THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

THE THERMAL DEGRADATION
of
POLY-<u>TERT</u>.-BUTYL METHACRYLATE

by

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THERMAL DEGRADATION OF
POLY-TERT.-BUTYL METHACRYLATE

SUMMARY.

Thermal degradation reactions of vinyl polymers can be classified into chain scission and non chain scisson reactions. Previous work on poly-tert.-butyl methacrylate had indicated that the only reaction to occur with this substance was of the latter type; a "classical" decomposition of the substituent ester groups into an acid, polymethacrylic, and an olefine, iso-butene. Further evidence had shown that this reaction displayed unexpected auto-catalytic features.

The theme of the present investigation was a more complete study of the thermal degradation of poly-tert.-butyl methacrylate with the aim of elucidating the mechanism of decomposition and accounting for this autocatalysis.

Because some polymer degradation reactions often show a close analogy with polymer synthesis reactions, it was thought logical to make a full investigation using established technique into the mechanism and kinetics of the polymerisation of tert.-butyl methacrylate. The results of these investigations show clearly that tert.-butyl methacrylate polymerises by a radical mechanism whose general features resemble closely those of other methacrylate esters which have been investigated. The measured values of the kinetic rate constants for the primary processes contribute to the body of information which is being accumulated about the effects

of structure on reactivity of monomers.

In the course of this work it was possible to confirm that one of the decomposition products of the polymerisation initiator $\alpha\alpha'$ azo-di-isobutyronitrile is methacrylonitrile, by the isolation and identification of polymethacrylonitrile.

The thermal degradation of poly-tert.-butyl methacrylate was elucidated by kinetic measurements in high vacuum supplemented by investigations into the products of the reaction mainly by infra-red and gas chromatographic techniques. These sensitive methods revealed that the degradation process is considerably more complex than had been reported previously. It is possible to distinguish at least four constituent reactions.

1. Depolymerisation.

It has been shown that poly-tert.-butyl methacrylate undergoes a chain scission reaction with production of monomer. In the initial stages this reaction resembles the depolymerisation of polymethylmethacrylate, but it is retarded by the accompanying ester decomposition reaction. In the course of this investigation it has been demonstrated that a copolymer of methyl methacrylate and methacrylic acid is more stable towards depolymerisation than is polymethyl methacrylate.

2. Olefine production.

It has been confirmed that iso-butene production is auto-catalysed. Evidence has been obtained that this decomposition has a non-radical chain mechanism showing a close resemblance to the acid catalysed hydrolyses of esters which are encountered in reactions in polar solutions.

3. Anhydride formation.

It has been found that polymethacrylic acid is unstable at temperatures above 150°C, eliminating water with the production of an infusible insoluble residue. This residue has been shown to be an anhydride closely similar to, but not identical with the product of polymerising methacrylic anhydride. Measurements of the rate of its formation have shown that diffusion of water vapour and hydrolysis of the initially produced anhydride are important factors controlling the rate and hence the temperature at which the reaction may be observed. These factors probably account for the previous failure to detect this thermal degradation reaction.

4. High temperature breakdown.

Reactions 1, 2 and 3 proceed consecutively in the thermal degradation of poly-tert.-butyl methacrylate at 200°C. A temperature 100°C. higher is required to break down the anhydride residue.

Preliminary investigations into this reaction suggest that it is a chain scission reaction with a radical mechanism, initiated by the decomposition of the anhydride links.

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PREFACE

The work described in this thesis was carried out between September 1956 and September 1959, at the University of Glasgow, in the department of Physical Chemistry, which is under the supervision of Professor J. Monteath Robertson.

Parts of the material contained herein have been published in various scientific journals. Reprints of these parts are appended to the thesis. These are, the polymerisation of *tert*.-butyl methacrylate (Chapter III), from the "Transactions of the Faraday Society" **55**, 1042, (1959); the identification of polymethacrylonitrile as a decomposition product of $\alpha\alpha'$-azoisobutyronitrile (Chapter III), from the "Journal of Polymer Science" **42**, 588, (1960); and the pyrolysis of polymethacrylic acid (Chapter V), from "Polymer" **1**, 125, (1960).

A further paper, on the pyrolysis of poly-*tert*.-butyl methacrylate (Chapters IV and VI) has been accepted by "Polymer", but has not yet been published.

My thanks are due to the Gas Council for a Scholarship during the tenure of which the present work was carried out, and to Imperial Chemical Industries Ltd. and to British Hydrocarbon Chemicals Ltd. for the gifts of samples

of methacrylic acid and <u>iso</u>-butene respectively.

I would also like to thank Dr. Eglinton, Mrs. F. Lawrie and Mr. F. Gisbey for instruction and help in infra-red and gas chromatographic techniques, and the interpretation of the results. I also thank Mr. A. Glennie for general technical assistance.

Finally I would like to express my thanks to Dr. N. Grassie for the suggestion of the problem and for the help and encouragement given me by him.

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CHAPTER I

INTRODUCTION

SYNTHESIS AND DEGRADATION

The dual approach to chemical problems by synthetic and degradative routes has been made use of throughout the history of chemistry. A short outline of the development of modern ideas about "vinyl polymers" will show how both routes have contributed to our understanding of the structure and properties of these substances.

Since polymers from both vinyl $CH_2=CHX$ and vinylidene $CH_2=CXY$ monomers are basically similar, the term "vinyl polymers" has come to be applied to both products. This is the sense in which it is used here.

The production of non-crystalline tars, gums and resins, was a feature which often took place during attempts to isolate the parent "vinyl" compound. The fact that in some cases these resins could be broken down to the parent compound helped to give rise to the idea that the bonding forces in these substances were secondary in nature. Polystyrene, known since 1839[1] was reported to break down on heating to styrene as early as 1866[2]. On the other hand polymethacrylic acid was reported in 1897[3] to decompose without the reproduction of monomer.

Until the work of Staudinger during the years 1920 - 1930 it was generally accepted that polymers were either of low molecular weight, or were aggregates of weakly bonded monomer units. Only since the 1930's has it been fully realised that polymers have a giant or macromolecular structure composed of covalently bound monomer units. Shortly afterwards, certain degradative studies, both by Staudinger and also by Marvel, showed that in many vinyl polymers the monomer units are arranged in a predominantly head to tail manner.

Much of the expansion in the plastics industry which has taken place since 1940 has been in the field of synthetic vinyl polymers such as polyethylene, polyvinyl chloride, polystyrene and polymethyl methacrylate. With this expansion has come an interest in the mechanism of the polymerisation process, and many kinetic studies have been carried out. At the same time it became clear that certain commercial plastics deteriorated rapidly by the action of such influences as milling, grinding, exposure to radiation, heat and to various combinations of these. Investigations of such deterioration or "degradation" reactions have been carried out under controlled conditions both from an industrial and an academic viewpoint. Results have shown that "degradation products" are rarely chemically simpler, and may in some cases even be compounds of higher molecular weight than the original polymer. It must be emphasised therefore that such reactions are degradations only in the sense that the product has deteriorated from a commercial point of view.

The reactions described in this thesis are principally "thermal degradation" reactions. Such reactions can be described by the term "pyrolysis" in the sense used by Hurd[4], viz., "... the transformation of a compound into another or other substances by the action of heat alone." In spite of the derivations of the words "degradation" and "pyrolysis" they will be used without necessarily implying a breaking down.

POLYMERISATION OF VINYL MONOMERS

The detailed kinetics of the polymerisation process will be considered later but a discussion of the general features will be given at this stage .

Under certain conditions vinyl monomers may polymerise by ionic mechanisms; recently such methods have produced polymers with important commercial potentialities. However, much more is known about radical chain polymerisation mechanisms. It is now accepted the polymerisation mechanism consists of at least three, or more distinct reaction steps.

The production of a free radical (R.) in the <u>initiation</u> step may be brought about by the action of heat or ultra-violet irradiation on the monomer alone. More commonly it results from the action of such agencies on a labile catalyst or "initiator" present in small amount. Peroxides and azo-nitriles are the commonest initiators used. Detailed investigations have shown that with both series of initiators, the initiation process is a complicated one. It is quite common for some of the initiator to be lost in side reactions. Since these do not result in polymer formation, the initiation process in these cases has been termed "inefficient".

The long molecular chain characteristic of vinyl polymers is built up by repeated <u>propagation</u> steps

$$R\cdot + CH_2{=}CXY \rightarrow RCH_2{-}CXY\cdot$$

The molecular chain growth may be interrupted without breaking the radical chain by the occurrence of interfering <u>transfer</u> reactions

$$RCH_2{-}CXY\cdot + R'{-}H \qquad RCH_2{-}CXYH \quad R'\cdot$$

in which R'H may be monomer or some other suitable substance.

Cases have been reported in which chain growth may be halted by the production of radicals which are unreactive, either by virtueof inaccessibility or by some stabilising feature; but by far the commonest <u>termination</u> mechanism is the interaction of two growing chain radicals. This radical destruction may proceed in two ways namely disproportionation and combination, which although kinetically equivalent, yield structurally distinct products:

Disproportionation

$$RCH_2\text{-}CXY\cdot + RCH_2\text{-}CXY\cdot \longrightarrow RCH_2\text{-}CHXY + RCH{=}CXY$$

Combination

$$RCH_2\text{-}CXY\cdot + RCH_2\text{-}CXY\cdot \longrightarrow RCH_2\text{-}CXY\text{-}CXY\text{-}H_2CR$$

Various methods have been devised to determine which mechanism occurs with any particular monomer. It appears likely that the preferred mechanism depends on a number of factors including the structure of the monomer and the polymerisation temperature.

Although the kinetics of such reactions are complex they may in favourable cases be capable of solution and the rate constants for the individual reaction steps have been determined for a number of monomers. Among these methyl methacrylate has been investigated by a number of workers, using a variety of methods[5]. Less detailed investigations have been made on certain of the higher alkyl methacrylate esters and attempts have been made to relate the value of the rate constants to the molecular structure in this homologous series.

PYROLYSES OF VINYL POLYMERS

The most extensive studies of polymer degradation reactions have been made of those induced by heat. Such thermal degradations or pyrolyses, generally carried out under high vacuum, may be classified into two groups depending on the nature of the product. In chain scission reactions the main backbone of carbon-carbon bonds is broken, usually with the production of quantities of monomer and related compounds. In non chain scission degradation reactions it is the substituent groups which react. Any polymer may of course undergo both types of reaction, resulting in a complex mixture of products.

Chain Scission Reactions - - - Depolymerisations

Almost all the polymers which have been examined undergo chain scission reactions to some extent and it seems likely that the reaction is quite general among vinyl polymers although the temperature required for it to proceed at a measurable rate may be greater than that at which substituent reactions predominate. Monomer is often the main product of such reactions, and even when it is not, the products are generally closely related to it being for example, dimers, trimers, etc. Chain scission reactions may therefore be regarded as reverse polymerisations or "depolymerisations".

Although the analogy between polymerisation and depolymerisation has been used to develop kinetic schemes to explain many features of degradation reactions[6], the complexity of the products and general experimental difficulties prevent a detailed determination of the individual rate constants in all but a very few favourable cases. However the general features of depolymerisation processes have been established.

Initiation. Depolymerisation occurs by a radical chain reaction initiated at labile centres. These may be externally added initiators but more often they are structures present in the polymer chain itself. The chain ends appear to be particularly susceptible; other "abnormal" structures which may be responsible for initiation include oxygenated groups, head to head linkages, and branches. Initiation by the direct breaking of a normal C-C link would require considerable energy (81 Cal/gm mole) and appears to occur relatively seldom as an initiation process. Clearly the stability of a polymer towards depolymerisation will depend upon the presence of potential initiator centres and a knowledge of the polymerisation mechanism and previous history of a polymer sample is thus a necessary pre-requisite to a study of its degradation.

Propagation and Transfer. The analogue of the propagation step is the "unzipping" of the polymer chain with production of monomer.

$$R-CH_2-CXY-CH_2-CXY\cdot \longrightarrow R-CH_2-CXY\cdot + CH_2=CXY$$

Competing with such depropagation reactions are transfer reactions, the non-monomeric products of which include substances such as di- , tri-, and tetra-mers.

$$R-CH_2-CXY-CH_2-CX\overbrace{Y\cdot CH_2-CXY\cdot}$$

$$\longrightarrow R-CH_2-CXY\cdot + \underset{\text{dimer}}{CH_2=CX-CH_2-CXYY}$$

Since the activation energies of transfer reactions are greater than those of propagation/depropagation reactions competition by transfer processes is more pronounced at the higher temperatures encountered during depolymerisation than with polymerisation.

The relative amounts of monomer and non-monomeric products vary with the particular polymer degraded. It has been found that the ratio depends on at least two factors as follows.

(i) High monomer yields are obtained from polymers in which the depropagating radical $R-CH_2-CXY\cdot$ is highly stabilised by resonance, that is, in which at least one of the groups $\underline{X}$ and $\underline{Y}$ is unsaturated, and the odd electron can be de-localised over a number of positions.

(ii) Conversely, transfer reactions are favoured when the readily abstracted "tertiary" hydrogen atoms are present, that is, when Y=H .

Thus monomer yields vary over a wide range from nearly 100% with poly-α-methyl styrene in which the radical is stabilised by the presence of a benzene ring to less than 1% with polyethylene in which no such stabilisation exists. An intermediate position is occupied by polystyrene (about 60%) in which the stabilisation by resonance is offset by the tertiary hydrogen.

Termination. In a depolymerisation reaction any termination is likely to be due to the interaction of two (de)propagating radicals, as in polymerisation.

Radical interactions are often profoundly affected by the reaction medium. This is certainly true of both initiation and termination steps in polymerisation, as will be discussed in greater detail in Chapter III. The few results available for depolymerisations suggest that the high viscosity of the reaction medium is an important factor controlling termination.

One interesting case is that of the "weak link" scission in the pyrolysis of polystyrene.[7] Radical production ("initiation") occurs by the decomposition of some, as yet unidentified, weak link within the polymer chain. However, these radicals, unable to diffuse apart, disproportionate to produce stable molecules. Not only does this radical destruction show an analogy with a polymerisation termination step, but since potential centres of initiation decompose without the occurrence of depropagation, the whole process resembles "inefficient" initiation of polymerisation (p. 4).

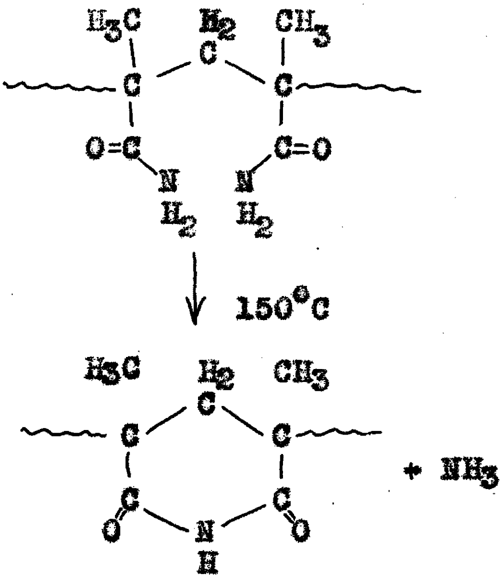
Non Chain Scission Reactions - - - Group Interaction.

Since they depend essentially on the macromolecular structure, depolymerisations are novel reactions in that they cannot occur with "simple" molecules, although radical oxidations and decompositions of hydrocarbons are similar in some respects. However, attached to the backbone of many polymers are reactive side groups which would be expected to participate in chemical transformations similar to those which occur in simpler compounds. It is of interest therefore to study the effect of the carbon chain and the presence of similar neighbouring groups on the rates and mechanisms of such reactions.

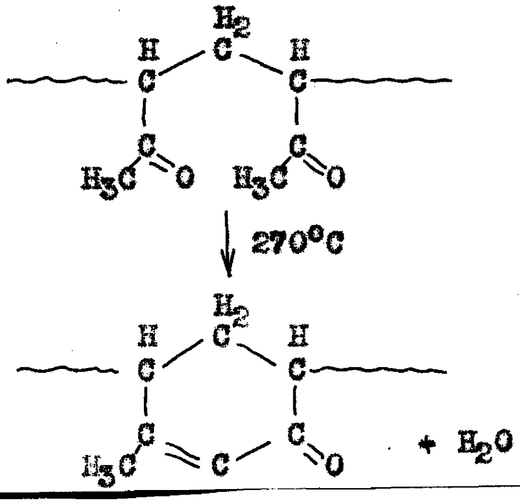
In the study of organic reaction mechanisms most progress has been made in the field of "ionic" mechanisms, generally in polar solvents. The investigation of rates and mechanisms of pyrolysis reactions have lagged behind those of reactions in solution. Consequently in some cases as much information has been obtained from thermal degradation studies on polymers as from the conventional pyrolytic studies on small compounds.

Certain polymers undergo pyrolytic substituent reactions at temperatures below that necessary for depolymerisation. Many of these reactions involve condensation of neighbouring groups. Among them may be mentioned:

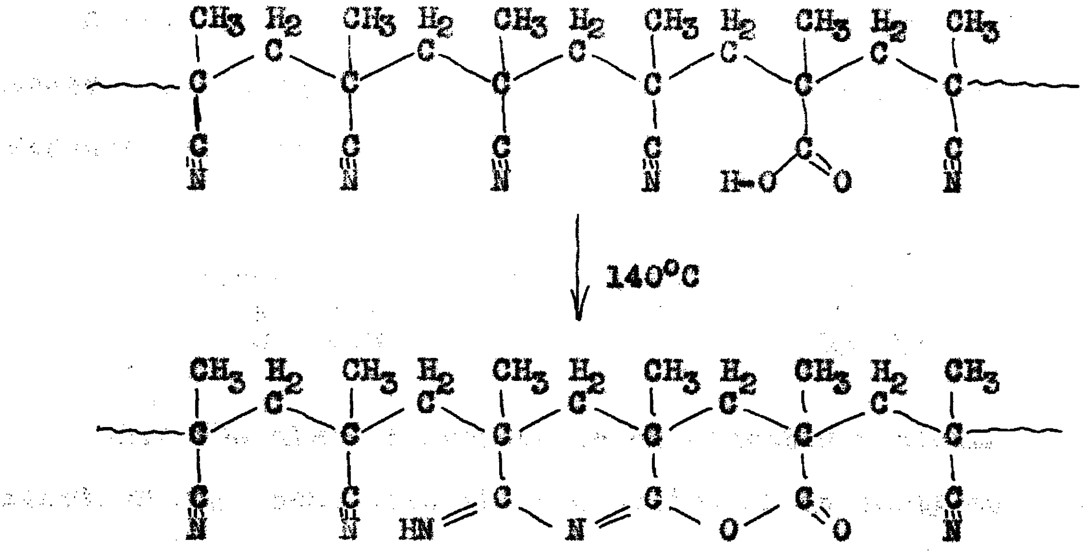
(i) The conversion of polymethacrylamide into an internal imide with elimination of ammonia.[8]



(ii) The condensation of groups in polymethyl vinyl ketone[9].



(iii) A condensation reaction, in this case without the elimination of any volatile products, occurs during the thermal degradation of certain polymethacrylonitrile samples which contain impurities in the form of acid units[10].

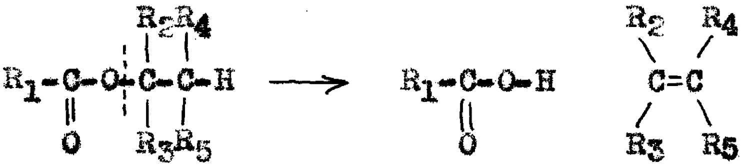


ESTER PYROLYSES

Since many vinyl polymers are esters it might be expected that the most detailed comparison of thermal degradation reactions of polymers with pyrolyses of low molecular weight compounds would be in this field, particularly as the thermal decomposition of "model" esters has been the subject of some study in recent years. It is therefore of interest to mention some of the more important types of ester decomposition processes.

1. Alkyl-Oxygen Scission.

The decomposition of ethyl acetate at a "dull red heat" into acetic acid and ethylene [11] provides the classical example of an ester decomposition reaction. The production of an acid and an olefine occurs with all esters which possess a hydrogen atom attached to the β carbon atom of the alcohol residue:



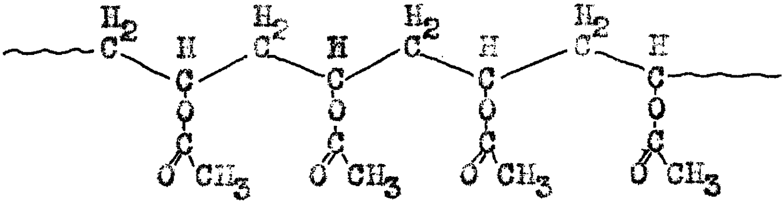
When the alcohol residue is unsaturated a similar reaction may occur with the production of an acetylene and an acid.[12]

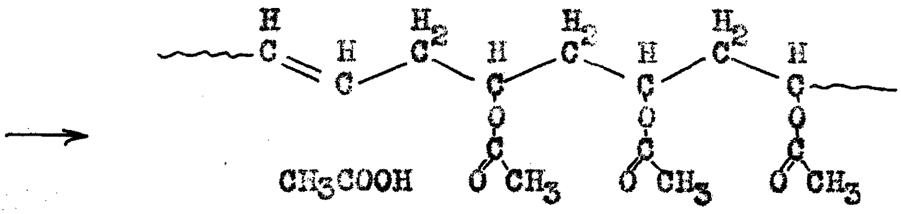
In considering the possible occurrence of ester decomposition reactions among polymers the most important features of results on model compounds are the relative stability of esters of different structures, and the temperature at which decomposition takes place. Methyl esters and others which do not possess the necessary H atom are particularly stable, while it has been clearly established by several workers that the relative stabilities of " reactive" esters are in the order, primary > secondary > tertiary. The question of the "decomposition temperature" is less easy to settle. Many of the reactions of model compounds have been performed in flow systems with short contact times during which measurable extents of decomposition are acheived only by using relatively high temperatures. Thus Houtman, van Steenis and Heertjes [13] report that suitable decomposition temperatures are

500 °C for primary esters
450 " " secondary "
300 " " tertiary "

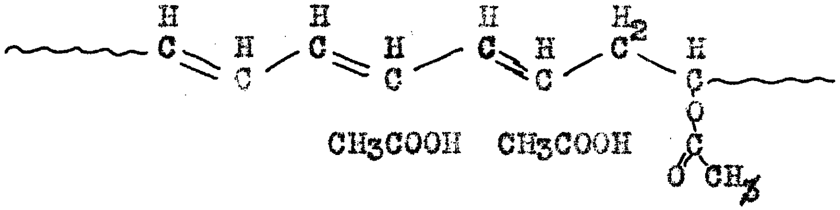
On the other hand more conventional kinetic measurements have been carried out at lower temperatures; the primary ester, n-propyl acetate, was studied at 340-380°C,[14] while iso-propyl acetate gives similar rates at 310-385°C.[14] Under similar conditions tert-butyl acetate decomposes at suitable rates at 240-300°C.[15] Even lower decomposition temperatures have been reported. As early as 1882, Menschutkin studied the decomposition of tert-amyl acetate in the liquid phase at 125-155°C.[16]

Polyvinyl acetate. An ester decomposition reaction of this type occurs in polyvinyl acetate at temperatures above 190°C.[17] The existence of the carbon-carbon backbone plays an important part in determining the rate of reaction . Thus the acid (acetic) is eliminated such that unsaturated centres appear in the chain.





These activate neighbouring groups which then decompose more rapidly than normally.

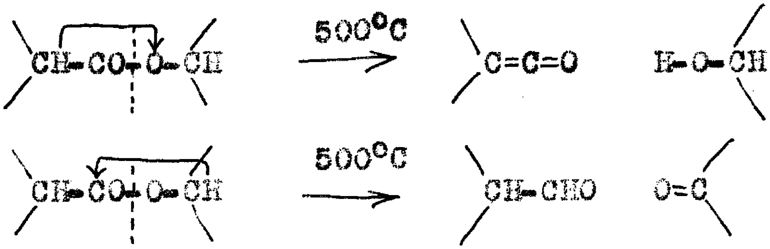


The overall reaction thus exhibits auto-catalytic features.

It seems likely that a similar reaction occurs in the thermal degradation of polyvinyl chloride.

2. Acyl-Oxygen Scission.

Until recently there have been only isolated reports of ester decomposition reactions other than those of the βH alkyl-oxygen scission type. However Ritchie et al.[18] have confirmed the existence of several other types, among which are some acyl-oxygen scission reactions. It seems likely that an αH either on acid or alcohol residue is necessary for this reaction



It has been suggested[19] that these reactions may compete with the alkyl-oxygen scission process.

Such reactions occur in the thermal degradation of condensation polymers such as polyethylene terephthalate but they have not so far been reported in vinyl polymers with ester side groups.

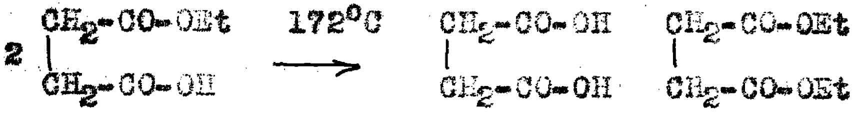
3. Other Ester Decomposition Reactions.

Other decomposition reactions of esters have been reported in which "Decarbonylation", "Decarboxylation" and "Intra-Acyl Scission" take place, generally with esters of unusual structure, in particular with unsaturated esters.

These reactions are unlikely to occur with vinyl polymers which contain such structures only on certain end groups. The temperature at which they have been observed, namely 500°C, is also considerably above that normally encountered in thermal degradation studies. In depolymerisation reactions, however, the monomer might decompose by these routes unless it is removed from the reaction zone, without delay.

4. Disproportionation - - - - Pyrolytic Ester Exchange.

Acid catalysed ester exchanges are well known among "polar solution" reactions; it seems likely that similar reactions can occur by pyrolysis under mild conditions, (temperature 300°C). Thus mono-ethyl succinate[20] and sebacate[21] on pyrolysis yield the corresponding di- esters and acids.



$$2\begin{array}{l}CH_2\text{-}CO\text{-}OEt\\ |\\ CH_2\text{-}CO\text{-}OH\end{array} \xrightarrow{172^\circ C} \begin{array}{l}CH_2\text{-}CO\text{-}OH\\ |\\ CH_2\text{-}CO\text{-}OH\end{array} \quad \begin{array}{l}CH_2\text{-}CO\text{-}OEt\\ |\\ CH_2\text{-}CO\text{-}OEt\end{array}$$

Similarly the slow distillation of glycol mono-benzoate yields glycol and glycol di-benzoate.[22]

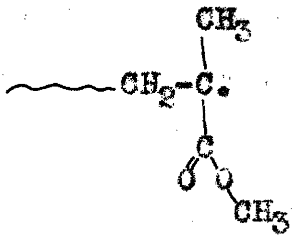
In the preparation of "poly-esters" the existence of ester exchange reactions is postulated to account for disproportionation at200°C in a molecular still[23]. Again in the field of condensation polymers, pyrolytic exchange reactions at 200°C have been suggested in other derivatives of carboxylic acids such as anhydrides[23] and amides.[24]

POLY-METHACRYLATE ESTERS.

Polymers from the homologous series of methacrylate esters provide an opportunity to study the various thermal degradation reactions of polymers since it would be expected that both chain scission and substituent ester decomposition might take place, the relative amounts varying according to the nature of the alkyl group of the ester. Such has been shown to be the case.

It is perhaps appropriate at this stage to point out that although strictly speaking the depolymerisation of poly-alkyl methacrylates could be described as "ester decomposition", this term will be reserved for side chain ester decomposition.

Lacking a βH atom the ester grouping in poly<u>methyl</u> methacrylate is stable and depolymerisation is the only reaction observed at temperatures upto and over 300°C. The propagating/depropagating radical



is not only resonance stabilised but also lacks a tertiary H atom. High monomer yields (100%) therefore characterise the depolymerisation. The simplicity of the product has contributed greatly to the ease of investigation of this reaction which is among the best understood of thermal degradations.[25]

In the absence of external catalysts the depolymerisation of polymethyl methacrylate can be detected above ~170°C. The structure responsible for initiation at 170-220°C is believed to be the unsaturated end produced on termination by disproportionation. Other initiating centres have been suggested for the reaction at higher temperatures. The kinetic chain length of the depropagation process is long and may exceed the molecular chain length if the latter is less than 200,000.

The depolymerisation of polymethyl methacrylate can also be initiated by ultra-violet irradiation at lower temperatures (~160°C) and a determination has been made of the individual rate constants of the primary processes under those conditions.[26]

Much less work has been reported on the higher methacrylates. Crawford[27] measured the relative rates of monomer production from a series of poly-alkyl methacrylates as monomer yields under standard conditions. (100 minutes heating in vacuum at 250°C). One of the factors determining such a rate will be the reactivity of the depropagating radical. It can be seen that the same radical

$$\sim\sim\sim CH_2-CXY\cdot$$

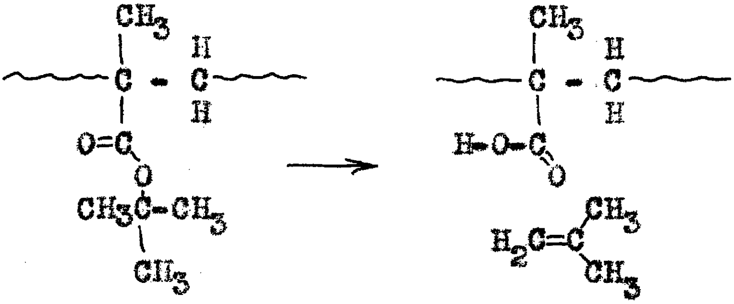
takes part in both propagation and depropagation reactions. It is therefore not surprising to find that Crawford's results bear some relationship to measurements of monomer and radical reactivity recently carried out in this department by means of copolymerisation experiments.[28]

The existence of ester decomposition side reactions might also affect the depolymerisation behaviour of the higher poly-methacrylates. Although Crawford suggests that olefinic impurities are present in the products from *secondary* esters it is only on recent re-examination of poly-ethyl and *n*-butyl methacrylates that it has been found that even these *primary* esters undergo side chain decomposition reactions.[29]

POLY-TERTIARY-BUTYL METHACRYLATE

Previous Work.

Poly-tert.-butyl methacrylate represents an extreme case in which no depolymerisation appears to take place. Crawford reported quantitative yields of iso-butene under the conditions described above.



The polymeric product polymethacrylic acid had been investigated previously and was reported to be stable to ultra-violet irradiation,[26] a known initiator for depolymerisations.

The simplicity of the products suggested that the kinetics of the reaction could be studied fairly readily. However, preliminary (unpublished) investigations by Grassie and Mathewson, in which the pressure developed in a closed system was used as a measure of iso-butene production, showed that the reaction displayed unexpected auto-catalytic features, as shown in figure 1.

The only other reference [30] in the literature to poly-tert.-butyl methacrylate degradation concerns the electron irradiation of it and polymethyl methacrylate.

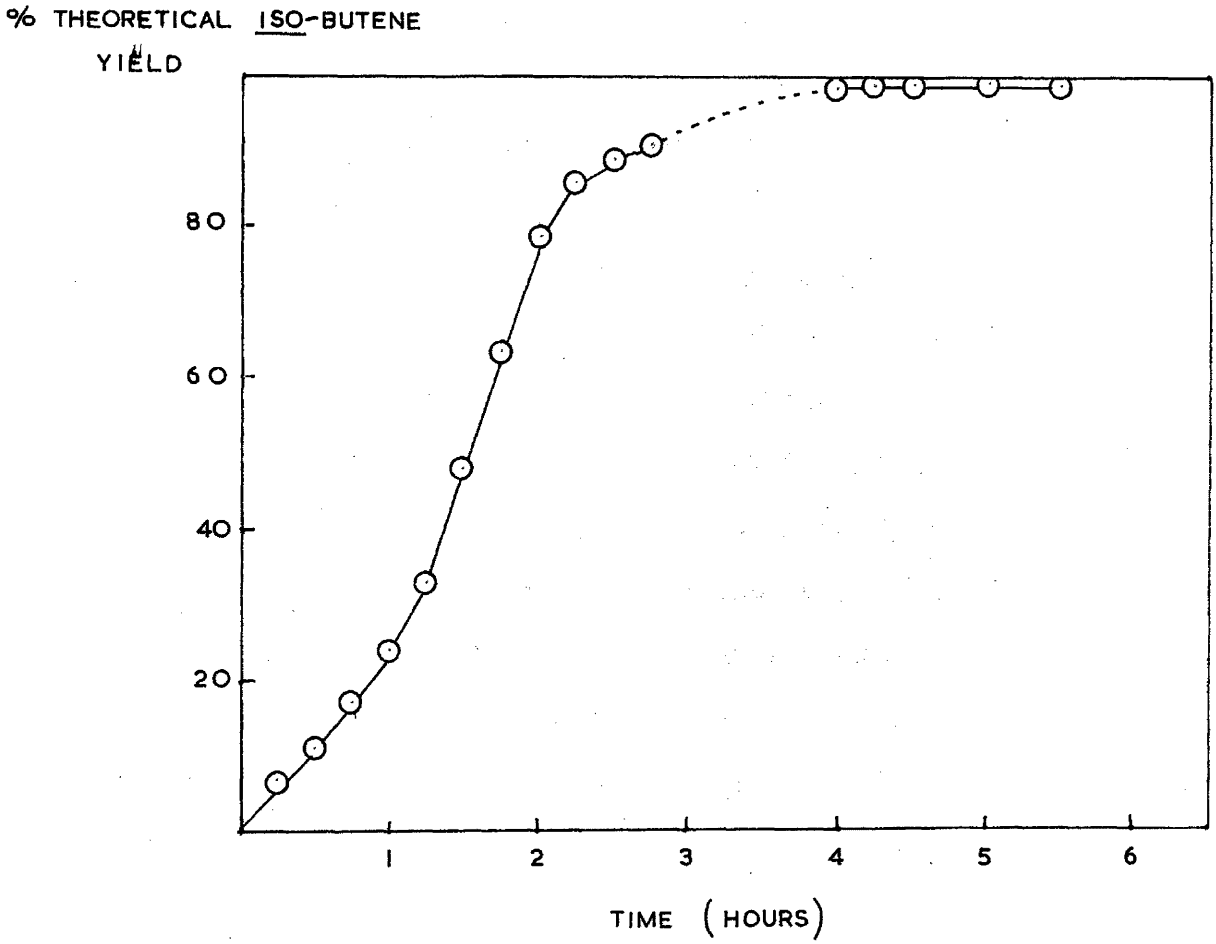


FIGURE I. DEGRADATION OF POLY-TERT-BUTYL METHACRYLATE AT 200 °C

RESULTS OF GRASSIE AND MATHEWSON

In this, it is suggested that the backbone of poly-tert.-butyl methacrylate may be somewhat weaker than that of polymethyl methacrylate. However since the degradation conditions are obviously so different from pyrolysis it would be unreasonable to expect that a direct comparison is possible.

Aim and Intended Scheme of Present Work.

It was the aim of the work described in this thesis to investigate the ester decomposition reaction in poly-tert.-butyl methacrylate and in particular the apparent auto-catalysis. It has already been pointed out that there is a close relationship between polymerisation and some degradation reactions and so it seemed logical to study first the polymerisation of the monomer. Determination of the rate constants of the polymerisation processes also allows comparison to be made with those of other methacrylate esters and contributes to the body of knowledge which already exists on the relationship between structure and reactivity of compounds of this type.

The simplicity of the reported products of degradation suggested that a suitable method of investigation would be by means of the dynamic molecular still[25] in which it is possible to measure the rate of production of volatile material, and particularly in the case of a single product to relate this directly to the rate of reaction.

In practice it was found that the reaction was more complex than suggested and it proved necessary in addition to examine the pyrolysis of polymethacrylic acid in some detail. Measurements in the dynamic molecular still were supplemented by measurements of the infra-red spectra of the polymers at various stages of degradation.

This thesis is therefore constructed as follows.

After a description of the various experimental techniques used in this work (Chapter II) the investigation of the kinetics of the polymerisation of _tert_.-butyl methacrylate is described in Chapter III. This is followed by a preliminary study of the pyrolysis of poly-_tert_.-butyl methacrylate (Chapter IV), the elucidation of the pyrolysis of polymethacrylic acid (Chapter V) and the mechanism of poly-_tert_.-butyl methacrylate pyrolysis (Chapter VI). In Chapter VII an account is given of the products of the high temperature breakdown of the residue from these degradations. Finally Chapter VIII contains a further brief discussion of the more important features of the results.

CHAPTER II

APPARATUS AND EXPERIMENTAL TECHNIQUES

PART 1 POLYMERISATION.

All polymerisations were carried out in dilatometers sealed under high vacuum. The reaction was followed by measuring with a cathetometer the decrease in the level of the liquid meniscus in the stem of the tube.

DILATOMETERS

A high vacuum system was constructed. Evacuation was provided by a mercury vapour diffusion pump backed by a rotary oil-pump. That part of the system used for the filling of dilatometers is shown in figure 2. With the exception of the burette tube this system and the degradation systems were constructed from a piece of normal ("soda") burette and a soft glass joint. All ground glass surfaces were lubricated with silicone grease.

It was found that the most satisfactory method of calibrating the narrow stem of the dilatometer was to determine the volume/length relationship of the bore of the individual length of tubing by a mercury thread technique before construction of the dilatometer. For the rate measurements described in chapter III the narrow tubing generally had a bore such that 20 cm ÷ 1 ml which with

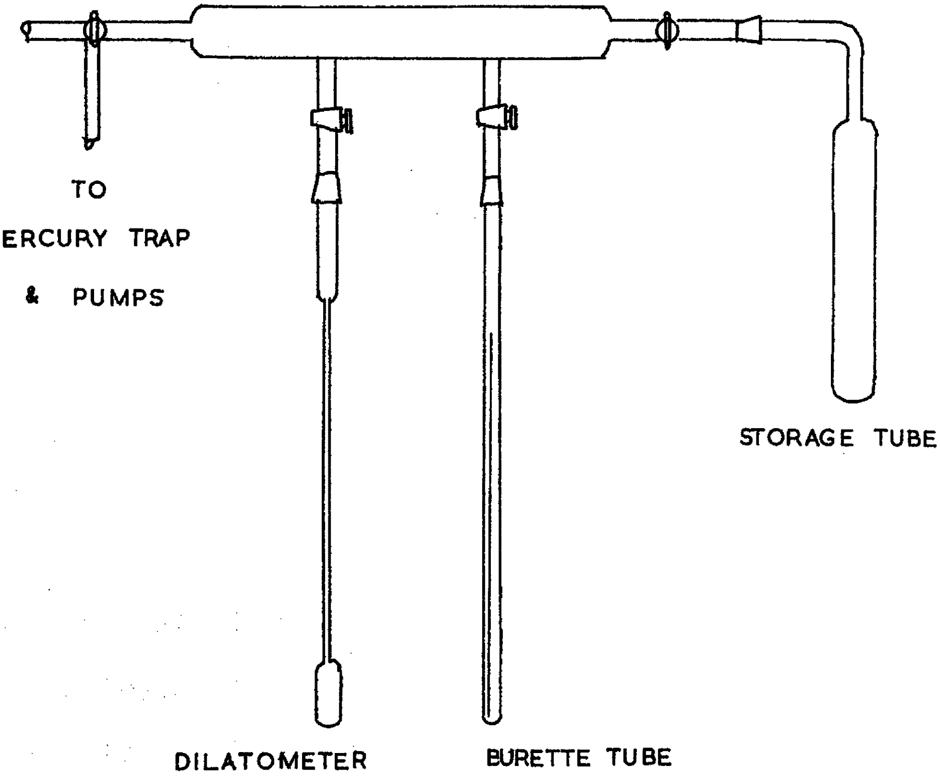


FIGURE 2 VACUUM SYSTEM FOR FILLING DILATOMETERS

bulbs of 5-6 ml capacity and a cathetometer reading to ±0.01 mm makes detectable, changes in the extent of polymerisation of ±0.01%. For the preparation of quantities of polymer for degradation experiments larger dilatometers of 25 or 50 ml capacity were used.

Before use dilatometers were cleaned by filling for 24 hour periods with chromic acid followed by sulphurous acid. They were then rinsed with distilled water and dried under vacuum.

Since the quantity of initiator and inhibitor used was extremely small, it was convenient to introduce them into the reaction tubes as standard solutions in chloroform. The solvent was removed at the water pump.

Freshly distilled monomer in the storage tube was degassed by repeated cycles of freezing in liquid oxygen, evacuation and thawing. Portions were transferred by "cold" distillation under high vacuum into the burette tube and measured volumes subsequently distilled into the polymerisation dilatometer. Since tert.-butyl methacrylate polymerises slowly by thermal and photo-initiation and cold distillation is a slow process, polymer is produced in the storage tube and in the form of a surface film it retards distillation. Use of a horizontal vacuum inlet and bent-arm storage tube made it possible to disturb this surface film by rocking the tube gently.

For some polymerisations a second liquid reagent had to be distilled into the dilatometer. This was the case for polymerisations in benzene solution and in the preparation of copolymers. It was distilled from a second vacuum chamber on the other side of the three-way tap.

While it was a feasible, although slow process to distil 1-2 ml of methacrylic acid under high vacuum, it was not practical to fill large tubes by this method and for the preparation of polymethacrylic acid (Chapter V) the monomer was degassed in the dilatometer.

After the dilatometers had been filled with a volume of liquid calculated to bring the meniscus about half way up the stem at the polymerisation temperature they were sealed still under high vacuum and stored at -183°C till required.

PHOTOPOLYMERISATION TECHNIQUES

Light Source

An Osram 125 watt mercury arc lamp was used. In order to avoid "skin effects" due to the non uniform absorbtion of light by a thick layer of monomer it was necessary to use wavelengths greater than 3300 Å. In the preliminary photoinitiation experiments shorter wavelengths were absorbed by the glass envelope. In the photosensitised "sector" experiments it was necessary to have a sharper source and the envelope was removed, however the soft glass lenses used with this system serve the same purpose.

Precautions were taken to minimise intensity fluctuations. Measurements were never started until the lamp had been running for at least an hour. The lamp was run at 240 volts from a "Variac" transformer with a voltmeter in parallel. Constant checks and adjustments were made to compensate for slight variations in "mains" voltage.

INTENSITY SCREENS

In order to determine the variation of the rate of polymerisation with the incident light intensity a means of cutting down the intensity by known relative fractions was required. This was done most conveniently by "intensity screens" of wire gauzes of different mesh sizes and wire gauges. Their transmission coefficients, relative to full intensity were measured using a uranyl oxalate actinometer[31].

The uranyl ion photosensitises the decomposition of the oxalate ion and over a certain concentration range the amount of decomposition is directly proportional to the incident light intensity. This condition holds provided the oxalate ion is never less than "half a molecule in excess".

Uranyl oxalate was prepared by mixing together hot solutions of equivalent amounts of Analar oxalic acid (2.52gm.) and Analar uranyl nitrate (10.04gm.). The precipitate was filtered off, washed thoroughly with cold water and dried in a vacuum desiccator.

Dilute solutions were made up of both uranyl oxalate and oxalic acid. Volumes of these solutions, such that the above condition holds, were mixed and the oxalate ion content measured by titration with potassium permanganate solution. Identical volumes were mixed in a glass weighing bottle which served as an actinometer cell and were exposed under standard conditions to either the full intensity or the intensity with one of the screens in position. Residual oxalate ion contents were measured by permanganate titration.

Transmission coefficient of screen

$$= \frac{\text{initial titre} - \text{titre after exposure to } I_x}{\text{initial titre} - \text{titre after exposure to } 100\% \ I}$$

A typical series of results is given below:

Exposure time --- 1 hour

$[UO_2C_2O_4] = 0.002$ M (5 ml of 0.006 M)

$[H_2C_2O_4] = 0.0067$M (10 ml of 0.010 M)

$[C_2O_4^=] = 0.0087$M $KMnO_4 \sim 0.06$ N

Screen	- -- -	A	B	C	**Blank**	
Titre (ml)	2.930	3.725	4.010	4.180	4.320	4.320
	2.935	3.735	4.035	4.175	4.310	4.310
	2.950	3.730	4.040	4.175	4.300	4.320
	2.925	3.720	4.030	4.160	4.310	4.305
		3.725	4.030	4.170	4.320	4.340
			4.020			
Average titre	2.935	3.727	4.027	4.171	4.315	
'Decomposition' (ml $KMnO_4$)	1.380	0.588	0.288	0.141	0	
% Transmission	100	42.6	20.9	10.4	0	

"Rotating Sector" Apparatus.

For the determination of the rate constants in the polymerisation of tert.-butyl methacrylate the average lifetime of the growing polymer radical must be measured. This was done by the established technique in which rates of polymerisation are measured under different illumination conditions; i.e. full intensity, and intermittent illumination with a range of exposure times. Repeated exposures of between 0.1 and 15 sec. were obtained by using the "rotating sector" apparatus shown in fig.3. The 1:1 rotating sector was driven through a reduction gearing system by a Citenco Type KQ/345 stirring motor.

For flash times of longer duration a manually operated shutter was used.

THERMOSTAT CONTROL.

Dilatometers were immersed in a 20 litre tank of water thermostatically controlled by a mercury-toluene regulator activating a Sunvic relay. Since the dilatometers act as very sensitive thermometers special attention has to be given to close temperature control. It was found that meniscus fluctuations due to temperature cycling were just on the limit of detectability indicating a temperature control of about ±0.02 C^{o} .

It is preferable to carry out photosensitised

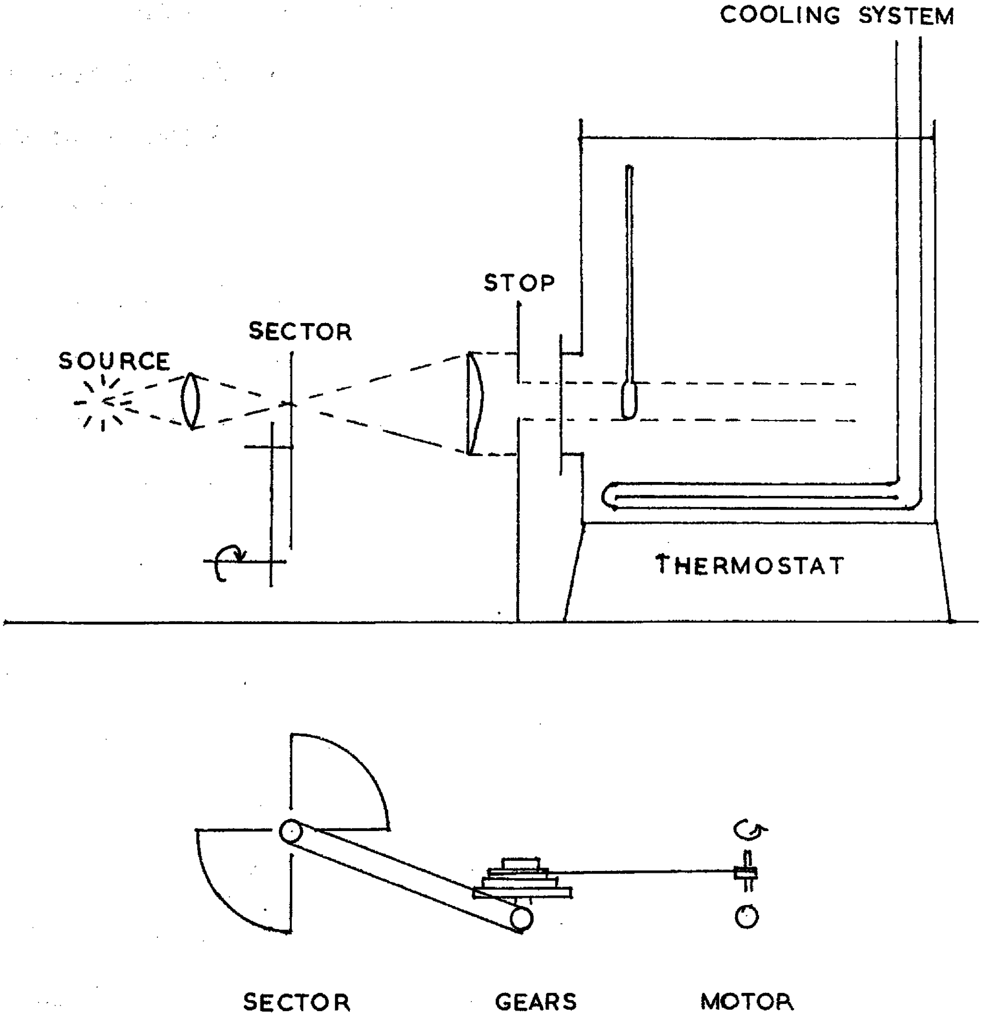


FIGURE 3 ROTATING SECTOR APPARATUS

experiments in as low a temperature range as possible. For temperatures below 30°C a cooling coil was immersed in the thermostat. Cold water was a satisfactory coolant for 25° and 20°C but for 15° and 10°C brine was circulated through a system in which an external coil was immersed in an ice/salt bath.

PRECIPITATION AND DRYING OF POLYMERS.

Both in the preparation of polymers for degradation studies and in some measurements in connection with the determination of the rate constants, the polymer must be isolated from the reaction mixture. It is important that the polymer should be obtained free from low-molecular weight impurities, particularly monomer and residual initiator. Precipitation of the polymer in a non-solvent is the most satisfactory technique.

Polymerisations of *tert*.-butyl methacrylate were halted at approximately 10% conversion. Even at such a relatively low conversion the reaction mixture was very viscous and was first dissolved in 1:4 dioxan before pouring into 70:30 methanol:water. While this non-solvent satisfactorily separates polymer from monomer and initiator, the polymer is still somewhat gummy. A second precipitation from dioxan into 50:50 methanol:water deposits the polymer in the form of a finely divided powder, which was collected in a sintered glass crucible.

Polymers whose molecular weights were to be measured in the determination of $k_pk_t^{-\frac{1}{2}}$ were dried to constant weight in an air oven at 70°C for 2-3 days. Some of the preliminary degradation experiments were carried out on polymer thoroughly dried by this method.

Cases have been reported in which even such mild pre-heating has caused changes in the degradation properties of polymers so another method of drying was employed for the polymers to be used for degradation studies. These were dried at room temperature in flasks attached to the high vacuum system. Since traces of solvent were detected among the degradation products from polymers dried by this milder method it is less efficient than the other. Apart from these impurities there was no difference in the degradation properties.

In the course of degradation studies, several copolymers were prepared. In these cases polymerisation was halted at 5% conversion in order to obtain uniformity of copolymer compositions. The solubility of these substances is not significantly different from poly-*tert*.-butyl methacrylate and similar precipitation techniques were employed.

The precipitation of polymethacrylic acid was somewhat different, and since it has some bearing on the degradation results it is discussed with them in chapter V.

OSMOTIC MOLECULAR WEIGHT MEASUREMENTS.

Number average molecular weights of samples of poly-tert.-butyl methacrylate were measured by osmometry. Osmotic pressures of dilute solution in redistilled methyl ethyl ketone were measured in osmometers of the Pinner-Stabin [32] design, supplied by Polymer Consultants Ltd.

Osmometer.

In this type of osmometer the solution is contained in a small (3ml) glass cell, separated from a large (~200ml) volume of solvent by membranes supported by stainless steel plates. There are two openings into the cell. One of these is used only for filling the cell and during operation it is closed by a mercury sealed positioning rod which can be used to adjust the initial level in the second opening, a fine capillary tube. A reference level is provided by a matching capillary tube dipping into the solvent.

Membranes.

Membranes were prepared from undried cellophane conditioned to methyl ethyl ketone. The initial aqueous medium in which the membranes had been stored was gradually replaced by acetone by immersing them for 24 hour periods in baths progressively richer in acetone till after five days they were in 100% acetone. A similar process was then used to replace the acetone with methyl ethyl ketone.

Temperature Control.

