THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

THE THERMAL AND PHOTOCHEMICAL DEGRADATION
of
POLY-n-BUTYL METHACRYLATE

by

James Richard MacCallum, B.Sc. (Glasgow)

SUPERVISOR:
Dr. N. Grassie

CHEMISTRY DEPARTMENT
GLASGOW UNIVERSITY

September 1961.

PREFACE

The work described in this thesis was carried out in the period October 1958 to September 1961 at the University of Glasgow in the department of Physical Chemistry, which is under the supervision of Professor J. Monteath Robertson.

Part of the subject matter of Chapter 4 has been submitted to the Journal of Polymer Science for publication.

My thanks are due to the Department of Scientific and Industrial Research for a Maintenance Grant during the tenure of which the work was performed.

Thanks are due to Dr. Reed for interpretation of mass spectra data, and Mr. I. Orr who gave general technical assistance.

Finally I would like to express appreciation of the encouragement and guidance given me by Dr. Grassie who suggested the problem and supervised the work described in this thesis.

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INTRODUCTION

The term "degradation" as used in the field of polymer science has no rigid meaning. The industrial chemist generally applies it to any process which leads to physical deterioration of a polymer. To the pure chemist it has become the description for almost any process of chemical modification of the polymer. Much of the early investigation of polymer degradation was done industrially, prompted by a need to prevent rather than to discover the cause of deterioration of physical properties.

Progress in understanding the breakdown of macromolecules was slow until the nature of polymerisation and polymer structure was fully appreciated. With the tremendous growth of the plastics industry in recent years however, research into the breakdown of plastics, particularly that caused thermally, photochemically or by oxidation has increased and is still increasing. A fundamental study of the causes of degradation is of great value, not only from the point of view of prevention but also since it should give guidance in planning stable macromolecular structures. Such a study can reveal new examples of well established reactions and often because of the unique conditions prevailing in macromolecular structures entirely new reaction types have been discovered. Thus for the pure chemist degradation is a rich field for the study of pure chemical processes. Our knowledge is now such that a classification of degradation reactions has been possible[1].

CLASSIFICATION OF DEGRADATION REACTIONS

Many different agencies both physical and chemical can bring about changes in polymer structure. Those most commonly encountered are:- all types of radiation, heat, mechanical working, oxygen, ozone and water. Often it is a combination of two or more which is operative, and for a fundamental study of the general phenomenon it is desirable to separate the complex reactions into their simple components.

This thesis is concerned with the effect of heat and ultra violet light on addition polymers under high vacuum. Reactions induced by these agencies can be loosely classified in the following way.

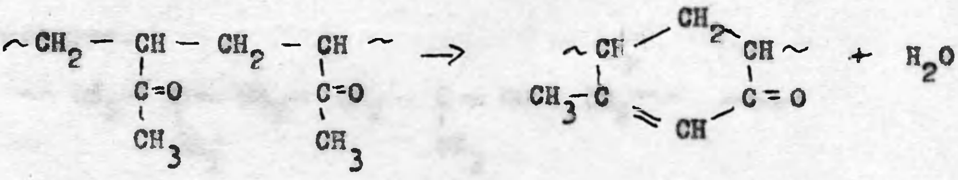
1. Reactions involving the main polymer chain
    - (a) Depolymerisation
    - (b) Cross-linking
2. Reactions involving substituent side groups of the polymer
    - (a) Decomposition
    - (b) Rearrangement

1. The two categories in this class are:- (a) depolymerisation and (b) cross-linking which respectively decrease and increase the molecular weight of the polymer.

(a) Depolymerisation

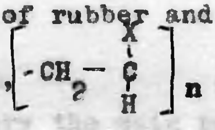
The polymer chain breaks into smaller fragments which have approximately the same empirical formula as the parent molecule. Frequently these fragments are monomer, which is liberated from the macromolecule in a manner which is the exact reverse of the propagation step of polymerisation. In general there are two ways in which this reverse polymerisation process may be initiated, namely at the chain-ends as in polymethyl methacrylate[2, 3], or at random along the length of the molecule as in polybutadiene[4]. The thermal degradation of polystyrene provides an interesting illustration of a random chain process and an end-initiated chain depolymerisation process occurring simultaneously[5]. A study of the change of molecular weight with extent of degradation has shown a sharp drop in molecular weight at very low percentage degradation. This drop in molecular weight is due to some "weak-link" in the polymer chain breaking to give two stable fragments. Simultaneously the polymer molecules unzipp from the chain ends giving monomer, with small amounts of dimer and trimer.

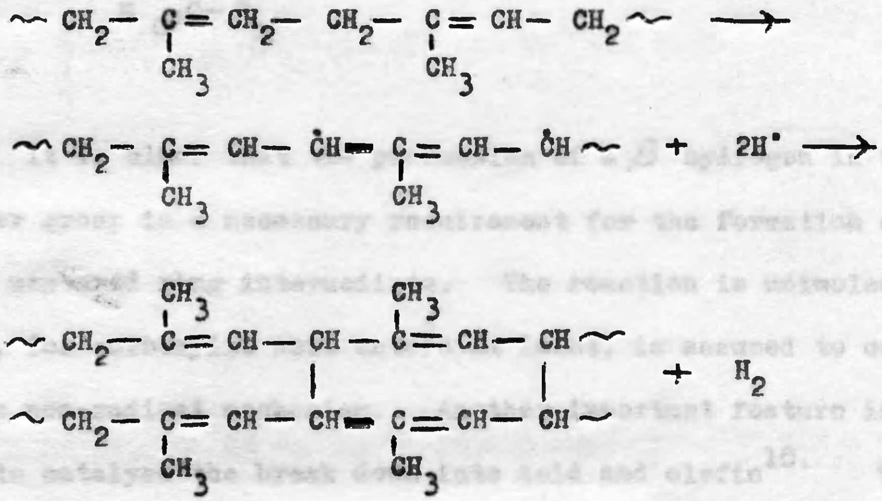
Depolymerisation processes can be brought about both thermally or photochemically. For example, polymethyl methacrylate has been studied using both agencies[2, 3]. However, polymethyl vinyl ketone behaves quite differently under the influence of heat and radiation. With ultra-violet light polymethyl vinyl ketone depolymerises[6], whereas on heating it undergoes side chain condensation[7] with elimination of water.



(b) Cross-linking reactions

In this type of reaction an intermolecular covalent link is formed which leads to a three dimensional network and the polymer ultimately becomes insoluble. The most common method of achieving this is by exposing polymers to high energy radiation, although in certain cases it may be achieved even with ultra-violet radiation.

The photo-gelation of rubber and vinyl polymers containing a tertiary hydrogen atom,  $\left[-CH_2-\overset{X}{\underset{H}{C}}-\right]_n$, is an excellent example of this type of reaction. When irradiated with wave length less than 4,000Å rubber rapidly becomes insoluble and hydrogen is evolved at a constant rate.[8] This observation has been accounted for by the following mechanism: bond scission at the carbon-hydrogen bonds of the α methylenic groups giving a hydrogen atom and an allylic radical. The α methylenic group is particularly susceptible to this reaction. The energy requirements of breaking the carbon-hydrogen bond are greatly reduced by virtue of the resonance stabilisation of the resulting allylic radical. Hydrogen atoms combine to form hydrogen molecules and the radicals combine in pairs or add to double bonds of adjacent chains, giving cross linked structures.



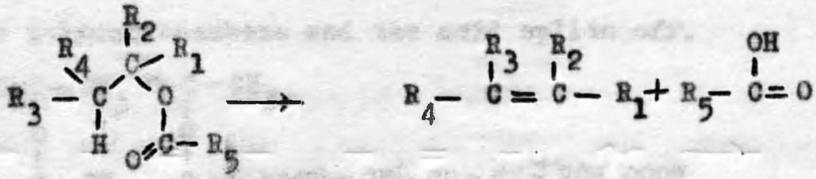
$$\sim CH_2-\underset{CH_3}{\underset{|}{C}}=CH_2-CH_2-\underset{CH_3}{\underset{|}{C}}=CH-CH_2\sim\ \longrightarrow$$

$$\sim CH_2-\underset{CH_3}{\underset{|}{C}}=CH-\dot{C}H-\underset{CH_3}{\underset{|}{C}}=CH-\dot{C}H\sim\ +\ 2H^{\cdot}\ \longrightarrow$$

(2) In this category the main polymer backbone remains unchanged, while substituent side groups either (a) decompose or (b) rearrange.

(a) <u>Decomposition reactions</u>

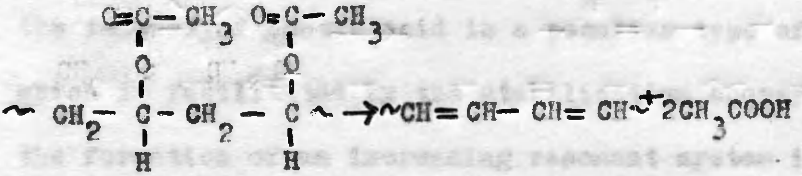
This class involves a chemical change in a side group induced by heat or light, giving a volatile product and an involatile residue. The best known and most widely encountered reaction of this type is ester decomposition; whereby an ester splits up into an acid and an olefine. This reaction has been thoroughly investigated among small organic molecules which may be regarded as models for high polymer molecules, and the following mechanism has been suggested[9].



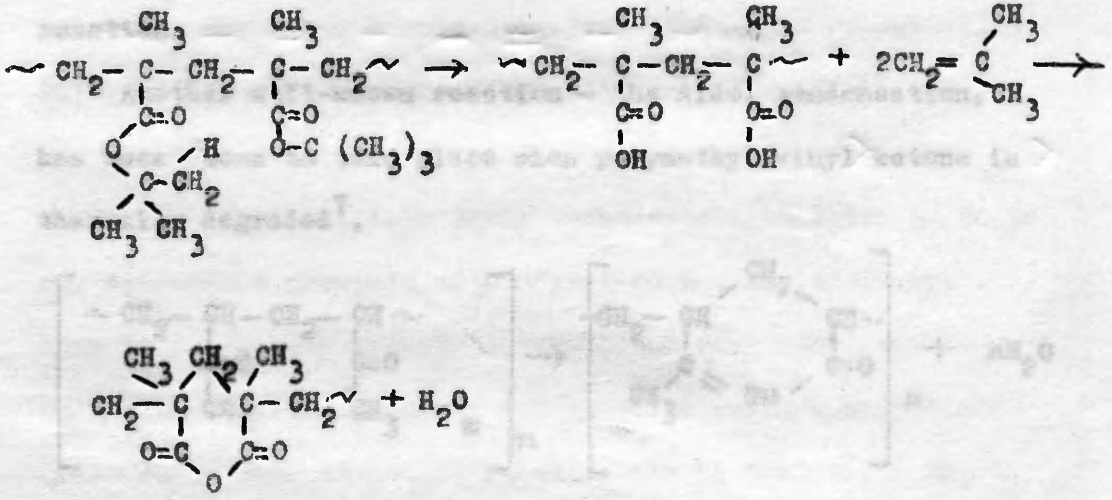
It is clear that the possession of a β hydrogen in the ester group is a necessary requirement for the formation of the six membered ring intermediate. The reaction is unimolecular and, for carboxylic acid esters at least, is assumed to occur by a non-radical mechanism. Another important feature is that acids catalyse the break down into acid and olefin[10]. The stability of model esters is in the order primary > secondary > tertiary, the temperature of onset of reaction being approximately, tertiary 250°C; secondary 300°C; and primary 350°C.

The decomposition of alkyl halides falls into this category, but in a number of cases a radical mechanism has been shown to be operative. Whether the decomposition involves a radical or unimolecular type of reaction depends upon whether the olefine formed inhibits the radical chain process. Any olefinic product which contains an allylic hydrogen atom will act as an inhibitor and under these circumstances the decomposition will be unimolecular.

High polymeric esters also undergo ester decomposition, although the reaction is usually modified by the macromolecular environment. Polyvinyl acetate decomposes[11] to give a polyene and acetic acid. In this case the olefine is part of the polymer backbone and the acid splits off.



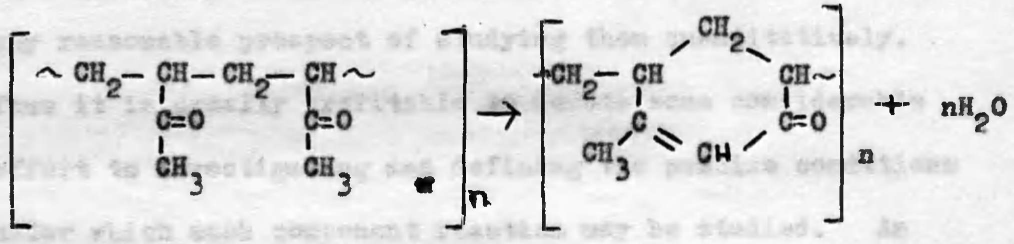
Conversely in poly-tert-butyl methacrylate[10] the olefine is expelled and the acidic group remains attached to the polymer backbone. In this case further reaction takes place, water being eliminated to give a polyanhydride.



Polyvinyl chloride as might be expected from a comparison with model compounds breaks down to a polyene and hydrochloric acid by a complex mechanism which is thought to involve radicals[12].

Great care must be exercised in comparing the behaviour of model compounds and polymers. The behaviour of polyvinyl acetate and poly-tert-butyl methacrylate illustrate the special circumstances which prevail in a macromolecule and which cannot be simulated in model compounds. In polyvinyl acetate the removal of acetic acid is a peculiar type of chain reaction which is facilitated by the stabilisation energy derived from the formation of an increasing resonant system in the polymer backbone. Again in poly-tert-butyl methacrylate[10] the formation of an acid unit catalyses the decomposition of its neighbours and auto-catalysis is observed, where normally the newly formed acid would be removed from the site of the reaction.

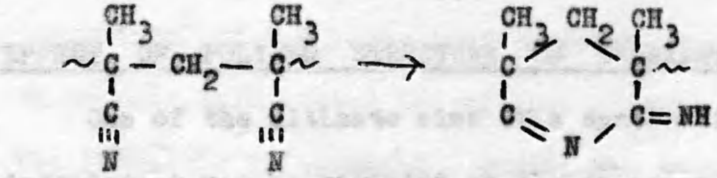
Another well-known reaction - the Aldol condensation, has been shown to take place when polymethyl vinyl ketone is thermally degraded[7].



This behaviour is to be contrasted with the depolymerisation which occurs on photochemical degradation[6].

(b) <u>Rearrangement</u>.

This type of reaction is associated with the development of colour in nitrile containing polymers. The mechanism has been studied by Grassie and co-workers who showed that in polymethacrylonitrile[13] and polyacrylonitrile[14] the following rearrangement takes place on heating.



The reaction is initiated in polymethacrylonitrile by acid units, present as impurity in monomer, copolymerised into the polymer. In polyacrylonitrile the tertiary hydrogen is thought to be the initiating centre.

CONDITIONS OF DEGRADATION

In many polymers a number of quite distinct degradation processes may occur simultaneously. Since the experimental difficulties encountered are usually considerable it is therefore important to separate such composite processes, as far as possible, into their constituents if there is to be any reasonable prospect of studying them quantitatively. Thus it is usually profitable to devote some considerable effort to investigating and defining the precise conditions under which each component reaction may be studied. An interesting example of the separation and study of component reactions in this way is provided by a series of papers by Grassie and McNeill[13] in which they have made a quantitative investigation of the three component reactions - depolymerisation to monomer, nitrile group condensation and ketone-imine decomposition - which make up the overall degradation process in polymethacrylonitrile.

EFFECT OF POLYMER STRUCTURE ON DEGRADATION BEHAVIOUR

One of the ultimate aims of a systematic study of polymer degradation may be regarded as the enunciation of the factors which could be used to predict how and under what conditions a polymer would degrade. At present although many systems have been studied, only qualitative postulates can be made regarding the effect of structure on degradation.

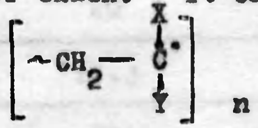
Early work proved that polymers which yielded high percentages of monomer degraded by a free radical reaction. It was shown that the propagation step in this depolymerisation process, or depropagation as it has come to be known, was the exact reverse of the propagation step in polymerisation, and, in fact, the process can be regarded as reversible and represented by

$$P_r + \text{monomer} \underset{\text{depropagation}}{\overset{\text{propagation}}{\rightleftharpoons}} P_{r+1}$$

Energetically we can write

$$E_{\text{depropagation}} = E_{\text{propagation}} - \Delta E_o .$$

where ΔE_o is the heat of polymerisation.. Since all polymerisations are exothermic ΔE_o is always negative. Thus the velocity of depropagation is negligible in comparison with propagation at room temperature. With increasing temperature the reverse reaction becomes relatively more and more important until at some temperature equilibrium is attained. Above this temperature the predominant reaction is depropagation. A comparison[1] of ΔE_o, the heat of polymerisation, with yield of monomer illustrates the utility of this generality. The lower the value of ΔE_o, the higher the probability of depolymerisation, up to a limiting value of about 14 Kcals, above which depropagation does not normally occur. In these circumstances ^{E}depropagation is of the order of magnitude of the activation energy of other reactions, for instance transfer or side-chain condensation, which can compete with and suppress depropagation.

The difference in heats of polymerisation is governed by many factors, principally the reactivity of the growing radical and steric strain in the polymer chain. It can be stated that generally the structures  $\left[\sim CH_2 - \overset{X}{\underset{Y}{C^{\bullet}}}\right]_n$ in which X and Y are substituents, yield high percentages of monomer due to the resonance stabilisation of X and Y on the radical. Where X is H, the radical is more reactive and the intramolecular disproportionation involved in depropagation is not effected. Polystyrene affords an interesting exception to this rule, as resonance in the aromatic nucleus stabilises the radical sufficiently to allow depropagation.

In a recent paper Bamford et al[15] have used the velocity coefficient of transfer of a growing polymer chain to toluene at 60°C as a measure of radical reactivity. Table I shows their values ^{K}tol., the heats of polymerisation and the yield of monomer on pyrolysis, from which it is obvious that low radical reactivity favours monomer production. This method of classification presents another means of predicting the mechanism of degradation, and the situation of polystyrene is no longer anomalous.

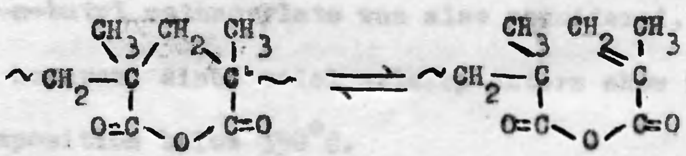
TABLE I

Monomer	$K_{toluene}$ 60°C	E_o Kcals/mols	Yield monomer on pyrolysis
Methacrylonitrile	2x10^{-2}	15	About 85%
Styrene	2.11x10^{-3}	17	65%
Methyl methacrylate	1.25x10^{-2}	13	90%
Methyl acrylate	0.56	20	1%
Acrylonitrile	0.785	17.3	1%
Vinyl acetate	7.73	21	0
Methyl	490		

THE METHACRYLATES

A survey[16] of the polymethacrylate esters as a group has shown that they all depolymerise to monomer on heating to 250°C., with the exception of poly-tert-butyl methacrylate.

The reactions which occur in this polymer have been studied by Grassie and Grant[10]. These authors showed that three distinct reactions occur: depolymerisation to monomer, ester decomposition to iso-butene and polymethacrylic acid, and liberation of water from the resulting acid to give polymethacrylic anhydride as the ultimate involatile residue. The formation of anhydride following ester decomposition inhibits the depolymerisation by stabilisation of the depropagating chain by a type of intramolecular repolymerisation,



Since all the other lower methacrylates depolymerise to monomer by a radical mechanism, the chain propagating radicals being identical with those involved in polymerisation, depolymerisation represents a third approach, in addition to polymerisation and copolymerisation, to the study of the effect of structure on radical reactivity. In this connection the thermal[2] and photochemical[3] degradation of polymethyl methacrylate in high vacuum has been thoroughly investigated. Both reactions yield monomer as the sole product, the reaction being initiated at the chain ends. During the photochemical work it was found that the high viscosity of the molten polymer affects the course of the reaction. From the wide variety of methacrylates available for study, therefore, poly-n-butyl methacrylate was chosen since it is reported[16] to have the lowest melting point of all the simple esters. This means that it should be possible to study its thermal and photochemical decomposition well above its melting point under which conditions it might reasonably be expected to exist as a relatively mobile liquid, thus reducing the effect of viscosity on controlling the reaction rate. The possibility of ester decomposition also occurring during thermal degradation of poly-n-butyl methacrylate was also considered. It seemed remote, however, since model primary esters show little sign of decomposition below 350°C.

The original object of the work described in this thesis was therefore to discover the best conditions for studying the depolymerisation process in poly-n-butyl methacrylate with the ultimate aim of elucidating the mechanism and determining the rate constants of propagation and termination for comparison with the data which exists for polymethyl methacrylate. How far this was achieved and how far the investigations were side-tracked into ester decomposition studies will be revealed by the Chapters which follow.

CHAPTER II

APPARATUS AND EXPERIMENTAL METHODS

Before studying the thermal degradation of an addition polymer, it is desirable to know its polymerisation characteristics. These could give an indication of any abnormalities which might occur in the chain and which might lead to abnormal degradation behaviour. The polymerisation of n-butyl methacrylate has been studied by Burnett, Evans and Melville[17]. The various rate constants are not very different from those of methyl methacrylate[18]. In view of the fact that both these polymers yield monomer on heating[16] one might reasonably use the knowledge which exists about the degradation of polymethyl methacrylate as a guide to the study of the n-butyl ester.

PREPARATION OF POLYMERS

n-Butyl methacrylate was supplied by I.C.I. Ltd. After washing four times with 5N caustic soda to remove the hydroquinone stabiliser, followed by four washings with distilled water, the monomer was dried overnight over anhydrous sodium sulphate, filtered and distilled under reduced pressure (b.p. 55-58°C. at 25 mms). Infra red spectra of liquid samples were taken at various stages of purification and the frequencies of the principal peaks compared with the values reported by Davison[19]. This evidence and the fact that only one peak was obtained on the vapour phase chromatogram were taken as strong evidence of purity of the monomer. For high purity monomer it is common to distil in high vacuum after degassing. n-Butyl methacrylate proved to be too involatile for this procedure, but it has been shown to have no effect on the rate of polymerisation[17].

Polymerisations were carried out in dilatometers at 60°C. with 2:2'-azo-isobutyronitrile, recrystallised from chloroform/methanol mixture (m.p. 105°C.), as initiator, and taken to 15% conversion using the data of Burnett, Evans and Melville for percentage contraction on polymerisation (17.5% for 100% conversion).

Polymers prepared in bulk have very high molecular weights. Two polymers of low molecular weight were prepared in benzene solution, the molecular weight being reduced by transfer to the solvent. These preparations were carried out in a three necked 500 ml. flask, fitted with a condenser, a dropping funnel and a gas inlet. 250 ml. of benzene were refluxed for one hour in a current of argon to purge the system of oxygen, the initiator being thereafter added, dissolved in the required amount of monomer. This final mixture was refluxed for two to three hours.

