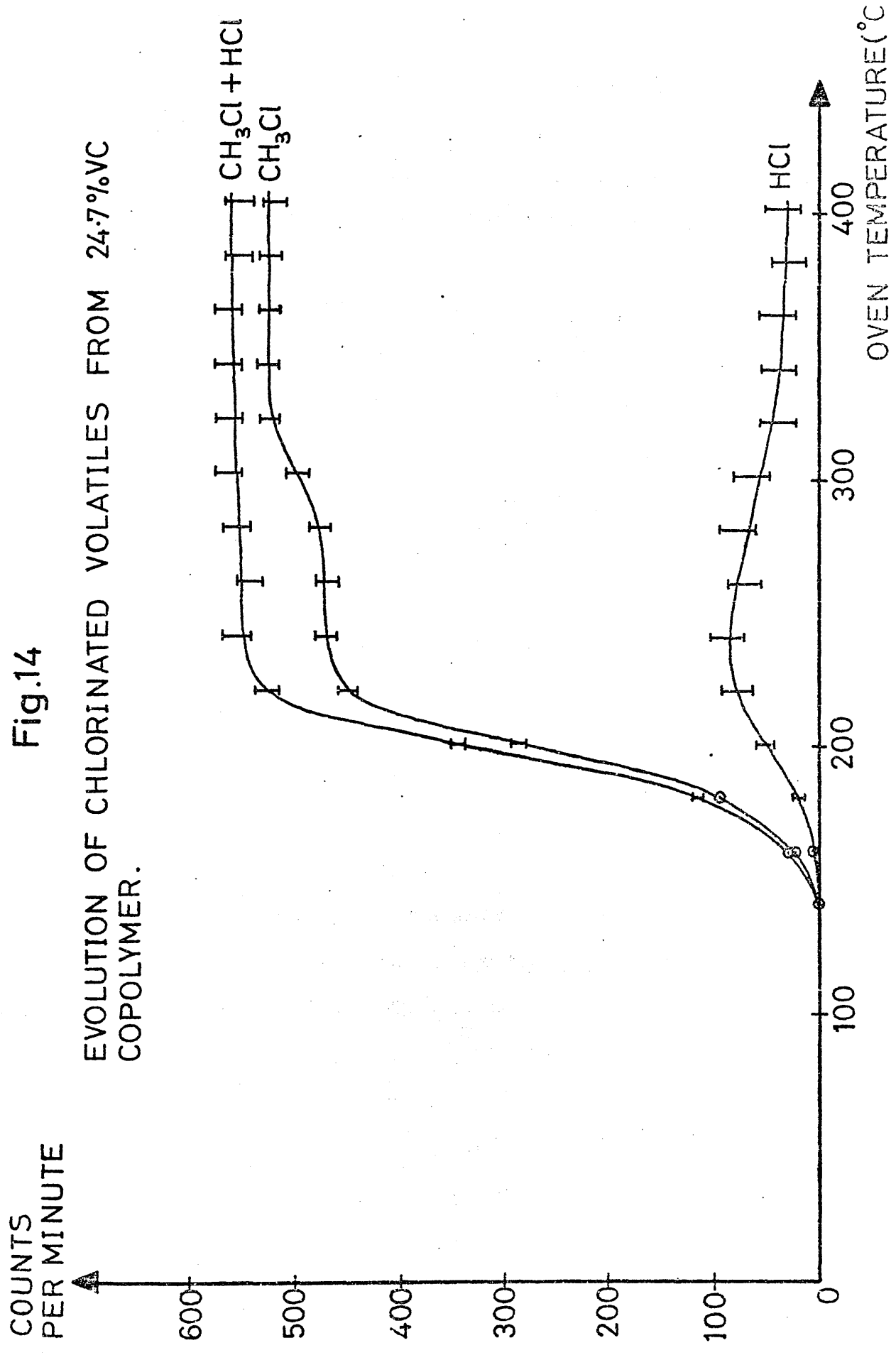
The slow heating-rate employed ensured that the time taken for opening/closing taps was insignificant and it allowed ample time for transferring fractions to the collectors. It was also quite possible to count fractions during the course of a run, but the accuracy of counting was naturally reduced.

The experimental method outlined above gave satisfactory results with a labelled PVC sample, but subsequent experiments on a labelled 25% VC copolymer, using the separation technique, showed the procedure to be technically imperfect. The results obtained for the copolymer are shown in Fig. 14, p.83. The most obvious anomaly is the apparent loss of accumulated HCl activity (as found by difference) towards the end of the experiment. The following possible sources of error were investigated:-

(1) Absorption of volatiles by greased surfaces in the counting volume at high gas pressures.

Fig.14

EVOLUTION OF CHLORINATED VOLATILES FROM 24.7%VC COPOLYMER.



- (2) Loss of some activity during the pumping out of non-condensable material.
- (3) A temperature difference between cold-finger and counting-tube.
- (4) Removal of some methyl chloride by ice at the low volatile flow-rates being used.
- (5) Inefficient HCl removal at low volatile flow-rates.
- (6) Inconsistency of sample weight and thickness.
- (7) Increased self-absorption of β^- by the volatiles at high pressures.

To check (1), the total volatiles from a radioactive 25% VC* copolymer were counted and then distilled into an evacuated tube whose walls were coated with a layer of Apiezon "L" grease (as used on the joints and stopcocks). After the tube had been warmed to ambient temperature, the volatiles were allowed to redistil into the counter for a few minutes. Times required for the quantitative distillation of such small amounts of material were normally of the order of a few seconds, yet a 10% reduction in activity was observed. Presumably, the methyl chloride component is more susceptible to absorption by a hydrocarbon grease — this would explain the apparent absence of the effect in experiments with PVC*. The problem was overcome by removal of all greased taps and joints from the counting volume and replacement by a single Teflon tap (Quickfit TF2/18), as in Fig. 15, p. 85.

To eliminate (2), the "pumping out" practice was stopped — vacuostat readings confirmed that leakage of air into the counting zone was negligible during the course of an experiment.

The number of moles of gas in the counting tube (and hence the number of counts/minute) will vary with the temperature of the cold finger when the counting volume is isolated, so that (3) was eliminated

Fig.15

GAS COUNTING ASSEMBLY

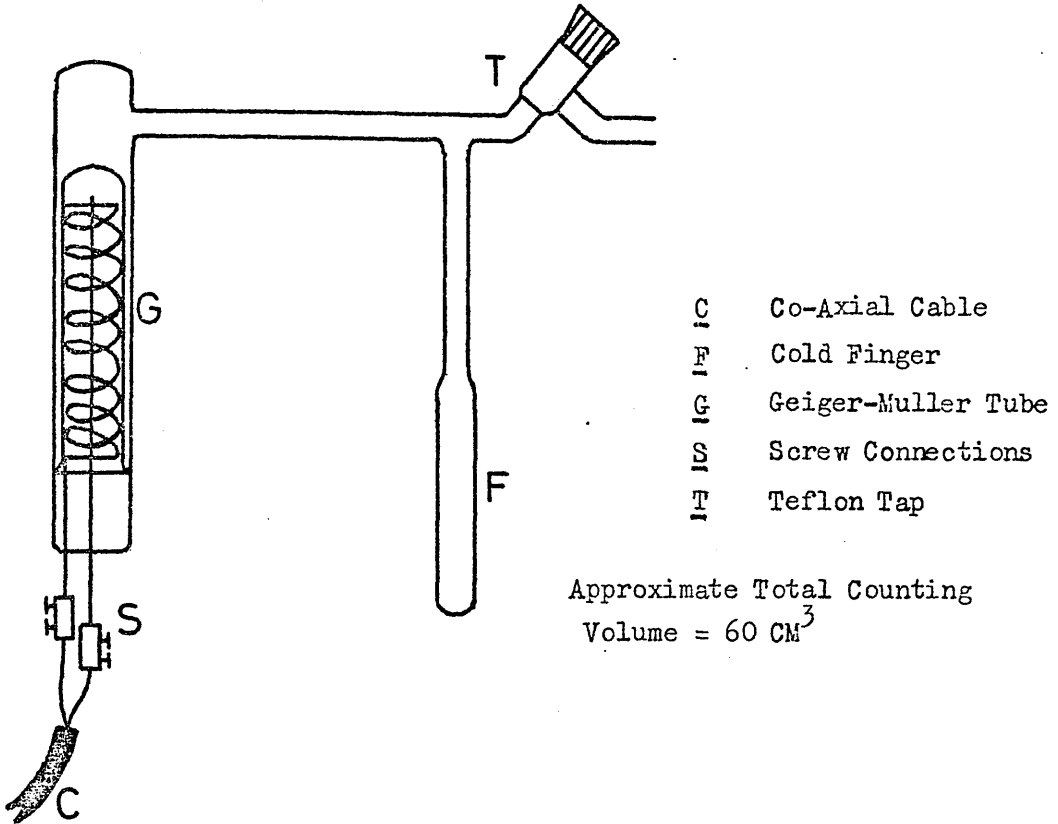
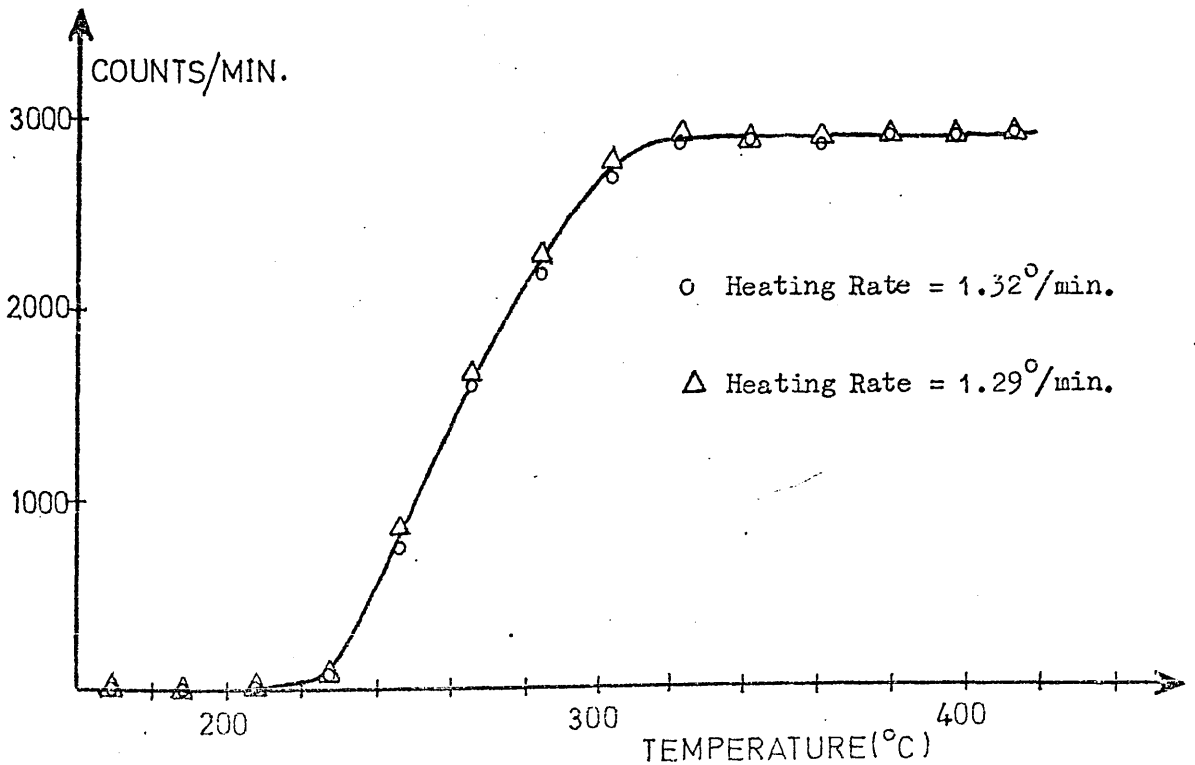


Fig.16

CURVE REPRODUCIBILITY FOR
100mg. OF PVC*



by always allowing the cold finger to reach ambient temperature after thawing the condensed volatiles.

In order to investigate (4) and (5), a Pirani gauge was incorporated into the system (as in Fig. 13, p. 81) and the initial "methyl chloride" TVA peak of a 10% VC* copolymer was monitored with/without ice in the trap. To avoid overlap of this peak with the one caused by the release of tetrahydrofuran, the solvent for the polymers was changed to cyclohexanone; this was condensable at -100°C and could therefore be removed in the initial trap. It was hoped that any removal of methyl chloride by the ice would produce a consistent difference in the TVA curves, but the experiments were inconclusive since small changes in the peak shape obtained by heating 100 mg. of polymer at $1^{\circ}/\text{min.}$ could be assigned to various other factors:-

- (i) Variation of trap temperatures between runs.
- (ii) Opening and closing taps, which caused small local variations in Pirani response.
- (iii) Changes in the liquid nitrogen levels in the -196°C traps, which effectively varied the distance from Pirani to cold trap.
- (iv) Slight differences in programmed heating rates (see p.90).
- (v) Variation in sample weight and thickness (see p.87).

Trap temperatures were monitored by fitting chromel-alumel thermocouples and passing the outputs into the recorder, but even with matched trap temperatures, the TVA curves obtained failed to reveal a trend which would indicate methyl chloride removal.

In another experiment, the 10% VC* copolymer was degraded to T_{max} of the initial "methyl chloride" peak and the activity of the ice was monitored. Methyl chloride dissolves in water at 20°C to the extent of 3.03 ml./ml. of water, so that sufficient water was present (on

thawing 2g. of ice) to dissolve the total theoretical methyl chloride evolved. The activity of the water rose only by about 2% and part of this might be due to traces of HCl*. Thus it was apparent that any CH₃Cl/ice interaction was insignificant.

As a final check, an inactive copolymer of intermediate composition was degraded until T_{max} of the "methyl chloride" peak was reached and a gas-phase I.R. spectrum was taken of the total volatiles non-condensable at -100°C. The experiment was repeated with ice in the trap and comparisons were made of the intensities of the main absorption bands of methyl chloride, but no indication of methyl chloride removal was obtained.

(5) was investigated as a source of experimental error by degrading labelled PVC at 1°/min. and measuring the activity of the volatiles which by-passed the ice film and collected in the -196°C traps. HCl removal was found to be quantitative, just as it had been at a heating rate of 10°/min. However, observation of the Pirani response led to the discovery that HCl removal is dependent upon the temperature of the ice film (see p. 79).

(6) proved to be an important source of error. The film-casting technique involved pipetting 5ml. of a solution of the polymer in cyclohexanone onto the base of the TVA tube, followed by slow evaporation of the solvent in a vacuum oven. The total HCl evolved from two PVC* films cast from "equal" volumes of the same solution was compared by gas counting and found to differ by an amount well outwith that expected from use of the 2σ confidence limit (about 10%, instead of a "statistical" 3%). The viscosity of the polymer solutions (concentration = 20mg./ml.) clearly prevents consistent volume transfer from a pipette.

Another related problem was the difficulty in preparing films of uniform thickness — slow removal of cyclohexanone in the vacuum oven did not give very satisfactory results. There will be two possible consequences of variation in sample thickness:-

(i) Diffusion control of the rate of volatile evolution in some experiments but not in others. The results of Neil⁽⁸⁴⁾ suggest that this effect can be neglected under the present experimental conditions if films of reasonably uniform thickness are used.

(ii) Changes in the extent of product - polymer interactions as a consequence of (i). A typical example of this is the downward shift of T_{max} , which is observed to occur with increasing film thickness, for the dehydrochlorination reaction in PVC. (see p.189).

To eliminate these effects and also the possibility of inaccurate polymer weights, a better film-casting method was sought:-

Solutions of known concentration were made up and a measured weight of the solution was transferred to the TVA tube, so that the exact weight of polymer in the film (100 ± 3 mg.) could be calculated. The solvent was removed by gentle blowing with oxygen-free nitrogen at a constant flow-rate, followed by heating in a vacuum oven for four hours at $60-70^{\circ}\text{C}$. Cyclohexanone tends to undergo peroxidation in presence of oxygen and the incorporation of peroxides into the polymer will naturally affect its degradation behaviour. Consequently, the solvent was distilled and stored under oxygen-free nitrogen prior to use.

Films cast by the new method were of uniform thickness and labelled PVC samples (corrected to 100mg) gave plots of counts/minute vs. temperature which were superimposable within the statistical

error limits of counting (see Fig.16 ,p.85).

Finally, errors due to self-absorption at high gas pressures (7) were found to be insignificant:-

The activity of a sample of radioactive HCl (from the degradation of 100mg. of PVC*) did not shift below the 20 error limit when benzene was added to the counter, even to the extent where the sample was saturated with benzene. Similarly, the activity of a sample of radioactive vinyl chloride was not reduced when a large volume of carbon dioxide was added.

After giving attention to factors (1) — (7) and making the necessary alterations to the technique and apparatus, satisfactory results were obtained with the copolymers as well as with PVC*. Incorporation of the Pirani gauge allowed a useful additional monitor of volatile evolution and the temperatures of the initial trap and ice-trap could be kept fairly consistent between runs by recording the output from the thermocouples.

SUMMARY

The apparatus which gave the most informative and reliable results is shown in Fig. 13, p.84, incorporating an initial trap at -100°C (to remove potential contaminants), an ice-trap maintained above -110°C (to remove HCl), followed by a Pirani gauge and a "greaseless" gas counting system (Fig. 15, p.85). Polymer films were cast from a weighed amount of cyclohexanone solution of known concentration.

PRESENTATION OF RESULTS

(i) Sample Temperatures

The sample temperature corresponding to any given oven temperature was obtainable after plotting the temperature lag between oven and

sample as a function of temperature (see Fig. 17, p.91). The standard method described on p.70 was used.

(ii) Sample Heating Rates

Since the average oven heating rate between the start and finish of each run was fairly constant, always being within $\pm 3\%$ of $1.32^\circ/\text{min.}$ (see Table V, p. 91), it can be assumed that the individual sample heating rates will be proportional to those for the oven.

(iii) Trap Temperatures

The variation in temperature of the initial and concentric traps during each run is shown in Table VI, p. 92.

(iv) Correction of Activity Measurements

The count-rate obtained after the accumulation of each volatile fraction was corrected for counter background (approximately 30 cpm) and dead-time and then corrected to 100 mg. of polymer. The data obtained for each copolymer were then further adjusted to allow for the differences in specific activity of ^{36}Cl , by multiplying each count-rate by the ratio:-

$$\frac{\text{specific activity of VC* used to make PVC*}}{\text{specific activity of VC* used to make copolymer}}$$

The 2 σ confidence limit was applied to all measurements.

The TVA and radiochemical volatile analysis curves obtained for PVC* and the copolymers are shown in Figs. 18 to 23. (pages 93 - 98) In both sets of data, the curves drawn as a continuous line (—) correspond to results obtained with no ice in the concentric trap, while those drawn as a broken line (.....) correspond to data obtained with a 2 g. ice film.

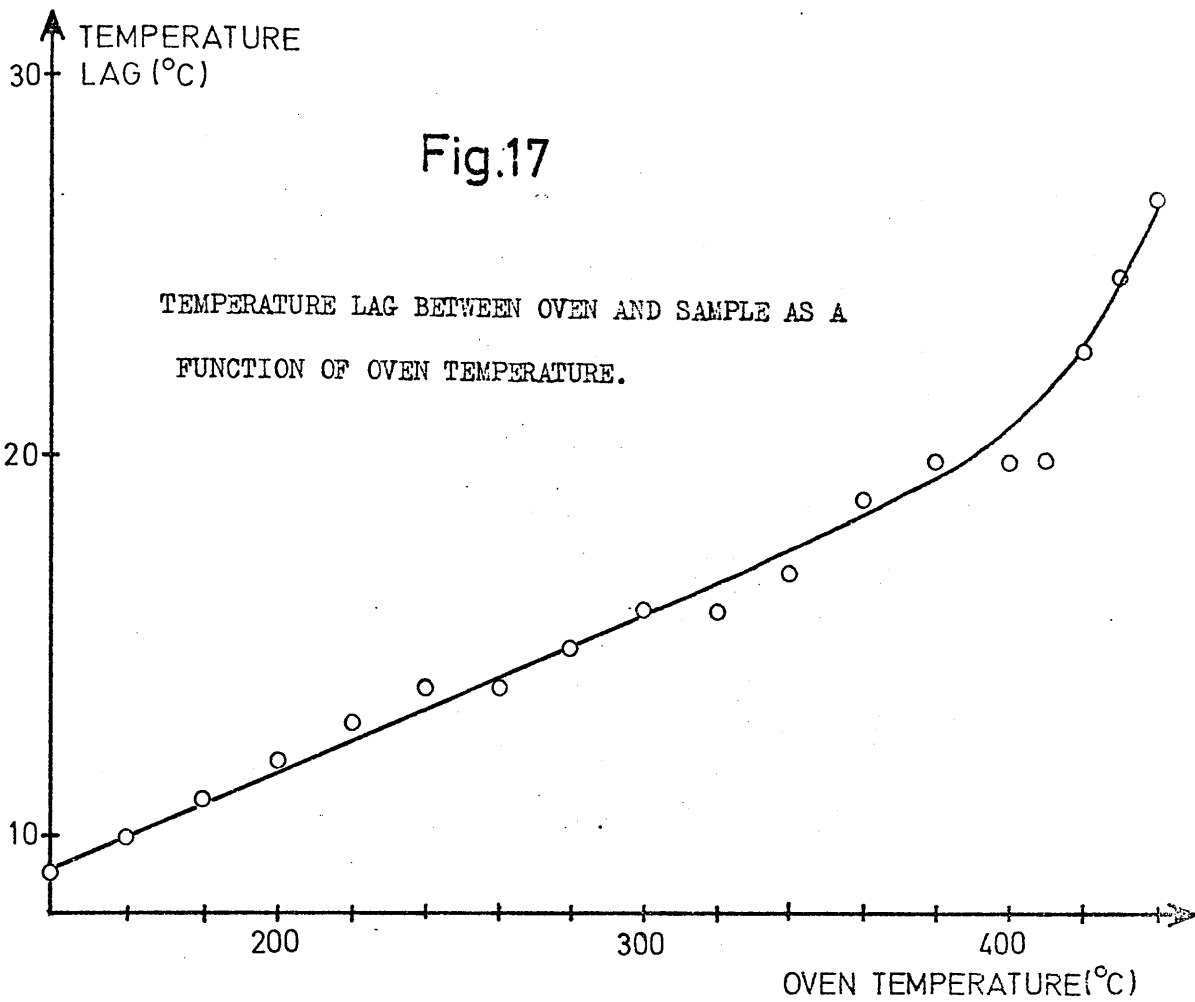


TABLE V

Average Oven Heating-Rates During Each Run (°C/Min.)

Polymer	Ice in Trap	No Ice in Trap
Copolymer 1	1.33	1.33
" 2	1.36	1.34
" 3	1.31	1.34
" 4	1.31	1.30
" 5	1.34	1.30
PVC*	—	1.30

TABLE VI

Trap Temperatures during each Run (°C)

Polymer	Trap	Ice in Trap	No Ice in Trap
Copolymer 1	I	→ -110 -105	→ -115 -105
	II	-110 -80	-110 -85
" 2	I	-115 -100	-115 -100
	II	-115 -80	-115 -85
" 3	I	-115 -100	-115 -95
	II	-120 -85	-115 -85
" 4	I	-115 -95	-110 -95
	II	-115 -85	-110 -85
" 5	I	-110 -100	-110 -100
	II	-110 -80	-110 -85
PVC*	I	—	-110 -100
	II	—	-120 -90

I and II refer to the initial trap and ice-trap respectively.

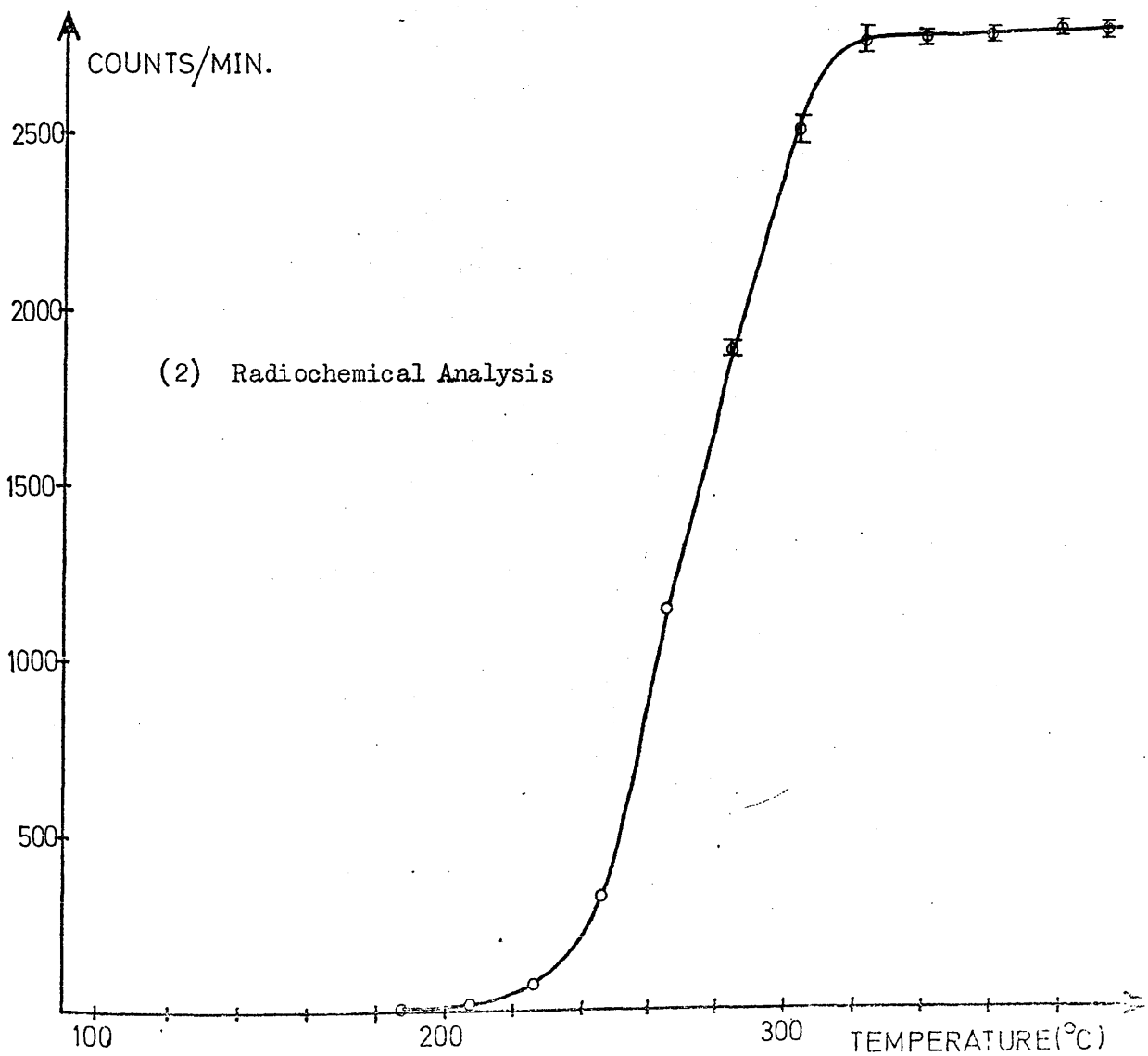
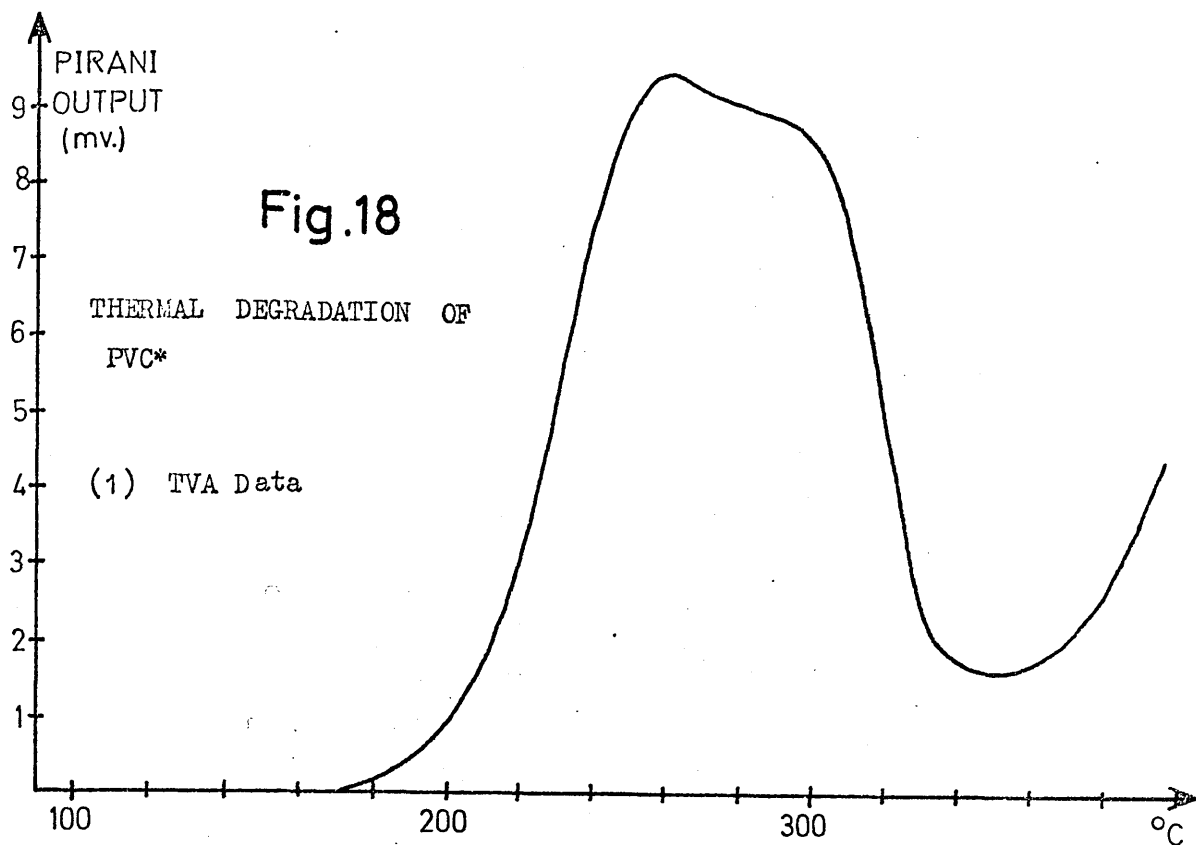


Fig.19

THERMAL DEGRADATION OF 88.6% VC* COPOLYMER

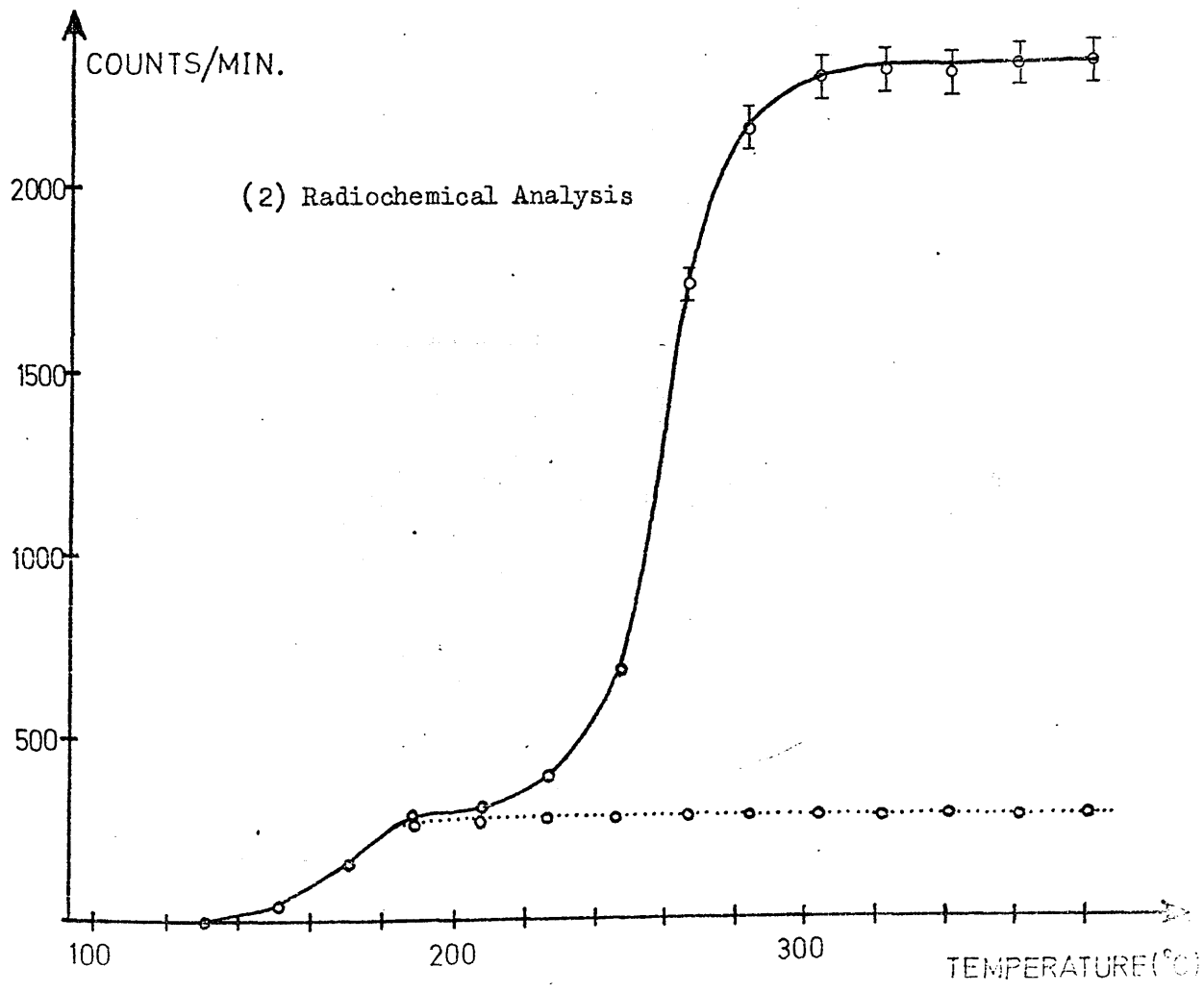
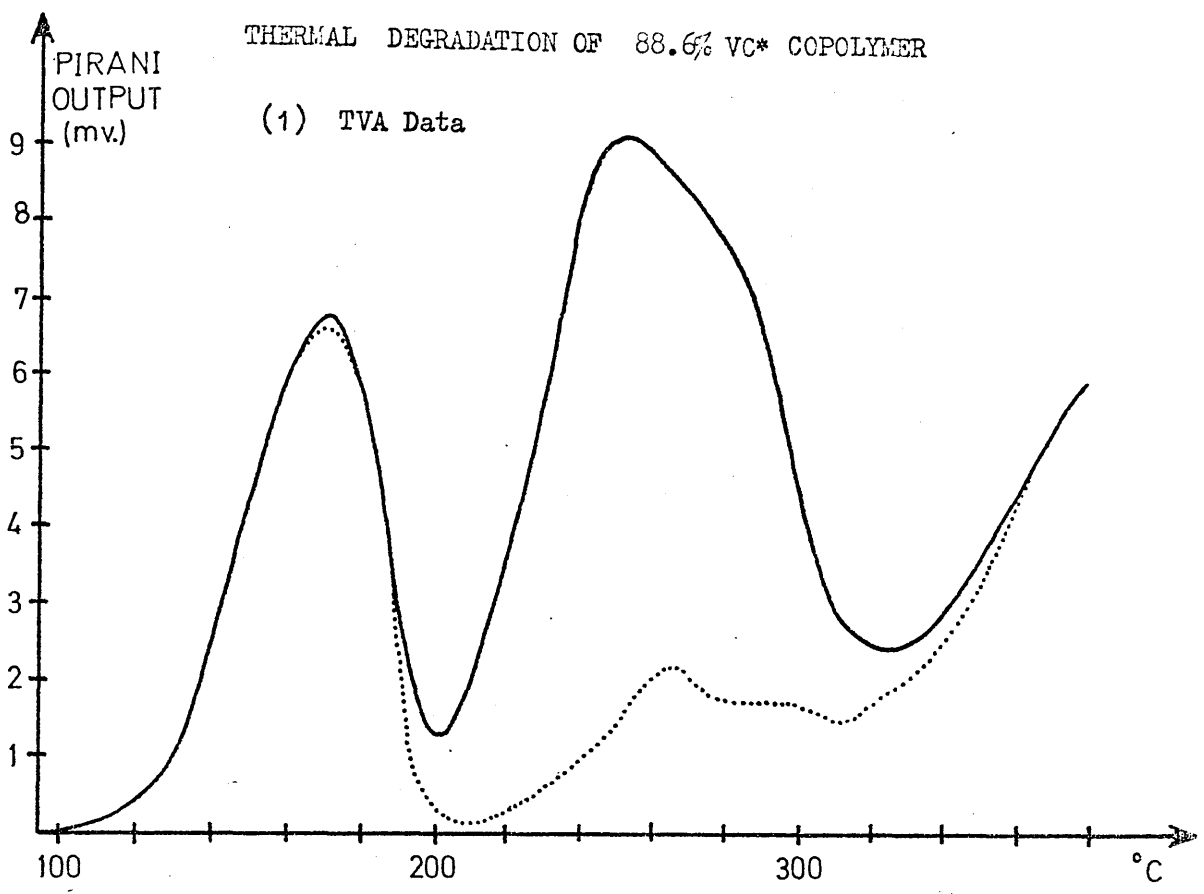