Accurate temperature control is necessary. The osmometers were set up in a 50 litre water thermostat controlled at 25°C by a Sunvic relay and spiral type mercury-toluene regulator. With the larger regulator, temperature control is probably better than the 0.02°C. obtained in the polymerisation thermostat. The difference in level of the liquid in the two capillaries was measured with a cathetometer and once equilibrium has been attained there were no detectable fluctuations due to temperature. The pressure head can be measured to within 0.005 cm.

Measurement technique.

As is usually the case with high polymer solutions non-ideal behaviour was encountered in the relationship between osmotic pressure and concentration; following the normal procedure osmotic pressure measurements were made for each polymer sample over a range of concentrations from 1 gm/100gm solution to 0.1 gm/100gm solution.

0.3 - 0.5 gm of polymer was dissolved in 50 ml solvent. After filtering to remove dust particles, different portions of this stock solution were weighed into tared 15 ml flasks. At the same time the concentration of the polymer in the stock solution in gm/100gm solution was determined by removal of a portion and evaporation, at 100°C in a tared bottle, to constant weight. Lower concentrations were prepared by diluting the stock solution in the flasks. To avoid errors due to evaporation losses these diluted solutions were weighed only immediately before use. The concentrations were therefore calculable on a weight basis.

Since the concentration was determined before the solution entered the osmometer, the latter had to be carefully rinsed with four portions of 2-3 ml of the solution before filling, to ensure that the calculated concentration was the true one. About one hour after filling, the pressure head was adjusted by means of the positioning rod so that it was close to the anticipated osmotic pressure. Thereafter the osmometer was left undisturbed. Readings were then taken at intervals till they became constant over a twelve hour period. This equilibrium was usually attained after about thirty hours.

The constancy of the osmotic pressure head after this time demonstrated that diffusion of low molecular weight polymers through the membrane was negligible. Since the molecular weights of all the polymer samples were in excess of 100,000 this was not surprising. In many cases the osmotic pressure head was confirmed by approaching it from both above and below the true value.

Cell Constant:

Ideally the equilibrium pressure head should be zero with pure solvent in the cell. In practise there was always a small "cell constant" which had to be subtracted from the observed pressure heads. Regular determinations of the cell constants of the osmometers were carried out. After the osmometers had been in use for several weeks these values did not show any great variation (0.00 ± 0.02 cm) during the six month period they were in use.

Calculation of Molecular Weight.

The product of the measurements outlined above was a series of osmotic heads h (cm) at concentrations c (gm/100 gm solution). A plot of h/c against c was made and the limiting value L determined.

$$\text{i.e.}\quad L = (h/c)_{c\to 0}$$

L can be related to M_2 the number average molecular weight of the polymer in the following way:

$$(\pi/C)_{c\to 0} = RT/M_2$$

where π = osmotic pressure in atmospheres

C = concentration of solution in gm solute/ml solution

R = Gas Constant, (82.06 cc atmos. per degree per mole)

T = Absolute temperature

Since 1 atmos. = 1033.3 gm/sq cm

π in atmos. = h x density of solution / 1033.3

Since C in gm/ml = c in gm/100 gm x $\frac{\text{density of solution}}{100}$

$$(\pi/C)_{C\to 0} = \frac{L \times \text{density}}{1033.3} \times \frac{100}{\text{density}}$$

$$= L / 10.333$$

Therefore M_2 = 10.333 RT/L = <u>252,800/L at 25°C</u>

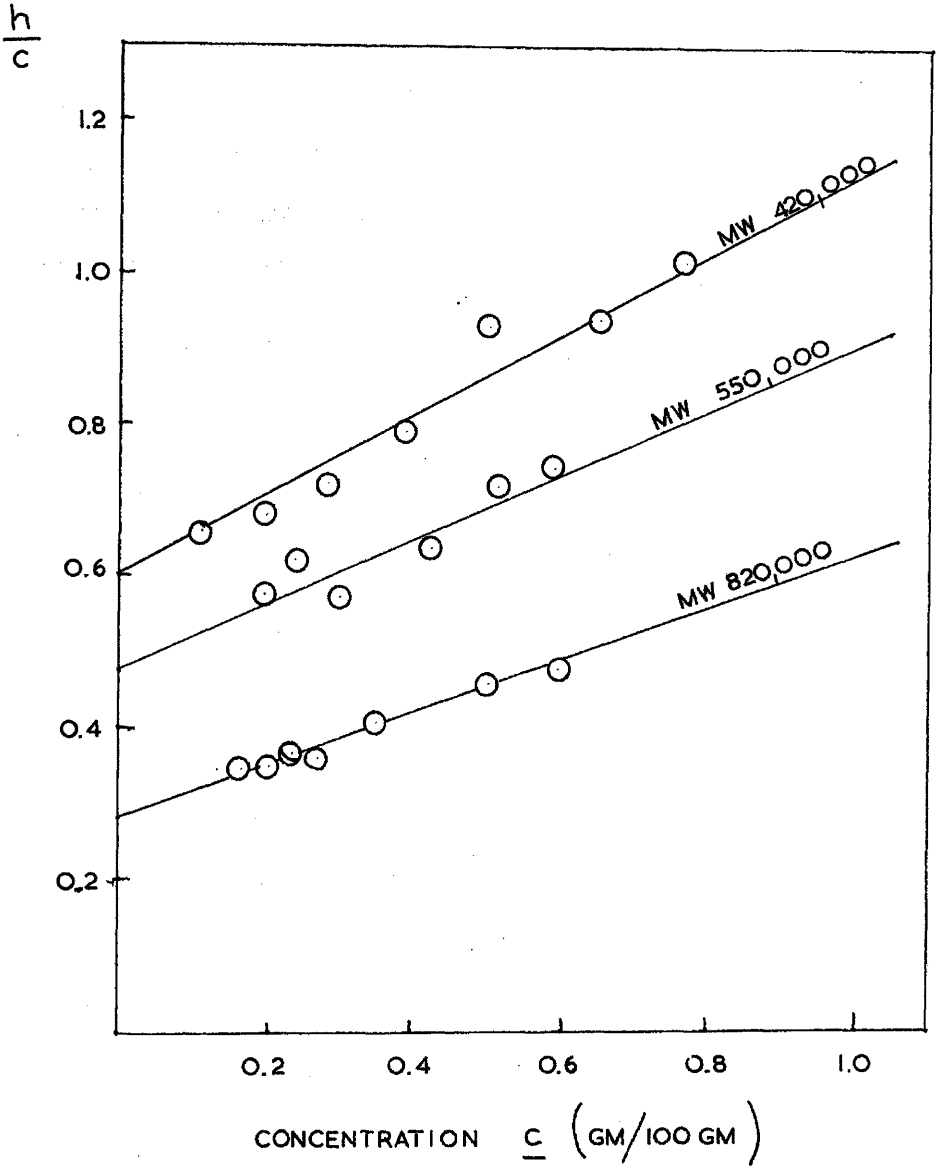


FIGURE 4 TYPICAL OSMOTIC PRESSURE DATA

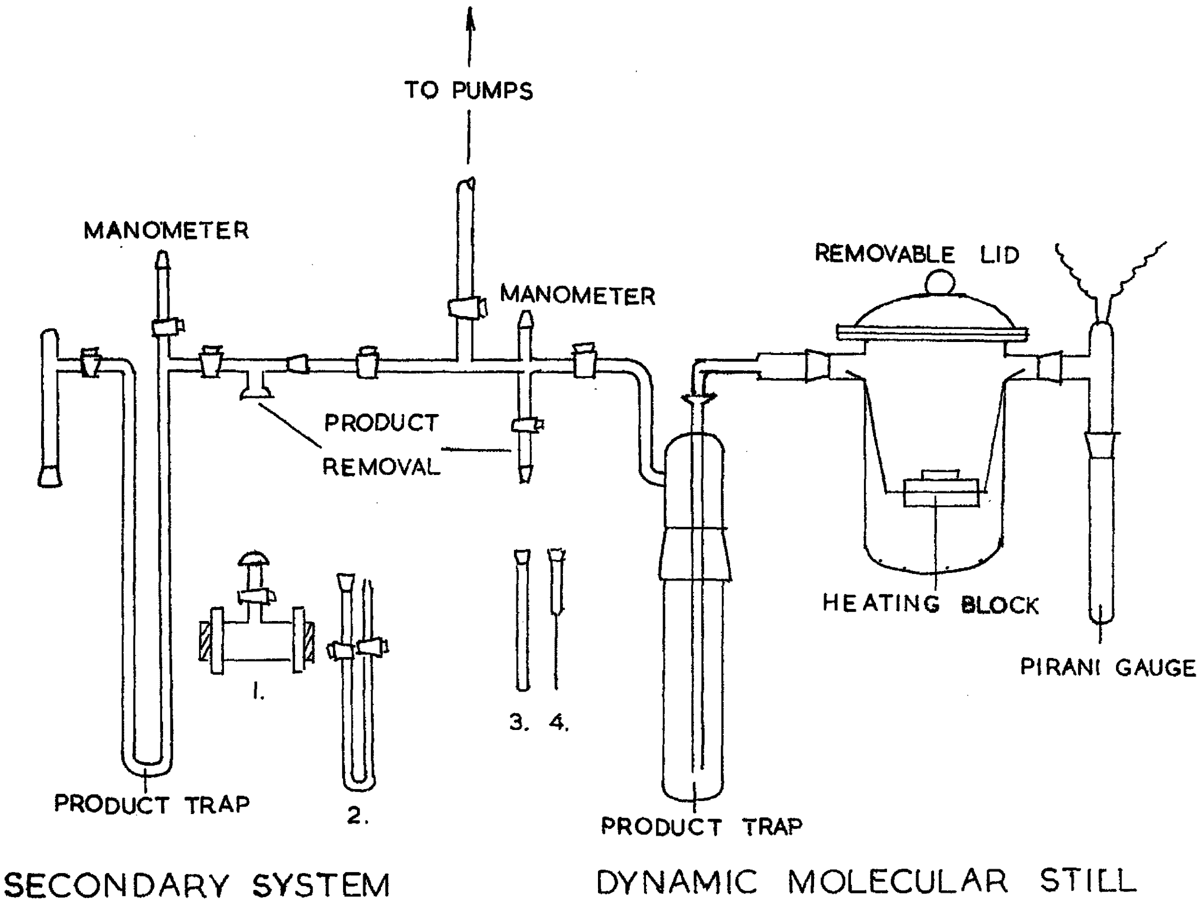
PART II DEGRADATION

Unless otherwise specified, degradations were carried out in vacuum. The general arrangement of the glasswork of the degradation apparatus is shown in figure 5. Basically it consists of a dynamic molecular still (d.m.s.) which was a modification of that first used by Grassie and Melville.[25] By this means rates of volatile production may be measured under conditions of high vacuum. The additional apparatus including a secondary degradation system was used in connection with the separation and removal of products for subsequent infra-red and/or gas chromatographic examination.

THE DYNAMIC MOLECULAR STILL

In the d.m.s. a layer of polymer is degraded thermally by being kept in contact with a hot surface. Since the system is continously evacuated during degradation, the volatile products have very little chance of further interaction once they escape from the polymer. Provided the rate of removal of volatiles is maintained constant by having an uniform pumping rate then the rate of production of volatiles will be measured by the small pressure developed inside the still. This pressure is measured by the Pirani gauge.

Two previous improvements on the original design have been incorporated in the present system. They are the introduction[17] of a product trap between hot surface and



1. INFRA-RED GAS CELL
2. GAS TRAP FOR V.P.C.
3. TARED TUBE
4. CALIBRATED CAPILLARY

FIGURE 5 GLASSWORK OF DEGRADATION APPARATUS mercury pump and the use of a thermostatted Pirani gauge on a side arm. The systems for heating, temperature recording and control are also different from the original systems.

The Product Trap.

During a degradation run the product trap was kept immersed in liquid oxygen. This prevents possible reaction of the mercury vapour with the degrading polymer or with the products in passing through the pump. Its main function, however, is in providing a constant "sink" for the removal of products condensable in liquid air which is independent of fluctuations in behaviour of the mercury pump.

For such substances the mercury pump merely provides a backing vacuum to enable the product trap to act as a pump. Since more volatile substances are only removed by the conventional pumping system it is possible to test for their presence among the products during degradation by closing a tap between mercury pump and still. The presence of "non-condensables" is shown by an immediate pressure rise indicated on the Pirani gauge. These tests will be referred to as "Pirani Tests".

It was shown that substances as volatile as carbon dioxide and iso-butene were trapped efficiently in the system. In addition propene can be trapped although no experiments were carried out to determine the efficiency of its trapping It seems likely that the only substances which can pass through the system are C_2-hydrocarbons, methane, carbon monoxide, oxygen, nitrogen and hydrogen.

The Pirani Gauge.

Pressure measurements by means of a Pirani gauge are based on the relationship between the thermal conductivity of a gas and its pressure at low pressures of the order of 10^{-1} to 10^{-4} mm of Hg. Thermal conduction of the heat away from an electrically heated hot wire by the gas would result in a decrease in temperature and consequently a decrease in the resistance of the wire. To prevent this, additional energy is supplied to the filament by an increase in voltage. This can be measured in a Wheatstone bridge circuit. At low pressures, the term $(V^2-V_0^2) / V_0^2$ is proportional to the pressure, where V and V_0 are the applied potentials required to balance the bridge at pressures p and zero respectively.

In the original d.m.s. the Pirani gauge was exposed to fluctuations of light and room temperature with consequent variations in the rate of heat loss by the wire. Even provided that V and V_0 could be measured under the same conditions it was necessary to evaluate the term $(V^2-V_0^2)/V_0^2$ in order to obtain the rate of production of volatiles from a calibration curve of $(V^2-V_0^2)/V_0^2$ against rate of flow of vapour through the system. In the darkened, thermostatted form of the gauge these fluctuations do not occur and

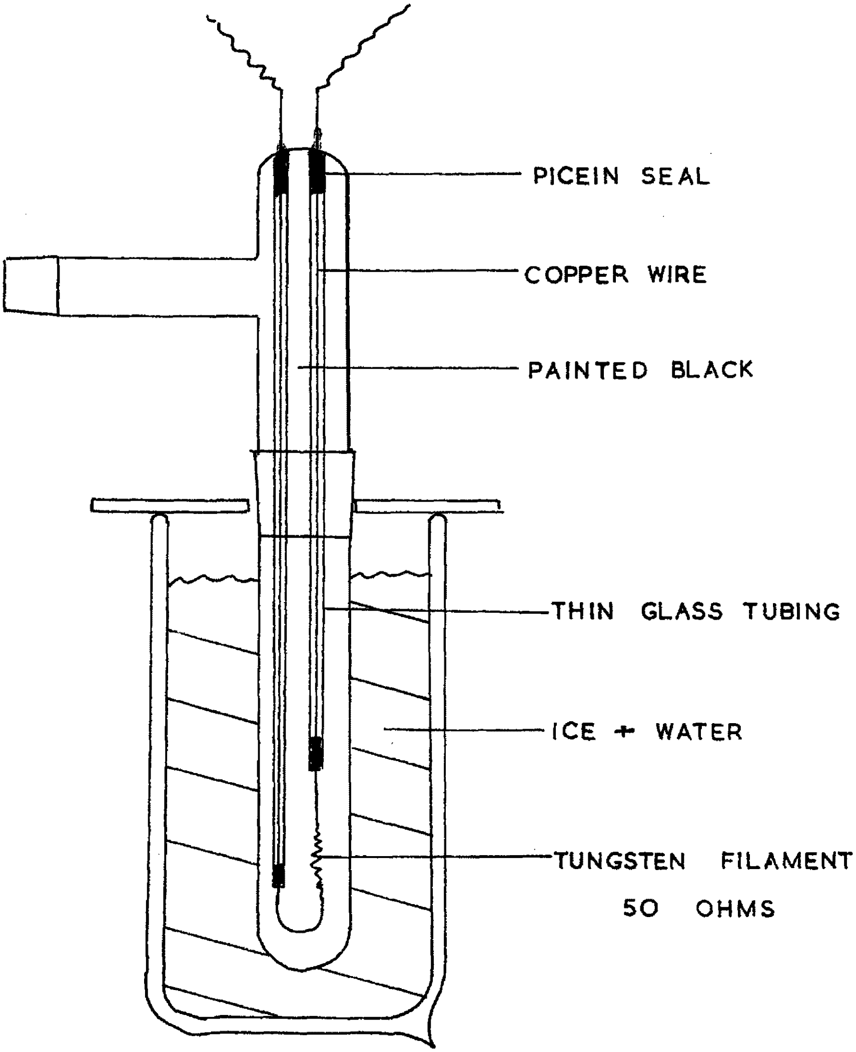
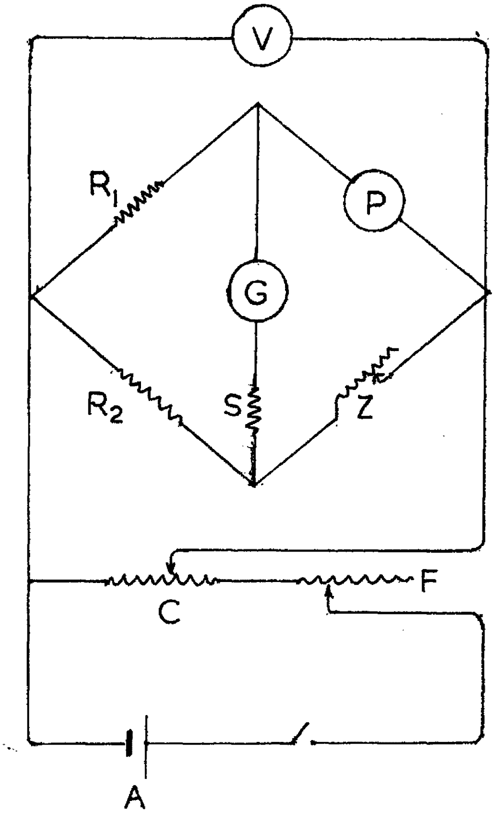


FIGURE 6 THERMOSTATTED PIRANI GAUGE



A	ACCUMULATOR	2 VOLTS
C	COARSE POTENTIOMETER	0–250 OHMS
F	FINE RESISTANCE	0–10 OHMS
Z	ZERO CONTROL	0–50 OHMS
R_1 R_2	FIXED RESISTANCES	37.6 & 23.5 OHMS
S	FIXED RESISTANCE	1,950 OHMS
V	VOLTMETER	0-2 VOLTS
G	GALVANOMETER	
P	PIRANI GAUGE	

FIGURE 7 PIRANI GAUGE CIRCUIT

calibration can take the form of a curve relating V to rate of flow of vapour.

The vacuum side-arm containing the hot-wire filament, figure 6 and the complete Pirani circuit, figure 7 are basically similar to those of McNeill (Ph.D. Thesis, Glasgow, 1957) although a number of modifications were made to the basic design to provide greater robustness and ease of operation.

Initially the circuit was adjusted so that $V_0 = 0.600$ volt. It was found that after a few degradations this decreased, presumably due to more thorough removal of volatiles, thereafter it remained constant at 0.582 ± 0.002 volt throughout the fifty to sixty degradations carried out in the d.m.s. These narrow limits are approximately the same as the limits of the error in measuring V.

As with any gauge operating on the thermal conductivity principle the Pirani gauge must be calibrated for the gas whose pressure is to be measured. Since it had been reported that iso-butene was the only degradation product from poly-tert.-butyl methacrylate it was calibrated in terms of rates of flow of iso-butene. The experimental system is shown in figure 8. The rate of flow of iso-butene into the d.m.s. was controlled by the needle valve and once equilibrium conditions had been set up this flow rate was equivalent to the rate of volatilisation of liquid iso-butene

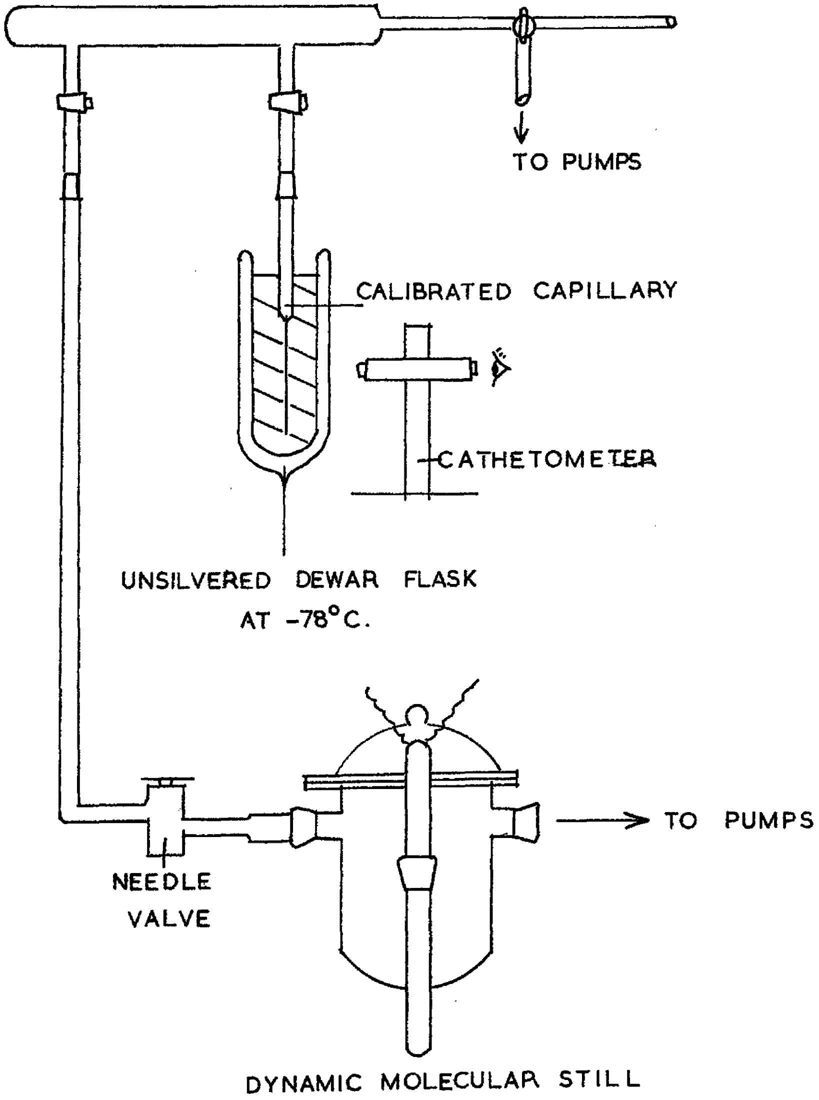


FIGURE 8 CALIBRATION OF PIRANI GAUGE

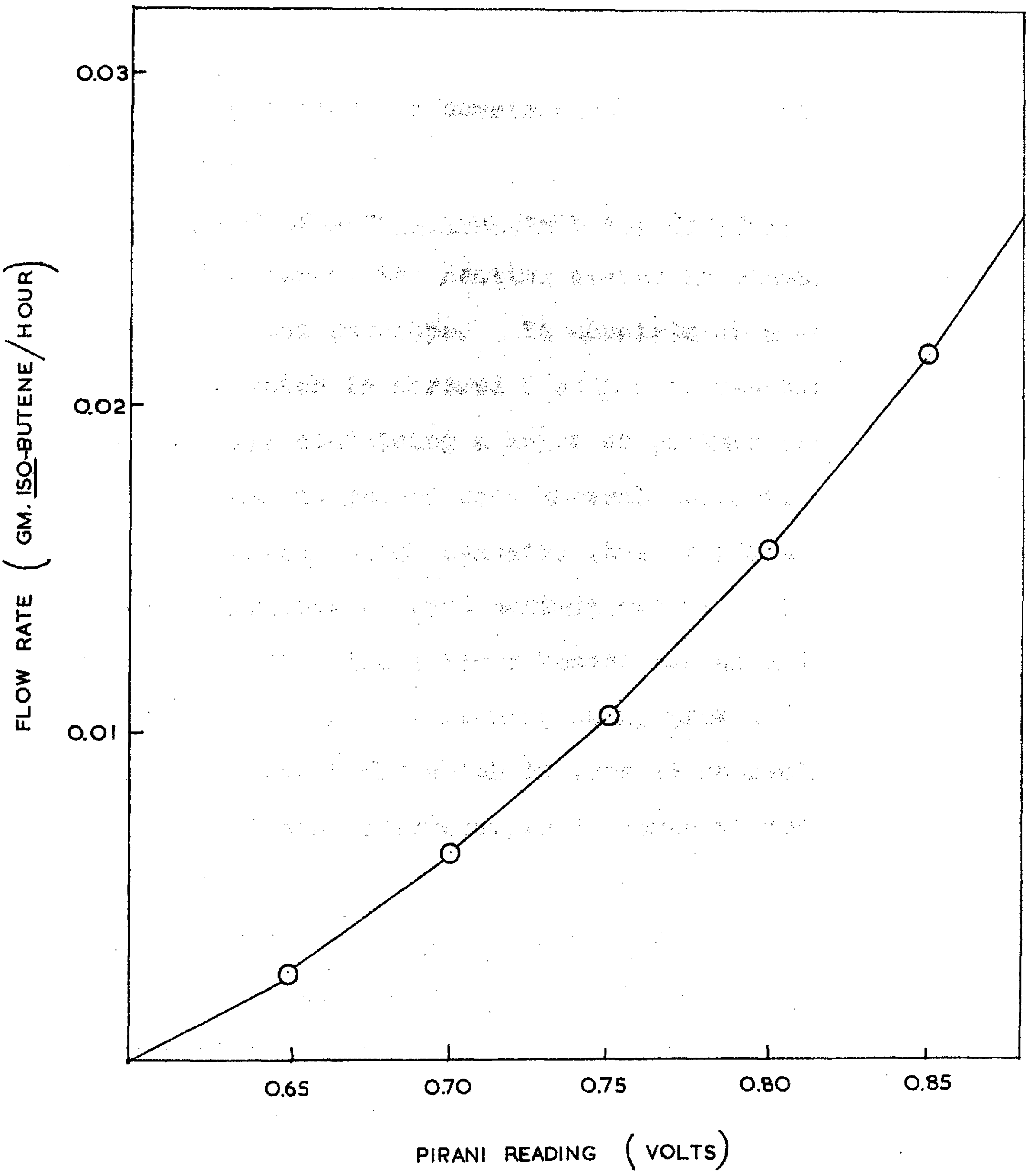


FIGURE 9 PIRANI GAUGE CALIBRATION CURVE

measured volumetrically. A calibration curve showing the relationship between Pirani readings and rates of flow of iso-butene was constructed and part of it is shown in figure 9.

Heating, Temperature Measurement and Control.

In the d.m.s. the heating system is contained in an evacuated glass envelope. It consists of a copper heating block onto which is screwed a copper degradation tray, (figure 10.), containing a layer of polymer covered with copper powder to ensure good thermal contact.

The heating block contains three cartridge-type heaters each of which has a rated maximum output of 50 watts at 24 volts. The single lower heater has an intermittent power supply, on/off switching being provided by means of an ETHER "Transitrol" which in turn is activated by a copper/constantan thermocouple soldered to the base of the degradation tray. The same thermocouple measures the temperature of the degradation surface.

The various electrical circuits are shown in figure 11. One aspect in which the present system differs from previous ones is in the method by which wires enter the vacuum system; instead of using borated copper wire to pass through the Pyrex glass, all wires whether of copper or of constantan were led through pieces of capillary tubing sealed with Picein wax. By this means bi-metallic junctions

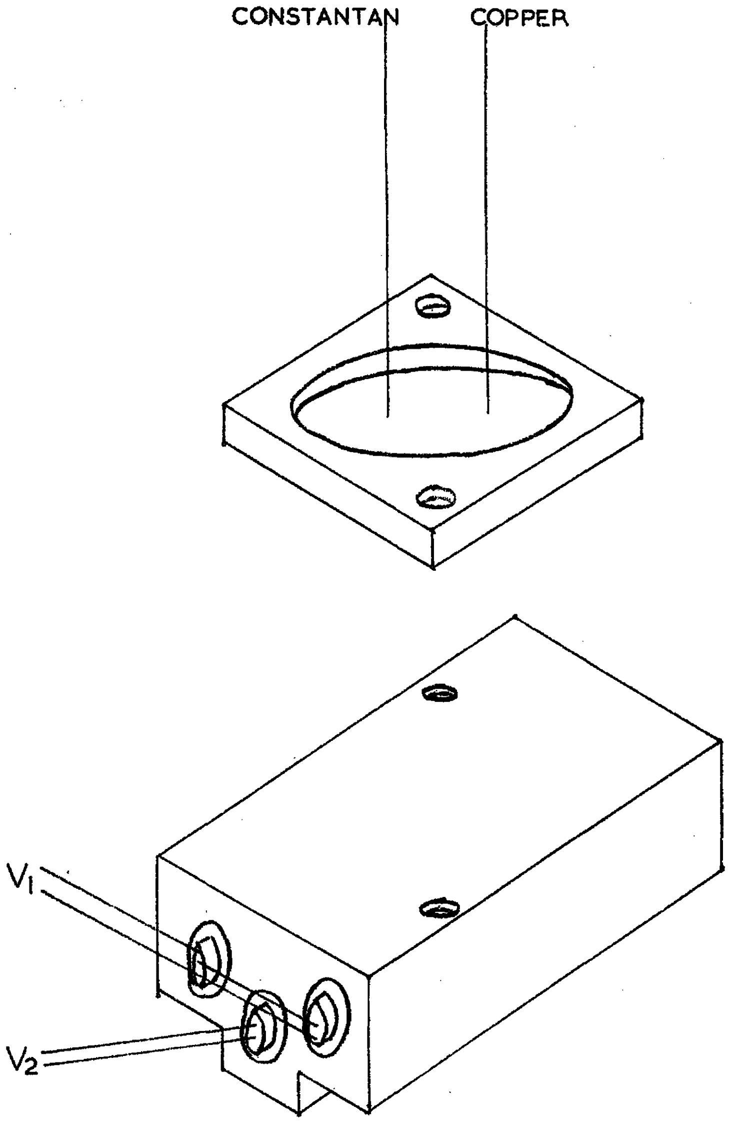


FIGURE 10 HEATING BLOCK & DEGRADATION TRAY

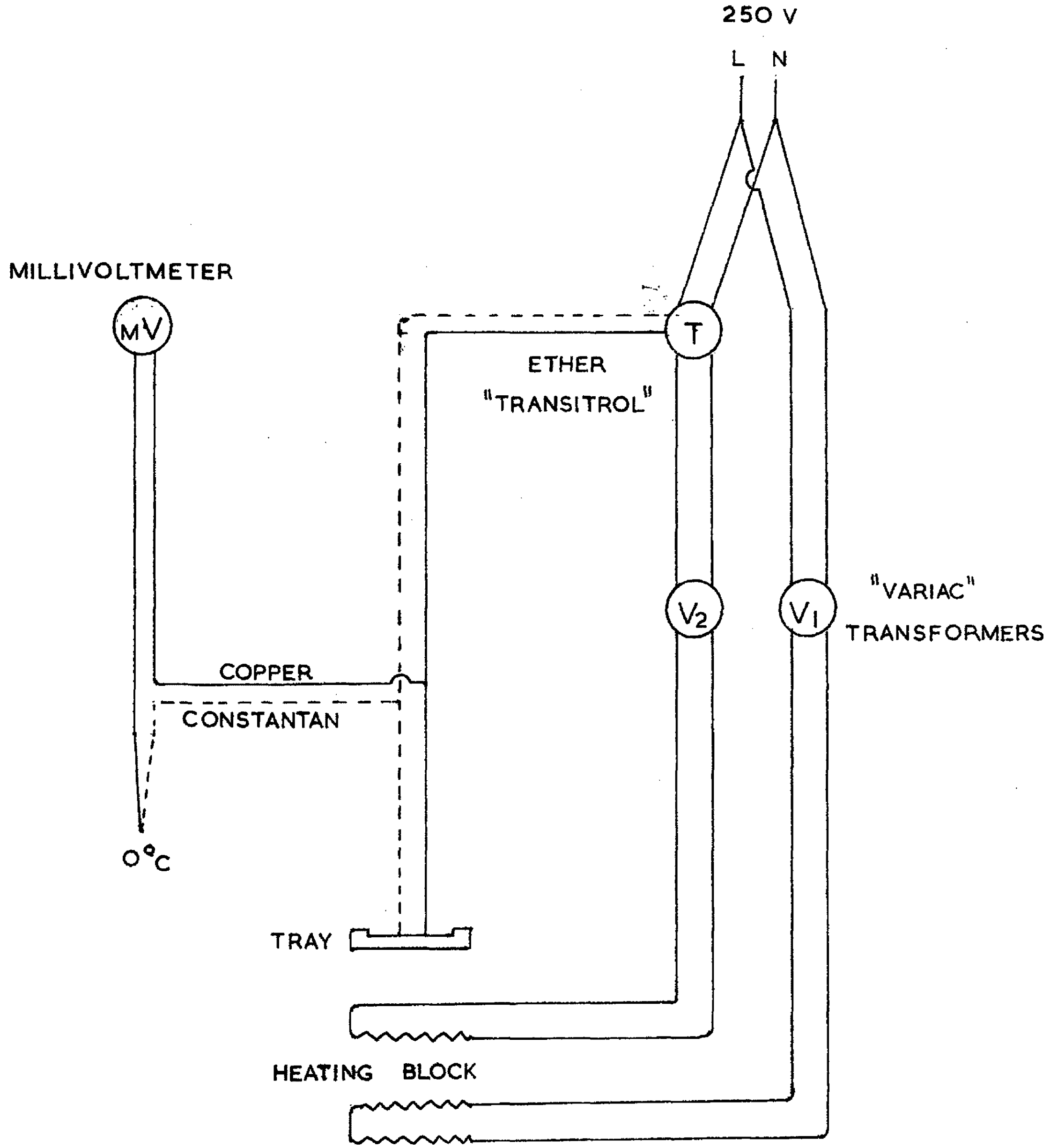


FIGURE 11 HEATING, TEMPERATURE MEASUREMENT & CONTROL CIRCUITS

were avoided and where joins were necessary wires were overlapped. Using the same tray thermocouple as part of a similar circuit it was found that the observed e.m.f. on the millivoltmeter was approximately the same as the "standard" value for the temperature recorded on a thermometer immersed in the same oil bath as the tray, at temperatures around 200°C. The temperature/e.m.f. calibration was therefore based on these standard e.m.f.'s with a small correction made for the slight drop in potential across the finite resistance of the wires of the circuit.

The finely divided copper powder used in the degradations came from two sources. Previously it had been prepared by the reduction of cupric oxide by coal gas; this material is generally contaminated with adsorbed hydrogen. Instead, coarse cupric oxide (does not pass 100 mesh) was reduced in formic acid vapour, a method based on that of Wehl[33]. Since the reduced product showed a tendency to absorb volatiles from the atmosphere it was kept stored under vacuum after heating to 250°C for 2 - 3 hours. Later 60 - 80 mesh copper was obtained from Hopkins and Williams.

Operating Technique.

In order to minimise the time necessary to evacuate the system, the d.m.s. was kept under vacuum except for the 1 - 2 minutes necessary to introduce the tray containing weighed quantities of polymer and copper, and connect the thermocouple leads. Even then the system had to be evacuated for several hours before a Vo Pirani reading was obtained. During this time the product trap was not immersed in liquid oxygen. This was only done immediately before raising the temperature of the block.

To raise the temperature to that required for degradation the following technique was found to be the most satisfactory compromise between prevention of overshooting and speedy attainment of temperature. Initially the temperature is raised rapidly by passing about 30 volts through the constant heaters until the temperature is about 40 °C* below the required degradation temperature, when it is reduced to zero so that the approach to degradation temperature is slow. Just as degradation temperature is reached and the controlling system comes into operation a constant low voltage (8 - 10 v) is applied which is maintained during the degradation. There is nothing to be gained by the use of the full power of all three heaters in the early stages since this leads only to overshooting difficulties, consequently the intermittent heater is kept on 8 - 10 v both during the temperature raising and normal running stages.

Degradation temperature is generally reached after 25 - 30 minutes and after some initial fluctuations of ±1 C° it remains constant to within the limits of detectable temperature change (±0.5 C°) throughout the degradation.

One disadvantage of the system is that the large size of the heating block (~ 350 gm copper) results in slow cooling after degradation. Before examination of the products it was usually necessary to leave the system to cool overnight under vacuum.

"Background" Products.

Pirani readings were made at intervals of one minute throughout the period of degradation. Even in the absence of polymer, volatiles were detectable in the early stages of heating. A typical example of a "background" Pirani curve is shown in figure 12. This feature of the d.m.s. appears to be peculiar to the present heating system since it has not been reported previously.

The first maximum in the rate of evolution of volatile material (peak A) occurs immediately power is switched on and is reached before there is any appreciable change in the tray temperature. Although the temperature at which peak B occurs is such that it could be due to volatiles from several parts of the still, it appears to be largely an artefact associated with the voltage reduction made at the end of the initial heating period. It seems likely therefore that the volatiles are produced from the porcelain of the cartridge heaters. Examination of the products revealed only water, in quantities of 0.5 - 1.5 mg. Presumably this is picked up during the time the still is open.

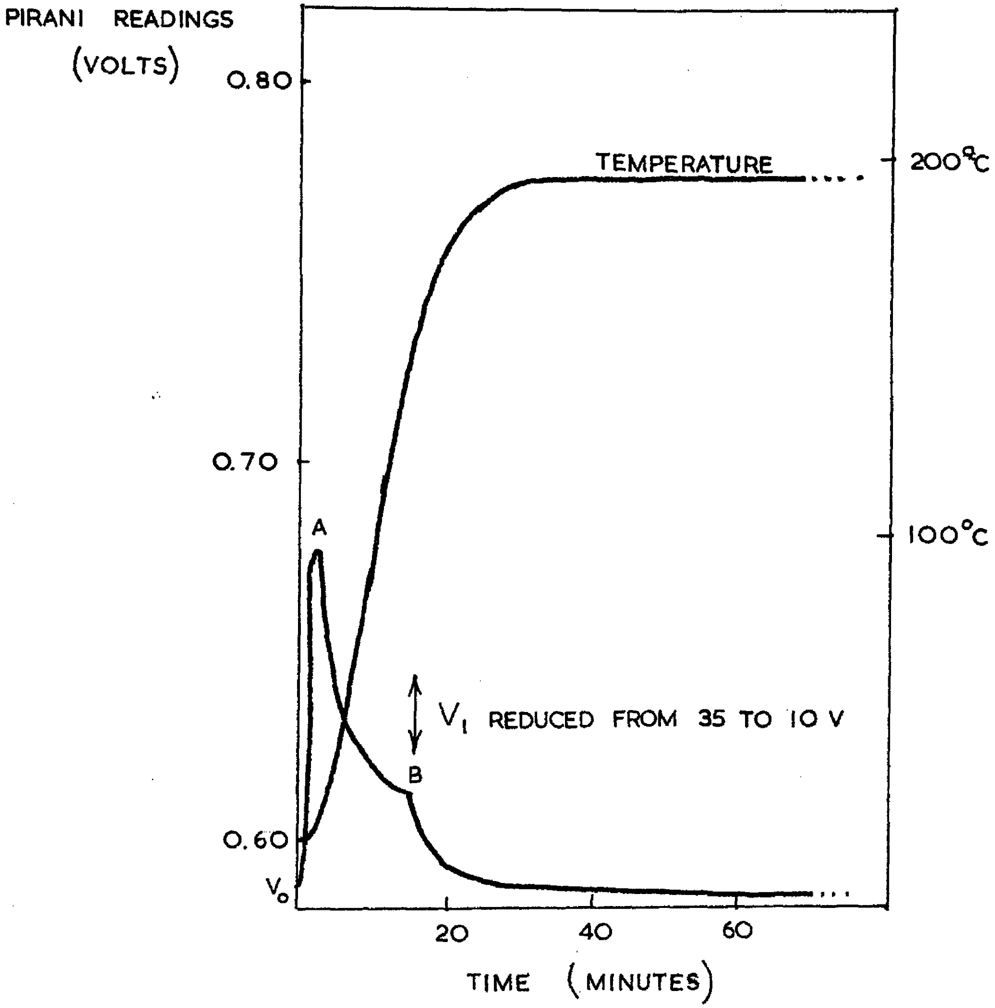


FIGURE 12 "BLANK" DEGRADATION SHOWING "BACKGROUND" PIRANI CURVE & TEMPERATURE ATTAINMENT

In "blank" degradations on the porous copper powder prepared by formic acid reduction of cupric oxide, peak B was slightly more pronounced and carbon dioxide was detected among the products by a combination of chemical and gas chromatographic techniques. The quantity was not sufficient to cause a measureable weight loss of tray and contents but both pressure and gas chromatography indicated that about 0.2mg of carbon dioxide was produced from 10 gm of powder. These observations were confirmed by heating copper samples in the secondary degradation system. It was shown by repeated heating and exposure to the air that the carbon dioxide arises from the atmosphere and not from the reduction method. The Hopkins and Williams copper which has a higher bulk density and was not porous did not give such effects.

THE SECONDARY DEGRADATION SYSTEM.

The best features of the d.m.s. are its direct measurement of volatilisation rate and the lack of uncertainty about uniform heating and temperature control. However in circumstances where volatilisation rates are not of primary importance and most interest lies in the reaction products the d.m.s. considered simply as a heating system possesses certain drawbacks.

Firstly, any non-volatile residue is contaminated with copper powder. It may of course be feasible to dissolve the residue and remove copper by filtration but in many cases, the residue is insoluble and infra-red methods of examination are the only ones available. Separation of copper and polymer in this case is a necessary but difficult operation.

Secondly, the slow heating-up period and the even slower cooling period make degradations for short intervals of time impracticable.

Thirdly, with regard to volatile products, not only will these contain the "background" products but if non-condensables are present, although detectable by the Pirani test (page 41), they will be lost in the normal method of operation. On the other hand if the reaction is carried out in a closed system the large volume (~ 2 litres) of the glass envelope would make it necessary to use a substantial quantity of polymer to obtain sufficient pressure of gas for an infra-red gas analysis.

For some degradation studies therefore it was more convenient to use the small-volume glass system already shown in figure 5. Analyses of the degradation products were generally confirmed by carrying out degradations in both systems. The secondary system was particularly useful in the high temperature breakdown of anhydropolymethacrylic acid (Chapter VII) where non-condensables were present. It was also used to degrade the KCl/polymer dispersions, where the ability to perform short time degradations was required.

Heating was provided by a metal bath controlled in the same manner as the heating block of the d.m.s. (Figure 13).

REMOVAL OF VOLATILE PRODUCTS OF DEGRADATION FROM SYSTEM

The vacuum system is designed to allow a certain flexibility in the after-treatment of volatile products. In general the products were redistilled under vacuum at room temperature into a relatively small weighed collecting vessel. A simple fractionation was then made by distillation from this vessel those products which were volatile at -78°C in vacuum.

Qualitatively these gases were examined by infra-red spectroscopy and gas chromatography after distillation into the appropriate collecting vessel. Quantitatively *iso*-butene was estimated in a calibrated capillary at -78°C with a correction for the vapour occupying the dead space.

The residual liquid non-volatile at $- 78^{\circ}$C was weighed directly, before it was examined further, generally by measuring an infra-red spectrum of a dried solution in carbon tetrachloride or chloroform.

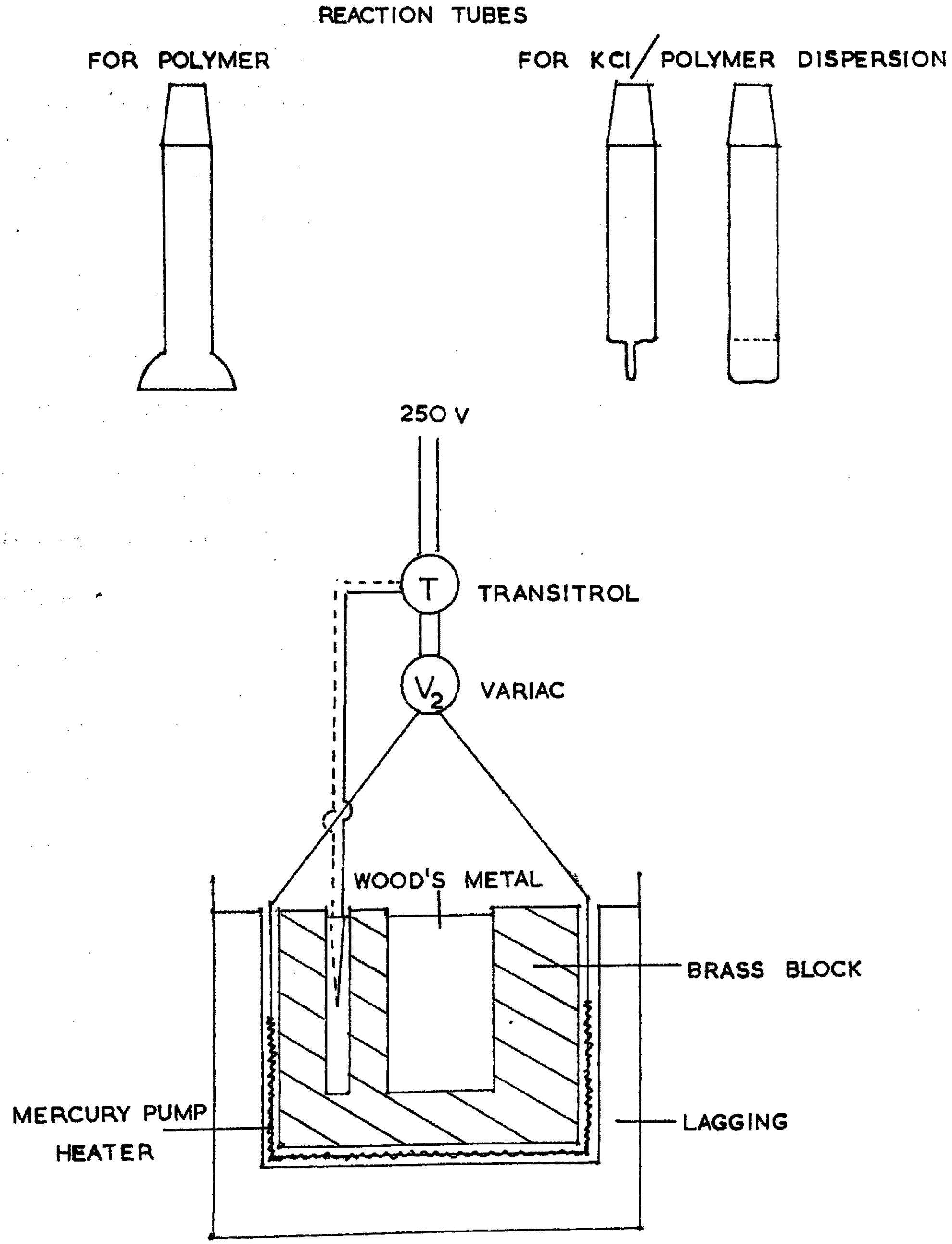


FIGURE 13 SECONDARY SYSTEM HEATING APPARATUS

VAPOUR PHASE CHROMATOGRAPHY

A useful analytical tool for the examination of degradation products is vapour phase chromatography (v.p.c.) owing to the ease with which the constituents of small samples can be separated.

Introduction of sample

All chromatograms were run on a Griffin & George Mark II apparatus. This machine is designed principally for use with liquids which can be introduced by syringe through a serum cap. One method of sample introduction which was used for gases was to withdraw a mixed sample of air and vapour with a 10 ml syringe and inject this into the system.

Since in many cases only one gas sample was required a less crude method could be used. The sample was distilled into a detachable U-shaped collecting vessel on the vacuum line, and isolated by turning the stopcocks. The serum cap was replaced by one limb of the U-tube, an air-tight seal being made by the rubber collar. The sample could then be introduced after the air was removed from the columns, by opening the stopcock.

Column Packing and Temperature

For gases non-condensable in liquid oxygen, satisfactory results were obtained by gas/solid chromatography on 60 - 100 mesh charcoal at room temperature with a flow rate of nitrogen carrier gas of 5 litres per hour: inlet pressure atmospheric.

For products volatile at -78°C gas/liquid chromatography on Silicone 301/Celite columns at room temperature was used. Inlet pressure atmospheric, nitrogen flow rate 1 litre per hour.

Little use was made of v.p.c. for the analysis of the liquid fractions since these generally contained either water, or acid or were obtained as dilute solutions. Infra-red methods were preferred.

INFRA-RED SPECTRA

Infra-red spectra between 4000 and 660 cm^{-1} were measured on a Perkin-Elmer Model 13 double beam spectrophotometer with sodium chloride prism. Spectra were measured of degradation products ranging from gases non-condensable in liquid oxygen to solids non-volatile in high vacuum at 380°C

Gases. (V_{-183} and V_{-78})

These were examined in a 10 cm gas cell with sodium chloride end plates.

Liquids ($V_{R.T.}$) and **Waxes** ($V_{D.T.}$)

For qualitative work these were examined preferably as thin films between sodium chloride "plates". Since in many cases of degradation water was a product this method could not always be used. In these cases the product was dissolved in carbon tetrachloride and dried over anhydrous sodium sulphate. The main functional groups present were detected from the solution spectrum between 4000 and 1500 cm^{-1} in a 5 mm cell with a similar cell containing pure solvent in the reference beam.

Quantitatively monomeric tert.-butyl methacrylate was estimated from the carbonyl peak heights of the spectra of solutions in chloroform of known volume. Figure 14 shows the Beer's Law calibration curve obtained from standard solutions, 0.5 mm sodium chloride cells were used.

Solids

Solid state spectra of polymers and related solid compounds were obtained from 0.5 - 2 mg of substance dispersed in a 300 mg disc of solid potassium chloride.

Qualitative Spectra: The solid was ground for two minutes in an agate mortar with dried potassium chloride under an infra-red lamp (to reduce adsorbtion of moisture from the atmosphere). The dispersion mixture was then pressed at 5000 lb. per sq. in. for five minutes, giving a transparent disc. In the measurement of the spectrum a "blank" disc containing only potassium chloride was placed in the reference beam.