The polymer was precipitated from the solution by adding to four litres of methanol. After filtering it was twice reprecipitated by dissolving in "Analar" acetone and then running the solution into a large volume of vigorously stirred methanol. Considerable difficulty was experienced in obtaining the polymer in a finely divided form. It tended to appear as a rubbery mass which adhered to the stirrer. After breaking up into small pieces, the filtered product was dried for two days under vacuum, ground to a fine powder and dried further under high vacuum. With high molecular weight polymers the grinding process was facilitated by precooling the material in a glass tube immersed in liquid air. In this case the drying time had to be increased since moisture tended to condense on the frozen polymer.

PREPARATION OF N-BUTHYLMETHACRYLATE / METHACRYLIC ACID COPOLYMERS

The reactivity ratios for this system have not been reported in the literature. However, the Alfrey-Price Q-e scheme[20], which is a semi-empirical approach to reactivity in copolymerisation reactions provides a reasonably reliable means of calculating the reactivity ratios (r) from data[21] which already exists on the copolymerisation of methacrylic acid esters with methacrylonitrile .

According to the Alfrey-Price Q-e scheme ,

$$r_1 = {}^{Q_1}/_{Q_2}\; e^{-e_1(e_1-e_2)}$$

$$r_2 = {}^{Q_2}/_{Q_1}\; e^{-e_2(e_2-e_1)}$$

Referring to methacrylic acid and n-butyl methacrylate as monomers 1 and 2 respectively then from reference21,

$$Q_1 = 1.15 \qquad e_1 = 0.52$$

$$Q_2 = 0.73 \qquad e_2 = 0.30$$

from which

$$r_1 = 0.82 \text{ and } r_2 = 1.11$$

The monomer compositions required for the preparation of a copolymer of given composition were calculated from the copolymer composition equation[22].

$$\frac{A}{B} \text{ in polymer} = \frac{A}{B} \text{ monomer } \frac{r_1 \ A + B}{r_2 \ B + A}$$

DEGRADATION APPARATUS

All degradations were carried out under high vacuum using a dynamic molecular still, essentially similar to that designed by Grassie and Melville. Figure 1 illustrates the general arrangement of the glasswork of the apparatus. The main features of the system are as follows. Firstly, volatile products are removed quickly so that there is little possibility of their reacting further. Secondly, since in the dynamic molecular still the heated surface is separated from the cold surface (the liquid air trap), a small pressure will be built up within the still. Provided the liquid air level is maintained constant then this pressure may be used as a measure of the rate of production of volatile material from the polymer. It is measured by a Pirani gauge (figure 2).

THE PIRANI GAUGE

The gauge circuit is shown in figure 3. The functioning

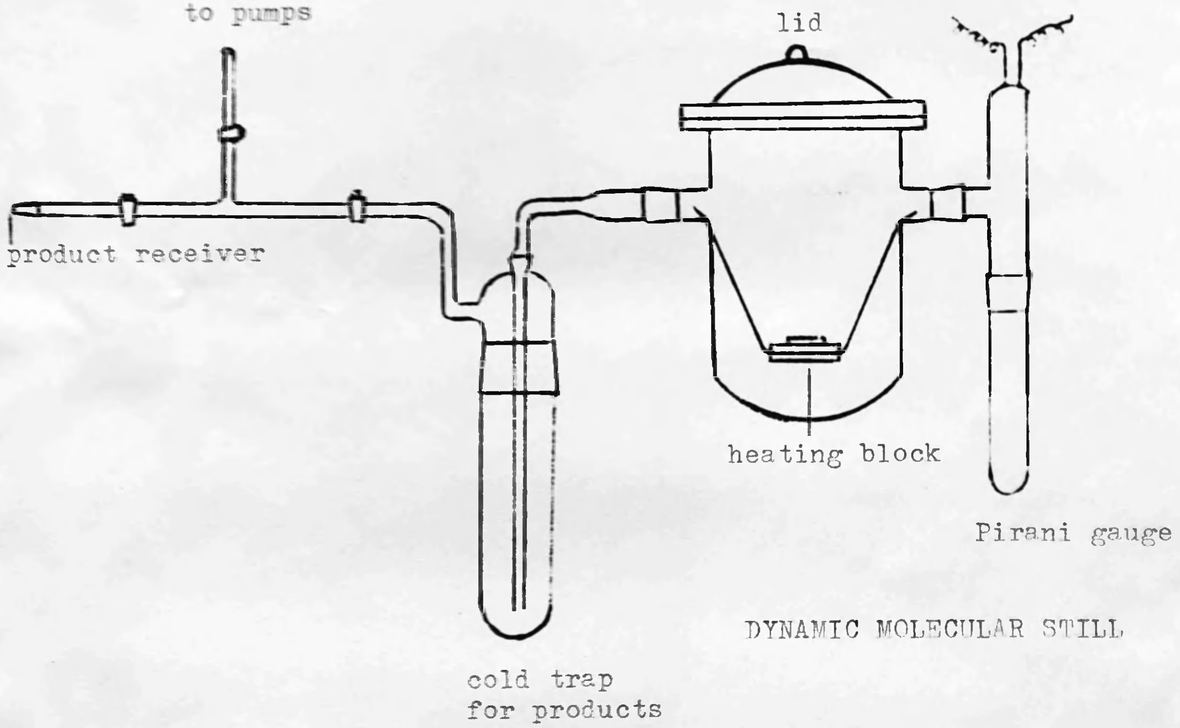


Figure 1. Glasswork of degradation apparatus.

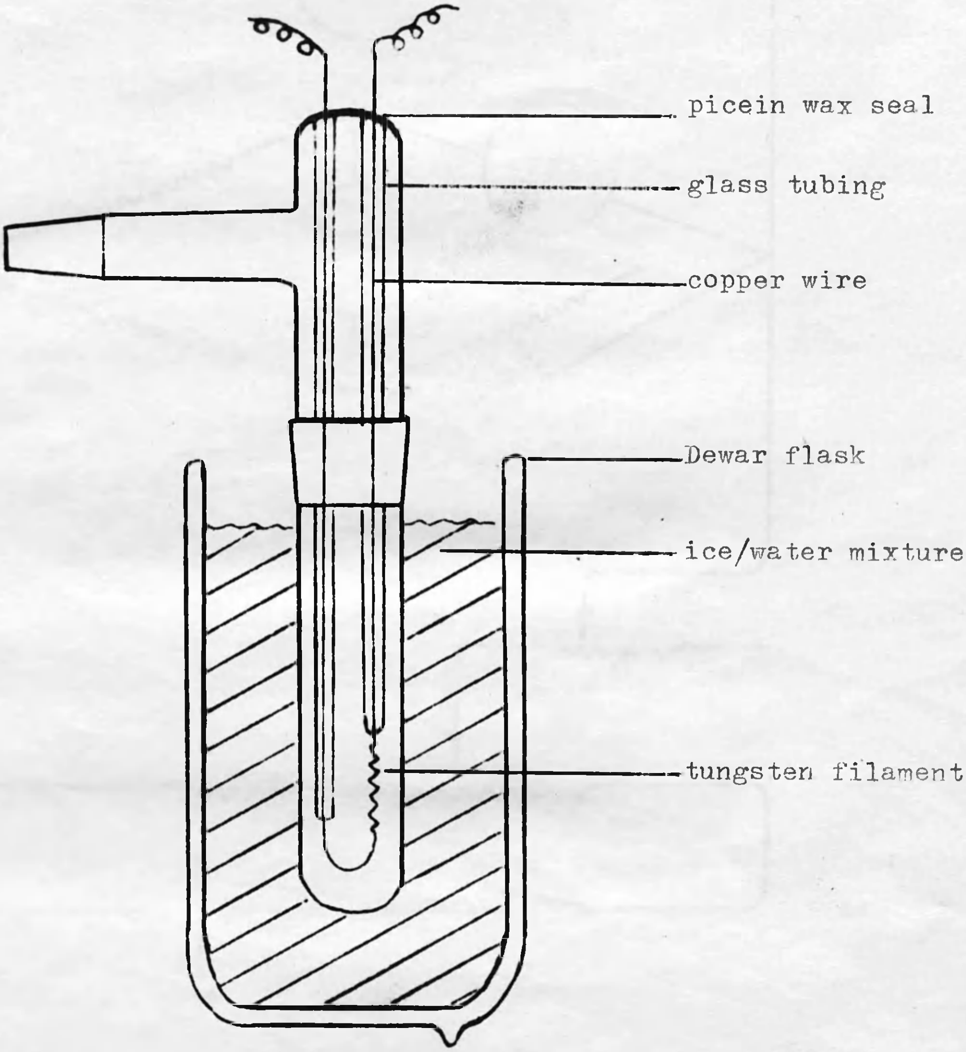
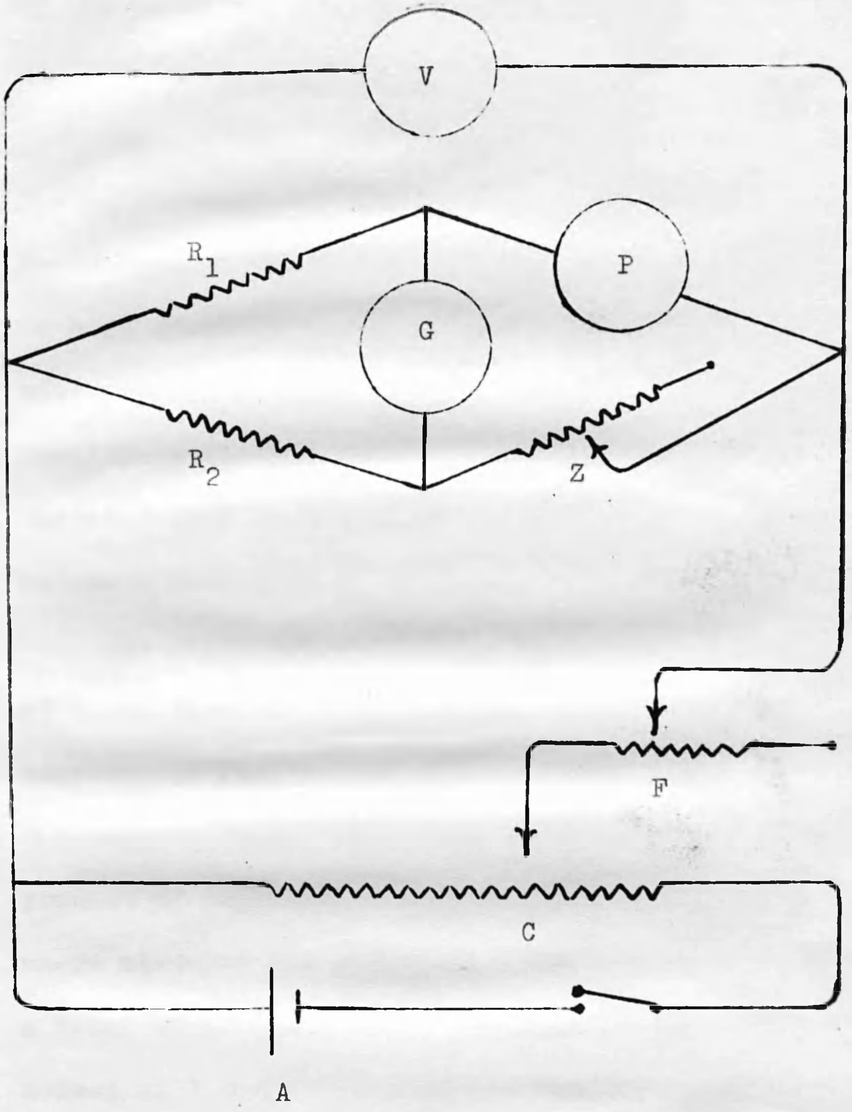


Figure 2. Pirani gauge



A	Accumulator 2 volts	C	Coarse potentiometer 0-100Ω
F	Fine potentiometer 0-10 ohms	R_1, R_2	fixed resistances
G	Galvanometer	P	Pirani gauge
Z	Zero control 0-50 ohms	V	Voltmeter 0-2 volts

Figure 3. Circuit for Pirani gauge.

of the gauge depends on the fact that the resistance of a hot wire varies inversely with the number of particles colliding with it. An increase of pressure increases the number of particles colliding and so lowers the temperature and thus the resistance of the wire. In this form of the gauge, resistance is kept constant by altering the voltage, thus a larger pressure will require a larger voltage to maintain the wire at a given resistance (temperature). It is necessary to have the gauge thermostatted in an ice/water mixture in order that the external heat loss is constant.

The gauge was calibrated by passing monomer into the still at known rates of flow by controlling and measuring the rate of evaporation from a calibrated reservoir and plotting V against the rate of flow. This procedure is only valid where the product of degradation is homogeneous, and could not be used where mixtures are obtained. The apparatus was calibrated for a value Vo of 0.600 using two lids on the still, firstly, the normal flat glass lid used for thermal degradations, the other a larger lid incorporating a quartz window for use in photochemical reactions. The plot of rate against voltage for the larger lid is shown in figure 4.

MEASUREMENT OF INITIAL RATE OF DEGRADATION

Thermal

Because of the bulk of the heating block ($\simeq$ 350g), about 15 minutes were required for the tray and polymer to reach the

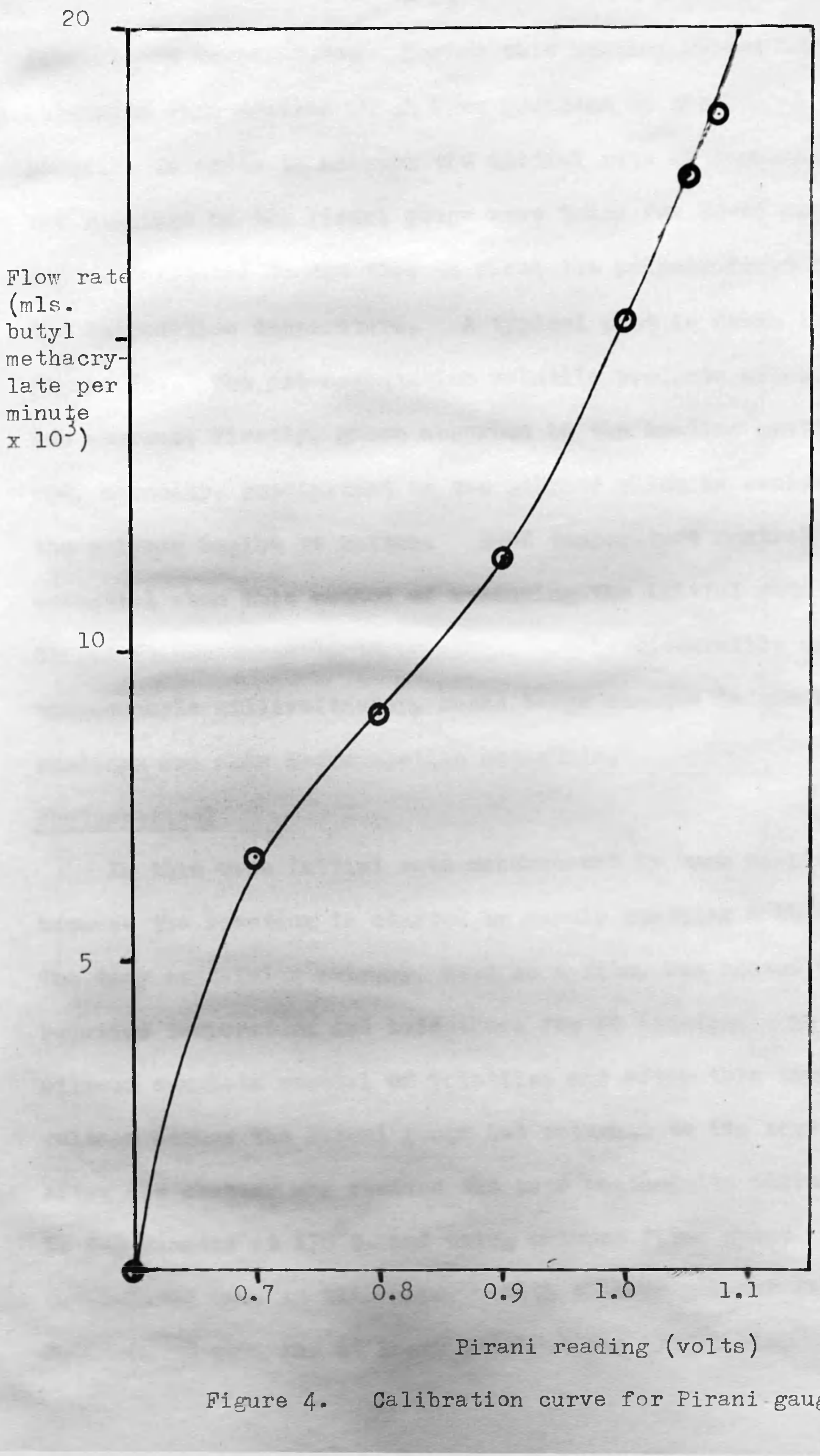
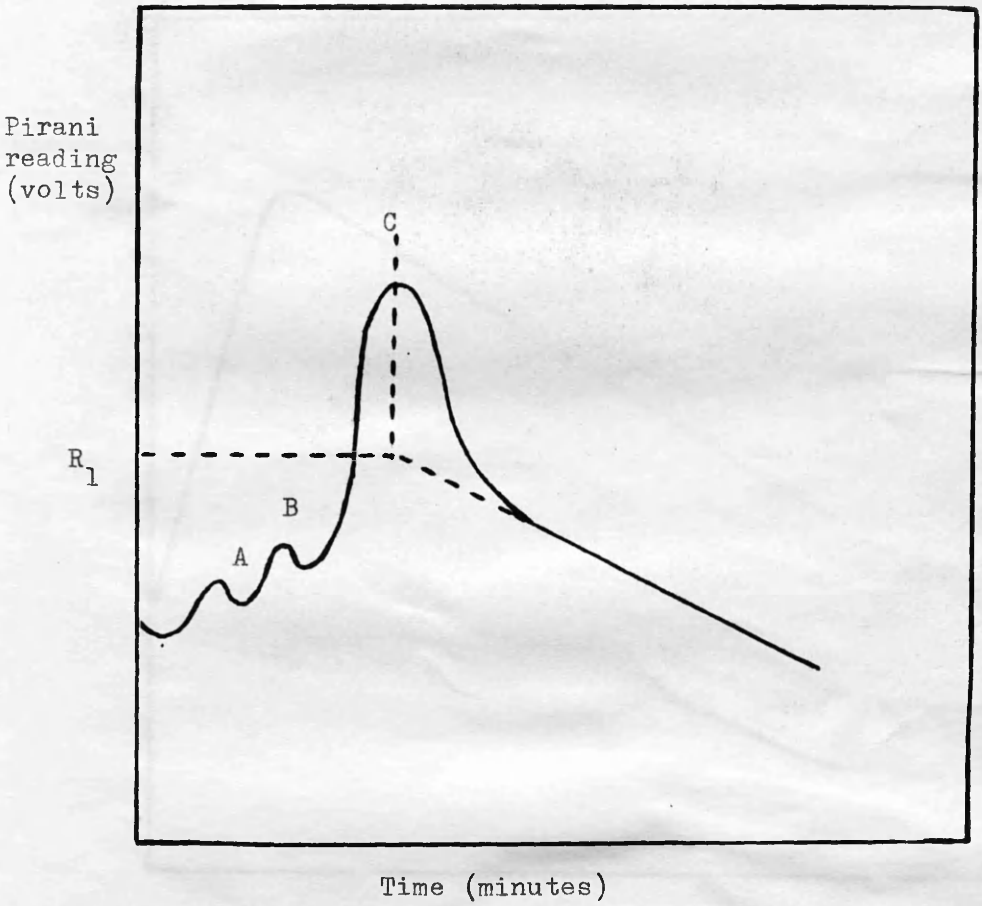


Figure 4. Calibration curve for Pirani gauge.

degradation temperature. During this heating period volatiles were evolved which were recorded by the Pirani gauge. In order to measure the initial rate of degradation the readings on the Pirani gauge were taken for 20-25 minutes and extrapolated to the time at which the polymer first reached the degradation temperature. A typical plot is shown in figure 5a. The pre-degradation volatile products arise from two sources, firstly, gases absorbed in the heating system and, secondly, precipitant in the polymer which is evolved when the polymer begins to soften. Good temperature control is essential when this method of measuring the initial rate is used. Slight fluctuations in temperature, barely discernible on the thermocouple millivoltmeter, cause large changes in the Pirani readings and make extrapolation uncertain.

Photochemical

In this case initial rate measurement is much simpler because the reaction is started by merely removing a shutter. The tray containing polymer, cast as a film, was heated to the required temperature and held there for 40 minutes. This allowed complete removal of volatiles and after this time the voltage across the Pirani gauge had returned to its zero value. After the shutter was removed the rate reached its maximum value in 2-3 minutes at 170°C. and using polymer films about 0.001-0.003 cms. in thickness. With thicker polymer films 0.006-0.008 cms. and at lower temperatures (150°C.-160°C.), some



Peaks A and B due to evolution of volatiles

C Polymer has reached degradation temperature

R$_1$ Initial rate of degradation

Figure 5A. Typical Pirani cure for thermal degradation.

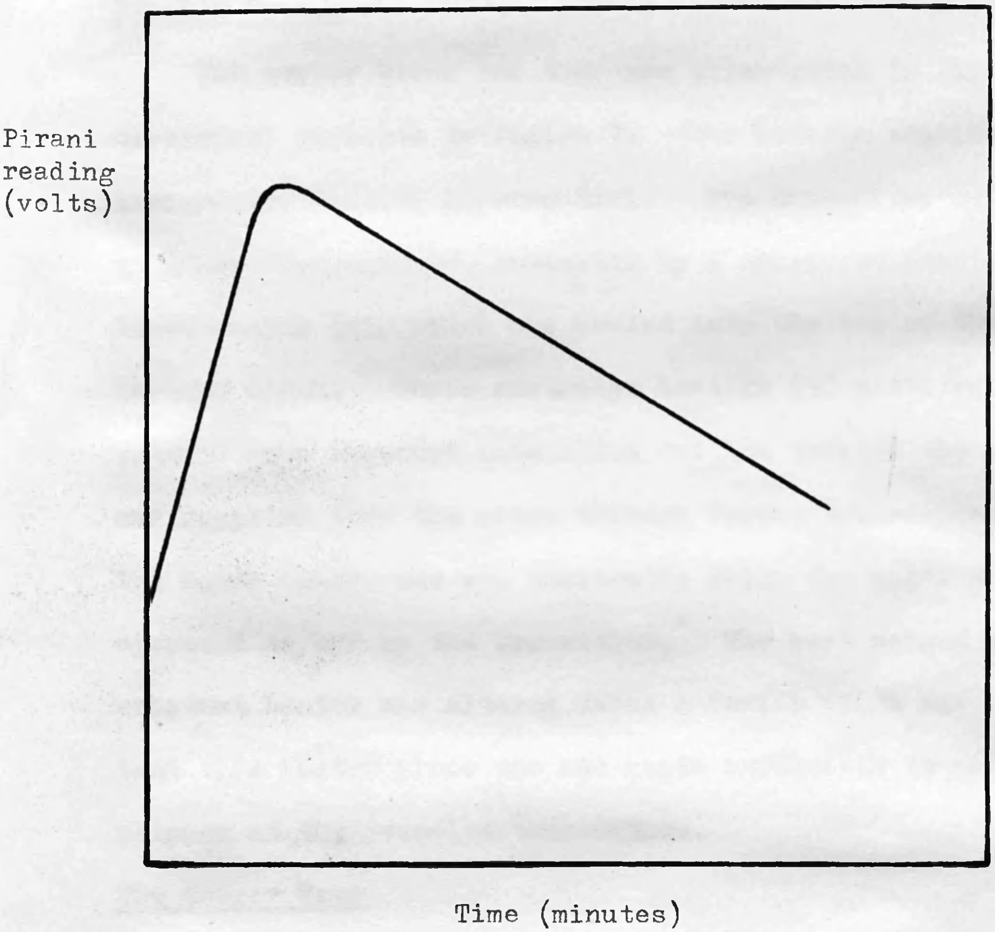


Figure 5B. Typical Pirani curve for photochemical degradation.