Fig.20

THERMAL DEGRADATION OF 82.4% VC* COPOLYMER

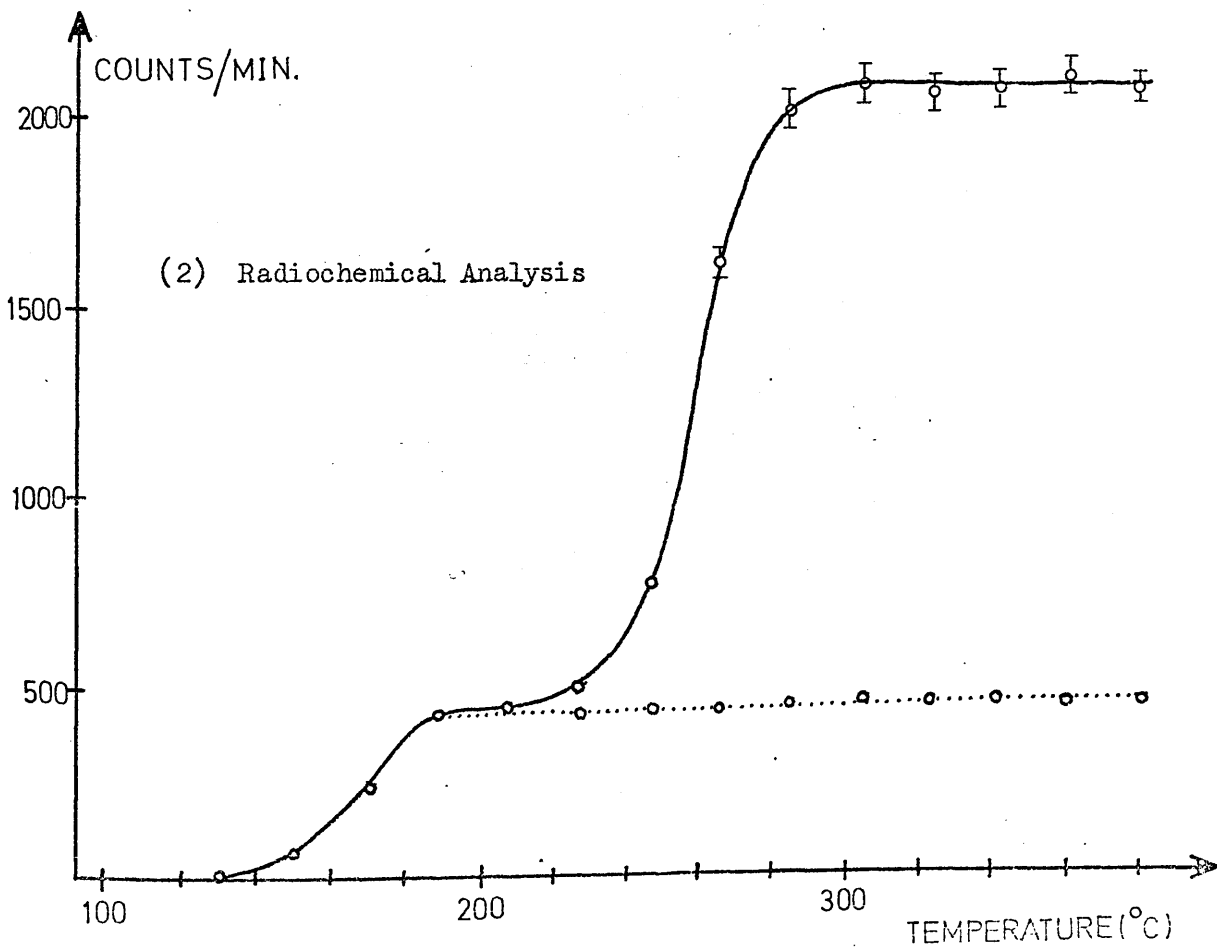
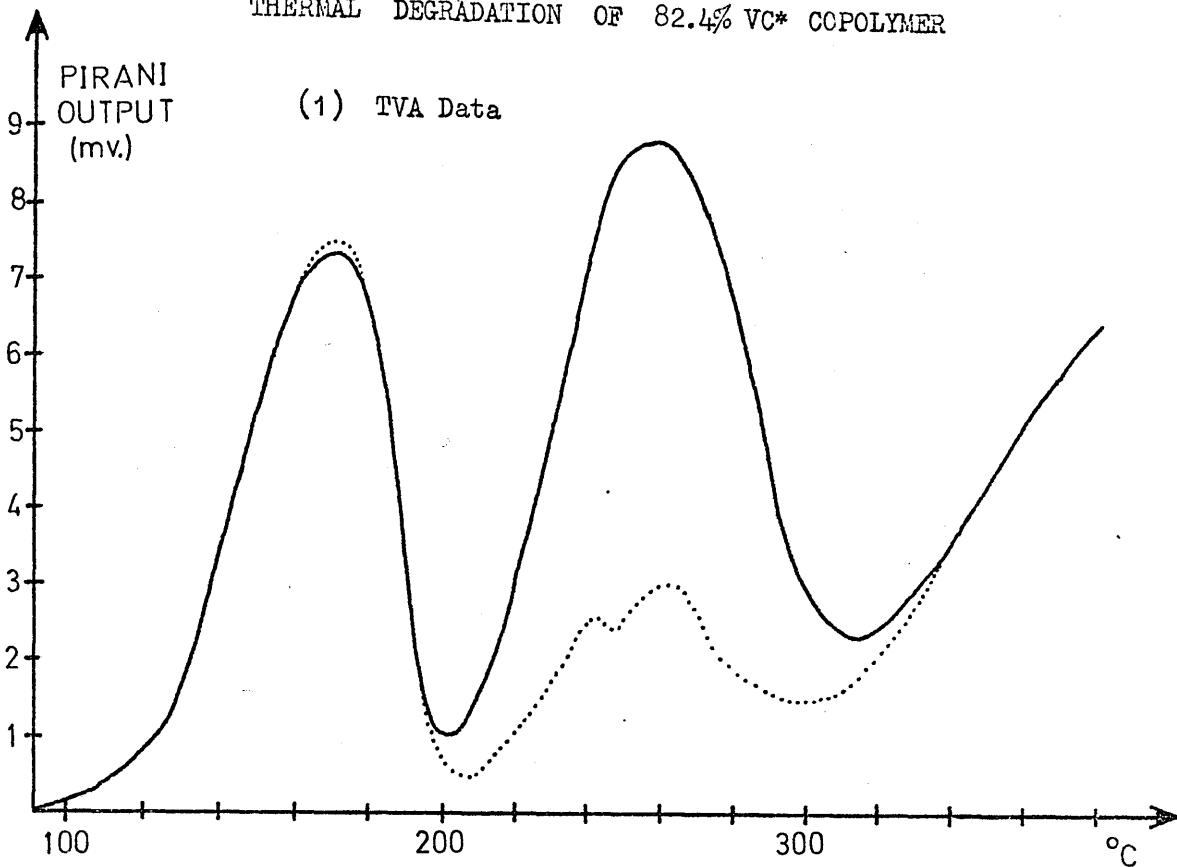


Fig.21

THERMAL DEGRADATION OF 62.6% VC* COPOLYMER

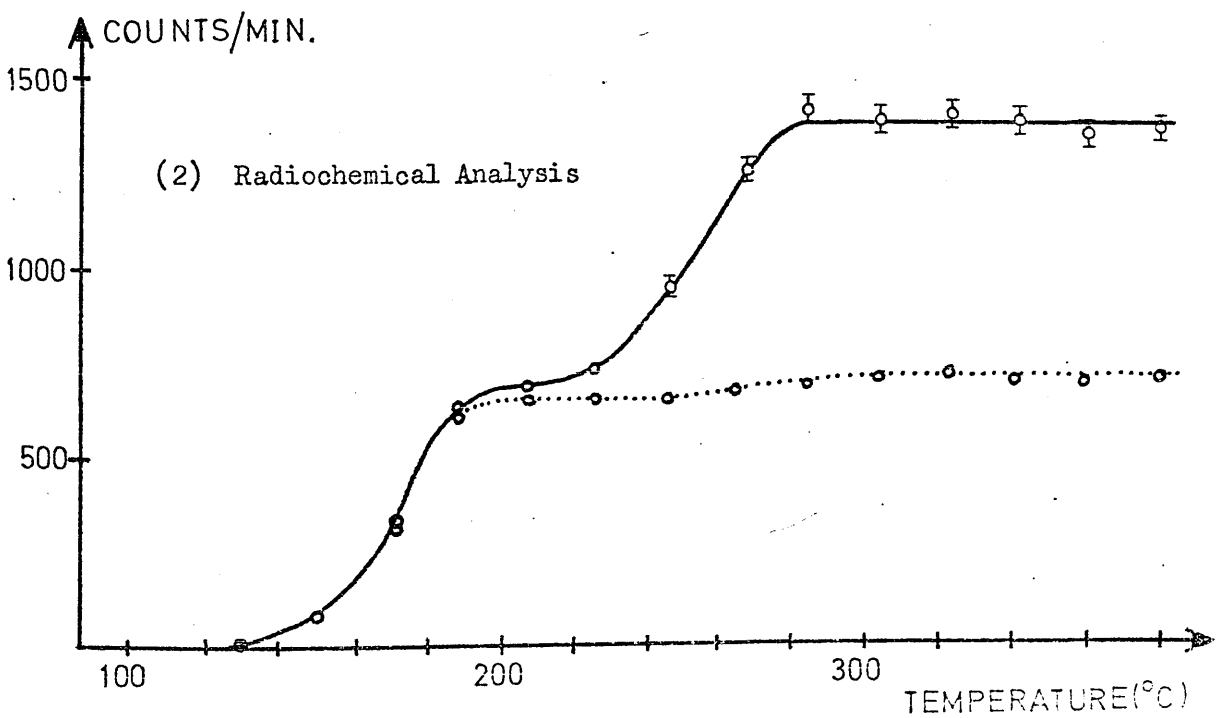
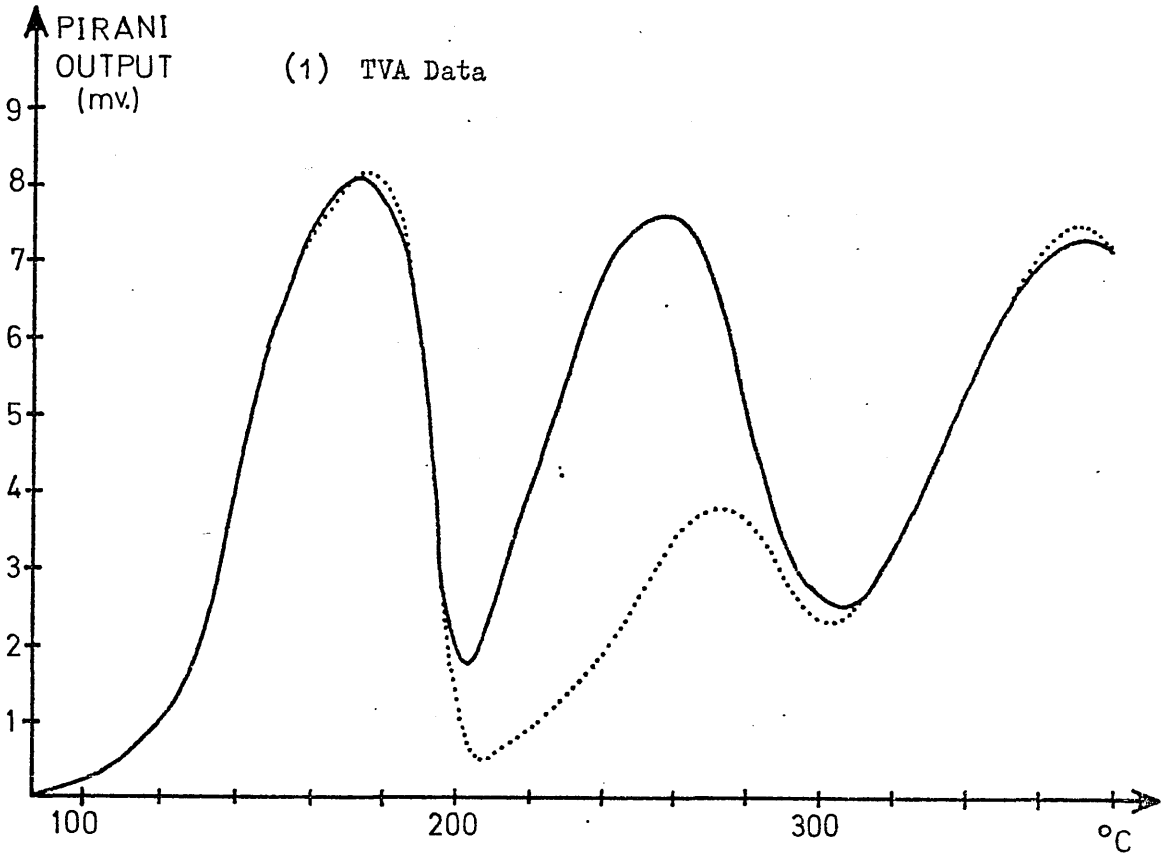


Fig.22

THERMAL DEGRADATION OF 24.7% VC* COPOLYMER

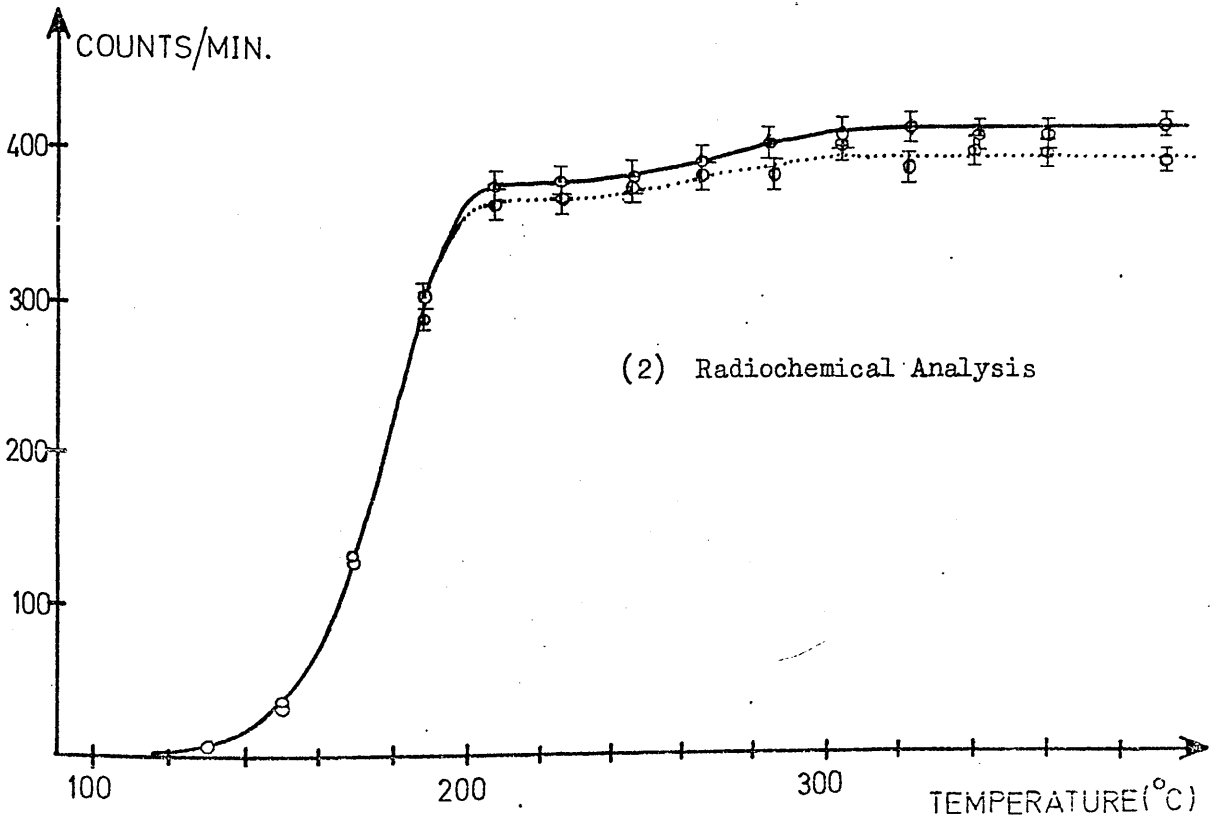
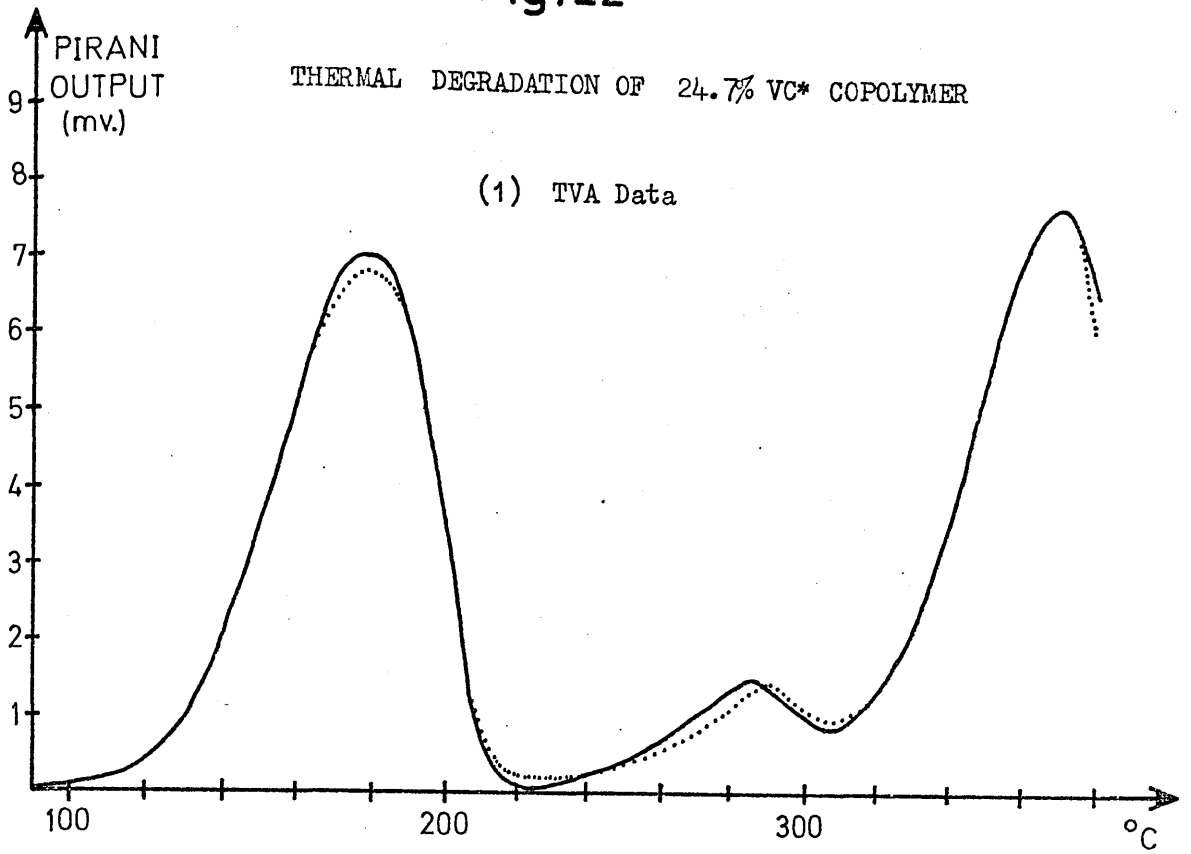
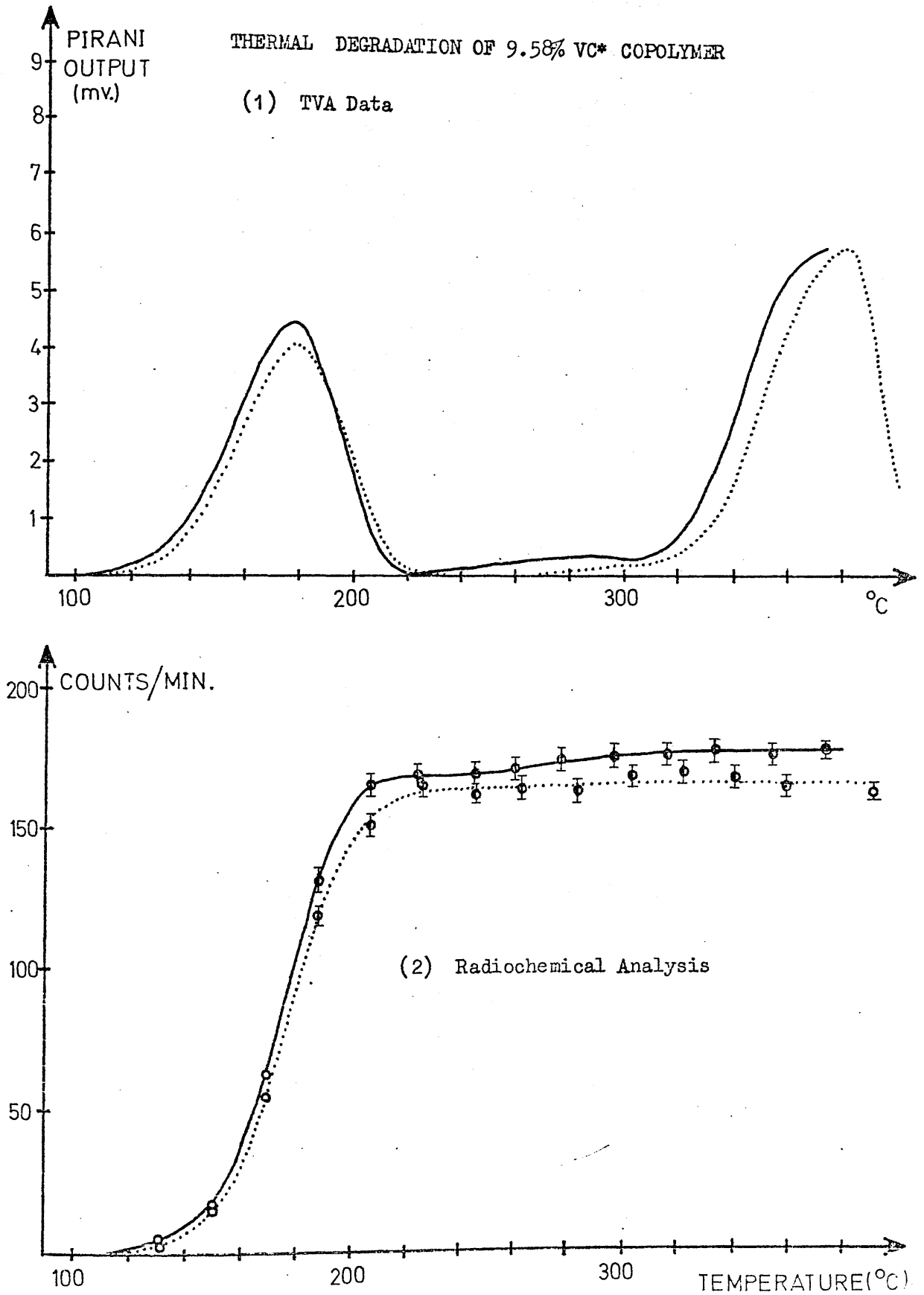


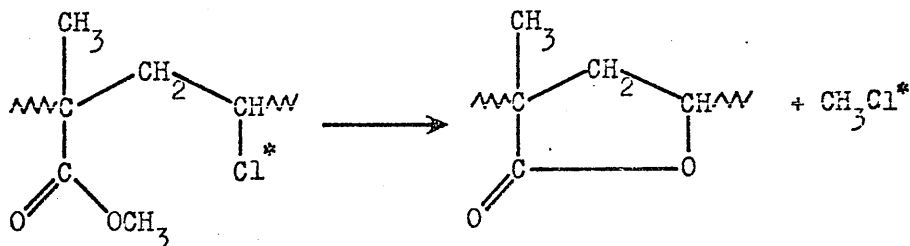
Fig. 23



(V) Relation between radioactivity and moles of product

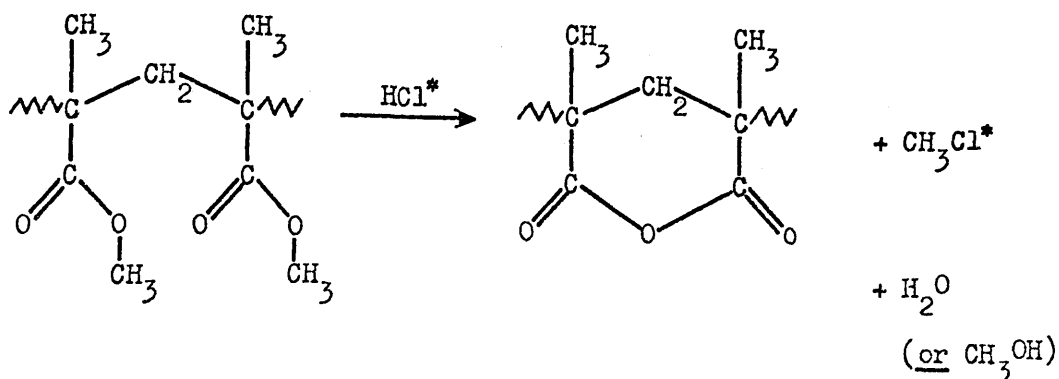
By titrating the volatiles against standard NaOH solution, it was shown that quantitative loss of HCl was obtained when 100 mg. of PVC* was heated to 400°C at 1°/min. It was thus possible to relate the total volatile activity obtained on degrading 100 mg. of PVC* to a specific number of moles of Cl, so that in Figs. 18 - 23 (and in all subsequent data), each count per minute can be equated with $5.694(\pm 0.036) \times 10^{-7}$ moles of chlorine-containing volatile product.

The only significant chlorinated products in the degradation of random VC - MMA copolymers are known to be HCl and methyl chloride, so that in each case, the first stage of radioactive volatile evolution must correspond to CH_3Cl^* produced by lactonization. i.e.,



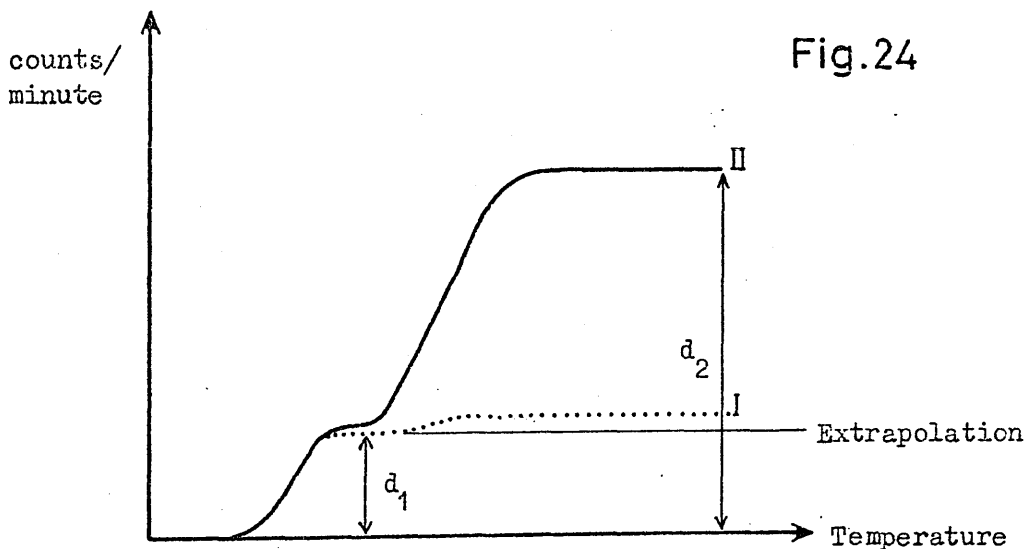
It will be recalled that this reaction involves randomly-selected pairs of adjacent VC and MMA units in the polymer chain.

A second phase of CH_3Cl^* evolution is observed (except in copolymers at extreme ends of the composition range) and this must correspond to reaction of HCl^* with unlactonized MMA units, as proposed by Guillot et al. (9) for this copolymer system and by McNeill and Neil (8) for PVC - PMMA blends:-



Consequently, the total HCl^* liberated by any copolymer is stoichiometrically equivalent to the summation of free HCl^* and CH_3Cl^* liberated in this secondary reaction.

The volatile analysis curves follow the general pattern shown below:-



At 400°C , all the traces are effectively parallel to the temperature axis. Comparison of the final ^{36}Cl activity obtained in each case (i.e., $\text{HCl}^* + \text{CH}_3\text{Cl}^*$), with the corresponding value for PVC^* degraded to 400°C , confirmed that removal of chlorine from the copolymers can

be regarded as complete at this temperature — copolymer compositions obtained by measuring the total volatile activities compare favourably with those predicted from the reactivity ratios obtained in Chapter II:-

TABLE VII: Copolymer Compositions from Radioactive Volatile Analysis

Copolymer	% VC by Volatile Analysis	% VC Predicted using r_1, r_2
(1)	9.81	9.58
(2)	21.8	24.7
(3)	60.9	62.6
(4)	82.5	82.4
(5)	89.6	88.6

For each copolymer, a curve corresponding to "lactonization" CH_3Cl^* can be obtained by extrapolating, parallel to the temperature axis, the horizontal portion of curve I which exists before the onset of the $\text{HCl}^*/\text{ester}$ interaction. A curve corresponding to total HCl^* evolution can then be obtained by subtraction of this extrapolated curve from curve II, while "free" HCl^* evolution is found by subtracting I from II. Figs. 25 and 26 (pp.102 and 103) show the evolution patterns obtained for total HCl^* and total CH_3Cl^* respectively. In the former case, the graphs have been drawn by subtraction of "best fit" curves, so that no error limits are included — the error on any point will be given by $\pm \sqrt{e_1^2 + e_2^2}$, where $(\pm e_1)$ and $(\pm e_2)$ are the errors on the curves being subtracted at that point and approximate values of these can be obtained by reference to Figs. 18 - 23.

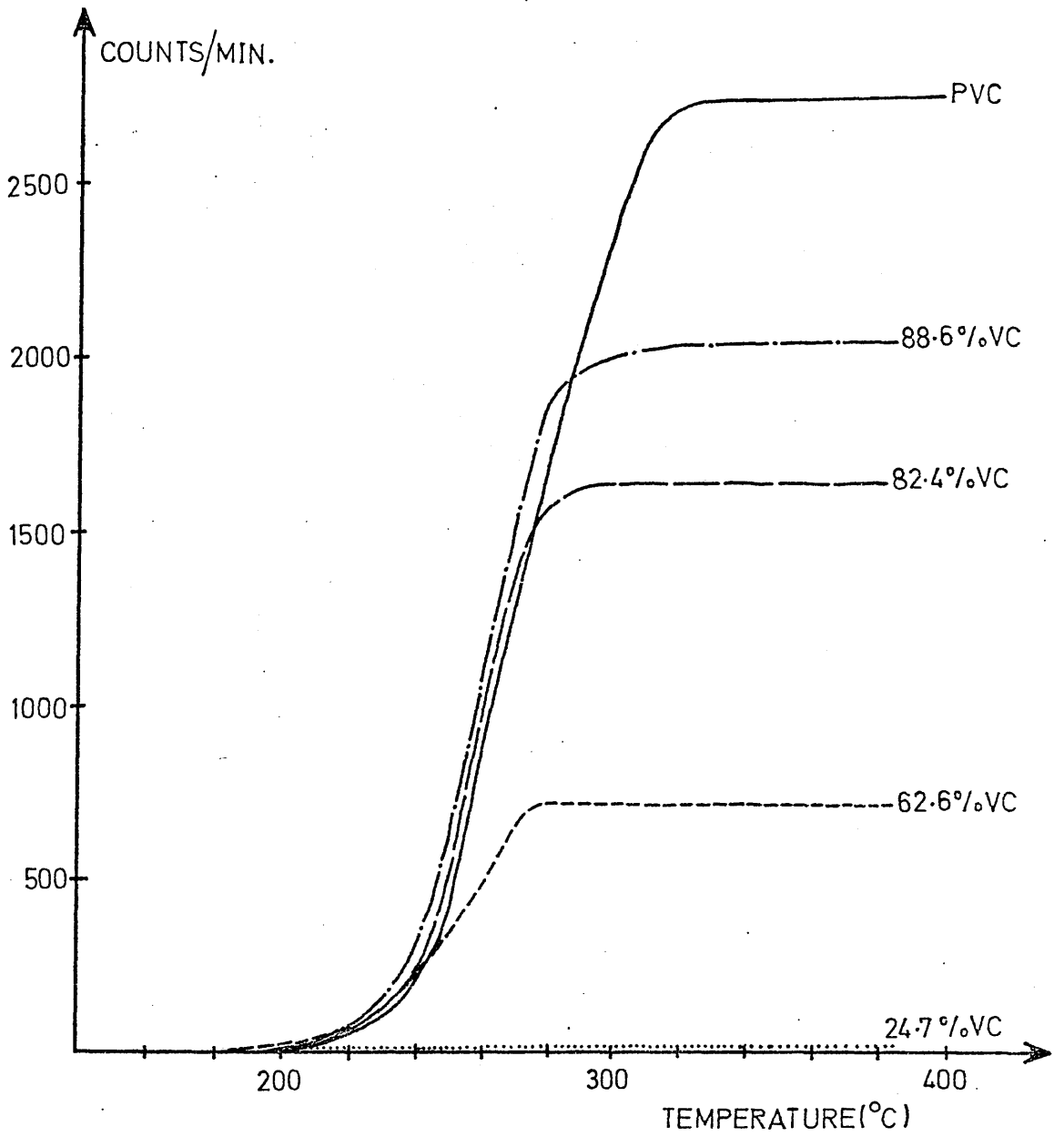


Fig. 25

EVOLUTION OF HCl* FROM PVC* AND THE COPOLYMERS.

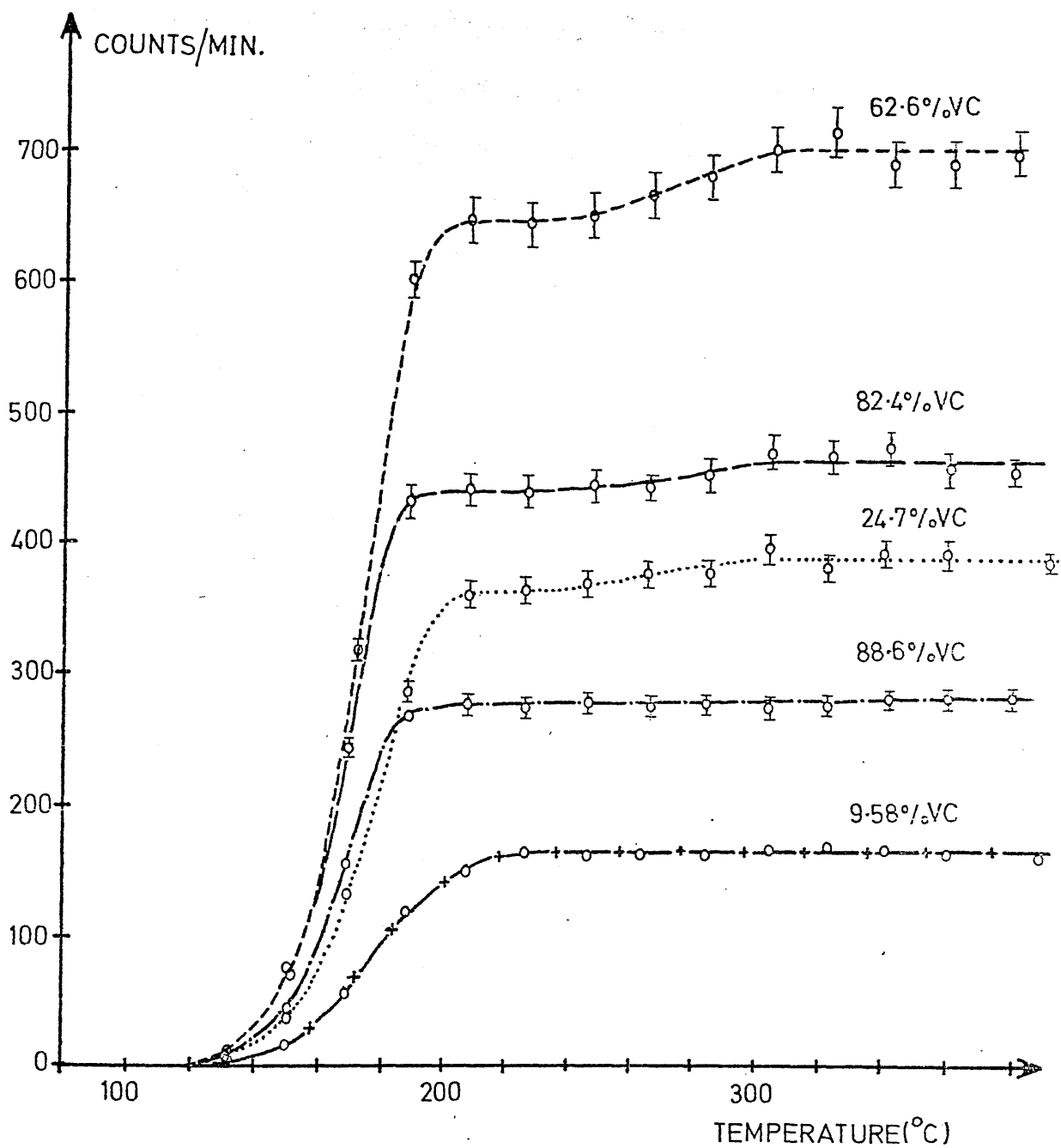


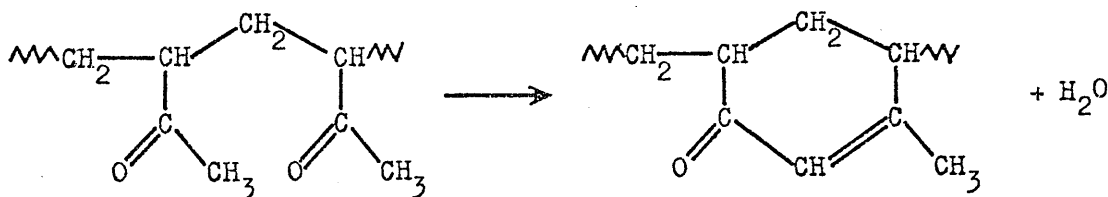
Fig.26

EVOLUTION OF CH_3Cl^* FROM THE COPOLYMERS.