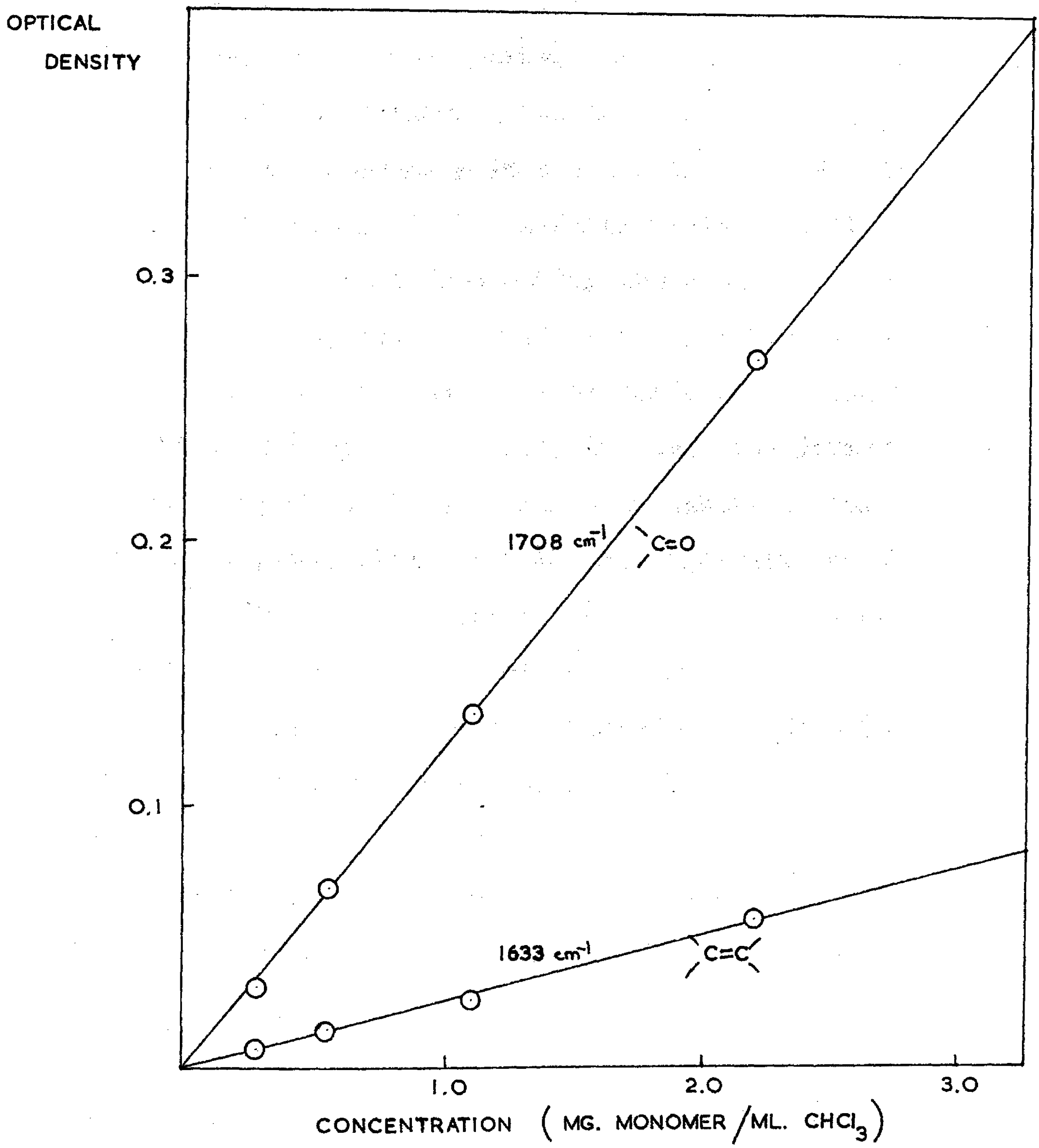


FIGURE 14 VERIFICATION OF BEER'S LAW

Since some of the degradation products cannot be ground to a satisfactory fine particle size, they give spectra with broad, ill-defined peaks. Better spectra were obtained by the following method. The undegraded polymers can be dispersed satisfactorily in KCl and the degradation products produced by heating the dispersion mixture in the secondary degradation system before making the disc.

Quantitative Spectra: Experimentally solid state spectra are usually regarded as the most difficult to place on a quantitative basis. Not only is there the difficulty in the handling of small quantities of materials for examination, but also there is the difficulty of the reproducibility of intensities depending to a great extent on particle size and particle size distribution.

Degradations have been followed semi-quantitatively by using heated intact KCl discs,[10] but only for reactions in which no volatile products occur

Some preliminary investigations were made into a method in which the disc was reground and the degradation carried out on the resulting powder before finally re-pressing the disc. It has been shown[34] that even with crystalline solids which grind readily, formation of a disc does not result in a solid solution but that particles retain their individuality. Degradation by this method should therefore still resemble solid phase reactions. It was found that the method was fairly satisfactory but had two drawbacks. Water adsorbed from the atmosphere could not be removed readily by heating in vacuum and after several cycles of grinding, heating and pressing KCl appears to lose some of its cohesive power since the discs become very brittle.

Instead of this "re-grinding" method an alternative method was used. Sufficient polymer for a number of discs was weighed and transferred to the agate mortar. The corresponding quantity of KCl was added slowly, with grinding. Since the agate mortar could not accommodate more than about 0.5 gm of mixture it was necessary to transfer the first quantity to a larger mortar. The remaining KCl after being finely ground was added to this. After being ground together the mixture was placed in a sealed vessel and shaken vigourously. Small quantities of this material were then ground again on the agate mortar. Finally the whole quantity was shaken again.

Approximately 320 mg of this dispersion mixture was heated for the required time. 300 mg of the degraded sample was then weighed accurately and pressed. It was shown by repeated sampling that the reproducibility of peak heights of spectra obtained by this method was about 5%.

CHAPTER III

PREPARATION, PROPERTIES AND POLYMERISATION OF <u>TERT</u>.-BUTYL METHACRYLATE

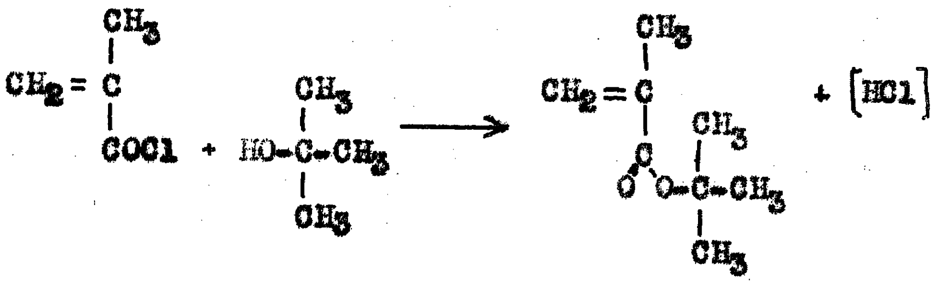
PREPARATION OF MONOMER AND RELATED SUBSTANCES

It is well known that it is difficult to prepare tertiary esters by the direct reaction between acid and tertiary alcohol. The forcing conditions sometimes used to overcome steric retardation cannot be used with compounds liable to polymerise and indirect methods have to be employed.

Because methyl methacrylate is commercially available alcoholysis or ester exchange methods have often been used to prepare other alkyl methacrylates, but this method is also unsuccessful when applied with <u>tert</u>.—butanol[35].

<u>Normal Method</u>

All previous preparations of <u>tert</u>.-butyl methacrylate have used the reaction between methacrylyl chloride and <u>tert</u>.-butanol or its sodium[36] or magnesium bromide derivative [27,37].



Pyridine is used to remove the HCl, in the method recommended by Heyboer and Staverman.[36] All the polymerisation and degradation studies were made using monomer prepared by this method.

1 mole methacrylyl chloride was added slowly, with stirring, to an ice-cold mixture of 1 mole <u>tert</u>-butanol, 2 moles pyridine, 1 gm copper powder and 0.1 gm hydroquinone. During the addition solid pyridine complexes precipitate, making stirring difficult.

After refluxing the reaction mixture for two hours and cooling, it was poured into two litres of normal hydrochloric acid to remove excess pyridine. The ester was extracted using 40 - 60° petroleum ether and dried over calcium chloride.

Petroleum ether was removed by distillation at atmospheric pressure and the monomer obtained by distillation under reduced pressure. Until required, monomer was stored at -18°C in the presence of hydroquinone (0.1%) as inhibitor. It was found that redistillation alone cannot remove the last traces of inhibitor and before use monomer was purified by washing with sodium hydroxide solution followed by distilled water. Finally, after drying overnight over calcium chloride, tert.-butyl methacrylate was distilled under reduced pressure. (38°C at 20 mm).

Yields average only 40% and the method could not be satisfactorily applied on a larger scale than described above; therefore it was necessary to repeat the reaction many times to obtain a reasonable quantity of monomer——in all about two litres were prepared.

Dimethyl aniline has been recommended as an alternative basic catalyst to pyridine [38]. It was found that tert.-butyl methacrylate could be prepared by this method in similar yields to the above. However it did not appear to offer any particular advantages and was not investigated further.

Methacrylyl Chloride.

Large quantities of this intermediate were required. Heyboer and Staverman[36] have discussed the objections to the action of the usual inorganic chlorinating agents on methacrylic acid and instead recommend benzene sulphonyl chloride. We used this substance in the early stages but found that benzoyl chloride [39] was cheaper and more satisfactory for large scale operation.

8 moles benzoyl chloride, 4 moles methacrylic acid and 0.8 gm hydroquinone were heated in a 2 litre flask, fitted with a 20 cm fractionating column. Methacrylyl chloride distills off directly, dissolved HCl being the only impurity. This may be removed by redistillation under reduced pressure. Yields 70 - 80%.

Anhydrides.

In connection with the identification of the degradation products (Chapters IV and V) it was necessary to prepare and to polymerise methacrylic anhydride. This monomer was obtained by the reaction between methacrylic acid and methacrylyl chloride in the presence of pyridine, a standard method of anhydride formation.[40] The corresponding saturated compound *iso*-butyric anhydride was prepared in the same way.

Glutaric anhydride was prepared by the action of acetyl chloride on glutaric acid.[41]

An Alternative Preparation of tert.-Butyl Methacrylate.

An alternative route to tertiary esters was suggested by Altschul.[42] For *tert*.-butyl esters it makes use of the equilibrium:

$$R{-}COOH + (CH_3)_2C{=}CH_2 \xrightleftharpoons{H^+} R{-}COOC(CH_3)_3$$

The method had not previously been applied to unsaturated acids but the mild conditions recommended[43] suggested that it might be suitable for such compounds.

1.5 moles *iso*-butene was condensed in a thick-walled reagent bottle cooled in CO_2/methanol (-78°C). A mixture of 0.5 mole methacrylic acid and 2 ml concentrated sulphuric acid was added, and the tightly stoppered bottle left overnight at room temperature. After recovering about 0.5 mole *iso*-butene from the reaction mixture, the residue was washed with sodium hydroxide to remove excess acid, then with distilled water and dried. Distillation as previously described yielded *tert*.-butyl methacrylate in 58% yield (based on methacrylic acid).

The method has since been applied to *tert*.-butyl acrylate with similar success.[44]

PREPARATION OF DIPHENYL PICRYL HYDRAZYL (DPPH)

For inhibition experiments the free radical DPPH was required. It was prepared by the method of Goldschmidt and Renn[45] outlined in figure 15. The only departure from the established method was the use of lithium aluminium hydride to reduce diphenylnitrosoamine.[46] The original reagent (zinc and acetic acid) gave only poor yields of impure products. Picryl chloride was prepared by the method of Boyer et al.[47]

The final product was recrystallised from an ether/chloroform mixture and obtained as violet-black prisms. It has been reported[48] that DPPH crystallised in this way

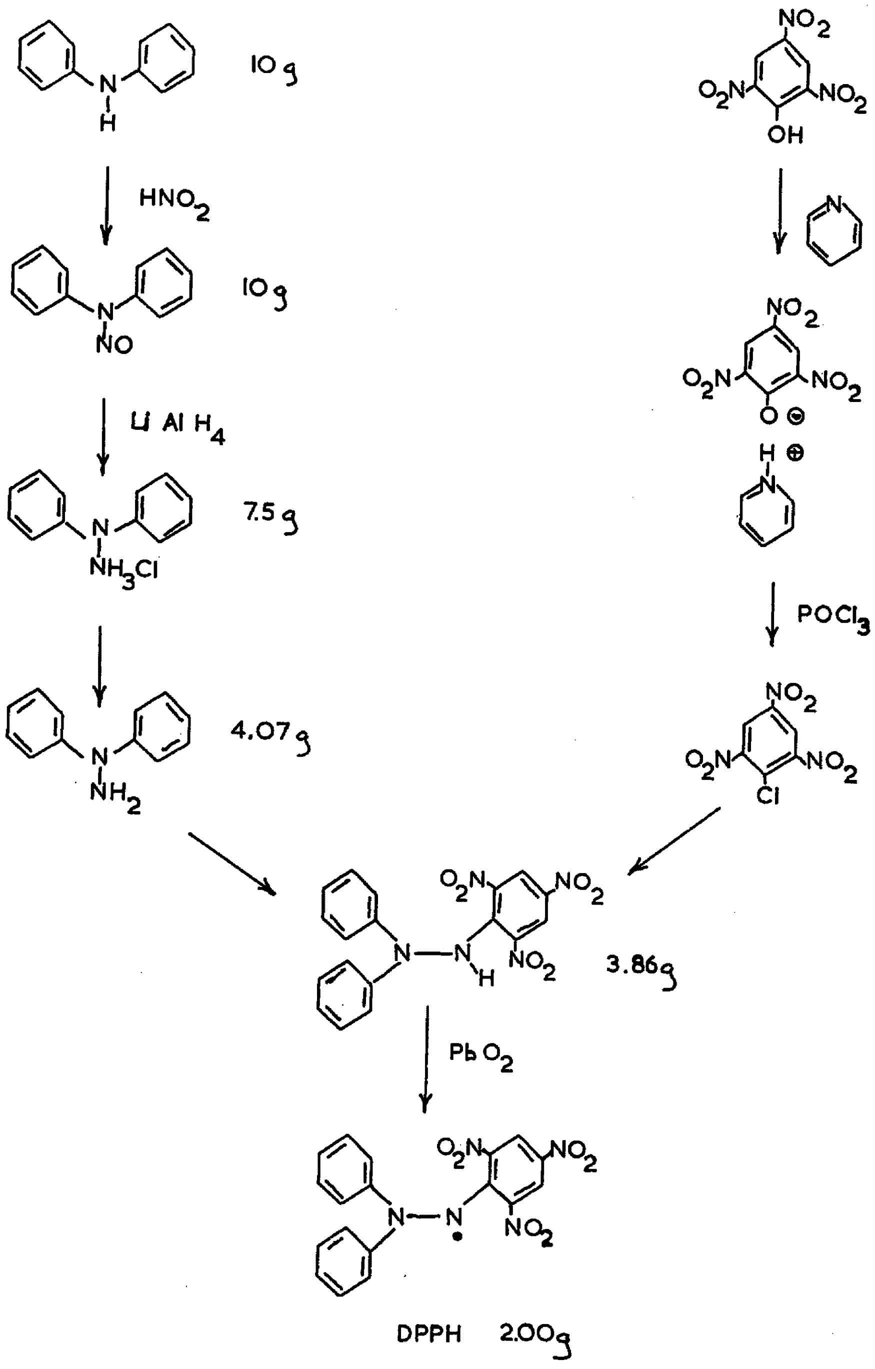


FIGURE 15. PREPARATION OF DIPHENYL PICRYL HYDRAZYL.

is a complex of approximate composition **n** DPPH : 1 $CHCl_3$ where **n**=3. Analysis of our product confirms the presence of chloroform but suggests that **n** lies somewhere between 3 and 4. In weighing the inhibitor corrections have been made for the presence of chloroform

Table 1. Analysis of DPPH

	%C	%H	%N	%Cl
Prepared as above	51.2	2.84	16.2	6.7
Lyons and Watson[48]	51.5	2.7	15.0	6.9
3 DPPH : 1 $CHCl_3$	50.7	2.84	16.2	8.2
4 DPPH : 1 $CHCl_3$	51.6	2.89	16.5	6.3

PHYSICAL PROPERTIES OF TERT.-BUTYL METHACRYLATE

Refractive Index.

Measurements of the refractive index of freshly distilled monomer were made on an Abbé refractometer These are seen to be in good agreement with those already available

Table 2. Refractive index of tert.-butyl methacrylate

Present work	$n_D^{21.5}$	1.4148
Bieber[37]	n_D^{25}	1.413
Crawford[27]	n_D^{20}	1.4143
Heyboer and Staverman[36]	n_D^{20}	1.4150

Ultra-Violet Spectrum

In order to control absorbtion during photochemical reactions and particularly to avoid "skin" effects it is necessary to know the absorbtion characteristics of the monomer in the visible and near ultra-violet.

The transmission curve of a 1 cm layer of monomer was therefore measured using a Hilger "Uvispek" spectrophotometer and is shown in figure 16.

Infra-red Spectrum

Checks on the purity of different samples of monomer were made by comparing the liquid phase spectra. Monomer prepared by the different routes mentioned above gave identical spectra; an example is shown in the appendix of Spectra, S1.

Assignment of frequencies. Most of the principal peaks in the spectrum can readily be assigned to specific vibrations using the accepted values quoted in standard reference works:

Bellamy, "Infra-red Spectra of Complex Molecules", (Methuen, 1954.)

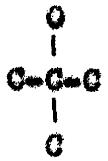
Techniques of Organic Chemistry, Volume IX, "Chemical Applications of Spectroscopy", (Interscience, 1956.)

Comparison was also made with the spectra of some other methacrylate esters and the saturated analogue tert.-butyl iso-butyrate (sample supplied by Mr R. W. Hay). The assignment of frequencies was of some help in considering the changes on degradation (Chapter VI).

Table 3. Assignment of frequencies of peaks in the infrared spectrum of tert.-butyl methacrylate.

Frequency (cm^{-1})	Intensity (relative)	Assignment
3570	w	Overtones of C=O and C=C stretching
3510		
3360		
3070	w	C-H stretching of $=CH_2$ group
2954	s	Assymmetrical C-H stretching of $-CH_3$'s
2910	s	Symmetrical " " " "
1993	w	? Overtone
1865	w	Overtone of 939 cm^{-1}
1708	s	C=O stretching
1633	s	C=C stretching
1474	s	Assymmetrical C-H bending of $-CH_3$'s in *tert.*-butyl group
1450	s	Assymmetrical C-H bending of $-CH_3$
1434	sh	Ethylenic C-H in plane bending
1390	s	Symmetrical C-H bending of $-CH_3$'s in *tert.*-butyl group
1366		
1331	s	Present in all methacrylate esters, probably arise from coupled stretchings of C-C and C-O of ester group. Only 1154 cm^{-1} is present in *tert.*-butyl *iso*-butyrate.
1308	s	
1154	s	
1011	m	
1254	s	*Tert.*-butyl skeleton. Suggested to be $C-CH_3$ rocking.
1205	sh	
1041	w	?
939	s	Out of plane bending of ethylenic C-H
867	m	? due to *tert.*-butyl group

Table 3. continued

Frequency (cm^{-1})	Intensity (relative)	Assignment
850	s	 $C-\overset{O}{\underset{C}{C}}-C$ skeleton
814	s	? $C=C$ torsion
755	m	? $C=C-C$ bending

DILATOMETRIC RELATIONSHIP

A convenient method of following a polymerisation reaction is by dilatometry since the density of a polymer is generally appreciably higher than that of the monomer from which it is derived. The method requires calibration by determining the relationship between decrease in volume of polymerising system and amount of polymer produced. Measurement of the quantity of polymer by precipitation and weighing has often been used but its accuracy depends upon the efficiency of precipitation. An alternative method, which was used in the present work, is independent of this limitation, and depends directly upon measurement of the densities of monomer and polymer.

The % shrinkage (%sh) on complete conversion of monomer to polymer is related to the volumes of initial monomer and derived polymer in the following way:

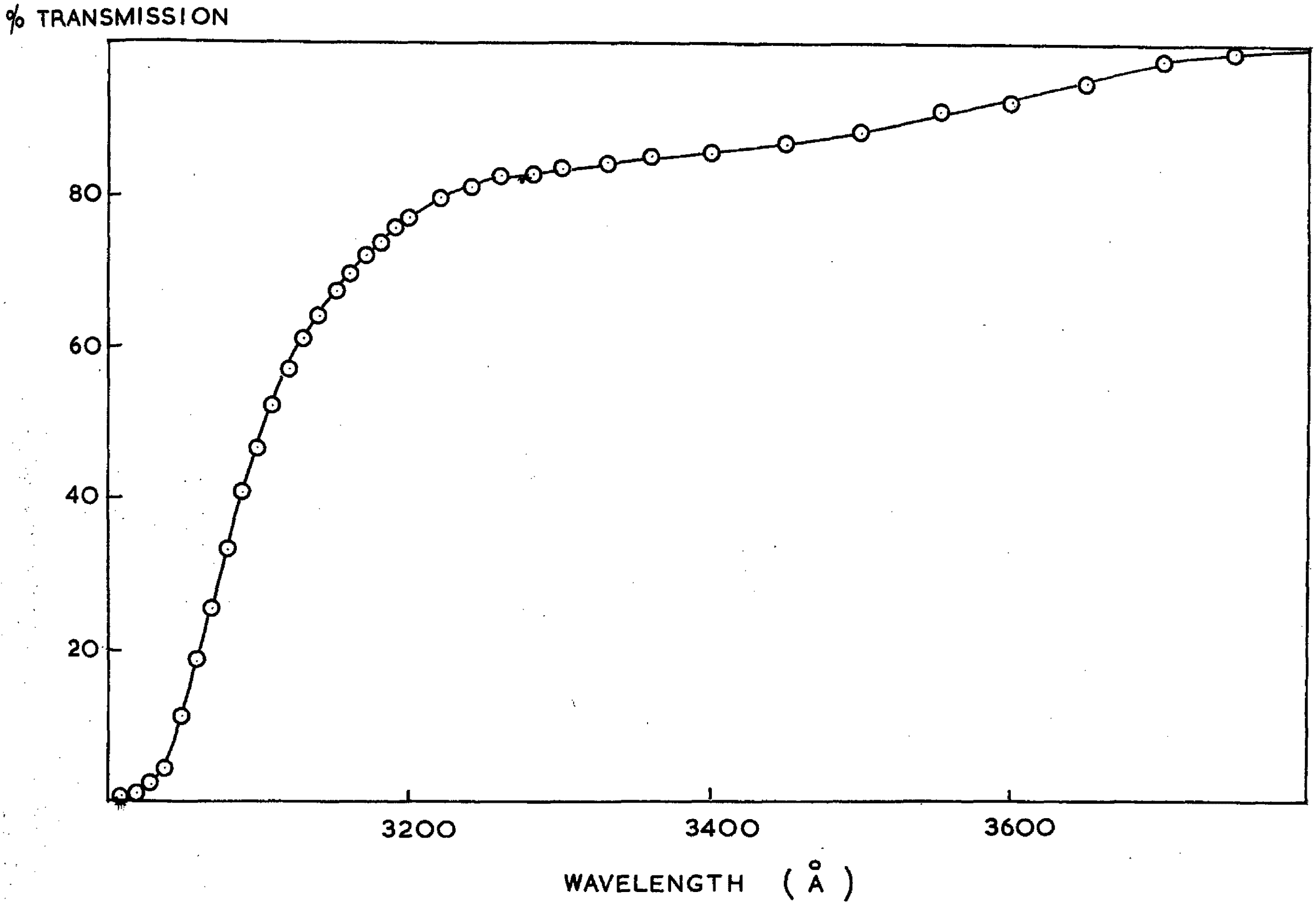


FIGURE 16. ULTRA-VIOLET SPECTRUM OF 1. CM. LAYER

OF TERT.-BUTYL METHACRYLATE

$$\%sh = \frac{V_m - V_p}{V_m} \times 100$$

$$= \frac{D_p - D_m}{D_p} \times 100$$

where V and D represent volumes and densities and m and p refer to monomer and polymer respectively.

Since D_m varies with temperature it is clear that %sh will also vary. Variations of D_p with temperature are usually small and it is quite common for %sh values to be obtained using D_p values (measured by flotation) at one temperature only. The main discrepancy in this method lies, however, in assuming that the density of the polymer in solution remains the same as in the solid state. It has been shown that this is not the case for polymethyl methacrylate and the use of the density of polymer in monomer solution has been recommended.[49] The method we have used is based on that of Matheson et al.[50]

An accurate determination of the density of freshly distilled monomer was made at a low temperature (20 and 30°C) using a large pyknometer constructed from Pyrex glass. It had previously been calibrated with distilled water at the same temperatures using densities obtained from the International Critical Tables. Results are

D_4^{20} (vacuo) 0.877_{16}

D_4^{30} (") 0.867_{26}

The cubical coefficient of expansion of monomer in Pyrex glass was measured over the range 20 - 90°C by observing the expansion and contraction in a dilatometer containing a known weight of monomer on raising and lowering the temperature in a large thermostat. Benzoquinone was added to the monomer to inhibit polymerisation. Reproducibility of readings at the same temperature showed that it was effective. Measurements were repeated several times and it was found that the volume of monomer at a temperature *t*°C is given by

$$V_t = V_{20} + V_{20}\alpha_t(t-20)$$

where V_t = volume at t°C

V_{20} = volume at 20°C

and α_t has the values in table 4

Table 4. Coefficient of expansion of monomer.

t (°C)	α_t
25	0.001125
30	0.001135
40	0.001150
50	0.001168
60	0.001185
70	0.001205
80	0.00122
90	0.00124

Knowing the weight of monomer it is now possible to calculate its volume at temperatures between 20 and 90°C.

Solutions of known weights of finely powdered polymer in monomer were made up in accurately calibrated dilatometers of about 25 ml capacity and after degassing the mixture, they were sealed in vacuum. The volume of the solution V_s was then determined at a range of temperatures.

$$V_p = V_s - V_m'$$

where V_m' is calculated from the weight of monomer as above. Corrections were made for the volume of the small quantity of benzoquinone added to inhibit polymerisation.

%sh could then be calculated since V_m, the volume occupied by a weight of monomer equal to the weight of polymer in the dilatometer, can also be calculated as above. The results of two determinations are shown in figure 17. and average values in table 5. This also gives the monomer concentration in the pure liquid, a term required in the evaluation of polymerisation rates in absolute units.

Table 5

t°C	[M] gm mole/l.	%sh
20	6.17	16.6
25	6.14	16.9
30	6.10	17.2
40	6.04	17.9
50	5.96	18.5
60	5.89	19.2

Table 5
(continued)

	t°C	[M] gm mole/l.	%sh
	70	5.81	19.8
	80	5.75	20.5
	90	5.68	21.2
by extrapolation			
	10	6.24	15.9
	0	6.31	15.3

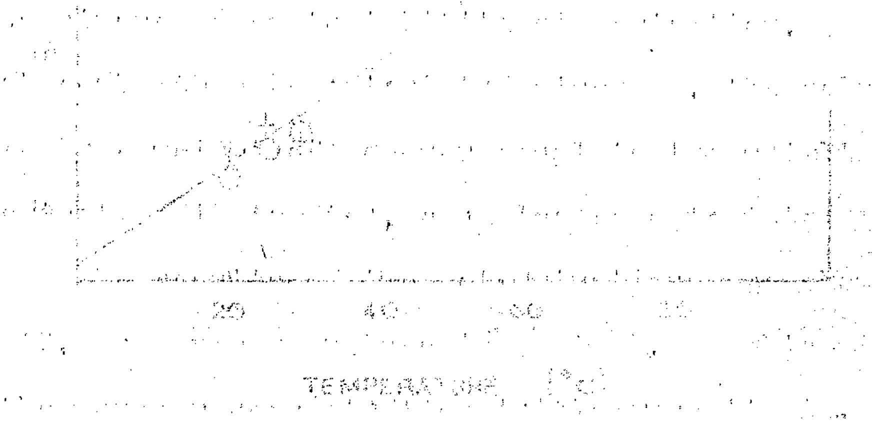


FIGURE 17 POLYMERISATION OF TERT-BUTYL METHACRYLATE

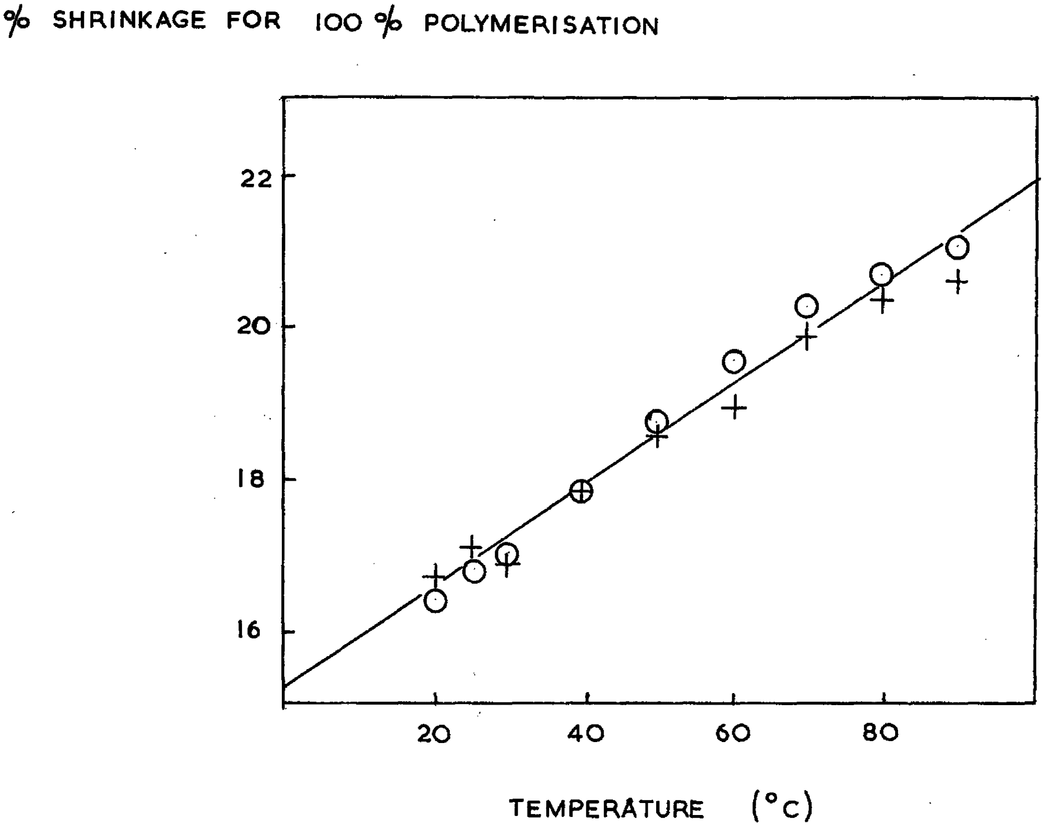


FIGURE 17 POLYMERISATION OF <u>TERT.</u>-BUTYL METHACRYLATE.

DILATOMETRIC RELATIONSHIP.

POLYMERISATION - PRELIMINARY INVESTIGATIONS

Thermal polymerisation

tert.-Butyl methacrylate resembles methyl methacrylate in polymerising slowly without added initiator. However the rates obtained are too low and irreproducible for kinetic work. Even at 80°C the rate is only approximately 2×10^{-6} mole $l.^{-1}$ sec^{-1} (~ 0.1% polymerisation per hour) which is negligible compared with "catalysed" rates.

Photopolymerisation

Rates of a similar order of magnitude are the highest obtainable when pure monomer at 25°C is irradiated using wavelengths greater than 3300 Å. On varying the intensity of the light by means of the intensity screens (page 28) it was shown that the rate varied with the square root of the incident light intensity (figure 18). The square root relationship is a feature of the kinetics of any system in which radical chain reactions are terminated by a bimolecular interaction, and is the "normal" behaviour of a vinyl radical polymerisation.

Thermally Catalysed and Photo-sensitised Polymerisation.

In order to obtain higher rates of polymerisation it is necessary to add a radical source or initiator to the system. When such an initiator decomposes by the action of heat alone then the polymerisation is described as

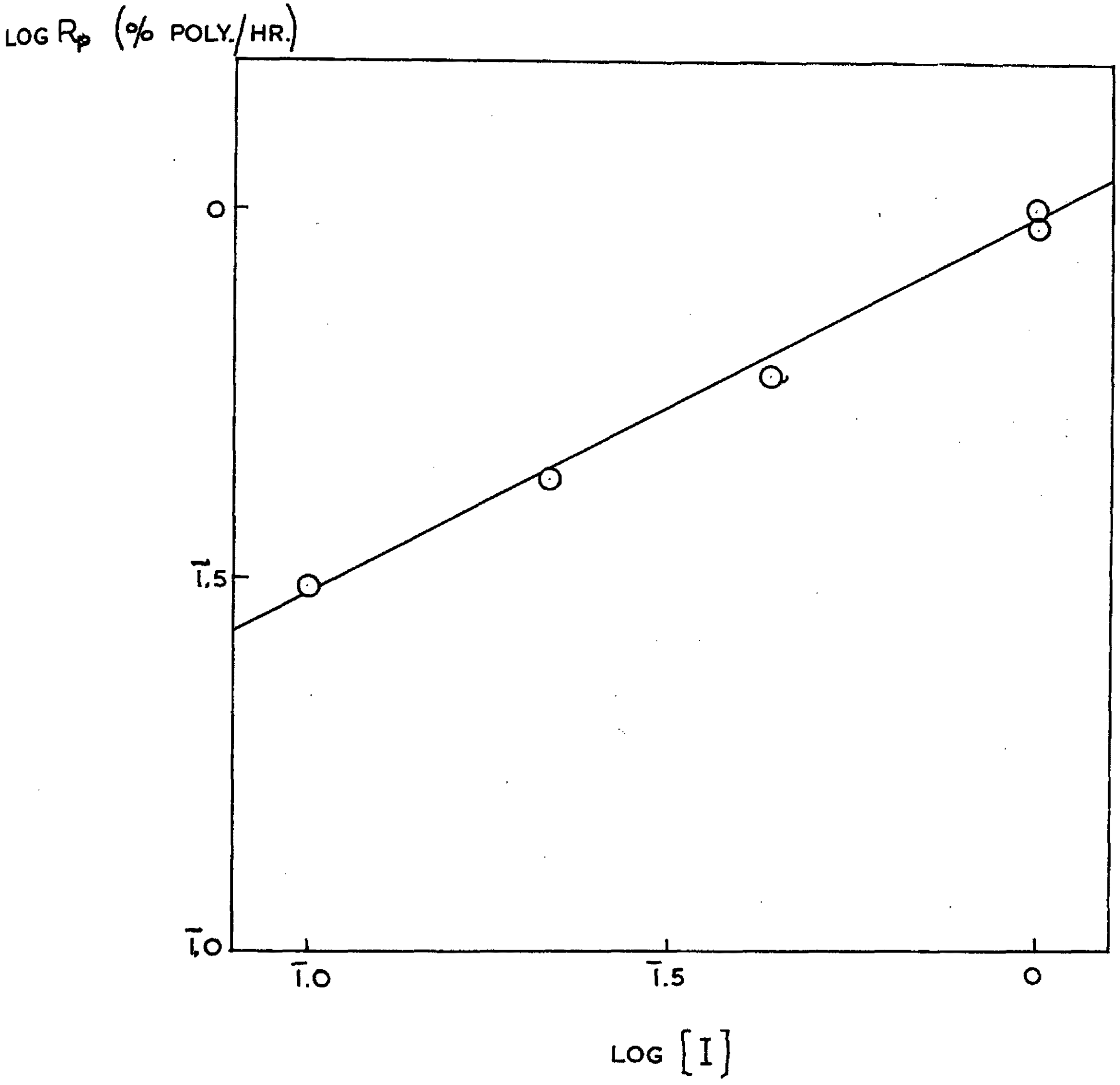
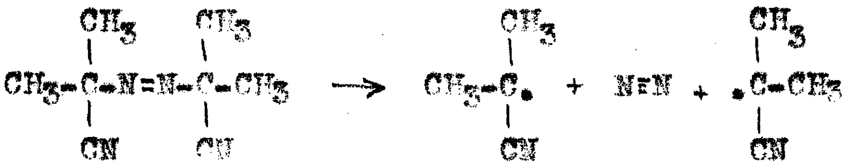


FIGURE 18 DEPENDENCE OF PHOTOPOLYMERISATION RATE ON INTENSITY.

LINE REPRESENTS THE CASE $R_p \propto [I]^{0.50}$.

thermally catalysed. The initiator may also decompose on irradiation, in which case the reaction is said to be photo-sensitised.

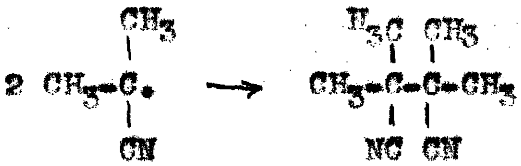
Choice of initiator and its decomposition mechanism. $\alpha\alpha'$Azo-di-iso-butyronitrile (AIBN) was used as polymerisation initiator. It is known to decompose to iso-butyronitrile radicals and nitrogen



$$\mathrm{CH_3-\overset{CH_3}{\underset{CN}{C}}-N{=}N-\overset{CH_3}{\underset{CN}{C}}-CH_3 \longrightarrow CH_3-\overset{CH_3}{\underset{CN}{C}}\cdot + N{\equiv}N + \cdot\overset{CH_3}{\underset{CN}{C}}-CH_3}$$

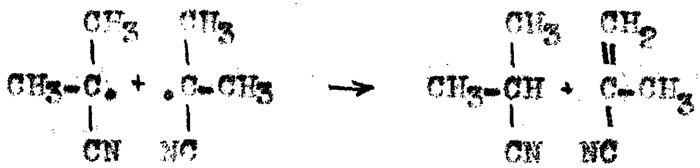
iso-Butyronitrile radicals can then initiate polymerisation, being themselves incorporated into the polymer chains as end groups, often important features in degradation reactions.

Only a fraction, f, of the radicals formed initiate polymerisation. Some indication of the fate of the remainder can be gained from the results of other investigators on the decomposition of AIBN in the absence of polymerisable monomers. Thus tetra-methyl-succinodinitrile (I), iso-butyronitrile (II) and methacrylonitrile (III) can arise from combination and disproportionation reactions between the radicals.



$$2\,\mathrm{CH_3-\overset{CH_3}{\underset{CN}{C}}\cdot \longrightarrow CH_3-\overset{H_3C}{\underset{NC}{C}}-\overset{CH_3}{\underset{CN}{C}}-CH_3}$$

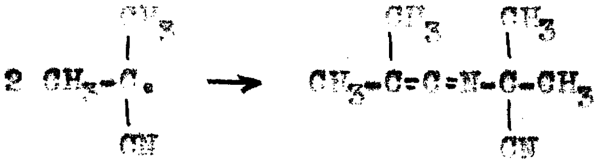
I



$$CH_3-\overset{CH_3}{\underset{CN}{C}}\cdot + \cdot\overset{CH_3}{\underset{NC}{C}}-CH_3 \rightarrow CH_3-\overset{CH_3}{\underset{CN}{CH}} + \overset{CH_2}{\overset{\|}{\underset{NC}{C}}}-CH_3$$

II III

Both tetra-methyl-succinodinitrile and *iso*-butyronitrile have been detected and estimated by an isotope dilution method.[51] A further unstable product which has been detected spectrophotometrically is the ketene-imine[52] (IV)



$$2\ CH_3-\overset{CH_3}{\underset{CN}{C}}\cdot \rightarrow CH_3-\overset{CH_3}{C}=C=N-\overset{CH_3}{\underset{CN}{C}}-CH_3$$

IV

AIBN was normally purified by a rapid recrystallisation from hot methanol. When heated in methanol for a longer period a small quantity of polymer-like products appeared. This was dissolved in acetone and reprecipitated in methanol. Sufficient material (2 mg) was obtained for the solid state (KCl disc) IR spectrum to be measured, (appendix of Spectra S2). This was identical with the spectrum of pure polymethacrylonitrile prepared at a similar temperature. While the existence of polymeric products has been reported previously, they do not appear to have been identified conclusively hitherto.

<u>Dependence of rate of polymerisation on initiator concentration.</u> Thermally catalysed polymerisation was studied over the temperature range 20 - 90°C. Figure

19 illustrates that the rate is proportional to the square root of the initiator concentration over a wide concentration range. Photo-sensitised polymerisation was studied over the temperature range 10 - 30°C and figures 20 and 21 illustrate that both intensity and sensitiser concentration exponents are 0.5 within experimental error. These results confirm that the termination reaction is normal, involving mutual destruction of pairs of radicals.

Dependence of rate of polymerisation on monomer concentration. Using a fixed initiator concentration of 7.8 x 10^{-3} gm mole/l. a value of 1.06 was obtained for the monomer concentration exponent at 50°C for polymerisations carried out in benzene solution, (figure 22). An order slightly greater than unity has been reported for methyl methacrylate and attributed to chain termination by solvent.[53] Alternatively a slight decrease in initiator decomposition rate or initiator efficiency with decreasing monomer concentration would have the same result.

Dependence of rate of polymerisation on extent of polymerisation. In kinetic work, initial rates of polymerisation are normally used. In practice, this is the average value over the first few per cent. conversion and unless otherwise stated the rates quoted have been obtained in that way. There is however, some interest

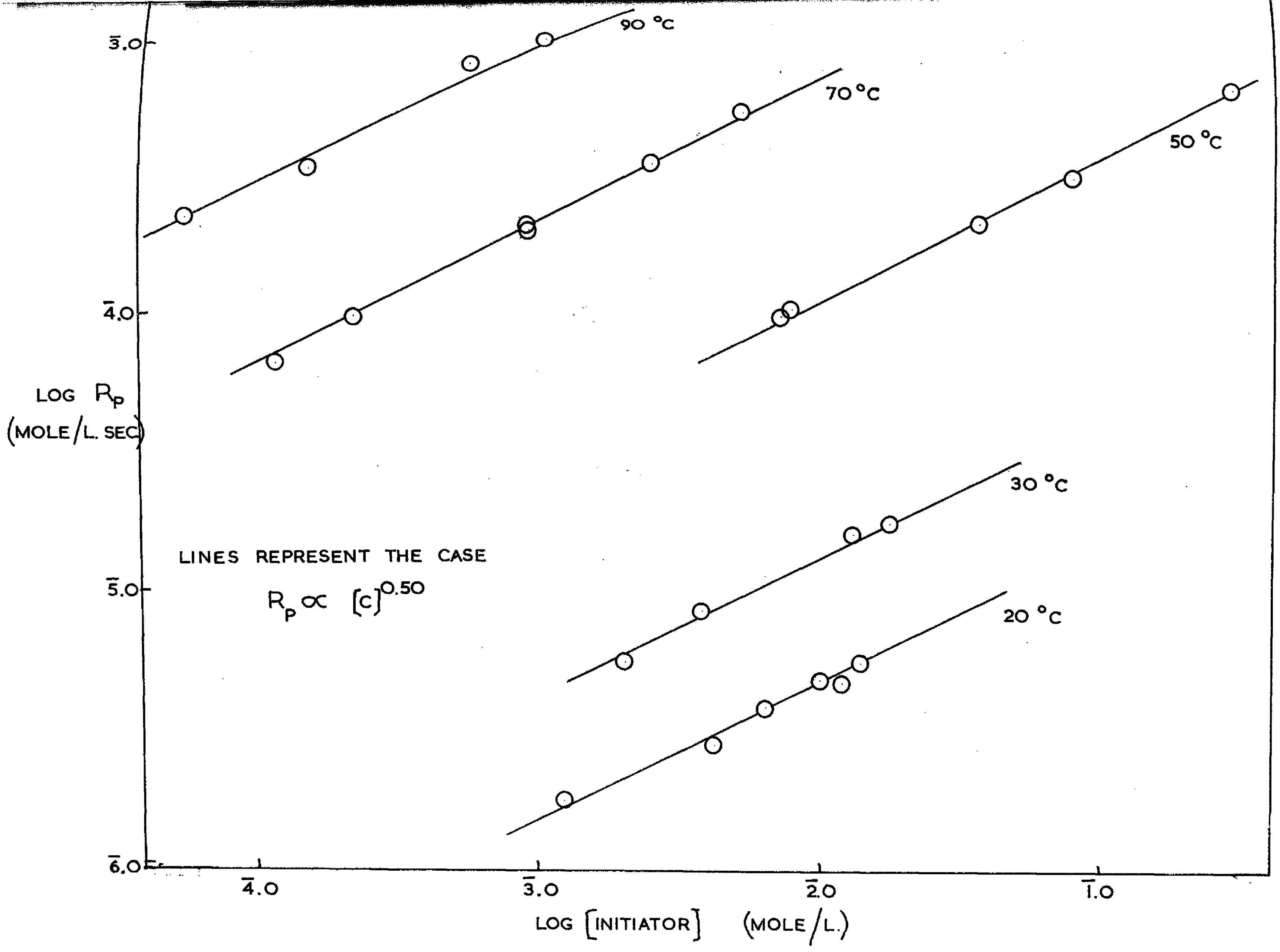


FIGURE 19 DEPENDENCE OF "CATALYSED" RATE ON INITIATOR CONCENTRATION

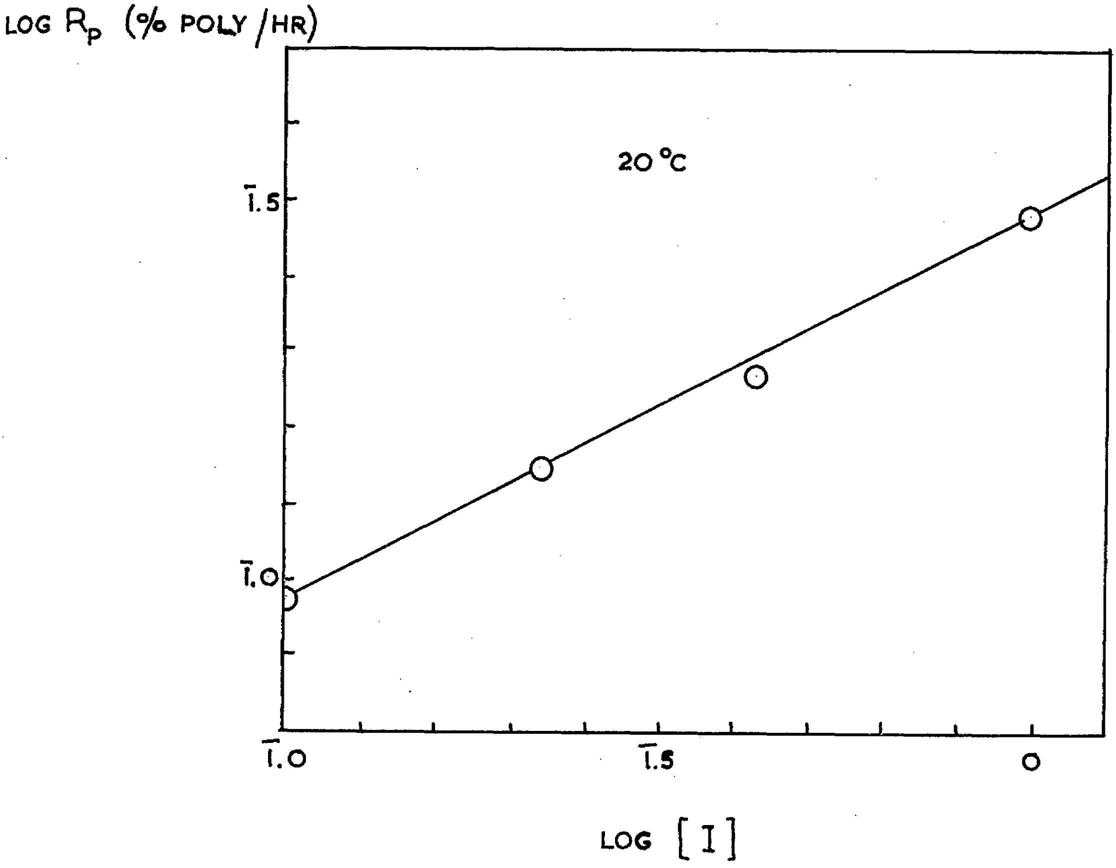


FIGURE 20 DEPENDENCE OF PHOTOSENSITISED RATE ON INTENSITY

LINE REPRESENTS THE CASE $R_p \propto [I]^{0.50}$

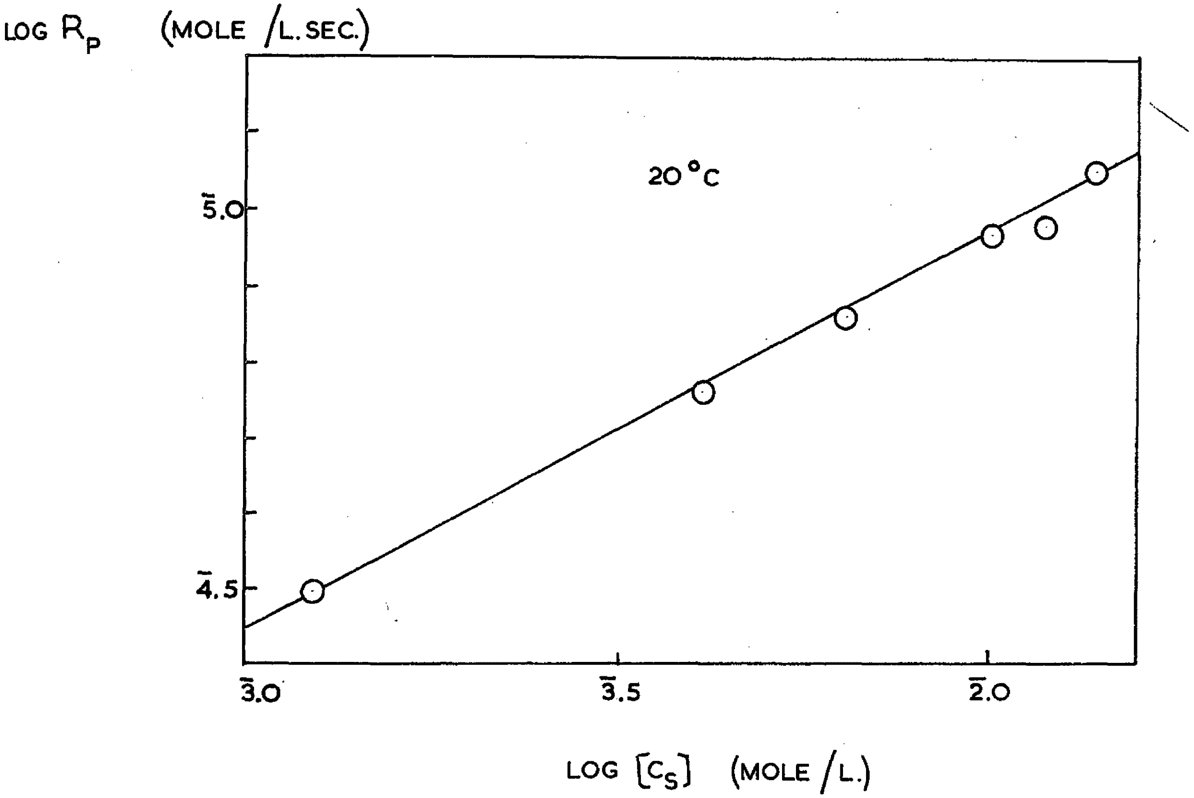


FIGURE 21. DEPENDENCE OF PHOTOSENSITISED RATE ON PHOTOSENSITISER CONCENTRATION.

LINE REPRESENTS THE CASE $R_p \propto [C_S]^{0.50}$

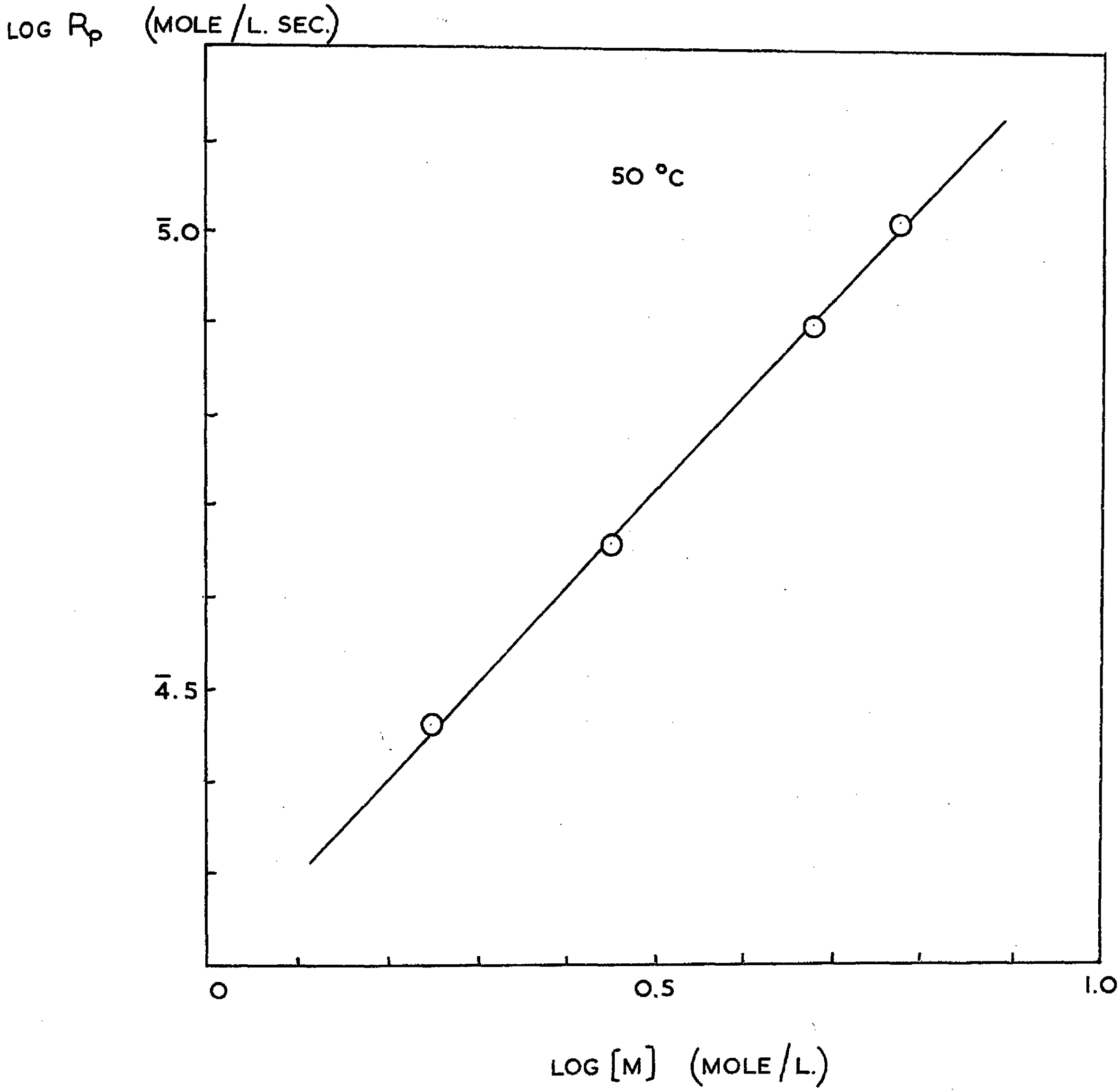


FIGURE 22. DEPENDENCE OF "CATALYSED" RATE ON MONOMER CONCENTRATION.