6 to 10 minutes elapsed before the maximum was attained. This time lag is due to slow diffusion of the monomer out of the polymer and will be discussed later. A typical plot is shown in figure 5b.

Heating System

The copper block and tray are illustrated in figure 6 and electrical circuits in figure 7. For kinetic studies good temperature control is essential. The controller used was an Ether "Transitrol", activated by a copper/constantan thermocouple (A), which was sealed into the top of the heating block. Three cartridge heaters (50 watts/24 volts rating) were inserted into holes drilled through the block and supplied from the mains through Variac transformers. The lower heater was run constantly while the upper two were operated on/off by the "Transitrol." The heat output of the constant heater was altered using a Variac which was set such that this heater alone was not quite sufficient to maintain the polymer at the reaction temperature.

The Copper Tray

The copper tray measured 37 mms. x 37 mms. x 7 mms. and had a circular hole 4 mms. deep and 32 mms. in diameter cut from the centre. The tray and block had been ground together to ensure even contact between the surfaces and, during operation, the tray was firmly screwed to the top of the block. The required weight of polymer was placed on the tray either as a

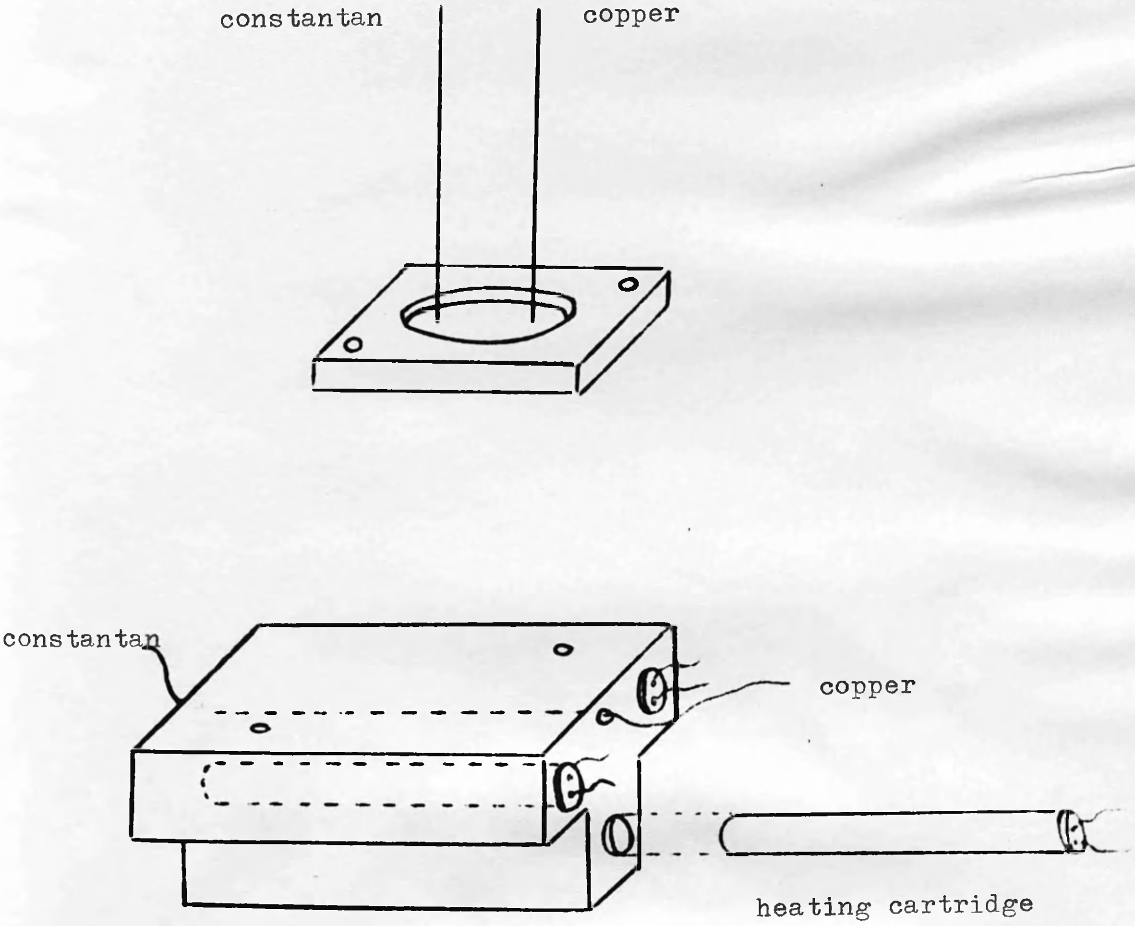


Figure 6. Degradation tray and heating block.

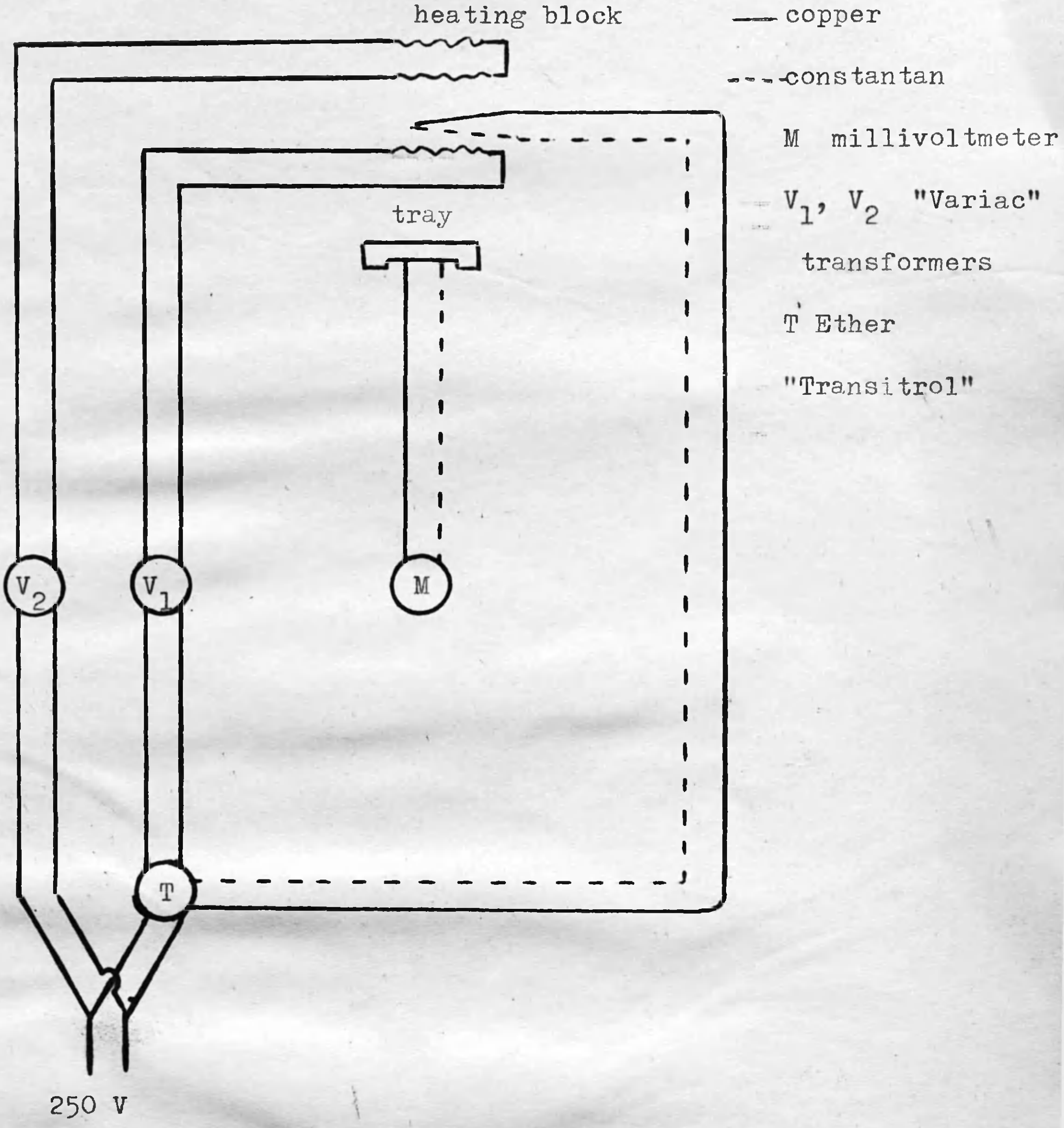


Figure 7. Temperature measurement, heating and control circuits.

fine powder (0.2-0.3 g.) for thermal degradation, or as a film (0.01-0.06 g.) for photodegradation. In the former case, the powder was covered by a layer of copper powder (10-12 g.) to ensure uniform heating. The copper powder, 60-80 mesh, was supplied by Hopkins and Williams Ltd.

The temperature of the tray was measured by a copper/constantan thermocouple soldered to the inside of the base. The thermocouple leads were led to a millivoltmeter through picien wax seals in the glass. The millivoltmeter readings were calibrated against a standard thermometer using a silicone oil bath and leads of the same resistance.

Photo-Degradation

An Osram 125 watt mercury arc lamp, with jacket removed, was used as light source. The output of this type of lamp has been studied by COWLEY AND Melville[3] and over 90% of the energy is emitted at 2537Å wave-length. The lamp was switched on for at least 30 minutes before commencing degradation to allow the lamp to reach an almost constant temperature.

Screens

The light intensity was varied by the use of intensity screens of known transmission. These were wire gauzes of different mesh sizes and wire gauges, the transmission having been measured using an uranyl oxalate actinometer[23] and checked by a photo-electric cell.

Investigation of Products

Two methods were employed in examining the volatile products of degradation, namely infra-red spectroscopy (I.R.) and vapour phase chromatography (V.P.C.). No quantitative measurements were made by either technique. On all occasions on which it was required to examine the products of degradation the liquid air trap was not put into place until the polymer had been heated beyond its melting point (150°C.) and the volatiles evolved, mainly adsorbed precipitant, removed to the secondary trap by pumping.

Infra-red spectra were measured on a Perkin Elmer Model 13 double beam spectrophotometer, with rock salt prisms. Volatile products were examined either in a 10 cm. cell or as liquid samples. Degraded polymer was examined in carefully filtered chloroform solution, using 0.5 mm. cells in the normal fashion, or in the solid state using films or the K Br. disc technique[24]. Spectra measured as films or in K Br. discs were identical with those run in solution.

Vapour phase chromatograms were run on a Pye Argon apparatus. Volatile compounds were transferred by molecular distillation from the liquid air trap to a smaller reservoir which had a narrow leg attached to its foot. Liquids collected in the leg and gases remained above the liquid. The vacuum was released slowly and a sample immediately sucked into either a syringe using a long needle for gases, or a micropipette for liquids, and then injected into the gas flow through a serum cap. A special copper spiral column immersed in ice/water was used for gaseous products. All columns were packed with Silicone 301/ Celite. Marker compounds were run and retention times used to identify the products. Analysis of liquid products was complicated by the presence of minute amounts of acid, which tend to be adsorped by the column packing.

Infra-red and V.P.C. used in conjunction proved to be extremely valuable tools in the investigation of the products of degradation.

Molecular Weight Measurements

Number average molecular weights were measured osmotically. Osmotic pressures were measured either on a Pinner-Stabin[25] type osmometer supplied by Polymer Consultants Ltd., or on a modified Fuoss-Mead instrument[26].

Solutions of degraded polymer were prepared by immersing the tray and contents in approximately 50 ml. of benzene for some hours and filtering off the copper powder.

Pinner-Stabin

In this osmometer, which is designed for static measurements, the solution is contained in a small glass cell (about 5 mls.) and separated from a larger volume of solvent (about 200 mls.) by two membranes, supported on stainless steel plates. The small volume of solution required makes it possible to carry out determinations with this instrument on very small samples of material.

Membranes

The solvent used was benzene, so the undried regenerated cellophane used as membranes had to be conditioned. It was stretched on a frame and treated in the following sequence:-

1 hour in distilled water

2 hours in 25 acetone : 75 water

2 hours in 50 acetone : 50 water

2 hours in 75 acetone : 25 water

2 hours in acetone

The process was repeated progressively replacing acetone by benzene.

Operation

Four instruments were employed. The osmometers were checked for leaks before using, in the manner recommended by the suppliers. Before filling, the cell was rinsed out six times with the solution under examination. After leaving for an hour to allow the system to settle thermally the difference in level between the two reference arms was adjusted to approximately the value expected, using the positioning rod. The change in level was followed for a period, usually about twenty-four hours, by which time normally equilibrium was attained. As it is impossible to obtain perfect membranes, the cell constant was determined before and after each measurement. Very little use was made of this type of osmometer as very variable results were obtained for the cell constant, and for the actual osmotic pressure at different concentrations. The probable reason for this behaviour is discussed below.

Fuoss Mead

Molecular weights were also measured on the Modified Fuoss-Mead osmometer described by Masson and Melville[26]. A bacterial cellulose membrane was used. The instrument was thermostatted at 30°C.± 0.05° by pumping water from a thermostatted water tank through the surrounding jacket. Before each measurement the cell constant was read and the osmometer washed out six times with solvent and then six times with the solution to be measured. Osmotic pressures were measured statically.

Over a period of time, some two months, the cell constant became variable, and was always positive. Careful examination of the polymer solutions led to the detection of a very fine gel which could apparently pass through the normal fairly coarse filter paper. The variation in cell constant is believed to be due to this gel being present in the osmometer, possibly by being absorbed into the membrane in some way. The gel would also explain the difficulties encountered with the Pinner-Stabin osmometers, and in this case the effect is more liable to be cumulative because of the method of emptying the cell of solution. The Fuoss-Mead osmometer does return to normal on persistent washing of the instrument with solvent.

The solvent used in both the above methods was "Analar" benzene, dried over calcium chloride and distilled through a fractionating column, discarding the first quarter of the distillate. Concentrations were found by taking a weighed amount of solution, evaporating to dryness in an air-oven at 110°C. for 24 hours, and weighing the resulting polymer.

Calculation

The number average molecular weight is related to the limiting value of $\frac{\pi}{C}$, obtained from the $\frac{\pi}{C}$ against C plot, by the following equation

$$\text{Limit}\left(\frac{\pi}{c}\right)_{c\to 0} = \left(\frac{\pi}{c}\right)_0 = \frac{RT}{M}$$

Where π = osmometer head (cms.)

C = concentration of solution in g. solute/ml. of solution

T = absolute temperature

M = the number average molecular weight of the polymer

R = the gas constant, 82.06 atmos./degree/mole.

Since 1 atmos. = 1033.3 gm./sq.cm.

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

Since C in gm./ml. = C in gm./100 g. x density of solution/100

$$\left(\frac{\pi}{c}\right)_{c\to 0} = L \times \frac{\text{DENSITY}}{1033.3} \times \frac{100}{\text{DENSITY}}$$

Where L is the limiting value of π/c in units of cm. and g./100 g. of solution

From which

$$M_2 = 10.333\ RT/L = 10.333 \times 82.06 \times T/L$$

$$= 847.9\ T/L$$

At 30°C. $M_2 = 257{,}000/L$

Viscosity Measurement of Molecular Weight

When the osmometers became difficult to use because of the variable large cell constants obtained, it was found necessary to employ viscosity measurements for molecular weight determinations. This is a rapid method of making such measurements, but is not absolute. The viscosity technique was used for measuring the change in molecular weight during photodegradation.

The intrinsic viscosity $[\eta]$ of a polymer solution is related to the molecular weight of the polymer by the equation

$$[\eta] = KM^{\alpha}$$

in which K and are dependent on the nature of solute and solvent, and M is the molecular weight. K and α must always be calibrated against some absolute method. The intrinsic viscosity is given by

$$\lim_{C \to 0} \left[\frac{(t_c - t_o)/t_o}{C} \right]$$

in which t_c and t_o are the times taken for solution of concentration C, in g. per 100 ml. solution, and solvent respectively to flow through the viscometer.

A suspended-level viscometer supplied by Polymer Consultants Ltd. was used for all measurements. The values for K and α are reported in the literature[27] as 0.437×10^{-4} and 0.80 for chloroform solutions at 25°C. Fair agreement was obtained for molecular weights measured by both viscosity and osmotic pressure methods.

CHAPTER III

THE THERMAL DEGRADATION OF POLY-n-BUTYL METHACRYLATE

INTRODUCTION

The kinetics of the polymerisation of n-butyl methacrylate have been studied[17] and the various rate constants found to be comparable with the corresponding values for the polymerisation of methyl methacrylate[18]. Since the same kind of radicals are involved in polymerisation and depolymerisation processes it might reasonably be deduced that the depolymerisation behaviour of the two polymers would at least be qualitatively similar.

Crawford, in a preliminary investigation[16] of the thermal degradation of some of the simpler methacrylate esters has indeed shown that with the exception of poly-tert-butyl methacrylate they all yield monomer exclusively. It would therefore be of considerable interest to measure the rate constants of the depolymerisation reactions of a range of polymers of methacrylic acid esters since in addition to polymerisation and copolymerisation studies this would give a third source of information about the relationship between structure and reactivity in this type of radical. This choice of poly-n-butyl methacrylate for study was intended to be the starting point of such a sequence of investigations.

In the work described in this thesis four polymers were studied extensively. Two were prepared in bulk and two by transfer in benzene solution. The molecular weights of these four polymers are given in table 2.

TABLE 2

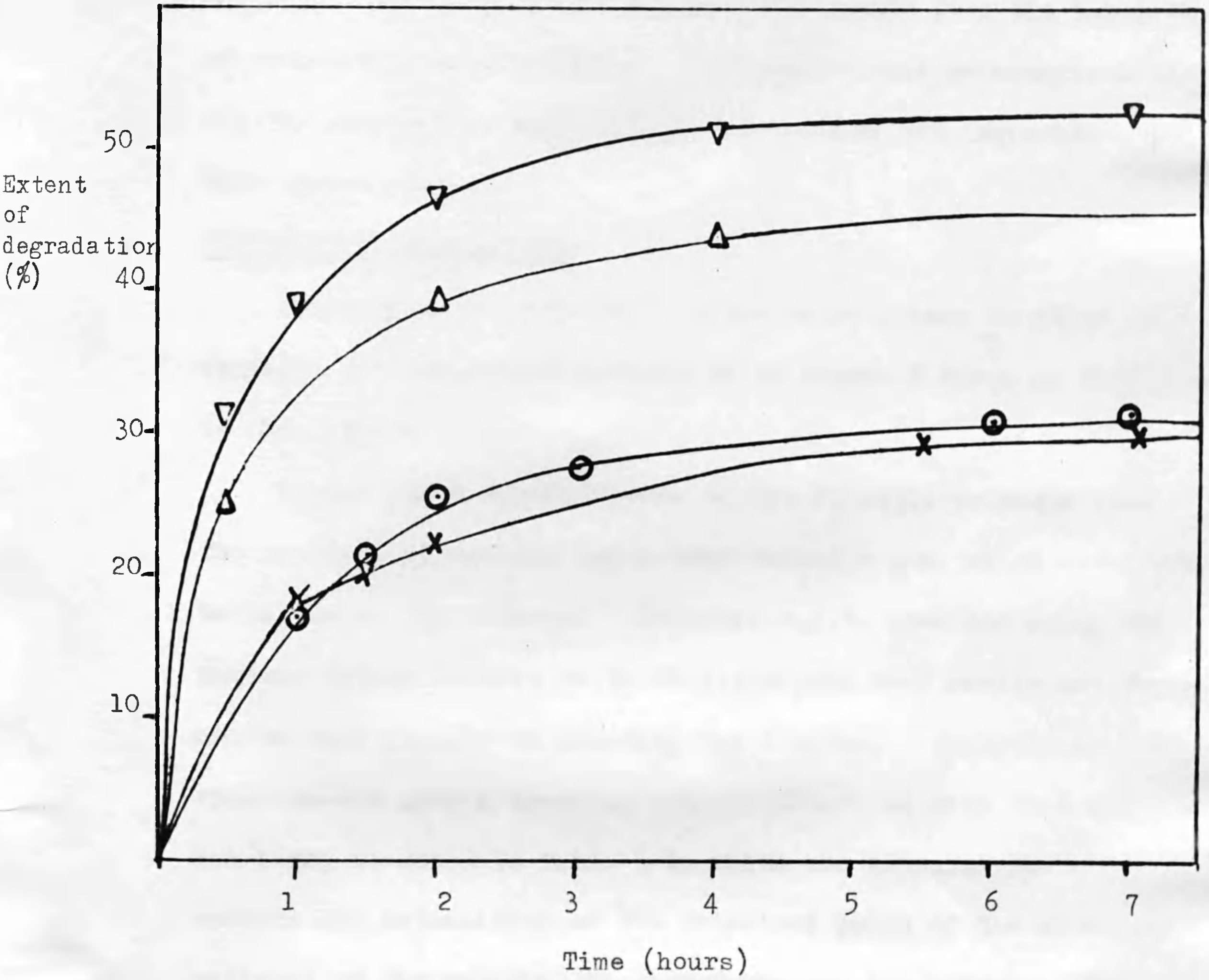
POLYMERS

	% Initiator (w/v) 2,2', azoisobutyronitrile	Preparation	Molecular Weight x 10^{-5}
N.B. 1	0.05	Bulk	11.0*
N.B. 2	0.50	Bulk	4.6
N.B. 4	0.20	Benzene solution 1 monomer: 10 benzene	0.4*
N.B. 6	0.03	Benzene solution 1 monomer: 2 benzene	1.1

* Viscosity measurement

SURVEY OF DEGRADATION

Before making a kinetic study of the degradation of poly-n-butyl methacrylate it seemed desirable to examine thoroughly the reaction at 250°C. At this temperature, only and exactly, 50% of polymethyl methacrylate degrades to monomer[2]. This proportion represents these molecules which have unsaturated structures at the chain ends. They are produced in the disproportionation reaction which terminates polymerisation and it is through these structures that depolymerisation is initiated at this temperature[28]. Figure 8 shows a graph of percentage degradation against time of heating at 250°C for a



▽ N.B.4
△ N.B.6
⊙ N.B.2
× N.B.1

Figure 8. Extent of degradation against time of heating at 250°C for a series of poly-n-butyl methacrylates.

series of poly-n-butyl methacrylates. It is immediately apparent that there is an inherent difference from the behaviour of polymethyl methacrylate. For poly-n-butyl methacrylate only the low molecular weight polymer approaches 50% degradation at this temperature.