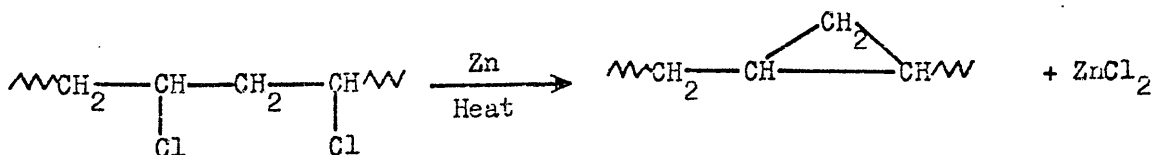
It is now required to correlate the theoretical sequence distributions, predicted from r_1 and r_2 , with volatile composition. Examination of Fig. 24 p.100 shows that the fraction of the total VC units which are lactonized in each copolymer can be found simply by measuring \underline{d}_1 and \underline{d}_2 . The calculation of the corresponding theoretical fractions demands a short discussion of the statistics of random intersequence cyclization reactions:-

THE STATISTICAL TREATMENT OF 1,3-CYCLIZATION REACTIONS OF VINYL POLYMERS

Marvel and Levesque⁽⁹¹⁾ found that the 1,3-cyclization reaction which occurs when poly(methyl vinyl ketone) is pyrolyzed at 300°C was non-stoichiometric, yielding only 85% of the total theoretically-available H₂O:-



Marvel and Sample⁽⁹²⁾ also showed that the 1,3-dechlorination of PVC with metallic zinc, to give cyclopropane rings, was likewise non-quantitative:-



Flory⁽⁹³⁾ explained these phenomena in terms of a random 1,3- interaction, in which some of the pendant substituents will remain

In both (i) and (ii), the total number of sequences of a given type is expressed as a function of the propagation probabilities of the copolymer system. For example, P_{AB} is the probability that, during the copolymerization process, a growing polymer chain of the type $\sim\sim\sim A\cdot$ will react with a monomer molecule of type B . Thus the total number of alternating sequences of type $A \left\{ (AB)_n \right\} A$, for example, is given as

$$(\text{Total number of } \underline{A} \text{ units in copolymer}) \times P_{AA}^2 \cdot P_{AB}^n \cdot P_{BA}^n$$

Similarly, the total number of "homopolymer" sequences of type $A \left\{ (B)_n \right\} A$ is given by

$$(\text{Total number of } \underline{A} \text{ units in copolymer}) \times P_{AB} \cdot P_{BB}^{n-1} \cdot P_{BA}$$

In all cases, P_{AA} and P_{BB} can be eliminated using the relations $P_{AA} + P_{AB} = 1$ and $P_{BA} + P_{BB} = 1$, giving as the final expression:-

$$f_u(B) = \left\{ \cosh \sqrt{P_{AB} P_{BA}} - \sqrt{\frac{P_{BA}}{P_{AB}}} \sinh \sqrt{P_{AB} P_{BA}} \right\}^2,$$

where $f_u(B)$ is the fraction of the total B units which cannot undergo cyclization.

The probabilities can be calculated⁽⁹⁵⁾ for low-conversion copolymers from the monomer reactivity ratios (r_A, r_B) and the percentage molar concentrations (A_f, B_f) of monomer units in the polymerization mixture:-

$$P_{AB} = 1 / (1 + r_A A_f / B_f)$$

$$P_{BA} = 1 / (1 + r_B B_f / A_f)$$

Alternatively, these probabilities can be calculated from the percentage molar concentrations (A,B) of A and B in the copolymer and the run number, $R^{(96)}$, by use of the following equations:-

$$P_{AB} = R/2A$$

$$P_{BA} = R/2B$$

Run number is defined as the average number of monomer sequences (runs) which occur per 100 monomer units in a copolymer. Consider, for example, the portion of copolymer chain shown below:-



The chain contains 20 monomer units arranged in 12 alternating runs (underlined). The run number associated with this structure is therefore 60.

Run number is a convenient parameter for characterizing sequence distribution in copolymers. It provides a useful mental picture of sequence distribution and its use simplifies considerably the calculations involved. One useful parameter which can be easily determined from R is the number-average length of a given type of sequence, denoted by $\langle A \rangle$ or $\langle B \rangle$. This is simply the total number of given type monomer units divided by the number of runs of that type present:-

$$\langle A \rangle = A/(R/2) \quad \text{and} \quad \langle B \rangle = B/(R/2)$$

The expression of propagation probabilities in terms of A, B and R also allows, for example, the fraction of A units centred in $\sim\sim$ BAAAB $\sim\sim$ type pentads to be determined:-

$$P_{\substack{\sim\sim \\ \uparrow \\ \text{BAAAB} \\ \uparrow \\ \sim\sim}} = P_{AA}^2 P_{AB}^2 = \frac{R^2(A - R/2)^2}{4A^4}$$

Run numbers themselves can be calculated for low-conversion copolymers from monomer reactivity ratios and monomer feed compositions, using the relation:-

$$R = 200 / (2 + r_{A_f} A_f / B_f + r_{B_f} B_f / A_f)$$

Johnston and Harwood⁽¹⁵⁾ have expressed the Alfrey-Lewis-Magel equation in terms of \underline{R} :-

$$f_u(B) = \left\{ \cosh(R^2/4AB)^{\frac{1}{2}} - (A/B)^{\frac{1}{2}} \sinh(R^2/4AB)^{\frac{1}{2}} \right\}^2$$

It is instructive to work with the equation in this form, for it indicates that $f_u(B)$ is very sensitive to \underline{R} and that copolymer cyclization reactions can be used very effectively to characterize copolymer structure.

EMPIRICAL AND THEORETICAL RESULTS FOR THE FRACTION OF LACTONIZABLE VC UNITS.

Using reactivity ratio values of $\underline{r}_A = \underline{r}_1 = 0.068(\pm 0.003)$ and $\underline{r}_B = \underline{r}_2 = 16.55(\pm 0.60)$ for VC and MMA respectively (mean values from the two Fineman-Ross determinations), together with values for \underline{A} and \underline{B} predicted using $\underline{A}_f, \underline{B}_f, \underline{r}_A$ and \underline{r}_B , theoretical values for the fraction, $f_L(A)$, of lactonizable VC units were obtained for each copolymer, by first calculating the run number and then using the relation:-

$$f_L(A) = 1 - f_u(A)$$

The results obtained are shown in Table VIII. Errors have been "worked through" using the standard methods, the ones associated with \underline{A}_f and \underline{B}_f being regarded as insignificant.

The corresponding empirical values of $f_L(A)$, obtained by measuring \underline{d}_1 and \underline{d}_2 , are shown in Table IX and, with the possible exception of the value obtained for copolymer(1), compare favourably with the theoretical predictions.

TABLE VIII: Theoretical determination of $f_L(A)$

Copolymer	A_f	B_f	R	A	B	$f_U(A) \times 100$	$f_L(A) \times 100$
(1)	63.4	36.6	17.1(+0.5)	9.58(+0.29)	90.4(+0.3)	1.92(+0.50)	98.1(+0.5)
(2)	84.0	16.0	36.3(+0.8)	24.7 (+0.6)	75.3(+0.6)	11.2 (+0.7)	88.8(+0.7)
(3)	96.3	3.74	45.5(+0.8)	62.6 (+0.7)	37.4(+0.7)	54.2 (+0.7)	45.8(+0.7)
(4)	98.6	1.40	28.5(+0.9)	82.4 (+0.5)	17.6(+0.5)	80.0 (+0.4)	20.0(+0.4)
(5)	99.1	0.860	20.0(+0.7)	88.6 (+0.4)	11.4(+0.4)	87.4 (+0.3)	12.6(+0.3)

TABLE IX: Empirical values for $f_L(A)$

Copolymer	$f_L(A) \times 100$
(1)	92.1(<u>± 2.7</u>)
(2)	88.0(<u>± 2.4</u>)
(3)	47.1(<u>± 1.0</u>)
(4)	20.2(<u>± 0.4</u>)
(5)	11.9(<u>± 0.3</u>)

For convenience, $f_u(A)$ and $f_L(A)$ have been expressed as percentages in Tables VIII and IX.

Reference to Fig.23, p. 98 shows that the empirical results obtained for the 9.58% VC* copolymer(1) must be treated with caution. The non-coincidence of the TVA traces between 100°C and 220°C probably indicates an inconsistency of sample weight and/or rate of pumping rather than an early elimination of HCl, since in the other copolymers coincidence of the traces is also observed for the peak above 300°C, while in this instance it is not.

DISCUSSION OF RESULTS

I Extent and Temperature Range of Lactonization

The variation in the extent of lactonization with copolymer composition is shown in Table X, where the yields of methyl chloride obtained experimentally are compared with those predicted using values of A, B and $f_L(A)$ calculated from the reactivity ratios. All data refer to 100 mg. of copolymer.

TABLE X : Yields of methyl chloride from lactonization

Copolymer	Empirical Yield (moles x 10 ⁶)	Theoretical Yield (moles x 10 ⁶)
(1)	94.0(+0.6)	97.4(+3.2)
(2)	207.8(+5.8)	241.5(+6.7)
(3)	370.1(+10.2)	374.5(+7.9)
(4)	252.0(+7.3)	238.4(+5.2)
(5)	159.4(+4.4)	167.2(+4.1)

The two sets of data are in quite good agreement. The main anomaly is the rather low value for the amount of methyl chloride produced by the 24.7% VC copolymer(2), but this is largely assignable to the difference of 2.9 in the percentage VC compositions of the copolymer, as found by use of the reactivity ratios and by radiochemical volatile analysis respectively.

The TVA data show that lactonization occurs over the temperature range 90 - 220°C, although the radiochemical assay of methyl chloride is not sensitive below 120°C. The maximum rate of CH₃Cl evolution occurs between 171°C and 178°C and there is some indication that T_{max} increases with MMA content. Guillot et al. have assigned a similar effect in their GC analysis of this system to differences in tacticity over the copolymer composition range⁽⁹⁷⁾, although the effect they observed was much greater than in the present study, with the maximum rates of methyl chloride evolution occurring between 150°C and 180°C.

II Extent and Temperature Range of Dehydrochlorination

The variation in the extent of dehydrochlorination with copolymer

The variation in the extent of dehydrochlorination with copolymer

composition is shown in Table XI, where empirical yields of HCl are compared with those predicted from r_1 and r_2 . The data again refer to 100 mg. of polymer. The errors quoted on the empirical results are only those associated with the "moles - activity" conversion factor (see p.99) and do not take account of the additional uncertainty introduced by curve subtraction (see p.104).

TABLE XI: Yields of HCl

Copolymer	Empirical Yield (moles x 10 ⁶)	Theoretical Yield (moles x 10 ⁶)
(1)	result suspect : see p.110	1.9(+0.5)
(2)	28.5(+0.2)	30.5(+2.1)
(3)	410.0(+2.6)	443.1(+8.7)
(4)	945.2(+6.0)	953.6(+9.3)
(5)	1184(+7.5)	1160(+9)

It is clear that dehydrochlorination differs from methyl chloride production (through lactonization) in that the extent of the former reaction decreases regularly as the VC content of the copolymers is reduced. Production of HCl becomes sensitive to radioactive assay above about 180°C and is generally observed between this temperature and 320°C. In copolymers of low VC content, HCl evolution becomes increasingly difficult to measure as its degree of radioactivity (c.p.m.) approaches the 2σ confidence levels for the curves corresponding to (CH₂Cl* + HCl*) and CH₂Cl* alone.

In the copolymers where HCl evolution is clearly defined, and also in PVC, the temperature at which the maximum rate of dehydrochlorination

occurs only varies between about 255°C and 265°C. At 260°C, the 88.6 and 82.4% VC copolymers have produced somewhat more HCl than the same weight of PVC, but the effect is much less pronounced than that found by Guillot et al. using argentopotentiometry⁽⁹⁾. In the latter instance, HCl evolution from an 86% VC copolymer was observed to commence at 110°C, attain its maximum rate at 210°C and reach completion at about 400°C. (In PVC, the corresponding temperatures were 200°C, 225°C and 400°C respectively). There is thus very little evidence in the present results to support the view of Guillot et al. that lactone groups in the polymer backbone lower the activation energy required for dehydrochlorination.

Guillot et al. also report that HCl evolution occurs over a broader temperature range in copolymers of high MMA content and that the maximum rate of dehydrochlorination in a 24% VC copolymer occurs about 150°C higher than in PVC. These effects are explained in terms of the isolation of increasingly short VC sequences between lactone structures, leading to an increased activation energy for the zip dehydrochlorination. There is little definite evidence in the present results to support this view, although the maximum rate of HCl evolution in the 62.6% VC copolymer could be as much as 10°C higher than in PVC and it must be admitted that the limit of accurate radioactive HCl analysis is approached at compositions of the order of 24% VC with the counting times and ³⁶Cl activities available.

III Extent and Temperature Range of the HCl/ester Interaction

This is a minor reaction, being only visible in copolymers of intermediate composition (see Fig. 26, p.103) and it reaches its maximum extent in the 62.6% VC copolymer, where the concentrations of uncyclized VC and MMA units will both be relatively high. The process necessarily

overlaps with HCl production and is generally observed between 220°C and 310°C. It is presumably a random reaction, although there is no simple way of relating it quantitatively to sequence distribution.

Guillot et al. found that with a copolymer composition of 46% VC, methyl chloride production by this mechanism was at least half as important as lactonization. The lesser extent of the reaction in the present study is probably due to the use of polymer films and high-vacuum conditions instead of the powder samples and dynamic nitrogen atmosphere adopted by Guillot et al. The diffusion of HCl out of the polymer can be expected to occur much more rapidly under the present conditions.

IV Degree of overlap of the lactonization and dehydrochlorination reactions

Reference to Figs. 18-23 shows that HCl evolution from the copolymers does not occur to a measurable extent until the lactonization reaction is almost complete.

GENERAL ASSESSMENT OF THE RADIOCHEMICAL METHOD OF VOLATILE ANALYSIS

Radiochemical analysis is suitable for the study of methyl chloride evolution over the copolymer composition range dealt with in the present work and although it becomes less reliable for monitoring the very small extents of HCl production in copolymers of low VC content, this problem could be overcome by incorporating ^{36}Cl of higher specific activity into the polymers or by extending counting times. The determination of HCl evolution using ^{36}Cl -labelled polymers is otherwise very useful for the study of this copolymer system, as it avoids the problems associated with argentopotentiometric estimation of the gas in presence

of methyl methacrylate (as found by Guillot et al.) and also any interference with titrimetric estimation (using NaOH solution), caused by the presence of carbon dioxide degradation product.

Finally, the use of ³⁶Cl-labelled PVC for a precise study of the thermal behaviour of polymer blends (see p.181), or of other PVC compounds, seems to hold particular promise, since radioactive PVC itself is comparatively easy to prepare.

CHAPTER FIVE

RELATED COPOLYMER SYSTEMS

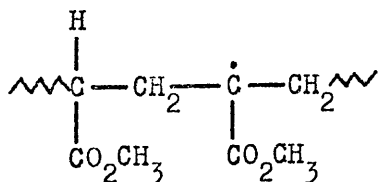
INTRODUCTION

Several other copolymer systems have been studied which are potentially capable of undergoing 1,3-interactions of the type found in VC - MMA copolymers. Some of these are novel copolymer systems, while the remainder have previously been prepared but not examined in detail for their thermal behaviour. Since reactivity ratios have been available for the latter systems, it has been possible to study a range of copolymer compositions, but for the novel systems only one copolymer has been prepared in each case, and it has been attempted to prepare copolymers of intermediate composition in order to maximise any 1,3-interactions. In the absence of reactivity ratios, Q-e data⁽⁹⁸⁾ have been employed. Relevant details of monomer and polymer preparation methods are contained in the Appendix.

In all cases, the behaviour of the copolymers is compared with that of the parent homopolymers using TVA data and this is presented graphically where most pertinent to the discussion. The previously prepared systems vinyl chloride-methyl acrylate, vinyl chloride-n-butyl methacrylate and vinyl bromide-methyl methacrylate will be discussed first.

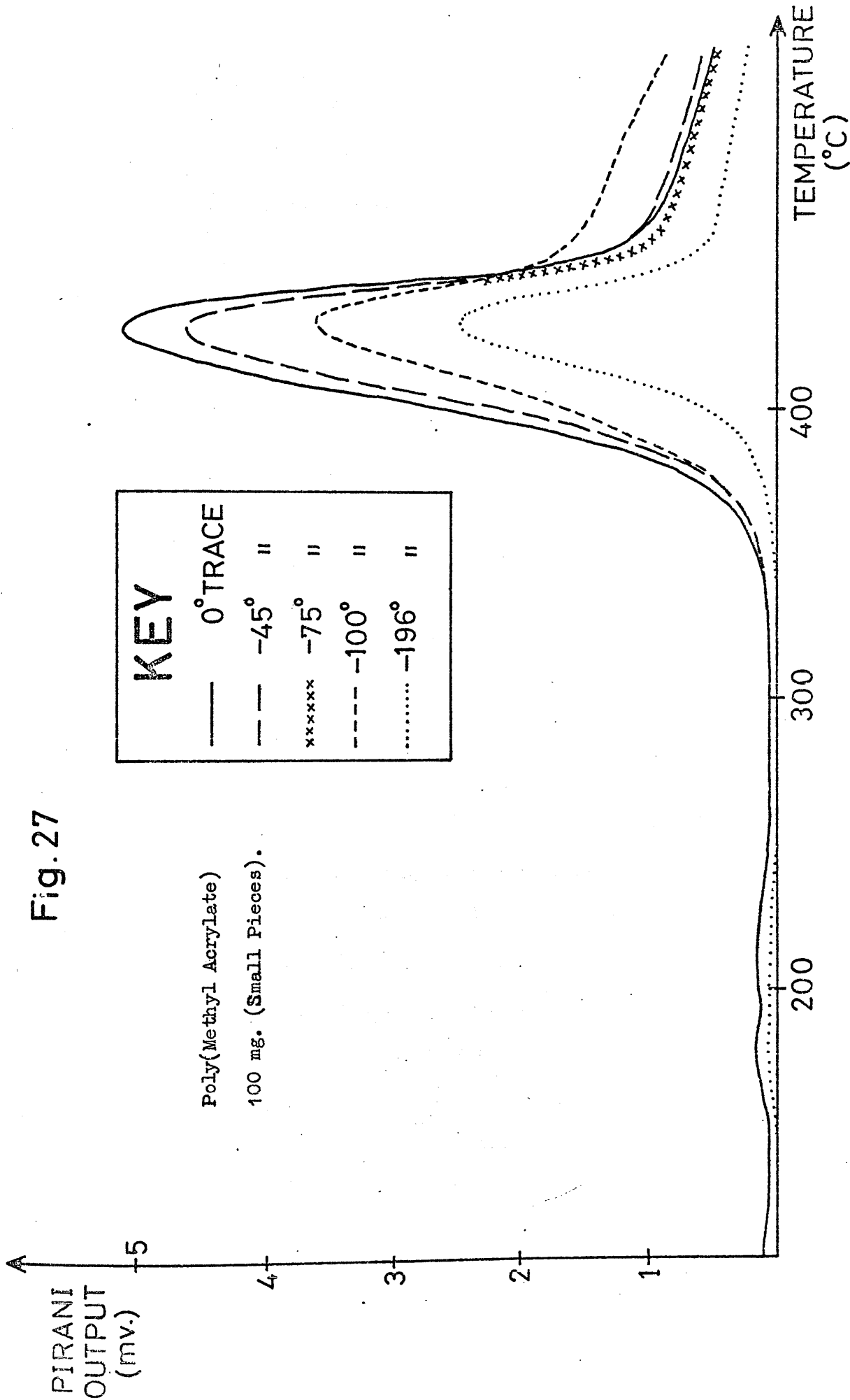
VINYL CHLORIDE - METHYL ACRYLATE COPOLYMERS

The preparation of these copolymers and their preliminary analysis by TVA and I.R. spectroscopy has been carried out by MacDonald⁽⁹⁹⁾. A detailed study of poly(methyl acrylate), PMA, degradation has been made by Cameron and Kane⁽¹⁰⁰⁾. In common with other monosubstituted ethylene polymers, PMA yields insignificant amounts of monomer and most of the total products comprise chain fragments, formed by extensive transfer reactions. The volatile products consist mainly of methanol and carbon dioxide and Cameron and Kane have explained the formation of all the products (and also the onset of colouration during degradation) in terms of competing reactions of a radical precursor of the type shown below, formed after transfer of a labile α -hydrogen atom.



Analysis of Volatile Products

The TVA curves of poly(methyl acrylate) [see Fig. 27, p. 118] comprise a single peak with $t_{\text{max}}^{\text{T}} = 430^{\circ}\text{C}$ and MacDonald has identified methanol, carbon dioxide and methyl acrylate among the condensable products. In the non-condensable fraction, only ethylene was identified, but it is likely that carbon monoxide and methane are also present, as found by earlier workers⁽¹⁰⁰⁾.



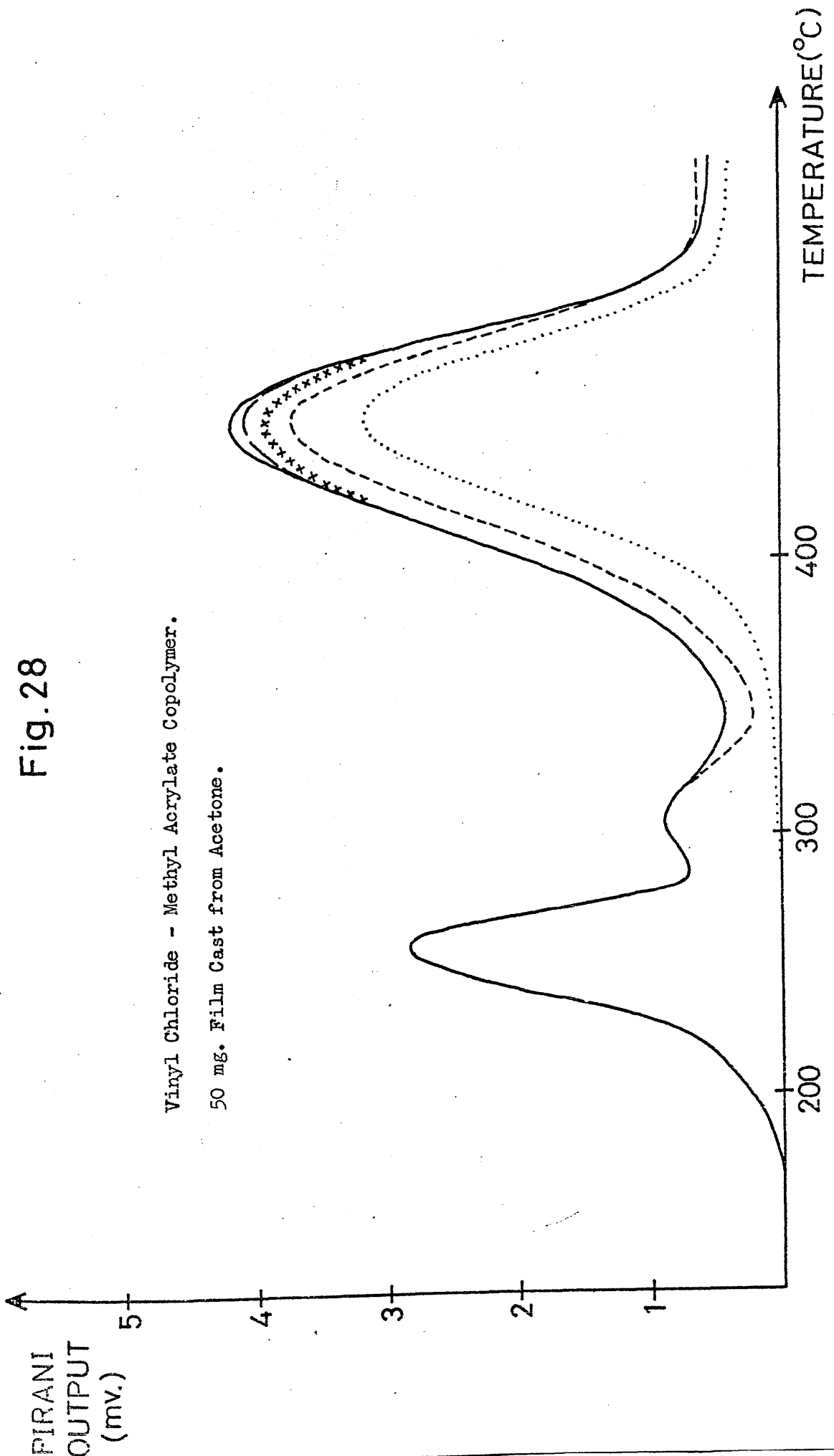
Copolymerization with only 5.13% (molar) VC leads to the appearance of a new peak in the TVA with $T_{\max} = 255^{\circ}\text{C}$, consisting entirely of material non-condensable at -100°C (but fully condensed at -196°C) and identified by I.R. analysis as methyl chloride. T_{\max} for the main stage of degradation remains at 430°C and carbon dioxide, methyl acrylate and methane were observed here. No methanol was identified.

Increasing the VC content to 51.2% (see Fig.28, p.120) leads to enhancement of the new peak (I.R. analysis : methyl chloride, HCl), which remains static at 255°C , and the appearance of a third peak, with $T_{\max} = 300^{\circ}\text{C}$, consisting mainly of material non-condensable at -100°C (but condensable at -196°C) and identified as HCl and carbon dioxide, with a small amount of methyl chloride. The main peak still shows T_{\max} at about 430°C , but it has been broadened, presumably by the volatiles from lactone decomposition. (It must be stated that the existence of lactone units can only be deduced in this case from the early elimination of methyl chloride at a constant T_{\max} , since no spectra were obtained for cold-ring fractions or residues).

Further increasing the VC content to 67.7% leads to enhancement of the second peak ($T_{\max} = 305^{\circ}\text{C}$; I.R. analysis—HCl, carbon dioxide and methyl chloride) at the expense of methyl chloride production ($T_{\max} = 255^{\circ}\text{C}$). The main peak ($T_{\max} = 450^{\circ}\text{C}$; I.R. analysis — carbon dioxide, methane, propylene and ethylene) is diminished somewhat, probably due to the smaller amounts of material being evolved from lactone breakdown, but is shifted to a higher temperature due to the increased polyene reactions of the VC sequences.

Fig. 28

Vinyl Chloride - Methyl Acrylate Copolymer.
50 mg. Film Cast from Acetone.



Discussion

The degradation pattern of the copolymers shows overall similarity to the VC - MMA system (see Fig. 29, p. 122) but lactonization occurs at a higher temperature (255°C vs. 206°C). HCl formation is evident in copolymers with greater than 50% VC, but, unfortunately, the effect of copolymerization on HCl production cannot be accurately defined, due to the overlap of the "HCl" peak (ca. 300°C) with other stages of degradation.

A puzzling feature of MacDonald's results is the failure to identify methanol as a product from the high - MA - content copolymers, especially when monomer is observed—methanol is the major condensable product in PMA degradation⁽¹⁰⁰⁾. Statistical calculations show that only about 5.3% of the MA units in a 5.13% VC copolymer can undergo lactonization and it is difficult to explain how one lactone unit per 20 MA units could interrupt any of the three methanol production mechanisms proposed by Cameron and Kane.

MacDonald has also noted the occurrence of strong carbonyl absorptions at 1738cm^{-1} and 1749cm^{-1} in the non-condensable fraction from the 67.7% VC copolymer, but these were not identified. A re-examination has shown that acetone (a solvent used for the copolymers) and formaldehyde exhibit strong carbonyl absorptions at 1738cm^{-1} and 1749cm^{-1} respectively in the gas phase, but both are fully condensed at -196°C in a continuously-pumped system. MacDonald's findings have not been further examined due to lack of sample, but this is clearly a system which deserves further attention.

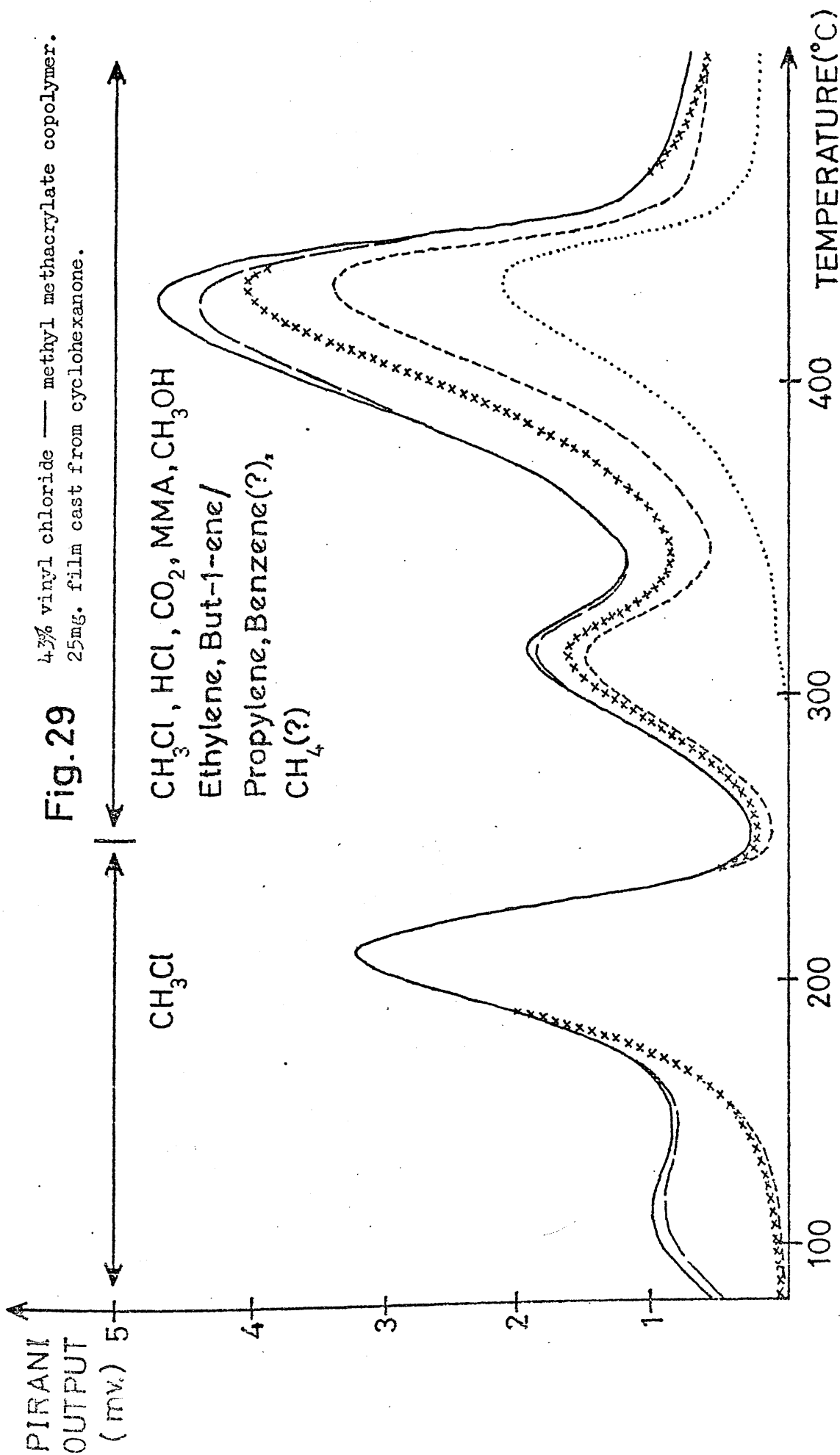


Table XII gives some of the more useful data relating to sequence distribution in the copolymers. The symbols used have already been discussed in Chapter IV.

TABLE XII

Mole Fraction of VC(A)	5.13%	15.8%	51.2%	67.7%
R	9.96	28.5	57.9	49.5
$\langle A \rangle$	1.03	1.11	1.77	2.74
$\langle B \rangle$	19.1	5.91	1.69	1.30
pAB	0.971	0.903	0.565	0.365
pBA	0.0525	0.169	0.593	0.767
$f_L(A)$	99.9%	97.6%	67.0%	42.1%
$f_L(B)$	5.32%	18.3%	70.3%	88.5%

The above data are based on monomer reactivity ratios of 0.12 and 4.4 for VC and methyl acrylate respectively. Strictly speaking, the figures refer to a polymerization temperature of 50°C, and not 40°C as used by MacDonald, but they are acceptable for a purely qualitative assessment.

It can be seen that the copolymer of lowest VC content consists essentially of long MA sequences, interrupted only occasionally by isolated VC units. As the 1:1 composition is approached, alternation

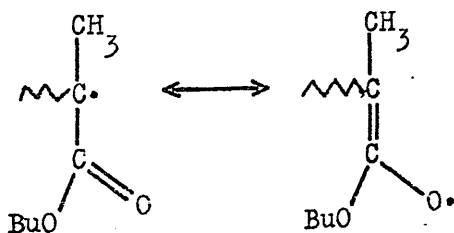
begins to predominate and this is associated with high values for both pAB and pBA and maximum lactonization. At the VC - rich end of the composition range, VC sequences are, on average, longer than those of MA, but are still very much shorter than those attained by MA units in the 5.13% VC copolymer.

VINYL CHLORIDE - n-BUTYL METHACRYLATE COPOLYMERS

This copolymer system was first studied as a B.Sc. project⁽¹⁰¹⁾.

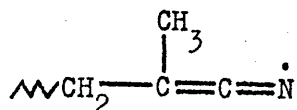
The thermal degradation of poly(n-butyl methacrylate) at 250°C has been studied by Grassie and MacCallum⁽¹⁰²⁾. Monomer was found to be the predominant volatile product, but depropagation proceeded only to the extent of about 40% and on prolonged heating the residue became progressively more stable. Grassie and MacCallum have explained these features in terms of a competing free-radical ester decomposition process, during which carboxylic acid units are initially formed in the polymer chain.

Their mechanism assumes the ability of a depropagating polymer radical to react in its alternative canonical form:-

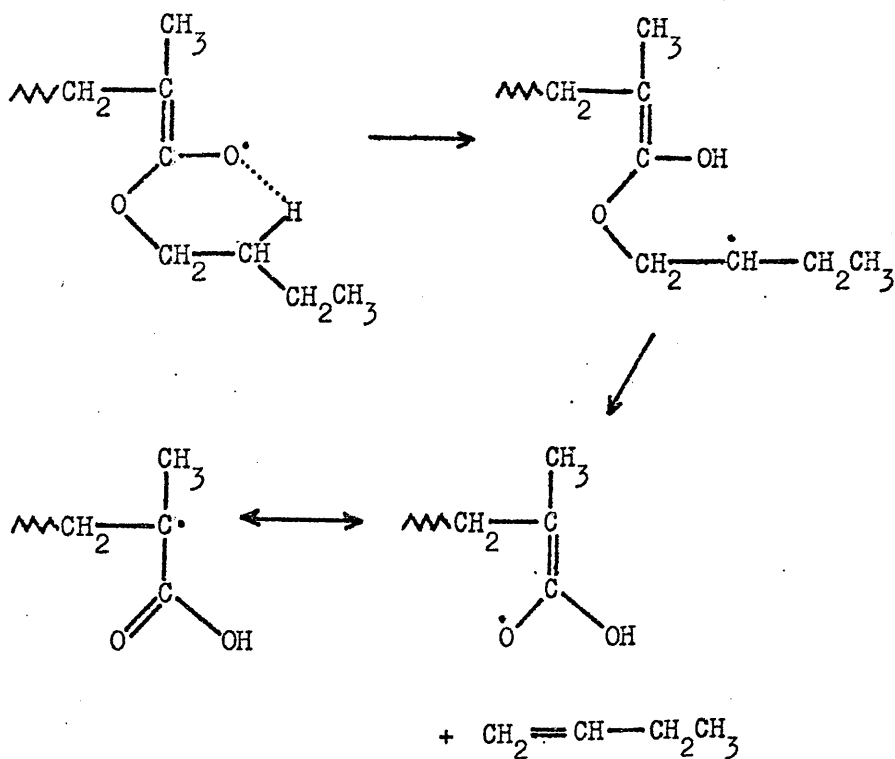


Such a situation is not without precedent. For example, the ketene-imine structures in poly(methacrylonitrile)⁽¹⁰³⁾ are known to result. imine structures in poly(methacrylonitrile)

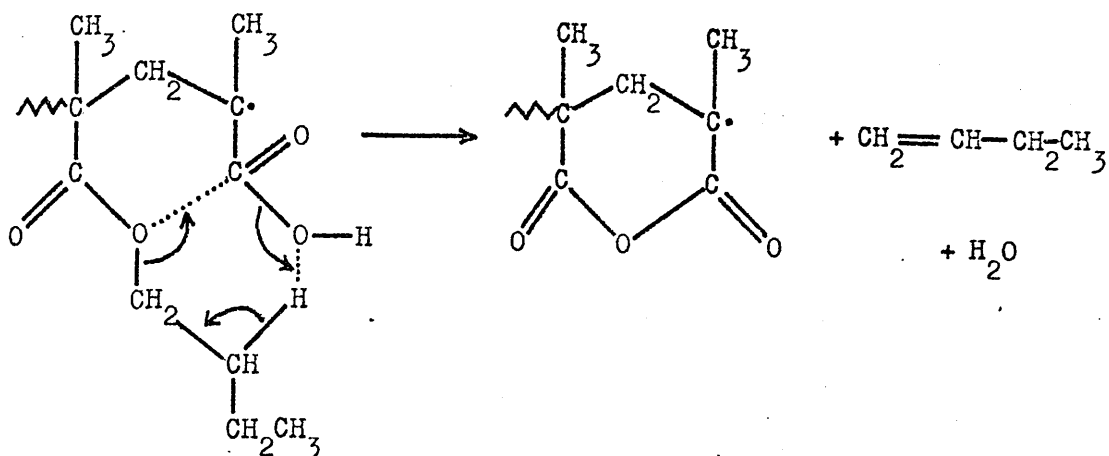
from reaction of the growing polymer radical in the form:-



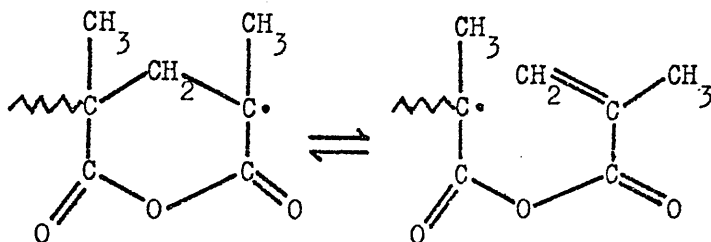
The ester decomposition is believed to proceed via a six-membered cyclic transition state, according to the following reaction scheme:-



Self-inhibition of the depropagation reaction then follows, due to the formation of terminal anhydride structures, which probably arise by the further reaction of a terminal acid unit with an adjacent ester function:-



Inhibition is believed to be the result of an equilibrium which will be set up between this anhydride radical and the radical formed by liberation of one more ethylenic unit from the chain end:-



Grassie and MacCallum have also used the first part of the above reaction sequence to explain the evolution of butene and formation of small amounts of carboxylic acid units in the polymer chain during the polymerisation of n-butyl methacrylate at 30°C (104°). Presumably, a copolymer of n-butyl methacrylate will also contain a small number of acid functions.