LINE REPRESENTS THE CASE $R_p \propto [M]^{1.06}$

in the rate at higher conversions and this was measured on some occasions.

It is to be expected that monomer depletion should cause a decrease in rate with increasing conversion, but in practice it has been found that several monomers including methyl and n-propyl methacrylates, exhibit an increase in polymerisation rate beyond 10% conversion. This "gel effect" has been attributed to diffusion control of the rate of termination in which interaction of two growing polymer radicals takes place in a viscous medium.

The rate of polymerisation of tert-butyl methacrylate decreases in the initial stages of conversion. Beyond 12 - 15% conversion, depending upon conditions, there is usually a period of steady rate followed by a gel effect. As with methyl methacrylate,[54] when the polymerisations are carried out in the presence of benzene, it is found that with increasing solvent concentration the steady rate and the gel effect shift to higher conversions or are suppressed completely. These properties of the system are illustrated in figure 23.

The initial decrease in rate is approximately first order with respect to monomer. It cannot be accounted for in terms of a decrease in initiator concentration which must be negligible during the course of the reaction.[55] The decrease in rate occurs in both thermally catalysed and photo-initiated and -sensitised polymerisations.

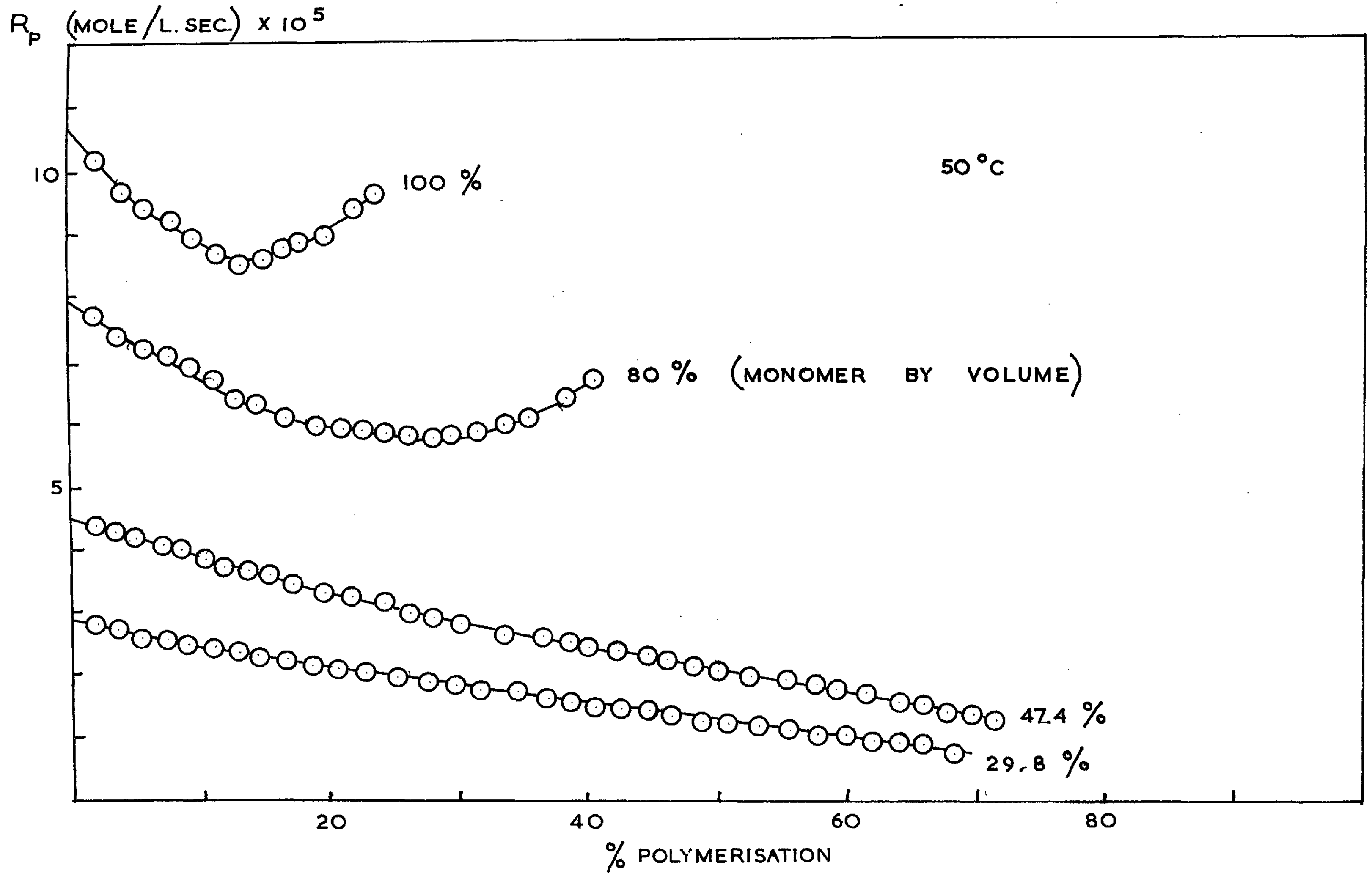


FIGURE 23. DEPENDENCE OF "CATALYSED" RATE ON EXTENT OF POLYMERISATION AND EFFECT OF DILUTION.

POLYMERISATION - DETERMINATION OF RATE CONSTANTS

The preliminary results outlined above are in accord with the usual kinetic scheme for radical polymerisation.[56] It follows that:

$$R_p = \frac{k_p}{k_t^{\frac{1}{2}}}[M]R_i^{\frac{1}{2}} \quad \ldots\ldots\ldots\ldots \quad (1)$$

in which k_p and k_t are the rate constants for propagation and termination respectively, $[M]$ is the concentration of monomer, and R_p and R_i are the rates of polymerisation and initiation respectively. k_p and k_t have been determined for a number of monomers and several established techniques are available.

Measurement of $k_p k_t^{-\frac{1}{2}}$ by the molecular weight method.

It can be shown that:

$$\frac{1}{P} = \frac{k_f}{k_p} + \frac{k_t}{k_p^2} \cdot \frac{R_p}{n[M]^2} \quad \ldots\ldots\ldots \quad (2)$$

in which k_f is the rate constant for transfer to monomer, P is the molecular chain length of the resulting polymer and n is 1 or 2 depending whether disproportionation or combination is the termination mechanism. Using this equation it was possible to obtain values of $k_p k_t^{-\frac{1}{2}}$.

Polymerisations were carried out at 50, 70 and 90°C over a range of initiator concentrations. Rates and molecular weights were measured and the results are represented in figure 24. $k_pk_t^{-\frac{1}{2}}$ values obtained from the slopes of the straight lines are shown in table 6 for $n=1$ and 2.

Table 6. $k_pk_t^{-\frac{1}{2}}$ values.

temp. (°C)	$k_pk_t^{-\frac{1}{2}}$ mol.-wt. method $n=1$	mol.-wt. method $n=2$	inhibitor method $m=1$
50	0.15	0.11	0.12
70	0.21	0.15	0.16
90	0.28	0.20	-

Intercepts on the $1/\bar{P}$ are small so that transfer is negligible: $(k_f/k_p \;\; 0.5 \times 10^{-4})$. These low k_f/k_p values combined with the relatively high $k_pk_t^{-\frac{1}{2}}$ values are reflected in the tendency to high molecular weights encountered with this polymer.

Measurement of $k_pk_t^{-\frac{1}{2}}$ by the inhibitor method.

The weakness of the molecular weight method resides in the doubt which exists about the value of n to be assumed. Direct determination of R_i (equation 1) by the inhibitor method is free from this complication. Using DPPH good agreement with other methods has been obtained in the benzoyl peroxide catalysed polymerisation of vinyl acetate[57] and the AIBN catalysed polymerisation of styrene.[58]

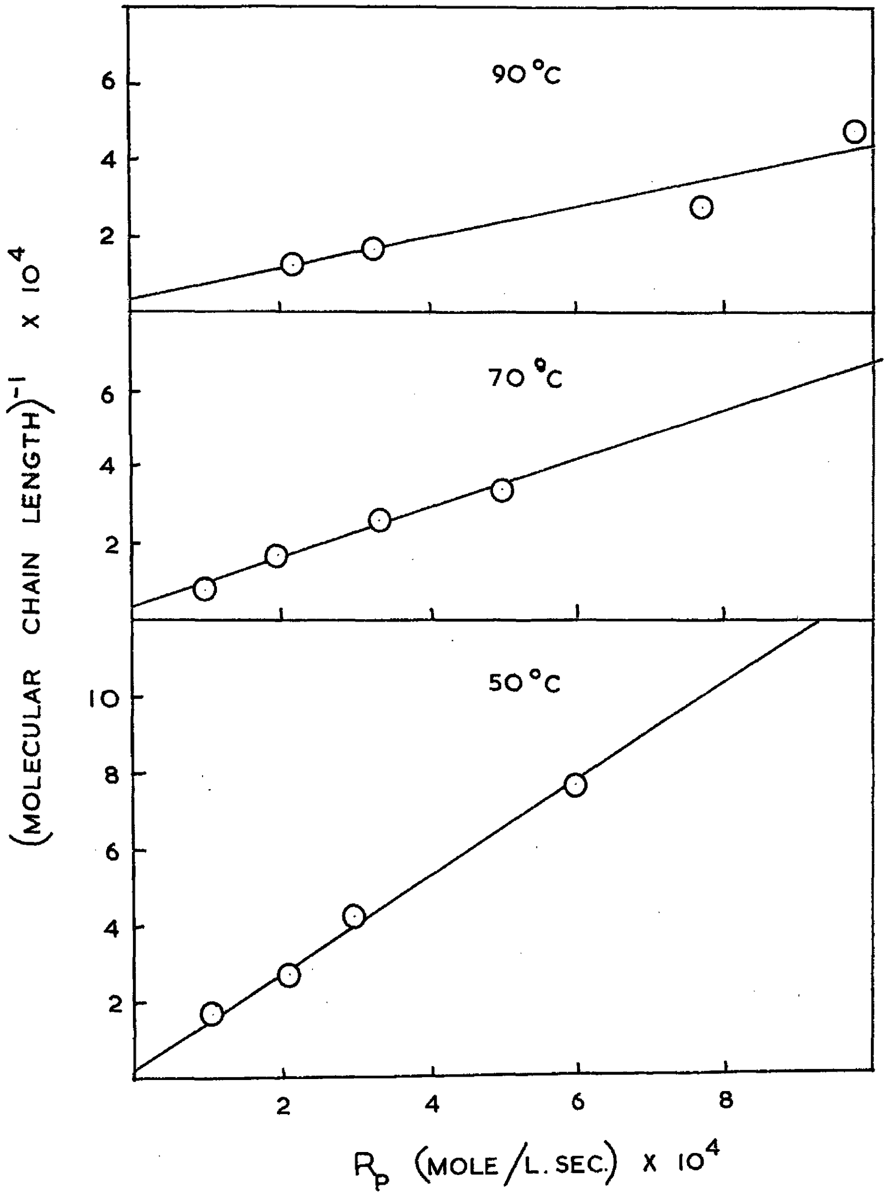


FIGURE 24. DETERMINATION OF $k_p k_T^{-1/2}$ BY THE MOLECULAR WEIGHT METHOD.

On the other hand, its use to measure the rate of radical production by various initiators in a variety of solvents[59] has recently been seriously questioned, a sensitivity to traces of oxygen and non-stoichiometry having been reported.[60] It has also been reported that this inhibitor underestimates the trapped radical concentration in polyacrylonitrile.[61] Since both molecular weight and inhibitor methods are applicable to the present system it was of interest to discover the extent of agreement which could be obtained between them.

The transition from zero to full rate is sharply defined in the inhibition of the polymerisation of tert.-butyl methacrylate by DPPH, (figure 25). The inhibition period obtained by extrapolation of the full rate portion of the curve back to the time axis is, however, exaggerated by two factors. First, there is the initial heating up period during which the rate of initiation increases to its maximum value, and secondly, an apparent inhibition period due to expansion by self heating at the onset of reaction counteracting contraction due to polymerisation.[62] Corrections were made in the following way and will decrease the error in our estimations of even the shortest inhibition periods reported to less than 5%. Soon after immersion of an uninhibited reaction mixture in the thermostat the dilatometer level passes through a maximum at which

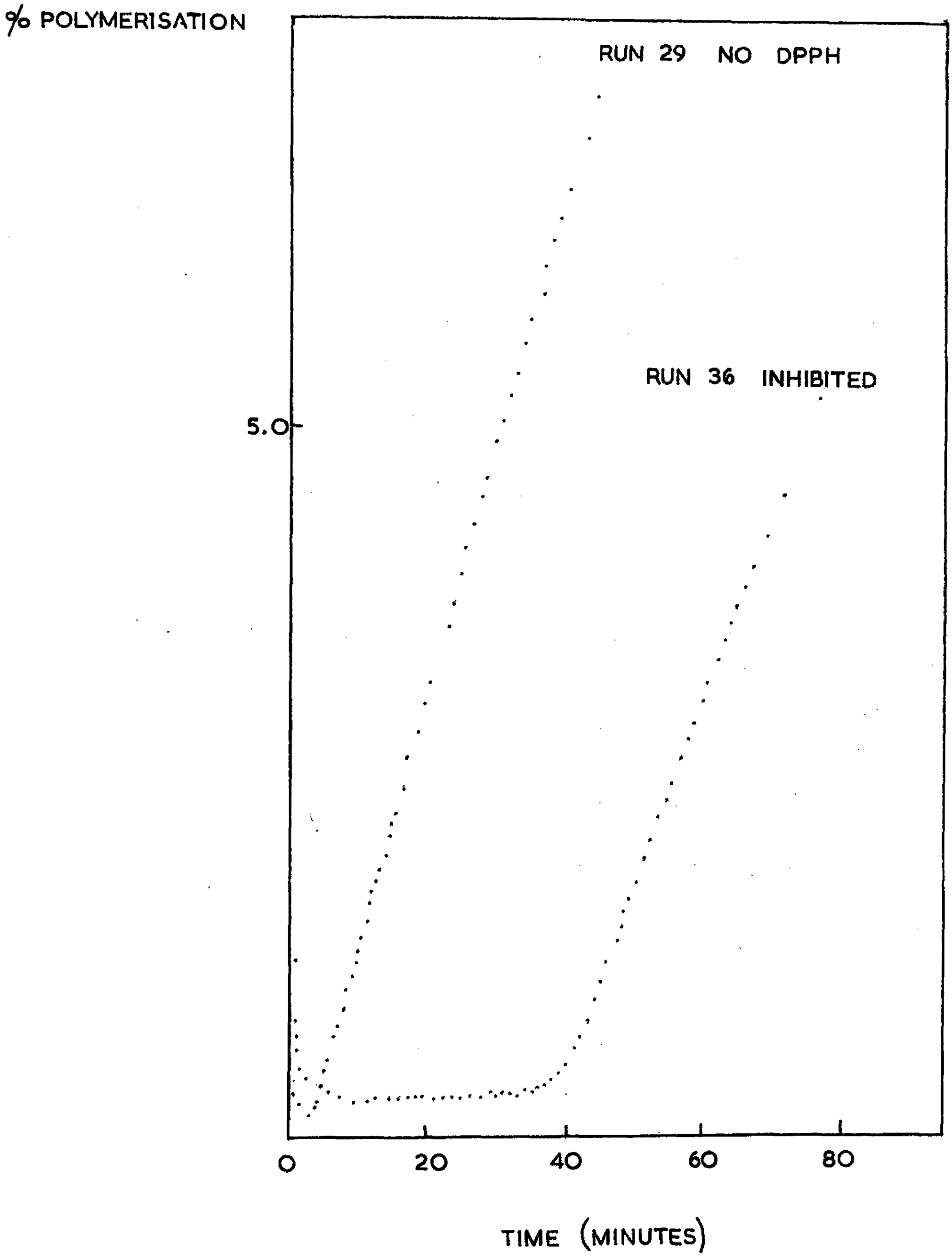


FIGURE 25. INDIVIDUAL READINGS DURING POLYMERISATION AT 50°C.

contraction due to polymerisation balances expansion due to rising temperature. The time at which this maximum occurs (usually about 3 minutes) was used as a correction for inhibited experiments whose rates of initiation were similar.

If the inhibition step can be represented by

$$mP\cdot + Z \longrightarrow \text{inactive products,}$$

in which **m** is the number of radicals destroyed by each inhibitor molecule, **Z**, then at constant initiation rate, inhibition periods will be proportional to the inhibitor concentration and

$$R_i = m\frac{[Z]}{t} \quad \ldots\ldots\ldots \quad (3)$$

in which **t** is the inhibition period. Since R_i is proportional to the catalyst concentration $[c]$ it follows from equation (3) that a plot of $[Z]/t$ against $[c]$ should be a straight line through the origin and this is confirmed in figure 26. If a value for **m** is assumed, R_i may be obtained from equation (3) and $k_p k_t^{-\frac{1}{2}}$ in turn from equation(1). $k_p k_t^{-\frac{1}{2}}$ Values obtained in this way at 50 and 70°C assuming $m=1$ are presented in the last column of table 6.

Initiation Efficiency and Choice of $k_p k_t^{-\frac{1}{2}}$ Values.

Values of the initiation efficiency, **f**, defined by

$$f = R_i/2k_d[c]$$

in which k_d is the rate constant for catalyst decomposition

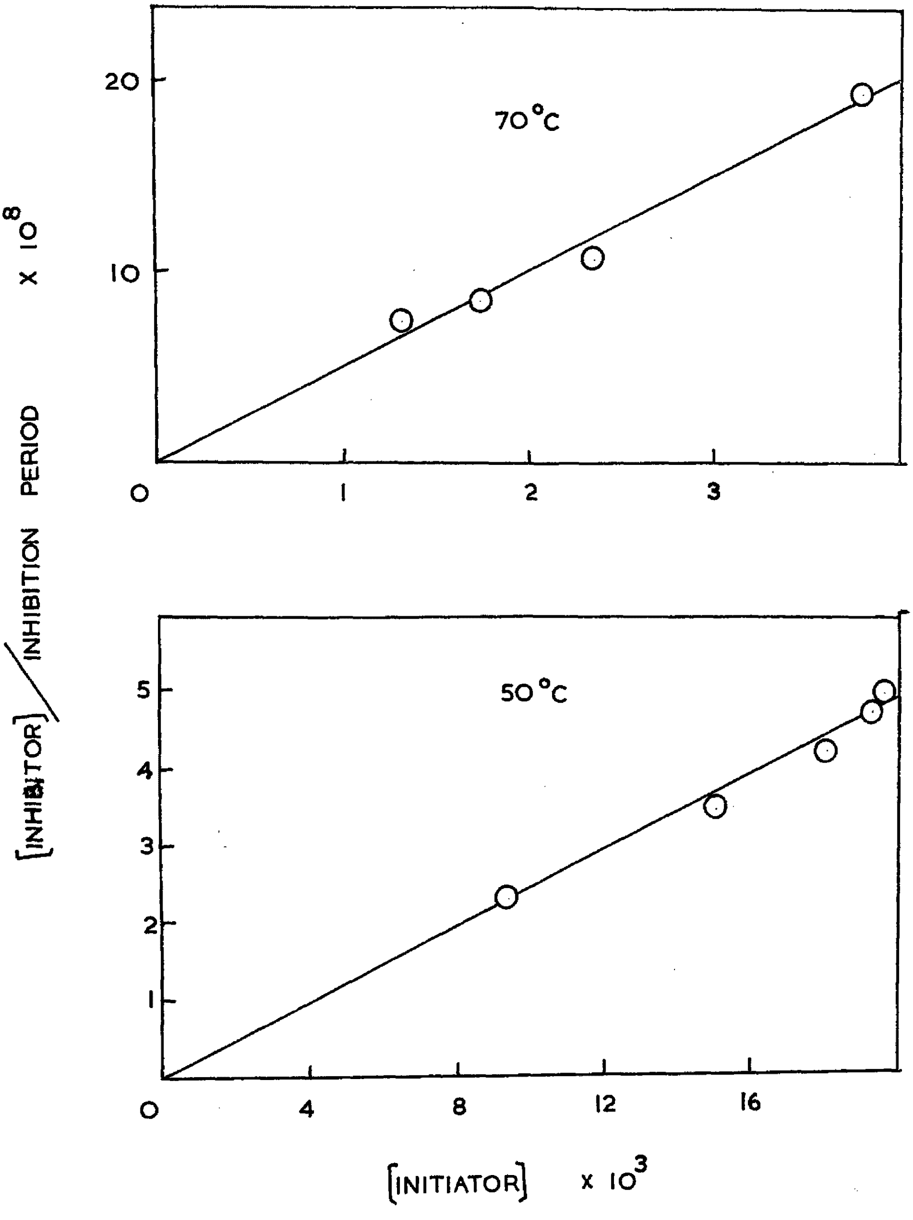


FIGURE 26. DETERMINATION OF $k_p k_T^{-1/2}$ BY THE INHIBITOR METHOD

have been calculated using[63] the value

$$k_d = 1.58 \times 10^{15} \exp(-30{,}800/RT)\ \mathrm{sec}^{-1}$$

and are presented in table 7.

Table 7. Initiation Efficiences

t (°C)	*f* (m.-w. method)	*f* (inhib. method)
50	0.32n	0.53m
70	0.38n	0.65m
90	0.35n	-

It has usually been assumed that *m*=1 so that it is tempting to conclude on the basis of tables 6 and 7 that *n*=2 and termination is by combination, and hence to use the $k_p k_t^{-\frac{1}{2}}$ values in column 3 of table 6. But independent evidence favours disproportionation as the dominant termination mechanism in the bulk polymerisation of methyl methacrylate in spite of the fact that this also leads to efficiency values of 0.3 - 0.4 [64] and 0.64 - 0.74 [65] using molecular weight and inhibitor methods respectively. These comparable discrepancies led us to examine more closely the mechanism of initiation by AIBN.

The existence of inefficient initiation processes was first discussed by Matheson.[66] It was suggested that there was competition for radicals between:

(1) reactions with substrate molecules (monomer or

inhibitor) and

(2) inter-radical reactions,

the latter being of importance in the early stages of initiator decomposition when the two radical fragments are contained in a cage of solvent molecules. On such a basis it would be expected that the efficiency of initiation would depend on the reactivity of the substrate. Later, Flory[67] pointed out that the inter-radical reactions within the cage would be much faster than diffusion out of the cage and that due to re-formation of initiator an equilibrium system is set up within the cage. Only those radicals which escape from the cage are capable of initiating polymerisation, and on this basis the efficiency would be independent of monomer reactivity.

At the time these ideas were put forward the only common initiator was benzoyl peroxide and it was on this compound that they were based. It seems not unreasonable to suggest that the mechanism of decomposition of AIBN is sufficiently different to show different kinetic features. It seems certain that the decomposition of the parent initiator is effectively into three entities, two _iso_-butyronitrile radicals and a nitrogen molecule. Re-formation of AIBN by a simultaneous attack of the two radicals on the nitrogen molecule seems a much more unlikely process than the corresponding combination of two benzoate radicals, and it is likely that any radical-radical interaction within the cage must lead to inactive products.

If this is the case then the results above would suggest that with the methacrylate esters DPPH is able to react with a large proportion of the radicals, while the smaller *f* value deduced from the molecular-weight method suggests that the monomer alone allows a larger amount of interaction between initiator fragment radicals.

This mechanism will also lead to a decrease in R_i or *f* with dilution. A small decrease in rate of polymerisation with decreasing monomer concentration has been observed with *tert*.-butyl (p. 85) and methyl methacrylates which could be the result of such a decrease in efficiency. Results have been reported[68] which show a lower efficiency in solution than in 100% monomer for the AIBN catalysed polymerisation of methyl methacrylate. These results may however be interpreted in a different fashion (p. 110)

With styrene the agreement between inhibitor and molecular weight methods is very much better, a fact which on the above hypothesis may be attributed to the greater reactivity of styrene monomer towards initiator radicals.[69]

The discrepancies between the results of molecular-weight and inhibitor experiments may thus be accounted for and $k_p k_t^{-\frac{1}{2}}$ values obtained by the molecular-weight method on the basis of disproportionation as the polymerisation termination mechanism accepted as the most reliable. Further evidence obtained in degradation experiments shows that poly-<u>tert</u>.-butyl methacrylate chain molecules contain ends capable of initiating depolymerisation at temperatures below 220°C. Similar results with polymethyl methacrylate have been interpreted,[25] as evidence for disproportionation as the termination mechanism. Extrapolating experimental results to 25°C: $k_p k_t^{-\frac{1}{2}} = 0.095_5$

Activation Energies.

From the above experimental results,

$$2E_p - E_t = 7.7 \text{ Kcal./mole.}$$

where E_p and E_t are the activation energies for propagation and termination respectively. Independent values of $2E_p - E_t$ have been obtained by standard methods from the overall energies of activation of the catalysed and photo-sensitised reactions: $2E_{overall} = 2E_p + E_d - E_t$ These depend upon assumptions being made about the energies E_d of the respective initiation processes and the agreement between the values obtained:

$$2E_p - E_t = 9.5 \text{ Kcal./mole.} \quad \text{(catalysed)}$$

$$2E_p - E_t = 6.6 \text{ Kcal./mole.} \quad \text{(photo-sensitised)}$$

and the previous value must be considered satisfactory. The first value is preferred because it is free of these assumptions.

Measurement of $k_pk_t^{-1}$.

In order to obtain individual values of k_p and k_t it is necessary to obtain another relationship between them. It can be shown that:

$$k_pk_t^{-1} = \tau . R_p . [M]^{-1}$$

in which τ is the lifetime of the growing radical. Thus determination of τ leads to the required relationship.

It has been established that both intensity and photosensitiser concentration exponents are close to 0.5. It is therefore possible to apply the method of intermittent illumination with Burnett and Melville's theoretical treatment[70] to obtain τ. Since the overall rate decreases in the initial stages of polymerisation, the rate at full intensity was measured before and after a period of intermittent illumination and the mean taken as R_o in calculating R_s/R_o in which R_s and R_o are the rates of polymerisation under intermittent and full illumination respectively. Radical lifetimes were obtained by the usual method of curve fitting to the experimental R_s/R_o against flash time curve, (figure 27). The theoretical curves were constructed from values quoted in reference 70 and by interpolation.

$k_pk_t^{-1}$ values obtained over a range of temperatures are presented in figure 28. The line was determined by the method of least squares and gives:

$$k_pk_t^{-1} = 2.60 \times 10^{-5} \text{ at } 25^\circ C$$

$$\text{and } E_p - E_t = 3.3 \text{ Kcal./mole.}$$

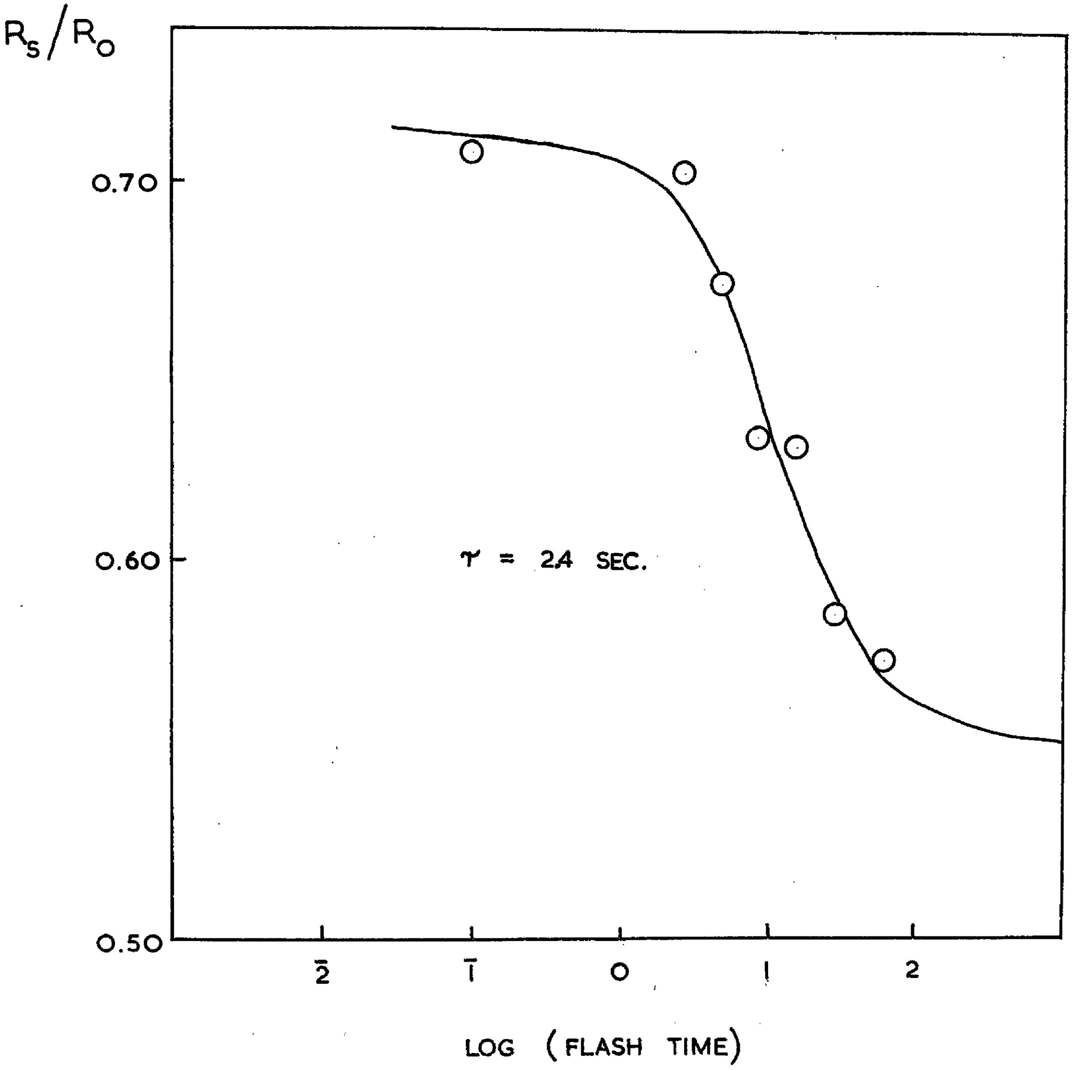


FIGURE 27. PHOTOSENSITISED POLYMERISATION

MATCHING OF EXPERIMENTAL POINTS WITH THEORETICAL CURVE.

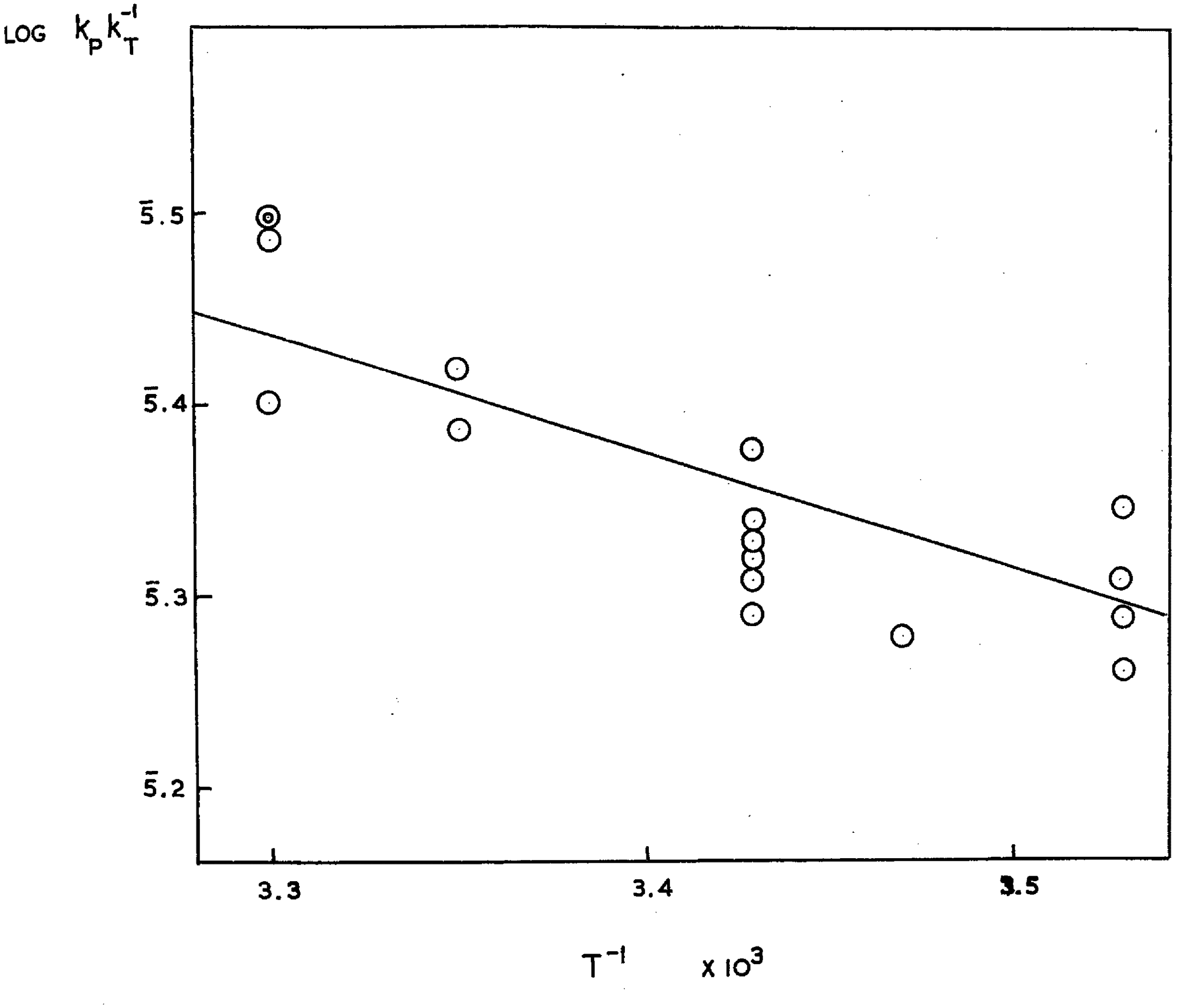


FIGURE 28. ARRHENIUS PLOT IN DETERMINATION OF $k_p k_T^{-1}$.

Individual Rate Constants and Comparison with other Monomers.

Individual rate constants and energies of activation were calculated and are given in table 8. along with those for other acrylate and methacrylate esters.

Table 8. Rate constants and energies of activation for acrylate and methacrylate esters.

monomer	t(°C)	k_p	$k_t(\times 10^{-6})$	E_p	E_t	Ref.
methyl methacrylate	30	286	24.4	6	2.8	50
	24	310	66	4.4	1	71
	24	313	47	3.6	-	72
n-propyl "	30	467	45	-	-	73
n-butyl "	30	369	10	4.5	-	73
tert-butyl "	25	350	14	4.4	1.1	present work
methyl acrylate	25	1580	55	-	-	73
	30	720	4.3	7.1	5.3	74
n-butyl "	25	13	0.018	2.1	0	75

The present result confirms Burnett, Evans and Melville's contention[73] that k_p is independent of the ester chain length in the methacrylate series and it is clear that the bulky *tert*.-butyl group decreases k_t only to a small extent, about the same as does the *n*-butyl group. The energies of activation available in the methacrylate series confirm that this is a steric effect. The decrease in k_t is relatively small compared with the decrease in the acrylate series; it is not known why this is so.

POLYMERISATION - RELATIONSHIP TO DEGRADATION REACTIONS

Investigation of the polymerisation of tert.-butyl methacrylate has not revealed any abnormal features by which it might differ from the usual vinyl monomer polymerisation. Determination of the rate constants for propagation and transfer and for termination together with the corresponding activation energies has shown that these do not differ greatly from the values reported for other methacrylate esters.

A comparable similarity in a wide range of methacrylate esters was also observed in the more limited investigation into the behaviour of tert.-butyl methacrylate and other methacrylates on copolymerisation.[28] These results show that the reactivity of tert.-butyl methacrylate towards a propagating radical resembles that of most other methacrylates, particularly the ethyl and iso-propyl esters.

It seems reasonable to conclude therefore that the structure of the polymer and probably some of its degradation characteristics should closely resemble those of polymethyl methacrylate.

POLYMERISATION - SOME COMMENTS ON THE TERMINATION MECHANISM

In considering the initiation and termination mechanisms in tert.-butyl methacrylate polymerisation a close examination was made of the evidence presented in the case of methyl methacrylate. This has revealed certain discrepancies in the evidence on which the termination mechanism has been concluded to be disproportionation.

The balance between disproportionation and combination seems to be a delicate one; thus it has been shown that changes in temperature of polymerisation can cause differences in termination mechanism. In all the results described below the same temperature (60°C) was used.

Using radio-active initiators Bevington[76] showed that the number of initiator fragments incorporated in a polymer chain was just over one in the case of methyl methacrylate polymerised in bulk (i.e. pure monomer). This is consistent with termination by disproportionation as the dominant mechanism. It was also shown that the number of initiator fragments was approximately the same when the polymerisation was carried out in 50% benzene solution. This was interpreted as showing that no appreciable transfer to benzene was occurring since this would reduce the number of initiator fragments per molecule.

From degradation studies Grassie and Melville[25] concluded that only one in two of the polymer chains possessed a readily degradable end. This, they suggested, was a double bond end. These results too, favoured disproportionation. Later, Grassie and Vance[77] made degradation studies on polymer prepared in 50% benzene solution. It was found that the proportion of readily degradable ends was reduced. This was interpreted as due to the occurrence of transfer reactions by which the number of saturated ends (including phenyl groups from the benzene) was increased relative to double bond ends which could arise only by disproportionation.

Now although both these sets of results favour disproportionation they are apparently in conflict as regards the occurrence of transfer in 50% benzene solution. One feature they have in common is the assumption that the termination mechanism does not change at all with dilution. If this assumption is not valid then the two results are no longer inconsistent. The number of initiator ends per molecule would be increased by combination and decreased by transfer and so the existence of small amounts of both might well leave the measured number of initiator ends per molecule apparently unchanged. On the other hand both combination and transfer would reduce the number of double bond ends and so explain the degradation results.

Reference has already been made to certain results which show a lower efficiency of initiation by AIBN in solution than in pure monomer.[68] The existence, in solution, of more termination by combination could provide an additional explanation of these results since the efficiency was determined from molecular weight methods, and as such its value depends on the assumption made for the termination mechanism.

It is suggested therefore that the balance between disproportionation and combination may be affected by the presence of solvent. It is certainly well established that the rate of termination can be altered by the viscosity of the medium as is shown by the 'gel effect' and it seems possible that the mechanism might also be altered. The gel effect is sometimes said to be evidence that methyl methacrylate is a 'bad' solvent for its polymer. With increasing concentrations of a 'good' solvent the gel effect becomes less pronounced so that in 50% benzene a gel effect does not occur.[54] As has been shown, tert.-butyl methacrylate behaves similarly. It may be significant that styrene which does not show any appreciable gel effect has a combination termination mechanism.

Finally it might be pointed out that early attempts to decide on the termination mechanism were made using model radicals.[79] Since the models were of low molecular weight, viscosity effects would be at a minimum, and it is interesting that destruction of the radicals is predominantly by combination.

CHAPTER IV

PYROLYSIS OF POLY-TERT.-BUTYL METHACRYLATE:

I: THE EXISTENCE OF SEVERAL REACTIONS.

PRODUCTS OF THE REACTION

The existence of several products.

A convenient point to start the discussion of the thermal degradation of poly-tert.-butyl methacrylate, at temperatures up to 200°C, is provided by the results of a re-examination of the work of Grassie and Mathewson (page 20).

Using the secondary degradation system (page 55) the reaction at 200°C was followed by measuring the pressure at room temperature developed in the U-tube by the degradation products. The method was similar to the one employed by Grassie and Mathewson and figure 29. shows the existence of an increase in rate as degradation proceeds, as was previously observed. The successful application of this simple technique requires that the volatile product should be completely vapourised at the temperature at which pressure measurements were made. This would be the case for iso-butene (b.p. -6°C). However, it was observed that in the U-tube there were drops of liquid which did not

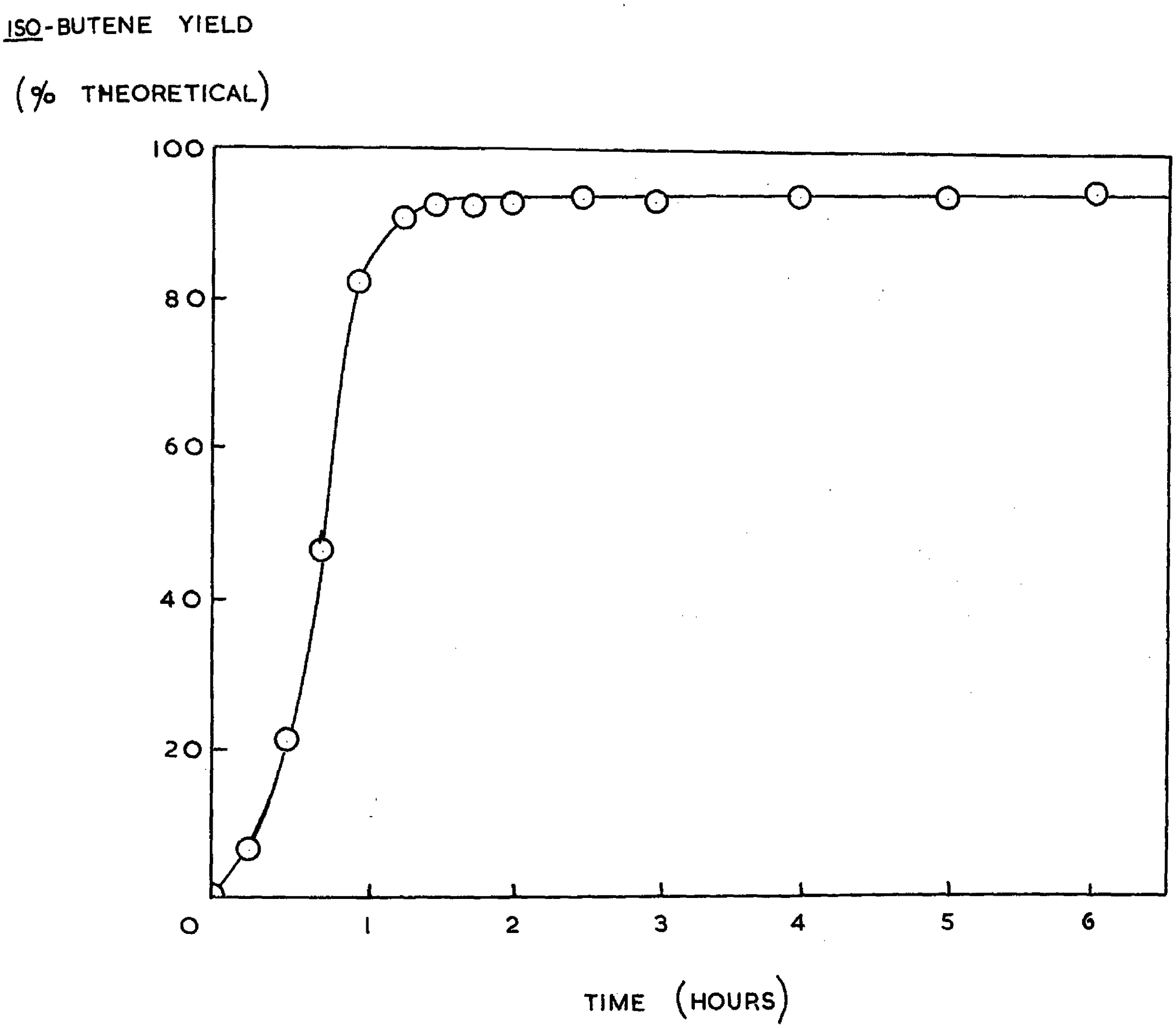


FIGURE 29. PYROLYSIS OF POLY-*TERT*.-BUTYL METHACRYLATE AT 200°C

AUTOCATALYSIS DEMONSTRATED IN "STATIC" SYSTEM.

evaporate at room temperature. It was concluded that iso-butene was not the only volatile product.

Identification of Products.

Degradations in closed systems and Pirani Tests (page 41) carried out during runs in the dynamic molecular still (d.m.s.) failed to detect any material which could not be completely condensed at -183°C.

The fraction (V_{-78}) which could be distilled in vacuum from solid CO_2/methanol mixtures was examined by infra-red and vapour phase chromatographic techniques. Although the spectrum of the gas was identical with that of a pure sample of iso-butene, v.p.c. showed that a trace of carbon dioxide was present. This could be accounted for as having been adsorbed on the copper powder, (page 55). The quantity of iso-butene was estimated in a calibrated capillary; it amounted to 35.3% by weight of the original polymer, compared with a theoretical content of 39.4%.

The liquid product (V_{RT}) volatile in vacuum at room temperature amounted to 10.7% of the original polymer. This was not homogeneous; two layers were observed. The characteristic smell of tert.-butyl methacrylate indicated that one of these was monomer. Positive identification of the denser liquid as water was made on the products of separate experiments by the usual tests, namely, colouration of anhydrous copper sulphate and a refractive index of 1.333.

Water would of course attack the sodium chloride "plates" used for infra-red samples but it was shown that a drop of this layer of product between pressed discs of pure potassium chloride gave the same infra-red spectrum as water does. The spectrum between 3600 and 1600 cm^{-1} of a dried solution in carbon tetrachloride of the liquid fraction was measured. In addition to the expected C-H, C=O and C=C absorbtion peaks of the monomer a small (sharp) peak occurred at 3525 cm^{-1}. This is the free O-H stretching frequency shown by <u>methacrylic acid</u> in dilute solution. By comparison with the spectra of standard solutions the amount was estimated at about 0.2% of the original polymer. The absence of similar peaks at higher frequencies showed that possible yields of <u>tert</u>.-butanol or methanol (polymer precipitant) were negligeable (certainly less than 0.5%). Additional C-H absorbtion attributed to $-CH_2-$ groups was also present. Since this did not appear in the spectrum of products from more thoroughly dried polymer (technique page 33) it was concluded that it arose from traces of <u>dioxane</u> (polymer solvent).

According to the previous work the residue (52.3%) should have been polymethacrylic acid. The additional loss in weight, associated with the production of water suggested that the residue might be an anhydride of polymethacrylic acid. Both the residue and authentic polymethacrylic acid were insoluble in the usual solvents suitable for infra-red spectroscopy and although polymethacrylic acid gave a satisfactory spectrum by the potassium chloride disc technique (page 61), the residue was soft and difficult to grind to the necessary fine particle size. Consequently the peaks were much broader than normal. In spite of this, it was immediately obvious by a comparison of the two spectra (Appendix of Spectra, S3 and S4.) that the residue was not polymethacrylic acid.

The spectrum of the residue shows the characteristic twin carbonyl peaks (1795 and 1750 cm^{-1}) of an anhydride together with the less distinctive C-O-C peak at 1022 cm^{-1}. This identification was later confirmed when it was shown that an identical spectrum was given by the product of the polymerisation of methacrylic anhydride. In spite of the identity of these two spectra there was a slight difference in physical properties of the two anhydrides and it will be convenient to refer to the pyrolysis product as "anhydropolymethacrylic acid" to distinguish it from the polymerisation product polymethacrylic anhydride.

Summary of Quantitative Analyses of Products.

Reactions in the d.m.s. were principally of interest in showing the variations in rates of production of volatiles but at the same time some of them were used to confirm the above analysis of the reaction products. These results are shown in table 9.

Table 9. Analysis of Reaction Products.

Temp. °C	Polymer mg.	Residue %	*iso*-Butene %	V_{RT} %	Monomer %
220	146.8	54.0	-	-	-
200	126.3	53.4	34.8	-	-
200	95.4	53.2	36.3	-	-
200	63.6	54.9	-	-	-
200	60.1	50.8	34.8	-	2.4
200	59.1	53.5	34.8	-	-
200	57.6	56.3	32.6	-	-
200	57.5	54.5	-	-	-
200	57.4	49.3	34.7	-	2.3
192.5	53.6	53.8	34.3	12.3	2.3
192.5	51.6	54.5	31.0	11.6	3.0
192.5	51.5	52.5	32.6	10.9	4.6
192.5	51.2	55.3	31.0	9.8	2.4
181	49.5	52.0	31.2	12.5	2.9

RATES OF PRODUCTION OF VOLATILES

The Existence of several Rate Maxima.

Because the volatiles produced from the degrading polymer contain several substances each with differing thermal conductivity it would not be expected that Pirani gauge readings could give a direct measure of the rate of *iso*-butene production; nevertheless, Pirani readings of the d.m.s. during a degradation should still give a qualitative picture of the changes in the rate of evolution of volatiles.

Series of thermal degradations in the d.m.s. were carried out at 200°, 192.5° and 181°C. A typical curve of Pirani readings against time is shown in figure 30. In discussing the various peaks, representing volatilisation rate maxima, it is convenient to use the notation shown in the figure.

Peaks A and B are independent of temperature and quantity of polymer, indeed they occur in the absence of polymer and are a feature of the degradation system (page 53). They need not be discussed further.