PRODUCTS OF DEGRADATION

Comparison of infra-red spectra of solutions or films of degraded and undegraded polymer as in figure 9 shows no difference in the polymer structure.

Vapour phase chromatograms of the volatile products show the presence of monomer and a very volatile gas, which was proved to be one of the butenes. However, v.p.c. does not allow the various butene isomers to be distinguished very easily and could not be used finally to identify the olefine. Analysis by mass spectrometer gave a cracking pattern identical with that of but-1-ene as shown in Table 3 in which are compared the mass numbers and intensities of the principal peaks of the cracking patterns of the unknown gas, but-1-ene and iso-butene. The values for but-1-ene and iso-butene were obtained from the U.S. Petroleum Institute Publications.

On raising the temperature to 260°C and thus increasing the extent of degradation it was possible to detect the twin anhydride carbonyl peaks at 1795 $cm.^{-1}$ and 1750 $cm.^{-1}$ in the residual polymer. Figure 10 shows a typical example of the carbonyl region of a polymer degraded at 260°C. The presence

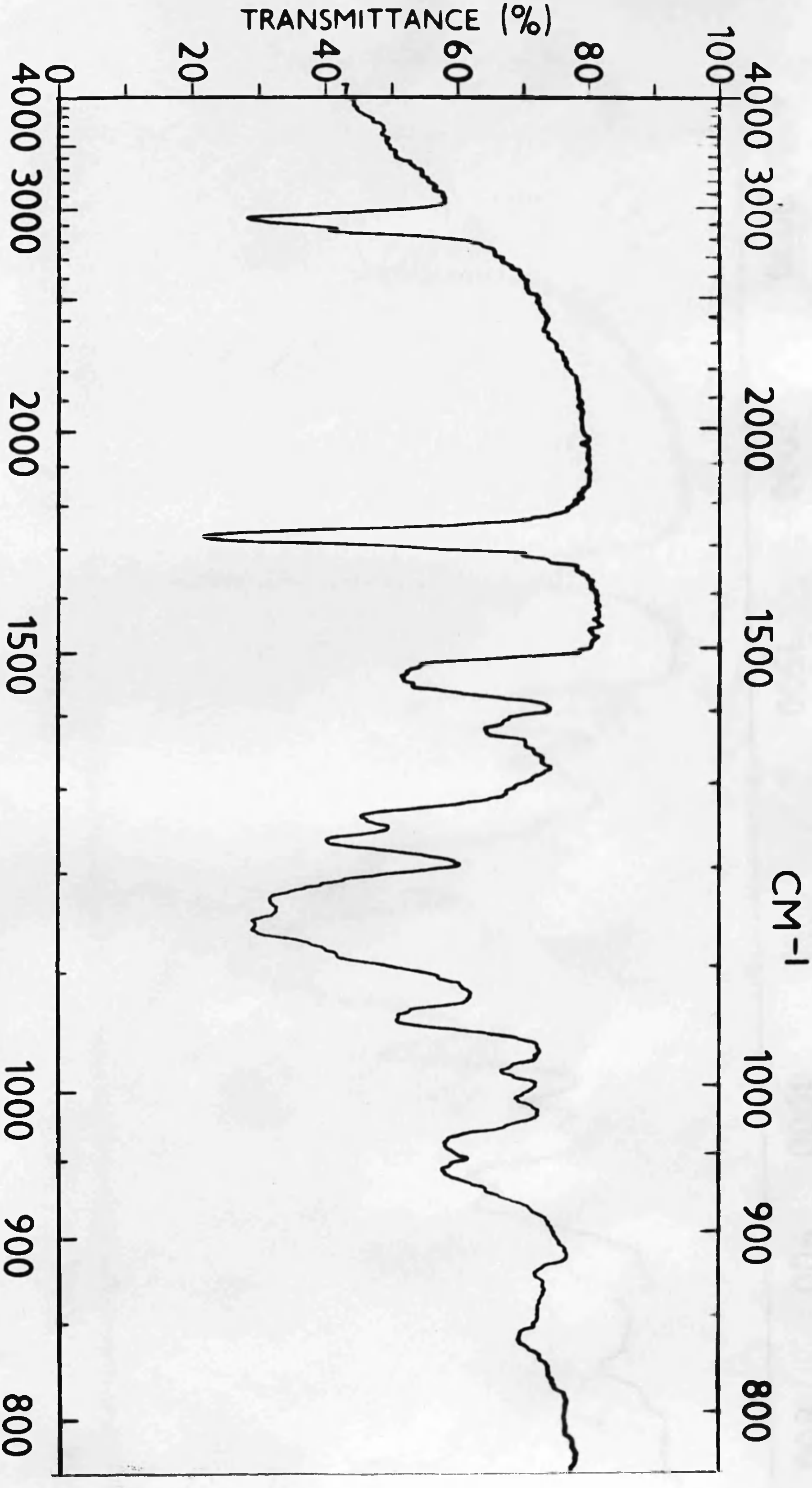


Figure 9A. Infra-red of undegraded poly-n-butyl methacrylate.

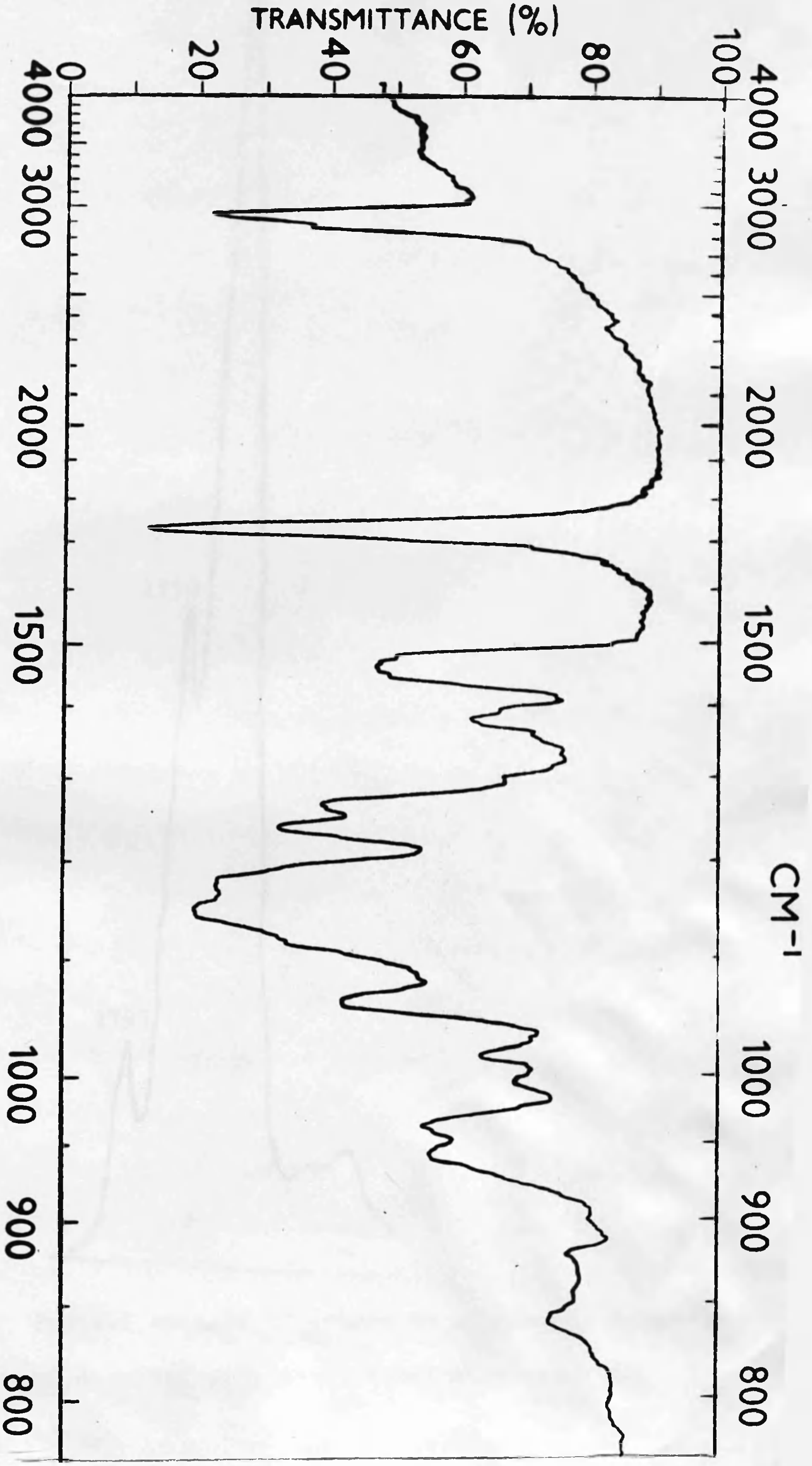


Figure 9B. Infra-red of degraded poly-n-butyl methacrylate.

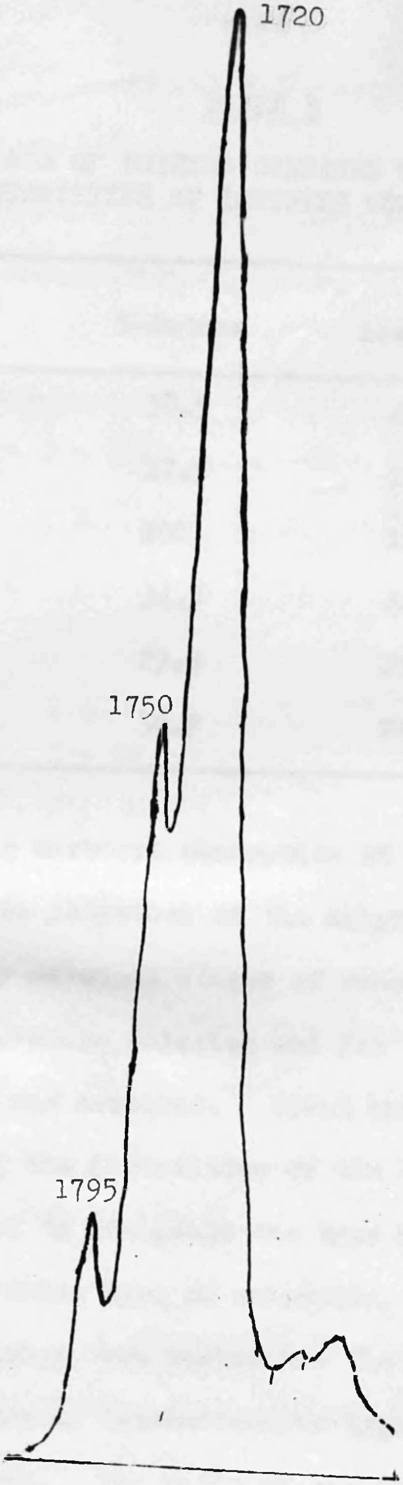


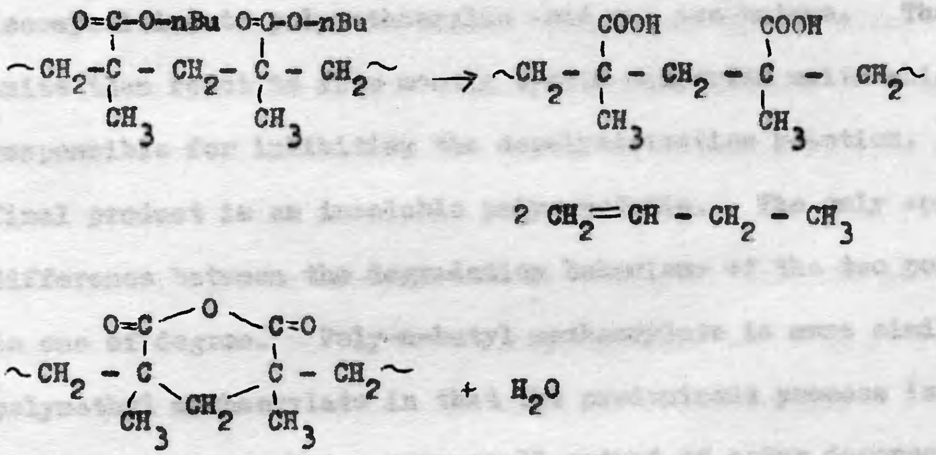
Figure 10. Typical example of anhydride showing in spectrum of degraded poly-n-butyl methacrylate.

TABLE 3

CRACKING PATTERNS OF BUTENES COMPARED WITH UNKNOWN BUTENE RELATIVE INTENSITIES AT IONISING VOLTAGE 50 VOLTS.

Mass : Charge ratio	1-Butene	iso-Butene	Unknown Butene
56	38.5	44.5	40.1
55	17.5	16.0	16.0
41	100	100	100
39	34.9	44.9	36.0
28	29.4	21.8	30.0
27	30.9	21.7	29.8

of a very strong carbonyl absorption at 1720 $cm.^{-1}$ due to the ester group makes detection of the anhydride peaks difficult, except at fairly advanced stages of reaction. The spectra were measured in chloroform solution and for this reason only the carbonyl region was examined. Grant and Grassie have shown[29] how the ratio of the intensities of the two anhydride carbonyl peaks can be used to designate the type of anhydride present. For an intermolecular type of anhydride, e.g. acetic anhydride, the peak with higher wave number has the higher intensity. The converse holds for an intramolecular type of anhydride, e.g. glutaric anhydride. The ratio of the intensities of the two peaks found in degraded poly-n-butyl methacrylate is identical to that found by the above authors for anhydropolymethacrylic acid, which is of the glutaric anhydride type, thus proving the presence of six membered cyclic anhydride units, of the type which would be formed as a result of ester decomposition of adjacent units and subsequent elimination of water.



Although the infra-red spectrum shows that the predominant type of anhydride present is intramolecular, the possibility of a few intermolecular units being formed, giving a small amount of cross-linking, is not precluded.

REVIEW OF DEGRADATION

At this stage it is convenient to summarise the thermal degradation of poly-n-butyl methacrylate thus:- firstly, depolymerisation to monomer occurs which ceases prematurely compared with polymethyl methacrylate; secondly, ester decomposition occurs yielding olefine and acid. The acid so formed must immediately react in some way to give the anhydride units which appear in the I.R. spectra. This sequence of events is somewhat similar to that which occurs in the thermal degradation of poly-tert-butyl methacrylate[10]. In this polymer Grant and Grassie showed that at 190°C. initially there was a small amount of depolymerisation to monomer, but the main process was ester decomposition to polymethacrylic acid and iso-butene. The acid units then react to form mostly cyclic anhydride units which are responsible for inhibiting the depolymerisation reaction. The final product is an insoluble polyanhydride. The only apparent difference between the degradation behaviour of the two polymers is one of degree. Poly-n-butyl methacrylate is more similar to polymethyl methacrylate in that the predominant process is depolymerisation, but a very small amount of ester decomposition can successfully inhibit this reaction and finally stop it completely. This competitive type of degradation process may be a general property of methacrylate polymers, with polymethyl and poly-tert-butyl representing the two extremes, namely total depolymerisation and total or almost total ester decomposition. The thermal degradation of polyethyl methacrylate was examined briefly and found to be similar to that of the n-butyl ester, that is mainly depolymerisation but with traces of ester decomposition leading to increasing stability of the residual polymer.

The non-occurrence of ester decomposition in polymethyl methacrylate can be explained by the fact that there is no hydrogen atom in the alcohol residue, one of the requirements of an ester before it can undergo this reaction[9]. It is interesting to speculate what would happen to the next higher ester lacking a β hydrogen atom, the neo-pentyl ester. It seems most probable that on thermal degradation this ester would yield 100% monomer in a manner analogous to the methyl ester.

It is now clear that a close comparison of the effect of molecular structure on the thermal depolymerisation of polymethyl and poly-n-butyl methacrylates cannot be attained because of the interference of the competing side-reaction in the n-butyl ester. However, it will be shown in the next chapter that the photo-reaction has none of the above complications and even poly-tert-butyl methacrylate can be made to yield 100% monomer. Nevertheless the ester decomposition reaction and its relationship to the depolymerisation process are of considerable interest and the rest of the chapter is concerned with this.

ACTIVATION ENERGY

The initial rate of degradation was measured at temperatures below 260°C and an Arrhenius plot (figure 11) gives an activation energy of 14 ± 1 kcals/mole for the production of volatile products. The kinetics of the reaction will be discussed later in Chapter V. Since there are two competitive reactions, depolymerisation and ester decomposition the overall rate will depend upon both, so it is not immediately obvious precisely to what this activation energy refers. For the thermal degradation of polymethyl methacrylate the activation energy was found to be

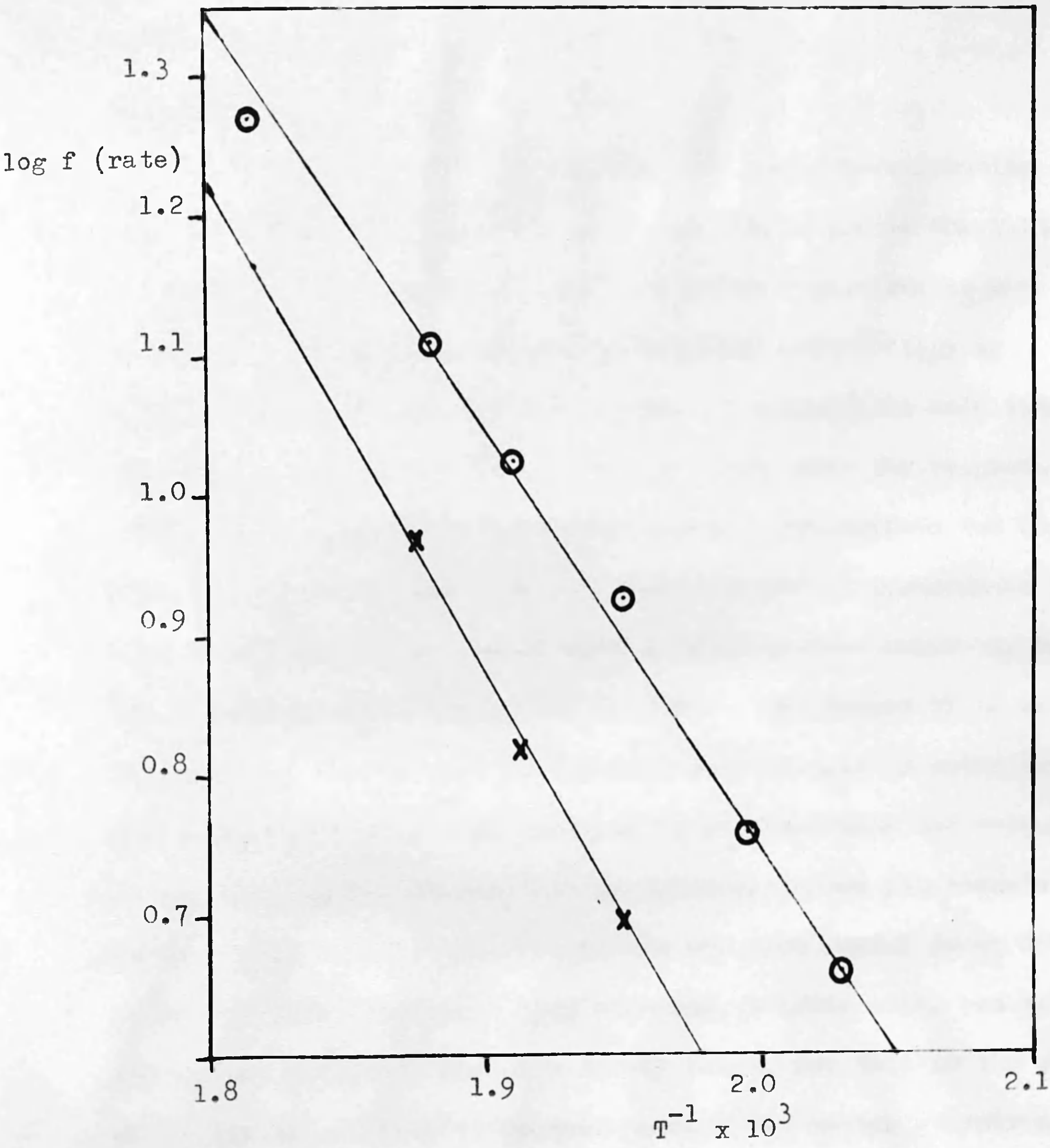


Figure 11. Thermal degradation of poly-n-butyl methacrylate. Arrhenius plot.

30 ± 1 kcals/mole[2].

ACID CATALYSES

Grant and Grassie[10] showed that the ester decomposition in poly-tert-butyl methacrylate is autocatalytic due to the fact that the newly formed acid which is retained in situ, acts as a catalyst. This catalysis can be produced artificially by copolymerising unsaturated acids such as methacrylic acid into the polymer chains and also by mixing acids with the polymer. Both methods were tried with poly-n-butyl methacrylate but as will be discussed below, the copolymer method is invalidated by the fact that all the acid units have reacted to form anhydride before the degradation temperature is reached. The choice of an external acid is very limited due to the fact that it must be relatively involatile at 250°C. In addition it is found that the copper powder used in the degradation experiments causes decarboxylation of the nitro-benzoic acids which are the most useful group of acids for this purpose. Zinc chloride, a Lewis acid, was tried and had no effect. The most likely reason for this is the problem of achieving intimacy of contact between the molten polymer and the added salt.

MOLECULAR WEIGHT CHANGES

A great deal of information regarding the nature of a depolymerisation process and the sites in the molecule at which it is initiated may be obtained from molecular weight measurements and particularly by plotting molecular weight changes against extent of volatilisation. If the process is a random one, i.e. if the volatile material is produced by the scission of the polymer chains at random then there would be a large drop in molecular weight before significant amounts of volatile material are produced. In figure 12 AD represents the extreme case. If chain scission at random led to radicals which could depropagate or "unzipp" and if these radicals were destroyed in a termination process before the molecule had completely disintegrated the reaction curve would lie between AD and the diagonal AC. At the other extreme, AB represents the situation in which after initiation to form radicals the molecules unzipp completely so that no involatile residue remains. This is the situation in low molecular weight polymethyl methacrylate. While a great deal of additional evidence is required for a complete analysis of any depolymerisation process it is also a useful generalisation to consider that a molecular weight against extent of degradation curve lying above the diagonal AC represents the situation where, on average, less than one involatile residue remains after the breakdown of a polymer molecule. A curve lying below the diagonal represents more than one involatile residue on the average.