Analysis of Volatile Products.

The TVA curves for poly(n-butyl methacrylate) are shown in

Fig. 30, p. 128. The rather involatile monomer gives a limiting rate effect in the -45°C trace and the major peaks ($T_{\text{max}} = 292^{\circ}\text{C}$ and 345°C) presumably represent chain-end-initiated and random-scission-initiated depropagations respectively — Grassie and MacCallum⁽¹⁰²⁾ have already shown that monomer production begins at chain ends during degradation at 250°C . Above 300°C , the response on the $-75/-100^{\circ}\text{C}$ trace probably indicates formation of but-1-ene, while the evolution of non-condensable material ($T_{\text{max}} = 425^{\circ}\text{C}$) is probably the result of breakdown of acid or anhydride structures.

Copolymerisation with only 5.6% (molar) VC results in considerable alteration of the TVA shape. A new peak appears with $T_{\text{max}} = 225^{\circ}\text{C}$, incorporating material which gives a limiting rate effect in the -100°C trap and identified by I.R. analysis as n-butyl chloride. The peak originally associated with low-temperature monomer production is almost removed, leaving only a small residual shoulder at 315°C on the 0°C trace. The main stage of monomer production is shifted upwards by 45°C to give $T_{\text{max}} = 390^{\circ}\text{C}$, although a small part of this shift can be assigned to the increased production of materials non-condensable at -100°C (but condensed at -196°C) and non-condensable at -196°C . T_{max} for the peak due to non-condensable production is shifted from 425°C in the homopolymer to 448°C in the copolymer.

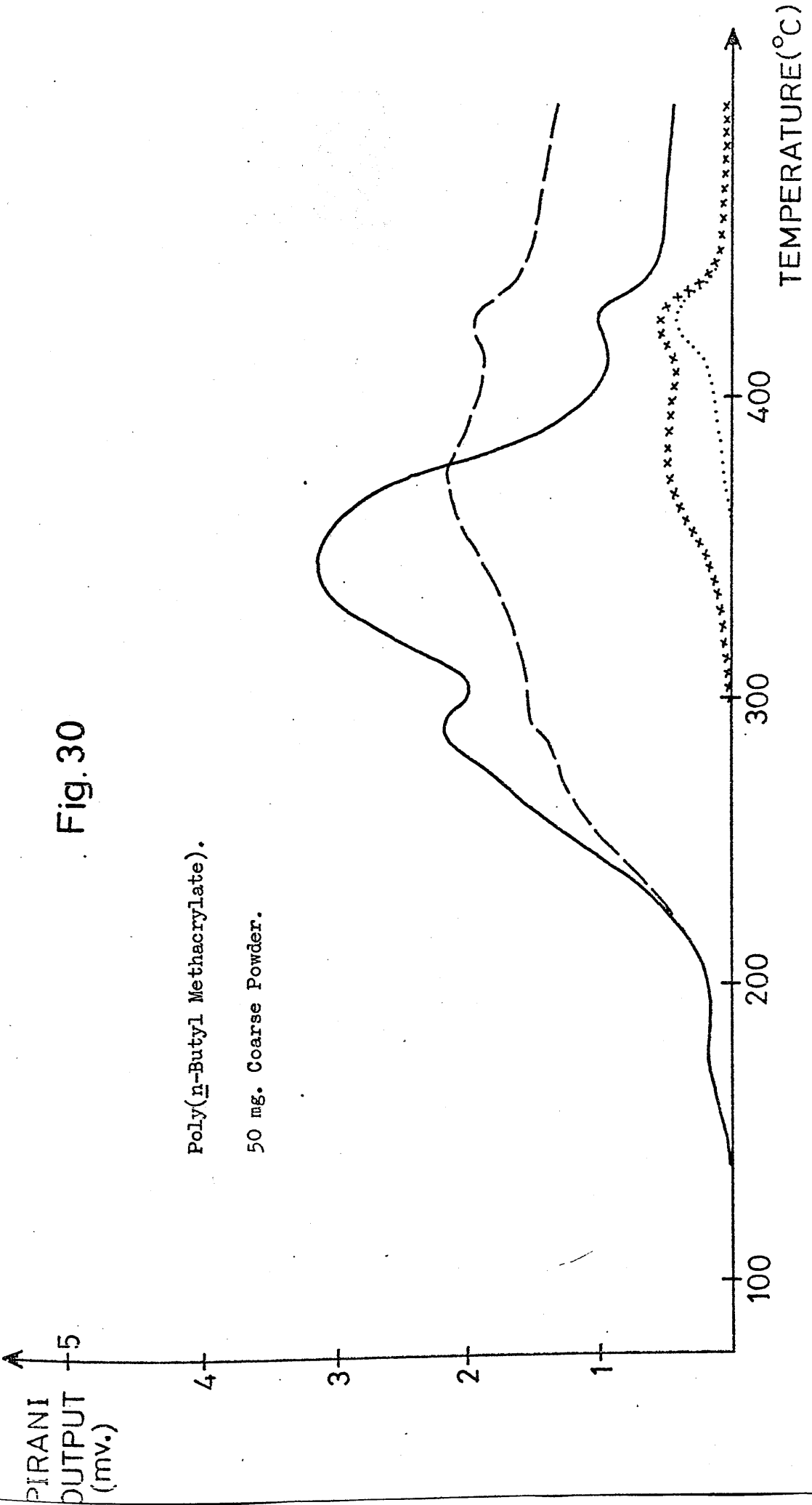
I.R. analysis has shown that in the main stage of degradation (i.e. above about 250°C), monomer, carbon dioxide, isobutene and but-1-ene (and/or propylene) are evolved, with methane (and probably also carbon monoxide) accounting for the non-condensable fraction.

In accordance with the earlier work on poly(n-butyl methacrylate)⁽¹⁰²⁾,

Fig. 30

Poly(n-Butyl Methacrylate).

50 mg. Coarse Powder.



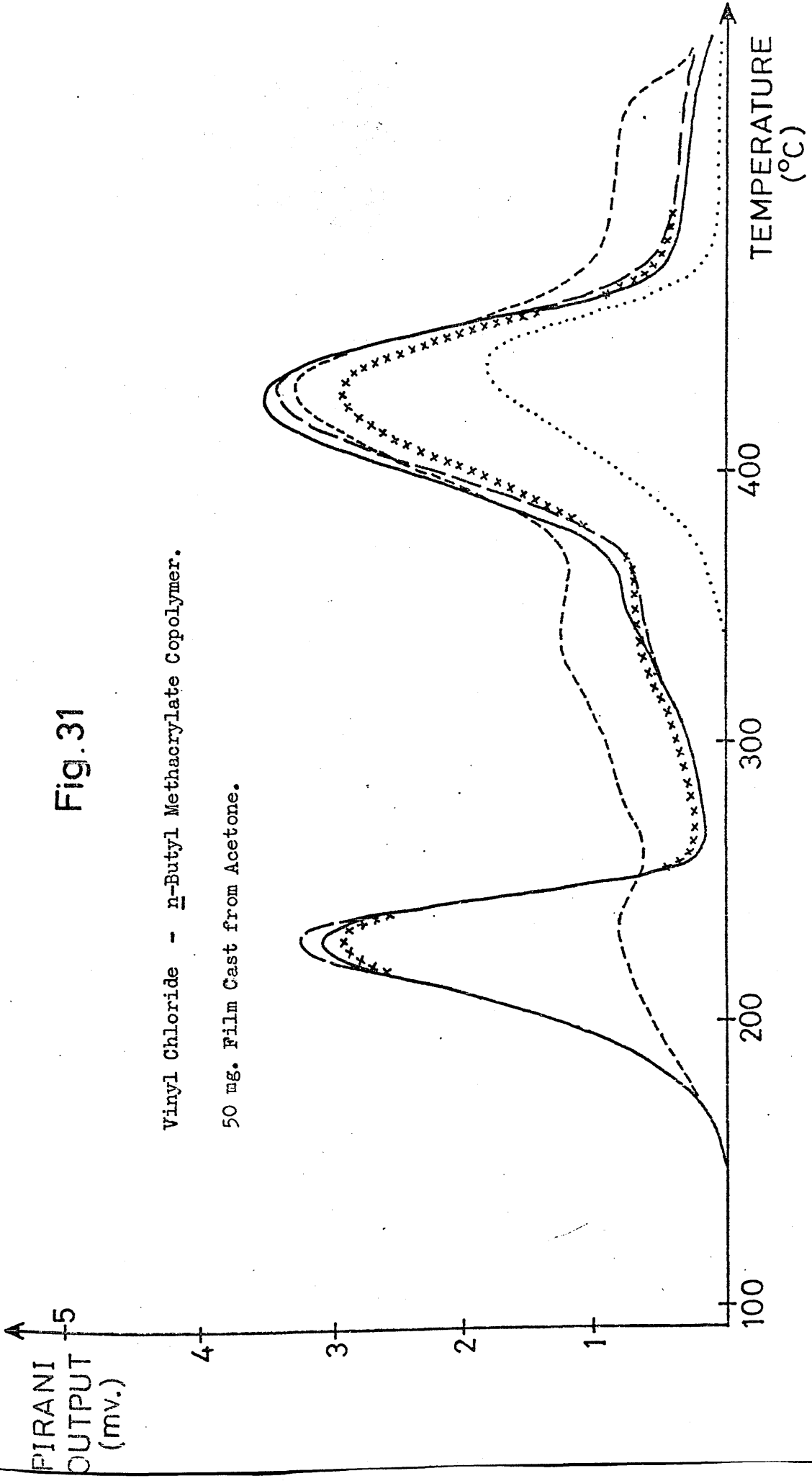
it is very likely that but-1-ene is produced in the copolymer, but propylene may also be present. It has not been possible, on infrared evidence alone, to clarify this point, due to the very similar absorption patterns of the two olefins.

Increasing the VC content from 5.6%, through 14.4% and 29.5% to 49.2% (Fig. 31, p.130) leads to a gradual enhancement of butyl chloride production, for which T_{\max} remains static at 225°C. T_{\max} for the main stage of degradation continues to move upwards from 390°C in the 5.6% VC copolymer to 425°C in the 1:1 copolymer and as the VC content is raised, materials non-condensable at -100°C (but condensable at -196°C) and non-condensable at -196°C begin to account for most of the volatile products in this temperature range. Monomer production is clearly in decline. In addition, a small shoulder appears on the 0°C trace and this shifts from about 320°C in the 14.4% VC copolymer to reach 365°C in the 1:1 composition. This new stage of reaction appears to represent largely material which is not condensed at -100°C (but condensed at -196°C) and probably consists in part of HCl, which has been identified among the products formed above 270°C in the 1:1 copolymer. The other products detected here by I.R. analysis were monomer, carbon dioxide, but-1-ene (and/or propylene), together with small amounts of isobutene and ethylene. Methane and carbon monoxide were identified among the non-condensables.

Finally, by raising the VC content from 49.2% to 74.6%, the butyl chloride peak begins to diminish, but maintains T_{\max} at 225°C, while a peak of comparable size emerges with $T_{\max} = 323^\circ\text{C}$. The final stage of degradation ($T_{\max} = 453^\circ\text{C}$) is now much less pronounced

Fig. 31

Vinyl Chloride - n-Butyl Methacrylate Copolymer.
50 mg. Film Cast from Acetone.



and still consists to a large extent of materials non-condensable at -100°C (but condensed at -196°C) and non-condensable at -196°C .

The second peak ($T_{\text{max}} = 323^{\circ}\text{C}$) does not suffer from excessive overlap with its neighbours, so products detected can be assigned almost specifically to this stage of reaction. These included a large amount of HCl with a smaller quantity of carbon dioxide. The -196°C trace showed the presence of a small non-condensable component and this was found to contain ethylene (with possibly some carbon monoxide).

The third stage of degradation in the 74.6% VC copolymer ($T_{\text{max}} = 453^{\circ}\text{C}$) is again fairly "clean-cut" and products evolved here, and identified by I.R. analysis, were mainly carbon dioxide, with some but-1-ene (and/or propylene), isobutene and ethylene.

Analysis of Cold-Ring Fraction

The cold-ring fraction obtained when the 1:1 copolymer was heated to 500°C showed strong infrared absorption bands at 1760cm^{-1} and 1700cm^{-1} . These probably represent γ -lactone and carboxylic acid structures respectively. 6-membered cyclic anhydride structures absorb at 1800cm^{-1} and 1760cm^{-1} , but the presence of these must remain speculative since the absorption at 1800cm^{-1} is obscured in this case. The existence of acid groups was supported by the presence of a broad absorption extending from 3600cm^{-1} to 2500cm^{-1} , while a medium absorption band at 1630cm^{-1} probably represents unsaturated hydrocarbon structures.

Discussion

As in the previous systems, lactonization is the first stage of degradation in the copolymers and this reduces the amount of n-butyl methacrylate monomer production (1) by removing available ester units.

(2) by "blocking" depropagation.

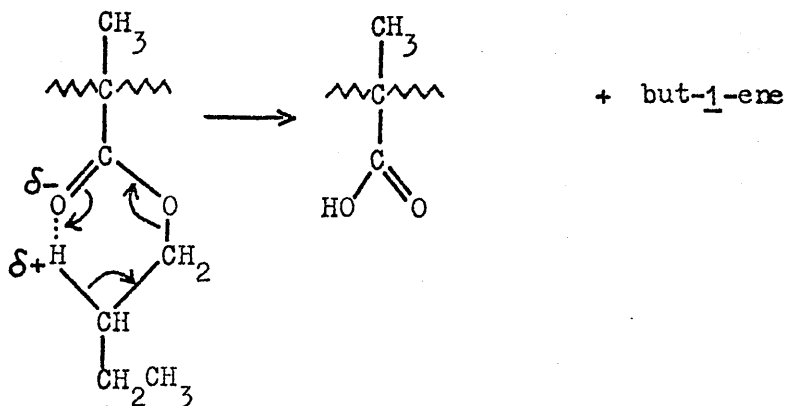
As before, chain-end-initiated depropagation is most drastically affected by introduction of lactone structures, whereas random-scission-initiated monomer production is not greatly reduced in extent but requires higher temperatures to achieve its maximum rate.

As usual, the effect of lactonization on dehydrochlorination is not clear, since HCl production is only observed in the 49.2 and 74.6% VC copolymers. As was seen, the peak with $T_{\max} = 323^{\circ}\text{C}$ in the 74.6% VC copolymer is largely due to HCl, but the other products may shift T_{\max} considerably from the dehydrochlorination value.

Breakdown of the lactone structures contributes largely to the composition of the volatiles in the copolymers of higher VC content, being notably responsible for the large-scale production of carbon dioxide.

The effect of copolymer composition on but-1-ene production cannot be accurately assessed without a more selective, quantitative investigation (e.g., by gas-phase chromatography), but it would undoubtedly be interesting. Copolymerization of n-butyl methacrylate with a small amount of VC will clearly reduce the number of units capable of undergoing a free-radical ester decomposition (by the mechanism of Grassie and MacCallum), so that ester sequences isolated between lactone units may be forced to undergo a different reaction

sequence — e.g., molecular ester decomposition:-



Such a mechanism is already known to occur in non-polymeric systems⁽¹⁰⁵⁾.

Isobutene (I.R. ; 890cm^{-1}) has been identified as a product over the entire copolymer composition range and it is quite conceivable that it is also evolved from poly(n-butyl methacrylate) at higher temperatures (previous analyses dealt only with degradation below 300°C). Backbone fragmentation is presumably its main source.

Table XIII gives a statistical correlation between copolymer composition, sequence distribution and extents of lactonization and provides a qualitative explanation of the trends observed in volatile composition. Lactonization is favoured when pAB and pBA are both high and occurs to a maximum extent in the 1:1 copolymer, whereas monomer production and dehydrochlorination are favoured at opposite ends of the composition scale.

The data are based on monomer reactivity ratios of 0.05 and 13.5 for VC and BMA respectively.

TABLE XIII

Mole Fraction of VC(A)	5.6%	14.4%	29.5%	49.2%	74.6%
R	10.8	25.7	44.9	51.8	40.2
$\langle A \rangle$	1.04	1.12	1.31	1.90	3.71
$\langle B \rangle$	17.5	6.67	3.14	1.96	1.26
pAB	0.96	0.89	0.76	0.53	0.27
pBA	0.057	0.15	0.32	0.51	0.79
$f_L(A)$	99%	98%	89%	66%	31%
$f_L(B)$	5.8%	17%	37%	64%	92%

VINYL BROMIDE — METHYL METHACRYLATE COPOLYMERS

The initial studies of this system were carried out in collaboration with B.Sc. student P. Anderson⁽¹⁰⁶⁾.

The thermal degradation of poly(vinyl bromide), PVB, has not been studied in detail since the behaviour of the polymer has been assumed to follow approximately that of PVC. The formation of longer polyene sequences in PVB than in PVC has already been discussed (p.55) and Braun and Thallmaier⁽⁶⁴⁾ have shown that an average polyene sequence comprises 12-13 double bonds. Mention has also been made of the work by Blauer and Goldstein on VB - MMA copolymers (p.55), in which it was found that copolymers of high VB content were less thermally

stable than pure FVB, but, up until now, no detailed study of thermal behaviour over the complete range of copolymer composition has been reported.

Analysis of Volatile Products

The TVA curves for FVB are shown in Fig. 32, p.136. The similarity to PVC is immediately obvious, although T_{\max} of the initial peak lies at 203°C , compared with 325°C in PVC (see Fig. 33, p.137). Above 370°C a second phase of reaction occurs in which a number of volatile products are formed, including some non-condensable material. This second phase of reaction closely resembles that of PVC, although T_{\max} is higher, being about 500°C in FVB, as opposed to 480°C in PVC.

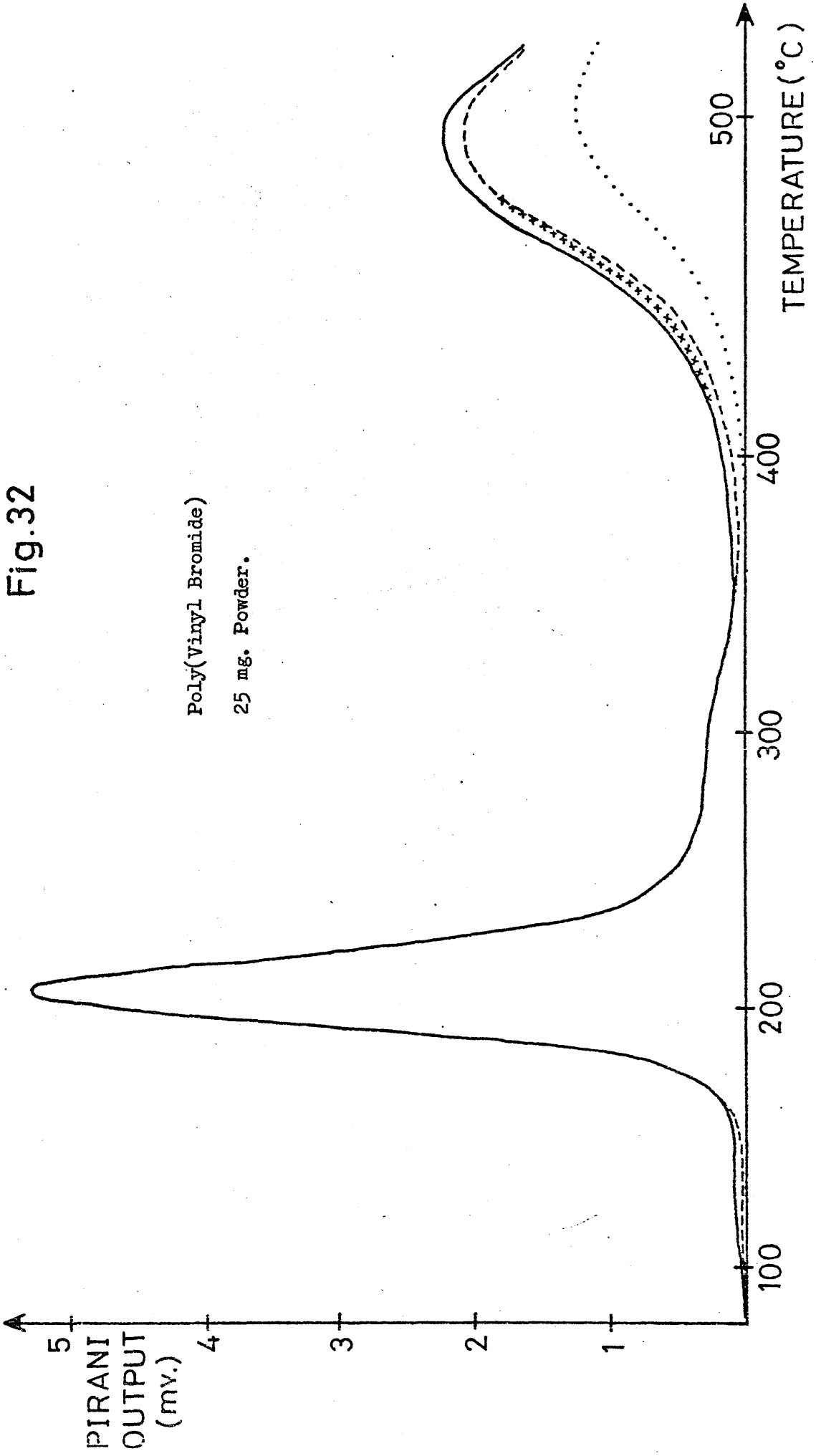
Comparison with PVC suggests that the initial peak in FVB represents loss of hydrogen bromide, while the second peak is caused by polyene cyclization and crosslinking processes.

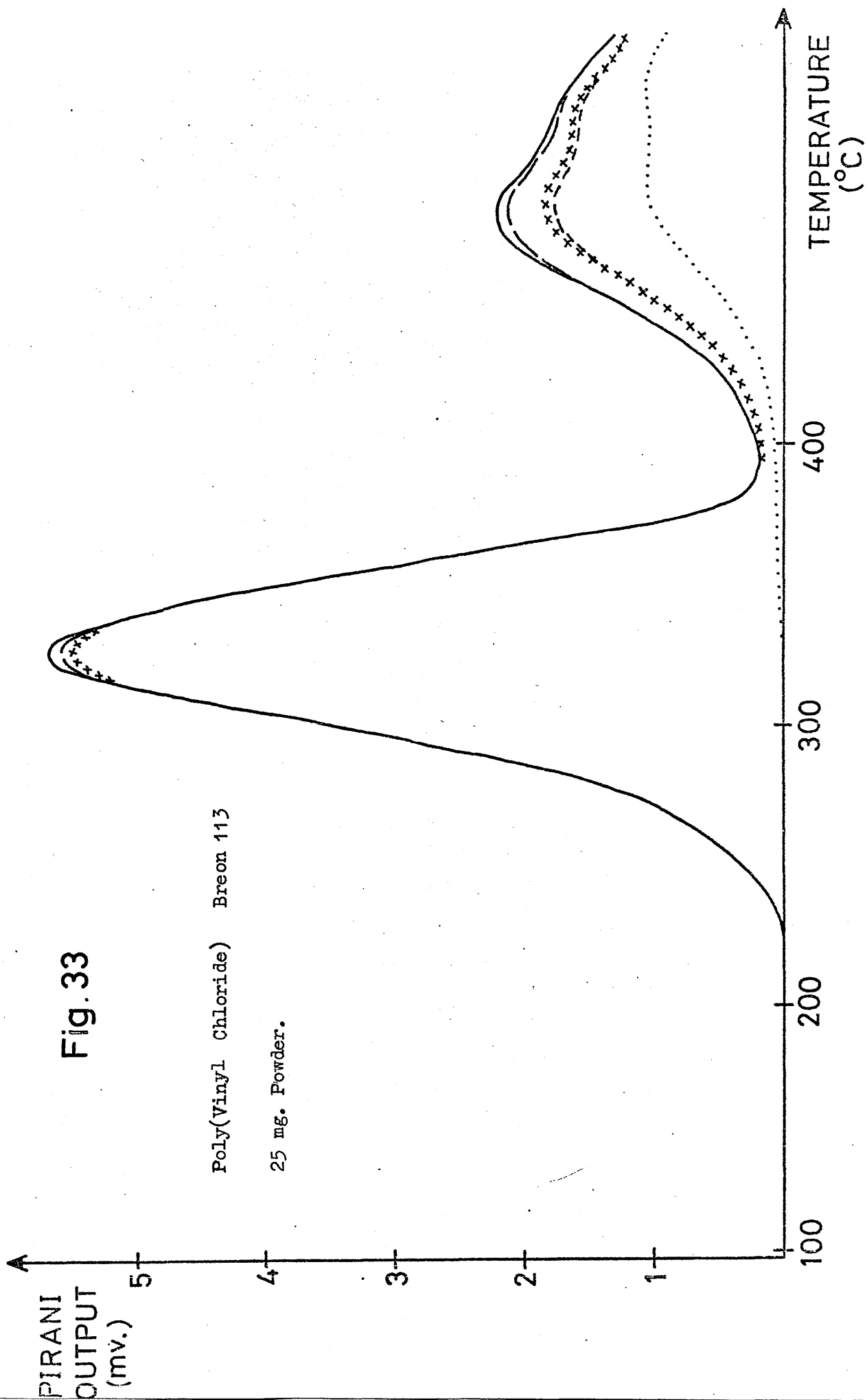
When an MMA copolymer containing only 4.87% (molar) VB is degraded, the TVA shape is considerably altered from that of PMMA (see Fig.34, p.138). A new peak appears with $T_{\max} = 175^{\circ}\text{C}$ consisting entirely of material non-condensable at -100°C and identified by I.R. analysis as methyl bromide. The peak with $T_{\max} = 295^{\circ}\text{C}$, associated with chain-end-initiated depropagation is almost removed, while the major stage of monomer production ($T_{\max} = 376^{\circ}\text{C}$) is shifted upwards to about 420°C . A small part of this shift can be assigned to the onset of a reaction phase ($T_{\max} = 444^{\circ}\text{C}$) which produces a mixture of volatiles, some of which are non-condensable at -196°C and others non-condensable at -100°C , but condensable at -196°C . Within the

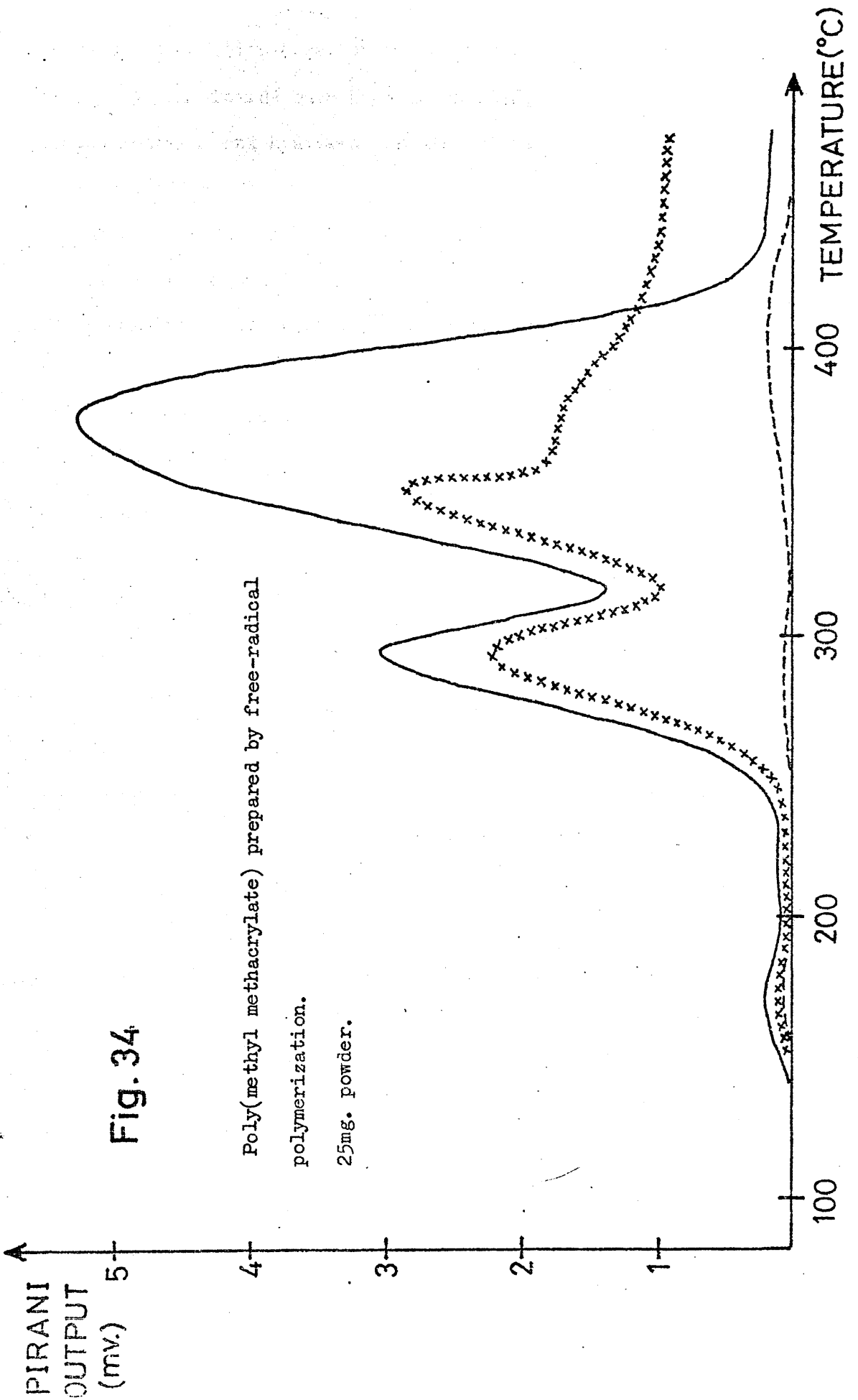
Fig.32

Poly(Vinyl Bromide)

25 mg. Powder.







main stage of degradation (i.e. above about 280°C), methyl methacrylate monomer and carbon dioxide have been identified, although it is likely that carbon monoxide and hydrogen are also present (see analysis below for 48.4% VB copolymer).

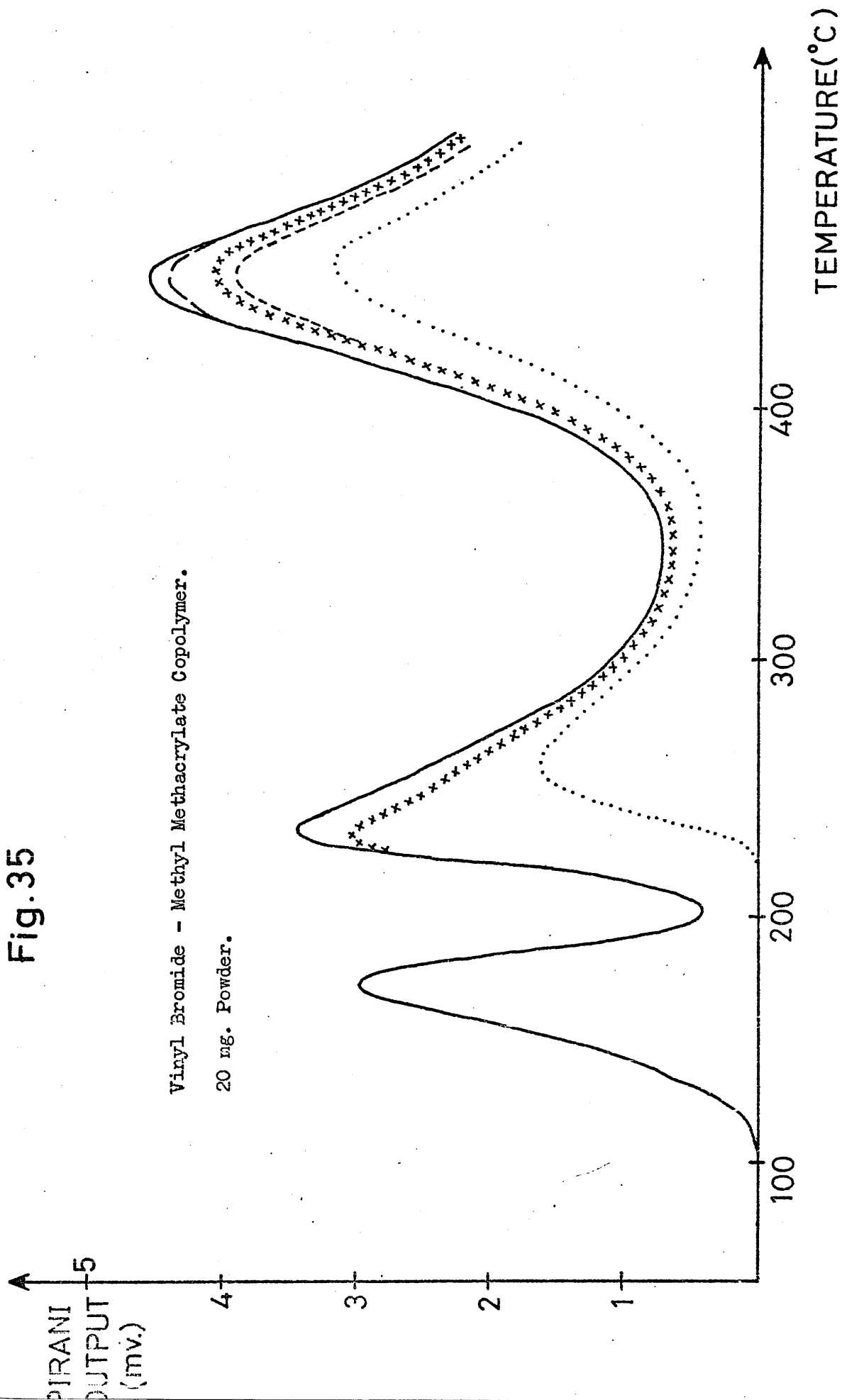
An increase in VB content from 4.87%, through 9.76% and 24.5% to 48.4% causes a large increase in size of the methyl bromide peak, whose T_{max} remains constant at 175°C (see Fig.35, p.140). The large peak originally associated with random-scission-initiated depropagation is shifted upwards on the temperature scale to give $T_{\text{max}} = 450^{\circ}\text{C}$ in the 48.4% VB copolymer, but the size of this peak is gradually diminished as methyl bromide formation increases and in the 48.4% VB copolymer it is seen to consist largely of non-condensable material, which has been identified as carbon monoxide and hydrogen by I.R. and mass-spectrometric analyses respectively. Carbon dioxide is the chief component of the volatiles which are non-condensable at -100°C , but condensable at -196°C .

The other major feature of the 1:1 copolymer is the appearance of an important peak with $T_{\text{max}} = 237^{\circ}\text{C}$, consisting of a mixture of volatiles which contains hydrogen bromide, carbon dioxide and some MMA monomer and also a non-condensable component. Evolution of the non-condensable material commences at approximately T_{max} and this fraction has been shown to consist of carbon monoxide (although hydrogen may also be present).

As the VB content is raised further to 73.2%, the methyl bromide peak ($T_{\text{max}} = 175^{\circ}\text{C}$) begins to diminish and the high-temperature peak ($T_{\text{max}} = 467^{\circ}\text{C}$) is less intense but broadened, presumably by the onset of the high-temperature polyene reactions of the VB sequences.

Fig. 35

Vinyl Bromide - Methyl Methacrylate Copolymer.
20 mg. Powder.