In the degradations at the lower temperatures peak C occurs at the attainment of the reaction temperature by the copper tray but the rate has already passed its maximum and is decreasing before 200°C is reached in that particular series. But for the failure to detect appreciable quantities of such solvents and/or precipitants among the

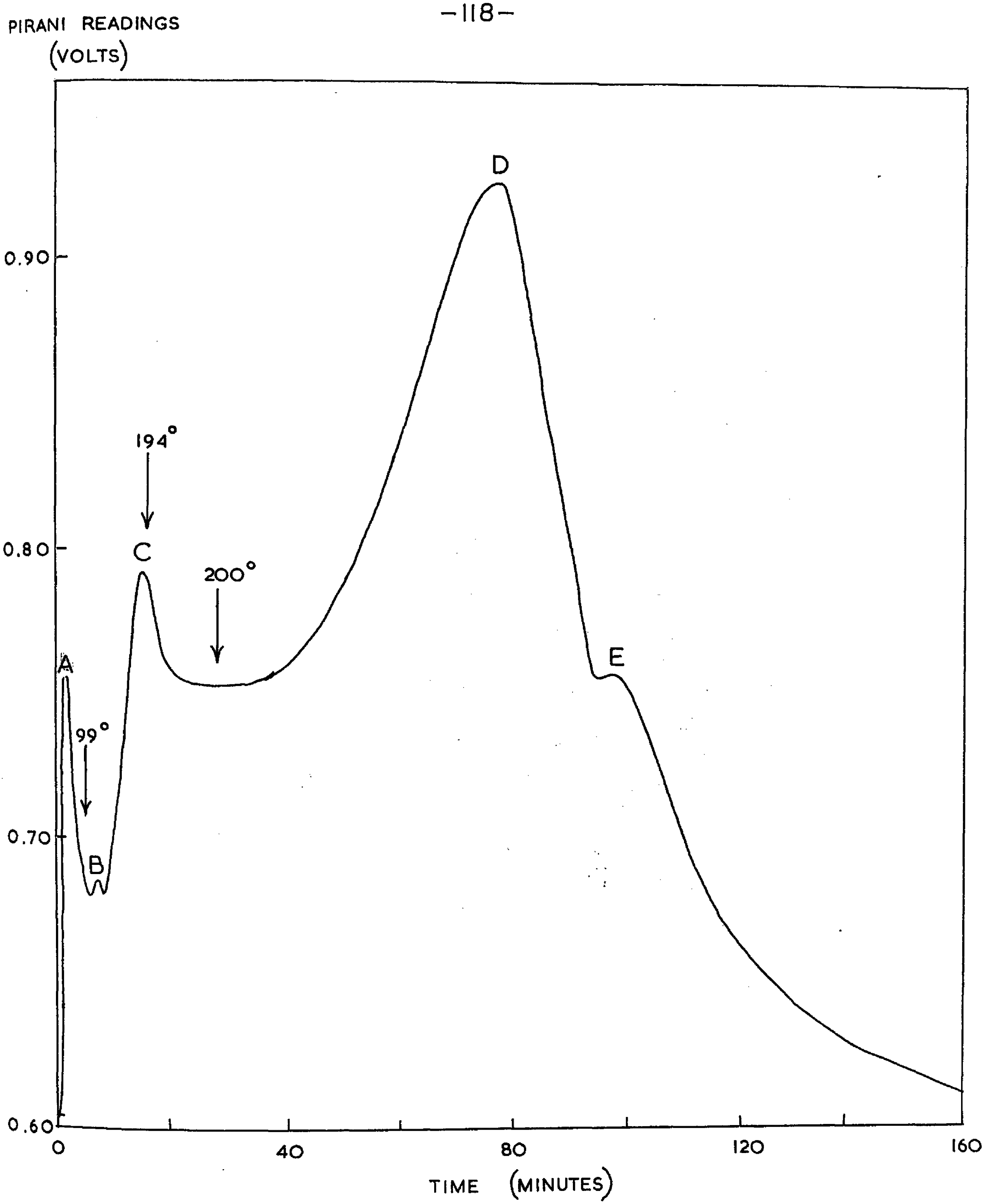


FIGURE 30. PYROLYSIS OF POLY-TERT.-BUTYL METHACRYLATE AT 200°C. PIRANI CURVE.

products of degradation this peak might have been attributed to a particularly large "impurities" content within the polymer. These volatile substances have been shown to cause such a peak as they escape from certain polymers when the softening temperature is reached[25].

The main phase of the degradation then follows. There is a fairly steady increase in rate reaching a maximum at D. Thus the d.m.s. method confirms the acceleration previously noted. It is however sufficiently sensitive to show that there is a subsiduary increase in rate at E. This latter is not always a sharply defined peak, some polymer samples showing only a broad inflection of the curve.

The general shape of the curve does not change with temperature but rates are lower and maxima D and E considerably later at lower temperatures, as is shown in table 10.

Table 10. Effect of Temperature on Pirani Curve.

Temperature °C	Peak D	Peak E
	minutes	
200	68	96
192.5	132	178
181	357	532

Separation of Rate Maxima.

The wider separation of peaks C, D and E at lower temperatures made it possible to stop the reaction at intermediate stages. In this way it was possible to associate the individual rate maxima with different products.

The Pirani curves during the three stages of degradation are shown in figure 31. and the yields of products at each stage in table 11.

Table 11. Product Yields at Different Extents of Degradation.

Stage	% Volatilisation Total	During Stage	*iso*-Butene %	V_{RT} %	Monomer %
I	10	10	6.0	7.7	3.4
II	35	25	22.3	5.2	0.1
III	47.4	12.4	6.5	7.0	0.0

These results show clearly that monomer is produced only in the early stages of degradation and must therefore be associated with peak C. *iso*-Butene occurs at all stages but mainly in stage II. The main ester decomposition is therefore the reaction whose rate increases to a maximum at D. The association of water with the "background" peak A has already been noted (page 53) and the presence of water at all stages is to be expected. Nevertheless the larger quantity in stage III shows that

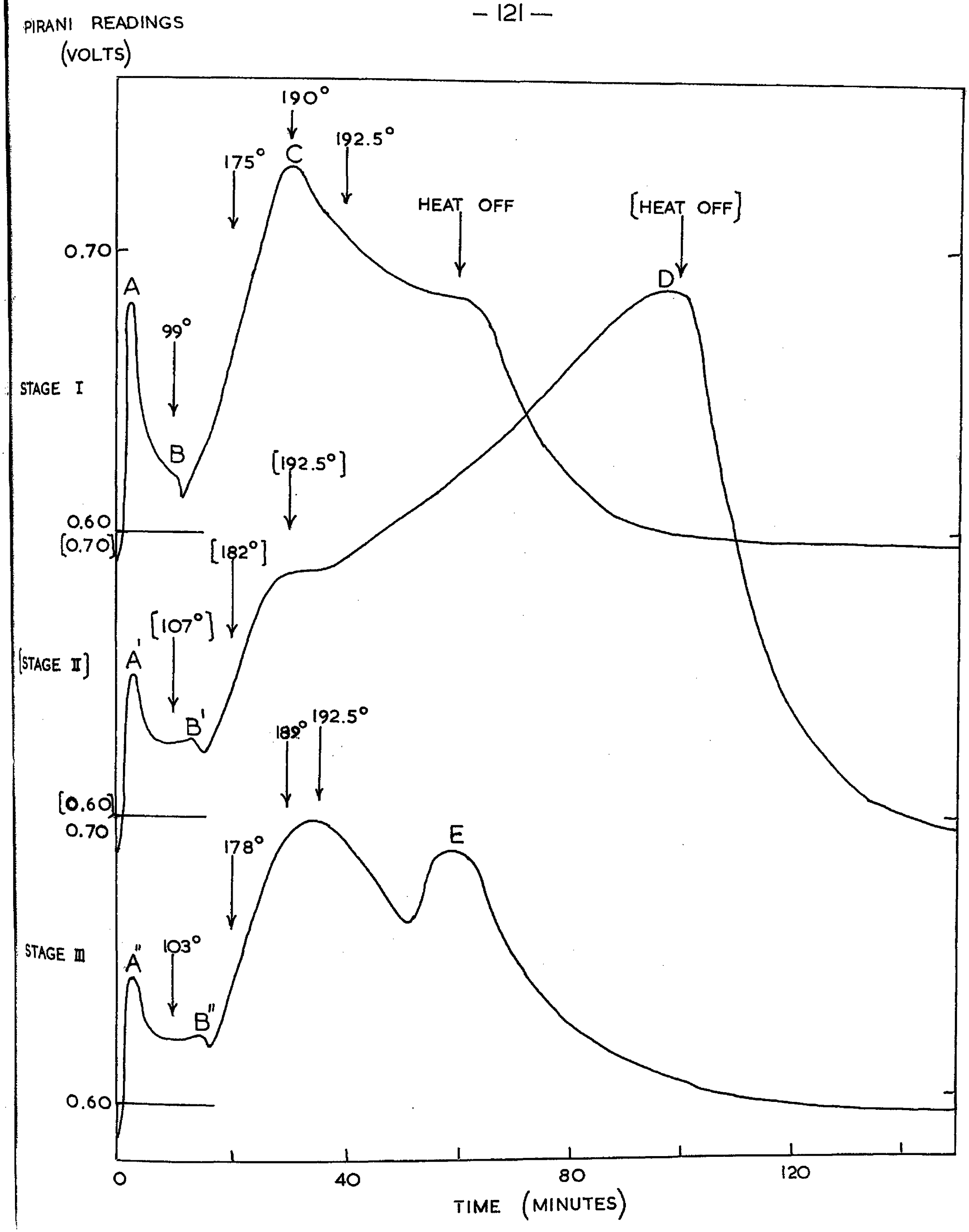


FIGURE 31. PYROLYSIS OF POLY-<u>TERT.</u>-BUTYL METHACRYLATE AT 192.5°C

peak E arises from a water producing reaction.

Effects of Physical Nature of Degrading Polymer on Rate of Volatilisation.

In common with any reaction which takes place in a solid or highly viscous liquid phase, the rate of diffusion of products may be slow and can in some cases be the rate controlling step in determining the rate of production of volatiles. Since polymers are generally poor conductors of heat it is also possible for heat conduction through a layer of polymer to become rate controlling.

It has been shown[25] that in the case of polymethyl methacrylate up to 0.5 gm. of polymer may be heated in a similar d.m.s. system, before either of these two processes becomes important. However in these degradations the residue is a clear, brittle glass showing that polymethylmethacrylate is a relatively mobile liquid at the temperatures (210 - 260°C) used. Anhydropolymethacrylic acid is a soft, opaque material indicating that although poly-tert-butyl methacrylate may have softened sufficiently to allow the particles to coalesce it has never been molten. An increase in degradation temperature even up to 220°C does not have any effect on the product. Because of these differences between the two systems, and the different products it was thought desirable to make a thorough examination of the whole question of heat conduction and volatile elimination in the poly-tert-butyl methacrylate system.

Varying weights of polymer from 12.6 to 126.3 mg. were degraded at 200°C. The Pirani curves were identical in shape, the various rate maxima occurring at approximately the same time, quite independent of the quantity of polymer. Since it had been shown that peak D may be associated almost exclusively with iso-butene production, these maximum Pirani readings can be related directly to rates of iso-butene elimination by means of the calibration curve (page 47). Figure 32. shows the relationship between the maximum rate of iso-butene production (peak D) and weight of polymer. These runs were made with polymer of the same particle size (60 - 80 mesh). In addition runs were made with polymer of different mesh sizes. Their maximum rates are also shown in figure 32.

These results would suggest that diffusion of heat through the layer of polymer can only maintain an uniform temperature when the weights of polymer are less than about 60 mg. Accordingly in other runs the quantity of polymer was kept to within 50 - 60 mg. Provided that the particle size of the polymer is finer than 60 mesh the rate of evolution of iso-butene does not increase with decreasing particle size showing that slowness of

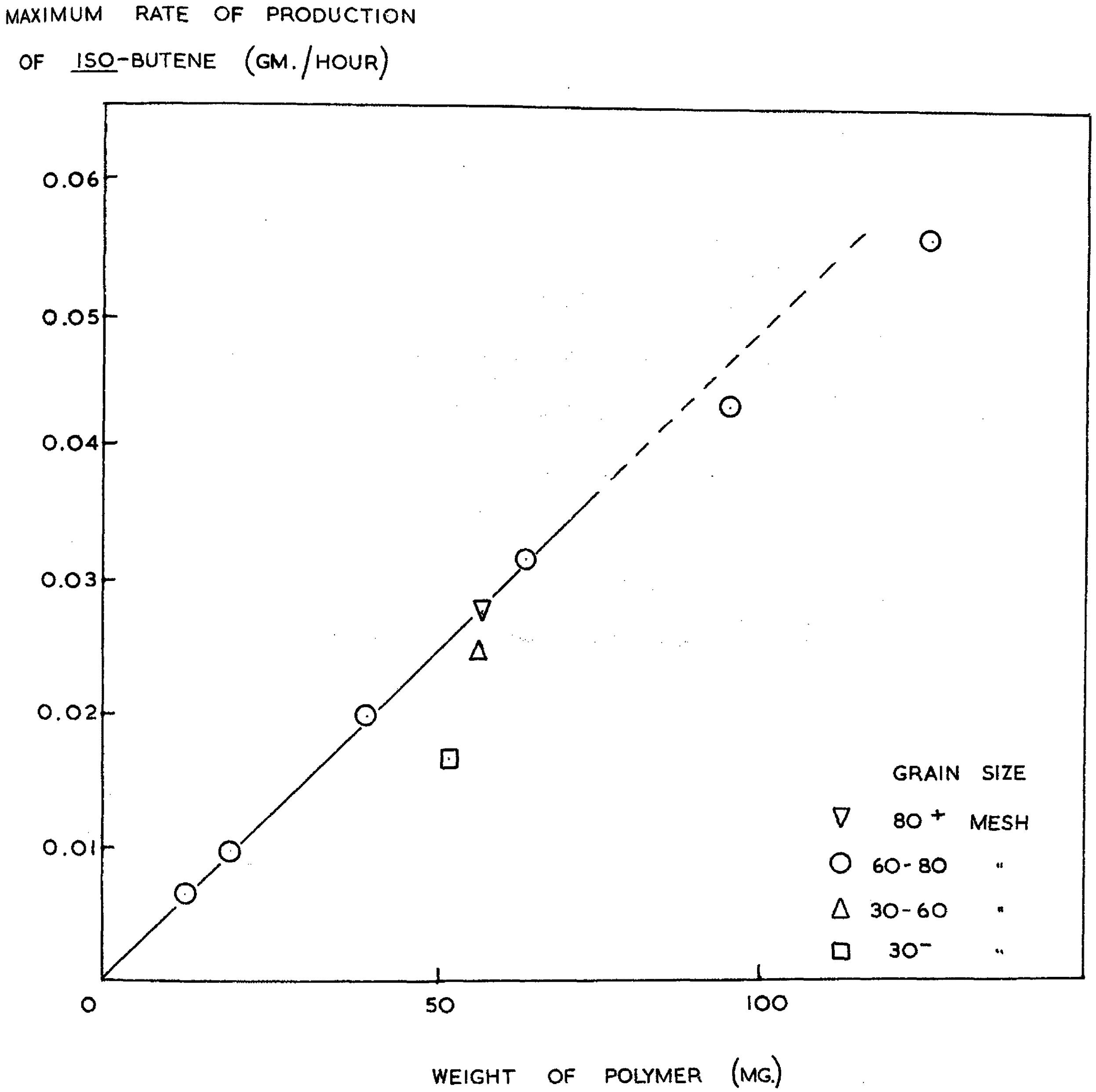


FIGURE 32. PYROLYSIS OF POLY-TERT-BUTYL METHACRYLATE AT 200° C.

RELATIONSHIP BETWEEN WEIGHT AND GRAIN SIZE OF POLYMER

AND MAXIMUM RATE OF PRODUCTION OF ISO-BUTENE.

diffusion cannot account for the acceleration phase of the reaction.

Only with very coarse particles which will not pass 30 mesh is there any alteration to the shape of the Pirani curve. In this case peak D is considerably broadened and at the same time the copper powder is disturbed by the swelling and bursting of the particles. These observations are consistent with the rate of diffusion of *iso*-butene becoming less than its rate of production.

The linear relationship between weight and rate and the identical shape of the Pirani curves show that contact between polymer and copper does not result in any surface catalysis; this conclusion was substantiated by carrying out runs with copper samples of very different bulk densities and particle surface areas. No difference in rates was detected.

THE DEPOLYMERISATION REACTION

In spite of the previous failure to detect monomer among the products[27], the existence of a monomer producing reaction in the degradation of poly-tert-butyl methacrylate should occasion no surprise, particularly in view of the close similarity shown by the tert-butyl methacrylate polymerisation to that of methyl methacrylate. What is more interesting is the comparative smallness of the monomer yield. Initial Pirani readings indicate that the initial rate is appreciable, but that there is a rapid decrease in rate. The following experiments were carried out, the results of which go some way towards explaining the behaviour.

Absence of trapped monomer.

The resemblance of peak C to an "impurities" peak has already been noted. However, the possibility that up to 4% monomer is trapped mechanically in the polymer is a remote one, particularly as the polymer is obtained as a fine powder, and by a double precipitation technique in which dioxane is present in much greater concentration than monomer at the second precipitation. That a true depolymerisation reaction occurs is further substantiated by the following pieces of evidence.

1. The Pirani curves of two polymer samples in the early stages of degradation are shown in figure 33.

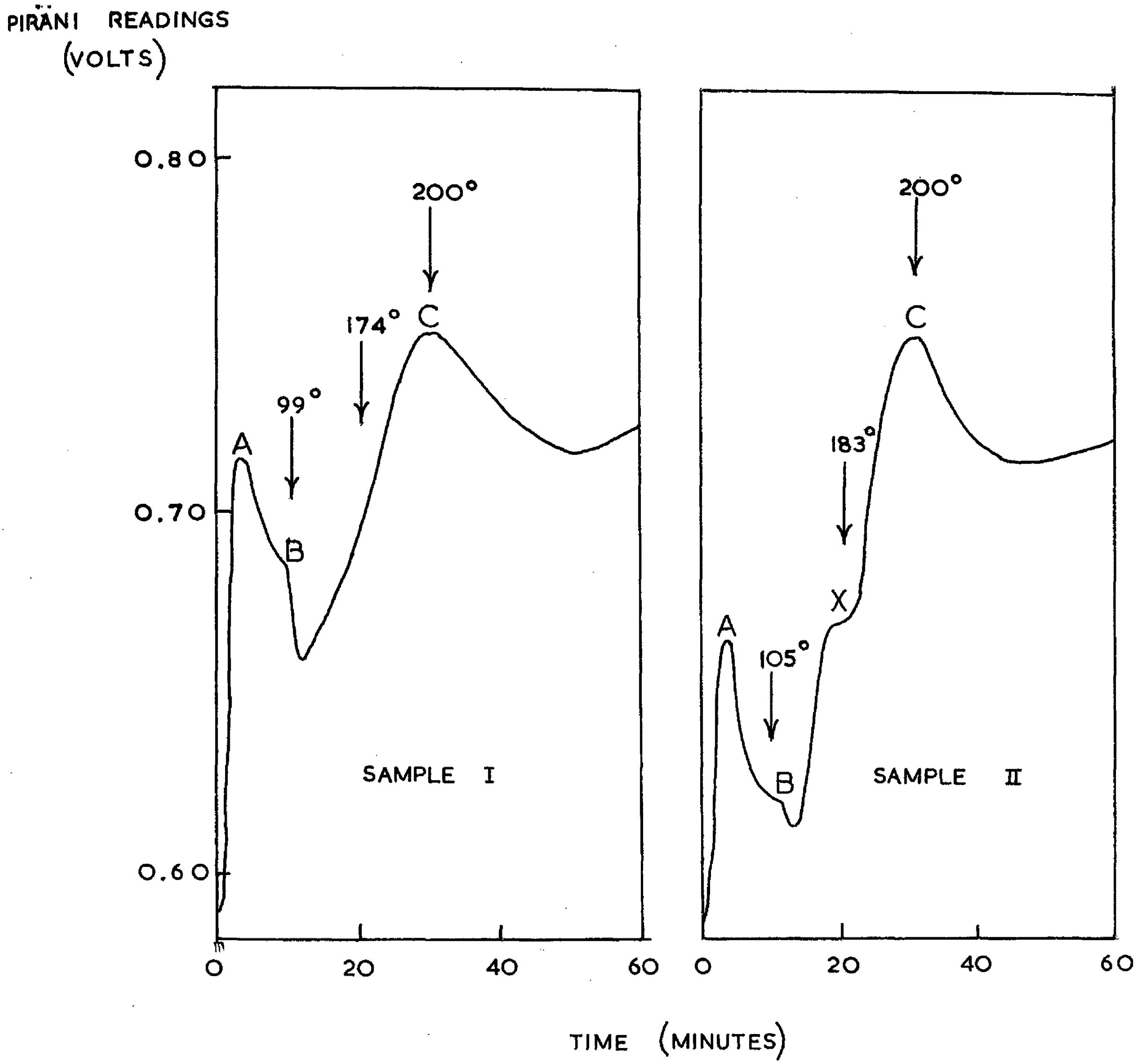


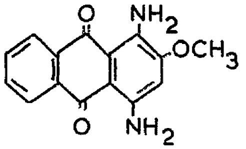
FIGURE 33. PYROLYSIS OF POLY-TERT-BUTYL METHACRYLATE

INITIAL PIRANI CURVES OF DIFFERENT SAMPLES.

Sample I had been dried by heating at 80°C, sample II by storing in vacuum, in the latter case a small trace of solvent had been detected among the degradation products (page 114). The extra step in the volatiles curve probably corresponds to a true "impurities" peak.

2. The degradation of poly-tert-butyl acrylate is similar to that of the methacrylate in that iso-butene is produced.[44] However, peak C is absent and no monomer was detected although the polymer precipitation technique was similar. Since tertiary hydrogen atoms are present little or no monomer would be expected from a depolymerisation type reaction.

3. Inhibitors. Radical depolymerisations are capable of inhibition; thus the depolymerisation of polymethyl methacrylate can be inhibited by 1,4-diaminoanthraquinone[25]. Attempts were made to inhibit monomer production from poly-tert-butyl methacrylate by grinding it together, before degradation, with a similar compound,



1,4-diamino-2-methoxyanthraquinone

No reduction in monomer yield occurred. It is believed that this was due to the non-molten state of the degrading polymer preventing diffusion of the inhibitor into it. A similar difficulty has been reported with polytetrafluoroethylene.[80]

Polymer films cast from a solution have sometimes been used in degradation studies[26]. With poly-<u>tert</u>-butyl methacrylate cast from chloroform it was found that during degradation the film became swollen with trapped degradation products and the Pirani curve showed the same distortion as encountered when the particle size of the polymer was too large (page <u>125</u>). Although Pirani curves of volatilisation rates are therefore unreliable in these cases, product yields were normal (monomer 4.3%). When the experiment was repeated using a solution of inhibitor in chloroform as the casting solvent the yield of monomer was decreased to 1.1%, showing that some inhibition was taking place. The other product yields were normal.

<u>Centres of Initiation.</u>

It seemed possible that the depolymerisation of poly-<u>tert</u>-butyl methacrylate might be initiated in one of two ways.

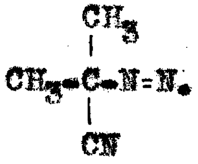
1. By radicals from trapped initiator.

The precipitation technique is designed to remove all traces of polymerisation initiators. In addition it was shown that polymer from a photo-polymerisation (i.e. in which external initiator was never present) degraded in the same way as AIBN thermally catalysed polymer.

2. At labile structures in the polymer.

Most of the work on the degradation of polymethyl methacrylate has been with polymer prepared with benzoyl peroxide as initiator. In this case the end groups of the polymer chains are phenyl and benzoate (from initiation) and saturated and unsaturated (from termination by disproportionation).

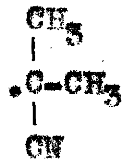
It was at one time suggested[81] that the initial decomposition of AIBN was into two dissimilar radicals



$$CH_3-\underset{CN}{\overset{CH_3}{C}}-N=N\cdot$$

I

and



$$\cdot\underset{CN}{\overset{CH_3}{C}}-CH_3$$

II

of which the azo-radical I was the more reactive initiator. This view was critisised[82] and it is now generally

This view was critisised[82] and it is now generally

taneously with radical production or very shortly afterwards. However, azo-radical I end groups if present even in a small amount could provide the necessary labile structures for initiation and it was thought that this hypothesis was worthy of investigation. It was shown however that polymer from benzoyl peroxide thermally catalysed polymerisation of <u>tert</u>-butyl methacrylate degrades in the same way as the corresponding AIBN. polymer.

It seems likely therefore that the centre responsible for initiation of depolymerisation is the same in both poly- methyl and *tert*-butyl methacrylates; i.e. the unsaturated centre arising by disproportionation.

While it is possible that the small yield of monomer is due to the presence of an abnormally small number of unsaturated chain ends the results discussed below indicate that decreased monomer production is due not to failure of the initiation reaction but to interference with the depropagation step.

Interference by the Ester Decomposition Reaction.

While the thermal degradation reaction at 181°C yields only 4% monomer, the photo-initiated reaction at 170°C gives high yields of monomer[29]. Since the monomer produced thermally appears at a rate which rapidly diminishes right from the start of the reaction, and since the above photo-process shows that the depropagation reaction *can* occur extensively in poly-*tert*-butyl methacrylate chains it seems reasonable to deduce that at the higher temperature something is being produced which inhibits the depropagation step.

In the photo-reaction no *iso*-butene was detected, while in the thermal reaction side chain ester decomposition is the main process. It would appear likely therefore that it is the simultaneous ester decomposition which is in some way responsible for inhibiting depropagation. In order to account for this it is of interest to consider the products of the tert-butyl ester decomposition and how they could act in this way. There would appear to be two main possibilities.

1. External inhibition by iso-butene. iso-Butene is a known inhibitor of radical chain reactions, and only a very small amount would be required to inhibit depolymerisation.

2. Internal inhibition by anhydride or acid units. Although the polymeric product of the ester decomposition is an anhydride (page 115) degradations at 181°C in which the reaction was interrupted in the early stages revealed that the intermediate solid products are copolymers of methacrylate ester and methacrylic acid (Appendix of Spectra S5, S6 and S7). The presence of acid groups is shown by the development of broad absorbtion about 2580 cm^{-1} and by the broadening of the carbonyl peak in the 1700 cm^{-1} region. A more detailed discussion of the spectral changes will be given later. It has been reported that polymethacrylic acid does not depolymerise to monomer so that production of acid units in the chain might interrupt depropagation. Alternatively the inhibiting unit might be the final anhydride unit.

Degradation of a Copolymer of Methyl Methacrylate and Methacrylic Acid

It has been possible to decide between the two possibilities discussed above. If methacrylic acid units can stop the depropagation in poly-*tert*-butyl methacrylate it seemed reasonable to suppose that they would do the same with any poly- methacrylate ester. Methyl methacrylate was the obvious choice both because its polymer degradation has been studied most thoroughly and because it is the least likely to undergo ester decomposition.

A copolymer of methyl methacrylate and methacrylic acid (ester:acid = 2.5:1) was prepared using AIBN initiation. Figure 34 shows the Pirani curve during degradation. Only a small quantity of volatile material was produced and this only in the early stages of reaction. Analysis of the products showed it to be mainly methyl methacrylate (3%) and water, although traces of methacrylic acid, methanol and hydrocarbon precipitants could be detected from a CCl_4 solution spectrum of the products.

Examination of a spectrum of the solid residue showed that the acid groups had been converted to anhydrides. Rather curiously, although the original copolymer was insoluble in chloroform, the degradation product dissolved slowly in that solvent.

At temperatures below 220°C polymethyl methacrylate degrades rapidly only to 50% conversion and thereafter more slowly. At higher temperatures (e.g. 250°C) it degrades smoothly to completion[25]. After being degraded at 200°C till evolution of volatiles had ceased

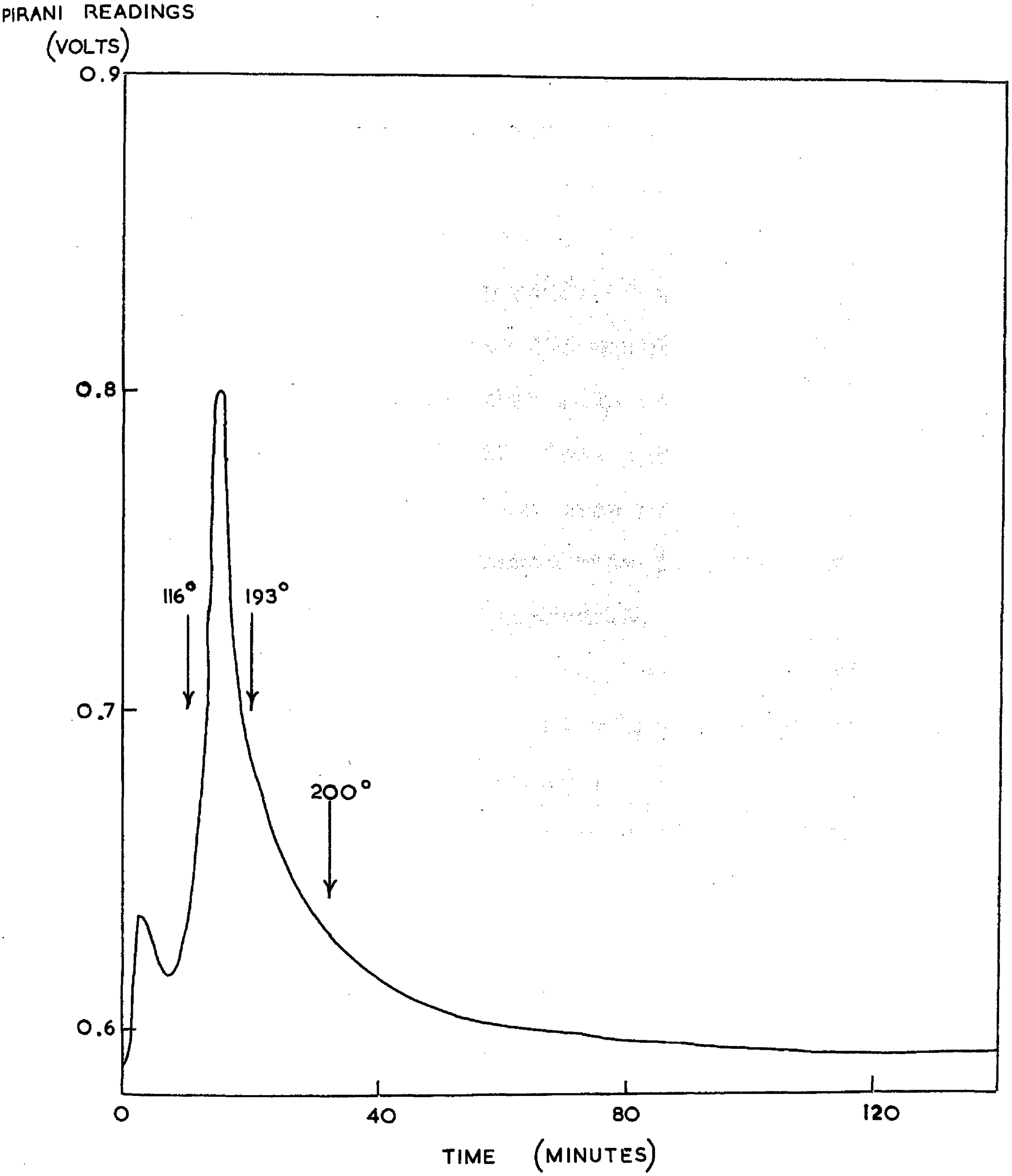
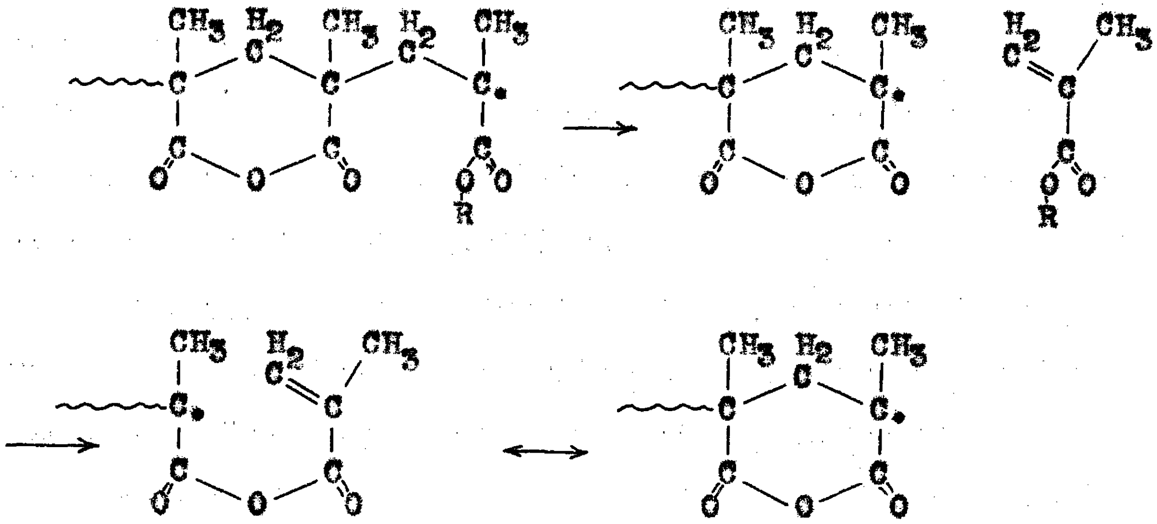


FIGURE 34. PIRANI CURVE DURING PYROLYSIS OF COPOLYMER OF METHYL METHACRYLATE AND METHACRYLIC ACID.

the methyl methacrylate/methacrylic acid copolymer was degraded successively at 220 and 250°C. In each case only trace amounts of monomer were produced. The total weight loss after all three stages was only 10%. The temperature must be raised to over 300°C before appreciable reaction occurs. Even at 330°C volatilisation is slow (60% volatilisation after 320 minutes, 80% after 645 minutes). It will be shown later that anhydropolymethacrylic acid breaks down at this temperature and although monomeric methyl methacrylate was the main product from the copolymer, there was infra-red evidence that it contained impurities arising from anhydride break-down.

These results show clearly that incorporation of methacrylic acid units can stabilise a poly- methacrylate ester against depolymerisation. It is not certain how they do this. Investigation of the reactivity of methacrylic acid in copolymerisations[28] reveals that the factors determining monomer and hence radical reactivity are quite different from that of the esters. It is possible that the acidic H atom can react with radicals in the same way as a tertiary H atom. On the other hand, although small traces of monomeric acid are produced on depolymerisation, methacrylic anhydride was never detected, even at 330°C. It would seem therefore that it may be the anhydride units which provide the block.

It is only possible to speculate about the manner in which it may operate. Being bound to the chain at two points may favour repolymerisation or allow time for interaction of radicals to occur.



long-lived radical ?

A study of copolymers of methyl methacrylate and methacrylic anhydride might help to solve this problem although such materials would be expected to be cross-linked and insoluble in the monomers, giving rise to considerable impurity effects.

SUMMARY

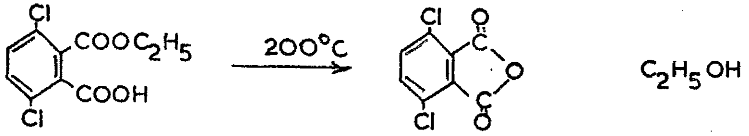
It has been established both from an examination of the degradation products and from the relative rates of production of volatiles during degradation that several reactions occur in the thermal degradation of poly-*tert*.-butyl methacrylate.

In the early stages there is a depolymerisation reaction such as takes place in other poly-alkyl methacrylates. This reaction however, is brought to a standstill when the side-chain ester decomposition becomes important. In the course of this investigation it has been demonstrated that a copolymer of methyl methacrylate and methacrylic acid is more stable towards depolymerisation than polymethyl methacrylate.

The ester decomposition reaction displays auto-catalytic kinetic features. It is more complicated than the simple alkyl-oxygen scission to *iso*-butene and polymethacrylic acid since the final products also include water and a polymeric anhydride. Poly-*tert*-butyl methacrylate does not possess the αH atoms necessary for acyl-oxygen pyrolytic scission and there is no evidence to suggest that such products might be present. The existence of two peaks D and E, and the detection of methacrylic acid units in the chain during degradation are both consistent with the reaction proceeding in two stages;

ester ⟶ acid ⟶ anhydride

and not by the direct production of anhydride from two ester units. Although tert. butanol might be dehydrated slightly at the degradation temperatures, the absence of even a trace of it among the degradation products renders unlikely the occurrence of a reaction such as occurs with certain mono-esters of substituted phthalic acids[83].



In any case none of these possibilities would lead one to expect the observed acceleration in rate.

With regard to this acceleration , the results reported so far are useful as "negative" evidence. It has been shown that it is not due to the physical nature of the degrading system, and the results with inhibitors and ultra-violet irradiation would suggest that free radicals are not involved in the ester decomposition. The possible ester decomposition mechanisms will be considered in a later chapter and evidence presented to show why the rate accelerates.

CHAPTER V

PYROLYSIS OF POLYMETHACRYLIC ACID.

Evidence for the belief that the thermal degradation of poly-<u>tert</u>.-butyl methacrylate proceeds through the intermediate formation of polymethacrylic acid has already been presented. It is obviously a critical test to show that polymethacrylic acid will form an anhydride at a sufficient rate under similar conditions.

PREVIOUS WORK

Polymethacrylic Acid.

There are very few reports of previous studies of the effect of heat on polymethacrylic acid.

Beilstein's "Organische Chemie" mentions only the work of Mjcen[3]. Believed at the time to be an octamer, polymethacrylic acid was heated in air with the following results: became yellow at 150°, began to "decompose" about 200° and volatilised at 300° without melting, no monomer was detected.

Schildknecht's "Vinyl and Related Polymers"[84] states that dry polymethacrylic acid is infusible but at 200° slow "polymer chain degradation" begins and at 350°

decomposition is rapid to CO_2 and volatile hydrocarbons. The source of this information is not given but it may possibly be connected with an abstract[85] of a Japanese paper. This states that at a temperature higher than 200° "methacrylic acid resins" depolymerised rapidly. The molecular weights of the depolymerised products were estimated by viscosity measurements of acetone solutions. Since polymethacrylic acid is virtually insoluble in acetone one must conclude that the work actually refers to methacrylic acid ester resins.

Cowley and Melville[26] briefly examined polymethacrylic acid. While no details are available it seems likely that this investigation was confined to determining whether there is an increase in the rate of production of volatiles on irradiating (ultra-violet) a sample maintained at about 160°. No such volatiles were detected.

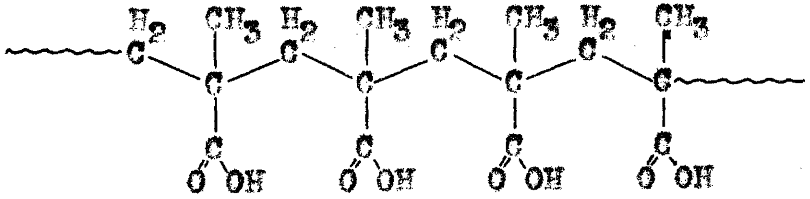
Crawford[27] makes no mention of water being produced from the degradation product of poly-tert.-butyl methacrylate even at 250°. A possible explanation for this will be discussed later.

Polymethacrylic acid in aqueous solution has been degraded by a variety of agents other than heat, namely X-rays[86], and ultra-sonic vibration[87]. In these cases polymer degradation has been attributed to a secondary reaction brought about by hydroxyl or other radicals produced from water. The results should therefore be expected to be quite different from those of thermal degradation.

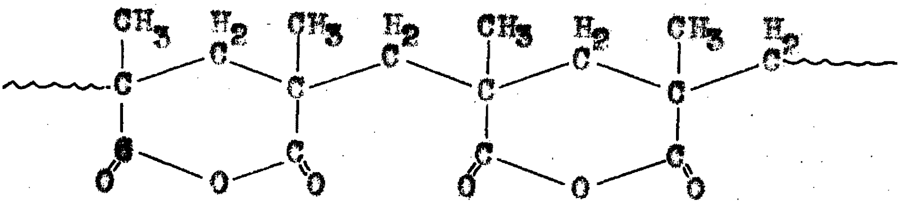
Shortly after these present studies on the pyrolysis of polymethacrylic acid were commenced, it was reported[88] that treatment of a commercial polymethacrylic acid ion exchange resin with thionyl chloride results in the production of a substance which contains anhydride as well as unreacted acid and the expected acid chloride units. Although obtained in this case by chemical and not by pyrolytic action, it does demonstrate that anhydride formation is not a difficult process with polymethacrylic acid.

<u>Pyrolytic Behaviour of Model Compounds.</u>

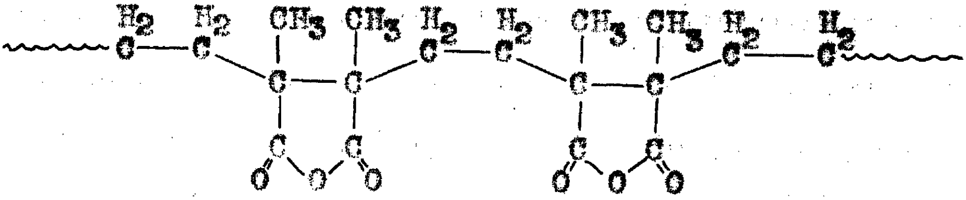
It has come to be accepted as well-nigh axiomatic that vinyl polymers have a predominately head-to-tail structure; in the case of polymethacrylic acid it would be



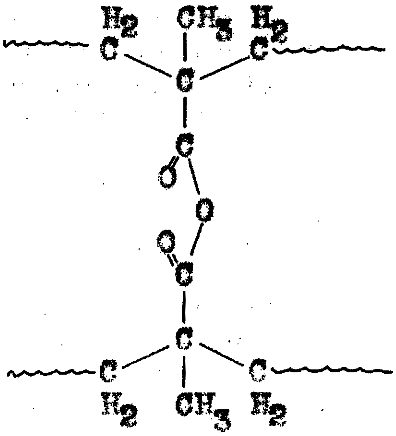
Formation of anhydride from adjacent carboxyl groups would lead to a structure in which six-membered glutaric anhydride type rings are the repeat unit:



If head-to-head, tail-to-tail structures exist then the expected anhydride would contain five-membered succinic anhydride type rings:



In the solid polymer it is likely that the chains are coiled and twisted together in a complex manner. It may therefore be possible for acid groups in non-adjacent positions of the chain, or on different chains to interact as if the acid groups belonged to different molecules of a saturated monobasic acid. Such a structure may be called the iso-butyric anhydride type :



While the formation of five- and six-membered ring anhydrides is well established no results of kinetic measurements are available. Such is the state of our knowledge of pyrolytic reactions that the view of Hurd[89] (1929) that only acetic acid among monobasic acids was capable of forming an anhydride by pyrolysis remained unchallenged until 1952 when Davidson and Newman[90] showed that a number of high boiling monobasic and dibasic acids formed anhydrides when refluxed in an open tube, at about 250°. They attribute the previous failure to detect anhydride formation to the existence of an equilibrium

$$\text{acid} \rightleftharpoons \text{anhydride} + \text{water}$$

which lies so far to the left that when the normal sealed tube method is used very little anhydride is ever present.

PRODUCTS

Absorbtion of foreign molecules by Polymethacrylic Acid.

A number of experimental difficulties peculiar to polymethacrylic acid pyrolysis may be traced to the ability of polymethacrylic acid to absorb foreign molecules. These difficulties were particularly noticeable while attempting a quantitative analysis of the volatile products. In addition the absorbtion may play some part in determining the rate of production of volatiles during degradation. The two materials which cause trouble are either ether or water.

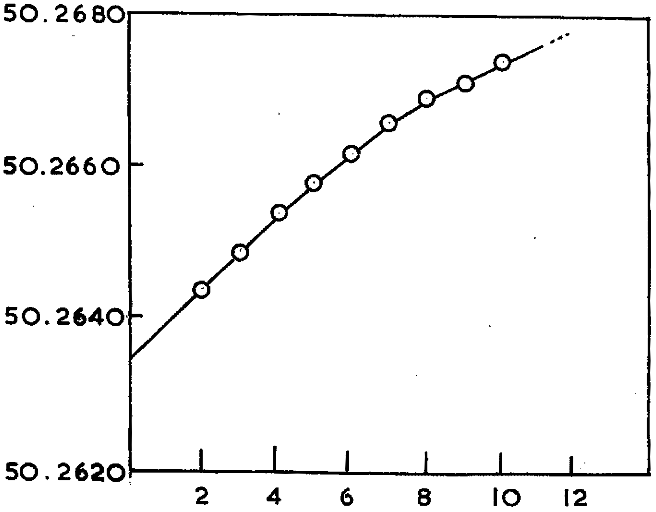
Ether. Polymethacrylic acid was prepared by the AIBN catalysed bulk polymerisation of methacrylic acid. The polymer was insoluble in most organic liquids (including monomer) but is soluble in very polar solvents such as methanol. It was purified by precipitation (twice) by ether (technical grade) from a methanol solution. Although apparently in a finely divided form before filtration, it formed a sticky gelatinous plug in the sintered glass crucible. When this was dried under vacuum it formed a brittle glass which was finely ground (passes 100 mesh) on a mortar.

When this sample was degraded at 200° considerable quantities of ether were detected among the products. Analysis by a V.P.C. method showed that it amounted to 5 - 7% of the weight of the polymer. Not only is this a large impurity content but subsequent investigation showed that it was removed only slowly on heating.

Mjoen noted the ability of polymethacrylic acid to absorb water from ordinary ether and recommended the use of anhydrous ether as the precipitant. Reprecipitation in this medium gave a product which although still requiring to be ground did not produce ether on degradation.

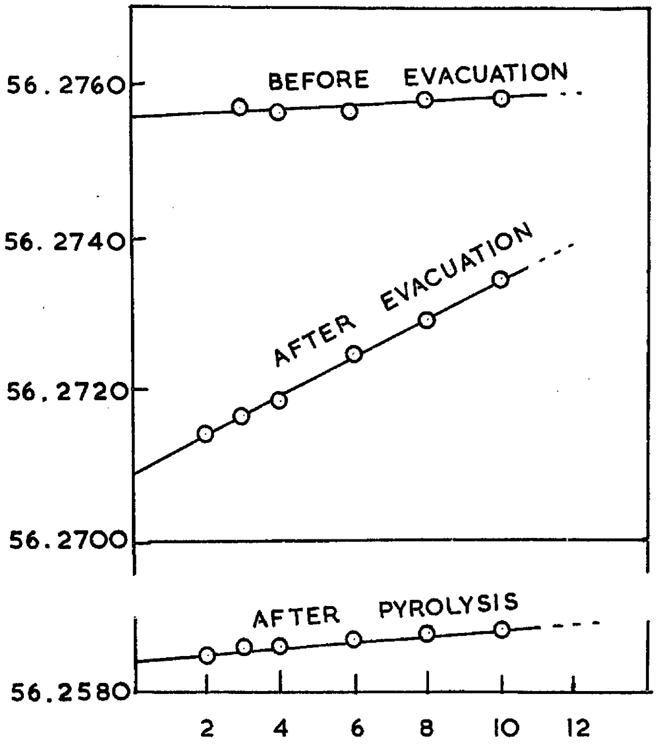
<u>Water</u>. The absorbtion of some substance , presumably water, from the atmosphere by polymethacrylic acid is demonstrated in Figure <u>35</u>. which shows the changes in weight of the copper tray containing approximately 50 mg. polymer during ten minutes immediately following the interruption of prolonged drying of the polymer in vacuum. It shows that the polymer gains 8% in weight in ten minutes.

FIGURE 35.



WEIGHT OF TRAY + CONTENTS

FIGURE 36.



MINUTES EXPOSURE TO ATMOSPHERE

ABSORBTION EFFECTS OF POLYMETHACRYLIC ACID.

Clearly this must introduce a considerable error in following the degradation by measuring weight losses, particularly when it is remembered that the theoretical weight loss for complete formation of anhydride is only 10.4%. This can be overcome to some extent by re-weighing the polymer sample after it has been dried by evacuation in the degradation system and using the extrapolated weight as the true weight of the polymer. Figure 36. shows the loss in weight on so vacuum drying a sample, and also demonstrates that the completely degraded product does not display the same absorbtive capacity. Neither does poly-tert.-butyl methacrylate.

Volatile Products.

After allowance has been made for the effects noted above there is still, on prolonged pyrolysis at 200°, a weight loss and water production both amounting to approximately 10% of the polymer, indicating that anhydride formation does take place.

More interesting is the fact that the aqueous product contains a trace (0.2% of polymer weight) of methacrylic acid. It is still produced from the polymer which is repurified by an additional precipitation by anhydrous ether. This suggests that a small amount of depolymerisation may occur before anhydride formation blocks the depropagation process.

Anhydropolymethacrylic Acid.

Because of the difficulties encountered with the volatile products it was natural that most attention should be focussed on the residue from the degradation. At first sight this did not seem to be a hopeful line of approach. Anhydropolymethacrylic acid whether obtained from the *tert.*-butyl ester or from the acid is a very intractable material. It is insoluble in all common organic solvents, it is infusible, and when it does break down at higher temperatures it produces a very complex range of products (Chapter VII). In addition attempts at C,H,O analysis suggest that there is a non-combustible residue.

The only method of approach which was found to be of any value was based on measurement of the infra-red spectrum.

Infra-red Spectra of Polymethacrylic and Anhydropolymethacrylic Acids.

The difficulty in obtaining good spectra from pre-formed anhydropolymethacrylic acid has already been mentioned. By using the method (Chapter II) in which polymethacrylic acid is dispersed in KCl and the degraded product formed *in situ* the peaks are considerably sharper but in the same positions; the reaction may also be followed semi-quantitatively using this technique.

Assignments of frequencies. In discussing the changes which occur during degradation it is necessary to assign as far as possible the absorbtion peaks to the individual vibrations of the polymer molecule or of groups within it. This has been done by making use of the accepted values for simple molecules (page 72. for sources). In addition the following monomeric or model compounds were examined:

methacrylic, iso-butyric and glutaric acids

" " " anhydrides.

Direct comparison between the spectra of these substances and those of the polymers is only of limited use particularly in the region below 1350 cm^{-1} where the model compounds give more complex spectra than the polymers due to additional C-O and C-C stretching vibrations of the skeletons, which are not always present in the polymer. In addition to comparison of the spectra of the three principal polymers studied (tert.-butyl ester, acid, and anhydride) it was also helpful to compare them with the specta of related polymers such as:

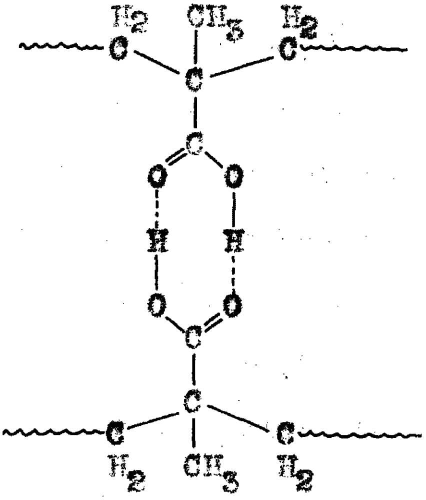
poly methyl and n-butyl methacrylates

polyacrylic acid and poly-tert.-butyl acrylate.

3600 - 2000 cm^{-1}. C-H stretching vibrations give rise to an absorbtion band in the range 2800 - 3000 cm^{-1}. With the KCl disc technique and the NaCl prism of the

Perkin Elmer instrument there is insufficient resolution to warrant a detailed discussion of the individual frequencies. As would be expected there are no appreciable changes on anhydride formation.

This "C-H absorbtion" is superimposed, in the acid, on a broad absorbtion band extending from 3600 to 2300 cm^{-1} with maxima at 3170 and 2580 cm^{-1} which is characteristic of acids in the pure liquid or solid state. In the case of simple acids this absorbtion is attributed to the O-H vibration of the hydrogen bonded dimer present in such condensed phases. In the case of polymethacrylic acid it must arise from similar hydrogen bonds. The structure shown here has intermolecular H-bonds, but it would seem likely that intramolecular bonds will also be present. On anhydride formation this broad absorbtion disappears although that about 3360 cm^{-1} is removed only slowly. While this might be attributed to isolated acid units it has been shown that water, which also can give a peak here, can be removed from KCl only very slowly under the same experimental conditions.



2000 - 1500 cm^{-1}. The broad peak at 1700 cm^{-1} arises from the C=O stretching vibration of the H-bonded acid groups. On anhydride formation it is replaced by the twin carbonyl peaks of the anhyride at 1795 and 1750 cm^{-1}. The intensity of the higher frequency peak is only about half that of the other peak. Important conclusions have been drawn from these observations. They are discussed below.