A simple illustration follows.

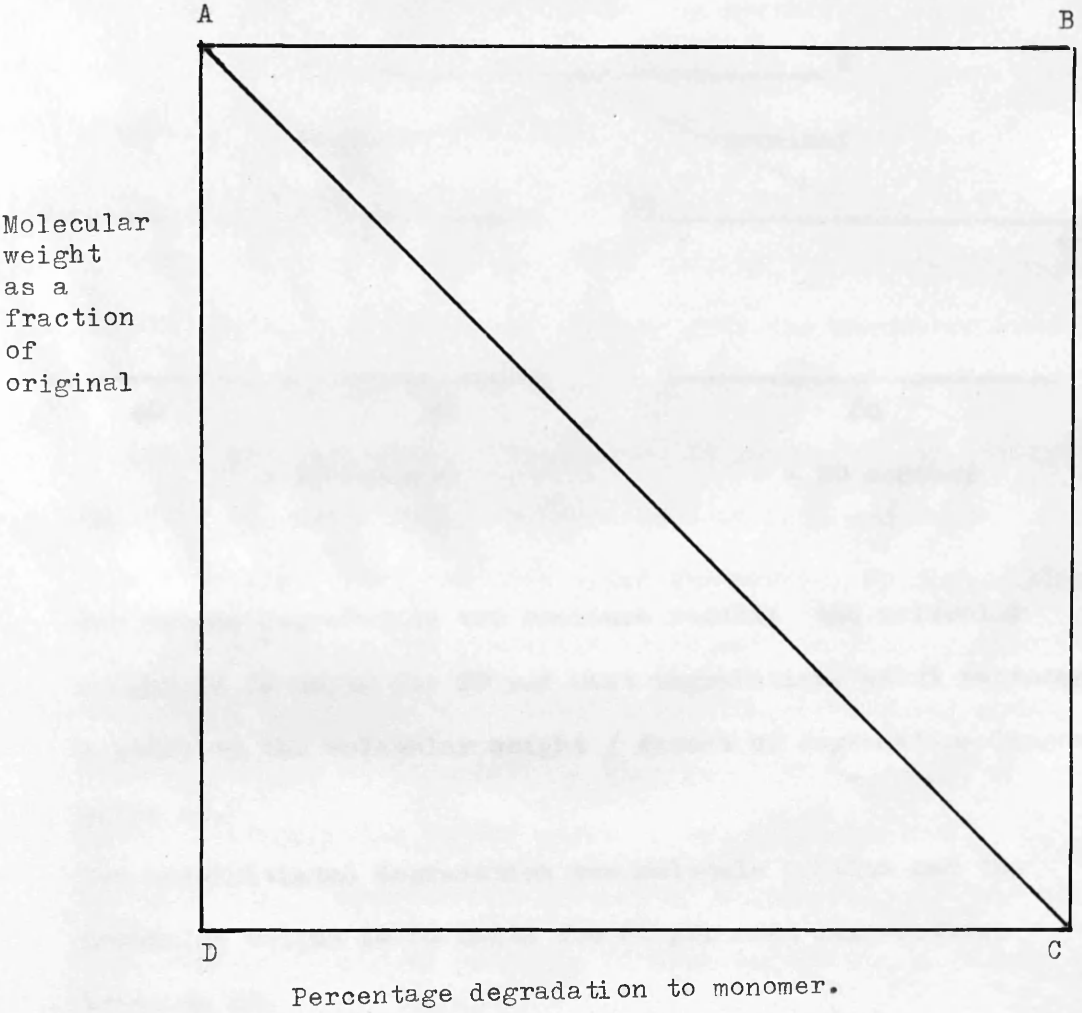
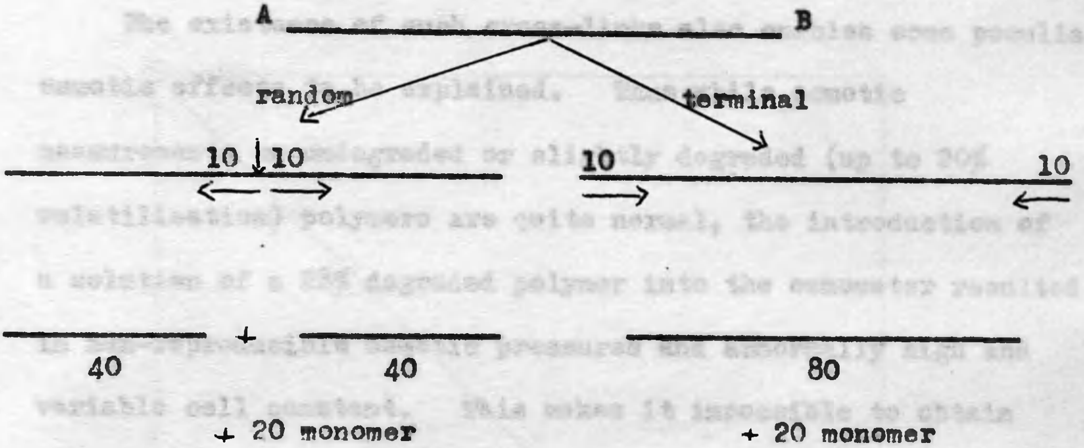


Figure 12. Theoretical molecular weight versus percentage degradation to monomer curves for various possible degradation mechanisms.

Suppose the molecule AB has a chain length of 100 units and the kinetic chain length of degradation is 10 units, that is 10 units are evolved from each initiated centre.



For random degradation two residues result; the molecular weight is 40 units for 20 per cent degradation, which represents a point on the molecular weight / extent of degradation diagram below AC.

For end-initiated degradation one molecule remains and the molecular weight is 80 units for 20 per cent degradation, lying on AC.

At advanced stages of volatilisation the polymer becomes progressively more insoluble in chloroform, the insoluble portion existing as a highly swollen gel. It is also at this stage that the anhydride structures become easily identifiable through infra red spectra. While it has already been shown (pages 44 and 45) that the bulk of the anhydride structures are cyclic due to elimination of water between adjacent acid units formed by ester decomposition in the chains, then insolubility is most easily explained in terms of a small proportion of intermolecular anhydride formation.

The existence of such cross-links also enables some peculiar osmotic effects to be explained. Thus while osmotic measurements on undegraded or slightly degraded (up to 20% volatilisation) polymers are quite normal, the introduction of a solution of a 28% degraded polymer into the osmometer resulted in non-reproducible osmotic pressures and abnormally high and variable cell constant. This makes it impossible to obtain reliable molecular weight measurements on such polymers. The effect persists for some time after the removal of the solution from the osmometer but gradually disappears on prolonged washing. In view of the definite insolubility which develops at more advanced stages of degradation, this peculiar behaviour is almost certainly due to the onset of gel formation and insolubility. Appreciable amounts of anhydride cross-links will of course only be possible at advanced stages of degradation when extensive ester decomposition has taken place. The use of molecular weight / degradation curves to obtain information about the nature of the reaction as discussed above will therefore still be quite valid at low degrees of volatilisation.

Osmotic molecular weights of a polymer degraded to 10% and 26% and are shown in figure 13. These points are undoubtedly

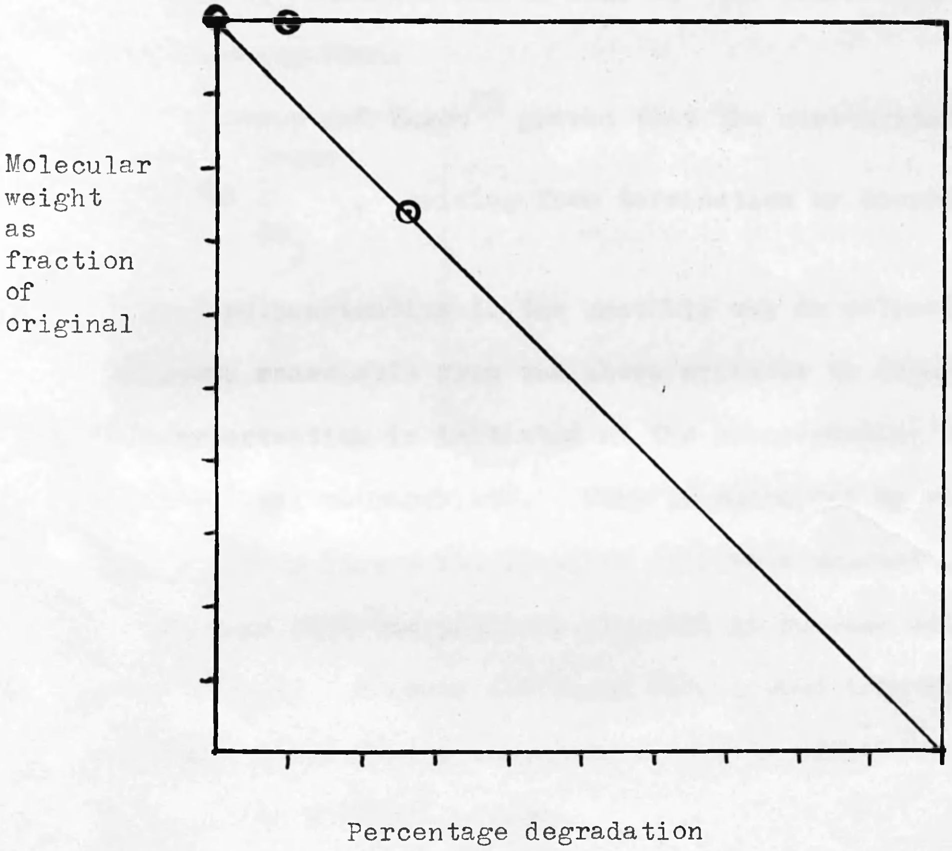


Figure 13. Molecular weight vs. percentage degradation for thermal degradation of poly-n-butyl methacrylate.

on or above the diagonal and it can thus be deduced that on the average not more than one involatile residue is produced from each degrading chain and so it is most likely that the depolymerisation is end-initiated as in polymethyl methacrylate. No definite decision can be made on this evidence as to which ends are breaking down.

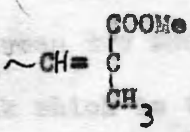
Grassie and Vance[28] proved that the unsaturated end,  $\sim CH=\underset{CH_3}{\overset{COOMe}{C}}$, arising from termination by disproportionation during polymerisation is the unstable one in polymethyl methacrylate It seems reasonable from the above evidence to assume that depolymerisation is initiated at the corresponding structure in poly-n-butyl methacrylate. This is supported by rate measurements (see table 4) which will be discussed in Chapter V, which show that the polymers prepared in benzene solution are more stable. Grassie and Vance showed that this is to be expected since they incorporate a smaller proportion of unstable unsaturated terminal groups.

TABLE 4

THERMAL RATES DEGRADATION AT 250°C FOR SOME POLY-n-BUTYL METHACRYLATES

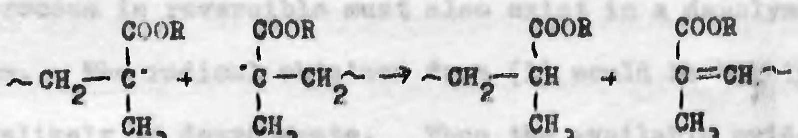
Polymer	Relative Rate
N.B.1	0.51
N.B.2	0.65
N.B.4	1.17
N.B.6	1.14

It is a well established fact that the bond β to a $>C=C<$ is weaker than a bond similarly placed to a saturated carbon-carbon link. The reason for this is the enhanced stability of the newly formed radical due to allylic resonance,

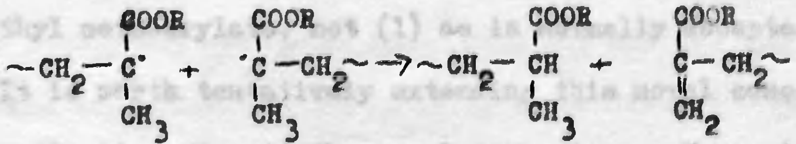
$$>\dot{C}-C=C< \qquad >C=C-\dot{C}<$$

In the polymerisation of methyl methacrylate it has been fairly well proved[30] that the termination step is disproportionation between two radicals, and it is at this stage that the unsaturated link which is the centre of initiation of depolymerisation[28] is introduced. On the other hand the bulk of evidence[31] to date supports the view that the termination step in the polymerisation of styrene is combination of two radical growing chains.

On examining the mechanism of disproportionation of a methacrylate it can be seen that there are two possibilities:-

(1) 

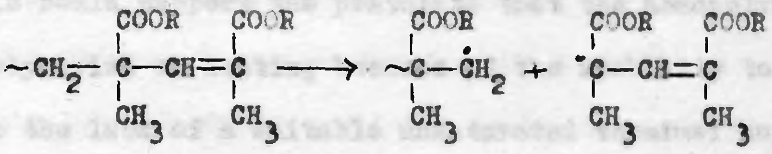
$$\sim CH_2-\overset{COOR}{\underset{CH_3}{C^{\cdot}}} + {}^{\cdot}\overset{COOR}{\underset{CH_3}{C}}-CH_2\sim \rightarrow \sim CH_2-\overset{COOR}{\underset{CH_3}{CH}} + \overset{COOR}{\underset{CH_3}{C}}=CH\sim$$

(2) 

$$\sim CH_2-\overset{COOR}{\underset{CH_3}{C^{\cdot}}} + {}^{\cdot}\overset{COOR}{\underset{CH_3}{C}}-CH_2\sim \rightarrow \sim CH_2-\overset{COOR}{\underset{CH_3}{CH}} + \overset{COOR}{\underset{CH_2}{\overset{\|}{C}}}-CH_2\sim$$

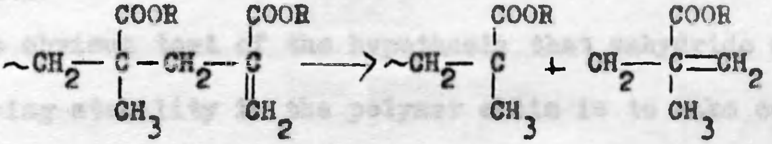
(1) involves the transfer of a hydrogen atom from a fairly sterically hindered methylene unit, whereas (2) is the transfer of a hydrogen atom from a relatively unblocked methyl group. There is no direct evidence to distinguish between (1) and (2) but it is interesting to note that styrene which has no

methyl group terminates by combination. Furthermore if we consider the situation in which the β carbon-carbon bond is ruptured homolytically, as is postulated in end-initiated degradation reactions we find that (1) gives



$$\sim CH_2-\underset{CH_3}{\overset{COOR}{C}}-CH=\underset{CH_3}{\overset{COOR}{C}} \longrightarrow \sim\underset{CH_3}{\overset{COOR}{C}}-\dot{C}H_2 + \cdot\underset{CH_3}{\overset{COOR}{C}}-CH=\underset{CH_3}{\overset{COOR}{C}}$$

and (2)



$$\sim CH_2-\underset{CH_3}{\overset{COOR}{C}}-CH_2-\underset{CH_2}{\overset{COOR}{\overset{|}{C}\!\!=}} \longrightarrow \sim CH_2-\underset{CH_3}{\overset{COOR}{C}} + CH_2-\underset{CH_3}{\overset{COOR}{C}}=CH_2$$

Thus it is the second of these which gives a radical identical to that normally assumed to exist in a polymerising system, and if the process is reversible must also exist in a depolymerising system. The radical obtained from (1) would be highly reactive and unlikely to depropagate. Thus the available evidence seems to suggest that (2) is the termination step in the polymerisation of methyl methacrylate, not (1) as is normally accepted.

It is worth tentatively extending this novel conception of the termination step to the acrylate series. Here, if the termination step in polymerisation were disproportionation (1) would hold, there being no α methyl group on the monomer. The fact that the acrylate group does not depolymerise on heating might be explained partly by the inability of the ruptured end unit to initiate an unzipping chain although a number of other factors probably contribute[1]. A study of copolymers of methyl methacrylate and methyl acrylate, containing a large proportion of the former would show whether a depropagating chain could pass through a methyl acrylate unit. If in fact it did, then this would support the postulate that the homopolymer does not depolymerise on heating because of the inability to initiate owing to the lack of a suitable unsaturated terminal unit, which is available in methacrylate polymers.

COPOLYMERS

The obvious test of the hypothesis that anhydride units are causing stability in the polymer chain is to make copolymers of methacrylic anhydride and n-butyl methacrylate. This cannot be done directly as the bifunctional methacrylic anhydride unit gives rise to cross-linked, insoluble, molecules. However, anhydride units can be usefully introduced into a polymer molecule by heating a methacrylic acid copolymer above 160°C [29, 32]. The time of preheating gives a good control of the amount of anhydride formed.

Two copolymers were made containing one and ten per cent methacrylic acid, C.N.B.1 and C.N.B.2, respectively. They were made under the same conditions as N.B.2 in order that their molecular weights would not be greatly different from that of N.B.2, thus eliminating any possibility of rate difference being due to differences in initial molecular weights. Table 5 shows the extents of degradation after two hours at 250°C after various times of preheating at 170°C. The extent of degradation does show a definite trend to increased stability with increased time of preheating, but the extent is similar for the two copolymers and not much less than that for the corresponding homopolymer. This suggests that during the time required to heat the polymer from room temperature to 250°C, a period of approximately 15 minutes, all the acid units have formed anhydride and so the effect of preheating at 170°C is rendered valueless.

TABLE 5

Polymer	Time preheating at 170°C	% Degradation after 2 hours at 250°C
N.B.2		29
C.N.B.1	0	36
C.N.B.1	1 hr.	33
C.N.B.2	0	28.4
C.N.B.2	½ hr.	27
C.N.B.2	2 hrs.	23.1
C.N.B.2	4 hrs.	22

Infra red spectra of KCl discs of the copolymers when heated to 170°C show the rapid disappearance of acid hydroxyl peaks. The rate of formation of anhydride is much faster in these poly-n-butyl methacrylate copolymers than in the methyl methacrylate / methacrylic acid copolymers studied by Grant and Grassie[29, 32]. The melting point and therefore presumably the viscosity of the n-butyl polymers are much lower than corresponding methyl polymers[16]

Thus the elimination of water to form anhydride is greatly facilitated in the less viscous poly-n-butyl methacrylate / methacrylic acid copolymers.

The fact that the copolymers are only slightly more stable than the homopolymer, and show little difference between each other is not easily accounted for. We would expect the polymer containing more acid (C.N.B.2) to be by far more stable than the homopolymer (N.B.2) and the copolymer (C.N.B.1) containing a fraction of the amount of acid. Intrinsic viscosity measurements suggested that increasing the acid content of the polymer lowered its molecular weight, which in turn, for an end initiated degradation process, would increase the extent of degradation in a given time. In order to eliminate the possible interference of molecular weight in the comparison, a portion of C.N.B.2 was esterified by treating a solution of the copolymer in chloroform with excess diazomethane and allowing to stand for several hours. After pouring the solution into methanol the resulting polymer was reprecipitated and vacuum dried. This treatment has been shown to have no effect on the polymer chain length[33]. The copolymer, now one of n-butyl and methyl methacrylate was pyrolysed at 250°C and a comparison (Table 6) made of the extent of degradation in a given time with that of the methacrylic acid / n-butyl methacrylate copolymer of the same chain length under the same conditions. The stabilising effect of the anhydride units is very clearly demonstrated.

TABLE 6

COMPARISON OF EXTENT OF THERMAL DEGRADATION FOR ESTERIFIED AND UNESTERIFIED COPOLYMER

Polymer	% Degradation after 2 hours at 250°C
C.N.B.2	28.4
Esterified C.N.B.2	45

PRODUCTS OF DEGRADATION OF COPOLYMERS

The volatile products of the thermal degradation of the copolymers were examined by infra red spectroscopy and vapour phase chromatography. Infra red spectra of liquid products showed the presence of n-butyl methacrylate only, the purity was checked by comparing with a spectrum of pure monomer, and found to be identical.

Vapour phase chromatography of gaseous products showed the presence of butene but no quantitative comparisons could be made as the sampling system of the instrument was not adapted for quantitative work. V.P.C. confirmed that the liquid products were nearly wholly monomer but traces of a high boiling constituent were observed. The retention time of this very small impurity was the same as that of methacrylic anhydride.

To find a probable explanation for the appearance of methacrylic anhydride in the degradation products it is necessary to examine the formation of anhydride units in the copolymer during preheating at 170°C. Although the anhydride does not show up clearly in infra red spectra it is reasonable to assume from Grant's work that the major part of the anhydride units are cyclic glutaric type structures. He found[32] that a type of ester exchange process takes place along a polymer molecule resulting in acid units occurring in pairs and then reacting to form intramolecular anhydrides. However, during this process it is possible that an occasional intermolecular anhydride unit might be formed. This view is supported by the fact that during the preheating period the polymer is not completely soluble in chloroform. It partially dissolves and forms a highly swollen gel. If all the anhydride units were intermolecular the polymer would be completely insoluble, whereas if all the units were intramolecular the polymer would dissolve completely.

Intermolecular anhydride links are analogous to the cross-linked glycol dimethacrylate copolymers studied by Grassie[2] in which the cross-links were found to have little influence on the course of the depolymerisation, and in fact the unzipping chain can pass through them. By applying the same type of mechanism to intermolecular anhydride links it is possible to account for the appearance of traces of methacrylic anhydride in the volatile degradation products.

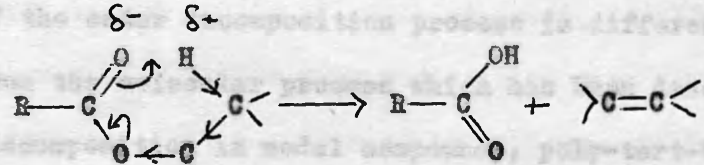
ESTER DECOMPOSITION

There has been much work in recent years on the pyrolysis of esters of "model" compounds, that is molecules of low molecular weight. Normally ester decomposition in model compounds or polymers only takes place at temperatures greater than 200°C.

This topic has been reviewed by Ritchie[34].

In order that this sort of reaction may occur it is necessary that the ester should possess a hydrogen atom on the β carbon atom of the alcohol residue. It is also well established that the stability of esters to breakdown is in the order primary > secondary > tertiary esters, the approximate relative rates of decomposition being 1 : 26 : 515[35]. The temperatures at which the rates of reaction become appreciable are approximately 250°C for tertiary esters, 310°C for secondary esters, and 350°C for primary esters.

The mechanism first suggested by Hurd and Blunck[9] has been elaborated on by McColl[36] who uses their six membered cyclic transition state in his discussion.



The bulk of evidence available supports the theory that for carboxylic esters the reaction is molecular rather than radical, whereas in the pyrolysis of alkyl halides both mechanisms are found. McColl suggests that the rate determining step is the formation of the hydroxyl bond, not the breaking of the alkyl oxygen bond, in constrast to the decomposition of the alkyl halides in which the critical step is the breaking of the carbon - halogen bond.