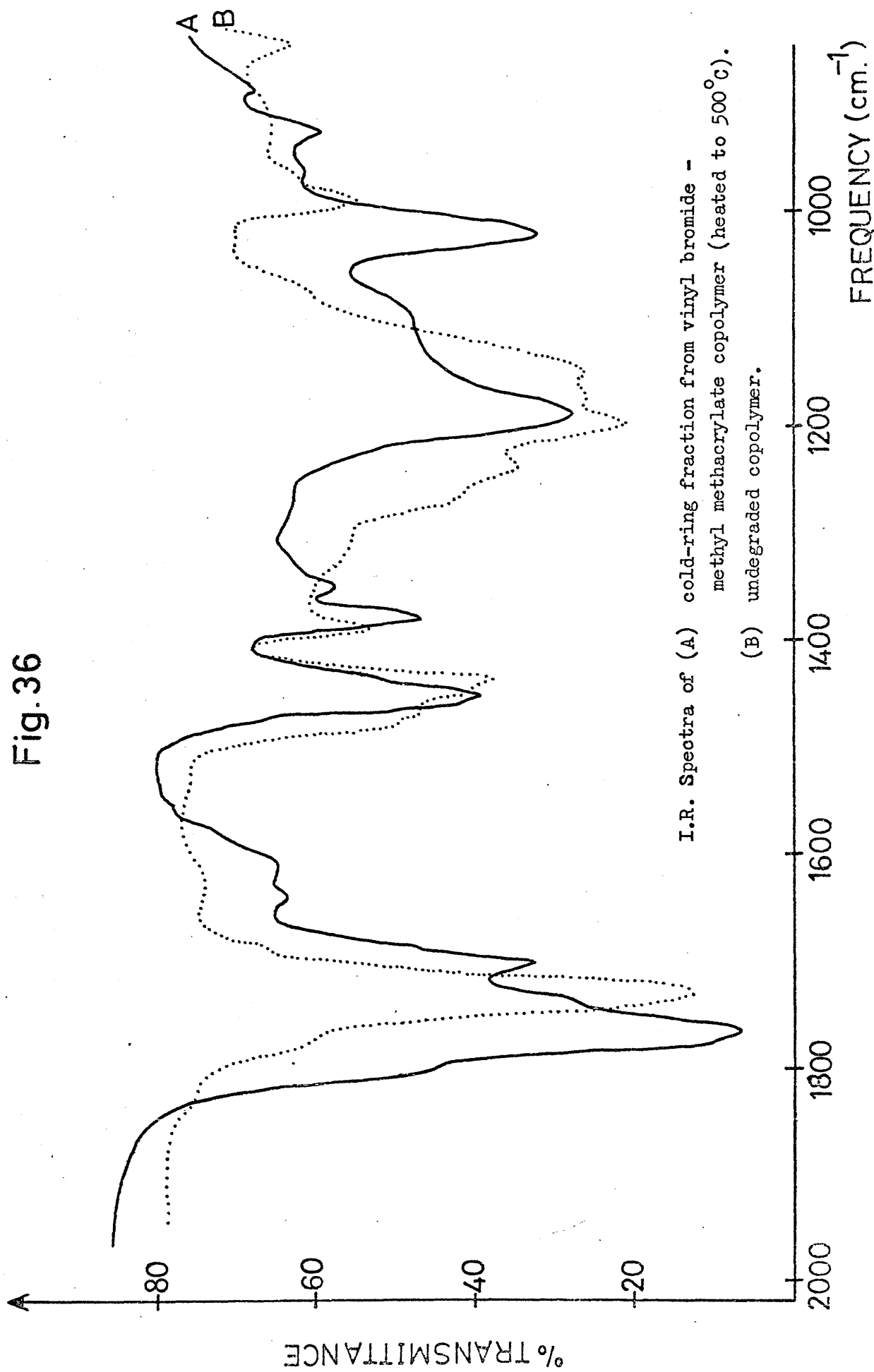
The middle peak is now strong, with $T_{\max} = 215^{\circ}\text{C}$ (comparable with T_{\max} for HBr elimination in FVB) and at this composition consists largely of material non-condensable at -100°C , but condensable at -196°C . A non-condensable component is still evident, though less important than in the 1:1 copolymer. Evolution of the non-condensable material again begins at T_{\max} for the total peak (i.e. 215°C).

Analysis of Cold-Ring Fraction

Fig.36, p.142 compares the I.R. absorptions of the cold-ring fraction of the 1:1 copolymer (heated to 500°C) with those of the undegraded polymer (both samples run as KBr discs). The strong ester absorption is still evident in the cold-ring fraction as a shoulder at 1740cm^{-1} , while new bands appear, as shoulders or distinct peaks, at 1800cm^{-1} , 1765cm^{-1} and 1700cm^{-1} , with a weaker, broad absorption between 1650 and 1600cm^{-1} . These new bands probably represent 6-membered cyclic anhydride, γ -lactone, carboxylic acid and unsaturated hydrocarbon structures respectively.

A surprising feature is the presence, even in the undegraded polymer, of an absorption at 1765cm^{-1} , evident as a shoulder on the main ester absorption. This phenomenon has also been noticed in the I.R. spectrum of a VC - methacrylic acid copolymer and becomes very pronounced in a VC - sodium methacrylate copolymer (see Fig. 46, p. 176). It may indicate that some lactonization occurs during the bulk copolymerisation process, but this "pre-lactonization" effect will be dealt with more fully under the VC - sodium methacrylate copolymer system.

Fig. 36



I.R. Spectra of (A) cold-ring fraction from vinyl bromide -
methyl methacrylate copolymer (heated to 500°C).
(B) undegraded copolymer.

Discussion

The degradation behaviour of VB - MMA copolymers roughly parallels that of the VC analogues, except that processes which involve scission of a carbon-halogen bond (i.e. lactonization and dehydrobromination) occur much more readily. Lactonization greatly reduces chain-end-initiated monomer production and raises its activation energy. Random-scission-initiated depropagation is not greatly reduced in extent but its activation energy is raised on copolymerisation with only a small amount of VB — T_{\max} shifts upwards by about 50°C . Presumably "blocking" by lactone structures is again responsible.

HBr elimination has only been observed in copolymers containing more than about 25% VB, but the effect of copolymer composition on the extent and temperature range of HBr formation is, as usual, difficult to interpret.

The presence of acid and anhydride units in the cold-ring fraction suggests that HBr may be reacting with unlactonized ester groups to give a second phase of methyl bromide formation (as in VC - MMA copolymers) but a more exact method of volatile analysis will be required to prove this.

The production of non-condensable material which begins abruptly at T_{\max} of the "HBr" peak and reaches its greatest extent in the 1:1 copolymer would appear to be related to the concentrations of lactone groups and of HBr and may involve a catalysed ring-opening process. No such effect is evident in VC - MMA copolymers and the relative bond strengths of HBr and HCl (86 and 102 kcal/mole, respectively)

may be a deciding factor. It is interesting to note that McNeill and Mohammed⁽¹⁰⁷⁾ have noticed an abnormally large production of non-condensable material during the thermal degradation of PMMA in presence of zinc bromide. No such effect is observed with zinc chloride additive.

It is useful to compare the trends observed in product composition against the statistical data contained in Table XIV. Lactonization reaches its maximum extent when pAB and pBA are both large (i.e. in a 1:1 copolymer), while monomer production will be highest in copolymers of low VB content, where long ester sequences are found, interrupted only by an occasional lactone ring. The highest degree of dehydrobromination should be observed in the 73.1% VB copolymer, but even here, the VB sequences are much shorter than those attained by MMA at the opposite end of the composition scale.

TABLE XIV

Mole Fraction of VB(A)	4.9%	9.8%	24.5%	48.4%	73.1%
R	9.26	17.6	37.0	50.0	32.3
⟨A⟩	1.05	1.11	1.32	1.94	3.72
⟨B⟩	20.6	10.3	4.08	2.07	1.37
pAB	0.951	0.903	0.755	0.516	0.269
pBA	0.0490	0.0980	0.245	0.484	0.731
$f_L(A)$	100%	99%	91%	66%	32%
$f_L(B)$	5.2%	11%	30%	61%	88%

The above data are based on monomer reactivity ratios of 0.05 and 20 for VB and MMA respectively.

VINYL CHLORIDE — n-BUTYL METHACRYLAMIDE (BMAC) COPOLYMER

The initial studies of this system were carried out in collaboration with B.Sc. student R.L.G. Nicoletti⁽¹⁰⁸⁾.

The copolymer was studied basically to determine whether a thermal lactamization process (analogous to lactonization) could be induced when the ester function is replaced with amide. n-butyl methacrylamide was chosen as comonomer since it is a liquid in its normal state (methacrylamide, for example, is a solid of melting point 102-106°C) and miscible with liquid vinyl chloride so that bulk copolymerization would be easy to achieve. The thermal degradation of poly(n-butyl methacrylamide), which itself has not been previously prepared, could also be compared with the degradation of its ester analogue, poly(n-butyl methacrylate).

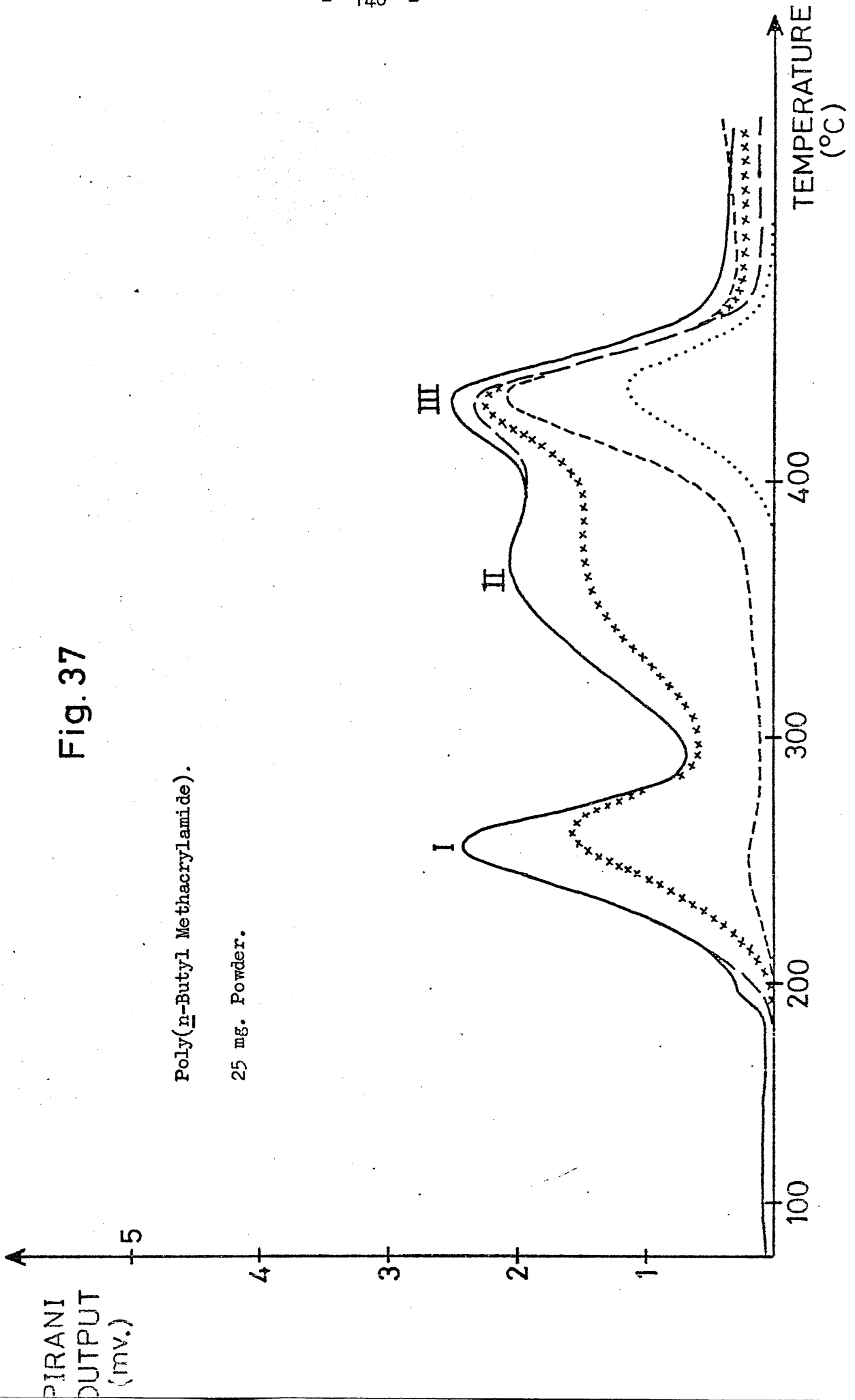
Poly(n-Butyl Methacrylamide) : Analysis of Volatile Products

The TVA curves of PBMAC homopolymer are shown in Fig.37, p.146. The first peak, I, ($T_{\max} = 258^{\circ}\text{C}$) can be resolved into two peaks ($T_{\max} = 189^{\circ}\text{C}, 258^{\circ}\text{C}$) by using a larger sample. With a 25mg. sample (as shown), the low-temperature peak only appears as a small shoulder. Thus there would appear to be at least two phases of reaction in Stage I and the products identified by I.R. analysis up to 265°C were butylamine, monomer and ammonia. Ammonia is non-condensable at -100°C ; the fraction condensable between -75°C and -100°C is probably

Fig. 37

Poly(n-Butyl Methacrylamide).

25 mg. Powder.

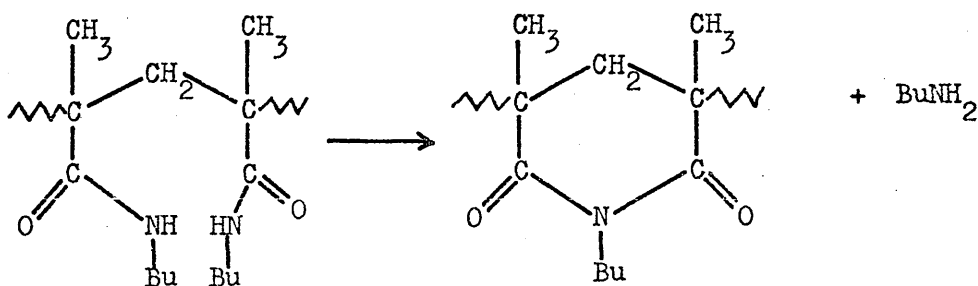


butylamine, while the least volatile component, which is condensed between -45°C and -75°C , is likely to be monomer.

In the remaining stages of degradation (peaks II and III ; $T_{\text{max}} = 370^{\circ}\text{C}$, 432°C), the products identified by I.R. analysis were butylamine, ammonia, monomer, isobutene, ethylene, but-1-ene (and/or propylene) and possibly methacrylonitrile (928cm^{-1}), with carbon monoxide and methane comprising the non-condensable fraction.

Stage I

The large-scale production of butylamine suggests that an imidization process may be occurring here:-



Bresler et al.⁽¹⁰⁹⁾ have noted the occurrence of a similar process during pyrolysis in vacuo of poly(methyl methacrylamide) between 315°C and 325°C , in which methylamine was evolved and cyclic structures formed in the residue. An analogous process in poly(n-butyl methacrylate) is not possible.

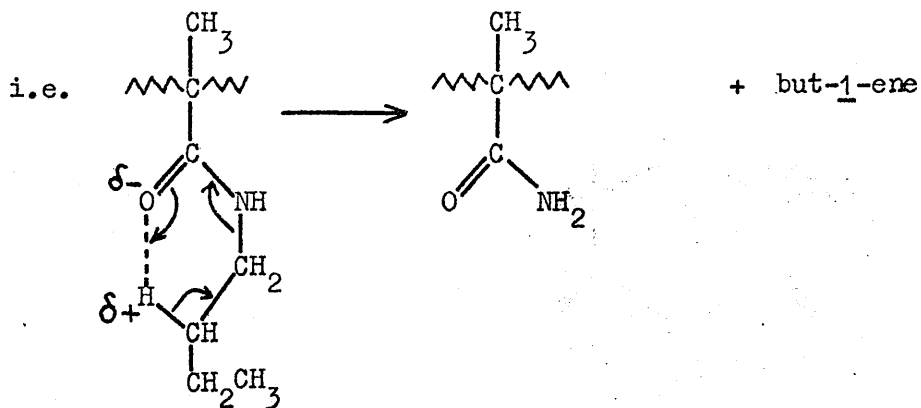
It is almost certain that ammonia production at this stage of reaction is the result of amide decomposition, exactly analogous to ester decomposition in poly(n-butyl methacrylate). It was not possible to identify but-1-ene specifically by gas I.R. analysis alone, since ammonia absorbs at 912cm^{-1} and the other strong band

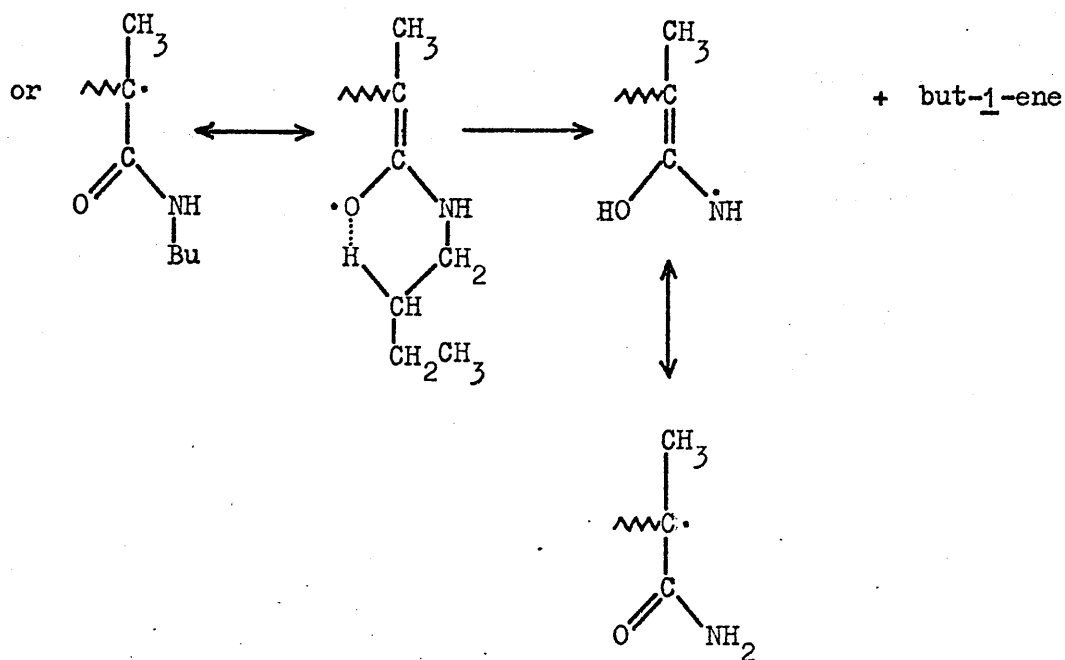
of but-1-ene (3010cm^{-1}) is obscured by butylamine. The presence of but-1-ene was deduced as follows:-

(i) The absorption at 912cm^{-1} was stronger in the degradation products than the band at 890cm^{-1} , whereas in pure ammonia, this situation is reversed.

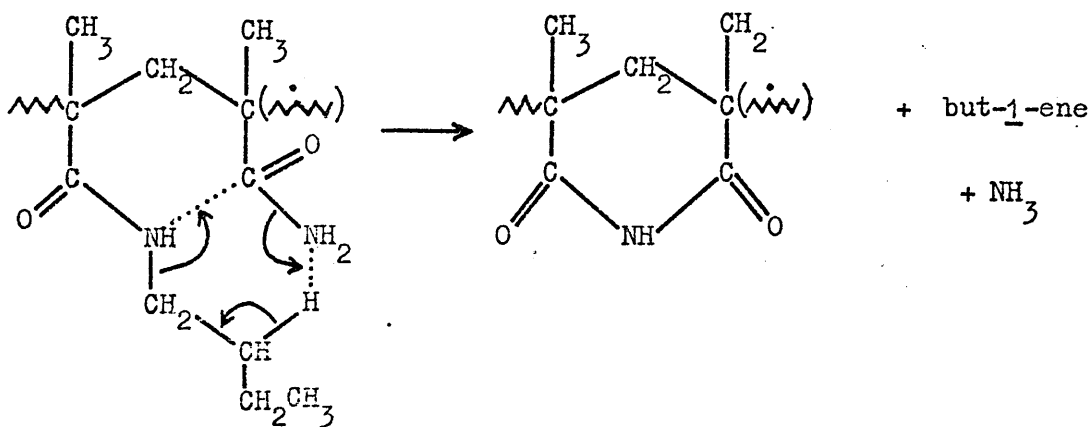
(ii) Gas chromatographic analysis of the products (collected to T_{max} of the first TVA peak) showed the presence of a material which had the same retention time as but-1-ene on Porapak at 130°C .

Amide decomposition appears to take place concurrently with imidization and depropagation, but it is not possible to say whether the mechanism is molecular (as proposed by Maccoll⁽¹⁰⁵⁾ for gas-phase ester decomposition) or involves a depropagating radical (as proposed by Grassie and MacCallum⁽¹⁰²⁾ for poly-n-butyl methacrylate decomposition).





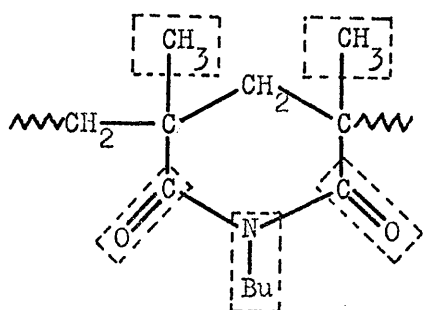
Regardless of which mechanism is involved, the primary amide group so formed presumably reacts with the adjacent secondary amide function to yield ammonia and more but-1-ene:-



Stages II and III

I.R. analysis has shown monomer to be a significant product in this region, together with but-1-ene (and/or propylene), while

butylamine and ammonia are still also important. The reason for the broad peak with $T_{\max} = 370^{\circ}\text{C}$ is not clear, but it may include a second phase of monomer production (as evidenced by the re-divergence of the -45°C and -75°C traces). Above 380°C , release of non-condensable material begins and this is probably due largely to decomposition of the structures:-



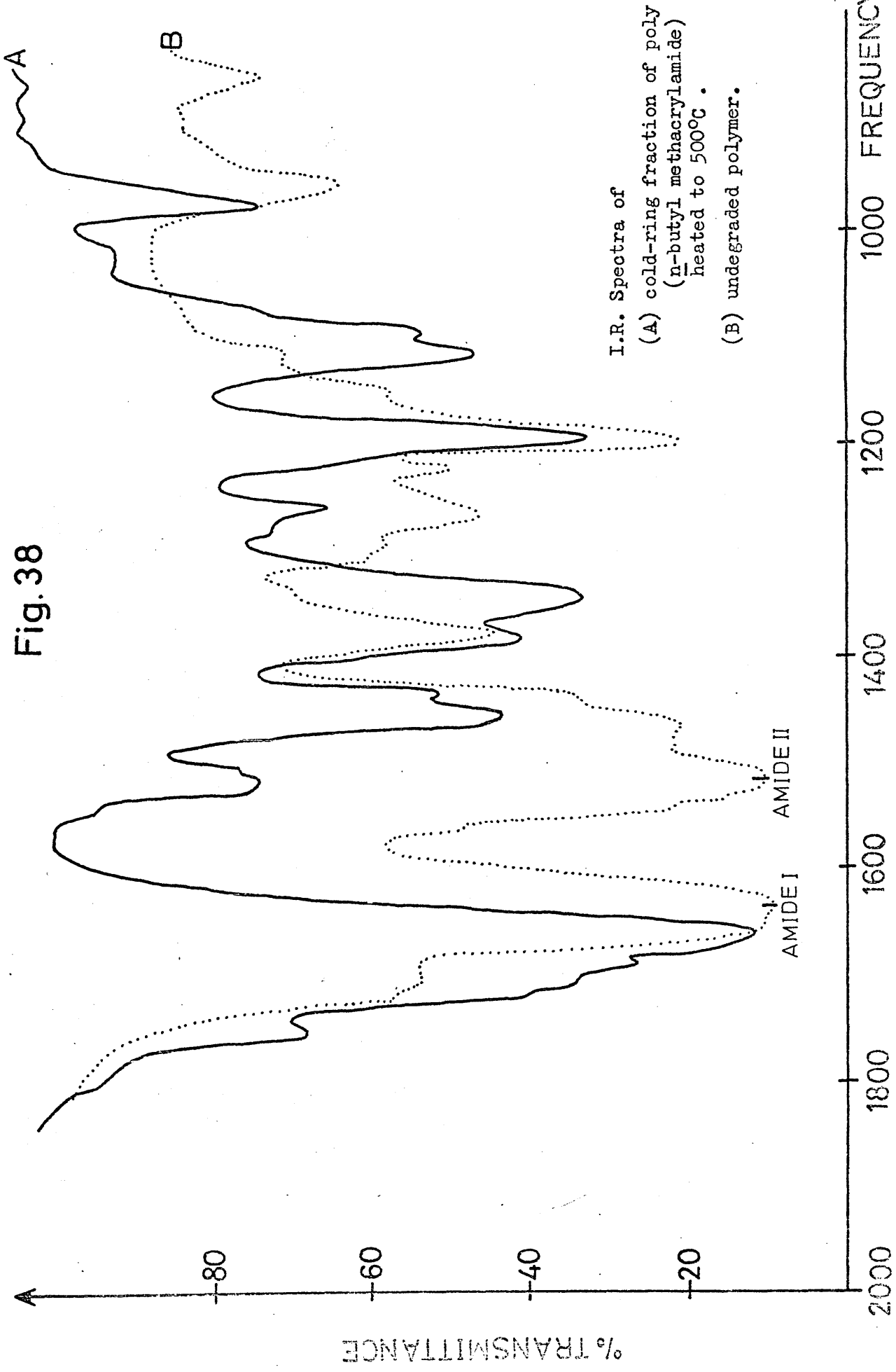
Carbon monoxide, butylamine and methane have been identified here, together with isobutene (and possibly propylene), which probably originates from scission of the residual backbone.

The apparent presence of methacrylonitrile among the volatiles from Stages II and III is not unexpected. McNeill et al.⁽¹¹⁰⁾ have already found I.R. and gas-chromatographic evidence for the formation of this product during degradation of poly(methacrylamide) and it is likely that it originates from dehydration of primary amide units, followed by splitting-out from the backbone.

Analysis of Cold-Ring Fraction

The solid-phase I.R. spectrum of the cold-ring fraction obtained when FBMAC is heated to 500°C is shown in Fig.38,p.151, where it has been superimposed on the spectrum of the undegraded polymer.

Fig. 38



I.R. Spectra of

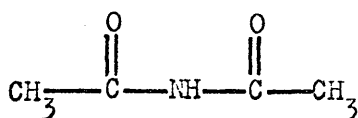
(A) cold-ring fraction of poly
(n-butyl methacrylamide)
heated to 500°C.

(B) undegraded polymer.

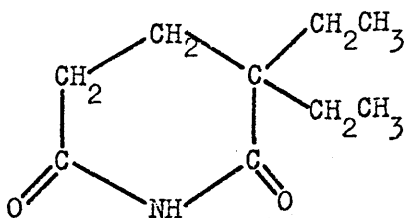
2000 1800 1600 1400 1200 1000 FREQUENCY (cm.⁻¹)

% TRANSMITTANCE

In the undegraded sample, the Amide I and Amide II bands of the secondary amide function appear at 1635cm^{-1} and 1520cm^{-1} respectively. A conspicuous shoulder at 1705cm^{-1} may indicate that some imidization occurs during the free-radical polymerisation process at 50°C , since the absorption is consistent with either acyclic or 6-membered cyclic imide structures (C = O stretch). Models of these structures (for which spectra were available)⁽¹¹¹⁾ are shown below together with their absorption frequencies in the carbonyl region.



1710cm^{-1} }
 1695cm^{-1} } (Strong)
 1760cm^{-1} }
 1740cm^{-1} } (Medium)



1715cm^{-1} }
 1655cm^{-1} } (Strong)
 1755cm^{-1} (Weak Shoulder)

The origin of these structures would be inter- and intra- molecular imidization respectively. Crauwels and Smets⁽¹¹²⁾ have already noted that imidization occurs during the free-radical polymerization of methacrylamide in aqueous solution, when the temperature exceeds 65°C .

In the cold-ring fraction, the Amide II band at 1520cm^{-1} is much weaker, indicating extensive removal of the secondary amide function, while a shoulder at 1710cm^{-1} and another absorption at 1695cm^{-1} correspond closely to acyclic imide. The maximum absorption occurs at 1665cm^{-1} and probably represents the cyclic imide, although it may be due in part to isolated primary amide structures (formed by amide

decomposition) which are unable to imidize. The remaining band at 1755cm^{-1} would be consistent with either type of imide structure.

It therefore appears possible that both inter- and intramolecular imidization operate concurrently during the thermal degradation.

VC - BMAC Copolymer : Analysis of Volatile Products

The TVA curves for a 23% (molar) VC copolymer are shown in Fig. 39, p.154. The most obvious features are the absence of the first homopolymer peak ($T_{\text{max}} = 258^{\circ}\text{C}$) and the appearance of a new peak ($T_{\text{max}} = 178^{\circ}\text{C}$), which consists to a large extent of material non-condensable at -100°C . The main stage of degradation has T_{max} at 402°C , compared with 432°C for the final stage of homopolymer breakdown.

I.R. gas analysis has shown the volatile products up to the end of the first peak to consist of HCl, butylamine and dioxane (precipitant used for isolating the polymer). Products identified by I.R. analysis in the remaining stage of decomposition (above 230°C) were butylamine, ammonia, monomer, but-1-ene (and/or propylene), isobutene, ethylene and possibly methacrylonitrile (928cm^{-1}), with methane and carbon monoxide contributing to the non-condensable fraction.

Analysis of Cold-Ring Fractions

A white solid cold-ring fraction formed during the first stage of degradation ($T_{\text{max}} = 178^{\circ}\text{C}$) was soluble in water and ethanol and showed I.R. absorption characteristic of a primary amine salt:-

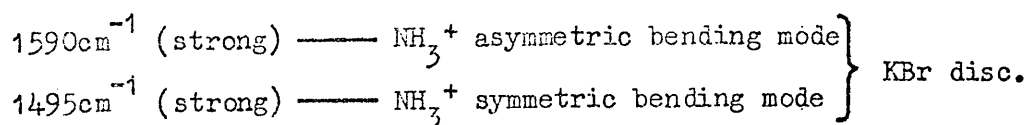
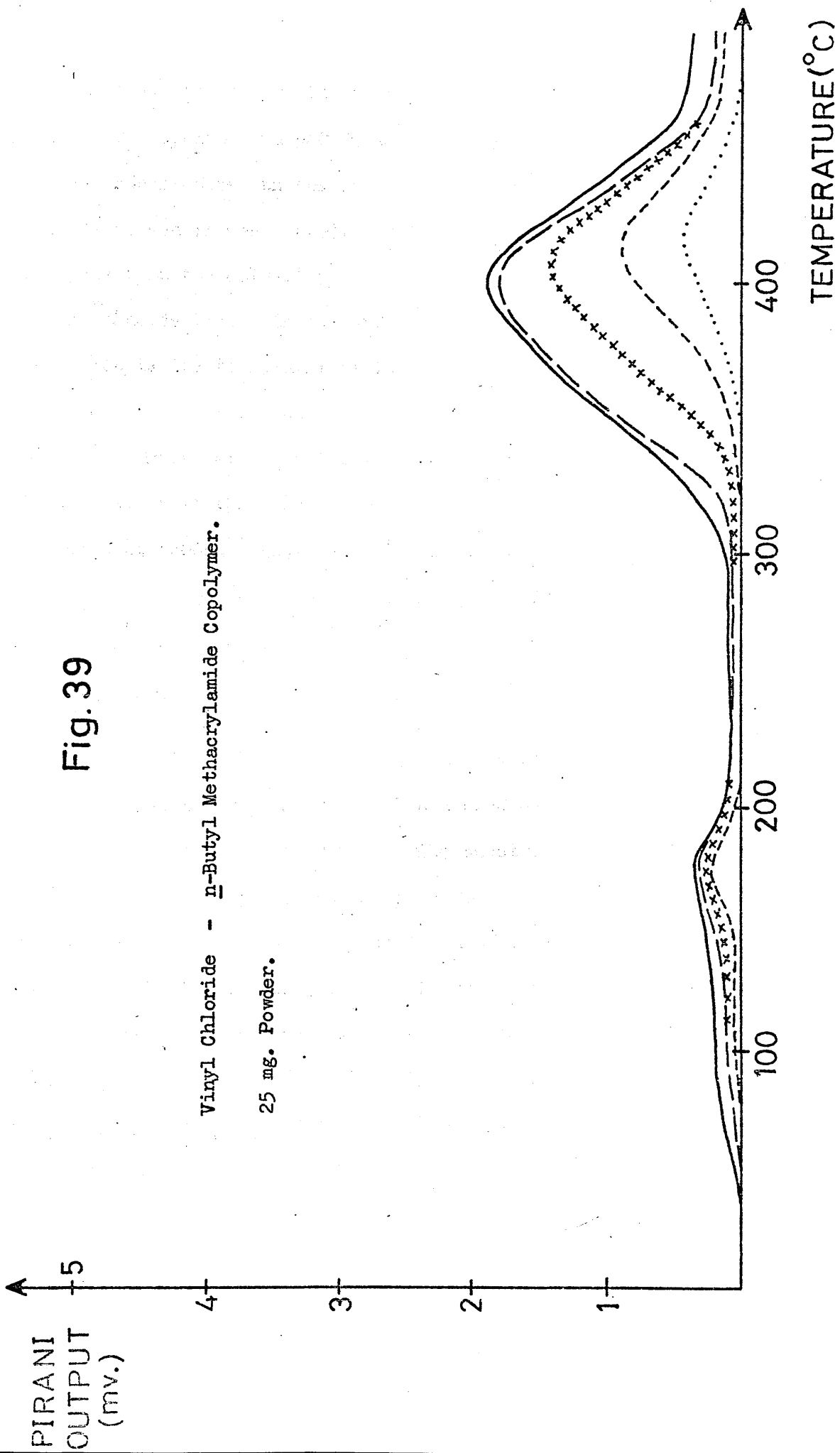


Fig. 39

Vinyl Chloride - n-Butyl Methacrylamide Copolymer.

25 mg. Powder.



The I.R. spectrum of the total cold-ring fraction, obtained by heating the copolymer to 500°C, is shown in Fig.40, p.156, where it has been superimposed on the spectrum of the undegraded polymer (KBr discs were used in each case). Residual secondary amide structures are present in the cold-ring fraction, as evidenced by the band at 1520cm⁻¹ (Amide II). In the undegraded copolymer the strongest absorption is due to Amide I at 1640cm⁻¹, but this becomes obscured in the cold-ring fraction, where the maximum absorption is shifted to 1665cm⁻¹. This latter absorption probably represents cyclic imide structures, as in the cold-ring fraction of the homopolymer (p.150). Shoulders at 1700cm⁻¹ and 1690cm⁻¹, which were also observed in the cold-ring fraction of the homopolymer, may again indicate the presence of acyclic imide groups.

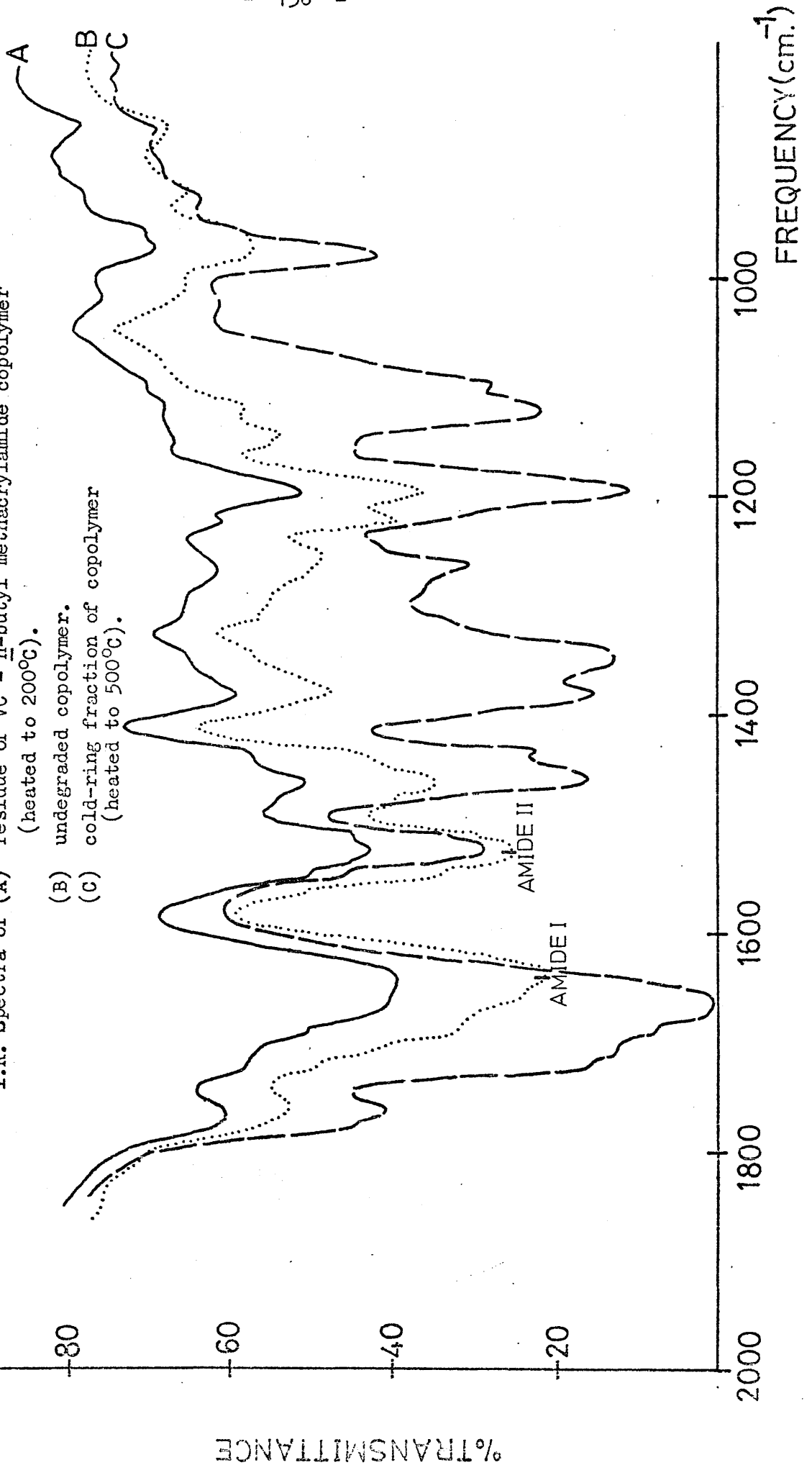
Analysis of Polymer Residue

To help elucidate the nature of the HCl loss, the copolymer was heated until the first TVA peak had been passed and the residue was examined for I.R. absorption. The spectrum obtained is shown in Fig.40, where it has been superimposed on the spectrum of the undegraded polymer. The most significant difference in the spectra is the growth of a shoulder between 1730cm⁻¹ and 1700cm⁻¹ on going from the undegraded to the partially degraded sample. Unfortunately, both acyclic and 6-membered cyclic imides absorb in this region, so that is not possible to assign this band specifically to a γ -lactam structure (carbonyl absorption : 1700cm⁻¹).