1500 - 1350 cm^{-1}. C-H bending vibrations give rise to a series of peaks in the frequency range 1500 - 1350 cm^{-1}. By comparison with polyacrylic acid it was possible to recognise the 1448 cm^{-1} peak as the "methylene scissoring" vibration frequency, leaving 1480 cm^{-1} as the assymmetrical C-H bending of the methyl group and 1390 cm^{-1} as the corresponding symmetrical vibration. A very weak absorbtion at 1368 cm^{-1} is assigned to $-CH_2-$ wagging by analogy with polyethylene.[91]

Acids generally show an absorbtion peak about 1400 cm.$^{-1}$ The only evidence for this absorbtion in the present case is a general reduction in the background in this region on anhydride formation.

The only other change on anhydride formation is that the 1480 and 1448 cm^{-1} peaks are replaced by a single broad peak with maximum at 1462 cm^{-1}. The two vibration frequencies are not always separable in other compounds (e.g. branched polythene[91] or polymethacrylonitrile) and the change is probably not of any great significance; factors such as changes in polarity, ring formation , or even melting alone have been known to cause small alterations to these frequencies.

Below 1300 cm^{-1}. C-C and C-O stretching vibrations have frequencies below 1300 cm^{-1}. Because there is considerable interaction between these skeletal vibrations the assignment of particular frequencies is less certain.

Acids normally have a peak about 1250 cm^{-1}. It seems likely that this is the main factor in the 1264 cm^{-1} peak but residual absorbtion on anhydride formation probably arises from a C-C skeletal vibration. The *tert.*-butyl skeleton is known to absorb here and one source attributes this to a C-CH$_3$ rocking vibration. Such structures are present in the polymer chain.

The broad peak at 1174 cm^{-1} is the most difficult to assign. After the "carbonyl peak" it is the most intense in the spectrum and almost certainly must involve C-O vibration. Acids do not normally absorb strongly in this region, certainly none of the model compounds has strong absorbtion here. One of the few oxygen containing vinyl polymers whose infra-red spectrum has been discussed in detail is polyvinyl alcohol; this too has a peak at a similar frequency (1144 cm^{-1}) whose assignment has been the subject of some controversy. Tadokoro et al.[92] suggest that it arises from C-O stretching in "crystalline" regions of the polymer while Krimm et al.[93] attribute it to an ether C-O-C linkage. In the present case it is unlikely to arise from trapped ether since similar spectra were obtained from samples which did and did not yield ether on pyrolysis. It seems likely that it arises from some combination of extended C-C linkages with C-O or C-O-H vibrations, a suggestion which is supported by the fact that only in the case of some <u>long chain</u> fatty acids has absorbtion by acids in this region been reported[94]. (Since these measurements were made in solution, crystallinity is probably not a critical factor.)

The most important feature on anhydride formation is the development of an intense peak at 1022 cm^{-1} which is quite characteristic of anhydrides, being shown by all the model anhydrides. It is due to C-O-C vibrations. The anhydride also has weaker peaks at 1134 and 1080 cm^{-1}. The shoulder at 963 cm^{-1} is present in all the polymethacrylates but absent from the polyacrylates.

The remaining broad absorbtion from 950 to 750 cm^{-1} present in the acid arises from at least two vibrations. O-H deformation is the cause of a broad ill-defined peak at about 920 cm^{-1} in most acids. The peak at 933 cm^{-1}

probably arises from this. Methylene rocking, which in polyethylene has a frequency of 720 cm^{-1}, is said to be variable in polymers and values of over 900 cm^{-1} have been reported for polyvinyl chloride, polyvinylidene chloride and polyvinyl acetate.[93,95] The peaks at 800 and 826 cm^{-1} in polymethacrylic acid may arise from this vibration. On anhydride formation the only detectable peak is at 737 cm^{-1} which is much nearer the normal methylene rocking vibration frequency.

The Carbonyl Peaks and the Structure of Anhydropolymethacrylic Acid.

Details of the structure of anhydropolymethacrylic acid can be deduced from three features of the twin carbonyl peaks of the anhydride spectrum, namely

1. The frequencies
2. The separation of the frequencies
3. The relative intensities of the peaks.

Frequencies. Strained ring anhydrides absorb at higher frequencies than strain free six-membered rings or open-chain anhydrides. The values for the model compounds are shown below.

Table 12.

	Frequency of carbonyl peak		
	Found	Lit.	Ref.
succinic anhydride	1855,1776	1865,1782	96
glutaric "	1802,1756	1802,1761	97
iso-butyric "	1803,1743	-	-
anhydropolymethacrylic acid	1795,1750	-	-

This shows quite clearly that no appreciable number of five-membered rings are present in the degraded polymer. Head-to-head, tail-to-tail, structures cannot therefore be present in detectable quantity in either polymethacrylic acid or its <u>tert</u>.-butyl ester.

<u>Separation</u>. Although the average separation of carbonyl frequencies in anhydrides is 60 cm^{-1}, it has been pointed out[98] that the range of values extends from 40 to 80 cm^{-1}, and an attempt has been made to correlate the separation with structure.

Six-membered anhydride rings generally have the least separation of frequencies. This being true the small separation (45 cm^{-1}) in the case of anhydropolymethacrylic acid would favour six-membered intramolecular anhydrides rather than the <u>iso</u>-butyric anhydride cross-link as the predominant structure.

<u>Relative Intensities</u>. For the identification of organic structures most interest has been in the frequency of absorbtion peaks, and much less attention has been paid to their intensities. As far as is known no previous attempt has been made to correlate the relative intensities of the two peaks with the anhydride structure. The only critisism to which the generalisations below may be open is that they are based on a fairly limited number of examples. This is due to the fact that while frequency values have been reported for many anhydrides, relative

intensities have not.

"In open-chain anhydrides the higher frequency peak is the more intense." This applies to acetic, crotonic and caproic anhydrides.[99] It also applies to propionic, perfluoropropionic, and chrysanthemum monocarboxylic anhydrides whose spectra are listed in the "Documentation of Molecular Spectroscopy" Index (Butterworths). We showed that it certainly applied to methacrylic anhydride and to iso-butyric anhydride.

"The lower frequency peak is the more intense in five and six-membered anhydrides." This is the case for glutaric anhydride, both by a previous report[97] as well as by our own measurement. The only six-membered ring anhydride in the DMS Index, N,N Phthaloyl-L-glutamic anhydride[100], also shows this relationship. We also showed that it applied to polymethacrylic anhydride which must have the glutaric anhydride ring structure as discussed further below ("Insolubility and Structure"). Among five-membered anhydrides the generalisation holds for succinic,[96] maleic and phthalic[99], each of which was checked by us and for three naphthalene dicarboxylic anhydrides[101]. It is also true for four other five-membered ring anhydrides whose spectra are listed in the DMS Index;

1:5-diphenylpentane-1:2-dicarboxylic

2:5 " 1:2 "

endo-1:2:3:4-tetrahydro-1:4-phenylimine-naphthalene-2:3-dicarboxylic

endo-1:2:3:4-tetrahydro-1-methyl-4-phenylimine-naphthalene-2:3-dicarboxylic.

Even if these relationships are not entirely general it would be difficult to understand why methacrylic anhydride on polymerisation, undergoes a reversal of the relative intensities if cyclisation is not the cause. The only other changes on polymerisation are that the product is saturated and is a solid. Saturation cannot be the cause since *iso*-butyric anhydride has the normal open-chain relationship, while we found that the relationship was unaltered by changes in state when methacrylic anhydride was examined in the pure liquid or in solution, and glutaric anhydride in the solid and in solution.

It is concluded therefore that the *predominant* structure in anhydropolymethacrylic acid is the glutaric anhydride type.

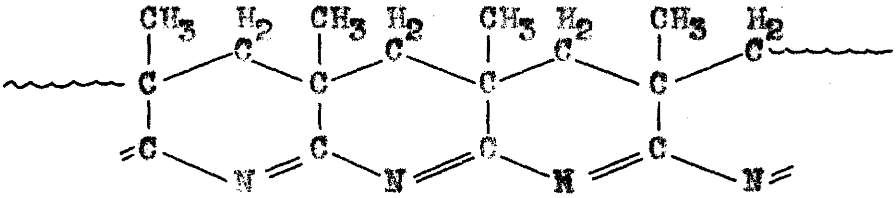
Insolubility and the Structure of Anhydropolymethacrylic Acid.

For the interaction of solvents with polymers to be sufficiently complete that a true solution is produced several conditions must be met.

1. *Polarity.* Polymethacrylic acid will only

dissolve in highly polar solvents such as water and methanol and is insoluble in all others. Poly-<u>tert</u>.-butyl methacrylate is insoluble in liquids at the ends of the "polarity scale" such as water, methanol and petroleum ether but is soluble in most organic liquids.

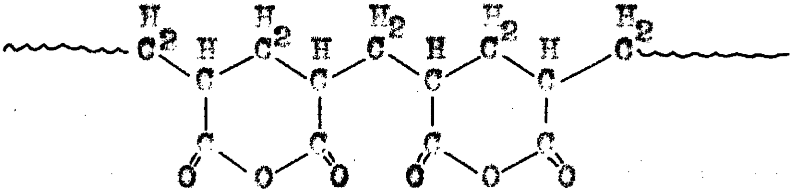
2. Mobility of Structure. Polymers with highly regular or "crystalline" structures such as isotactic polystyrene are difficult to dissolve, so also are polymers in which rigidity of the chain is present due to some additional chemical bonding. Thus in the insoluble highly coloured degraded polymethacrylonitrile[10] there is a conjugated -C=N- chain in addition to the normal -C-C- backbone:



3. Absence of Cross-links. The linear polymer molecules produced from vinyl monomers are, subject to the above requirements, generally soluble, but three dimensional networks produced when chains are linked together are insoluble. In many cases it has been shown that only a few cross-links are necessary to alter the solubility completely.

The insolubility of anhydropolymethacrylic acid in a wide range of possible solvents, including acetic anhydride, indicates that the insolubility is not due to failure to meet condition 1. A rigidity of structure might be expected to arise from the linked six-membered glutaric anhydride rings. The presence of a small number of iso-butyric anhydride type links could not be ruled out either. It has been possible to decide between these two possible causes of insolubility in the following way.

Although acrylic anhydride is an effective cross-linking agent when copolymerised with other monomers, it has recently been shown[102] that when polymerised alone it undergoes a form of "internal copolymerisation" with the production of a linear molecule containing linked glutaric anhydride type rings:



This compound is soluble in polar solvents such as dimethyl formamide, showing that any rigidity is not sufficient to prevent solution. Methacrylic anhydride was polymerised in bulk and the product polymethacrylic anhydride examined. Although identical in infra-red spectrum with anhydropolymethacrylic acid it is soluble in dimethyl formamide and can be precipitated substantially unchanged by pouring the solution into ether.

This demonstrates that although anhydropolymethacrylic acid has substantially the same linked glutaric anhydride type structure as polymethacrylic anhydride it must also possess a few cross-links of some description. It seems likely that these must be *iso*-butyric anhydride structures. This is the type of cross-link which is produced when methacrylic anhydride is used as a cross-linking agent for the preparation of cross-linked polymers from several monomers. It has been reported that as little as 0.5% methacrylic anhydride in methyl methacrylate can render the polymer insoluble[103].

It is certainly possible to demonstrate that the cross-link is alkali sensitive. The only reagents which have any effect on anhydrpolymethacrylic acid are concentrated solutions of sodium, potassium or ammonium hydroxides, in which it "dissolves" readily. By pouring the viscous ammoniacal solution into acetone it is possible to isolate a polymer whose spectrum (Appendix of Spectra S.7.) shows it to be mainly a polymethacrylic acid with certain additional groups, probably amide or ammonium salt.

RATES OF REACTION

Rate of formation of Anhydropolymethacrylic acid.

The formation of anhydropolymethacrylic acid was followed by heating samples of polymethacrylic acid dispersed in KCl (Chapter II for details of technique). There are no suitable peaks in the infra-red spectrum of the acid which can be used as a measure of concentration, but two of the peaks (1795 and 1022 cm^{-1}) of the product are reasonably well separated from interference and were used for this purpose.

It was found that at 200°C the reaction was too rapid to be followed by this method. Figure 37. shows the results obtained at 192.5°C, the highest temperature at which the reaction was studied. The ordinate, "the extent of reaction" is given by the ratio

$$\frac{\text{Increase in peak height at time t}}{\text{'' \quad '' \quad '' \quad '' \quad ''}} \times 100$$

$$= \frac{\text{Absorbtion at time t - Absorbtion at time 0}}{\text{'' \quad '' \quad '' \quad '' \quad '' \quad '' \quad 0}} \times 100$$

In practice the infinity reading was taken as the result of 12 hours pyrolysis at 200°C. The results show quite clearly that both absorbtion peaks give approximately the same measure of the extent of reaction, and that the reaction is a rapid one ($t_{\frac{1}{2}} \sim 12$ minutes).

Measurements were also made at 181, 169, and 153°C. Figure 38. shows that different batches of polymer/KCl

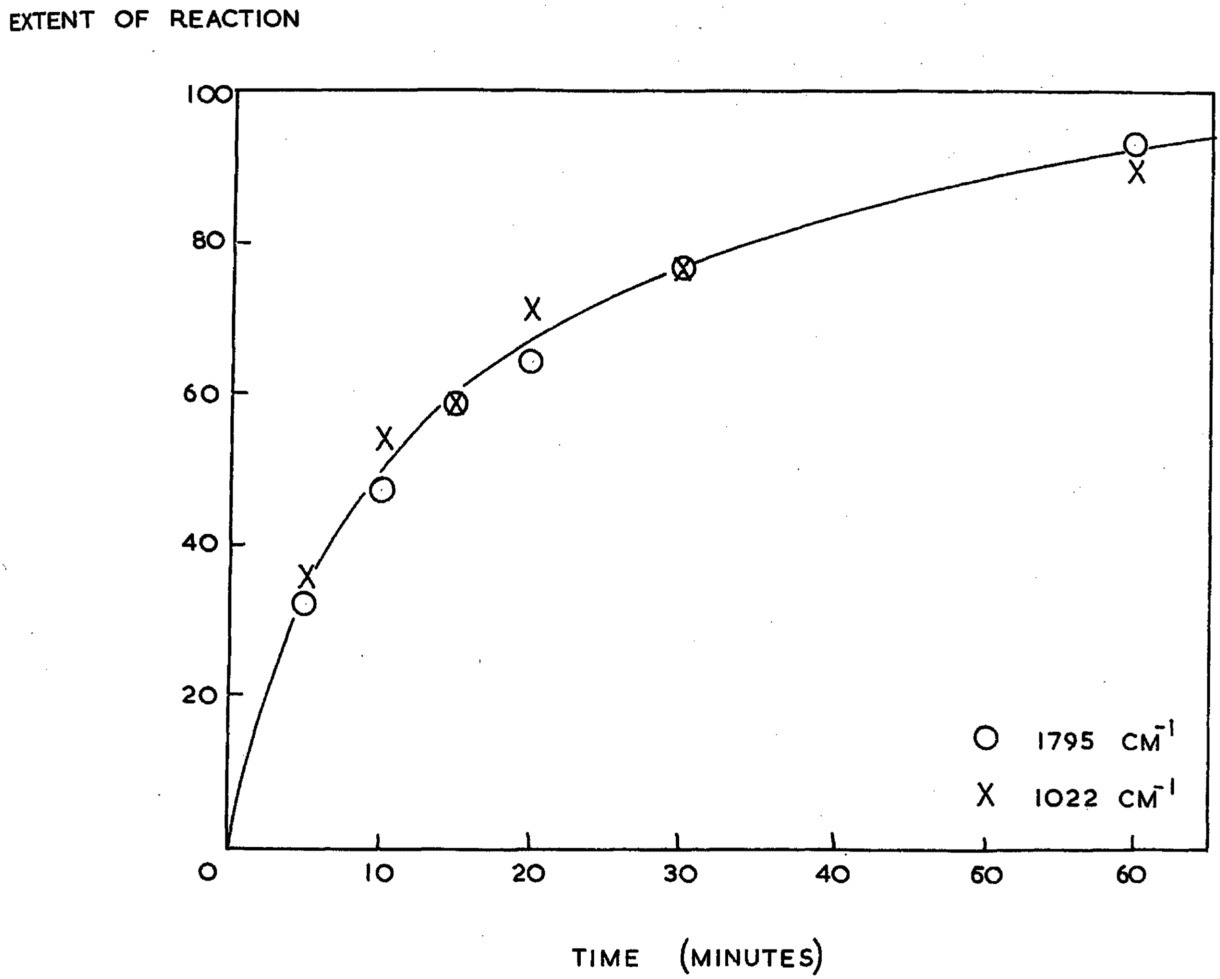


FIGURE 37. PYROLYSIS OF POLYMETHACRYLIC ACID AT 192.5 °C.

INFRA-RED CHANGES

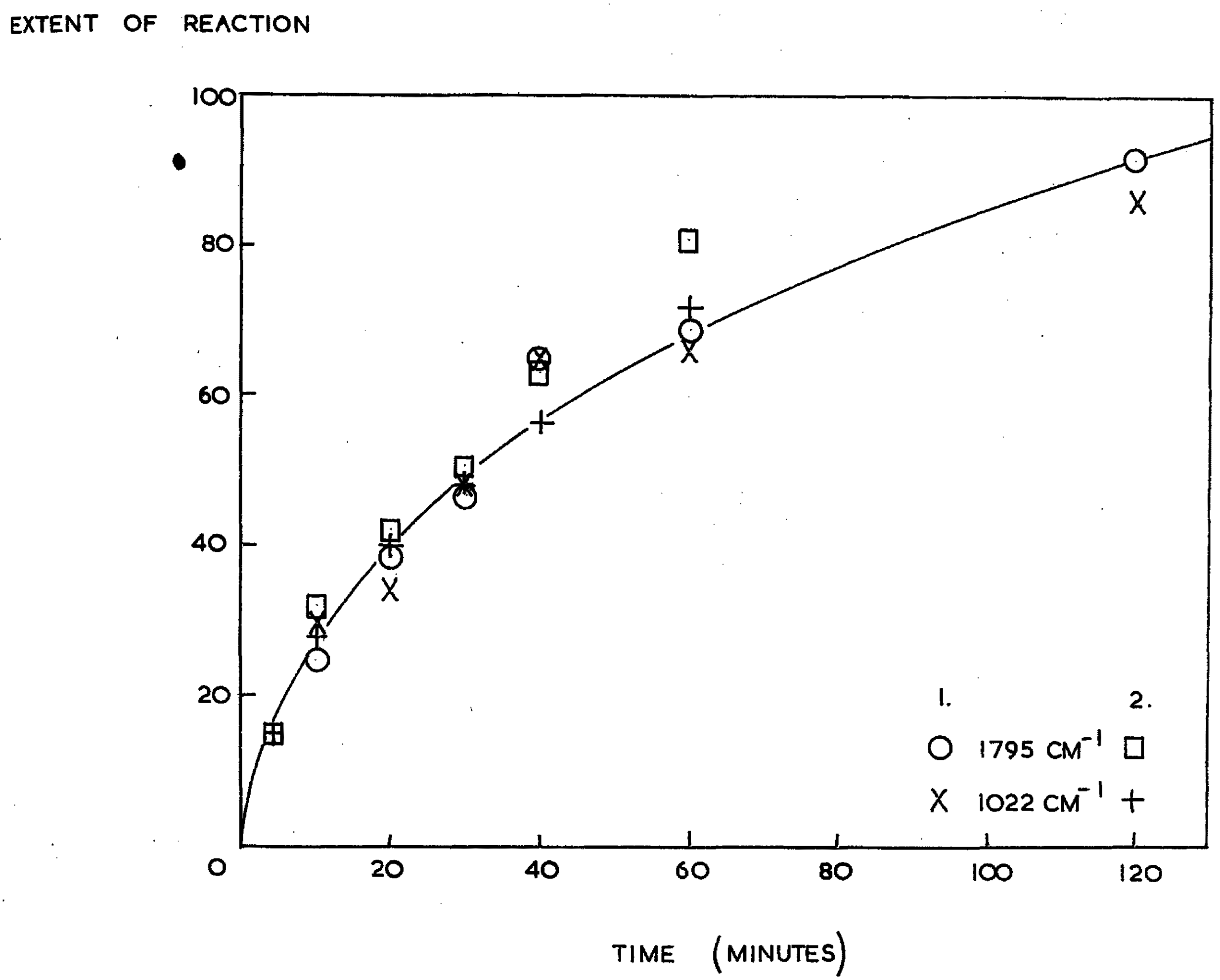


FIGURE 38. PYROLYSIS OF POLYMETHACRYLIC ACID AT 181°C.

DIFFERENT KCl/POLYMER DISPERSIONS

dispersion give results which are indistinguishable from one another within the admittedly appreciable experimental error. Figure 39. shows the effect of temperature on the rate of the reaction of the same batch of dispersion mixture.

"Activation Energy"

In order to calculate the activation energy of the reaction it is necessary to determine some form of rate constant for the reaction at each temperature. From the nature of the reaction it was reasonable to expect that it might show second order kinetics. The usual expression for the rate constant of a reaction of the second order is

$$k = \frac{1}{t}\left(\frac{1}{a - x} - \frac{1}{a}\right)$$

$$\text{or} \qquad kt = \frac{1}{a - x} - \frac{1}{a}$$

Provided that there is a normal Beer's Law relationship between peak heights and concentrations then it is possible to equate x with the extent of reaction as measured above, while the initial concentration of acid a will be 100%. Plots of $1/\overline{a - x} - 1/a$ against t are shown in figures 40. and 41.

Bearing in mind the experimental technique and the above assumption the results show satisfactory agreements with second order kinetics, and rate constants have been

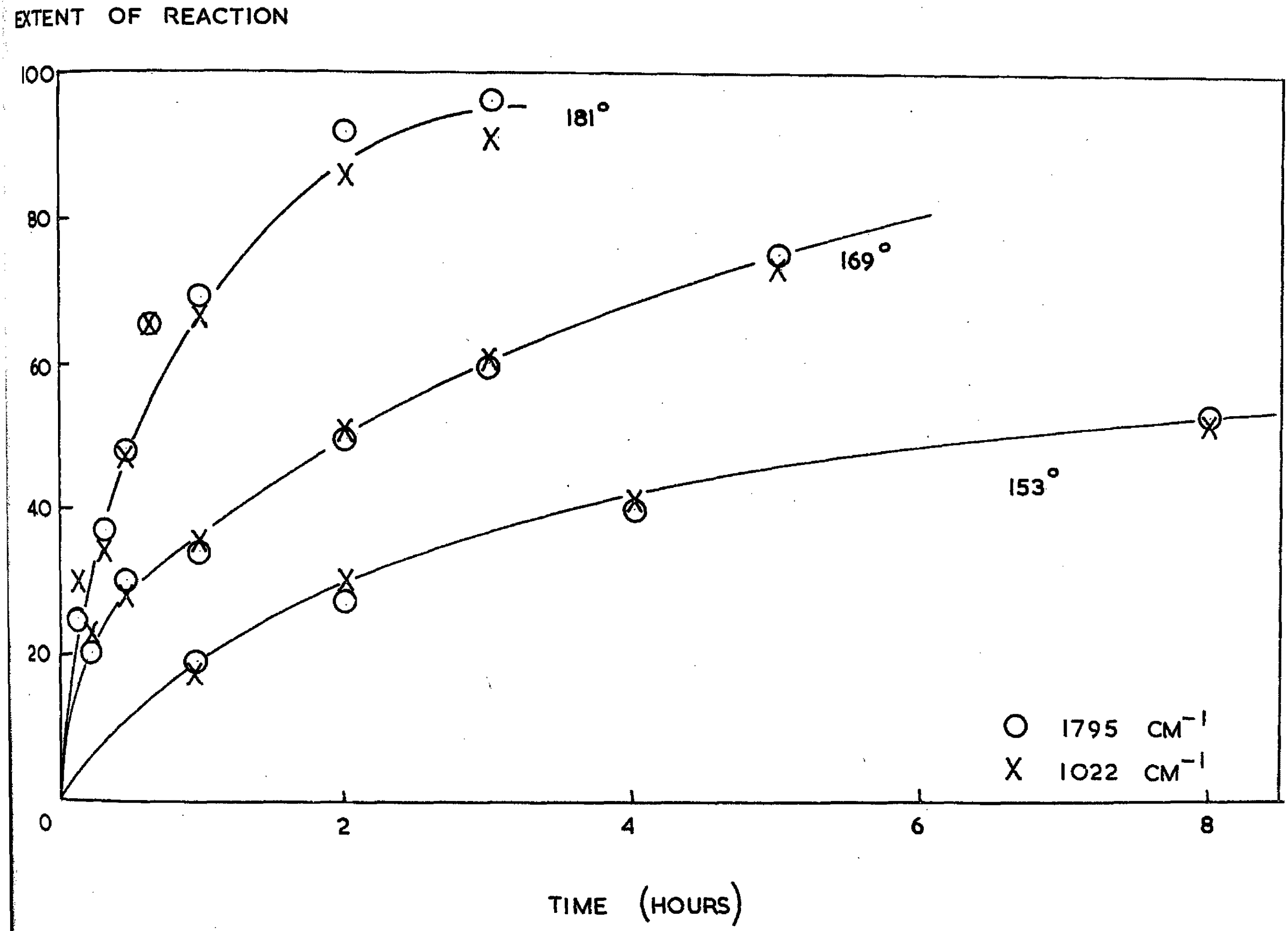


FIGURE 39. PYROLYSIS OF POLYMETHACRYLIC ACID AT DIFFERENT TEMPERATURES

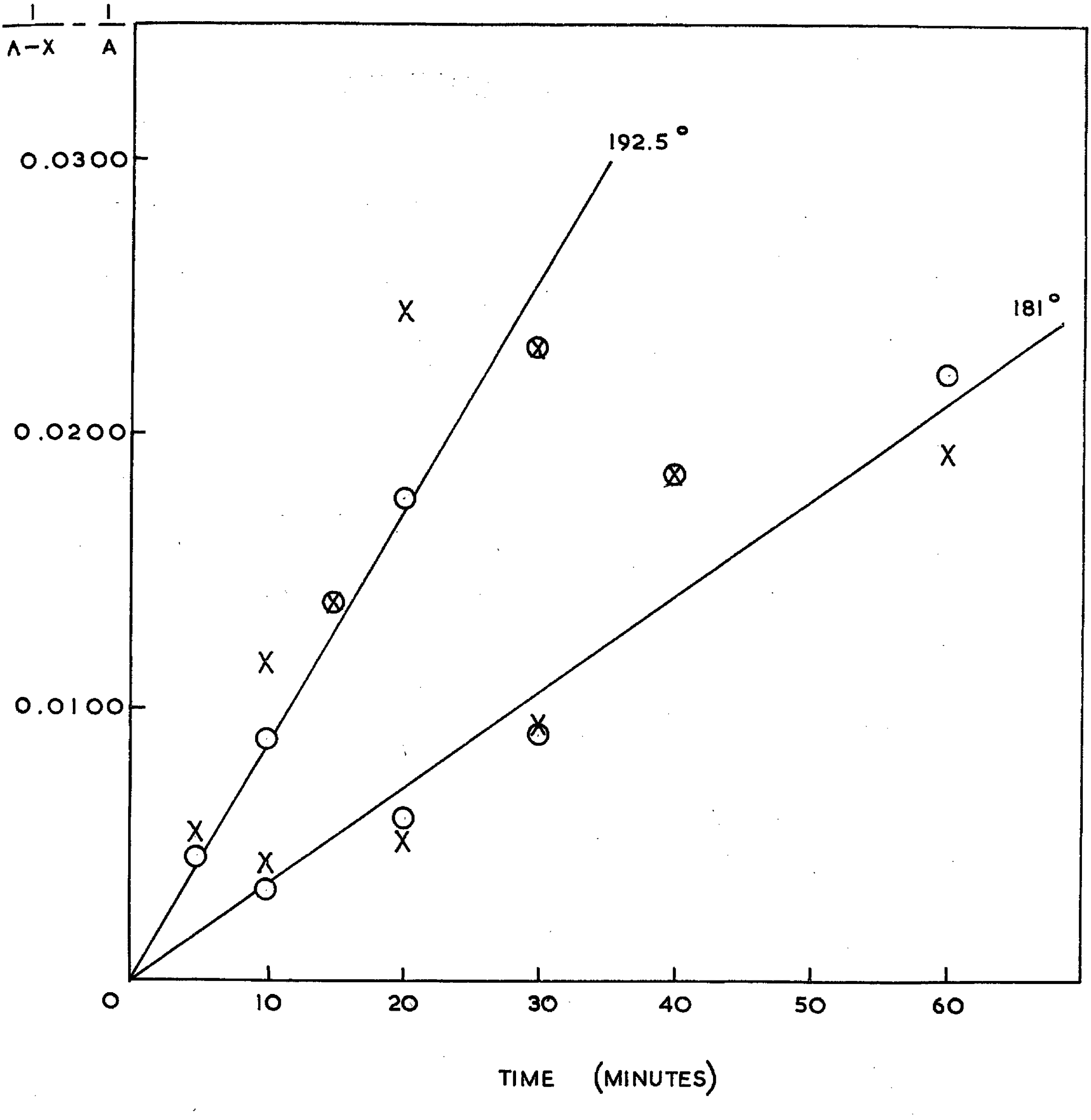


FIGURE 40. SECOND ORDER PLOT.

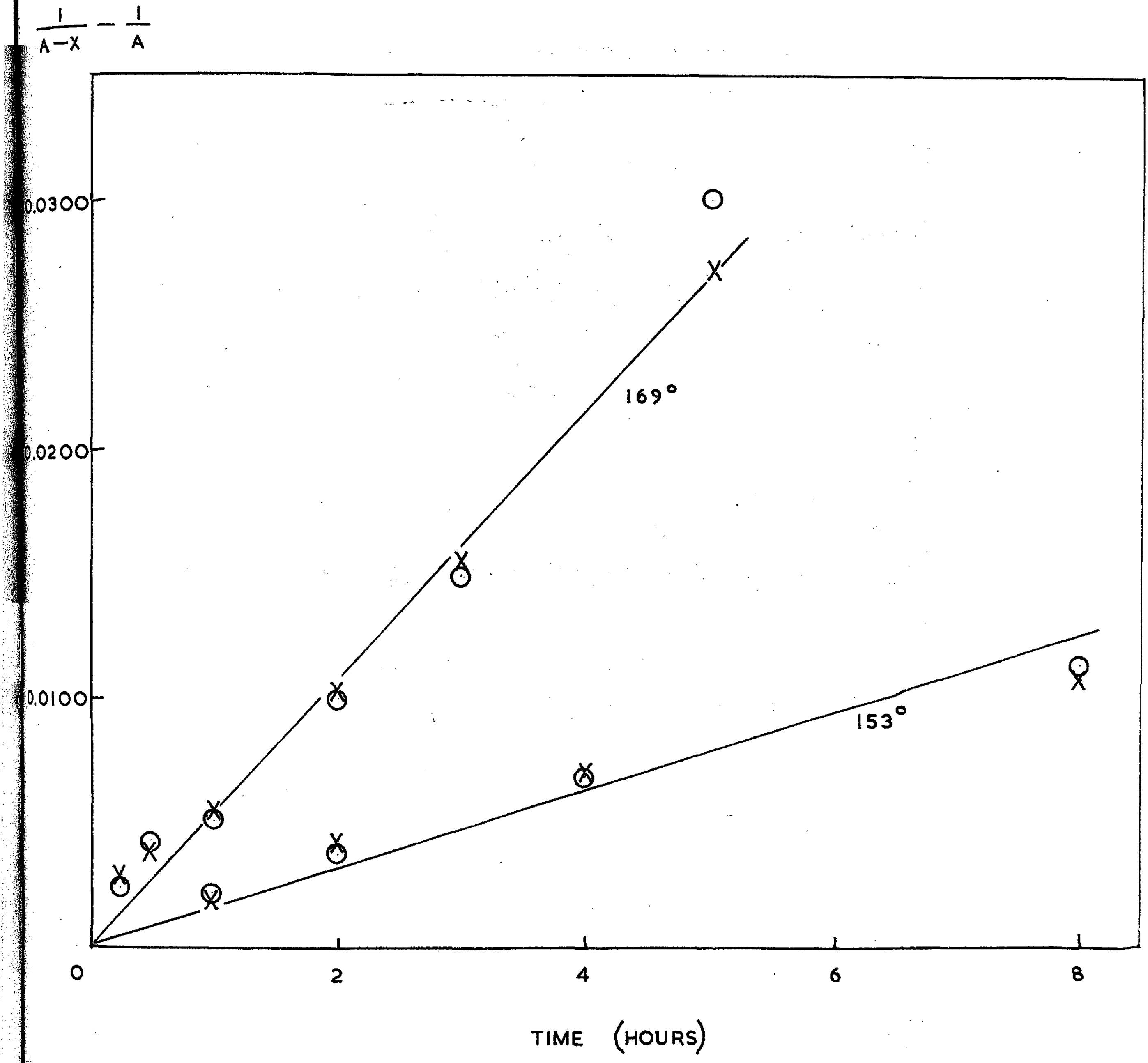


FIGURE 41. SECOND ORDER PLOT.

calculated from the slopes of the lines. They are given in Table 13. together with the approximate times at which half the acid has reacted.

Table 13. Kinetics of anhydride formation.

Temp. ($^{\circ}$C)	k (1/%.sec.)	$t_{\frac{1}{2}}$ (hours)
192.5	14.3×10^{-6}	0.2
181	5.9×10^{-6}	0.5
169	1.4×10^{-6}	1.8
153	0.4×10^{-6}	6.5

An Arrhenius plot (Figure 42.) gives a value of the "activation energy" of the reaction as 37±3 Kcal./mole.

Rates of Production of Volatiles.

Attempts were made to measure the rate of the reaction by measuring the rates of volatile production in the dynamic molecular still. With the reaction occurring so rapidly at 192.5°C (Figure 37.) it might have been expected that a considerable part of the reaction would have taken place during the finite time necessary to raise the temperature of the degradation system and that still lower temperatures would have to be used. The opposite proved to be the case. At 192.5°C there is an approximately constant slow evolution of volatiles over about two hours, before the rate begins to fall off. In order to obtain a clearer view of the Pirani curve during

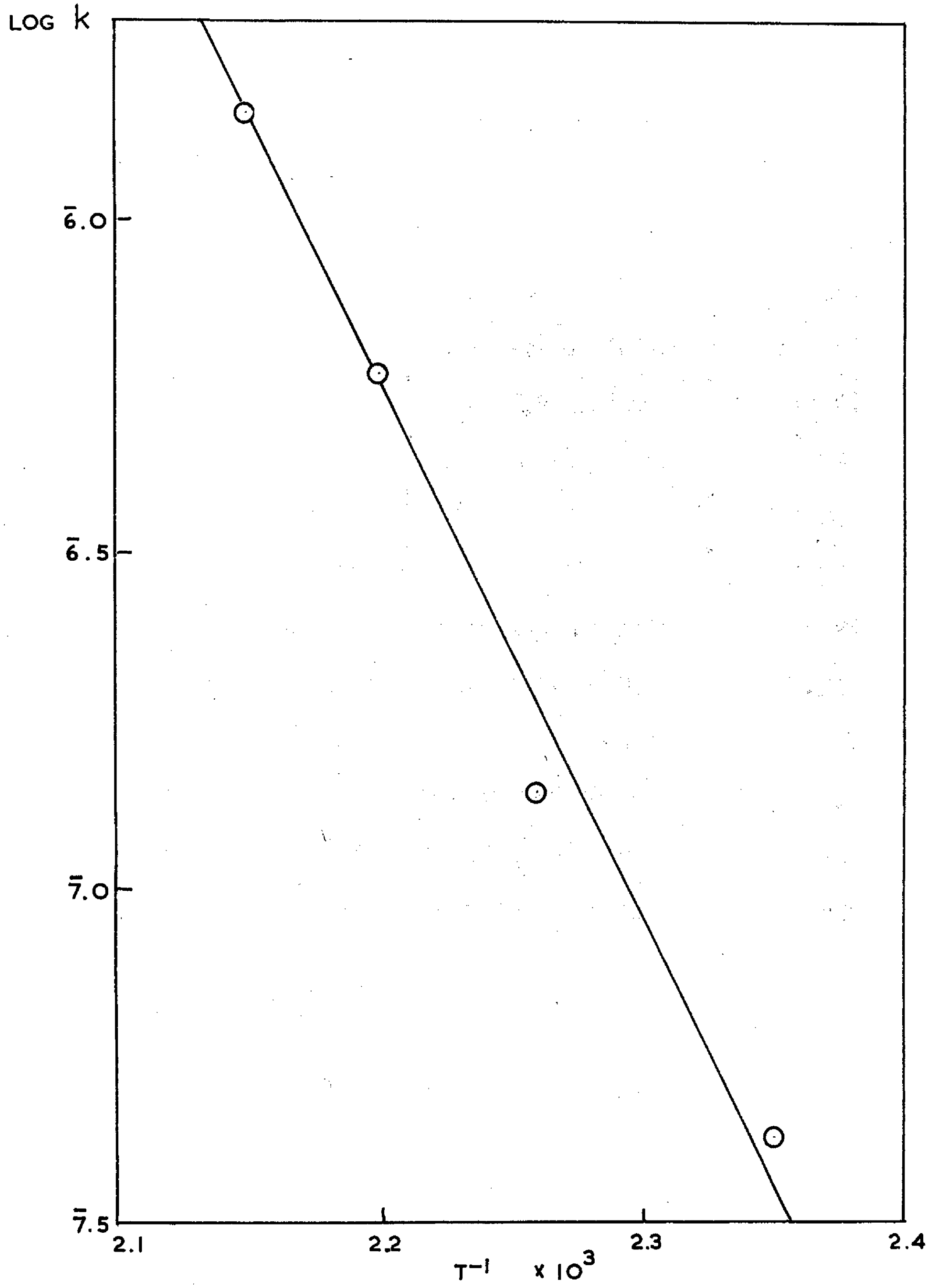


FIGURE 42. PYROLYSIS OF POLYMETHACRYLIC ACID, ARRHENIUS PLOT.

degradation it was necessary to use higher temperatures. Figure 43 shows the Pirani curves of two samples degrading at 200°C.

The lower curve (B) shows that there is a period of about 40 minutes during which the volatiles are produced at an approximately constant rate, followed by a slow decrease in rate. Curve A was given by the sample containing trapped ether. It appeared likely from this curve that ether was not removed rapidly during the heating period. It was possible to confirm this, and at the same time to make a direct comparison of the rates of reaction under the different conditions by interrupting the degradation before elimination of volatiles was complete. The spectrum of the residue after 45 minutes degradation at 192.5°C is shown in the Appendix of Spectra (S.8) A similar spectrum can be obtained using the KCl dispersion method by heating the polymer for only 10 minutes. After 45 minutes the reaction would be 90% complete using the dispersion method

Examination of the volatile products of the first stage of the interrupted degradation showed that ether was present. However when the residue was heated again till all volatile material had been evolved, a further trace of ether was detected among the products, showing that it was removed only slowly from the degrading polymer.

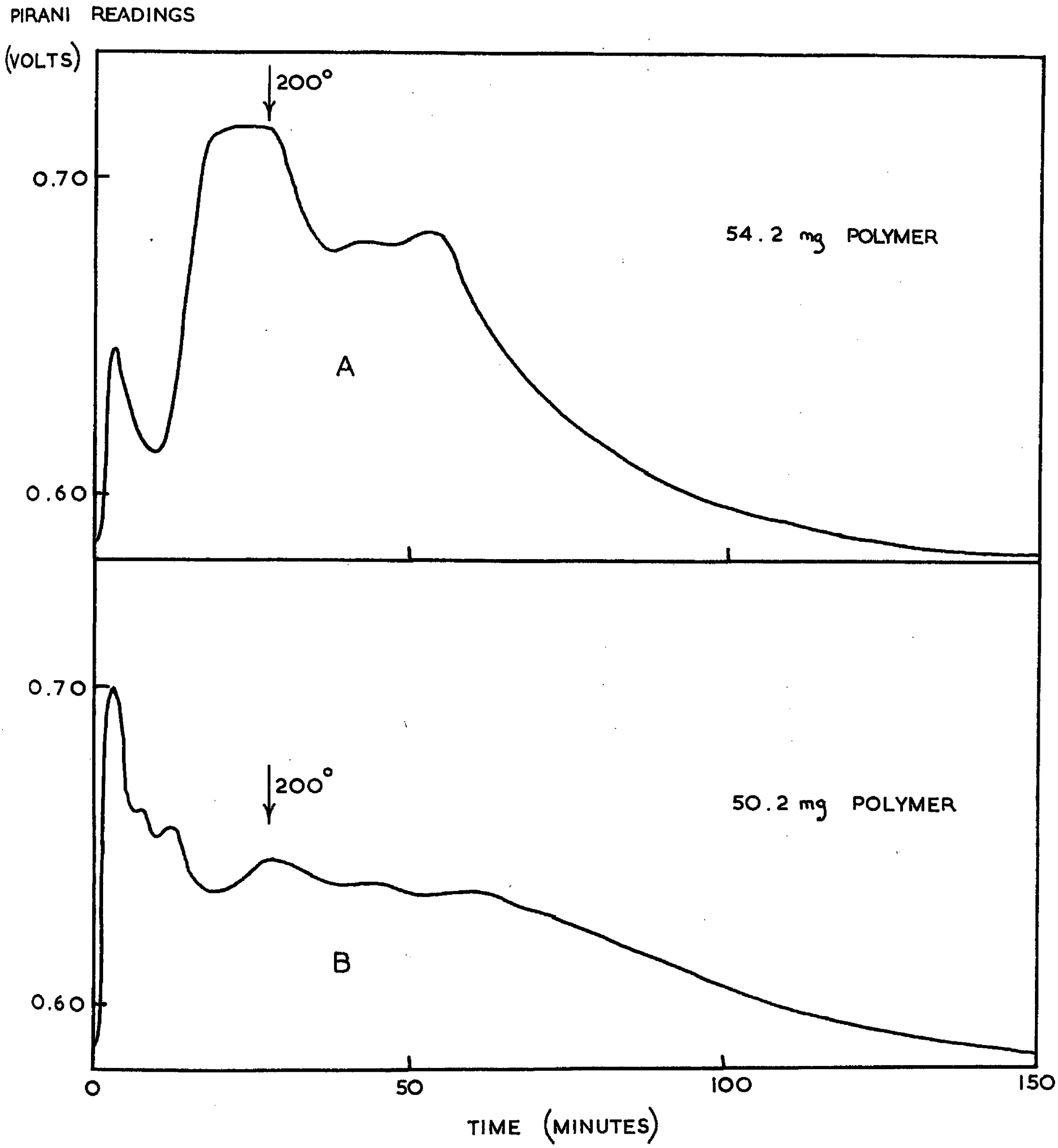


FIGURE 43. PYROLYSIS OF POLYMETHACRYLIC ACID AT 200°C
PIRANI CURVE.

Comparison of Rate Measurements (Methods).

Diffusion Control. It has already been mentioned that the rate of diffusion of products from polymers may be a slow process. We believe that this is an important factor in polymethacrylic acid degradation. It has been shown that polymethacrylic acid readily absorbs both ether and water, and further that ether is not removed readily during the degradation. It seems probable therefore, that water, produced within the polymer particles, will not escape very readily. If this is the case then it would be expected that partial hydrolysis of the anhydride might easily occur. The system is similar to the one discussed by Davidson and Newman with respect to simple molecules. The "rate of reaction" would be dependent on the ease with which water molecules can escape from the polymer, and might show a zero order phase if this depends on the surface area of the polymer. The reaction can be represented thus:

$$\text{acid} \rightleftharpoons \left[\text{anhydride} + \underset{(\text{trapped})}{\text{water}}\right] \longrightarrow \text{anhydride} + \underset{(\text{free})}{\text{water}}\uparrow$$

The existence of such a diffusion control of the reaction may explain the previous failure to detect anhydride formation. The polymer used by Crawford was initially in the form of a block 2 x 1 x 0.3 cm^3. Diffusion of water from such a system would be very slow.

Action of KCl. There are a number of possible reasons why the reaction should be appreciably higher in the dispersion method.

1. It may provide a more polar medium. Since the polymer is still in the form of fine particles which make contact with KCl only at the surface this is not very likely.

2. It may remove the water rapidly as it is formed. Although KCl does not form a recognised hydrate it is very difficult to remove traces of water from it.

3. By grinding with KCl a fine particle size is produced, in addition the KCl will prevent the particles from coalescing as they do in the other method. Diffusion control would be less likely in this case. This is probably the simplest explanation.

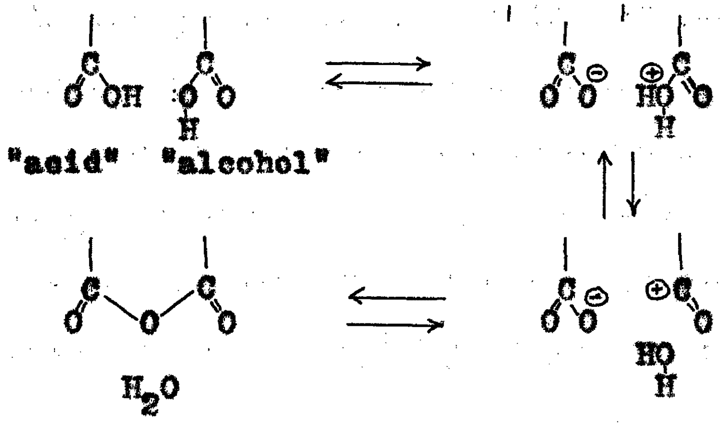
It therefore appears that diffusion effects tend to retard reaction to a relatively greater extent under molecular still conditions while dispersion in KCl appears to be more favourable for reaction.

MECHANISM OF THE REACTION

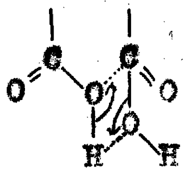
General.

There is no evidence to suggest that anhydride formation is a radical reaction, nor is it likely that the reaction proceeds with the intermediate formation of ketenes as was suggested at one time. The suggestion of Davidson and Newman[90] that the mechanism "is likely to be analogous to the esterification of a carboxylic acid by an alcohol" certainly seems the most reasonable one.

It is becoming increasingly clear that many "unimolecular" pyrolytic reactions show analogies with heterolytic reactions in polar solutions and may be considered formally at least as proceeding through the same ionic intermediates. There are a number of esterification mechanisms known, but it seems likely that anhydride formation may be considered analogous to an acid catalysed esterification:



The complete reaction may be represented as passing through a transition state with the structure:



Effect of Polymer Structure .

There have been no direct kinetic measurements on rates of formation of anhydrides, but it does seem that the presence of the polymer backbone has a favourable influence on anhydride formation, since anhydropolymethacrylic acid is formed readily at temperatures well below that at which glutaric anhydride is normally formed (300°C).[104] Although the influence of possible back reactions cannot be entirely neglected it is probable that this is due to a favourable steric or probability factor, as has been suggested to account for the lower temperatures required for anhydride formation from branched chain glutaric acids.

Polymers from 1:1 disubstituted monomers generally possess a strained chain structure. Methacrylates are no exception to this rule Examination of a model of a section of the polymethacrylic acid molecule shows that a conformation in which the acid groups are fairly close together is at least no more strained than any other, and might well be the preferred conformation over considerable segments of the chain. The very favourable geometry present in 1:8-naphthalene dicarboxylic acid in which the acid groups are held in a similar position probably accounts for the ease with which an anhydride is formed (140 - 150°C).[105]

Extent of reaction.

In the reactions studied by Marvel et al.[9] conclusions were drawn about the polymer structure from considerations of the statistical probability of the isolation of some groups when the pyrolysis reaction consisted solely of the interaction of two adjacent groups. Thus, for a purely head-to-tail arrangement of monomer units, it has been shown[106] that approximately 13% of the units should be isolated after "complete" reaction of pairs of adjacent units.

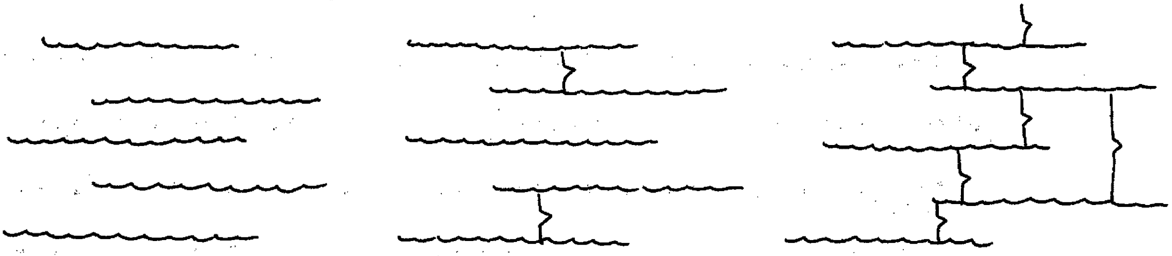
Superficially, the anhydride formation reaction of polymethacrylic acid might have been expected to show this behaviour. There is, however, no infra-red evidence to suggest that isolated carboxylic acid groups are left after prolonged degradation. This observation is consistent with the conclusions drawn from the study of the product and the measurement of the rates of reaction, regarding the greater complexity of the anhydride formation reaction.

i.e. 1. Cross-link formation is a reaction between pairs of non-adjacent units.

2. Diffusion control, subsequent hydrolysis and re-formation of anhydride would also prevent the isolation of units.

DEGRADATIONS OF COPOLYMERS CONTAINING METHACRYLIC ACID

It has been shown that there are likely to be two different anhydride structures in anhydropolymethacrylic acid, internal and cross-link. The insolubility has been attributed to the latter. It would be expected that in the early stages of degradation, formation of such a cross-link would be detectable by a molecular weight increase before the product becomes insoluble.



1. 2. 3.

1. Before degradation
2. Increased molecular weight
3. Insoluble

Since the only solvents for methacrylic acid are those which would break down an anhydride link provided they can penetrate the polymer, it is not practical to attempt such an investigation with polymethacrylic acid.

It was thought that the production of a cross-link might be confirmed in another fashion. If copolymers had a purely random structure then in a copolymer containing less than 50% methacrylic acid units, the chances of methacrylic acid units occurring in paired sequences would be less than that in which the units are separated by inert "spacer" units. In fact, copolymers do not have a random structure, but it has been found almost invariably that in the growing polymer chain, radicals ending in one type of unit add on the co-monomer rather than the same monomer, i.e. any deviation from randomness is towards alternation rather than bunching.

On degrading such a copolymer one would expect that if only a few acid units reacted to form anhydrides, leaving many unreacted acid units on "complete" reaction, it would be due simply to the internal reaction of the few paired units which might be present. In this case the degraded copolymer would be soluble. Alternatively, if anhydride formation went to completion, the majority of the bonds would be cross-links and the degraded copolymer would be insoluble.

Copolymers of methacrylic acid with both methyl methacrylate and styrene were prepared and degraded. Results were in complete contrast to those expected.

Methyl methacrylate/ methacrylic acid copolymer.

(Composition 2.5 ester : 1 acid)

The formation of an anhydride has already been mentioned (page 123.) and the effect on depolymerisation discussed. Examination of the spectrum of the fully degraded product failed to reveal any residual acid groups yet the polymer is soluble and therefore not cross-linked.

There would appear to be three possible explanations.

1. Direct formation of anhydride from an acid and an ester unit. Since the major volatile product is water, not methanol, this is not likely.

2. Contrary to expectations considerable bunching of acid units has occurred during copolymerisation.

3. We think that the most likely explanation is that at the degradation temperature acid and ester groups are not fixed in position but may undergo exchange reactions. This could continue till two acid units are adjacent when anhydride formation would occur. The existence of such reactions has already been discussed (page 17.) and further evidence of their existence will be discussed in Chapter VI.