In the polymeric ester field Grassie has studied the break-down of polyvinyl acetate[11] and Grant and Grassie, poly-tert-butyl methacrylate[10], both of which undergo ester decomposition by non-radical processes. Polymethyl methacrylate cannot react in this manner as it does not have the necessary hydrogen atom in the alcohol residue.

The decomposition of poly-tert-butyl methacrylate was studied by Grant and Grassie[10] at temperatures around 200°C - 50° below the onset temperature quoted above. This apparent enhanced instability may be due partly to the autocatalytic nature of the reaction or to a steric effect which may be associated with the occurrence of the reaction in a polymer chain environment. The ester decomposition reaction in poly-n-butyl methacrylate is occurring at 250°C at a reasonable rate :-100° less than the onset temperature quoted above. This could be an indication that the mèchanism of the ester decomposition process is different in this case from the molecular process which has been described above to explain decomposition in model compounds, poly-tert-butyl methacrylate, and polyvinyl acetate. This is further borne out by the fact that once the depolymerisation process is completely blocked by the products of ester decomposition no further increase in anhydride or butene formation appears to occur, in spite of the fact that the large majority of ester units on the polymer chains are still intact. This leads us to suspect that the ester decomposition process in this case may be closely linked with the depolymerisation process and thus involve radical intermediates. This will be discussed more fully in a later section of this Chapter.

ABNORMALITY OF POLYMERISATION

The polymerisation of n-butyl methacrylate has been studied by Burnett, Evans, and Melville[17], who observed that during thermal polymerisation at 30°C bubbles of gas were evolved and the polymer became insoluble in monomer. A similar occurrence was observed during the thermal polymerisation of n-propyl methacrylate[37]. The gas was not identified but the above authors suggested that it might be butene or carbon dioxide. Whilst the study of the thermal degradation of poly-n-butyl methacrylate was progressing it was thought that identification of these bubbles might be of value and it was decided to attempt to identify the gas or gases using the new techniques such as infra-red and v.p.c. now at our disposal.

A reaction vessel of 100 ml. bulb capacity, as illustrated in figure 14, was half filled with redistilled pure monomer and thoroughly degassed. It was then sealed off and set in a water bath thermostatted at 30°C. After some twenty hours bubbles of gas appeared and polymer was deposited. The reaction was allowed to continue for about two hours during which time a large amount of polymer, about 10% of the contents of the vessel, deposited. The reaction tube was then removed and end A. dipped into liquid air. After five minutes immersion the stopcock was closed and the tube broken into two parts such that the volatile products remained under vacuum, and the reaction mixture dissolved in acetone. All the polymer dissolved. The vacuum in the sealed part of the

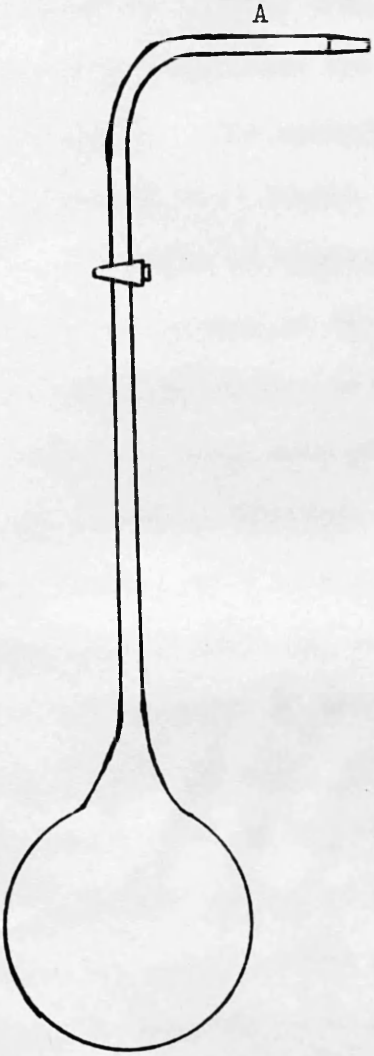


Figure 14. Polymerisation vessel.

tube was released slowly and a sample withdrawn by syringe for analysis by v.p.c. as described in Chapter II. The gas was found to be exclusivaly butene. The polymer was precipitated and reprecipitated by pouring the acetone solution into methanol. After drying in vacuum its spectrum was measured using the pressed disc technique[24]. The appearance of broad hydroxyl peaks at about 3000 cm.$^{-1}$ showed that traces of acid were present in the polymer. Great care was taken to eliminate the possible incorporation of water during the making of the discs. Grinding of the polymer-potassium chloride mixture was done under infra red lamps, a sample disc containing pure potassium chloride made under these conditions showed no hydroxyl peaks, thus the peaks which appear on adding polymer must belong to the polymer.

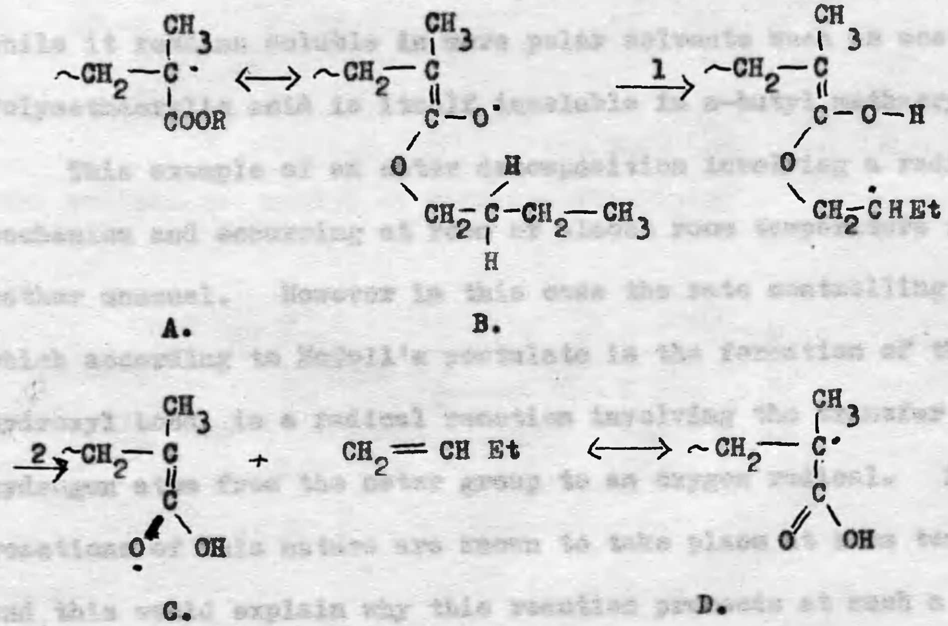
These observations can only be explained in terms of an ester decomposition reaction to acid and olefine.

MECHANISM OF DECOMPOSITION

The elucidation of the mechanism of ester decomposition during the polymerisation of n-butyl methacrylate might assist in explaining the peculiarities of the thermal reaction. The occurrence of an ester decomposition process at 30°C is extraordinary and in fact no other example is reported to take place at such a low temperature.

It is possible that ester decomposition occurs during polymerisation of n-butyl methacrylate due to localised heating as a result of slow dissipation of the heat of polymerisation.

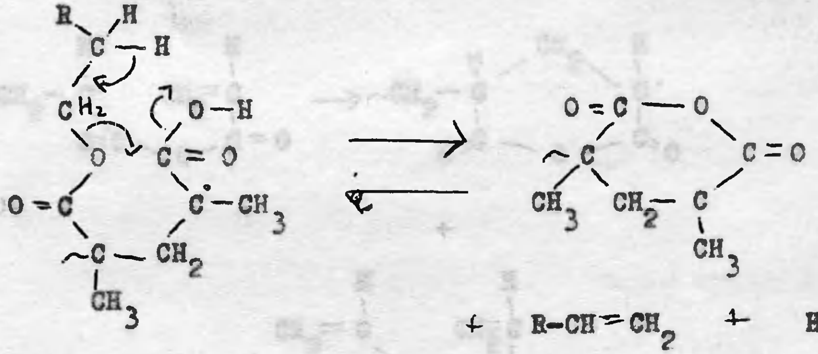
If polymerisation were carried out adiabatically there would be enough heat available to raise the temperature of the solution by several hundred degrees. Explosions can occur during polymerisation in this way, particularly at intermediate conversions when the high viscosity of the mixture inhibits the diffusion of heat out of the system. However Bengough[38] has studied the rise in temperature of several polymerising systems, similar to n-butyl methacrylate and has shown that the maximum rise under the sort of experimental conditions used in the present work is of the order of a few degrees. Thus the possibility of a purely thermal reaction is eliminated and the following mechanism, which is envisaged to occur in competition with the normal propagation step during polymerisation, is proposed to account for this unusual ester decomposition.



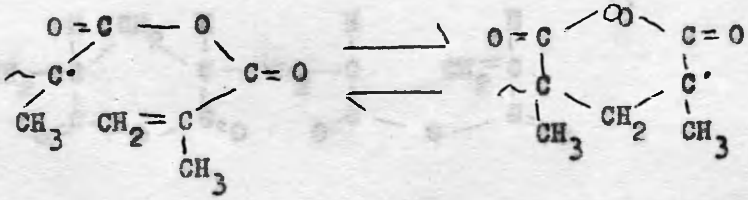
Radical A is the normal growing polymer radical, B a canonical form. The contribution of B to the stability of the radical has been discussed in copolymerisation studies[21], and is favoured by hyperconjugation with the methyl group. Step 1 is transfer of a hydrogen atom from the alcohol residue and is facilitated by the six membered cyclic intermediate which is the same as the cyclic intermediate structure postulated for the molecular mechanism of ester decomposition. Step 2 is an intramolecular disproportionation giving radical C and butene. C is one of the structures contributing to the stabilisation of the growing radical in which D has most weight. The overall effect is to introduce a methacrylic acid unit into the polymer molecule, liberating butene. The presence of methacrylic acid would account for the insolubility of the polymer in monomer, while it remains soluble in more polar solvents such as acetone. Polymethacrylic acid is itself insoluble in n-butyl methacrylate.

This example of an ester decomposition involving a radical mechanism and occurring at room or almost room temperature is rather unusual. However in this case the rate controlling step, which according to McColl's postulate is the formation of the hydroxyl bond, is a radical reaction involving the transfer of a hydrogen atom from the ester group to an oxygen radical. Radical reactions of this nature are known to take place at room temperature and this would explain why this reaction proceeds at such a low temperature.

This postulated mechanism for the reaction taking place during polymerisation can readily be extended to the ester decomposition which occurs during thermal degradation. The explanation for the fact that very few acid, andthus anhydride units, have such a profound effect on the depropagation would follow if the radical mechanism is invoked. In this way, by the same mechanism, the acid unit would appear at the end of the depropagating molecule, with the added effect of the possibility of a newly formed acid unit catalysing the molecular break-down of its ester neighbour to give a cyclic anhydride, water, and butene, in a manner analogous to the degradation of poly-tert-butyl methacrylate

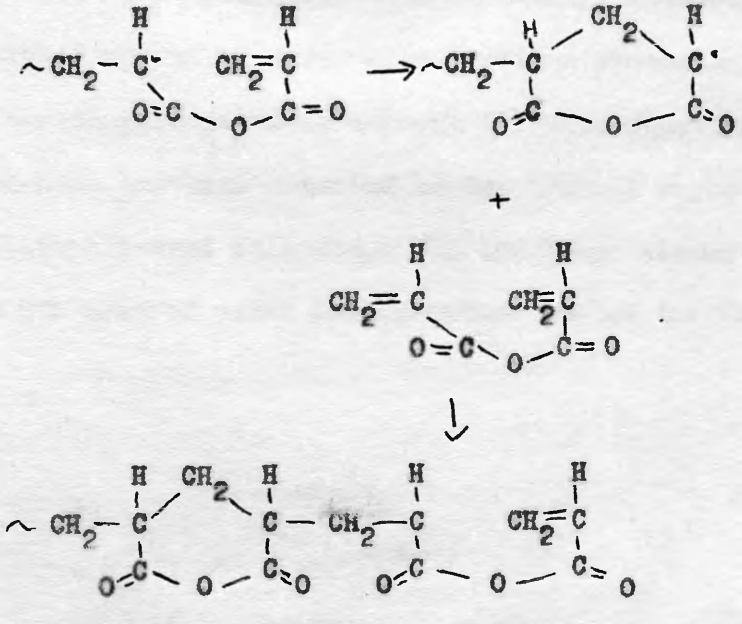


The radical can unzipp on further unit giving



B

The extra chemical link of fragment B to the main polymer chain via the anhydride would tend to anchor the newly formed $>C=C<$ in the vicinity of the radical and a pseudo equilibrium between propagation and depropagation would exist, giving a stabilised radical at the chain end. Normally the monomer unit formed in depropagation is rapidly removed from the neighbourhood of the free radical and the probability of equilibrium is very much diminished. This type of intramolecular polymerisation has been studied by Butler et al[39] who have made soluble polyacrylic anhydride and suggest the following mechanism



The above stabilised depropagating radical may have a dual inhibiting effect. Not only is it able to inhibit the depropagation of its own molecule but it may also act as an inhibitor by terminating the depolymerisation of another molecule by combining or disproportionating with the depropagating radical.

SUMMARY

The preceding chapter has dealt with the thermal degradation of poly-n-butyl methacrylate in the region of 250°C. The original object of the work was to evaluate the velocity coefficient of the various steps in the depolymerisation process. It has been shown how this purpose was baulked by the occurrence of ester decomposition. The overall effect of this reaction is to introduce anhydride units into the polymer molecule which inhibit the depolymerisation. Study of degradation of copolymers substantiate this view.

A previous observation that bubbles of gas were evolved during thermal polymerisation of n-butyl methacrylate has been followed up and an ester decomposition proceeding by a radical mechanism postulated to account for this reaction. This mechanism has been extended to the thermal degradation and tentatively used to account for the large effect which only a few per cent of ester decomposition has on the thermal degradation

CHAPTER IV

THE PHOTOCHEMICAL DEGRADATION OF POLY-n-BUTYL METHACRYLATE

INTRODUCTION

In the preceeding Chapter it has been shown how the occurrence of an ester decomposition reaction led to complications in the depolymerisation process. As Cowley and Melville[3] had already made a kinetic study of the photodegradation of polymethyl methacrylate it seemed feasible that a similar investigation could be undertaken with poly-n-butyl methacrylate. The investigation of the thermal reaction showed that the onset of thermal degradation takes place in the region 215 - 220°C. No volatiles are evolved at an appreciable rate below 215°C, thus below this temperature there is a fair range in which it was hoped that the photochemical reaction could be isolated, and studied on its own, as Cowley and Melville did with polymethyl methacrylate.

The mechanism of break-down of polymethyl methacrylate on irradiation with light of wave length 2537Å in high vacuum at temperatures below 200°C was found to be very similar to the mechanism of its thermal degradation[2]. The unsaturated terminal units formed during the polymerisation reaction in the disproportionation termination process were the centres of initiation which was followed by unzipping of monomer from the polymer chain. The intensity exponent was found to be 0.5 which demonstrated that the termination reaction involved the mutual interaction of the radical chain carriers. The rate constants for the initiation, depropagation and termination reactions were measured using a combination of sector and inhibitor techniques. The overall reaction was apparently straightforward with the exception of the effect of viscosity on the termination step. With increasing molecular weight and therefore increasing melt viscosity, the termination constant seemed to decrease. The situation is in fact somewhat similar to that which prevails at high conversions during the bulk polymerisation of a number of monomers,[40] methyl methacrylate among them, and which manifests itself in the so called "gel effect".

A preliminary investigation showed that poly-n-butyl methacrylate also degraded to monomer photochemically. As a matter of interest the behaviour of one or two other polymers on irradiation was examined. The most outstanding result of this cursory examination was the discovery that poly-tert-butyl methacrylate when irradiated at 160°C yielded pure monomer in almost quantitative amounts in spite of the fact that its thermal decomposition is predominantly ester decomposition. Examination by infra red and v.p.c. of both the volatile products and residual polymer from poly-n-butyl methacrylate and poly-tert-butyl methacrylate showed that the sole reaction occurring in both polymers was depolymerisation to monomer. This result now provides a means of arriving at the original objective which was to study the kinetics of depolymerisation of a series of polymethacrylate esters.

It is interesting that neither polystyrene nor polymethacrylonitrile depolymerise to monomer on irradiation in spite of the fact that both degrade thermally in this way to give monomer. Since it is clear that depolymerisation, once initiated, can occur in both these polymers it seems that ultra-violet radiation is incapable of bringing about the necessary initiation process. This may be regarded as further evidence in favour of the fact that chain ends and particularly the unsaturated chain ends, formed in a disproportionation termination reaction during polymerisation, are all important particularly in photo-initiation[3] since the balance of evidence is in favour of disproportionation as the termination step in methacrylates[30] while combination seems predominantly to occur in polystyrene[31] and polymethacrylonitrile[41]. It is interesting to speculate whether these polymers would yield monomer once the process of depolymerisation has been initiated. In this connection a study of the photochemical degradation of copolymers of styrene or methacrylonitrile with one of the methacrylates is clearly of vital interest.

PHOTO DEGRADATION

It is already known that light of wave length 2537Å initiates the photo-reaction in polymethyl methacrylate[3]. Before commencing a kinetic study of the photodegradation of poly-n-butyl methacrylate it was necessary to ascertain that there is no "skin effect". This comes about in a photo-initiated reaction when the surface layers absorb a large proportion of the light which causes degradation with the result that practically all the reaction is confined to those surface layers. Obviously such an occurrence would complicate the kinetics of the reaction tremendously. To test the possibility of such a situation it is necessary to measure two things, firstly an accurate spectrum of poly-n-butyl methacrylate in the ultra violet region, and secondly the wave length range of the radiation capable of causing degradation.

The measurement of the ultra violet spectrum of polymers, particularly the methacrylates, in solution is difficult as the solvents in which the polymers dissolve readily, e.g. chloroform benzene and acetone themselves absorb strongly in the ultra violet region. Conventionally measurements are usually made on cast film. This method however has certain quite serious drawbacks, not the least of which is the problem of removing the last traces of solvent from the film. Grassie[42] has shown how tenaciously the last few per cent of solvent cling to a polymer and if the solvent has a high extinction coefficient this can seriously affect the appearance of the polymer spectrum. Another, although not quite so serious difficulty is the measurement of film thickness. With very thin films this can be rather awkward. To overcome these difficulties a small cell was constructed by fixing a square of silica plate (25 mms. square) to the end of a short piece of glass tubing (16 mms. diameter, 16 mms. depth). The adhesive used was Araldite. After baking at 100°C for two days in order to set the adhesive the cell was soaked in chloroform for one day to ensure that all soluble material was removed. Knowing the area of the cross-section of the cell, and the density of the polymer, any thickness of film could be cast by weighing out the required amount of polymer, adding one or two drops of chloroform then evaporating to dryness. The drying process was completed by placing in an oven at 110°C for one hour. The cell could then be placed in a spectrophotometer and the absorption spectrum of the polymer measured. Figure 15 shows a spectrum run on an automatic recording Perkin Elmer Model 137 U.V. for a film 0.003 cm. in thickness, which is about the average used in the degradation experiments to be described.

The second factor to be ascertained in connection with the possibility of a "skin-effect" was the wave length of the light responsible for initiating the reaction. This is relevant to the information gained from the measurement of the absorption spectrum for, as has already been mentioned, the light causing the photo-degradation must not be strongly absorbed by the polymer. This was done by starting a photo-reaction in the normal manner, allowing it to proceed, and then interposing a sheet of thick pyrex glass between the light source and the degrading polymer. Pyrex glass is known to cut out all light of wave length less than 3200Å[43].

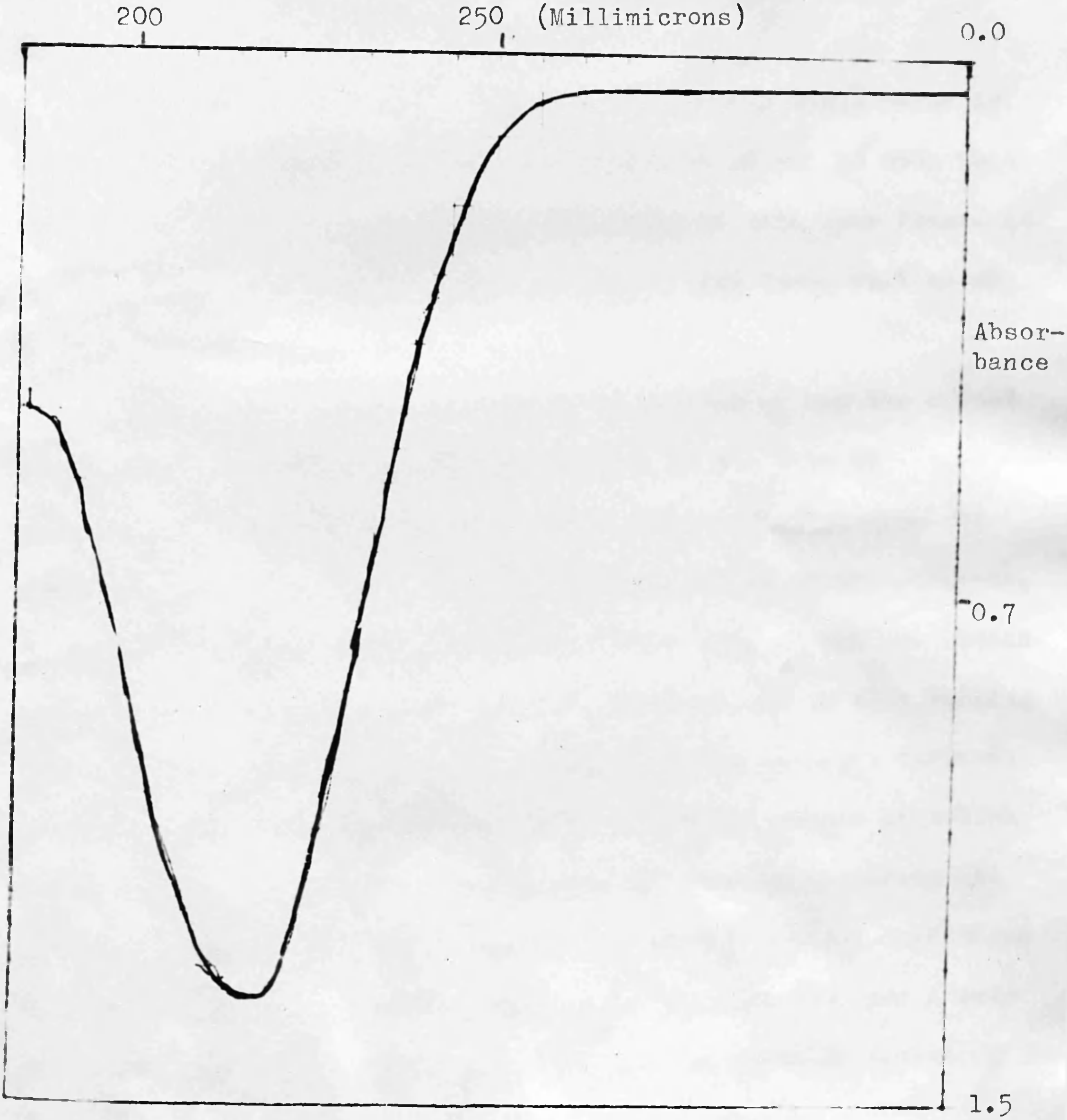


Figure 15. Ultra violet spectrum of poly-n-butyl methacrylate film 0.003 cms. thick.