One other interesting feature is the occurrence in the undegraded copolymer of a medium absorption at 1765cm⁻¹, which is retained on

A Fig.40

I.R. Spectra of (A) residue of VC - *n*-butyl methacrylamide copolymer
(heated to 200°C).
(B) undegraded copolymer.
(C) cold-ring fraction of copolymer
(heated to 500°C).

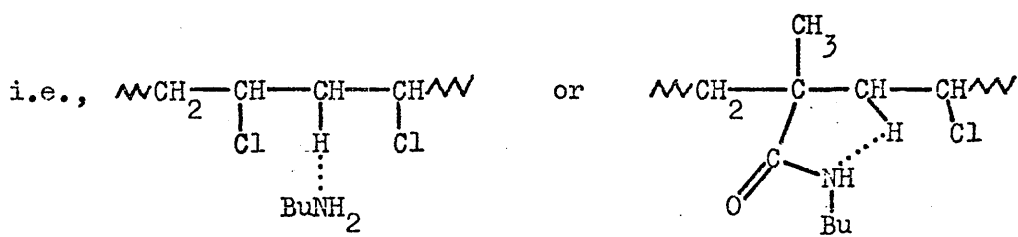


heating. It is again possible that this is due to intermolecular imidization during polymerisation.

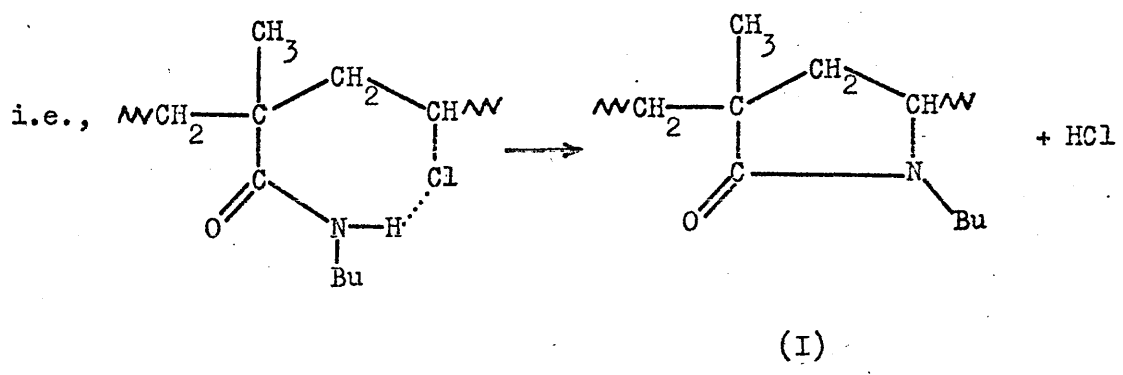
Discussion

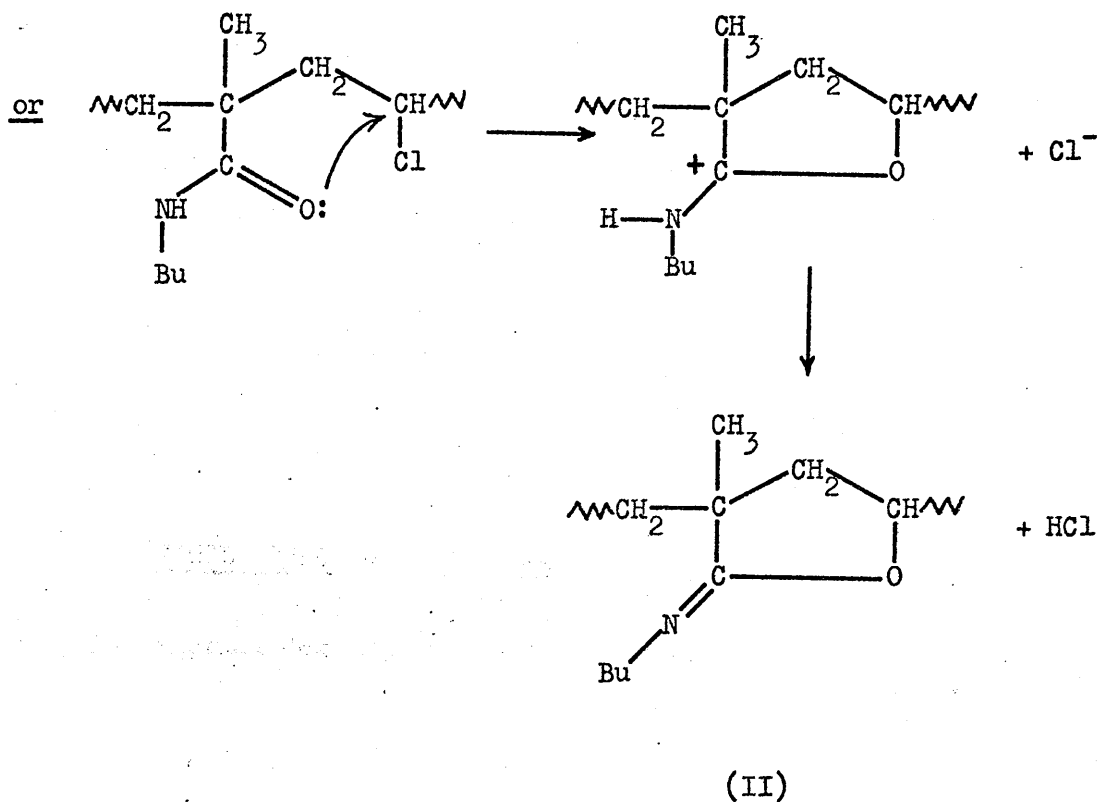
The most interesting feature of the copolymer is clearly the elimination of HCl very early in the degradation ($T_{max} = 178^{\circ}C$, compared with about $300^{\circ}C$ in PVC). The possible reasons for this early elimination are outlined below:-

(i) HCl may be eliminated by the usual "zipper"-type process, its early release being the result of base catalysis by butylamine or possibly neighbouring group participation by the amide group.



(ii) HCl elimination may be the result of a lactamization process.





No definite spectroscopic evidence has been obtained for the formation of either (I) or (II).

A brief study has been made of the thermal degradation of PVC in presence of poly(n-butyl methacrylamide) [see Fig.48, p.186 .] An interaction is observed in which HCl elimination is apparently divided into two overlapping stages and begins about 20^oC sooner than in pure PVC. Base catalysis by butylamine seems the most likely explanation of this and presumably the effect is much enhanced when mixing is on a molecular scale — i.e., in a copolymer.

The fact that no HCl was detected at higher temperatures may of course be due to the low VC content of the copolymer. Studies of a high VC content copolymer would therefore be interesting.

Regardless of the true mechanism involved, the HCl released reacts

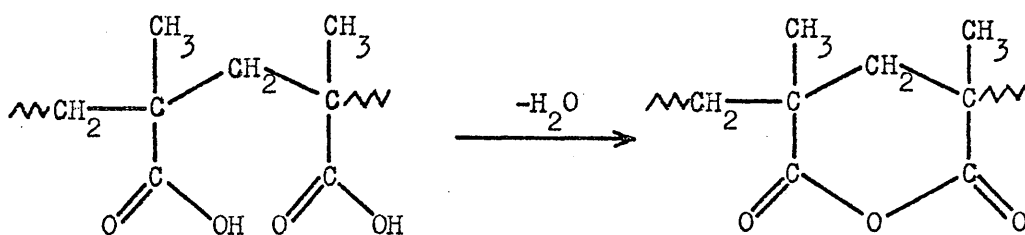
with butylamine (from imidization) to give an involatile amine salt:-



Because of this effect, the size of the initial "imidization" peak in the TVA is much reduced. Similarly, the "HCl" peak, because of its overlap, only represents a fraction of the total HCl released from the polymer.

VINYL CHLORIDE — METHACRYLIC ACID COPOLYMER

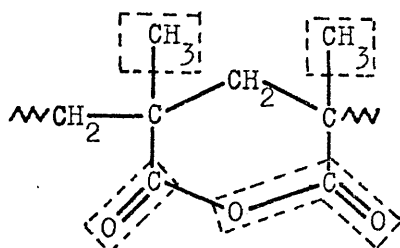
The thermal degradation of poly(methacrylic acid), PMAA, has been studied in some detail by Grant and Grassie⁽¹³⁾. At 200°C, monomer was found to be only a minor product, with the major reaction being the loss of water to form a residue which contained glutaric anhydride type units:-



The mechanism of anhydride formation was considered to be analogous to an acid-catalysed esterification (see p. 10). Vacuum-dried PMAA rapidly absorbs atmospheric moisture and the release of this was observed before the onset of anhydride formation.

More recent studies, using TVA and I.R. analysis of products,^(28,113) have confirmed these findings and shown that at higher temperatures

the anhydride structures decompose to give carbon dioxide, carbon monoxide, methane, ethylene, propylene and isobutene. Presumably, these products arise by fragmentations of the type shown below:-



The olefins must originate from scission of the residual backbone.

The TVA curves for PMAA are shown in Fig.41, p.161. The limiting rate effect in the -75°C trace is characteristic of water and the release of this begins as soon as heating commences. Above about 170°C , the main source of water becomes anhydride formation and T_{max} for this process occurs at 249°C . Water elimination ceases after 325°C , as shown by the return of the $0^{\circ}/-45^{\circ}\text{C}$ traces to the base-line. The main stage of degradation has $T_{\text{max}} = 444^{\circ}\text{C}$ and can be seen to include a large proportion of non-condensable material.

Copolymer -- Analysis of Volatile Products

The TVA for a 65% (molar) VC - MAA copolymer is shown in Fig. 42, p.162. The large response on the $0^{\circ}/-45^{\circ}\text{C}$ traces at low temperatures is mainly due to the solvent cyclohexanone, but the limiting rate in the -75°C trace also suggests the desorption of water. The displacement of the -100°C trace to give a peak with $T_{\text{max}} = 168^{\circ}\text{C}$ is due neither to cyclohexanone nor water (since both are fully condensed at this temperature) and I.R. gas analysis has shown HCl to be responsible.

Fig. 41

Poly(Methacrylic Acid).

25 mg. Film Cast from Methanol.

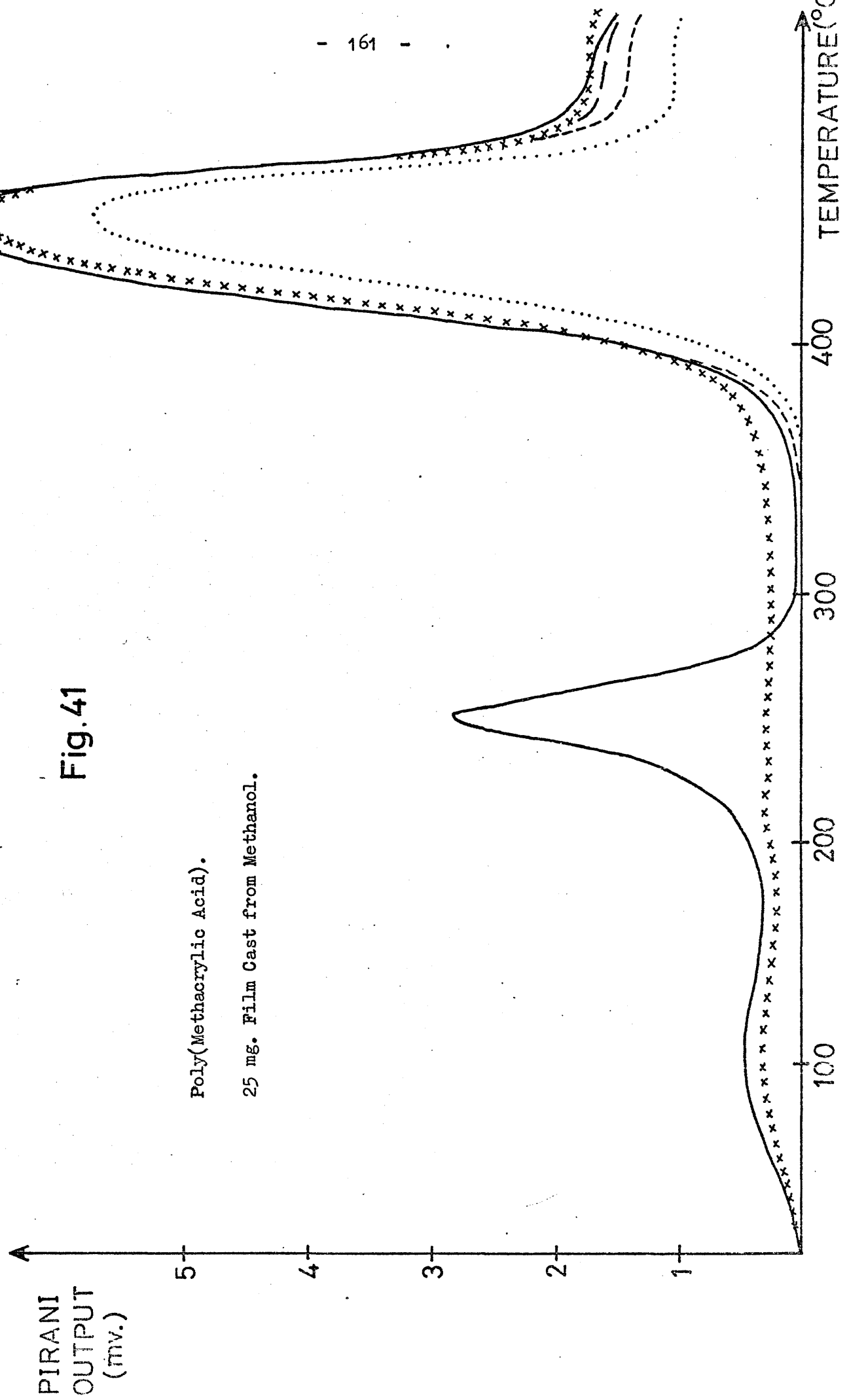
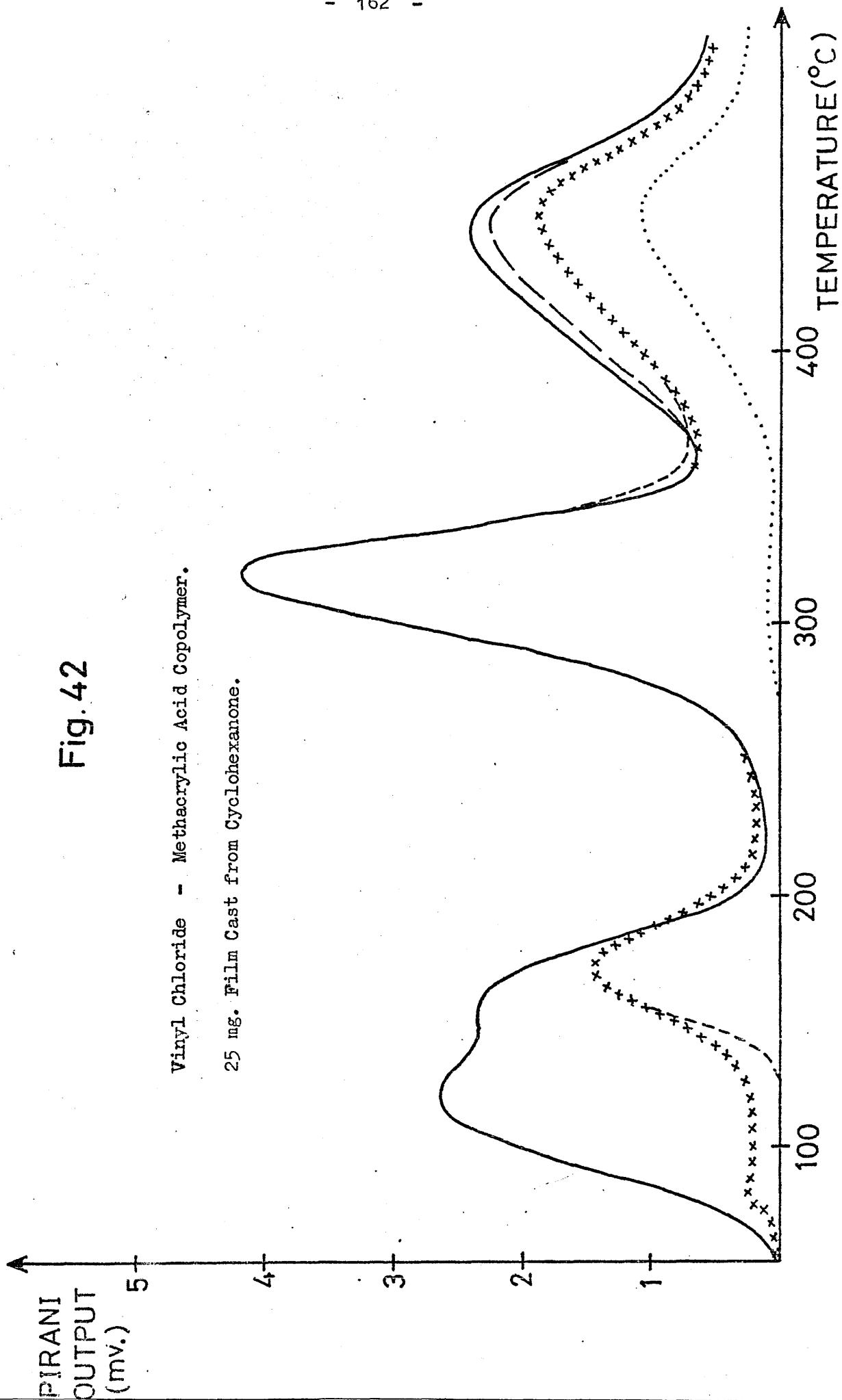


Fig. 42

Vinyl Chloride - Methacrylic Acid Copolymer.

25 mg. Film Cast from Cyclohexanone.



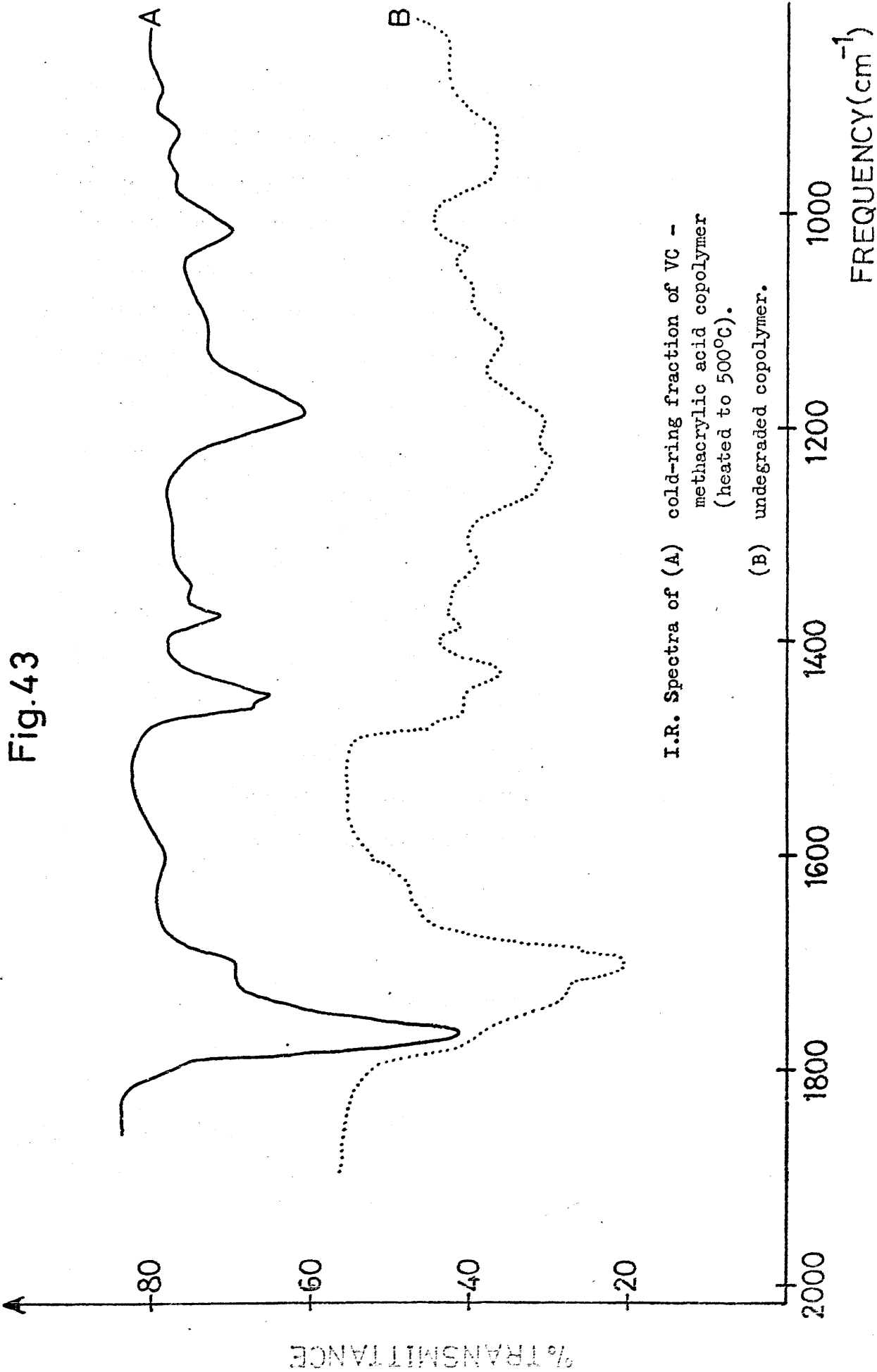
Above 220°C, a second and more important phase of HCl elimination begins to give $T_{\max} = 319^{\circ}\text{C}$. Smaller amounts of benzene and carbon dioxide have also been identified here and the displacement of the -196°C trace shows that a very small quantity of non-condensable material is also being released.

The final stage of degradation shows T_{\max} at 444°C (as in PMAA) and the volatile products were identified as carbon dioxide, but-1-ene (and/or propylene), ethylene and possibly some isobutene. The non-condensable fraction included carbon monoxide and methane.

Analysis of Cold-ring Fraction

The cold-ring fraction obtained by heating the copolymer to 500°C was dissolved in chloroform and cast as a film onto a NaCl plate. Its I.R. absorption is shown in Fig.43, p.164, where it has been superimposed on the spectrum of the undegraded copolymer (KBr disc). In the latter, maximum absorption occurs at 1700cm^{-1} and this is immediately assignable to the carboxylic acid function. Shoulders are also apparent at 1765cm^{-1} and 1720cm^{-1} . It is possible that the first of these is due to the occurrence of a limited amount of lactonization during the polymerization process (see p.168), whereas the second is probably caused by trapped cyclohexanone solvent.

The maximum absorption in the cold-ring fraction occurs at 1765cm^{-1} and this is probably due largely to lactone structures — glutaric anhydride type structures also absorb at this frequency, but the "twin" carbonyl peak which should appear at 1800cm^{-1} ⁽¹³⁾ is not distinct (only a weak shoulder is visible). A band at 1020cm^{-1} which has also been associated by Grant and Grassie with glutaric anhydride type units, is probably caused mainly in this case by a C - O - C stretching mode of



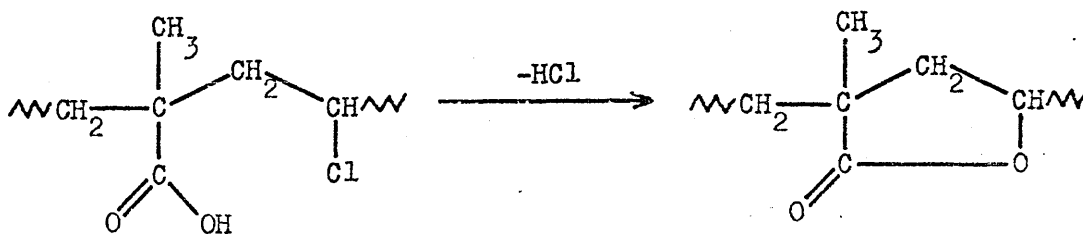
γ -lactone. The same band was noted in an undegraded VC - sodium methacrylate copolymer (see p.176) in which γ -lactone structures were known to be present, while a liquid film spectrum of γ -butyrolactone showed a strong absorption at 1030cm^{-1} . A strong absorption at 1190cm^{-1} in the cold-ring fraction can be assigned to the other C - O - C stretching mode of γ -lactone by comparison with a sample of γ -butyrolactone. The latter absorbs strongly at 1170cm^{-1} . The other main carbonyl absorption at 1705cm^{-1} must be due to unreacted $-\text{CO}_2\text{H}$ groups and finally, a weak, broad absorption at 1605cm^{-1} probably represents unsaturated hydrocarbon structures.

Analysis of Polymer Residue

The residue obtained by heating the copolymer to 500°C was examined for I.R. absorption by casting it as a film onto a salt plate as before. Apart from the expected alkane absorptions, unsaturated hydrocarbon structures were evidenced by bands at $3100\text{-}3000\text{cm}^{-1}$, 1600cm^{-1} , 875cm^{-1} and 820cm^{-1} . A weak absorption at 1760cm^{-1} may have been due to residual lactone units.

Discussion

HCl elimination at anomalously low temperatures is clearly the result of an intramolecular lactonization process:-



This appears to reduce drastically the number of acid units available for anhydride formation — evidenced by the almost total removal of the "water" peak at 249°C on going from PMAA to copolymer and also by the I.R. analysis of the cold-ring fraction, which shows that lactone structures outnumber those of anhydride and isolated $-\text{CO}_2\text{H}$.

The effect of copolymerisation on the main stage of HCl loss ("unzipping") is, as usual, difficult to assess, since small amounts of carbon dioxide and benzene are concurrently released, but on an overall basis, T_{max} is only shifted from 325°C in pure PVC to 319°C in the copolymer. (25mg. film samples used in each case)

VINYL CHLORIDE — SODIUM METHACRYLATE COPOLYMER

The thermal behaviour of polyelectrolytes has not been studied in much detail in the past, probably due largely to their mode of application. For example, typical uses of acrylic-type polyelectrolytes include water conditioning and waste treatment and they have also been employed as soil dispersants and processing additives in the paper and textile industries. It seems likely, however, that polyelectrolytes will be used increasingly to extend the uses of the more important commercial polymers, either in the form of copolymers or as polymer blends, so that a prior knowledge of their thermal degradation characteristics will be useful.

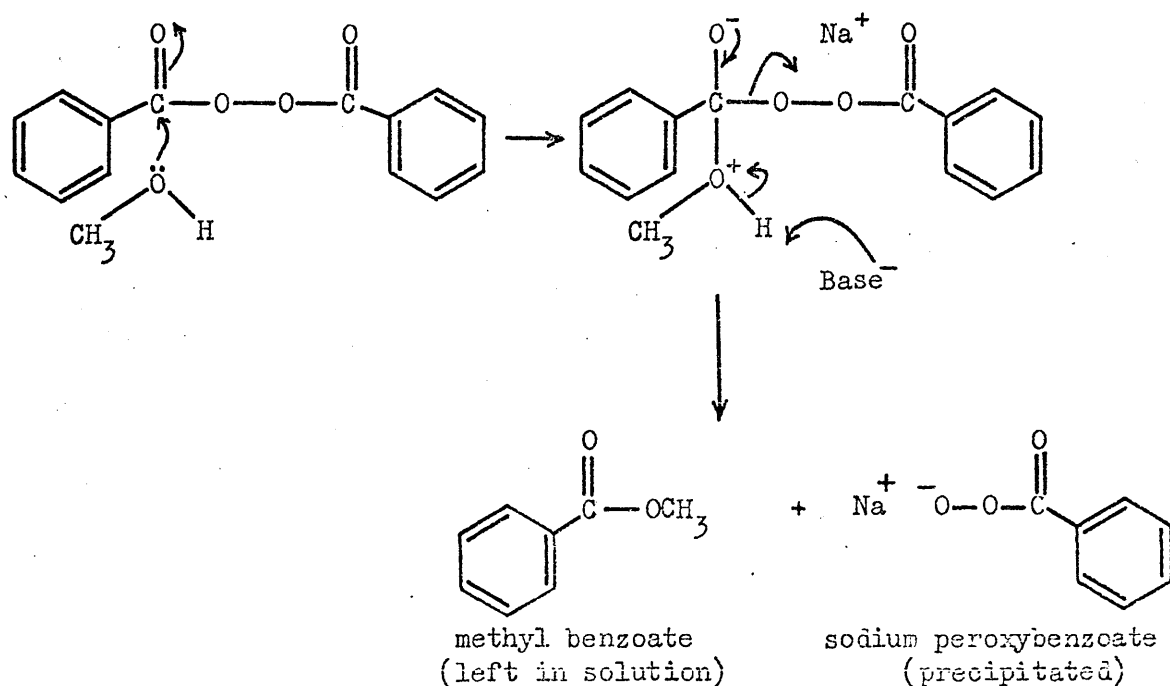
A wide range of metal salts (and also the ammonium salt) of polymethacrylic acid is currently under study by McNeill and Zulfiquar⁽¹¹³⁾, and, in general, the polymers have been found to be highly crystalline powders which are relatively stable to heat. In the present work, the major aim has been first of all to prepare a VC - sodium methacrylate copolymer and then to examine its thermal behaviour, with particular reference to the effect of replacing the

the ester function (as in VC - MMA copolymers) with a highly polar carboxylate group.

Choice of Polymerisation Initiator

Benzoyl peroxide failed to operate as an effective initiator for the copolymerisation in methanol solution at 45°C. The yield of polymer was less than 1%, even after several days, and on opening the dilatometer, a smell very similar to that of methyl benzoate was observed. A similar effect has been noted during the copolymerisation of sodium acrylate with vinyl acetate at 70°C in alcohol solution,⁽¹¹⁴⁾ but here the effect was attributed to the inhibiting properties of decomposition products of vinyl acetate.

A more rational explanation of these effects would seem to be the destruction of the initiator by methanolysis, in presence of monomeric anion as base. For example, in the present system, $\text{CH}_2=\text{C}(\text{CH}_3)\cdot\text{CO}_2^-$ is a moderate base. Benzoyl peroxide can be considered to be a mixed anhydride of benzoic and peroxybenzoic acids and base-assisted methanolysis will occur as shown below:-

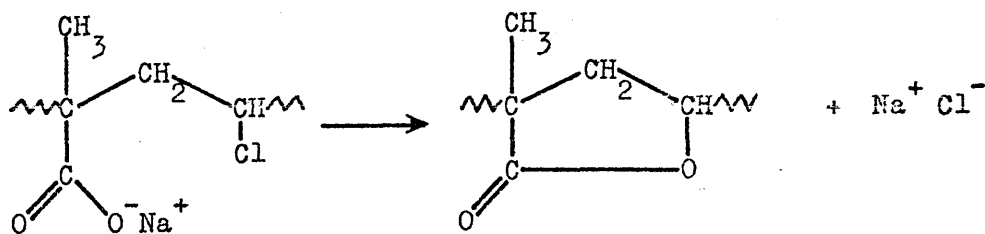


This reaction scheme is directly comparable with that found in the preparation of peroxybenzoic acid from benzoyl peroxide⁽¹¹⁵⁾ in which the peroxide is reacted with sodium ethoxide in ether-alcohol solution at -5°C . Azo-bis-isobutyronitrile cannot be competitively removed from the system in this way and it was found to give satisfactory initiation of the copolymerisation.

Pre-Lactonization

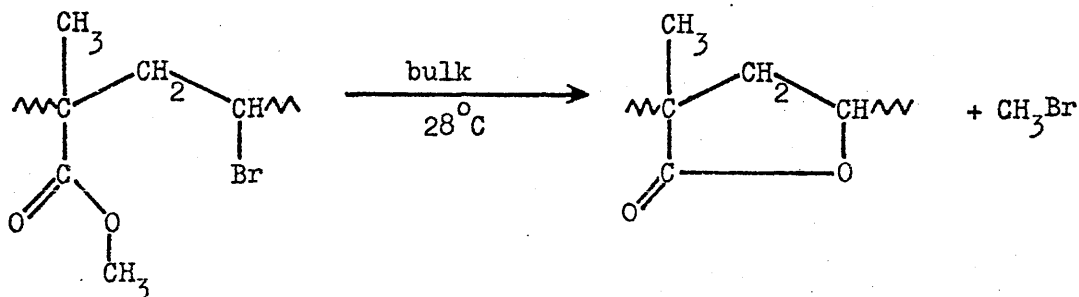
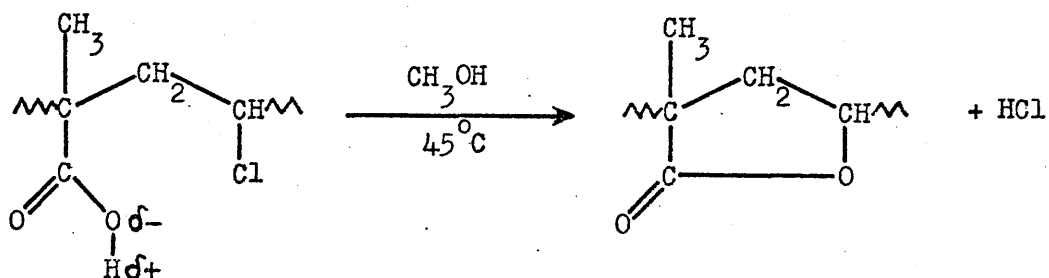
There appears to be a strong tendency for adjacent VC and salt units to lactonize during the polymerisation process. From the point of view of comparing the degradation behaviour of this system with the previous ones, this was a disappointing factor and also a complicating one, since the product of the polymerisation would effectively be a terpolymer and not a copolymer. The presence of lactone structures in the undegraded polymer was deduced from the presence in the I.R. spectrum (KBr disc) of strong bands at 1765cm^{-1} and 1195cm^{-1} .

The carboxylate anion is a very good nucleophile for attack at saturated carbon and it seems likely that the following reaction is able to take place in methanol solution at 45°C :-



Although not investigated, NaCl is presumably a by-product of the polymerization.

Analogous reactions can be envisaged for the VC - MAA and VB - MMA systems, where there was also some spectroscopic evidence for pre-lactonization:-



The first of these reactions probably occurs by virtue of the high polarity of the O - H bond and the polarity of the solvent, while the second process may result from the relative weakness of the C - Br bond (see p.179) and/or from the ability of the Br⁻ ion to function both as a good leaving group and as a good nucleophile.

Neither reaction can occur as readily during polymerization as it does during thermal degradation of the polymer.

Thermal Degradation of Poly(Sodium Methacrylate)

The TVA curves for PNaMA are shown in Fig. 44, p.171. McNeill and Zulfiqar have shown that the slow release of absorbed water begins as soon as heating is commenced and this is seen as the initial "plateau" region in the 0°/-45°/-75°C traces. Above about 215°C, the release of more volatile material commences, including a non-condensable fraction, and the volatile products identified by I.R. analysis were similar to those evolved in the later stages of degradation — isobutene, but-1-ene, ethylene, methyl ethyl ketone, di-ethyl ketone, methyl cyclopentanone, dimethyl cyclopentanone, carbon dioxide and carbon monoxide.

On heating the polymer to 500°C, the residue was identified as a mixture of carbon and sodium carbonate, while the cold-ring fraction was mainly monomer. No anhydride structures have yet been identified and this would appear to discount the possibility of splitting out Na₂O in an analogous fashion to water elimination from PMAA.

The uniformity of the volatile product composition throughout the degradation suggests that the reaction of isotactic, syndiotactic and atactic segments of the polymer chain may occur at different temperatures. Sodium carbonate probably originates from two sources:-

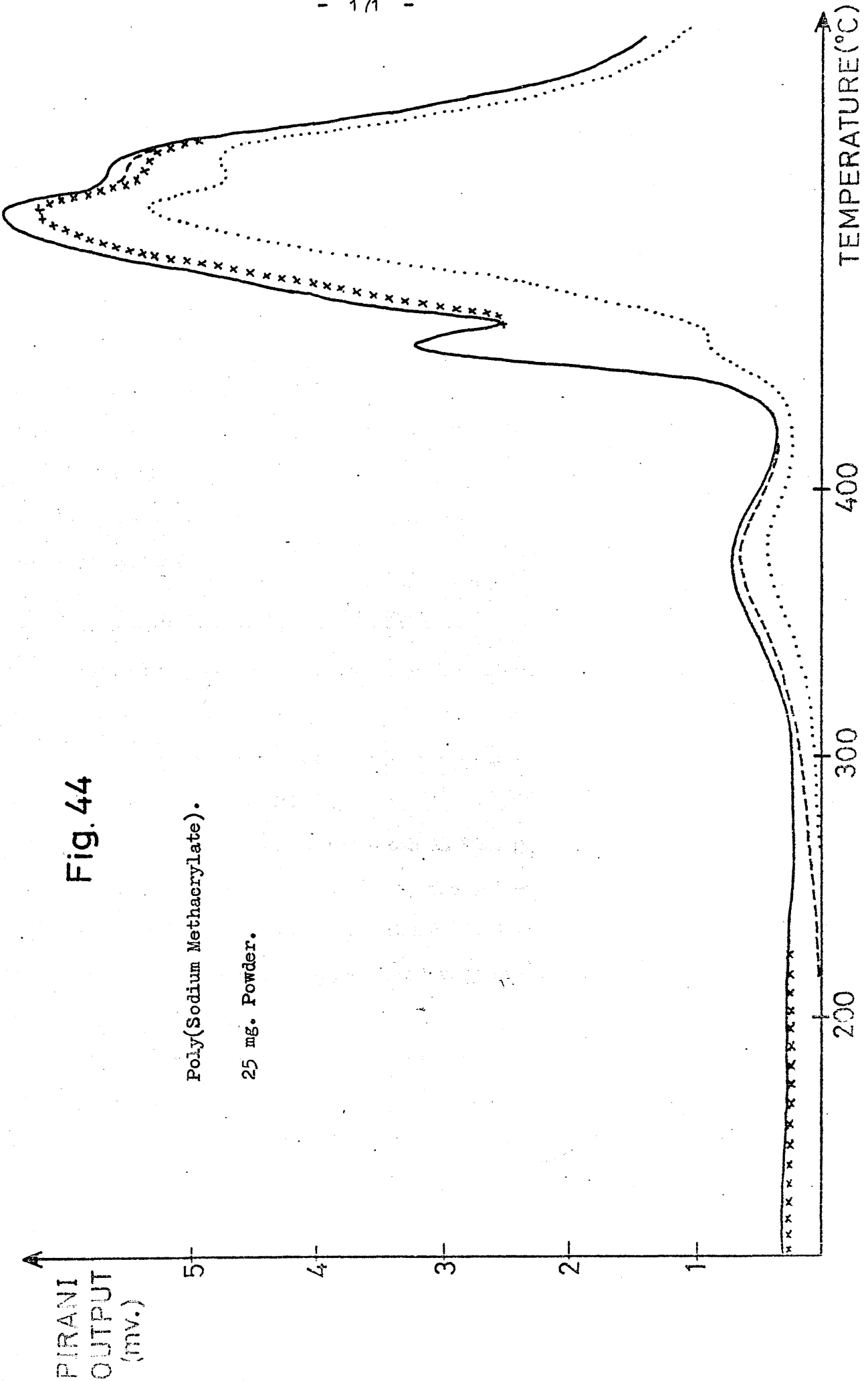
(i) decomposition of monomer — McNeill and Zulfiqar have shown that this yields a mixture of carbon and Na₂CO₃ on heating to 500°C.