Styrene / Methacrylic Acid Copolymers

(Compositions 2.6 : 1 and 4.3 : 1
styrene : acid)

These copolymers initially soluble in dioxan, on degradation at 200°C become insoluble in dioxan until a trace of alkali is added. These would appear to be the expected cross-linked products

However, examination of the spectra of degraded copolymers shows that while some anhydride formation is detectable, there has been very little change in the acid unit concentration, and that further anhydride formation cannot be brought about on further heating.

Even more curious is the production of a trace of some volatile organic material during degradation. It is certainly not styrene, but while not positively identified it could be benzaldehyde, since there is a smell of almonds and the solution spectrum shows both carbonyl and phenyl groups.

It is possible that the anhydride decomposes after it has been formed, with the reproduction of acid units by interaction with the tertiary H atoms of the styrene units. Alternatively, one has to consider the possibility that during copolymerisation styrene adds to the methacrylic acid in the same way as does <u>iso</u>-butene (page 69.), in which case the copolymerisation product is not a true copolymer of styrene and methacrylic acid.

In view of these possibilities it would not be safe to draw any conclusions from these experiments without a more complete investigation of the system.

SUMMARY

It has been shown that polymethacrylic acid will form an anhydride under the same conditions as does poly-*tert*.-butyl methacrylate.

It has been established that the pyrolysis product from both polymers is the same, and a more detailed consideration has been given to its structure, mainly by means of infra-red analysis. The head-to-tail structure for the polymers has been confirmed, while the degraded product has a structure composed mainly of linked six-membered anhydride rings with occasional cross-links.

When polymethacrylic acid is degraded in bulk the rate of degradation becomes diffusion controlled and liable to vary with different polymer samples, which probably accounts for the irregularities noted with peak E (page 119.)

Under conditions where diffusion control is less likely the reaction was measured over the range 153 - 192.5°C Activation energy was 37 Kcal/gm. mole.

CHAPTER VI

PYROLYSIS OF POLY-*TERT.*-BUTYL METHACRYLATE:

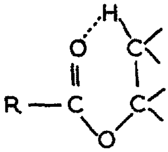
II. THE MECHANISM OF ESTER DECOMPOSITION.

Although radical mechanisms for ester decomposition have been suggested as occurring at temperatures above 500°C the decomposition of the ester group in the polymer is apparently not associated with a radical mechanism since it is not affected, for example, by the usual radical initiators and inhibitors. The mechanism of the reaction which will be postulated here is simply a modification, due to the presence of the polymer chain, of the mechanism by which simple (model) esters decompose.

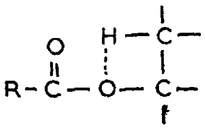
ESTER PYROLYSIS IN MODEL COMPOUNDS

It is now generally accepted that the decomposition of esters having β^H atoms proceeds through a unimolecular transition state. This has been confirmed by experiments in which it was shown that the molecule does not dissociate into reactive fragments such as separated ions or radicals.[107]

Two possible structures of the transition state are:



I



II

The six-ring structure I is generally preferred on steric grounds although there is no direct evidence to allow a choice between them. This structure is associated with the names Hurd and Blunk[108] who postulated that the comparitive instability of esters with a βH atom was due to their ability to form such an 'intermediate'. It was in fact one of a number of possible intermediates considered earlier by Bilger and Hibbert[109].

THE "CHAIN" REACTION

It is apparent that a simple random decomposition of isolated ester units in the polymer chain would lead to a normal "exponential" decrease in rate with extent of degradation. Since this does not occur with poly-<u>tert</u>.-butyl methacrylate the decomposition cannot be entirely a random one. It seems therefore that the polymer chain plays a significant part in the reaction mechanism.

The kinetics of the elimination of acetic acid from polyvinyl acetate have been studied[17]. The rate of elimination of volatile products shows a steady increase with time, qualitatively similar to the <u>iso</u>-butene elimination phase of the degradation under consideration. This overall kinetic resemblance suggests that the mechanism of decomposition of ester groupings in the two polymers may be basically similar.

The kinetics of polyvinyl acetate decomposition have been satisfactorily explained on the basis of the occurrence of two basic reaction steps. The overall decomposition may be described as a (non-radical) chain reaction, in the sense that the kinetic scheme can be derived on the basis of a difficult first step ("initiation") followed by the repetition of a relatively easier step ("propagation").

The initiation reaction is the normal decomposition of a saturated ester with the production of an "active centre" in the chain. In polyvinyl acetate the acid product is volatile and is removed, while the unsaturated group is left in the chain. The double bond is the active centre. In poly-tert-butyl methacrylate the unsaturated centre is removed and the acid unit left in the chain. The kinetic features of the pyrolysis of poly-tert.-butyl methacrylate would be explicable if it were possible to show that acid groups are active centres for further decomposition.

THE THERMAL DEGRADATION OF COPOLYMERS CONTAINING TERT.-BUTYL METHACRYLATE

The hypothesis that the ester decomposition of poly-tert.-butyl methacrylate proceeds by a chain mechanism in which the reproduced active centre is an acid group, was tested by the study of a series of copolymers. These were composed of large proportions of tert.-butyl methacrylate together with traces of the second monomer which was either methacrylic acid, styrene or methyl methacrylate.

1. Copolymers with methacrylic acid.

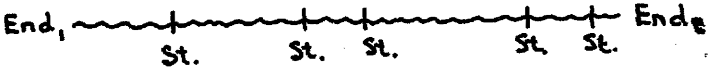
(Compositions 7.10 : 1 and 2.55 : 1
ester : acid)

If the active centres are indeed acid units then the introduction of additional methacrylic acid units would be expected to decrease the stability of the copolymer relative to the polymer. The Pirani curves obtained during the degradation of copolymers with methacrylic acid are shown in figure 44. The relative instability of the copolymers is shown both by the earlier attainment of the maximum rate, and also by the higher maximum rate at all temperatures. (Table 14, page 185)

2. Copolymer with Styrene.

(Composition 3.4 : 1 ester : styrene)

The small proportion of styrene may be assumed to be distributed in a random manner along the chain. In all but the very lowest polymers there will be many styrene units in one chain. These break up the sequences of *tert*.-butyl methacrylate units. Thus the copolymer of *tert*.-butyl methacrylate and styrene may be represented as;



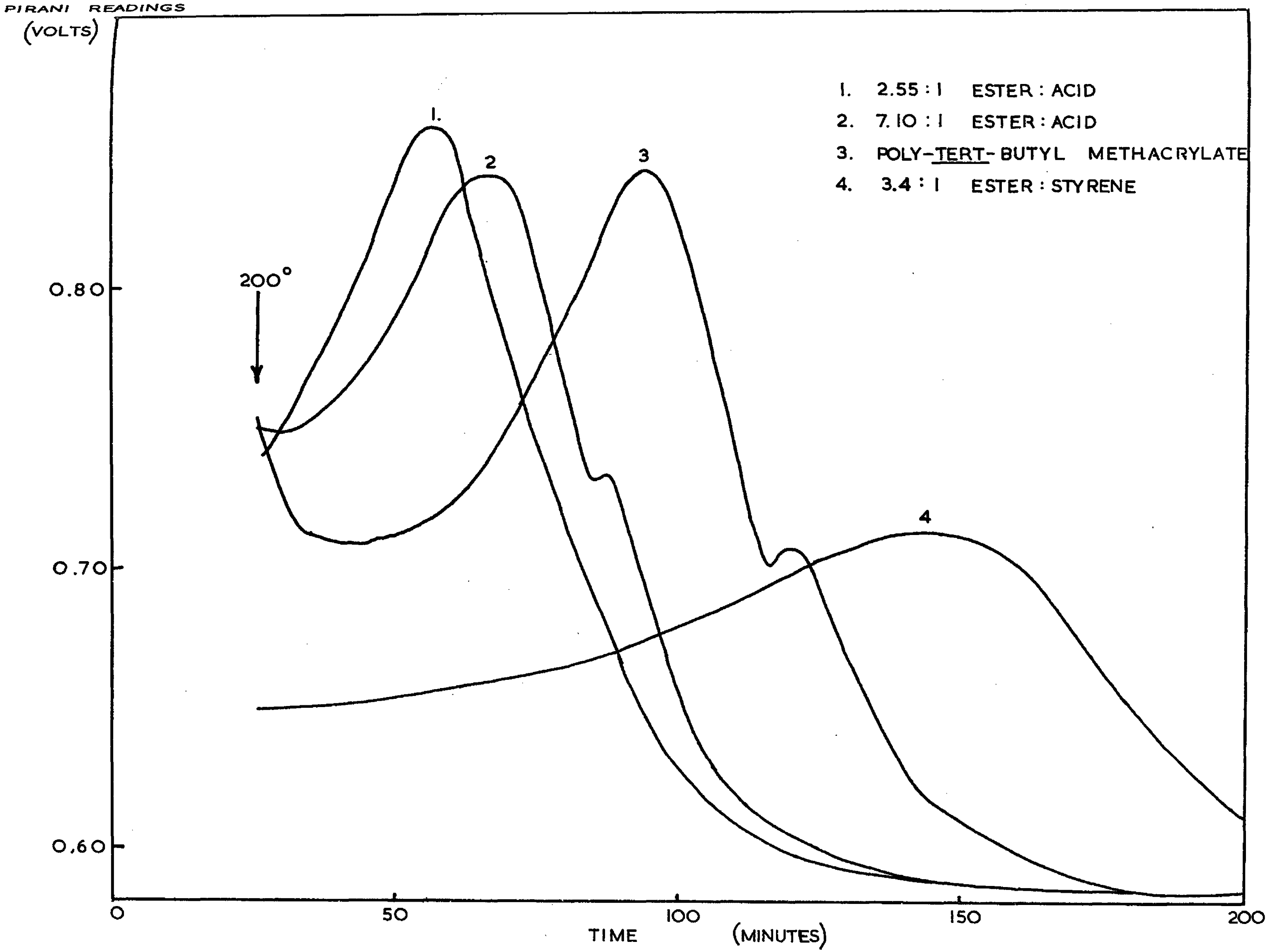


FIGURE 44. PYROLYSIS AT 200°C OF COPOLYMERS, PIRANI CURVES.

Table 14. Maximum rate of production of *iso*-butene from copolymers.

	181°C		192.5°C		200°C	
	1.	2.	1.	2.	1.	2.
2.55 ester : 1 acid	184,	37.6%	70,	88.0%	32,	169%
			71,	87.0%		
7.10 ester : 1 acid	-		83,	68.7%	45,	122%
poly-*tert*.-butyl	357,	22.9%	136,	51.3%	69,	99%
methacrylate	365,	23.6%	132,	51.0%		
			133,	50.7%		
3.4 ester : 1 styrene	-		222,	29.2%	119,	53.5%
3.5 *tert*.-butyl : 1 methyl	-		117,	47%	61,	115%

1. Time (in minutes) between attainment of pyrolysis temperature and maximum D of *iso*-butene production rate.

2. The maximum *iso*-butene production rate as a percentage of the total *iso*-butene content per hour.

If the "easy" propagation step consists of the reproduction of acid units along the chain it is likely that the introduction of unreactive foreign units would block the propagation step, and limit it to the sequence in which it was initiated.

Two possibilities arise: if the reaction can only be initiated at a limited number of specific points, such as the chain ends, then the reaction will stop once the first blocking group is reached, in much the same manner as the anhydride groups appear to stop the depolymerisation process. On the other hand if the initiation process can occur at random along the chain, the overall reaction will be slower but will go to completion.

Results show that the reaction is appreciably slower than normal, but in time, normal yields of iso-butene result. Infra-red analysis of the polymeric residue from the degradation shows that it contains the original styrene units, together with the usual anhydride. No residual unreacted ester groups can be detected in this residue.

This shows quite clearly that the chain propagation mechanism stops at styrene units but that initiation occurs in each sequence, i.e. initiation is a random process.

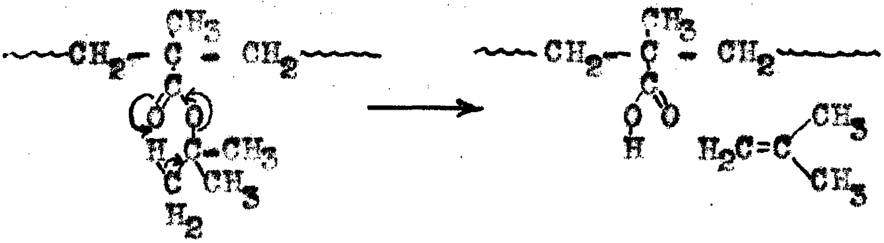
3. Copolymer with methyl methacrylate.

(Composition 3.5 : 1 tert.-butyl : methyl)

In contrast to styrene units, methyl methacrylate units have no appreciable effect on the ester degradation reaction. It has already been suggested that methyl ester groups and acid groups can undergo some form of exchange process (Chapter V). If this is the case then methyl methacrylate units would not be expected to check the reproduction of acid units along the chain. There is no evidence from the nature of the volatile products of decomposition of methyl ester groups, and infra-red examination of the residue shows that ester groups are present after prolonged degradation, in contrast with the product from the pure polymer.

POSSIBLE NATURE OF THE "PROPAGATION" REACTION

In view of the evidence obtained from copolymers of tert.-butyl methacrylate with methacrylic acid and styrene there can be little doubt that some form of "chain" reaction occurs in the pyrolysis of poly-tert.-butyl methacrylate. The active centres are acid units. The initiation step is likely to be by a normal ester decomposition:



The next question to be considered is why the decomposition of neighbouring groups is an easier process. The most likely explanation seems to lie in some form of reaction in which the initial acid group plays a direct part. We did however, consider another possibility which will be discussed first.

The "Steric Strain" Hypothesis.

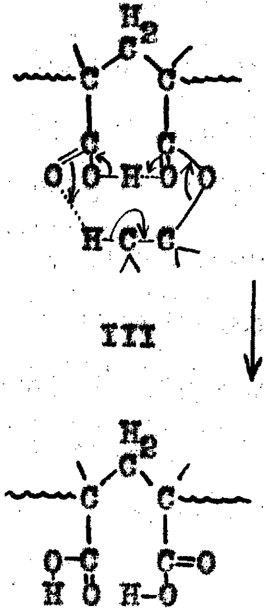
The presence of both methyl and ester groupings on every alternate carbon atom in the polymer chain results in considerable strain in the poly-methacrylate structure.[110] It therefore seemed possible that the attainment of a conformation suitable for a six-membered transition state to be produced might be a difficult process. Since a carboxylic acid group will occupy less space than an ester group, particularly a *tert*.-butyl ester, production of a six-membered transition state adjacent to an acid unit would be an easier process than when it is adjacent to an intact *tert*.-butyl group. In this way one might account for the occurrence of two ester decomposition reactions with different rate constants.

This hypothesis has been tested (N.W.Weir B.Sc. Thesis 1959). Much of the strain in the polymer structure can be avoided by replacing the methyl groups with hydrogen. Thus it would be predicted that poly-*tert*.-butyl acrylate would be able to form the necessary transition state more readily, but the decrease in strain on replacing ester by acid groups would be much less. Iso-butene production from this polymer would be expected to be more rapid initially but would not be expected to increase to the same extent during degradation.

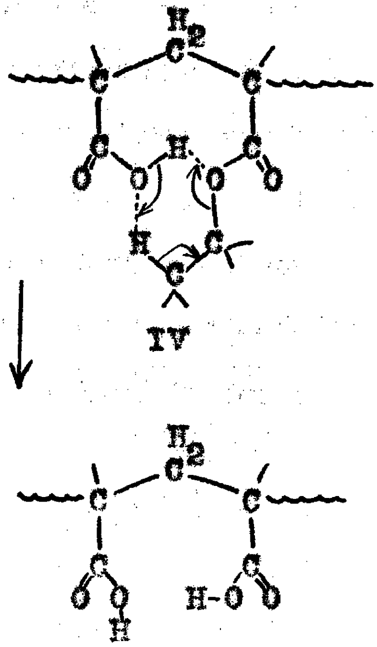
In fact it was found that the ester decomposition phase of poly-tert.-butyl acrylate degradation shows an acceleration at least as great as that of the methacrylate. One must conclude therefore that the propagation reaction is not easier than the initiation by virtue of a steric effect.

The Group Interaction Mechanism.

It is possible to formulate a reaction mechanism for olefin elimination from the interaction of a pair of neighbouring acid and ester groups. Two possible transition states III and IV shown below, display a close similarity to the two possible transition states of the "unimolecular" reaction, I and II respectively (page 180), particularly in having βH "interaction". In cases I and III the H interaction is with an acyl (carbonyl) oxygen, in II and IV with an alkyl (ether) oxygen. The group interaction cases III and IV have, additionally, oxygen interaction with an acidic H. It would also be possible to formulate eight-membered transition states with mixed acyl and alkyl oxygen interaction but this would only unnecessarily complicate the discussion.



III



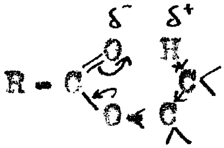
IV

Solution analogies. In order to show why decomposition by this process is an easier reaction than "mono-unit" decomposition it is necessary to consider possible analogies which the pyrolysis reaction shows to reactions in polar solutions.

Consideration of either "mono-unit" transition state I or II shows that one can distinguish at least two processes, these are the making of the O-H bond and the breaking of the C-O bond. A summary has been given[111] of evidence showing that it is the forming O-H bond which primarily determines the rate, and not the breaking alkyl-oxygen bond, in the normal vapour phase pyrolysis of esters.

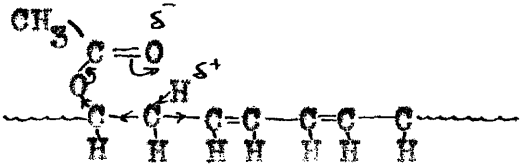
Elimination. Regarding the pyrolysis principally from the standpoint of an olefin producing reaction, Maccoll considers it as the analogue of an elimination (E) reaction, in particular the bimolecular E2 reaction, since the alternative E1 mechanism depends on the breaking of a C-X bond as the rate determining step. In the E2 mechanism proton removal is brought about only on the approach of a nucleophilic reagent. It is possible therefore to regard the pyrolysis as due to the nucleophilic attack of the acyl oxygen atom on the βH atom

The mono-unit process on this basis may be represented



Clearly the reactivity of the ester will be a function of the electron displacements affecting the fractional charge on the attacked H atom

In the "propagation" step in polyvinyl acetate decomposition, double bonds act as active centres by virtue of their electron withdrawing power.

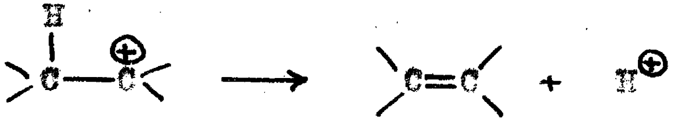


Similarly in the "bi-unit" propagation reaction in poly-<u>tert</u>.-butyl methacrylate decomposition the cyclic process will be started by the attack of the acyl (carbonyl) oxygen atom on the acid hydrogen atom. Being attached to an electron withdrawing oxygen atom instead of to a carbon atom the fractional positive charge on the attacked hydrogen atom will be greater and consequently the "bi-unit" process much easier than the "mono-unit" process.

In using the elimination analogy only interaction between carbonyl oxygen and acid hydrogen has been mentioned (structures I and III) since Maccoll only makes use of the six-ring structure I. However an identical argument can be made out for interaction between ether oxygen and acid hydrogen using structures II and IV.

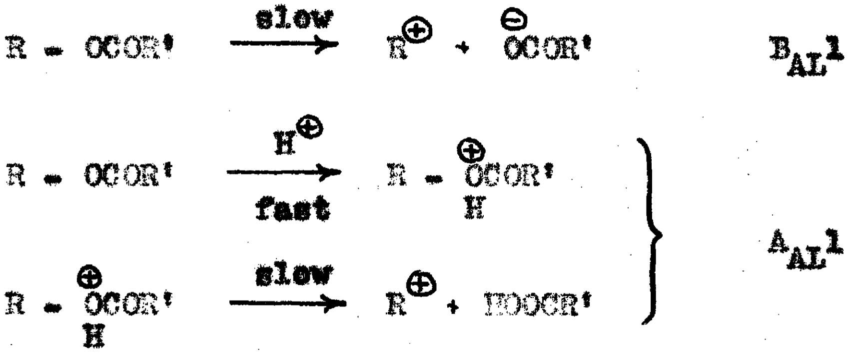
Hydrolysis. While the elimination analogy is the most useful when considering the olefin formed it is also possible to consider ester pyrolyses as similar to the decomposition reactions of esters in solutions. In aqueous and alcoholic solutions such decompositions are "hydrolysis" and "alcoholysis" respectively.

Ingold[112] has discussed no fewer than eight distinct mechanisms for ester hydrolysis. Of these, four have acyl/oxygen scission, and might prove to be useful analogies with acyl scission pyrolytic reactions, about which comparatively little is known. Of the four alkyl/oxygen scission reactions, three involve the expulsion of the alkyl group as a carbonium ion. The production of alcohol may be regarded as a purely secondary process, occurring only in the presence of water. In the absence of water it would be expected that the carbonium ion would decompose to an olefin and a proton.



In fact olefin by-products have been detected in at least one of the two mechanisms established experimentally

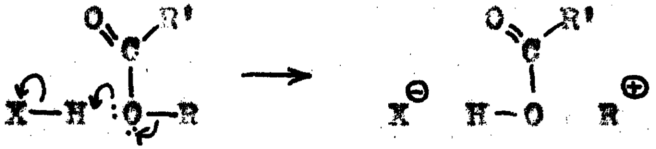
It is in the production of the carbonium ion that the three mechanisms differ. In the two mechanisms established experimentally ($B_{AL}1$ and $A_{AL}1$) alkyl/oxygen scission is the sole factor in the rate determining step:



$$R - OCOR' \xrightarrow{\text{slow}} R^{\oplus} + \overset{\ominus}{O}COR' \qquad B_{AL}1$$

$$\left.\begin{array}{l} R - OCOR' \xrightarrow[\text{fast}]{H^{\oplus}} R - \underset{H}{\overset{\oplus}{O}}COR' \\ R - \underset{H}{\overset{\oplus}{O}}COR' \xrightarrow{\text{slow}} R^{\oplus} + HOOCR' \end{array}\right\} \qquad A_{AL}1$$

In the presence of an acid, mechanism $A_{AL}1$ is the preferred route, but it is possible to imagine the effect of using a series of acids of decreasing strength. In conditions favourable to the formation of ions, mechanism $B_{AL}1$ would be expected to take over, as it does in all the reported cases in solution.. However in circumstances less favourable for ion formation, the proton uptake would become involved in the rate determining step. Such would be the hypothetical $A_{AL}2$ mechanism.



"$A_{AL}2$"

It is to such a mechanism that the pyrolysis of esters is most closely allied, and one would predict as from the elimination analogy that their reactivity would be a function of the acidity of the hydrogen atom.

From such considerations, the pyrolysis of poly-tert.-butyl methacrylate may be described truly as a reaction autocatalysed by acid.

INFRA-RED STUDIES ON THE ESTER DEGRADATION.

One feature of the proposed mechanism is that it should be possible to bring about iso-butene production by the use of external acids; while the presence of a polymer backbone is favourable for the formation of the "bi-unit" transition state it is not vital. It would also be expected that the catalytic effect of different acids would be in the same order as their acid strengths.

One way in which these ideas might be tested would be by studying the effect of acids on the polymer in non-polar solutions. However it was felt that the tests should be made under conditions as close as possible to those present in the polymer during the actual thermal degradation, i.e. virtually solid state conditions.

For use in high vacuum conditions such as encountered in the dynamic molecular still, the acids would have to be involatile and therefore of relatively high molecular weight. Even if stable compounds of this description had been available one would still have expected the same difficulties over diffusion as had been encountered with the inhibition experiments.

The method which was found to be reasonably satisfactory was to use low molecular weight acids in a sealed system, and to follow the reaction by infra-red spectroscopy.

It was first necessary to confirm the general features of the degradation reaction on pure polymer, following the reaction by this infra-red spectroscopic method. At the same time it proved possible to confirm certain observations made previously in reactions in the d.m.s., namely:

the presence of acid units during degradation,
acceleration by additional methacrylic acid units and
retardation by additional styrene units.

Assignment of frecuencies and changes of spectrum during pyrolysis.

The spectra of polymethacrylic acid and the changes on anhydride formation have already been discussed (page

148). Similar spectral changes occur during the degradation of poly-*tert.*-butyl methacrylate, additional changes being explicable in terms of *iso*-butene production from the ester group, or loss of material by depolymerisation.

3600 - 2000. C-H stretching vibrations have two distinct maxima at 2965 and 2925 cm^{-1}, probably the assymmetrical and symmetrical C-H stretchings of the methyl groups respectively. On degradation the C-H intensities are reduced.

Using the KCl disc method there is also O-H absorbtion, but since the nujol mull method does not show this absorbtion it can be attributed to water in the KCl, not to acid groups in the polymer. On degradation however the maximum shifts to lower frequencies, as would be expected for acid formation.

A more satisfactory indication of an acidic intermediate is the rise and fall of weak broad absorbtion about 2580 cm^{-1}.

2000 - 1500. The ester has a sharp C=O stretching peak at a frequency of 1715 cm^{-1}. Acid formation is shown by a broadening to the low frequency side before the anhydride peaks develop on the high frequency side.

1500 - 1350. 1478 and 1458 cm^{-1} the assymmetrical C-H bending of the methyl groups and the methylene scissoring vibration frequencies respectively, are not well separated;

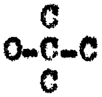
on degradation the intensity is reduced and the peaks coalesce as found for the acid.

Symmetrical C-H bending of the methyl groups of the chain contributes to the 1392 cm^{-1} peak and this contribution remains on degradation. Similar vibrations in the *tert.*-butyl group are known to give two peaks. One of these also contributes to the 1392 cm^{-1} and is lost on degradation. The other is the 1367 cm^{-1} peak. This disappears completely on degradation.

Below 1300. The *tert.*-butyl skeleton is known to give two peaks at about 1250 and 1200 cm^{-1}, and will contribute to the absorbtion in these regions. The 1140 cm^{-1} peak is at a normal C-O-C vibration frequency for an ester. It is likely however that basic vibrations of the methacrylate chain also occur in these regions; the picture is also complex in the acid and the anhydride (page *151*).

Weak absorbtion peaks at 1042, 967 and 878 cm^{-1} cannot be definitely assigned to any particular vibration.

The fairly strong peak at 848 cm^{-1} arises from the



$O-\overset{\displaystyle C}{\underset{\displaystyle C}{C}}-C$ skeleton,[113] i.e. the *tert.*-butyl ester group. It disappears completely during degradation and was used as a measure of the ester concentration in semi-quantitative measurements.

Methylene rocking is probably the cause of the 754 cm^{-1} absorbtion.

Results of Degradation in KCl Dispersion Method.

Degradations were carried out in the same system as used for polymethacrylic acid (pages 56, 63 and 160.), using pure poly-*tert*.-butyl methacrylate, a methacrylic acid / *tert*.-butyl methacrylate copolymer and a styrene / *tert*.-butyl methacrylate copolymer.

Figure 45 shows the changes in intensity which occur in regions of ester, acid and anhydride absorbtion during the degradation of the pure polymer at 192.5°C. The presence of acid groups is clearly demonstrated. The decrease in ester intensity is consistent with an initial depolymerisation followed by an auto-catalytic ester decomposition.

Acceleration by additional acid units and retardation by styrene units are demonstrated in figure 46, which shows the relative decrease in ester intensity for both copolymers and pure polymer.

Catalysis by External Acids.

Slight modifications were made to the experimental technique in order to demonstrate external acid catalysis. The acid and polymer were first ground together before adding the KCl, and the degradations were carried out in evacuated, sealed ampoules of about 2 ml. capacity immersed in an oil bath. Control experiments showed that the ester decomposition phase of the reaction was not

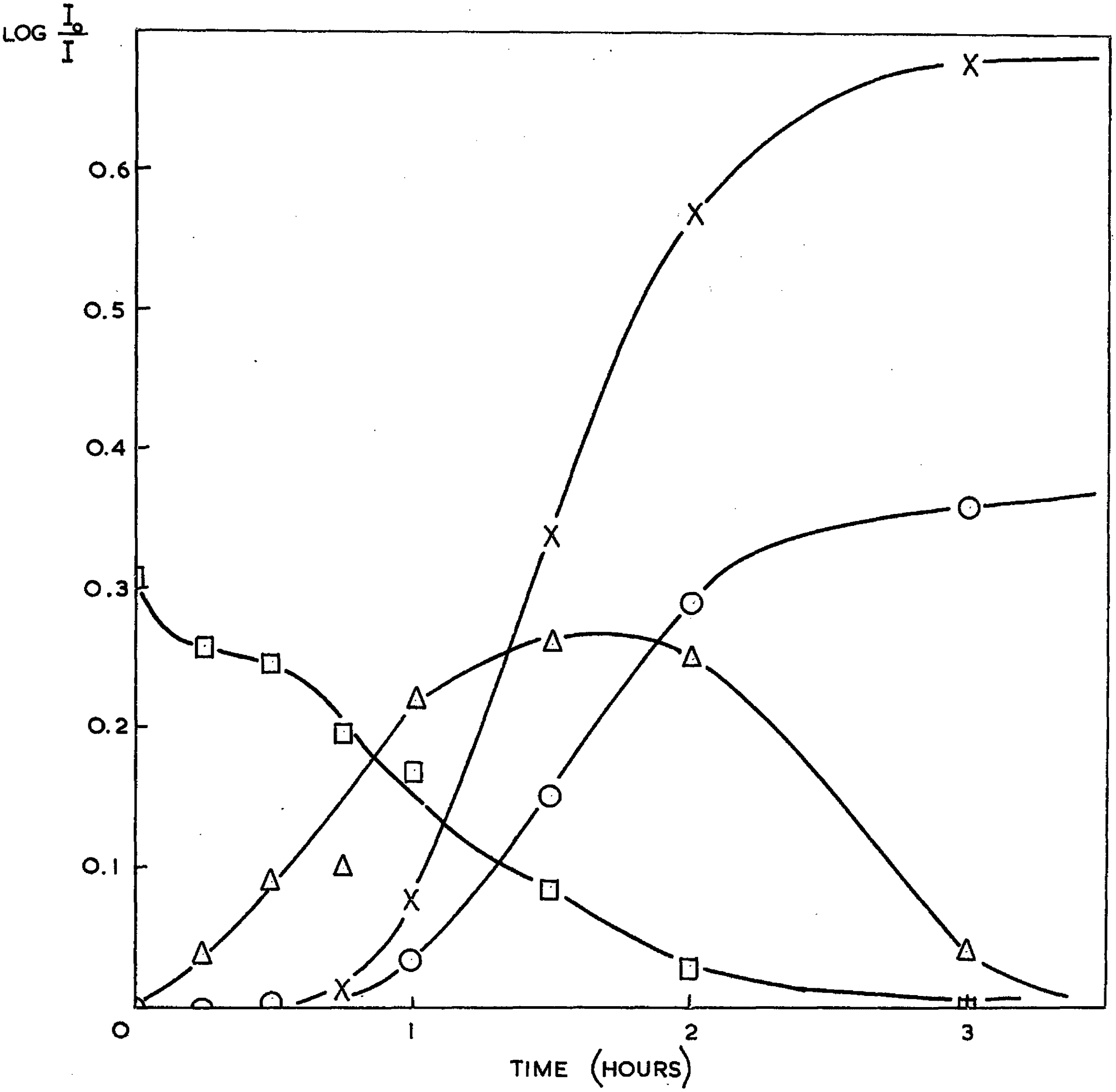


FIGURE 45. PYROLYSIS OF POLY-TERT.-BUTYL METHACRYLATE AT 192.5 °C ABSORBTION OF ESTER (□ 848 CM^{-1}), ACID (△ 2580 CM^{-1} x10), AND ANHYDRIDE PEAKS (○ 1795 CM^{-1} AND X 1022 CM^{-1}).

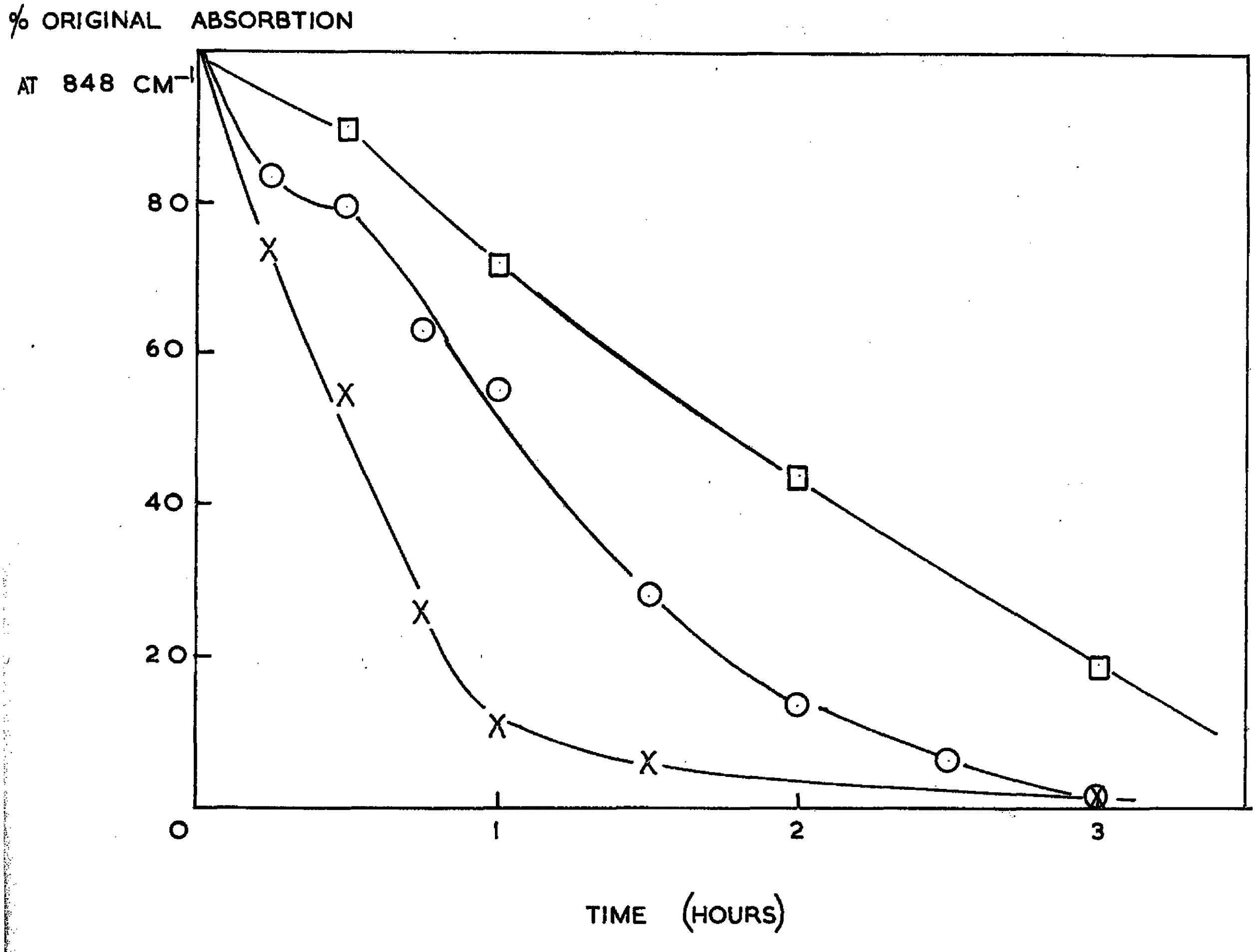


FIGURE 46. PYROLYSIS OF COPOLYMERS AT 192.5°C.

□ 3.4 : 1 ESTER : STYRENE

○ POLY-TERT-BUTYL METHACRYLATE

X 2.55 : 1 ESTER : ACID

significantly modified by the sealed system.

Although it is possible to demonstrate that both acid and polymer are uniformly distributed within the KCl, it is unlikely that the acid is uniformly distributed in the polymer. Most of it will be in inactive sites and the true concentration of acid in the polymer will be very much less than that given by the ratio of weight of acid to weight of polymer.

Figure 47 shows the results of using the same weight ratio (1:6) of different acids. It would be difficult to distinguish from experimental error the deviation from normal behaviour caused by both benzoic and naphthoic acids. No such doubt exists about the effect of the much stronger acid, 3:5 dinitrobenzoic acid.

Figure 48 demonstrates that smaller weght ratios of this acid are sufficient to produce detectable deviations from normality.

COMPARISON BETWEEN THE PYROLYSES OF POLYVINYL ACETATE AND POLY-TERT.-BUTYL METHACRYLATE.

While the pyrolyses of the two ester polymers, polyvinyl acetate and poly-*tert*.-butyl methacrylate, show some general similarities a more detailed consideration shows that there are some differences. These would have to be taken into account in any attempt to examine the kinetics of poly-*tert*.-butyl methacrylate degradation

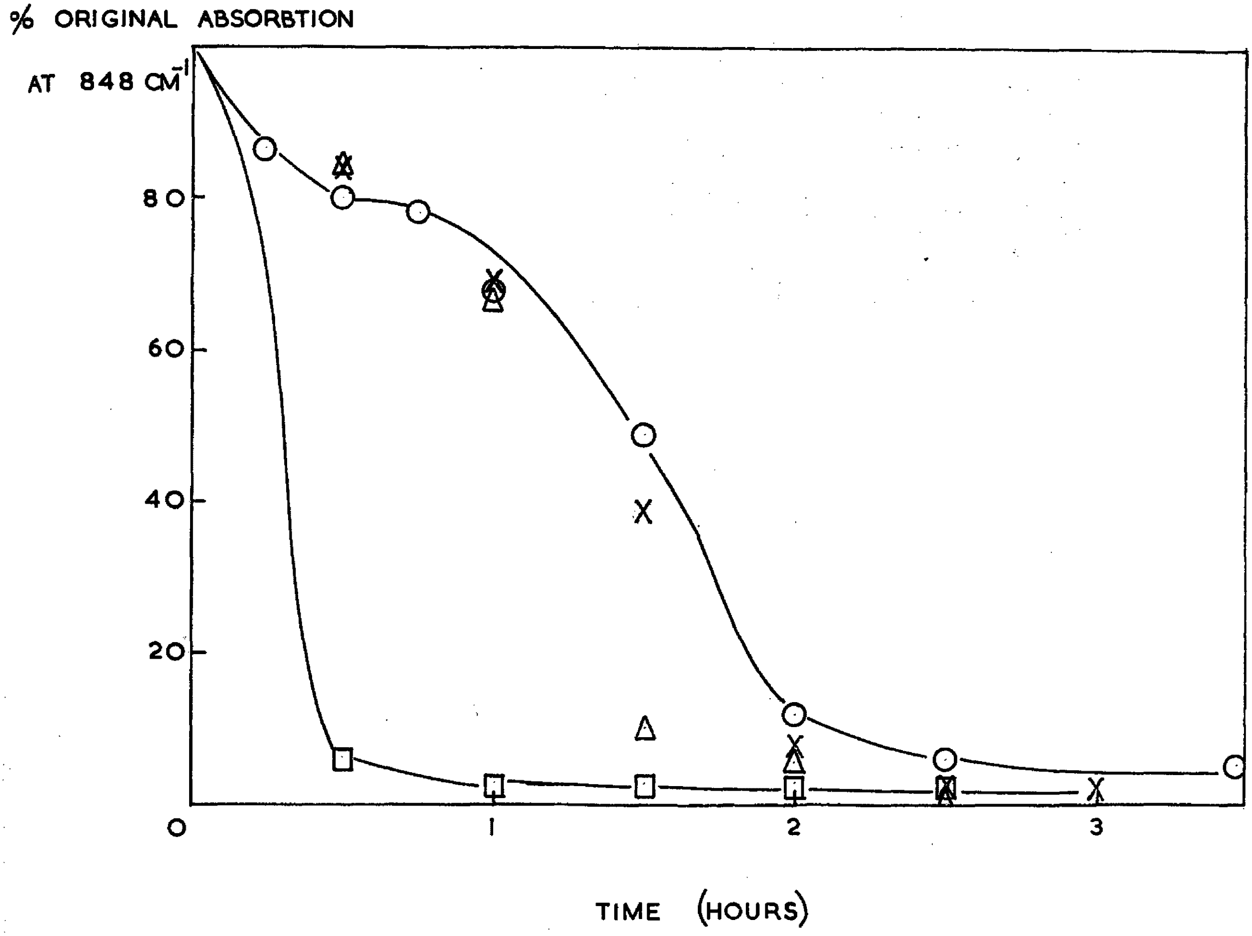


FIGURE 47. PYROLYSIS OF POLY-TERT.-BUTYL METHACRYLATE AT 192.5 °C ○ IN PRESENCE OF BENZOIC X, NAPHTHOIC Δ AND 3:5 DINITROBENZOIC □ ACIDS.

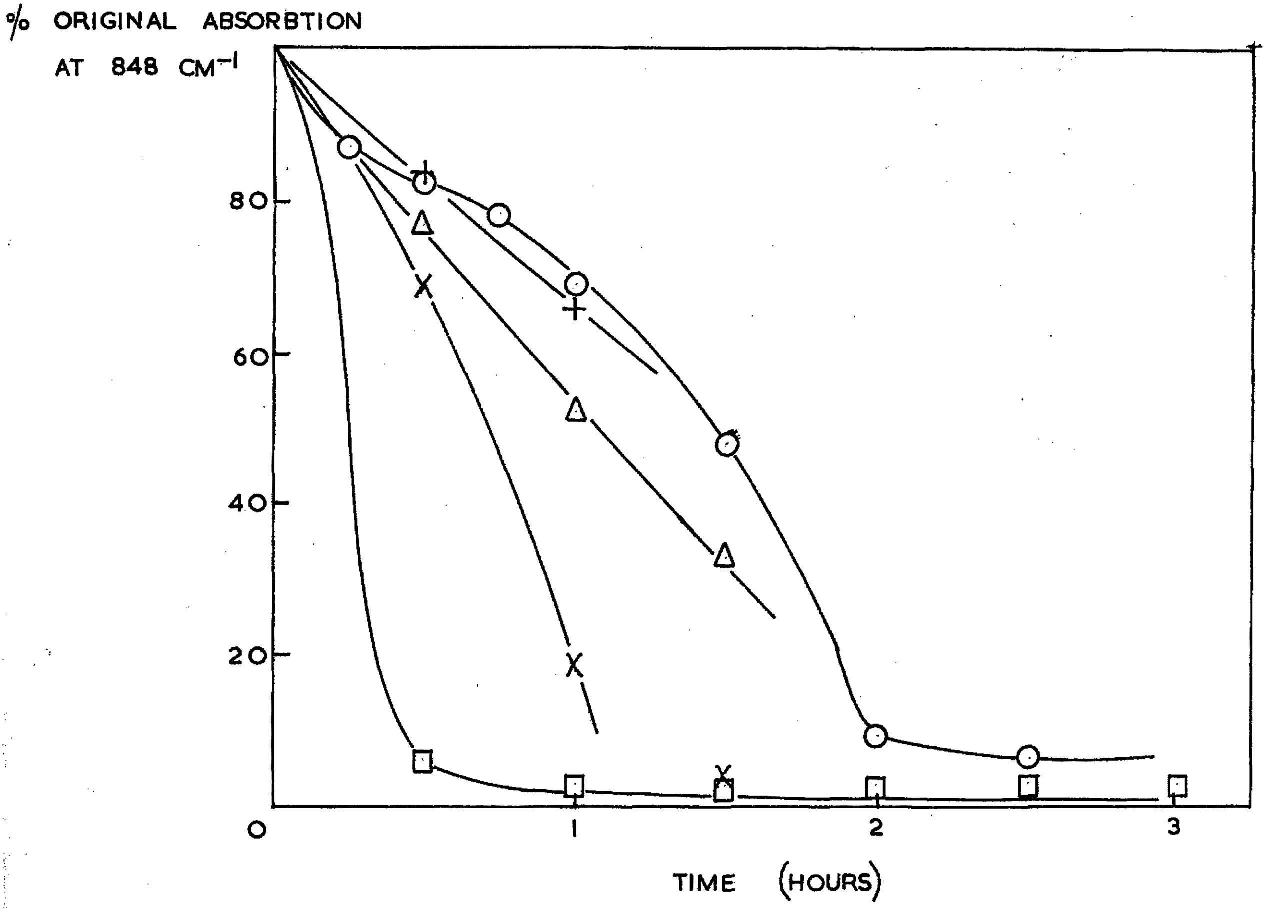


FIGURE 48. PYROLYSIS OF POLY-TERT.-BUTYL METHACRYLATE AT 192.5°C. ○, IN PRESENCE OF 3:5 DINITROBENZOIC ACID

□	6:1	POLYMER	: ACID
X	10:1	"	"
Δ	20:1	"	"
+	50:1	"	"

in greater detail.

The most obvious difference is, of course, the occurrence of a depolymerisation reaction, which raises experimental difficulties in the determination of the initial *iso*-butene production rate. Apart from this difference there are distinctions within the ester decomposition reaction itself.

The chain ester decomposition in polyvinyl acetate is initiated only in the region of the chain ends. The quantity of volatile product from this decomposition of a secondary ester group is regarded as negligeable compared with the quantity produced by the propagation step. With poly-*tert*.-butyl methacrylate initiation is apparently a random process and being the decomposition of a tertiary ester it may not be quantitatively negligeable as an *iso*-butene producing step.

Although the propagation step in poly-*tert*.-butyl methacrylate pyrolysis is predominately a reaction along the chain, the ability of external acids to catalyse the reaction shows that acid groups on one chain may cause decomposition on a neighbouring chain. Such inter-chain propagation does not occur in polyvinyl acetate.

Interaction and termination of growing reaction chains in polyvinyl acetate pyrolysis are uncommon. With poly-*tert*.-butyl methacrylate, removal of acid active centres occurs on anhydride formation. It is probably the neutralisation of acid groups by this process which prevents the inter-chain propagation from becoming important. It will confine the propagation to intra-chain reactions in which each acid group takes part in the "bi-unit" process only once.

Two other reactions which may occur in poly-*tert.*-butyl methacrylate pyrolysis but have no parallel in the case of polyvinyl acetate are "transfer" and alcohol production ("termination")

1. "*Transfer*" It may be possible for acid centres to pass through *tert.*-butyl ester groups without decomposing them, much as they do with methyl ester groups. (page 137).

2. *Alcohol Production*. Although the direct formation of alcohol from an acid and an ester group is not quantitatively detectable (pages 114 and 138.) it might be important from a kinetic aspect since it would represent a breaking of the intra-chain propagation reaction.

ESTER DEGRADATION IN POLYMERS IN RELATION TO ESTER DECOMPOSITION IN OTHER MEDIA.

It has been shown that the polymer structure favours an "acid catalysed pyrolysis reaction". The analogy with certain types of ester decomposition reactions in polar solvents has been pointed out. It is interesting to consider to what extent similar reactions occur in less polar media.

The existence of an auto-catalytic reaction in the liquid phase pyrolysis of *tert*.-amyl acetate is very clearly demonstrated in the results of one of the earliest investigations into pyrolysis reactions.[16] The reproduced figure 49 shows a quite remarkable resemblance to the results obtained in the static system (pages 21 and 112) and presumably are due to auto-catalysis by acetic acid.

The acid catalysed reversal of the liquid phase pyrolysis has been demonstrated by the alternative synthetic route to *tert*.-butyl esters by the reaction between methacrylic acid and *iso*-butene (page 68).

One would not expect dilute vapour phase pyrolysis to show acid catalysed effects particularly when flow systems are used. However, such conditions may be regarded as ideal and in practice many pyrolyses which are apparently "vapour phase" do in fact take place on surfaces, where the conditions are likely to be similar to those in the liquid phase or in the polymer chain. Under these conditions catalytic effects of acid have been postulated on several occasions. Thus Houtman, van Steenis and Heertjes[13] reported that primary esters did not decompose at 500°C unless a carbon deposit was present, and also that traces of acids were associated with the deposit in

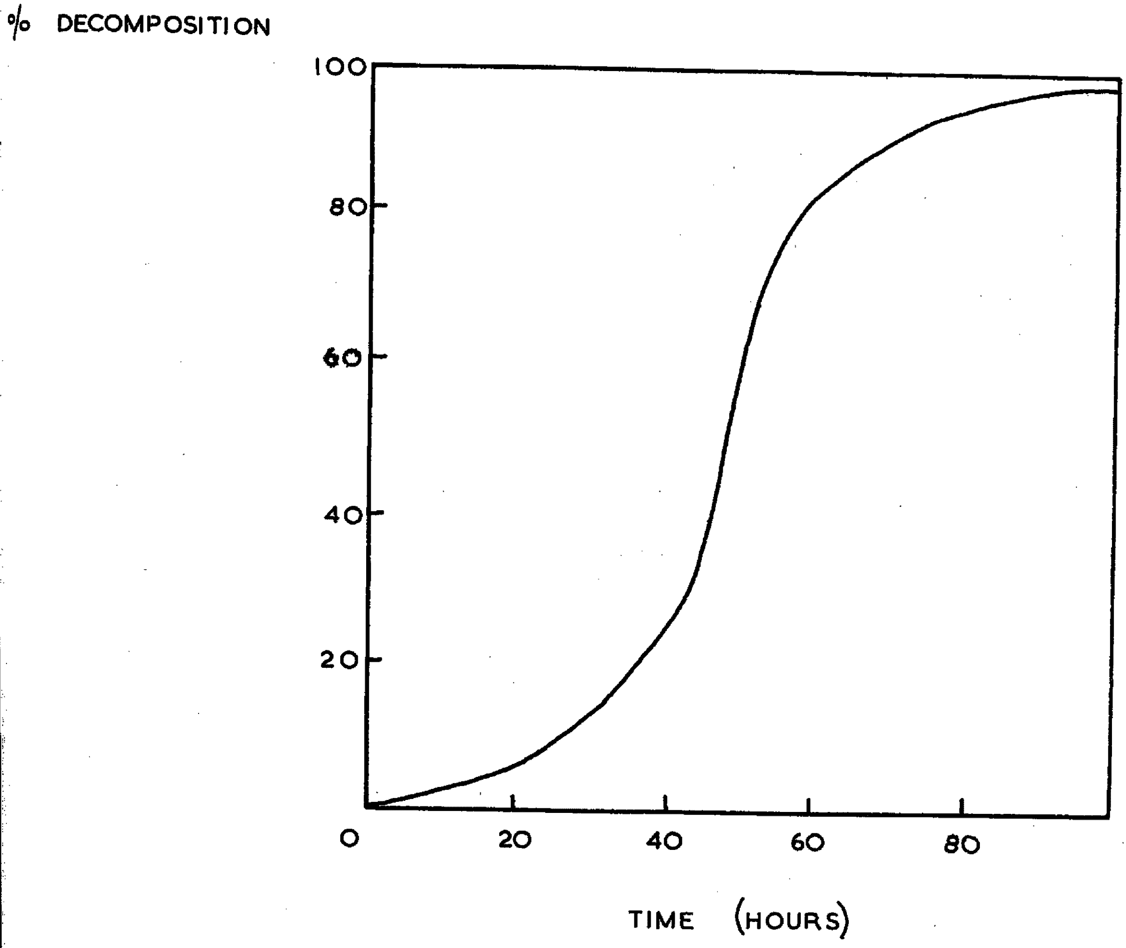


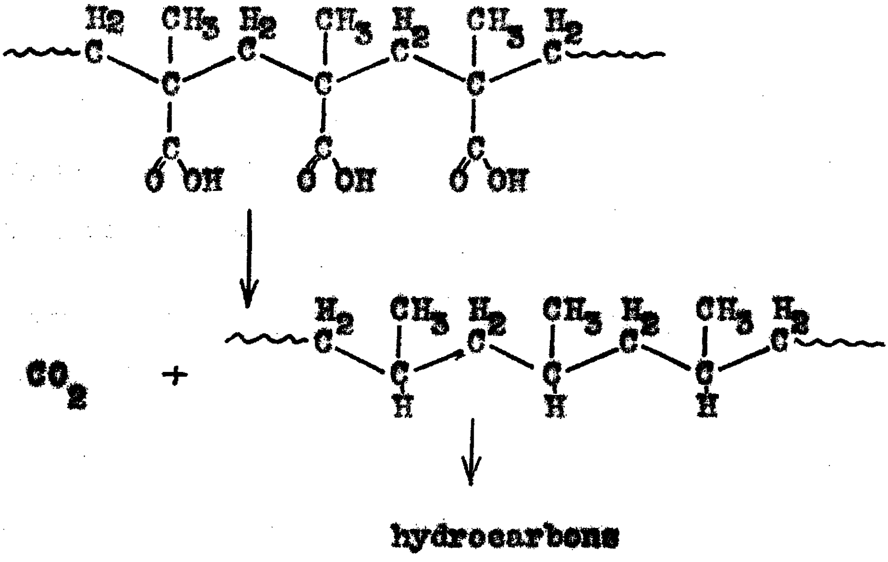
FIGURE 49. PYROLYSIS OF TERT.-AMYL ACETATE AT 155°C

causing reaction. On the other hand Rudy and Fugassi[15] found that clean glass surfaces catalysed the decomposition of *tert.*-butyl acetate and propionate and that reproducible results are only obtained when the surface was coated with a "light brown film". In recent years Bailey et al.[114] have shown that not only does the presence of an "acidic carbon deposit" increase the rate of pyrolysis but have also claimed that the presence of this material can affect in some cases the direction of elimination from unsymmetrical esters in a manner comparable to that which occurs on a change from an E2 to an E1 mechanism.