Figure 16 shows how the rate of the reaction fell away almost to zero when the sheet of glass was put in place. This indicates that the light causing the reaction has a wave length less than 3200Å and the fact that silica, the material of which the top plate is made, absorbs light less than 2000Å[44] means that the light causing the reaction must be that of wave length 2537Å which constitutes 90% or more of the radiation emitted from the low pressure mercury lamp.

Thus knowing that it is light of wave length 2537Å which is initiating the degradation and from figure 15 it can be seen that the polymer transmits practically all light of this wave length it is reasonable to proceed on the assumption that there will be no "skin effect".

Another point which required to be cleared up was the effect of the state of polish of the copper tray on the rate of degradation. It seemed possible that light reflected from the metal surface might significantly affect the rate of the reaction, particularly from a highly polished surface such as one can obtain with copper. Indeed a wide range of surfaces can be made ranging from a highly polished to a very dull, partially oxidised surface. Evaluation of the actual effect of the differing states of polish of the copper surfaces on the reaction was done by measuring the rate of degradation of the same polymer under identical conditions except that a highly polished tray, a fairly dull tray and a very dull tray were used. Table 7 shows that the state of polish of the

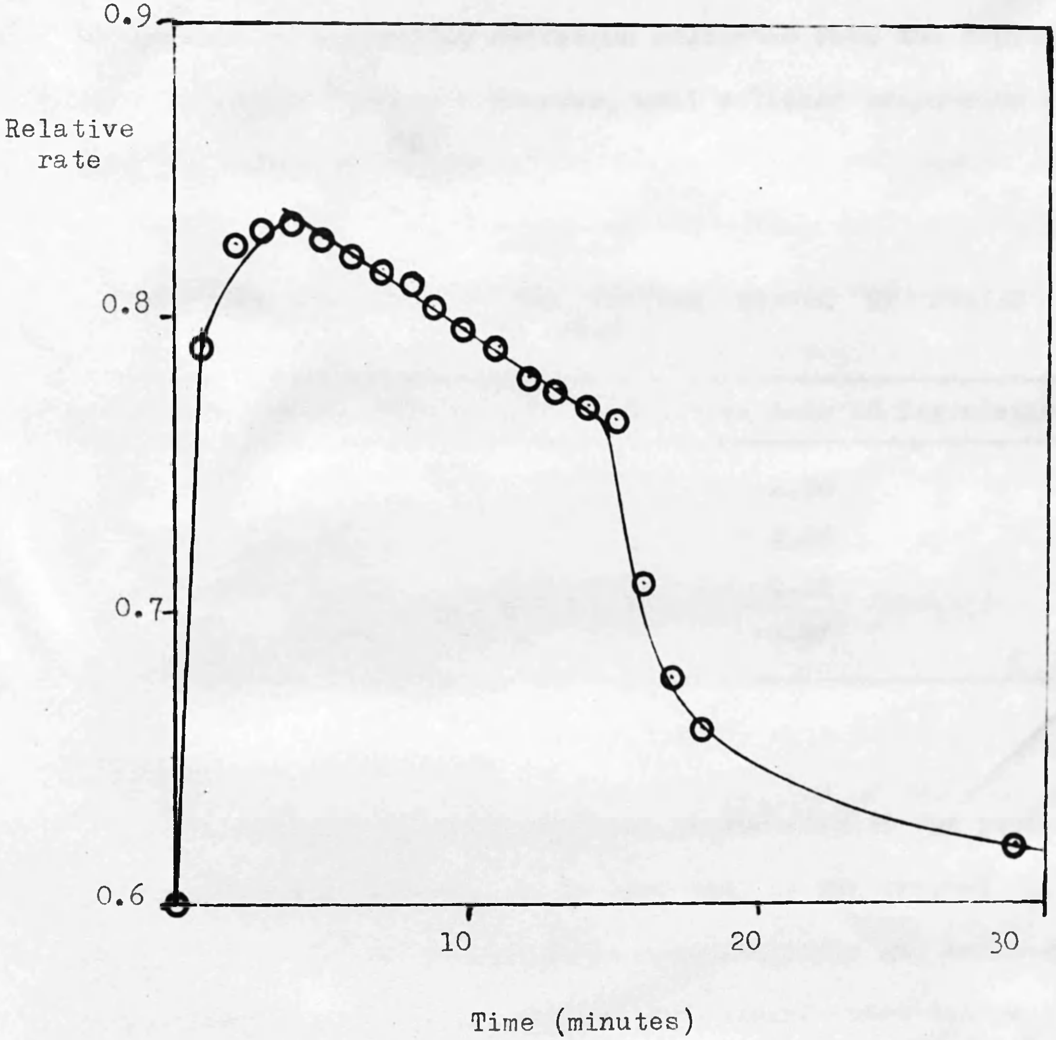


Figure 16. Photochemical degradation of poly-n-butyl methacrylate showing fall in rate at A when plate of pyrex glass interposed between polymer and light source.

tray has no effect on the rate of degradation. Thus the proportion of activating radiation reflected from the copper tray must be insignificant. However, well polished trays were always used for degradation runs.

TABLE 7

RATE OF DEGRADATION FOR VARYING STATES OF POLISH OF TRAY

State of Polish of Tray	Relative Rate of Degradation
Very dull	4.90
Dull	4.66
Moderate polish	4.46
Highly polished	4.92

PRODUCTS OF DEGRADATION

The same methods were employed to investigate the products of photochemical degradation as were used in the thermal degradation, namely, vapour phase chromatography and infra-red spectroscopy. Yields of monomer were always quantitative within experimental error and although a careful check was made for traces of butene none was ever detected. Thus the reaction is an uncomplicated depolymerisation.

RATE MEASUREMENTS

For quantitative measurement of the rate of depolymerisation of polymethyl methacrylate it is found[3] that the thickness of polymer film is critical. Up to a certain limit, the rate of degradation is proportional to the weight of polymer (and therefore the film thickness), beyond this limit the rate falls off rapidly. There are two principal reasons for this. Firstly, the finite time required for the monomer to diffuse out of the molten polymer allows the possibility of repolymerisation and secondly uniform heating becomes increasingly difficult with thick film. Because of the nature of the degradation copper powder cannot be used as in thermal work to assist heat transfer within the polymer mass. It is obviously necessary for a quantitative investigation that rate measurements be made within the region of proportionality of rate and weight.

In order to investigate the possibility of fulfilling those conditions in poly-n-butyl methacrylate, a series of experiments was undertaken to investigate the relationship between weight of polymer and rate of degradation. The results of these experiments were very perplexing. It was found that the rate of degradation was not proportional to the weight of polymer taken, no matter how thin a polymer film was used. After a considerable accumulation of data became available it was apparent that the rate of degradation is proportional to the square root of the weight of polymer taken as illustrated in figure 17. The relationship is undoubtedly genuine and covers a wide range of film thicknesses and polymer samples. A full discussion of the kinetics of degradation will be given in Chapter V, but this rather unusual dependence of the rate on the square root of the quantity of polymer taken makes the direct measurement and comparison of initial rates of degradation impossible.

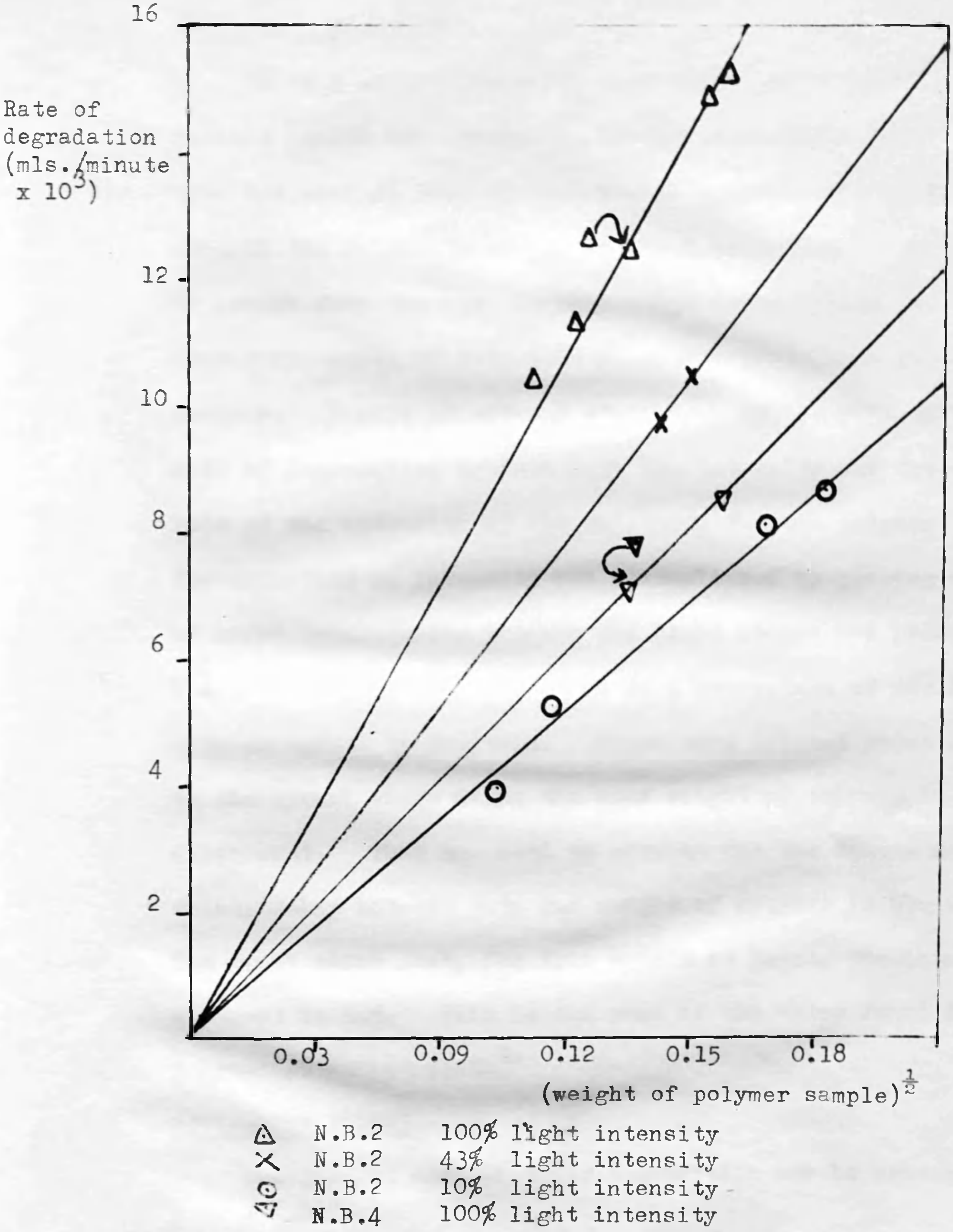


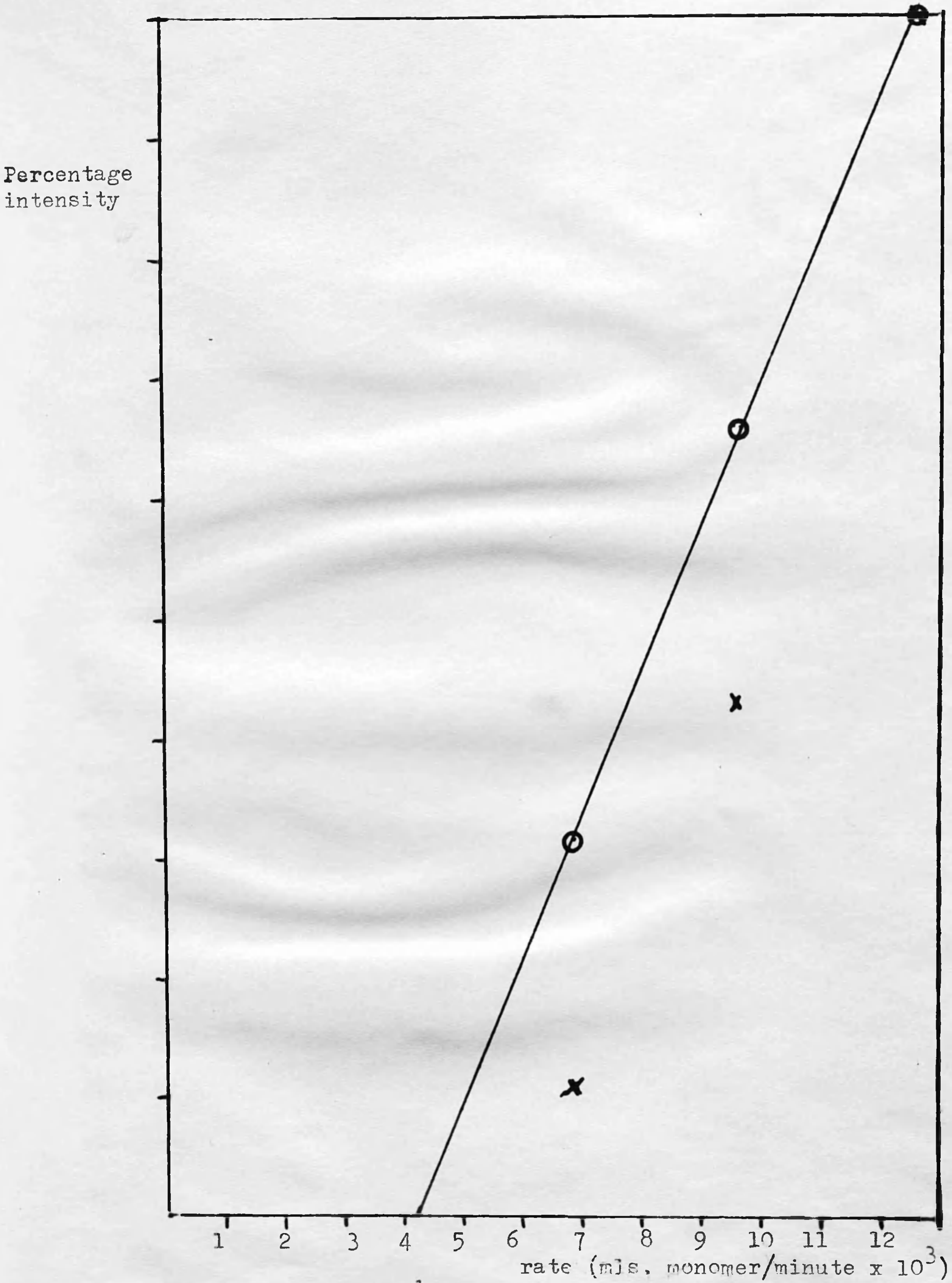
Figure 17. Photochemical degradation of poly-n-butyl methacrylate showing rate against (weight)$^{\frac{1}{2}}$ relationship.

INTENSITY EXPONENT

It is a well established fact for a photo reaction that if radical chains are terminated by the interaction of two radicals then the overall rate of reaction is proportional to the square root of the intensity of the absorbed radiation. It is reasonable to assume from the work on polymethyl methacrylate that the photo depolymerisation of poly-n-butyl methacrylate is a radical chain process. Figure 18 shows a comparison of the plot of initial rate of degradation against both the intensity and the square root of the intensity of the radiation for one polymer sample. The variation in intensity was accomplished by placing screens of known transmission between the light source and polymer sample. The intensity is then expressed as a percentage of the intensity with no screen in position. Rates were initial rates recorded on the Pirani gauge using the same weight of polymer in each experiment. Thus the need to correct for the square root relationship between rate and weight of polymer is obviated. The graph shows that, for this sample at least, the intensity exponent is 0.5. This is the same as the value found for polymethyl methacrylate[3].

ACTIVATION ENERGY

The general mechanism for degradation may be written ;



⊙ - (intensity)$^{\frac{1}{2}}$. X - intensity, lying on curve

Figure 18. Photochemical degradation of poly-n-butyl methacrylate showing rate against intensity and (intensity)$^{\frac{1}{2}}$.

		rate
Polymer $\longrightarrow P_n$	Initiation	I
$P_n \longrightarrow P_{n-1} + M$	Depropagation	$k_d [P]$
$P_r + P_s \longrightarrow$ Stable polymers	Termination	$k_t [P]^2$

From the above kinetic scheme, it may be easily deduced that the rate of monomer production ($^{dM}/dt$) is given by,

$$\frac{dM}{dt} = k_d \, k_t^{-\frac{1}{2}} I^{\frac{1}{2}}$$

from which the overall activation energy $E_o = E_d - \frac{1}{2} E_t$ ——— (1)

Since depropagation is the exact reverse of propagation the value E_d will be given by the activation energy of the propagation step, less the heat of polymerisation. The heat of polymerisation has been given by Dainton, Ivin and Walmsley[45] as -13.3 kcal/mole, and from Burnett, Evans and Melville[17] the activation energy of the propagation step is 4.5 kcal/mole. Therefore $E_d = 4.5 + 13.3 = 17.8$ kcal/mole. Thus equation (1) becomes $E_o = 17.8 - \frac{1}{2}E_t$ ——— (2).

The experimental results obtained using a series of poly-n-butyl methacrylates of varying molecular weight are shown in figure 19. The rates used in the graph are measured initial rates divided by the square root of the weight of polymer. The span of temperature at which measurements can be made is restricted at the upper end by the onset of thermal degradation and at the lower end by diffusion effects. The points lie on a fairly good straight line and give a value of 5 ± 1 kcal/mole for the overall

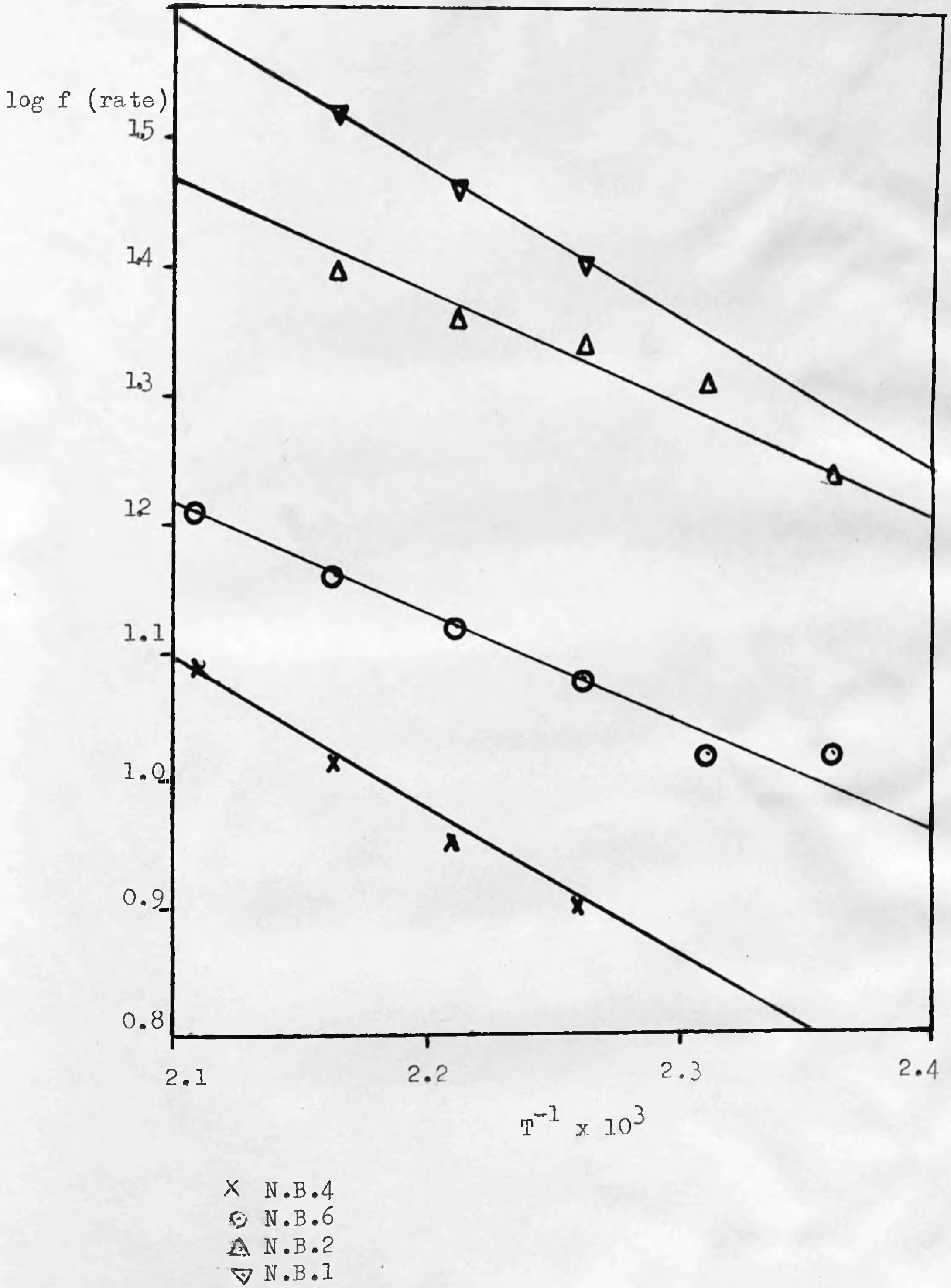


Figure 19. Photochemical degradation of poly-n-butyl methacrylate

Arrhenius plot.

activation energy (E_o). From equation (2) $E_t = 26$ kcal/mole. This result compares with the value of 20 kcal/mole obtained by Cowley and Melville in their work on polymethyl methacrylate. Both values are very high compared with that normally obtained for the activation energy of a reaction involving two radicals, and Cowley and Melville explained the large discrepancy as being due to diffusion control of the termination process.

Since the heat of polymerisation used in this calculation refers to liquid monomer an allowance ought to be made in the above energetic scheme for the heat of evaporation of monomer as under the experimental conditions used the monomer is produced in the vapour phase. The heat of evaporation of monomer is of the order of 9 kcal/mole. Thus, making this allowance, $E_t = 43.6$ kcal/mole and applying the same correction to Cowley and Melville's results a value of $E_t = 38$ kcal/mole is obtained for polymethyl methacrylate. This correction clearly makes the already abnormally high activation energy of the termination step even larger and these values can only refer to a viscosity or diffusion controlled reaction. The activation energy for diffusion of large polymer radicals might well be in this region. The value for the diffusion of monomer in polymethyl methacrylate is about 30 kcal/mole[3]. Taking into account the extra bulk of the polymer radicals it is not inconceivable that E_t is in fact a measure of their activation energy of diffusion.