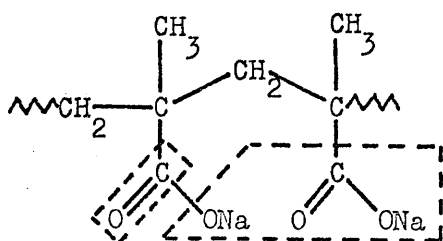
(ii) elimination from adjacent salt groups as shown below — the resulting cyclobutanone structure rearranges by bond scission to give the substituted cyclopentanones, which are then released:-

Fig. 44

Poly(Sodium Methacrylate).

25 mg. Powder.





Methyl ethyl ketone and diethyl ketone presumably arise by secondary fragmentation of the ketone structures. Carbon monoxide may be formed in place of ketone as shown. Carbon dioxide probably arises by the decomposition of single $\text{-CO}_2\text{Na}$ units (Na_2CO_3 does not decompose below 500°C), but the fate of the resultant Na^+ ions is not clear. The olefins presumably arise by scission of the residual backbone, as in previous systems.

"Copolymer" : Analysis of Volatile Products

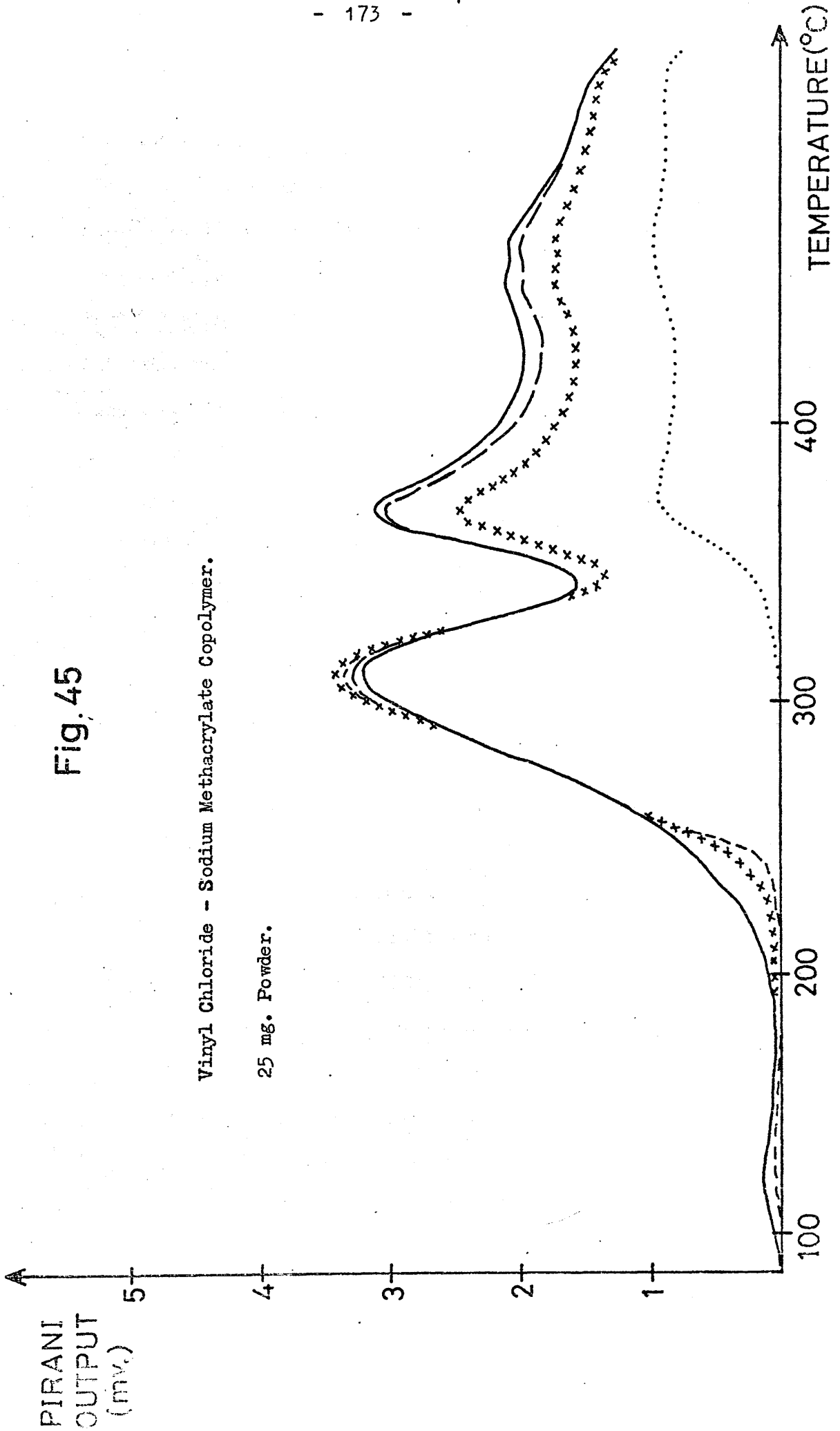
Due to the pre-lactonization reaction, microanalysis figures for the "copolymer" were rendered useless and it can only be stated that the "copolymer" was of approximately intermediate composition, on the basis of the Q-e data used.

The TVA curves obtained are shown in Fig. 45, p. 173. The small peak below 160°C is probably caused by the solvents used for washing the polymer (tetrahydrofuran and methanol) and also some absorbed water (sodium methacrylate polymers are very hygroscopic). Above 190°C , the large-scale evolution of volatile material begins and I.R. gas analysis has shown that the products evolved up until T_{max} of the first peak (313°C) are those associated with the degradation of VC sequences — HCl and benzene. A very small amount of carbon dioxide is also present. The initial separation of the traces is characteristic

Fig. 45

Vinyl Chloride - Sodium Methacrylate Copolymer.

25 mg. Powder.



of HCl evolution in presence of water and it is likely that this effect is due to the limited adsorption of HCl on ice deposited in the traps — a similar effect has been noticed during studies of a PVC - PMAA blend (see p.188), in which water is released just before the onset of HCl elimination. In the present case, I.R. analysis showed that water was present among the volatiles obtained on heating to 500°C and it is likely that most of this is liberated before T_{\max} of the "HCl" peak — a small amount of liquid product released below 313°C was insoluble in carbon tetrachloride and chloroform, but dissolved immediately on adding acetone. It is likely that the water produced is merely absorbed moisture and not the result of substituent reactions in the polymer.

The second peak in the TVA ($T_{\max} = 373^{\circ}\text{C}$) coincides with the first major stage of degradation of PNaMA, but it is probable that this phase of reaction in the copolymer is due partly to lactone decomposition — T_{\max} for the stage of reaction which includes lactone breakdown is 420°C in a 1:1 VC - MMA copolymer. Extensive peak overlap, however, precludes an accurate interpretation in the present case.

I.R. analysis of the condensable fraction has shown that the other volatile products released below 500°C include a large amount of carbon dioxide with smaller quantities of but-1-ene (and/or propylene) and ethylene. No absorptions associated with ketonic products have been observed, despite the strong and clearly defined absorptions of the other components. Analysis of the non-condensable fraction showed the presence of methane and carbon monoxide and the TVA traces reveal that evolution of these begins above about 310°C.

Analysis of Cold-Ring Fraction

Part of the I.R. spectrum of the cold-ring fraction obtained on heating the "copolymer" to 500°C is shown in Fig.46, p.176, where it has been superimposed on the spectrum of the undegraded polymer. (Both samples were run as KBr discs). In the undegraded polymer, the bands at 1765cm⁻¹ and 1575cm⁻¹ can be attributed to γ-lactone and unreacted -CO₂Na groups respectively. In the cold-ring fraction, a new band is observed at 1700cm⁻¹ and this is probably due to carboxylic acid units formed by HCl attack on the salt groups. To investigate this possibility, the following experiment was carried out:-

PVC and poly(sodium methacrylate) were ground together in approximately 1:1 proportions and the I.R. spectrum of the mixture was recorded. The mixture was then heated until the "HCl" peak of the PVC had been passed and an I.R. spectrum was taken of the residue. Shoulders were found to have developed at 1800cm⁻¹, 1750cm⁻¹ and 1010cm⁻¹ and these are indicative of glutaric anhydride type structures. In contrast, when a sample of PNaMA was heated to the same temperature in absence of PVC, the spectrum was virtually unchanged. It can be fairly confidently assumed, therefore, that the following conversions of the salt groups take place on reaction with HCl:-

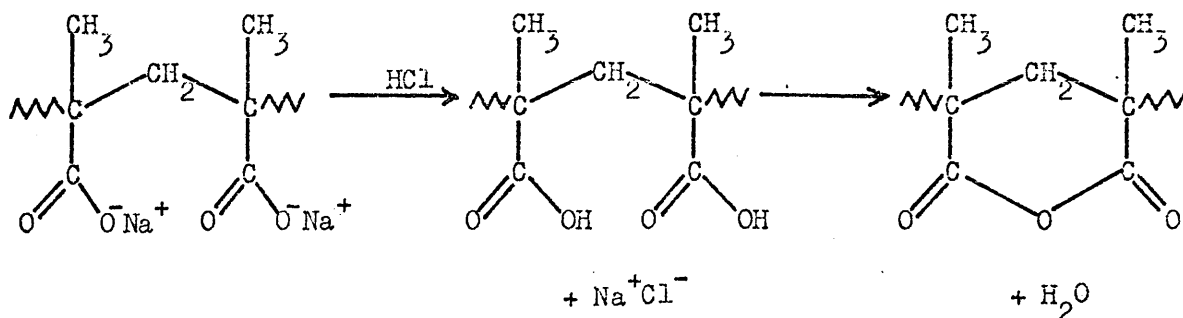
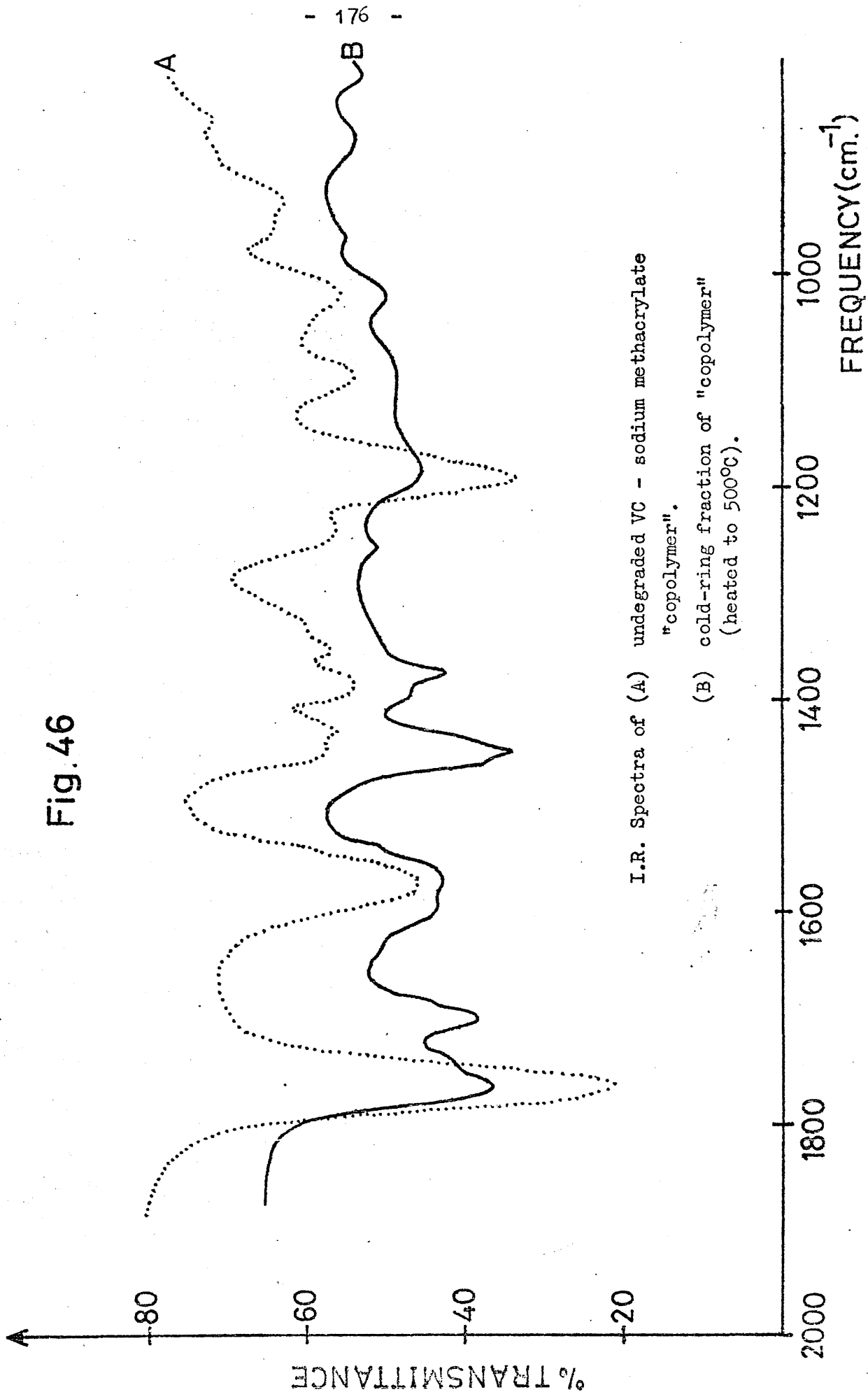


Fig. 46



A similar process for ester modification has already been discussed (p. 7).

The band formerly assigned to $-\text{CO}_2\text{Na}$ is broadened in the cold-ring fraction and this is probably due to the presence of some sodium methacrylate monomer, which shows carbonyl absorption at 1560cm^{-1} . Sodium carbonate is also present in the cold-ring fraction, being evidenced by a strong absorption at 1450cm^{-1} . A shoulder between 3100cm^{-1} and 3000cm^{-1} , together with bands at 875cm^{-1} and 820cm^{-1} , suggests that the same type of unsaturated structures are present as were found in degraded VC - MAA copolymer.

Analysis of Polymer Residue

The residue obtained by heating the "copolymer" to 500°C was found to be alkaline in aqueous solution. Examination as a KBr disc showed a strong I.R. absorption band at 1450cm^{-1} and another medium absorption at 880cm^{-1} , both of these being characteristic of sodium carbonate. A weaker, broad absorption between 1600 and 1550cm^{-1} was probably due to residual carboxylate anion, while another small absorption between 3100cm^{-1} and 3000cm^{-1} , together with a band at 820cm^{-1} , again suggests unsaturated hydrocarbon structures.

Discussion

The most puzzling feature of the "copolymer" is its readiness to produce Na_2CO_3 in absence of ketones. The spectroscopic evidence suggests that unreacted $-\text{CO}_2\text{Na}$ groups are relatively scarce, most having pre-lactonized or undergone conversion to acid. It seems likely, therefore, that most of the Na_2CO_3 must come from monomer

decomposition — there was some evidence for the presence of monomer in the cold-ring fraction. The apparent absence of anhydride structures, however, suggests that sequences containing more than one $-\text{CO}_2\text{Na}$ group are uncommon, so that monomer production may occur largely by splitting out of isolated units.

In the TVA of the copolymer, there is considerable overlap of the "HCl" peak with the succeeding one, so that the T_{max} for HCl production may well be less than 313°C . This should be compared with a T_{max} of 325°C in Breon 113 (powder sample), where little overlap is observed. VC sequences will be shielded from $-\text{CO}_2\text{Na}$ or $-\text{CO}_2\text{H}$ groups by the lactone structures, so that destabilisation with respect to HCl elimination may well be due to interaction with lactone. Alternatively, the effect may be the result of base catalysis by small amounts of sodium carbonate.

GENERAL CONCLUSIONS

To conclude this chapter, it will be instructive to compare the T_{max} values observed for the lactonization reaction in the various copolymer systems studied. These values — the temperatures at which the maximum rate of lactonization occurs when the copolymers are heated linearly at $10^\circ\text{C}/\text{minute}$ — may be taken as an approximate guide to the ease with which the reaction occurs in each case. The results are presented in Table XV.

TABLE XV

T_{max} Values for Lactonization in Various Copolymer Systems

System	T _{max} (°C)	Copolymer Composition
VC — methyl acrylate	259	15.8% VC
VC — <u>n</u> -butyl methacrylate	228	49.2% VC
VC — methyl methacrylate	206	43.0% VC
VB — methyl methacrylate	175	9.76% VB
VC — methacrylic acid	168	65.0% VC

T_{max} values have been taken from those copolymers in which there is minimum overlap of the TVA curves for lactonization with those for subsequent reactions.

The high T_{max} value for the VC — methyl acrylate system is in accordance with the findings of earlier workers (see p. 58) and supports the view that absence of α-substitution on the ester unit makes cyclization more difficult.

By contrast, the results for the VC - BMA and VC - MMA systems do not corroborate the findings of Zutty and Welch that varying the ester group in the methacrylate series has no effect on the ease of lactonization. Possibly, the steric effect of the butyl group in a predominantly S_N2 reaction is responsible for this phenomenon.

The fact that lactonization occurs at a lower temperature in a VB - MMA copolymer than in the VC analogue will be due to the first (or both) of the following factors:-

- (i) the lower bond strength of C-Br compared to C-Cl (65.9: 78.5 kcal/mole).

(ii) the superiority of Br^- over Cl^- both as a leaving group and as a nucleophile in substitution at saturated carbon.

The very low T_{max} value for the VC - MAA copolymer can be assigned to the high polarity of the O — H bond. In this case at least, it seems very unlikely that radical intermediates are involved.

In addition to the TVA data, the pre-lactonization effect observed in the VC - NaMA system shows that an ionic lactonization mechanism is quite possible under certain conditions.

Finally, it must be added that cotacticity of the monomer units in the copolymer may have an important influence on this type of cyclization and until these effects are fully known, the above thermal data must be treated with some caution.

CHAPTER SIX

THE THERMAL DEGRADATION OF POLYMER BLENDS

INTRODUCTION

The blending of one polymer with another, just like copolymerization, can often be used to modify the properties of the polymer and extend its applications. Typical advantages derived from blending are better processing properties, increased impact and flame resistance. On a commercial scale, blending has been largely applied to the modification of poly(styrene) and PVC to give "high-impact" properties. To this end, poly(styrene) has been blended with natural and synthetic rubber, while typical PVC blends include those with butadiene-containing rubbery copolymers, some acrylates, ethylene-vinyl acetate copolymers and ABS plastics.

The study of copolymer degradation has shown how the presence of foreign monomer units in the polymer chain can greatly influence the stability of the polymer. Similarly, the degradation behaviour of one polymer is often affected by intimate contact with another. A typical case of this is the degradation of PMMA in contact with PVC, which has already been cited by McNeill and Neil as evidence for the free-radical degradation of the latter polymer (see p.51). Clearly, the study of polymer blends is often of considerable use in extending our knowledge of polymer degradation in general.

PURPOSE OF THIS CHAPTER

In the preceding chapters, the thermal degradation of the following copolymer systems has been discussed:-

1. VC - methyl methacrylate
2. VC - methyl acrylate
3. VC - n-butyl methacrylate
4. VC - n-butyl methacrylamide
5. VC - methacrylic acid
6. VC - sodium methacrylate
7. VB - methyl methacrylate

In this chapter, a brief investigation is made of the thermal behaviour of the analogous polymer blends, largely to supplement the information already collected for the copolymers, but also to study any novel effects induced by blending. Secondly, an attempt has been made to elucidate further the nature of the lactonization reaction occurring in VC - MMA copolymers by comparing the thermal degradation of 1:1 blends of a VC - MMA copolymer with PVC and PMMA with that of the respective homopolymers.

GENERAL ASPECTS OF THE THERMAL DEGRADATION OF POLYMER BLENDS

Unlike macromolecules are, in general, incompatible in the solid state, so that attempts to prepare a polymer blend, either by melt mixing or by casting them together as a film from a common solvent, usually result in a heterophase system which, at best, consists of domains or micelles of one polymer in a continuous matrix of the other. Thus, a polymer blend is neither a true mixture, nor a solid solution.

During pyrolysis of a polymer blend, therefore, any interaction between the components (or with the products of degradation) must occur at phase boundaries or, alternatively, by the diffusion of small molecule products into the second phase. Unless the reaction environment is one of a polymer melt, the second of these possibilities will be severely restricted.

The methods used for studying polymer blends by TVA have already

been described by McNeill and Neil⁽⁶⁸⁾. In the present work, mixed and unmixed samples have been degraded using a twin-limbed "trouser tube" (Fig.47), which allows simultaneous degradation of the unmixed samples under the same conditions and ready comparison with the blended form.

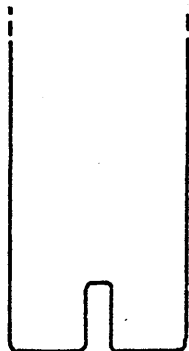


Fig. 47

In the first experiment, 10-15mg. of each polymer are degraded separately (as powders or films) in the different limbs, while in the second experiment, the same total weight of each polymer is degraded as a blend in both limbs. In absence of a suitable common solvent, mixing has been achieved by grinding together the two solid polymers. In this case, true blending will only be obtained after fusion of the two polymers.

BLENDS OF PVC WITH POLY(METHYL METHACRYLATE), POLY(METHYL ACRYLATE) AND POLY(n-BUTYL METHACRYLATE)

The thermal degradation of these systems has been studied by other workers and the results obtained are summarized in Table XVI, p.184. Premature degradation of the ester polymers is observed in all cases and is generally assumed to be the result of attack by chlorine radicals from the degrading PVC. In PMMA and PBMA, modification of the ester group by HCl is also observed.

TABLE XVI

Polymer Pair	Solvent used for Film Preparation	Behaviour of mixed sample compared to unmixed	Reasons postulated to explain Behaviour	Ref.
PVC - PMMA	Cyclohexanone	MMA evolved initially at lower temperatures, but subsequent breakdown occurs at higher temperatures. HCl evolution slightly retarded.	Chlorine Radicals from PVC breakdown enter PMMA phase and cause early depropagation. PMMA competes with PVC for reaction with the Cl· radicals. HCl interacts with PMMA to give anhydride structures in the Polymer chain which then "block" depropagation at higher temperatures.	(68) (8)
PVC - PMA	Cyclohexanone	PMA breakdown occurs at lower temperatures.	Chlorine Radicals from degrading PVC abstract tertiary H-Atoms from PMA to give the familiar radical precursor:- $\begin{array}{c} \sim\text{CH} \text{---} \text{CH}_2 \text{---} \dot{\text{C}}\text{---} \\ \qquad \qquad \qquad \\ \text{CO}_2\text{CH}_3 \qquad \qquad \text{CO}_2\text{CH}_3 \end{array}$	(116)
PVC - PBMA	Cyclohexanone	Increased BMA monomer production in the lower temperature range, accompanied by decreased monomer formation at higher temperatures. At about 400°C., there is an increase in the amount of material non-condensable at -100°C.	Attack on PBMA by Cl· radicals as before. HCl reacts with ester groups to yield Acid/Anhydride structures which decompose to give highly volatile material.	(117)

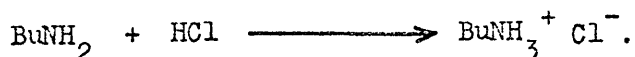
BLEND OF PVC WITH POLY(n-BUTYL METHACRYLAMIDE)

This system has already been mentioned briefly in connection with the VC - BMAC copolymer (p.153).

Poly(n-butyl methacrylamide) did not dissolve in the common solvents for PVC (tetrahydrofuran, toluene, cyclohexanone and methyl ethyl ketone), so that a "blend" could only be prepared by grinding the two polymers together into a fine powder. The TVA curves obtained for the mixed and unmixed systems are shown in Fig. 48, p.186 and two main features are immediately obvious:-

- 1) The shifting of T_{max} for the initial stage of PBMAC breakdown from $231^{\circ}C$ in the unmixed sample to $209^{\circ}C$ in the blend.
- 2) The splitting and broadening of the "HCl" peak ($T_{max} = 292^{\circ}C$) to give two overlapping stages of reaction with $T_{max} = 270^{\circ}C$, and $313^{\circ}C$ respectively.

Even in the unmixed form, T_{max} for butylamine and monomer production is about $27^{\circ}C$ below its value in the pure homopolymer, so that the shift to lower temperatures is not due to any interaction in the polymers themselves. It is likely that the flow of butylamine to the Piranis is curtailed as soon as dehydrochlorination begins, because of the formation of the involatile amine salt (see p. 158) i.e.,



This effect is also evident in the blend, where, because of the earlier loss of HCl, evolution of butylamine ceases to be observed at even lower temperatures and a downward shift of T_{max} is brought about. For the same reasons, the intermediate stage of PBMAC

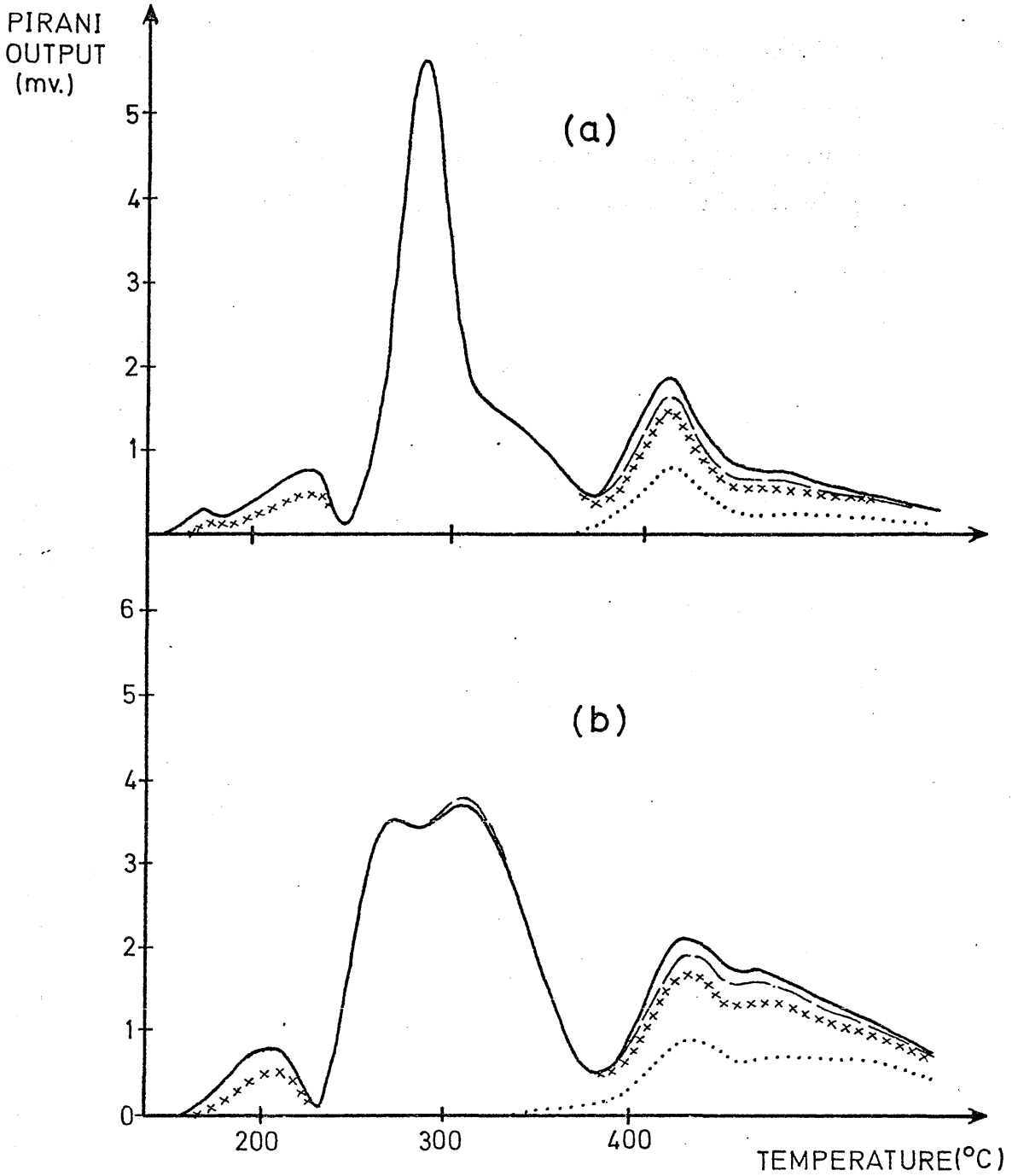


Fig. 48

TVA traces for equal weights (15 mg.) of Poly(n-Butyl Methacrylamide) and PVC degraded simultaneously as (a) unmixed (b) mixed samples.

Powder samples; heating-rate $10^{\circ}/\text{min}$.

degradation ($T_{\max} = 370^{\circ}\text{C}$), where butylamine is again a major product, appears to have been removed in both the mixed and unmixed cases.

Although any influence which degrading PVC might have on the stability of PBMAC is obscured by the above effect, there is no real evidence for increased BMAC monomer production at lower temperatures — the separation of the -45°C and -75°C traces is not markedly affected by blending.

Dehydrochlorination, on the other hand, begins at least 20°C sooner in the blended sample and the splitting of the HCl peak suggests that two stages of HCl loss are in operation. The first of these may be elimination at the PVC/PBMAC phase boundary, where base catalysis by butylamine or bound amide groups is most effective, while the second is normal dehydrochlorination of "non-superficial" PVC.

One final interesting feature of the blend degradation is the increased production at higher temperatures of non-condensable material and of material condensed between -100°C and -196°C . The most likely explanation of this is an increase in the amount of imidization taking place in PBMAC (at the expense of the other processes), possibly due to acid catalysis by HCl. The cyclic imides subsequently decompose to give carbon monoxide, methane, butylamine and isobutene.

BLEND OF PVC WITH POLY(METHACRYLIC ACID)

PMAA was insoluble in the common solvents for PVC, so that a powder "blend" was again used. The TVA curves obtained for the mixed and unmixed systems are shown in Fig.49, p.188.

T_{\max} for the peak corresponding to anhydride formation is 228°C in the unmixed sample and this is close to the normal value for a PMAA

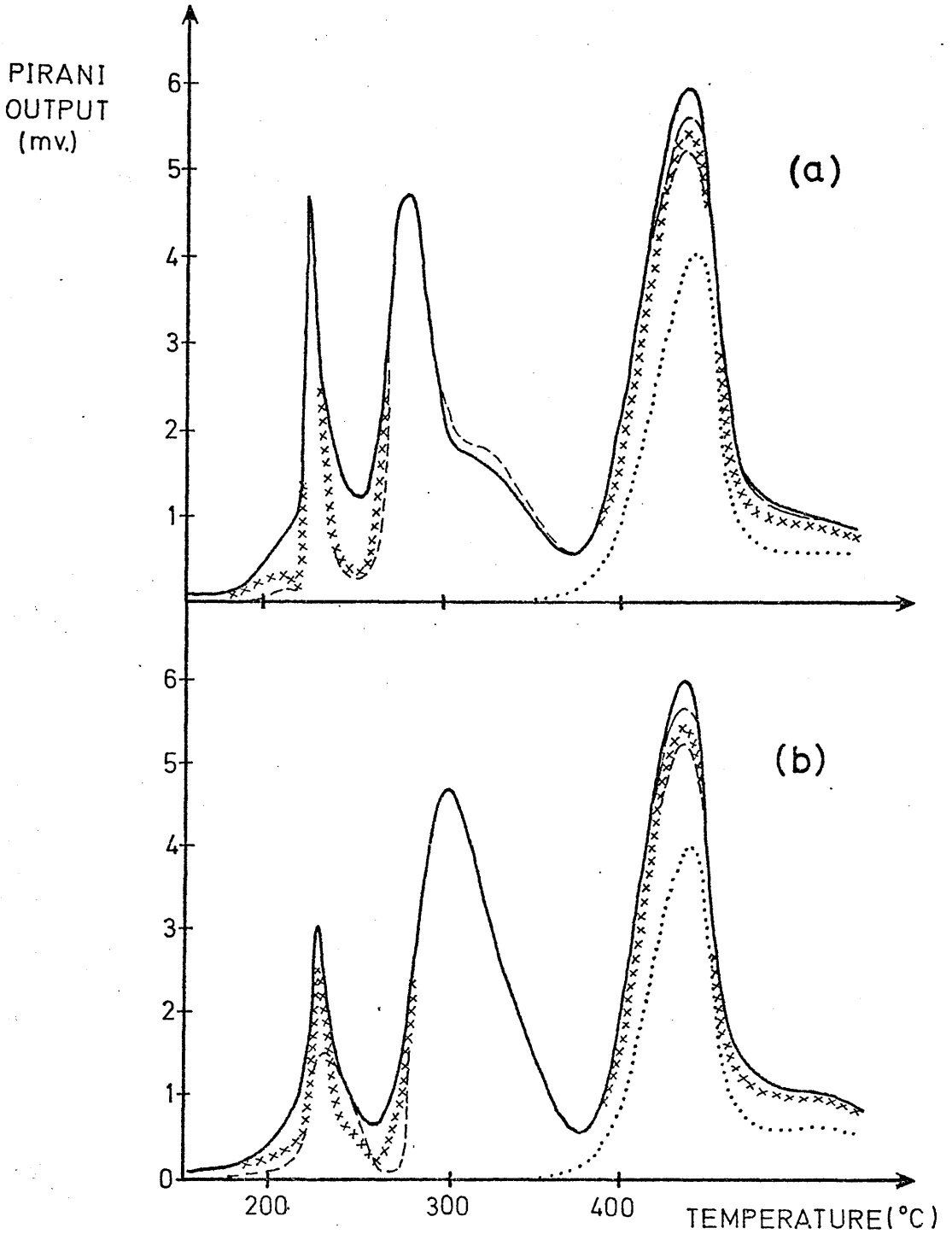


Fig. 49

TVA traces for equal weights (15 mg.) of Poly(Methacrylic Acid) and PVC degraded simultaneously as (a) unimixed (b) mixed samples. Powder samples; heating-rate 10^oC/min.

powder sample (the value for a PMAA film is 249°C). The value is unchanged in the polymer blend. The high-temperature peak associated with anhydride fragmentation is also unaffected by blending.

By contrast, the dehydrochlorination peak is altered both in shape and in T_{max} value ($283^{\circ}\text{C} \longrightarrow 301^{\circ}\text{C}$), on going from unmixed to mixed samples. McNeill and Neil⁽⁶⁸⁾ have already observed that the shape of the TVA curves for PVC are a function of sample form — thin films show a distinct single peak, while thicker films or powders show two overlapping stages of degradation, with the main peak showing a prominent shoulder on the high-temperature side. T_{max} is about 30°C lower for the thicker samples. These effects have been explained in terms of the autocatalytic effect of HCl, which diffuses more slowly out of thick samples.

In the present case, the unmixed PVC shows the typical TVA shape for a powder sample, whereas the mixed sample more closely resembles the uncatalysed degradation. It seems likely that the effect is caused here either by increased subdivision of the PVC (through grinding) or by dispersion of the polymer in PMAA, both of which effectively minimise the interaction with HCl.

In conclusion, there would appear to be no true chemical interactions in this blend which affect the overall stability of the constituent polymers.

BLEND OF PVC WITH POLY(SODIUM METHACRYLATE)

Blending in this system was again achieved by grinding together the two polymers. The TVA curves obtained for the mixed and unmixed samples are shown in Fig.50, p.190.