CHAPTER VII

PYROLYSIS OF ANHYDROPOLYMETHACRYLIC ACID.

According to Schildknecht's "Vinyl and Related Polymers" polymethacrylic acid breaks down at 350°C to " CO_2 and volatile hydrocarbons ". It would be simple to explain this result as the decomposition of polymethacrylic acid by decarboxylation to CO_2 and a polypropylene chain which at this temperature is known to break down to hydrocarbon fragments:



However, as has been shown, polymethacrylic acid would almost certainly lose water with formation of anhydropolymethacrylic acid at much lower temperatures, and it is not immediately obvious how such products as those above might arise from the anhydride. Accordingly it was thought that it might be interesting to investigate the breakdown of an authentic sample of anhydropolymethacrylic acid.

The high temperature breakdown of anhydropolymethacrylic acid is also of interest in connection with the depolymerisation of polymethacrylic derivatives. Although traces of methacrylic acid arise from the depolymerisation in the pyrolysis at 200°C of both polymethacrylic acid and its *tert*.-butyl ester, monomeric methacrylic anhydride was never detected. It would therefore be useful to find out if, when the residue does break down, chain scission only occurs after "side chain" anhydride decomposition, or if chain scission can occur with production of methacrylic anhydride or fragments containing intact six-membered anhydride rings.

DEGRADATIONS IN THE DYNAMIC MOLECULAR STILL.

For the first degradation of anhydropolymethacrylic acid, a 50 mg. sample was prepared from polymethacrylic acid by prolonged heating at 200°C by the usual method in the dynamic molecular still.

The temperature was then raised to 330°C, at which temperature volatile materials are evolved slowly. The rate of production of volatiles decreases slowly from the start of the reaction but is still detectable after 14 hours heating. The simplicity of the variation of volatilisation rate with time, contrasting markedly with both acid and tert.-butyl ester degradations, is offset however, by the complexity of the reaction products. Closed system "Pirani Tests" carried during the degradation showed that the products include substances (V_{-183}) which do not condense in liquid oxygen. At the other extreme of volatility there are products (V_{DT}) which, although volatile at the degradation temperature, condense to form a yellow layer on the sides of the glass envelope and on its contents, including even the cooler parts of the copper powder covering the degradation tray. At the end of the 14 hour period of heating investigation showed that products (V_{-73} and V_{RT}) of intermediate volatility were present. Their analysis is discussed below. The residue of non-volatile material and that part of the yellow fraction still on the copper amounted to 32% of the original anhydropolymethacrylic acid.

In an effort to bring about more complete reaction in a reasonable time, the degradation was continued at 380°C till production of volatiles was negligeable (5 hours). The most noticeable feature of the degradation during this stage was that the yellow surface layer on the hot copper steadily darkens till it is black. Even after this prolonged degradation there is still a residue of 21% of the original anhydride. It was found that this is a black substance present throughout the copper powder and not simply as a layer on the bottom of the tray. This suggests that much of the reaction takes place not on the uniform temperature surface, but within the covering copper powder, and consists of the secondary breakdown of the yellow partially volatile material. Even if the copper is not exerting a chemical "catalytic" influence, the reaction is taking place in non-uniform temperature conditions.

Further degradations at 380°C of the product from both polymethacrylic acid and poly-<u>tert</u>.-butyl methacrylate confirmed that a wide range of volatile products occurs and that there is always a residue amounting to 20 - 25 % of the anhydropolymethacrylic acid, no matter the length of the degradation. These experiments also confirmed that the d.m.s., at least in its present form, is not suited even for qualitative investigation of this degradation.

In view of the complexity of the problem further investigations were limited to a preliminary qualitative examination of the products by infra-red analysis supplemented by gas chromatography.

DEGRADATIONS IN THE SECONDARY SYSTEM AND THE PRODUCTS OF THE REACTION

All the results discussed below were obtained from anhydropolymethacrylic acid prepared from polymethacrylic acid. Unless otherwise specified the anhydropolymethacrylic acid was heated in the closed secondary system for three hours at 380°C, no copper was present.

V_{-183} (Products non-condensable in liquid oxygen).

With the U-tube product trap immersed in liquid oxygen a measurable pressure develops in the system, during degradation. That the reaction is a rapid one at 380°C can be gauged from the observation that more than half the total pressure develops within the first ten minutes. At 300°C this "half life" of the reaction is approximately 24 hours.

After three hours at 380°C these products were allowed to expand into the evacuated infra-red gas cell. Although the pressure of the products was only 30 mm. and consequently the spectrum weak, the number of gases volatile at -183°C is limited, so that identification of the products was fairly simple. Carbon monoxide was identified by the twin absorbtion peaks at 2111 and 2156 cm^{-1}. A hydrocarbon (C-H absorbtion at 3080, 3000, and 2929 cm^{-1}) was identified as methane by the sharp absorbtion peak at 1307 cm^{-1}.

In order to confirm the identification of these products a sample, unavoidedly mixed with air, was withdrawn from the cell and injected onto a powdered charcoal gas chromatographic column. The pattern of elution peaks, shown in figure 50, bears a striking resemblance to the pattern given by a coal-gas/air mixture. The individual peaks were identified by injecting samples of air and single component/air mixtures onto the column. Not only does this result confirm the presence of carbon monoxide and methane but it also indicates that hydrogen is a degradation product.

V_{-78} (Products volatile at -78°C in vacuum).

The elution peak pattern obtained from a sample of these products on a Silicone 301 / Celite column is shown in figure 51. The largest of the three separated components has a similar retention time to either a C_2 hydrocarbon or carbon dioxide. The least volatile substance has a similar retention time to C_4 hydrocarbons such as butene-1 or *iso*-butene. Since this particular column packing is known to exert no specific absorbtion effect and compounds are usually eluted from it in the order of their boiling points the small second peak is likely to be due to a C_3 hydrocarbon.

The products were identified by examination of the infra-red spectrum of the gases at 65 mm. Hg pressure. Carbon dioxide was recognised by the strong single peak

FIGURE 50

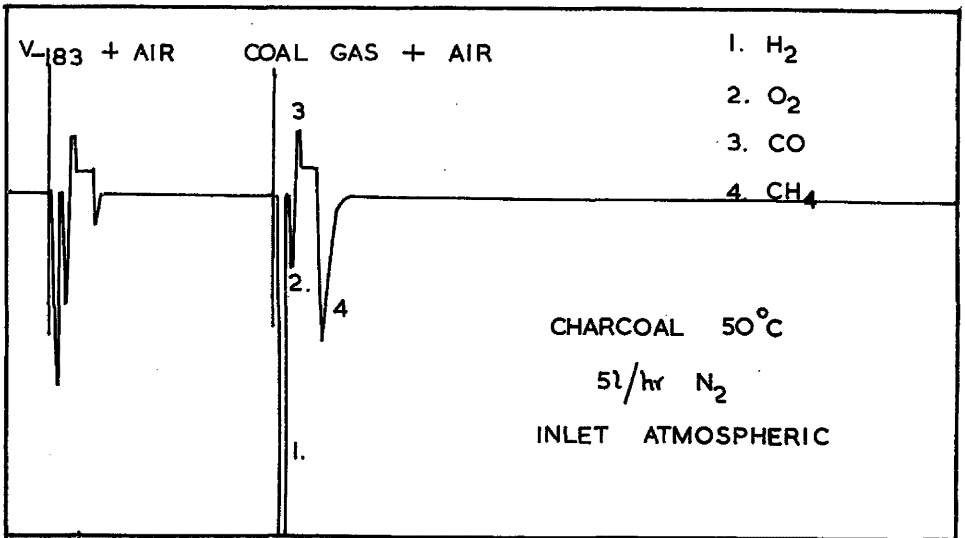
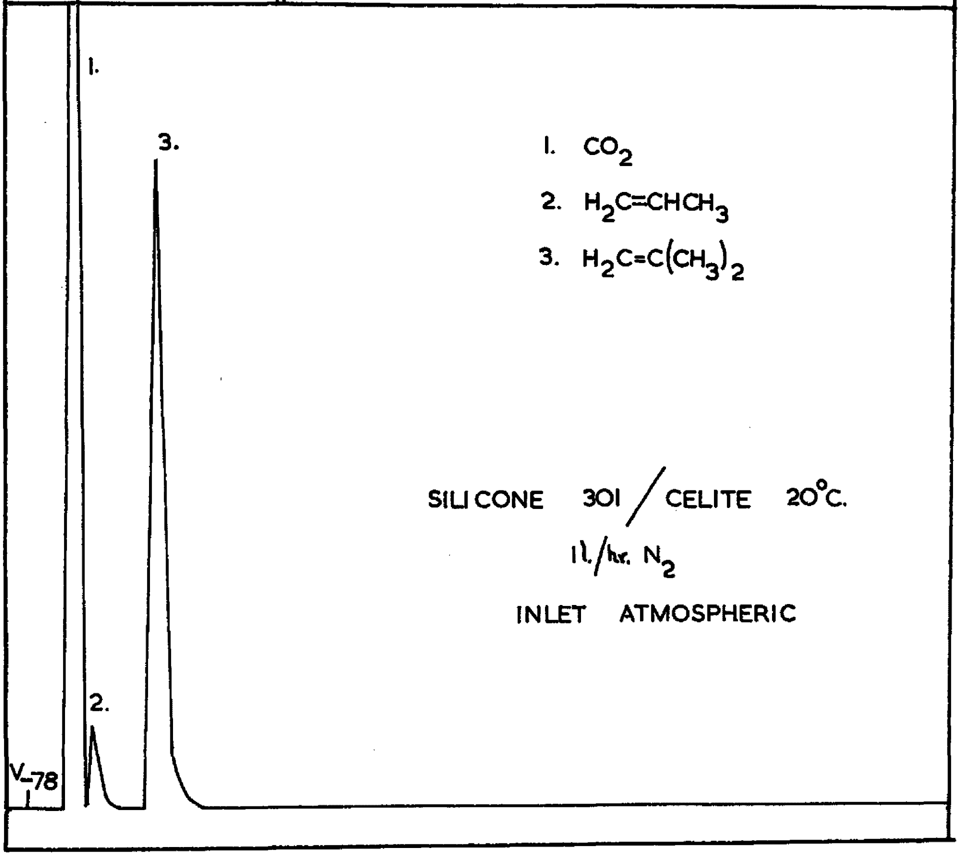
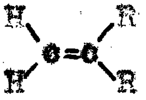


FIGURE 51.

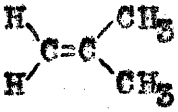


PYROLYSIS OF ANHYDROPOLYMETHACRYLIC ACID, GAS CHROMATOGRAMS.

at 2350 cm^{-1}, with weaker peaks at 3640, 3540, 720 and 669 cm^{-1}. The presence of an unsaturated hydrocarbon is indicated by C—H stretching vibrations at 3070 and 2930 cm^{-1}, C=C stretching at 1660 cm^{-1} (weak) and C-H bending about 1448 cm^{-1} (weak). Identification was provided by the presence of a sharp peak at 887 cm^{-1}, which is characteristic of olefins of the structure

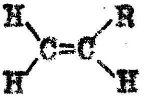


The only compound consistent with the gas chromatography results and containing this grouping is the simplest,



<u>iso-butene</u>.

The smallest component has been identified, with a fair degree of certainty, as <u>propene</u> by the presence of a small but distinct peak at 912 cm^{-1}. Absorbtion in this region is characteristic of olefins with the structure



and it is the strongest peak in the spectrum of compounds such as propene and butene-1.

In addition to being produced in the degradation at 380°C in the closed system, similar products were detected from runs at 330°C and 300°C in the same system and from runs in the d.m.s. at 380°C and 330°C.

By measuring the pressures developed in the same volume by V_{-183} and V_{-78} the volume ratio V_{-183} / V_{-78} was shown to be approximately 1/2. Since V_{-78} consists mainly of carbon dioxide, the latter is undoubtedly the largest single "simple" degradation product of anhydropolymethacrylic acid. Rough estimations based on the pressure at -78°C in a known volume indicated that it amounts to about 20% of the original anhydride.

V_{RT} (Products volatile at room temperature).

Unlike the products previously discussed there is no clear-cut separation of V_{RT} from less volatile products, and it generally contains some of the yellow material characteristic of V_{DP}, which as will be shown, is closely related to the degrading polymer, and the non-volatile residue.

Only two products could be positively identified.

Even from degradations in the secondary system the products include water, recognised by its insolubility in organic solvents; tests showed it to be acidic.

Examination of the spectrum of a dried solution in carbon tetrachloride confirmed the presence of an acid (non-bonded O-H stretching at 3550 cm^{-1}, C-H and bonded O-H stretching 3200 - 2800 cm^{-1}, C=O stretching of monomer at 1735 cm^{-1} and of bonded dimer at 1700 cm^{-1}).

The low carbonyl frequency and the presence of a C=C stretching peak at 1635 cm^{-1} suggested that the acid was unsaturated. By a crude fractional distillation it was possible to obtain a sample free from water, and so obtain the complete spectrum. This contains all the peaks consistent with it being methacrylic acid.

V_{RT} (and V_{DT}) samples always possess a distinct, although unrecognised smell, quite different from that of methacrylic acid or anhydride. This appears to be associated with the yellow colouration and certain infra-red absorbtion peaks additional to those of methacrylic acid. These are extra C-H stretching and bending vibrations together with a peak at 1760 cm^{-1}. Although this latter absorbtion disappears on treatment of the carbon tetrachloride solution with either water or NaOH solution, the fact that it seems to be a single peak argues against it being an anhydride carbonyl. This reasoning and stability considerations make a peroxide carbonyl even less likely. The most reasonable assignment would seem to be either an ester or large ring lactone carbonyl.

V_{DT} (Products volatile at the degradation temperature).

This substance is deposited as a yellow layer on the sides of the reaction tube used in the secondary degradation system. Physical examination shows clearly that it is not a single simple substance but a range of products, from a brown solid glass closest to the degradation surface to a light-yellow viscous liquid at the top of the tube.

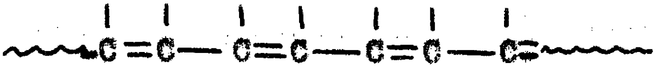
The solid state infra-red spectra of different samples shows too that it has a variable composition. Some spectra are basically similar to those of anhydropolymethacrylic acid with additional O-H and C=O absorbtion consistent with the presence of acid units. Other samples in which there is very little residual anhydride absorbtion at 1795 and 1026 cm^{-1} show, in addition to the acid groups, still more complex spectra in the C=O stretching region with peaks at 1760 and 1735 cm^{-1}.

It seems reasonable to conclude that this fraction consists largely of small fragments of the polymer chain and that under most degradation conditions it is undergoing further decomposition.

Non-volatile Residue

This material is black. A typical KCl disc spectrum is shown in the Appendix of Spectra, S 9.

Probably the most significant feature of the spectrum is the presence of a broad absorbtion peak at 1600 cm^{-1}, a region associated with extensive -C=X- conjugated chains. Other samples show this peak as low as 1555 cm^{-1}. Together with the black colour, this suggests that the backbone of the polymeric residue consists of a highly unsaturated conjugated chain



$$\sim\sim\overset{|}{C}=\overset{|}{C}-\overset{|}{C}=\overset{|}{C}-\overset{|}{C}=\overset{|}{C}-\overset{|}{C}=\sim\sim$$

Because of the presence of many unsaturated groups it would not be safe to draw any conclusions from the frequency (about 1700 cm^{-1}) of the carbonyl peak. Even the presence of O-H absorbtion does not necessarily prove that acid units are present since the observed separation of O-H and C-H stretching frequencies is not usually obtained with solid state spectra of acids. The O-H absorbtion could be due to moisture in the KCl.

Minimum Degradation Temperature.

With so much of the degradation product volatile the use of the KCl dispersion degradation method was not very satisfactory. It was however possible to show that prolonged heating (24 hours) in vacuum at 250°C had no effect on the spectra of anhydropolymethacrylic acid samples. However, 15 hours heating in vacuum at 270°C resulted in appreciable loss in intensity due to volatilisation, and the development of 1700 and 1600 cm^{-1} peaks in the residue.

Sensitivity to Air.

Similar experiments showed that anhydropolymethacrylic acid was stable in air at 200°C but changes in the spectra similar to those above, occurred on heating samples for 24 hours in air at 250°C.

DEGRADATION OF ANHYDROPOLYMETHACRYLIC ACID BY ULTRA-VIOLET IRRADIATION.

A KCl disc containing anhydropolymethacrylic acid was exposed in air to the unfiltered radiation of the ultra-violet lamp. Even at room temperature, infra-red spectral changes take place, which are consistent with the occurrence of reactions similar to those whose products have been discussed above.

The anhydride carbonyl peaks steadily decrease on irradiation. The first detectable products are acid units, shown by the production of a 1700 cm^{-1} carbonyl and broad ("bonded") O-H absorbtion in the region 3000 - 3300 cm^{-1}, and carbon dioxide trapped within the disc, shown by a peak at 2350 cm^{-1}. Later, when most of the anhydride has been removed, peaks at 1760 and 1735 cm^{-1} can be distinguished, but as before cannot be assigned to a definite structure. After prolonged exposure (10 days) only the 1760 cm^{-1} peak is left.

The instability of the anhydride to ultra-violet irradiation is not due to the polymer structure. It was shown using the same technique that both succinic and glutaric anhydrides decompose on irradiation. In these cases only acid and carbon dioxide were detected.

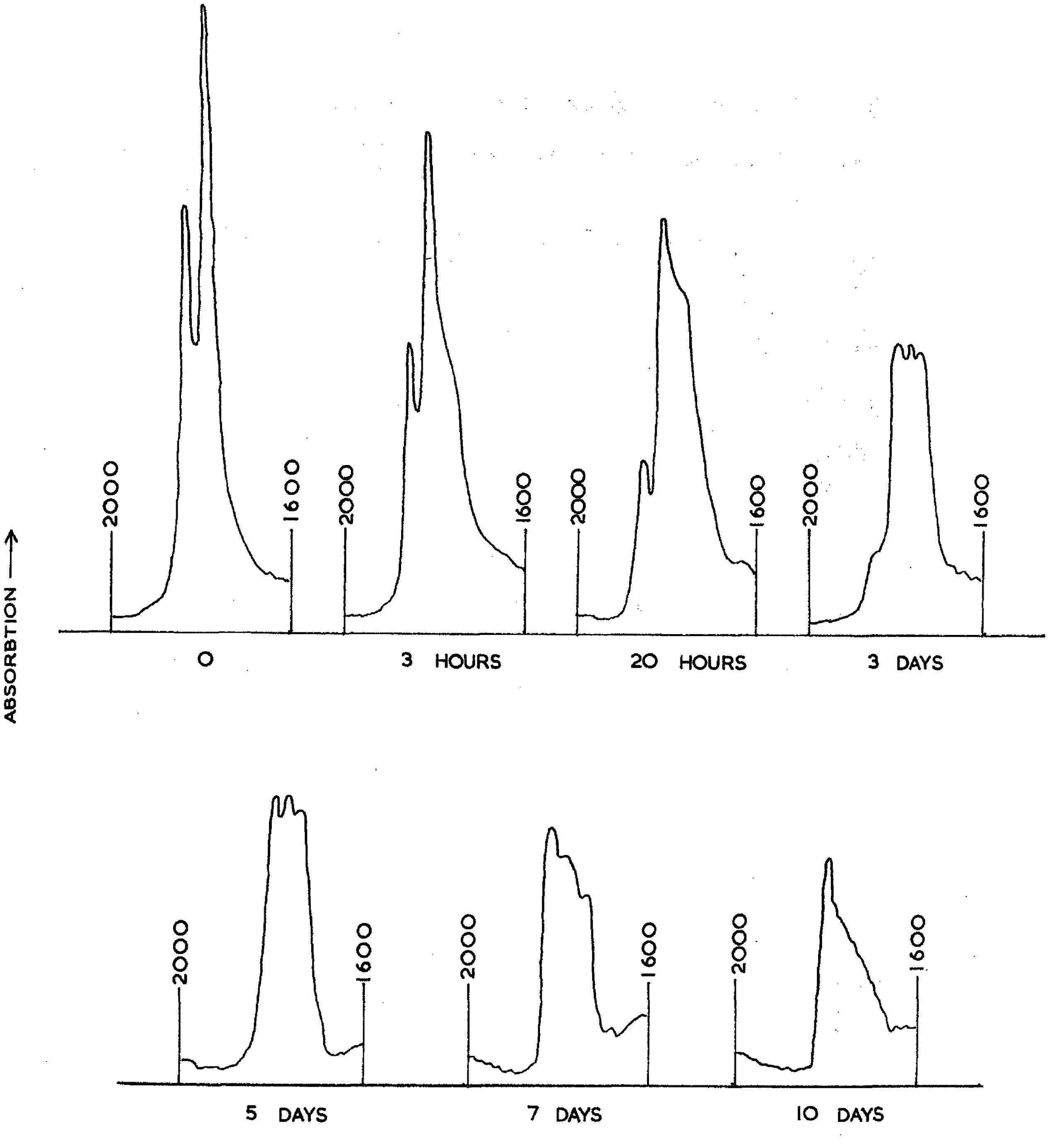


FIGURE 52. PHOTOLYSIS OF ANHYDROPOLYMETHACRYLIC ACID. SPECTRAL CHANGES IN THE CARBONYL REGION.

Iso-butyric anhydride in a silica tube also decomposes on irradiation, with the development of a deep golden-brown colouration, only an acid product was detected.

INSTABILITY OF "ANHYDROACRYLIC ACID".

During the investigation of the degradation at 200°C of poly-*tert*.-butyl acrylate[44] it was never possible to obtain a spectrum of the residue which would show as complete anhydride formation as obtainable with the methacrylate. Nevertheless the water production was consistent with anhydride formation, and the weight loss was, in some cases, even in excess of that theoretically required. It was suggested that a further slow decomposition of "anhydroacrylic acid" was occurring.

The problem has since been re-examined and the latter conclusion confirmed; thus it has been shown that on prolonged degradation at 200°C, appreciable quantities of carbon dioxide are produced, particularly in the later stages. The residue has been shown to contain very little anhydride but many *acid* units.

POSSIBLE ROUTES TO FURTHER STUDY.

Any future investigations of the pyrolysis of anhydropolymethacrylic acid, or polymethacrylic anhydride, must surely start with a detailed quantitative analysis of the products.

For a conventional analysis of the gaseous products it would be necessary to work on a somewhat larger scale, consequently increasing difficulties of non-uniform temperature and slow diffusion. However it should prove possible by the adaptation and calibration of gas chromatographic apparatus to analyse the gaseous products by this means. Alternatively or additionally, the analysis of all the gaseous products except hydrogen could be fairly simply done by an infra-red technique.

It may be possible to identify the "lactone" by the preparation of a larger quantity and studying its chemical properties. For the quantitative analysis of the liquid products the presence of water and acid raises difficulties to the use of vapour phase chromatography. The organic components could probably be analysed more readily by quantitative infra-red methods.

With regard to V_{II}, its solubility in benzene should allow molecular weight measurements by cryoscopy to be made, to determine if it is in fact a low polymer.

One technique which has proved useful in the investigation of pyrolytic reactions of polymers which break down to a range of products, is mass spectrometry.[115] This would be useful both for a qualitative and quantitative analysis, and might even be used for rate measurements in association with a dynamic molecular still along the lines suggested by Zemany.[116]

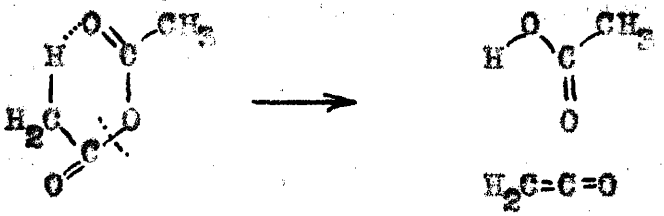
POSSIBLE BREAKDOWN ROUTES.

Without a detailed quantitative analysis of the products and rate measurements, any mechanisms for the pyrolysis of anhydropolymethacrylic acid which can be proposed must be largely speculative. Nevertheless the following suggestions may serve as a basis for further investigation.

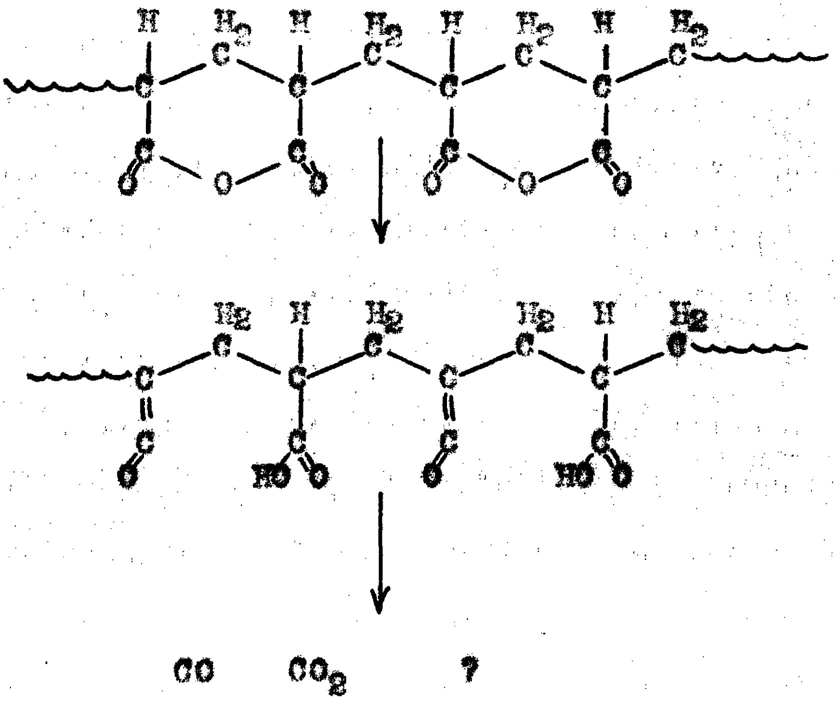
The presence of quantities of a material volatile only at the degradation temperature suggests that chain scission reactions are occurring, but the absence of methacrylic anhydride shows that depropagation is unimportant, unless methacrylic anhydride is being rapidly and completely decomposed. It seems likely that the initial reaction is actually the decomposition of the anhydride grouping.

Not a great deal of work has been reported on the decomposition of simple anhydrides. One study on the decomposition of acetic anhydride[117] suggested that at

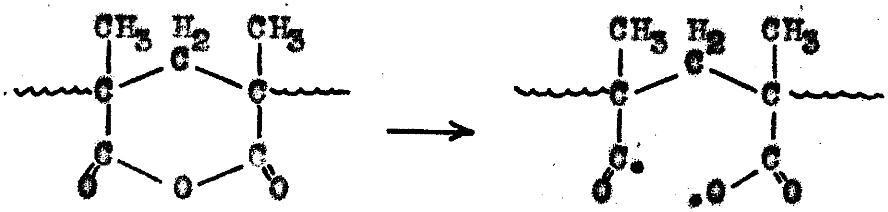
300°C it decomposes by two mechanisms, one radical and one intramolecular. The latter, with the production of acetic acid and keten, is analogous to both the βH alkyl/oxygen and αH acyl/oxygen scission reactions of esters:



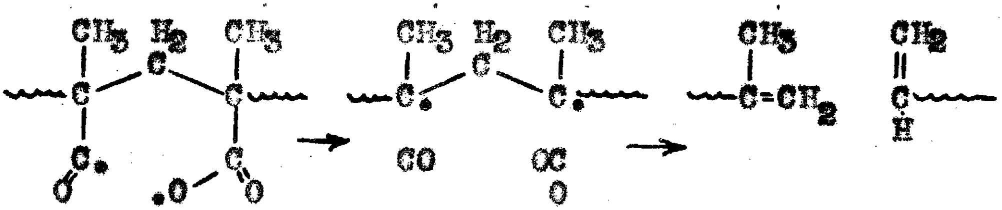
While anhydropolymethacrylic acid does not possess the necessary α(β)H atom, anhydropolyacrylic acid does, and its greater instability may be due to the occurrence of this reaction, followed by further decomposition from the keten groups.



In anhydropolymethacrylic acid only the radical reaction is likely:



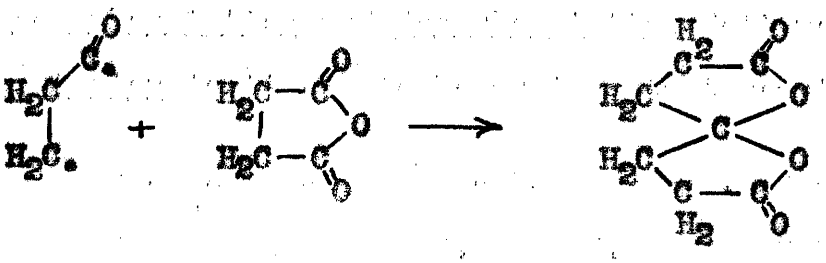
Decarbonylation and decarboxylation followed by chain scission is likely to be an important reaction:



Decomposition from such chain ends might account for iso-butene and propylene production.

It is clear from the V_{-183} / V_{-78} ratio that decarboxylation and decarbonylation cannot be the only reactions undergone by the two radicals. The presence of products retaining carbonyl groups suggests that other reactions occur. Hydrogen abstraction would result in acid (detected) and aldehyde (undetected) groupings respectively.

Anhydrides with rings larger than six-membered decompose to ketones with elimination of carbon dioxide. Formally at least this can be regarded as arising from the union of the two parts of a di-radical after decarboxylation. With rings of smaller size ketone formation has never been reported, but in the case of succinic anhydride[119] there is some formation of a di-lactone by the addition of a three-atom fragment to the carbonyl group of an anhydride molecule



An analogous reaction might account for the formation of additional carbonyl peaks in the degradation products.

With the ratio H / C of most of the volatile products fairly high, it is not surprising that the non-volatile residue is highly unsaturated. Elimination of methyl groups as methane may play some part in the development of the dark colour.

SUMMARY.

It has been shown that anhydropolymethacrylic acid decomposes at temperatures above 270°C. There is a wider range of products than can be covered by the term "carbon dioxide and volatile hydrocarbons", but monomeric methacrylic anhydride is not detectable. The reaction mechanism is probably a complicated one, initiated by the radical decomposition of the anhydride.

CHAPTER VIII

GENERAL DISCUSSION

Although summaries have been made at the ends of each chapter giving the main conclusions drawn from the results contained therein, it is perhaps appropriate to consider briefly a more general outline of the work completed and at the same time to suggest possible lines of further investigation.

It has been established that the ester decomposition reaction is quantitatively the most important reaction leading to production of volatiles during the thermal degradation of poly-tert.-butyl methacrylate. The previous report that the reaction displays auto-catalytic features has been substantiated both by measurements of rates of iso-butene production in high vacuum, and also by infra-red studies of the residual non-volatile fraction during degradation. Principally from studies, by both these methods, on the degradation of copolymers of tert.-butyl methacrylate with other monomers, it has been possible to show that the ester decomposition reaction consists of two processes related to each other in a manner resembling the initiation and propagation processes of a chain reaction. These have respectively a "mono-unit" and a "bi-unit" transition state and show close analogies both with olefin elimination and ester hydrolysis reactions such as occur in polar solvents. The "acid-catalysed" nature of the propagation step has been further demonstrated by the action of external acids on the ester decomposition.

With regard to further work on the ester decomposition it would be interesting to see whether there is any correlation between the efficiency of the external acid as a catalyst for the pyrolytic ester decomposition and its acid strength as measured by its reaction with water (pK value), as has been indicated (figure 47, page 202). While it would obviously be desirable to measure the individual rate constants of the two or more ester decomposition processes, the occurrence of depolymerisation and anhydride formation reactions raises difficulties in the accurate measurement of the rate of production of *iso*-butene, particularly in the important early stages of the reaction. One way in which this difficulty might be overcome would be by a refinement of the present technique by combining the temperature stability and rapid removal of volatile products of the molecular still, with the ease of separation and estimation of small quantities of material made possible by gas chromatography.

If this was possible then direct measurement of iso-butene production could be achieved.

It has been clearly established that polymethacrylic acid is not nearly as stable to heat as had previously been supposed. It has been shown that the main reaction occurring with polymethacrylic acid at temperatures well below 200°C is anhydride formation by the interaction of pairs of adjacent acid units. Studies on this reaction in particular and to a lesser extent on the other pyrolytic reactions demonstrate the usefulness of infra-red techniques in following reactions of polymers. It has been shown that the rate of degradation in bulk is controlled by the rate of diffusion of the water produced in the reaction. This fact together with the non-availability or non-application of infra-red examination probably accounts for the failure by previous workers to detect this fairly simple thermal degradation reaction. With regard to further work, we feel that the infra-red techniques employed in studying this reaction may prove useful in the study of other reactions in which structural changes take place with the formation of both volatile and non-volatile products.

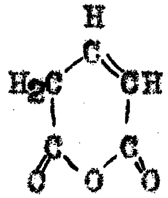
Both the ester decomposition and the anhydride formation reaction are examples of pyrolyses occurring by non-radical mechanisms. Although it is possible to formulate intramolecular transition states for the mechanisms of these reactions such that charges are never separated, it does seem clear that they possess a close relationship to certain reactions which are heterolytic in polar solutions. Similar conclusions have been arrived at in recent years by several workers studying the pyrolytic reactions of model compounds.

The remaining pyrolytic reactions described in this thesis are of the usual radical type. They include the depolymerisations of poly-_tert_.-butyl methacrylate and polymethacrylic acid and the final breakdown of anhydro-polymethacrylic acid at an elevated temperature. The depolymerisations of both poly-_tert_.-butyl methacrylate and polymethacrylic acid had not previously been detected. Although quantitatively they are less important than the side chain ester decomposition and anhydride formation reactions, they would seem to offer the most scope for further investigation.

All the available evidence obtained in the present work is consistent with the depolymerisation in chains of pure poly-_tert_.-butyl methacrylate units being similar to the well established depolymerisation of polymethyl methacrylate. The most interesting feature of the depolymerisation is however, the effect of the production of acid and anhydride units in these chains. They bring about inhibition of the depropagation or monomer producing reaction.

The behaviour of copolymers in general towards depolymerisation is very largely an unexplored field worthy of future investigation. However, the particular case of degrading poly-*tert*.-butyl methacrylate is itself singularly unsuited as a starting point for this study, since not only are there three units to consider (*tert*.-butyl ester, acid and anhydride) but also the occurrence of the side chain reaction results in a continually varying composition of the ter-copolymer. This latter objection has been overcome, while still staying within the methacrylate series of polymers, by the study of a copolymer of methyl methacrylate and methacrylic acid. As expected this material is more resistant to depolymerisation than is pure polymethyl methacrylate. Because this substance does form an anhydride it was not possible to decide directly from this experiment whether the acid or the anhydride unit is responsible for the inhibition. However the production of traces of methacrylic acid from the degradation at 200°C of copolymers of methacrylic acid with both *tert*.-butyl and methyl methacrylates, from poly-*tert*.-butyl methacrylate and from polymethacrylic acid, together with the absence of monomeric anhydride from these degradations and from degradations carried out at temperatures as high as 380°C all combine to suggest that it is the anhydride unit which is resistant to depropagation.

Logically the next step in this investigation should be the examination of copolymers of methyl methacrylate containing pre-formed anhydride units. One possible co-monomer is methacrylic anhydride. This is likely to result in both cross-link and internal six-membered ring units. The close similarity of structure between esters, acid and cross-link anhydride lead one to suspect that the ring unit is that responsible for inhibition of depropagation. It is obviously desirable therefore to examine copolymers in which only ring units are present. The known[119] copolymers of methyl methacrylate and maleic anhydride offer the possibility of studying the effect of a five-membered anhydride ring unit. In order to obtain the more strictly comparable six-membered anhydride ring unit it would be necessary to attempt to copolymerise methyl methacrylate with an $\alpha\beta$ unsaturated glutaric anhydride:



The study of the high temperature breakdown of anhydropolymethacrylic acid is still in its preliminary stages and an indication of possible approaches to further study has been given. In addition to its bearing on the stabilising influence of anhydride units, the pyrolytic and photolytic breakdown of this substance would have to be examined before any progress could be made in the study of the pyrolyses of poly-alkyl methacrylates possessing βH atoms and therefore susceptible to ester decomposition and subsequent anhydride formation.

The behaviour in polymerisation of acrylic anhydride is somewhat abnormal, we have suggested that this is also the case with methacrylic anhydride. The work described in this thesis started with an investigation of the polymerisation of <u>tert</u>.-butyl methacrylate from the results of which it was concluded that polymethyl and poly-<u>tert</u>.-butyl methacrylates should be similar in properties. This has been borne out by the existence of a depolymerisation reaction. It is perhaps appropriate to conclude this thesis with a suggestion that a similar complete investigation into the polymerisation of methacrylic anhydride would be helpful in elucidating the reason for the stability of anhydropolymethacrylic acid towards depolymerisation.

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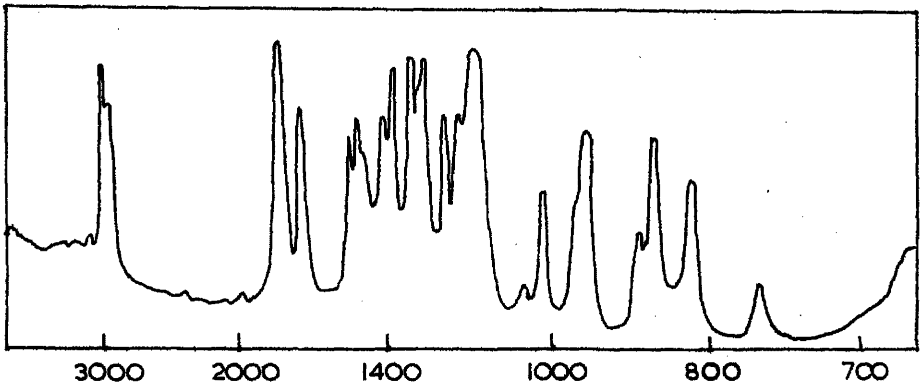
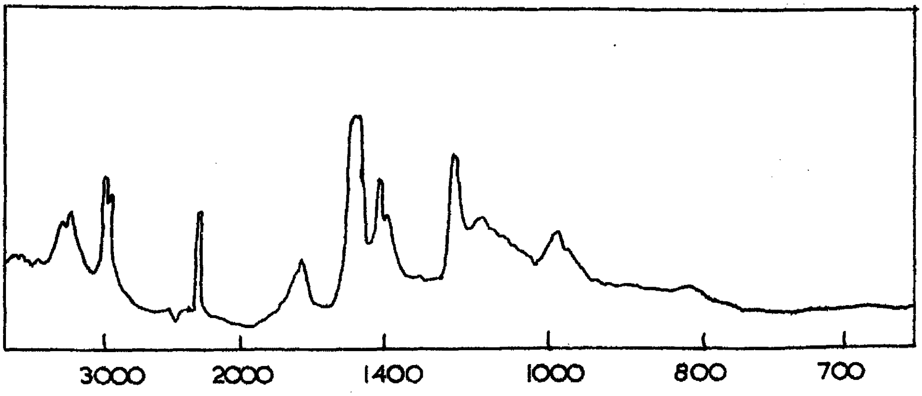
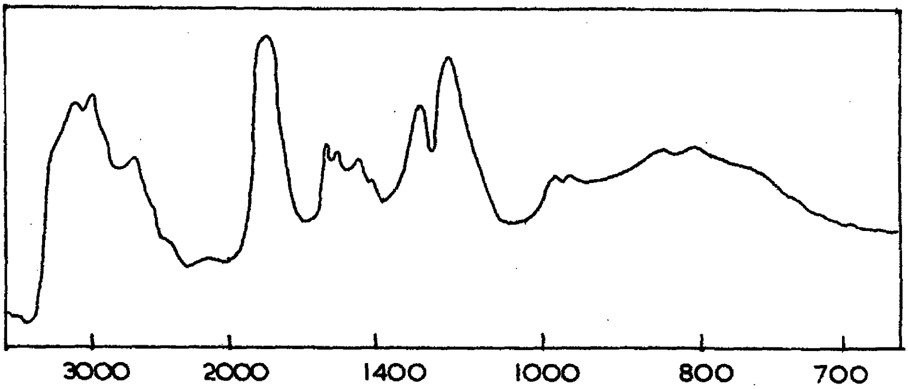
APPENDIX OF SPECTRA



S. 1. <u>TERT.</u>- BUTYL METHACRYLATE

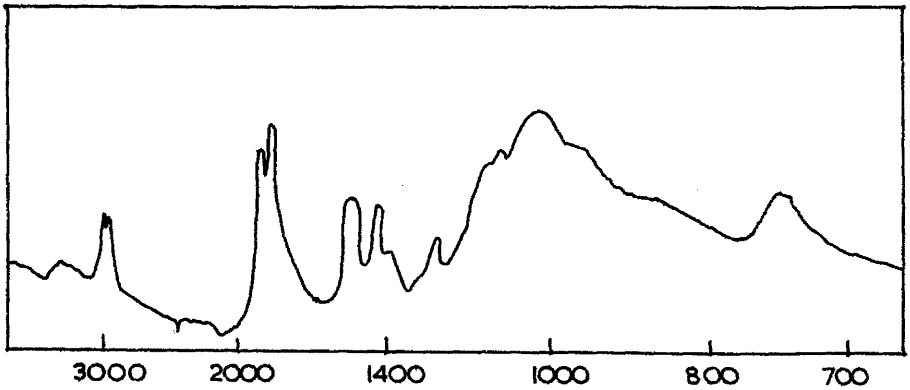


S. 2. POLYMETHACRYLONITRILE FROM AIBN



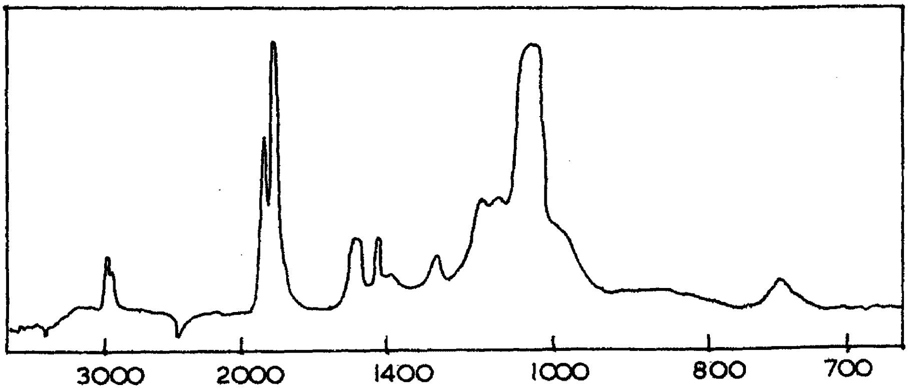
S. 3.

POLYMETHACRYLIC ACID



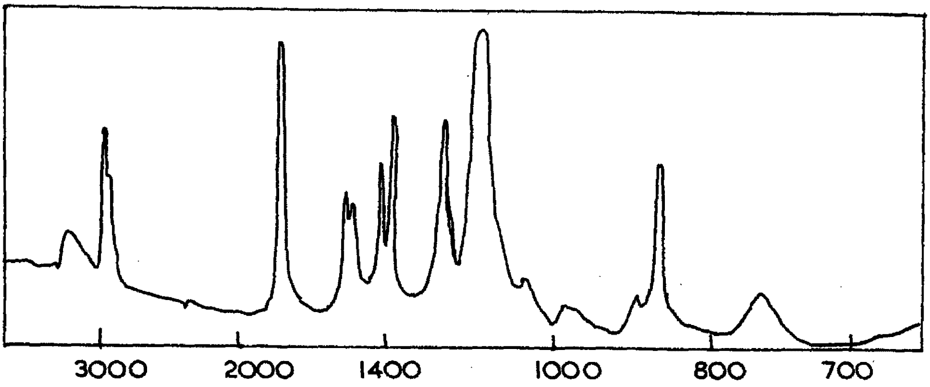
S. 4A

ANHYDROPOLYMETHACRYLIC ACID BY BULK DEGRADATION

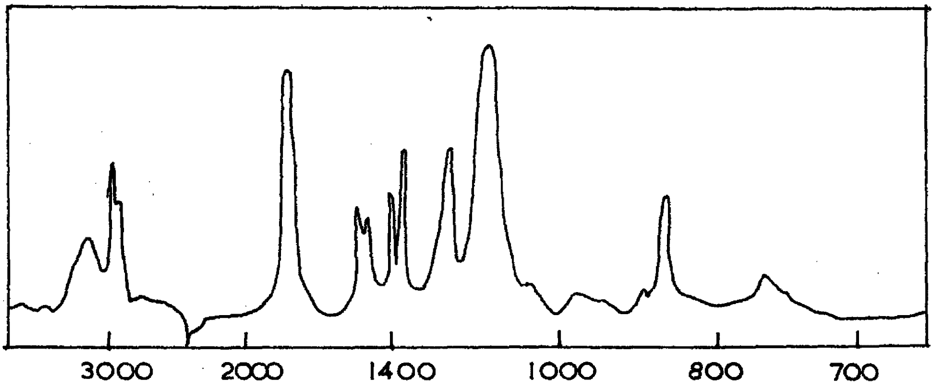


S 4B

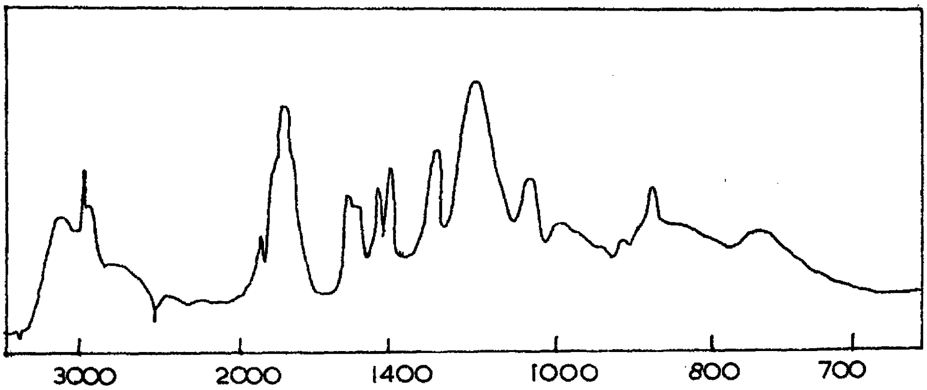
ANHYDROPOLYMETHACRYLIC ACID BY KCl DISPERSION



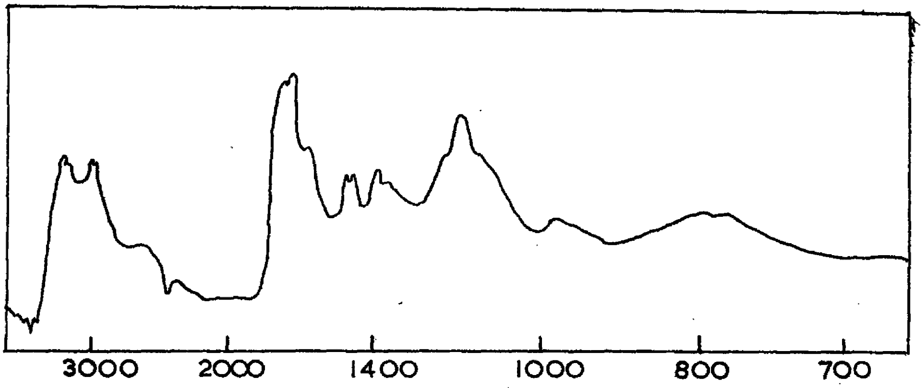
S. 5. POLY-<u>TERT</u>-BUTYL METHACRYLATE.



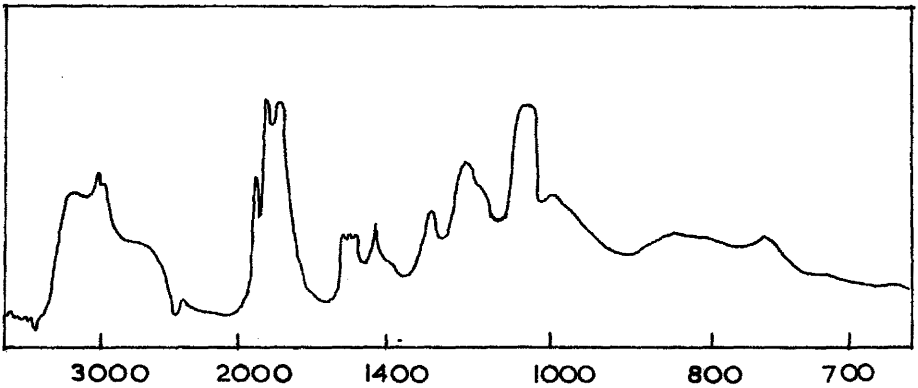
S 6A POLY-<u>TERT</u>-BUTYL METHACRYLATE AFTER 12.1% VOLATILISATION



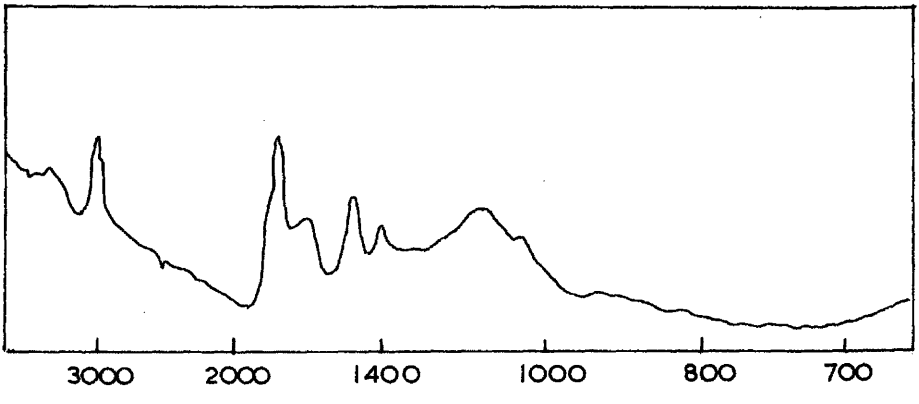
S 6B POLY-<u>TERT</u>-BUTYL METHACRYLATE AFTER 25.5% VOLATILISATION



S. 7. ANHYDROPOLYMETHACRYLIC ACID TREATED WITH 0.880 NH_4OH



S. 8. POLYMETHACRYLIC ACID AFTER 45 MINUTES AT 192.5°C IN BULK.



S. 9. RESIDUE FROM PYROLYSIS AT 380°C

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