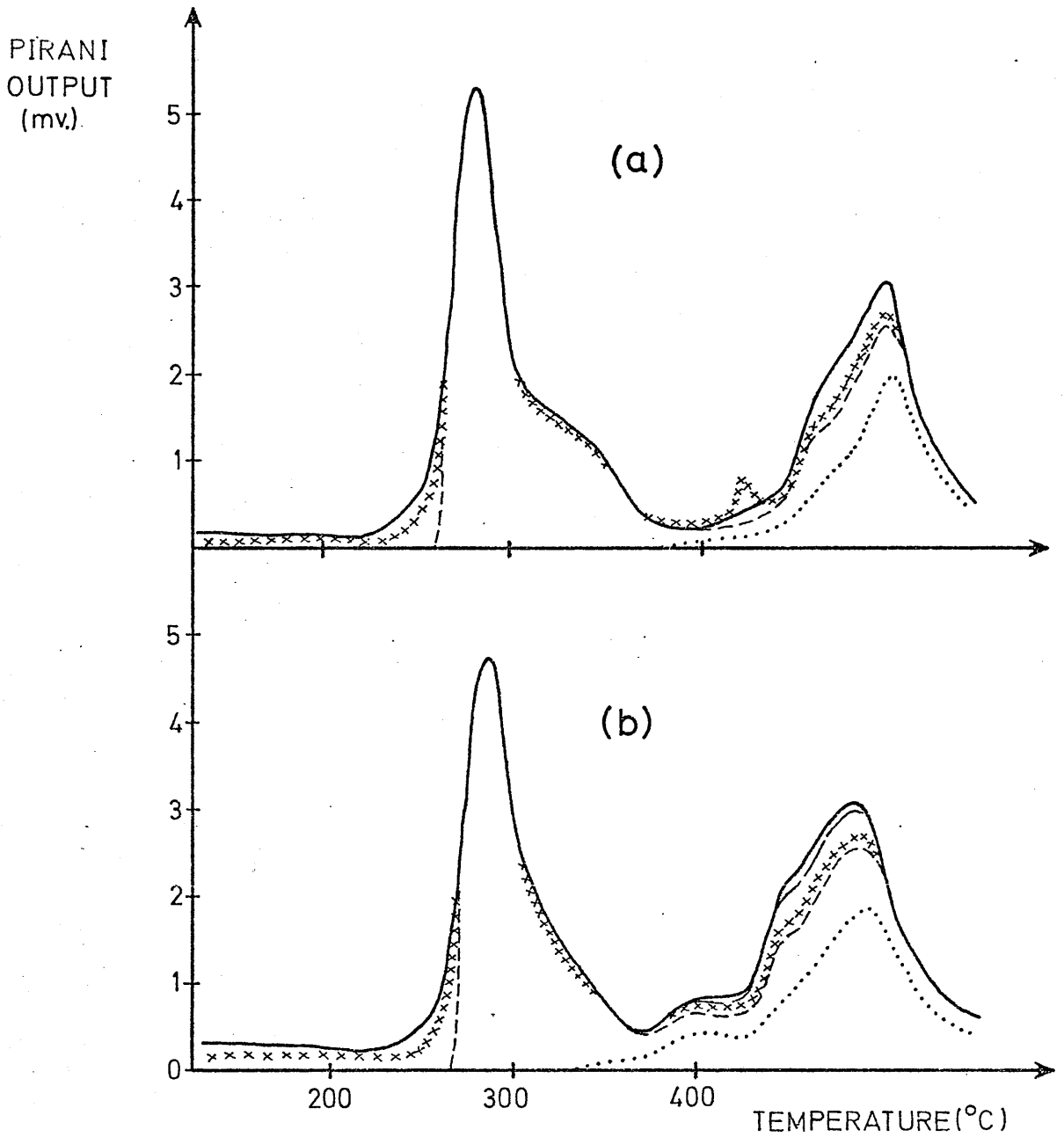


Fig.50

TVA traces for equal weights (15 mg.) of Poly(Sodium Methacrylate) and PVC degraded simultaneously as (a) unmixed (b) mixed samples. Powder samples; heating-rate $10^{\circ}\text{C}/\text{min}$.

T_{\max} for the dehydrochlorination reaction is unchanged on blending, although the coalescence of the shoulder with the main peak suggests that the effect of HCl catalysis is again reduced in the blended sample.

Much more significant is the appearance in the TVA of the blend of a small peak with $T_{\max} = 403^{\circ}\text{C}$, consisting largely of material which is non-condensable or is condensed between -100°C and -196°C . This is probably caused by decomposition of anhydride structures, which originate by interaction of HCl with the salt groups (see p.175). The temperature at which this process occurs is close to that observed for a similar decomposition in a PVC - PMMA blend⁽⁶⁸⁾.

BLEND OF POLY(VINYL BROMIDE) WITH POLY(METHYL METHACRYLATE)

Mixed and unmixed samples were prepared by casting films from redistilled tetrahydrofuran. The TVA curves obtained are shown in Fig.51, p.192. In both cases, the peak preceding HBr elimination represents loss of solvent.

T_{\max} for dehydrobromination and chain-end-initiated monomer production are both unchanged in the blend, but the extent of the latter process is greatly curtailed. The peak associated with random-scission-initiated depropagation has T_{\max} shifted upwards by about 17°C , but part of this shift is associated with the increased production of non-condensable material and of material which is condensed between -100°C and -196°C . T_{\max} for the release of these more volatile products is 420°C .

Discussion

If FVB degrades by a free-radical process (analogous to the one proposed for PVC) and bromine atoms are able to diffuse into the PMMA

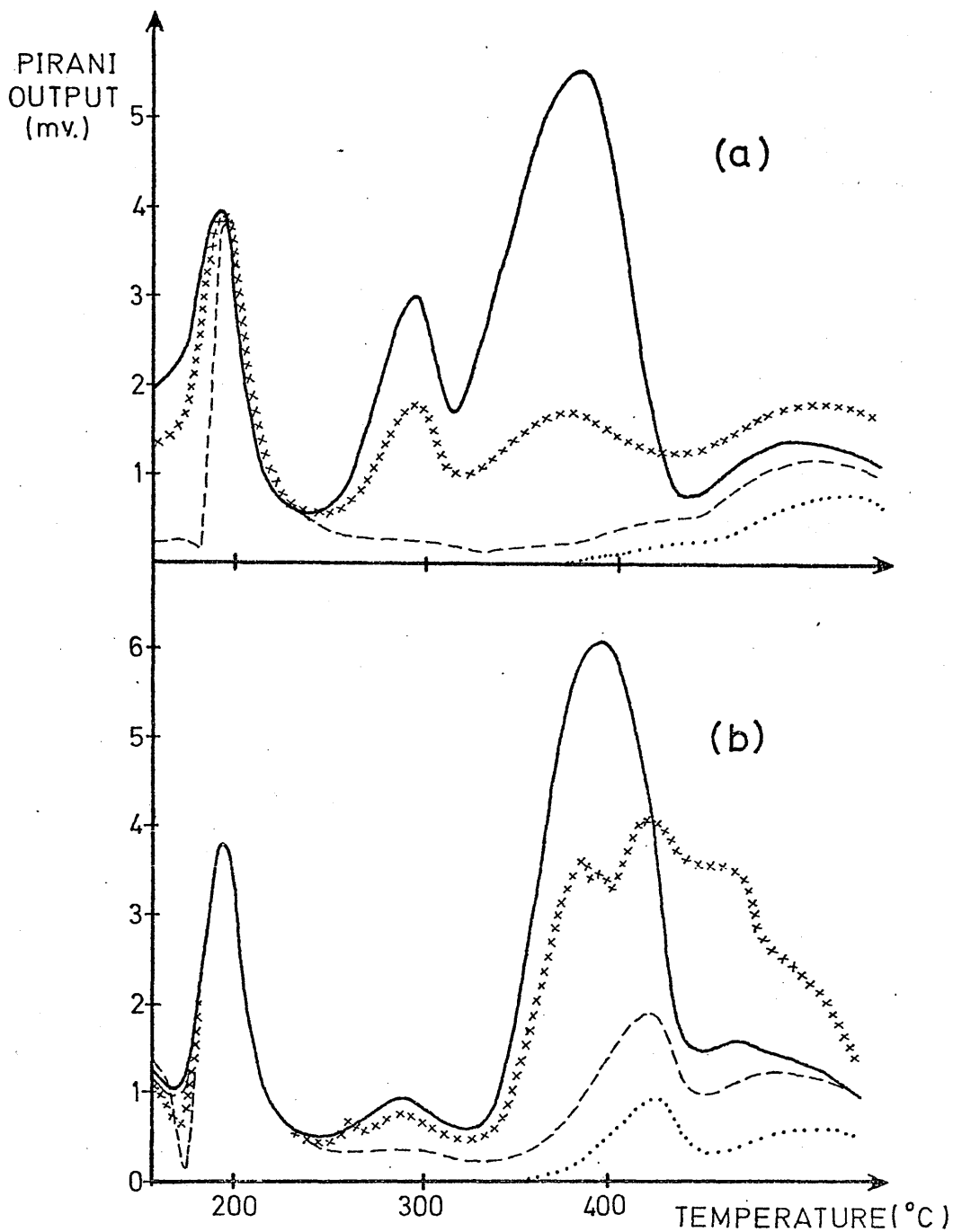


Fig. 51

TVA traces for equal weights (15 mg.) of Poly(Vinyl Bromide) and PMMA degraded simultaneously as (a) unmixed (b) mixed samples.

Films cast from THF; heating-rate $10^{\circ}\text{C}/\text{min}$.

phase, then they appear to be incapable of causing premature degradation of the PMMA. It is possible that radicals are present, but that the temperature is too low to overcome the activation energy required — T_{max} for the dehydrohalogenation reactions of PVC and PVB are about 300°C and 200°C respectively.

The reduction in the extent of low-temperature monomer production is probably caused by the conversion of some of the ester groups to anhydride (possibly via the acid) by reaction with HBr. The anhydride structures then "block" depropagation from the chain ends. The release of the highly volatile material above about 340°C can then be explained by the breakdown of the anhydride units to yield carbon dioxide, methane and carbon monoxide, as in previous systems. It is surprising, however, that T_{max} for the initial monomer production is not shifted to a higher value. Possibly, overlap with methyl bromide formation (from the HBr/ester interaction) is responsible.

The area enclosed between the $0/-45^{\circ}\text{C}$ and -100°C traces is lowered in the blend for the peak associated with random-scission-initiated depropagation and this would again be consistent with anhydride formation at lower temperatures.

A STUDY OF THE LACTONIZATION REACTION IN VC - MMA COPOLYMERS USING POLYMER BLENDS

The purpose of this investigation was two-fold:-

- (i) To study the mechanism of lactonization.
- (ii) To help elucidate any effects which lactonization may have on the stability of VC and MMA sequences in the copolymer.

It was considered possible that reactive intermediates formed during

lactonization in the copolymer could induce the premature degradation of either PMMA or PVC. For example, if radical species were involved, then an early production of MMA monomer might be anticipated. A copolymer which contained 43% VC (and could therefore be expected to undergo a high degree of lactonization) was blended in turn with PVC and PMMA.

BLEND OF THE COPOLYMER WITH PVC

The TVA curves obtained for the mixed and unmixed systems are shown in Fig.52, p.195. In both cases, films cast from cyclohexanone were used, giving rise to broad solvent peaks prior to methyl chloride evolution.

T_{max} for dehydrochlorination is clearly unaffected by blending and in both cases, the splitting of the HCl peak to give T_{max} at 295°C and a shoulder at 320°C is assignable to overlap of the corresponding processes in PVC and in the copolymer — a sample of pure PVC degraded under identical conditions showed the symmetrical single peak ($T_{max} = 331^{\circ}\text{C}$), associated with thin film behaviour, while pure copolymer showed T_{max} at 298°C .

The only significant change obtained on blending is the shift of T_{max} for the high temperature peak from 414°C to 435°C . It is likely that this is due mainly to a large reduction in the amount of MMA monomer being released from the copolymer, due to conversion of the ester function in presence of the high concentration of HCl. This view is supported by a reduction in the area between the $0/-45^{\circ}\text{C}$ and the -100°C traces in the blend TVA and a corresponding increase in the amount of material non-condensable at -100°C . The latter effect is

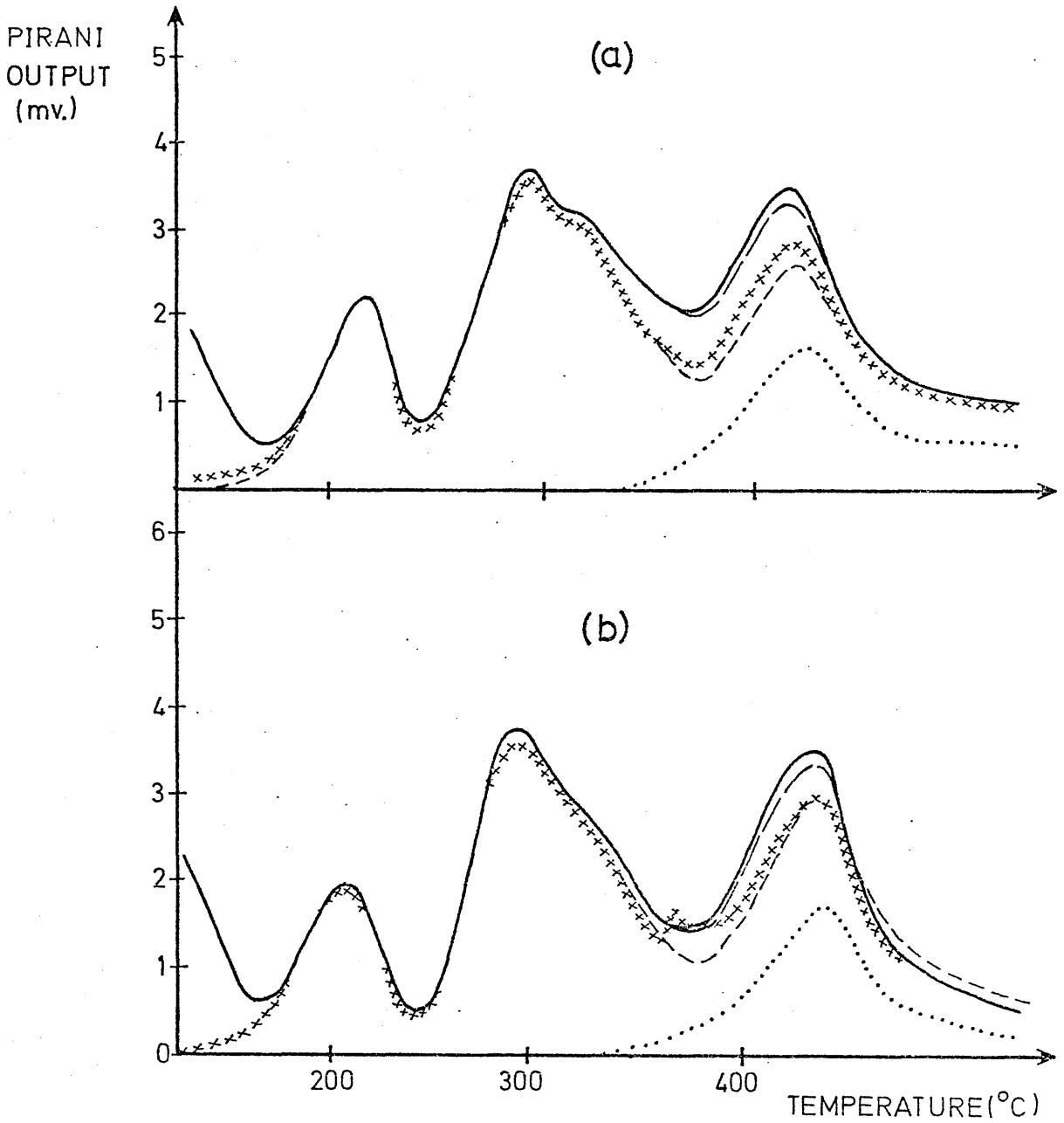


Fig. 52

TVA traces for equal weights (15 mg.) of 43% VC - MMA copolymer and PVC degraded simultaneously as (a) unmixed (b) mixed samples. Films cast from Cyclohexanone; heating-rate $10^{\circ}\text{C}/\text{min}$.

consistent with the decomposition of acid or anhydride structures.

BLEND OF THE COPOLYMER WITH PMMA

The TVA curves obtained for the mixed and unmixed systems are shown in Fig.53, p.197. The large initial response on the 0/-45°C trace is again due to cyclohexanone.

In the unmixed sample, comparison with the curves obtained for PMMA degraded alone showed that the peaks with $T_{\max} = 289^{\circ}\text{C}$ and 373°C are largely due to monomer production by chain-end and random-scission-initiated processes respectively. Comparison with the curves obtained for the copolymer degraded alone showed that the peak on the -100°C trace with $T_{\max} = 316^{\circ}\text{C}$ can be associated mainly with HCl production in the copolymer, while the larger peak on the same trace at 414°C is due mainly to lactone decomposition. The evolution of non-condensable material ($T_{\max} = 414^{\circ}\text{C}$) will be largely the result of polyene reactions and lactone breakdown.

In the blended sample, there is an overall decrease in the total monomer production (the area enclosed between the -45°C and -100°C traces is lowered by 10%), but the amount of depropagation occurring at low temperatures is enhanced and T_{\max} for this initial monomer production is shifted upwards to coincide with T_{\max} for dehydrochlorination of the copolymer. The lowering of monomer production at high temperatures is accompanied by an increase in the amount of highly volatile material being produced around 400°C . T_{\max} for dehydrochlorination in the copolymer is unchanged by blending.

In order to explain this behaviour, I.R. spectra were obtained for the volatiles produced between 250°C and 500°C by (i) pure copolymer and

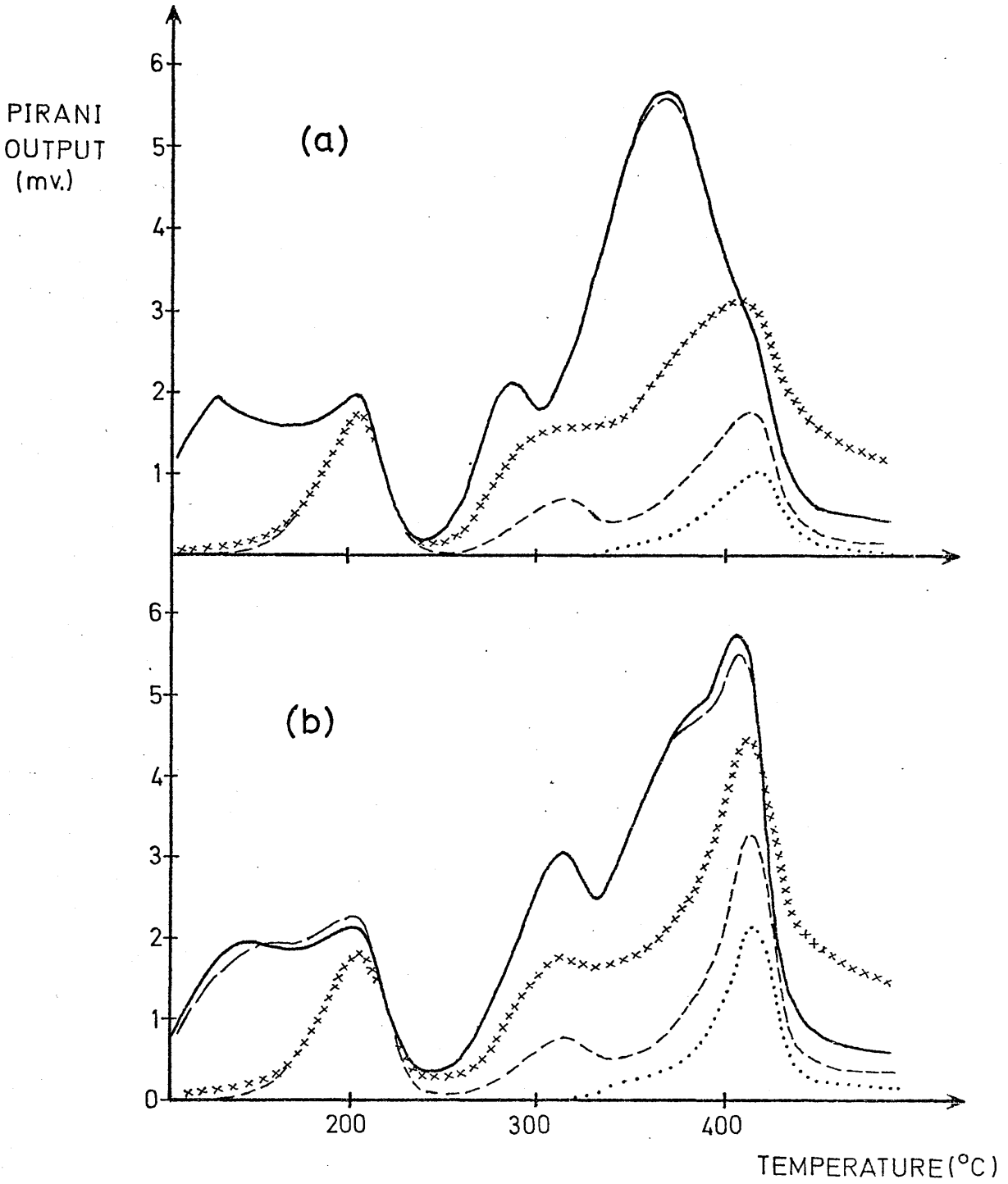


Fig.53

TVA traces for equal weights (15 mg.) of 43% VC - MMA Copolymer and PMMA degraded simultaneously as (a) unimixed (b) mixed samples. Films cast from cyclohexanone; heating-rate 10°C/min.

(ii) the same weight of copolymer blended with an equal weight of PMMA. The following features came to light:-

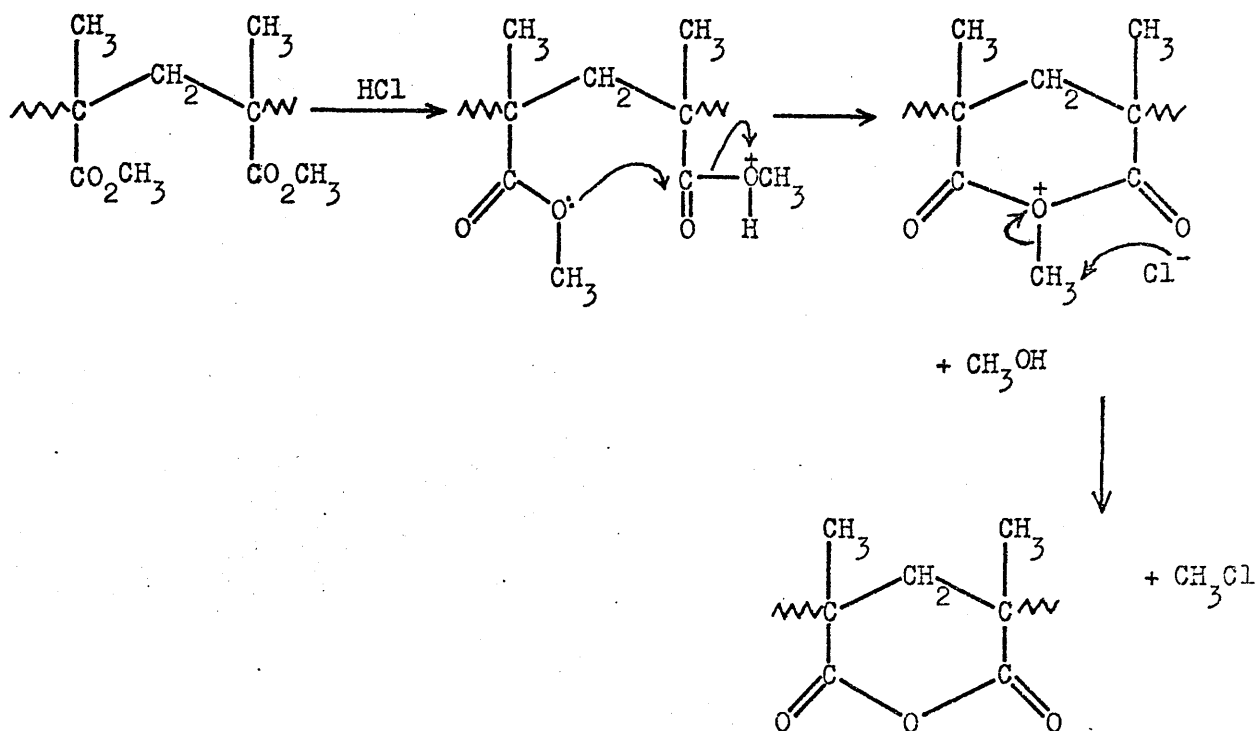
(a) In addition to the products identified by previous workers (see p. 65), a 43% VC - MMA copolymer yields a significant amount of methanol (a strong absorption at 1035cm^{-1}), together with but-1-ene and/or propylene (912cm^{-1}) and ethylene (950cm^{-1}).

(b) In the same temperature range, the blend yields a relatively larger amount of methanol and also some isobutene, in addition to MMA and the copolymer products. Absorption due to free HCl was also observed to be relatively weaker in this case.

Statistical calculations predict that a 43% VC - MMA copolymer will lose 29% of its total chlorine content as HCl, so that the alteration of the TVA characteristics on blending is explainable in terms of attack by $\text{Cl}\cdot$ radicals on PMMA to give higher yields of monomer at dehydrochlorination temperatures (as in PVC - PMMA blends) and conversion of the ester function by HCl to release methanol and leave behind anhydride structures in the chain, which, in turn, "block" depropagation at higher temperatures and decompose to give the highly volatile material around 400°C .

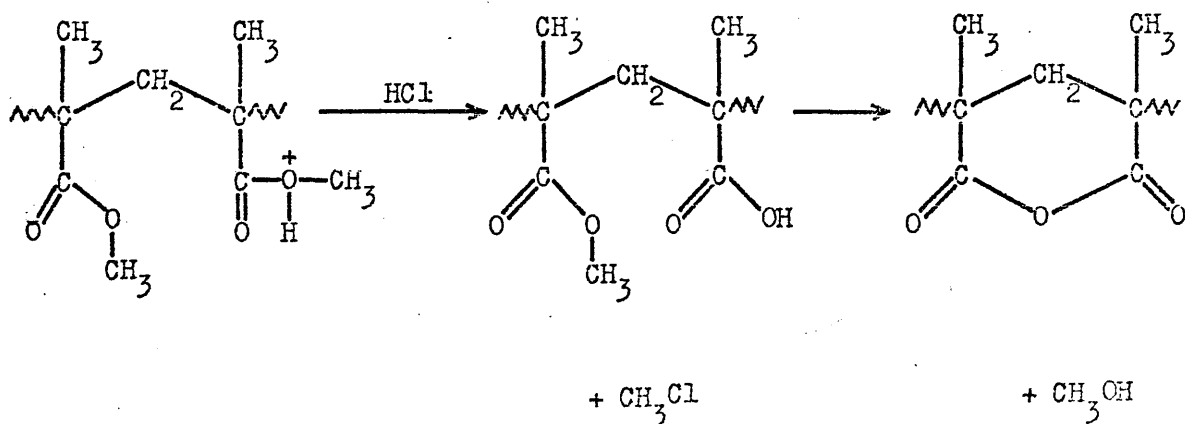
The precise mechanism of methanol formation is uncertain. McNeill and Neil⁽⁸⁾ have cited the following reaction sequence to explain the behaviour of PVC - PMMA blends, although methanol was never identified among the major products (mass spectral and G.C. analyses):-

(1)

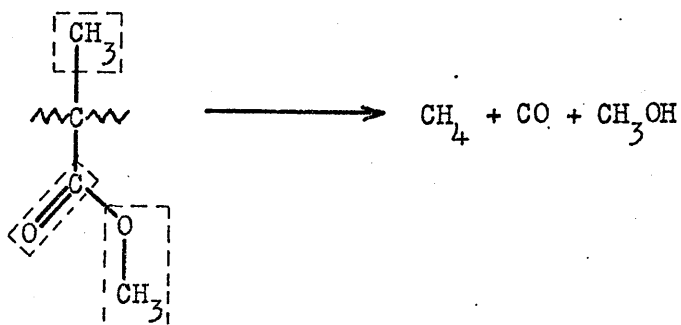


Alternatively, partial conversion of the ester groups by HCl may be followed by a process which is analogous to the one proposed by Jamieson and McNeill for cyclization in MMA - methacrylic acid copolymers⁽¹¹⁸⁾, for which methanol is a major degradation product.

(2)



Jamieson and McNeill also suggest that part of the methanol production in MMA - MAA copolymers must arise by the high-temperature decomposition of MMA sequences isolated between anhydride structures, in competition with depropagation. In the present case, the formation of methanol by this process will, of course, be dependent on (1) or (2):-



GENERAL CONCLUSIONS

There is no indication in the present results that reactive species formed during lactonization of the VC - MMA copolymer have any influence on the degradations of either PVC or PMMA. The increased production of monomer at low temperatures by PMMA heated in presence of the copolymer can be assigned to the effects of Cl· radicals, formed during dehydrochlorination of the copolymer, entering the PMMA phase. The lesser extent of the phenomenon in this instance, compared with PVC - PMMA blends, can be explained in terms of the lower concentration of VC units which are capable of dehydrochlorination.

A P P E N D I X O N E

POLYMER PREPARATION

The methods of preparation of the polymers and copolymers discussed in Chapters V and VI are summarized below:-

(1) VINYL CHLORIDE — METHYL ACRYLATE COPOLYMERS

Purification of monomers: VC was distilled from a cylinder, degassed and distilled on the vacuum line. MA was shaken with dilute NaOH solution to remove inhibitor, washed with distilled water until neutral, dried over anhydrous calcium chloride and finally degassed as for VC.

Reactivity ratios: MA 4.4 }
VC 0.12 } at 50°C in benzene solution (119)

Type of polymerization: bulk.

Monomer feed composition: the weight of MA used was found from volume, the density being known. The weight of VC used was found by weighing the dilatometer.

Initiator: 0.05% (W/V) azo-bis-isobutyronitrile.

Temperature: 40°C.

Polymerization times: 25-32 hours.

Conversion: approximately 4%.

Isolation and purification of polymer: precipitated in methanol.

Reprecipitated into methanol from acetone solution.

(2) VINYL CHLORIDE — n-BUTYL METHACRYLATE COPOLYMERS

Purification of monomers: as for (1)

Reactivity ratios: BMA 13.5 }
VC 0.05 } at 45°C (35)

Type of polymerization: bulk.

Monomer feed composition: as for system (1).

Initiator: 0.3% (W/V) azo-bis-isobutyronitrile.

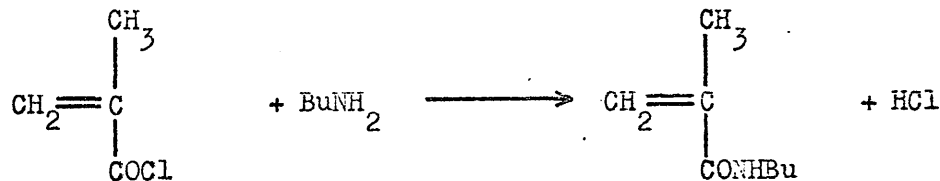
Temperature: 40°C.

Conversion: Not exceeding 4.3%.

Isolation and purification of polymer: as for system (1).

(3) POLY(n-BUTYL METHACRYLAMIDE).

Synthesis of n-butyl methacrylamide (120,121):- this involved the reaction of n-butylamine with methacrylyl chloride in aqueous solution.



The preparation details for methacrylyl chloride and n-butyl methacrylamide are described under (a) and (b) respectively:-

(a)

A mixture of 424.5 ml. (5 moles) of methacrylic acid, 1049ml. (10 moles) of benzoyl chloride and 0.85g. of hydroquinone was distilled at a fairly rapid rate through a Vigreux column. The fraction which boiled at $\leq 100^\circ\text{C}$ was collected in a receiver (immersed in ice) which contained 0.85g. hydroquinone. The crude product was then redistilled through a shorter column packed with glass beads. Methacrylyl chloride distilled at $98-100^\circ\text{C}$ and was obtained in about 70% yield.

(b)

125g. of n-butylamine (168.4ml.), dissolved in 1500ml. of water, was transferred to a 2-litre flask fitted with a stirrer, dropping funnel and narrow-bore outlet tube. The flask was immersed in ice. 88.5g. of methacrylyl chloride (81.5ml.) was gradually added to the cooled solution from the dropping funnel. The product, n-butyl methacrylamide, gave a pink emulsion which separated as a reddish layer after standing in a separating funnel. The aqueous layer was twice shaken with ether and the ether extracts were combined with the main product. This was washed with water and then dried over anhydrous calcium chloride. After filtering, the ether was removed in a rotary evaporator. A small amount of hydroquinone inhibitor was added to the crude amide, which was then distilled under vacuum. The amide distilled at 60-62°C. at 0.1mm. Hg as an almost colourless liquid. The yield was approximately 55%.

Purification of monomer: as for methyl acrylate [see system (1)]

Type of polymerization: bulk.

Initiator: 0.1% (W/V) azo-bis-isobutyronitrile.

Temperature: 50°C.

Polymerization time: 160 min.

Conversion: 18.4%.

Isolation and purification of polymer: precipitated in water from methanol solution. Reprecipitated into water/dioxane mixture from methanol solution.

(4) VINYL CHLORIDE — n-BUTYL METHACRYLAMIDE COPOLYMER

Purification of monomers: as for system (1).

Reactivity ratios: unknown; no Q-e data available.

Type of polymerization: bulk.

Monomer feed composition: as for system (1). A molar monomer feed ratio of 1.27 : 1 (VC : BMAC) gave a 23% VC copolymer.

Initiator: 0.1% (W/V) azo-bis-isobutyronitrile.

Temperature: 50°C.

Polymerization time: 48 hours.

Conversion: 17%.

Isolation of polymer: precipitated in dioxane.

(5) POLY(VINYL BROMIDE)

Purification of monomer: as for VC [see system (1).]

Type of polymerization: bulk.

Initiator: 30% hydrogen peroxide (0.5ml./10g. of VB).

Temperature: 60°C.

Polymerization time: 10 hours.

Conversion: 4.09%.

Isolation and purification of polymer: precipitated in methanol.

Reprecipitated into methanol from tetrahydrofuran solution.

(6) VINYL BROMIDE — METHYL METHACRYLATE COPOLYMERS

Purification of monomers: as for system (1).

Reactivity ratios:
VB 0.05
MMA 20 } 28°C (bulk polymerization)(76)

Type of polymerization: bulk

Monomer feed composition: weights of VB and MMA used both found from volume, densities being known.

Initiator: 0.35% (W/V) azo-bis-isobutyronitrile.

Temperature: 28°C.

Conversion: not exceeding 5%.

Isolation and purification of polymer: precipitated in 40-60 petroleum ether. Reprecipitated in methanol from benzene solution.

(7) VINYL CHLORIDE — METHACRYLIC ACID COPOLYMER

Purification of monomers: VC was purified as in system (1). MAA was distilled under vacuum, in presence of a small amount of copper powder to inhibit polymerization, and then transferred direct to the dilatometer and degassed on the vacuum line.

Reactivity ratios: unknown; Q-e values used⁽¹²²⁾.

Type of polymerization: solution in methanol (0.685 ml. methanol/g. of VC).

Monomer feed composition: the weight of MAA used was found from volume, the density being known. The approximate weight of VC used was found by the same method. A molar monomer feed ratio of 43.6 : 1 (VC : MAA) gave a 65% VC copolymer.

Initiator: 0.3% (W/V) of azo-bis-isobutyronitrile.

Temperature: 45°C.

Polymerization time: 195 min.

Conversion: 4.4%.

Isolation and purification of polymer: precipitated in distilled water to remove MAA. The polymer was then re-dissolved in acetone and

reprecipitated twice in water. To remove initiator, the polymer was next re-dissolved in tetrahydrofuran and precipitated in toluene. Finally, to avoid a THF peak in the "lactonization" region of the TVA trace, the polymer was re-dissolved in cyclohexanone and precipitated in toluene.

The copolymer was found to be insoluble (or only sparingly soluble) in chloroform, methanol and ethanol.

(8) POLY(SODIUM METHACRYLATE)

Preparation of monomer: a stoichiometric excess of distilled methacrylic acid was reacted with sodium hydroxide in dry methanol at 0°C. The reaction mixture was then poured into a large volume of anhydrous diethyl ether. The salt precipitated as a gelatinous mass, while the unreacted acid remained in solution. The salt was filtered off and dried in a vacuum oven prior to re-precipitation from dry methanol.

Type of polymerization: solution in methanol (8g. monomer/100ml. methanol).

Initiator: 0.05% (W/V) azo-bis-isobutyronitrile.

Temperature: 60°C.

Polymerization time: 210 minutes.

Conversion: 25%

Isolation of polymer: precipitated in methanol.

(9) VINYL CHLORIDE — SODIUM METHACRYLATE COPOLYMER

Purification of monomers: VC purified as in (1), NaMA as in (8).

Reactivity ratios: unknown; Q-e data used⁽¹²²⁾.

Type of polymerization: solution in methanol (2.46ml. methanol/g. of VC).

Monomer feed composition: a known weight of salt was added to the dilatometer as a solution in dry methanol and the solvent was pumped off on the vacuum line. The approximate weight of VC added was estimated from the volume at -75°C , the density at -15°C being known. A molar monomer feed ratio of 15.7 : 1 (VC : NaMA) was used.

Initiator: azo-bis-isobutyronitrile (0.36% W/W of monomers).

Temperature: 45°C .

Conversion: 4.8%

Isolation and purification of polymer: the polymer precipitated as a fine powder from the polymerization mixture. It was found to be insoluble in water, acetone, cyclohexanone, chloroform, ethanol, toluene, tetrahydrofuran, methyl ethyl ketone, dimethyl formamide, dioxane and methanol. Some swelling was observed in a mixture of tetrahydrofuran and methanol and the polymer was shaken in this medium for several hours to remove initiator and residual monomer.

(10) POLY(VINYL CHLORIDE)

Breon 113 is a British Geon sample, stated to be free from impurities and to have a molecular weight of 45,600.

(11) POLY(METHYL METHACRYLATE)

Sample prepared by free-radical polymerization in bulk at 60°C using azo-bis-isobutyronitrile as initiator. Conversion less than 10%. Molecular weight (\bar{M}_n) = 134,000.

A P P E N D I X T W O

MOLECULAR WEIGHT DATA FOR THE COPOLYMERS

Molecular weight figures for the VC - MMA copolymers studied in the present work have already been presented on p. 34.

Data obtained for the VC - MA, VC - BMA and VB - MMA systems by MacDonald, Straiton and Anderson respectively are shown below:-

VC - MA Copolymers (p.117)

% VC	molecular weight (\bar{M}_n)
5.13	233,000
15.8	241,000
51.2	269,000
67.7	176,000

VC - BMA Copolymers (p.124)

% VC	molecular weight (\bar{M}_n)
5.6	766,000
14.4	291,000
29.5	139,000
49.2	57,500
74.6	31,500

VB - MMA Copolymers (p.134)

% VC	molecular weight (\bar{M}_n)
4.87	324,000
9.76	85,500
24.5	35,600
48.4	159,000
73.1	21,900

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