MECHANISM OF DEGRADATION

It has been shown on page 49 how a study of the change in molecular weight with extent of degradation can give valuable information about the mechanism of degradation of a polymer. In the case of the thermal degradation of poly-n-butyl methacrylate the application of this method was partially prevented by the competitive side reaction of ester decomposition. The reaction in the photochemical degradation, being pure depolymerisation is suitable for molecular weight / extent of degradation analysis. Figure 20 shows such an analysis for two polymers of widely different molecular weights. In the case of N.B.2 (M.W. 460,000) the curve lies on or just above the diagonal and for N.B.6 (M.W. 110,000) the curve is well above the diagonal. This immediately suggests an end-initiated mechanism since in high molecular weight material a random initiation process would result ultimately in more than one involatile fragment per degrading chain so that the molecular weight / degradation curve would fall below the diagonal.

It may be possible as in the polymethyl methacrylate degradation process to obtain more information about the type of chain end through which initiation occurs by a study of the change in rate as the reaction proceeds. For the thermal degradation of polymethyl methacrylate Grassie and Melville found that, below 250°C, the rate reduced to zero at fifty per cent degradation. Later Grassie and Vance showed that for polymers

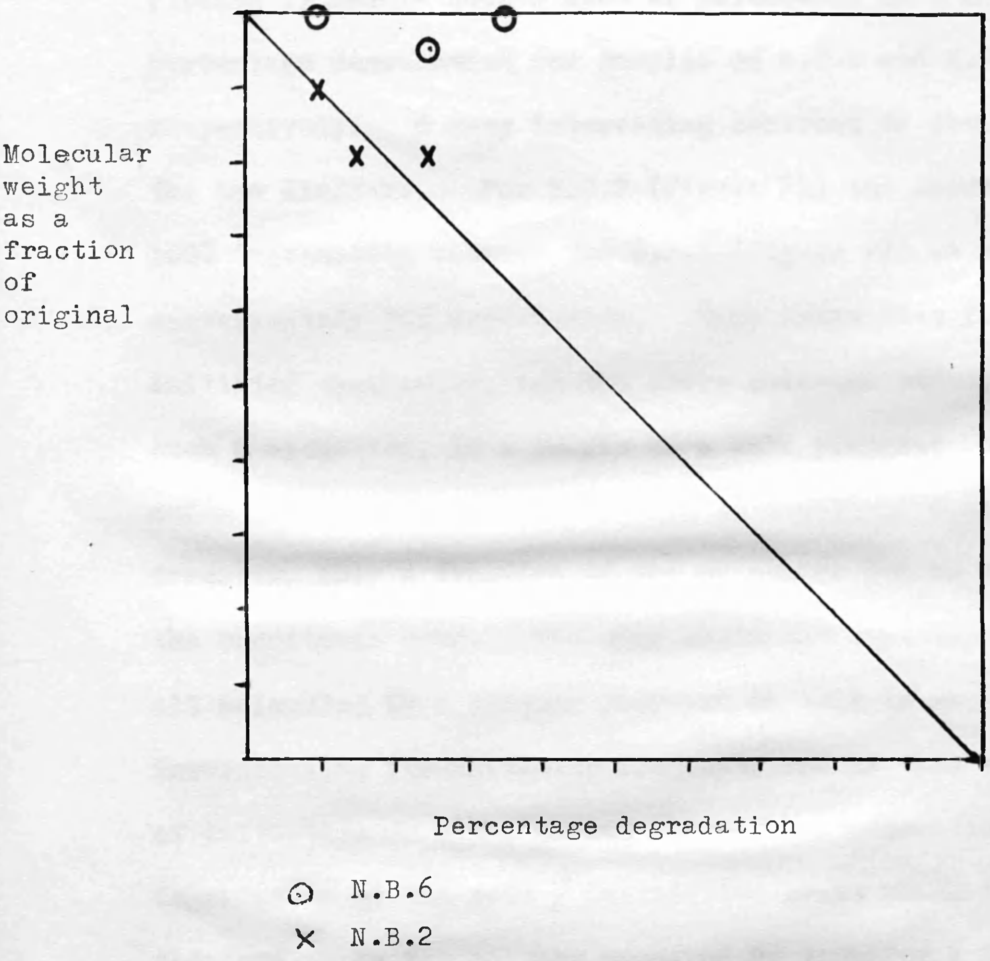


Figure 20. Molecular weight change with extent of photochemical degradation for poly-n-butyl methacrylate.

prepared in benzene solution, so that transfer to benzene took place, the rate becomes zero at less than fifty per cent degradation, due to the smaller proportion of molecules in the transferred polymer having an unsaturated terminal unit. Figures 21 and 22 show a plot of percentage rate against percentage degradation for samples of N.B.2 and N.B.6 respectively. A very interesting contrast is obvious from the two diagrams. For N.B.2 (figure 21) the curve extends to 100% degradation whereas for N.B.6 (figure 22) it extends to approximately 50% degradation. This means that for an end initiated mechanism, and the above evidence strongly favours such a situation, in a sample of a bulk prepared polymer all molecules are degradable, whereas in a polymer prepared by transfer, only a fraction of the molecules can be degraded under the conditions used. The only chain end structure common to all molecules in a polymer prepared in bulk is that incorporating the initiator fragment, and if this were the centre of initiation we would expect a smooth extrapolation to 100% degradation on the rate / degradation graph which is in fact obtained. In the polymer prepared by transfer a fraction of the molecules will have no initiator fragment as some of the polymer chains will have been initiated by a phenyl radical resulting from the transfer of a hydrogen atom from the solvent (benzene). It is possible to calculate roughly the proportion of molecules having an initiator fragment by the following scheme.

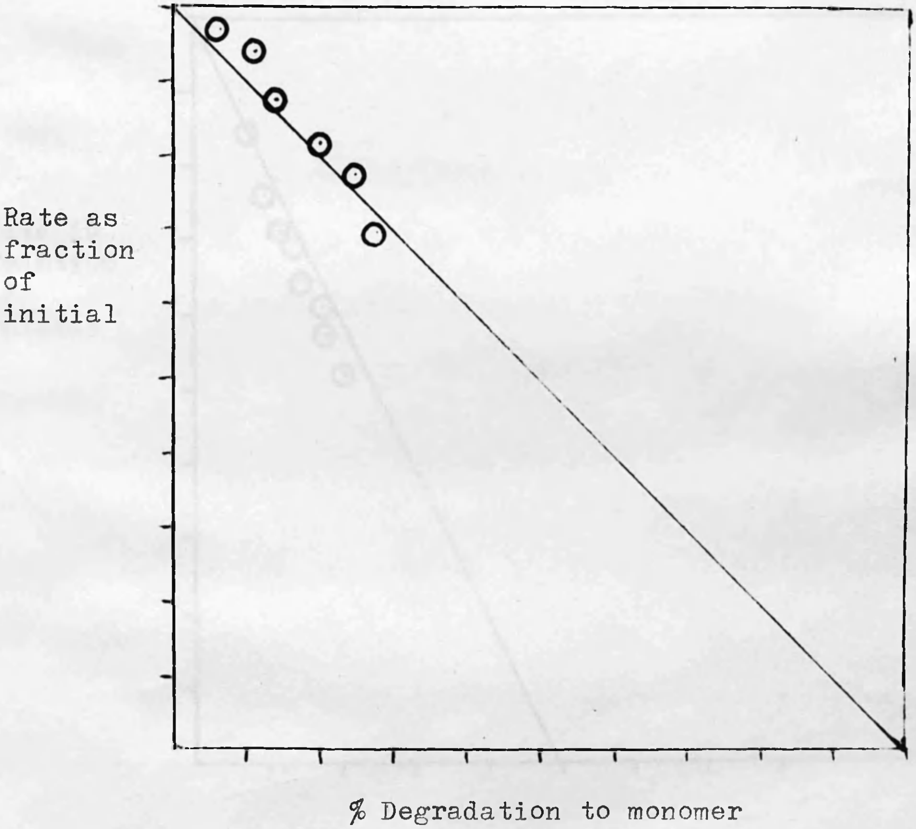


Figure 21. Change of rate with extent of degradation during photochemical degradation of poly-n-butyl methacrylate (N.B.2).

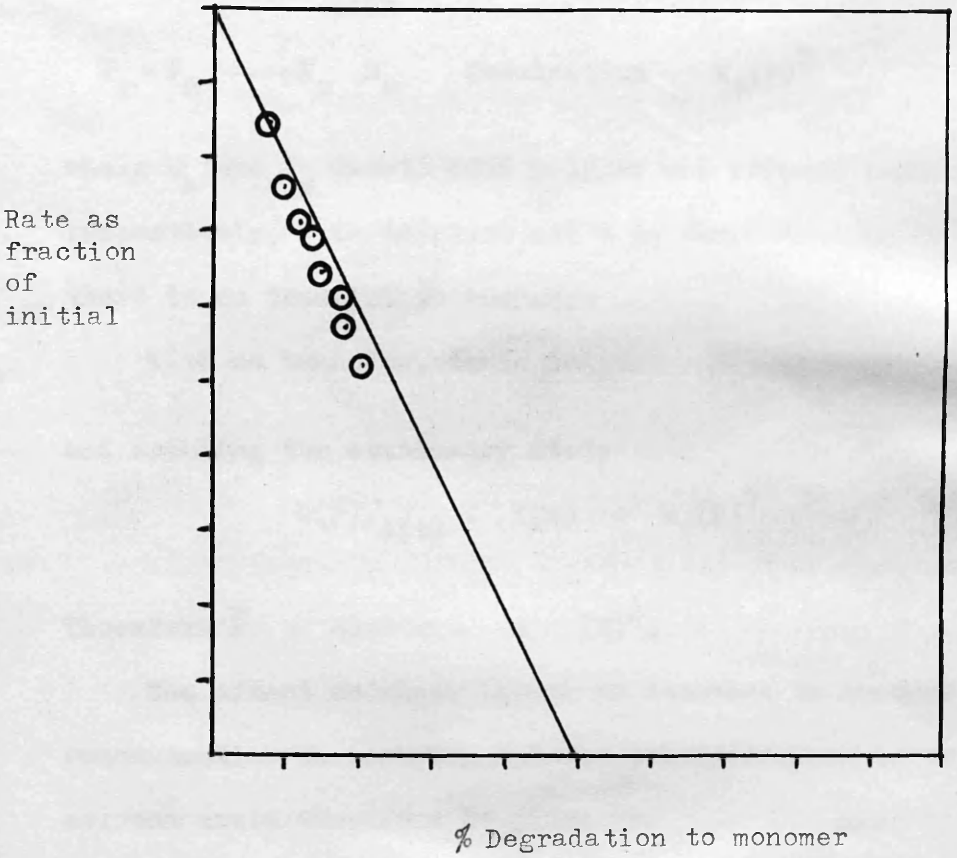


Figure 22. Change of rate with extent of degradation during photochemical degradation of poly-n-butyl methacrylate (N.B.6).

		rate
$C + M \longrightarrow P_1$	Initiation	$K(M)$ (if catalyst concentration constant)
$P_n + M \longrightarrow P_{n\ 1}$	Propagation	$k_p(P)(M)$
$P_n + S \longrightarrow M_n$ new chain	Transfer	$k_f(P)(S)$
$P_r + P_s \longrightarrow M_r\ M_s$	Termination	$k_t(P)^2$

where M_n and P_n denote dead polymer and polymer radicals respectively, C is catalyst and S is benzene. It is assumed that there is no transfer to monomer.

With no transfer, chain length $\bar{P} = \dfrac{k_p(M)(P)}{k_t(P)^2}$

and assuming the stationary state

$$d(P)/_{d(t)} = K(M) - k_t(P)^2 = 0$$

Therefore $\bar{P}$ = constant x $(M)^{\frac{1}{2}}$.

The effect on chain length of decrease in monomer concentration on carrying out the polymerisation in an inert solvent would therefore be given by

$$\bar{P} = \bar{P}_o \frac{(M)^{\frac{1}{2}}}{(M_o)^{\frac{1}{2}}}$$

in which $\bar{P}$ and $\bar{P}_o$ are chain lengths and (M) and (M_o) are monomer concentrations in inert solvent and pure monomer respectively.

Thus in Ag polymer prepared in inert solvent there are $\dfrac{A}{2P_o \dfrac{M^{\frac{1}{2}}}{M_o^{\frac{1}{2}}}}$ moles each of double and single bond end structures due to disproportionation assuming that this is the sole termination process.

If however $\overline{P}_c$ is the actual chain length with transfer there will be a total of $\frac{A}{P_c}$ ends in Ag of polymer. From this it can be deduced that the proportion of double bond ends will be

$$\frac{\overline{P}_c}{2\overline{P}_o \dfrac{M^{\frac{1}{2}}}{M_o^{\frac{1}{2}}}}$$

The above deductions are based on the assumption that the catalyst concentration is constant and that a change in medium has little effect on the rate of decomposition of catalyst. Thus it is only necessary to know monomer concentrations and molecular weights with and without benzene to calculate the number of double bond end structures in a polymer prepared by transfer in benzene solution. It is also apparent from the above calculation which was originally made by Grassie and Vance[28] that the number of initiator fragment ends is equal to twice the number of unsaturated end units, that is

$$\frac{P_c}{\overline{P}_o \dfrac{M^{\frac{1}{2}}}{M_o^{\frac{1}{2}}}} \quad \underline{\qquad\qquad\qquad} \text{(a)}$$

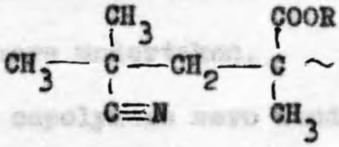
The molecular weight of N.B.6 is 110,000 and the molecular weight of a polymer prepared in bulk using the same concentration of catalyst (0.033 g./100 mls.) was estimated to be about 1.2×10^6 (using the approximate relationship that the molecular weight is inversely proportional to the square root of the catalyst concentration). (M_o) and (M) were 1 and 0.33 respectively. From equation (a) the proportion of chain ends which incorporate an initiator fragment is

$$\frac{110{,}000}{1{,}200{,}000 \times (0.33)^{\frac{1}{2}}} = 16\%$$

This value falls far short of the intercept of the rate / degradation curve on the degradation axis, which is about 50%.

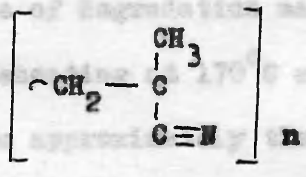
This result apparently does not support the suggestion that it is the chain ends containing initiator fragments which initiate the degradation reaction. However the value for the molecular weight $(\overline{P}_o)$ of the polymer prepared in bulk is an approximation which might lead to a considerable error in the final result. Furthermore the actual kinetic scheme employed in the derivation of (a) is possibly an oversimplification. No allowance has been made for the possibility of copolymerisation of benzene with the monomer. Recent work[46] has shown that benzene does become incorporated into the polymer chain.

All the polymers used in the work described in this thesis were prepared using 2, 2' - azoisobutyronitrile as initiator which gives the following end unit



$$CH_3-\overset{CH_3}{\underset{C\equiv N}{C}}-CH_2-\overset{COOR}{\underset{CH_3}{C}}\sim$$

It is not apparent why this particular grouping should be labile photochemically, particularly in view of the fact that polymethacrylonitrile which has the structure



$$\left[\sim CH_2-\overset{CH_3}{\underset{C\equiv N}{C}}\right]_n$$

does not itself degrade photochemically.

In the photo degradation of polymethyl methacrylate which was prepared using bensoyl peroxide as catalyst it was thought that the terminal unsaturated links were the centres of initiation of break down, however, no measurements were made using 2, 2' - azoisobutyronitrile catalysed polymer. Similarly in the present work no polymers prepared using benzoyl peroxide as catalyst were studied. It would appear that a comparative study must be made using the same polymer but varying the initiator in order to clear up this point. It is of interest to note that Bywater[47] found that polymers with hydroxyl end units degraded very readily thermally.

DEGRADATION OF COPOLYMERS

The radicals concerned in depolymerisation initiated photochemically are probably the same as those which occur in the thermal degradation of poly-n-butyl methacrylate. It was thought that it would be of value to the study of the thermal degradation if an investigation of the effect of anhydride on photodepolymerisation were undertaken.

The same two copolymers were used as in the thermal work, C.N.B.1 and C.N.B.2. As previously the amount of anhydride formed was controlled by preheating at 170°C. After the copolymer film had been preheated for the desired time, the shutter was removed and the initial rate of degradation measured. Figure 23 shows a graph of time of preheating at 170°C against the initial rate. In these experiments approximately the same weight of polymer was taken in order to obviate the absolute rate measurement difficulty.

The normal methods were used to investigate the volatile products. Very little could be done, however, with the degraded polymer as it was always, at least partially, insoluble.

For copolymers which had little preheating the liquid products showed definite broadening with slight peaks in the 2500 - 3400 $cm.^{-1}$ region which is characteristic of acid hydroxyl groups. This, plus positive results from test-paper examination, indicated that acid was appearing among the volatile products. V.P.C. cannot be used very successfully for tracing acids as the polar acid molecules tend to stick on the column. In fact vapour phase chromatograms showed only one peak - that of monomer.

MECHANISM

From figure 23 it can be seen that the stability of the polymer rises with time of preheating. The fact that acid appears in the volatile products from polymer which has had little preheating

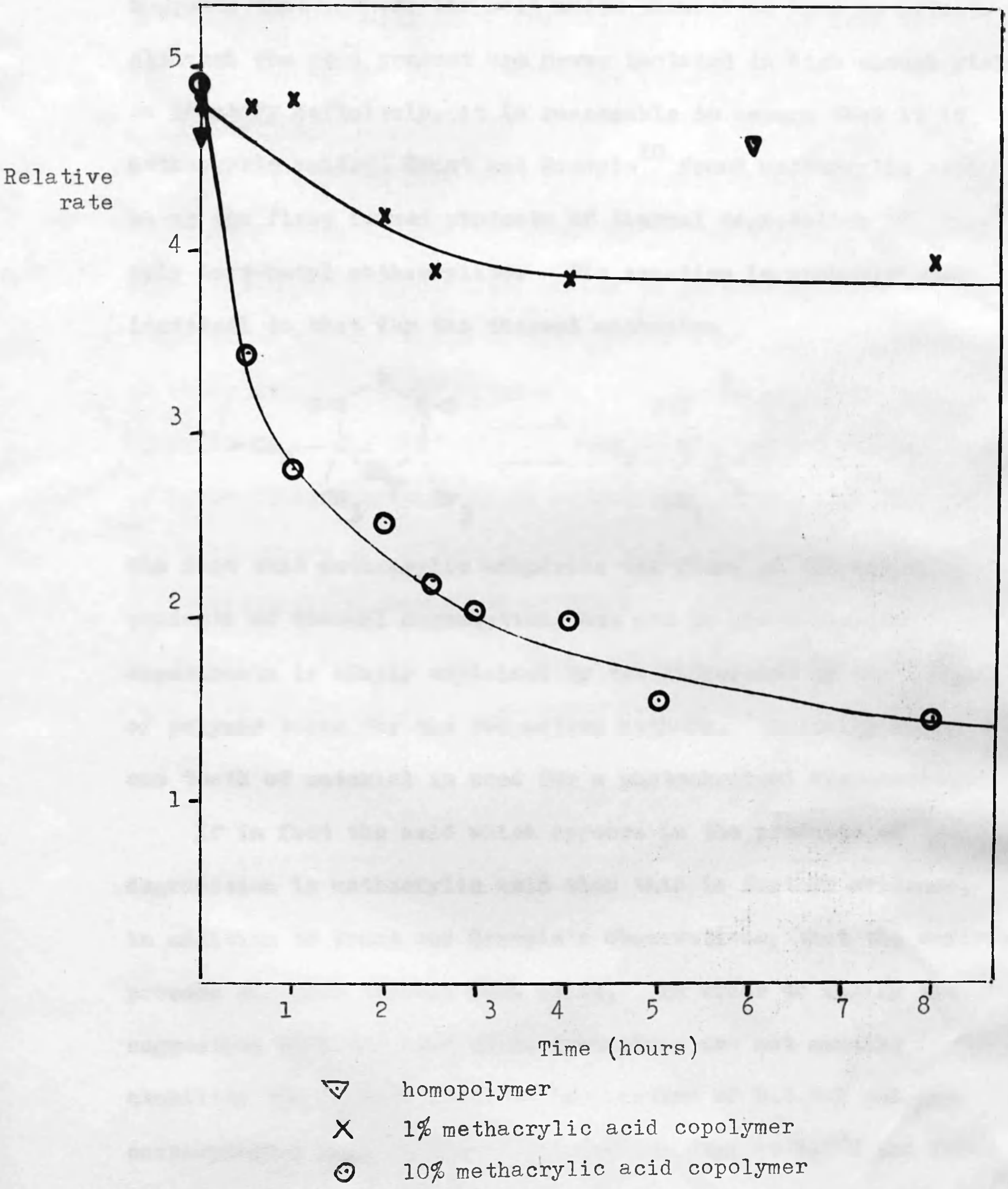
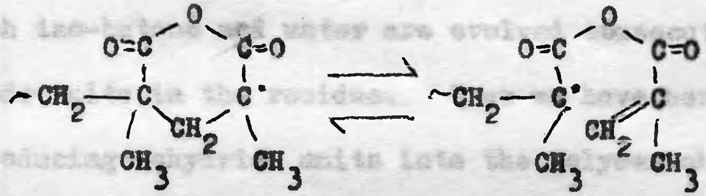


Figure 23. Effect of preheating at 170°C on initial rate of photodepolymerisation of poly-n-butyl methacrylate.

suggests that methacrylic acid units themselves have no effect. Although the acid product was never isolated in high enough yield to identify definitely, it is reasonable to assume that it is methacrylic acid. Grant and Grassie[10] found methacrylic acid among the first formed products of thermal degradation of poly-tert-butyl methacrylate. The reaction is probably identical to that for the thermal mechanism



The fact that methacrylic anhydride was found in the volatile products of thermal degradation, but not in photo-chemical experiments is simply explained by the difference in the quantity of polymer taken for the respective methods. Normally about one tenth of material is used for a photochemical degradation.

If in fact the acid which appears in the products of degradation is methacrylic acid then this is further evidence, in addition to Grant and Grassie's observations, that the unzipping process can pass through such units. In order to verify the suggestion that the acid units themselves are not causing stability the initial rates of degradation of C.N.B.2 and the corresponding homopolymer N.B.2 were compared at 125°C and found to be similar. It has been shown[29] that the conversion of acid to anhydride at this temperature region is negligible. Preheating had no effect on the initial rate of degradation of C.N.B.2 and therefore this result gives further proof that the acid units do not have any effect on the depropagation reaction.

POLY-TERT-BUTYL METHACRYLATE

It has already been stated that almost quantitative yields of monomer could be obtained from the photochemical degradation of poly-tert-butyl methacrylate, heated to just under 170°C. This temperature is very close to the threshold of thermal degradation in which iso-butene and water are evolved consecutively leaving anhydride units in the residue. Thus we have here another means of introducing anhydride units into the polymer chain, and figure 24 demonstrates the effect of preheating a sample of poly-tert-butyl methacrylate at 178°C on the initial rate of photochemical degradation. Once again it is apparent that the formation of anhydride brings about stability in the polymer chain.

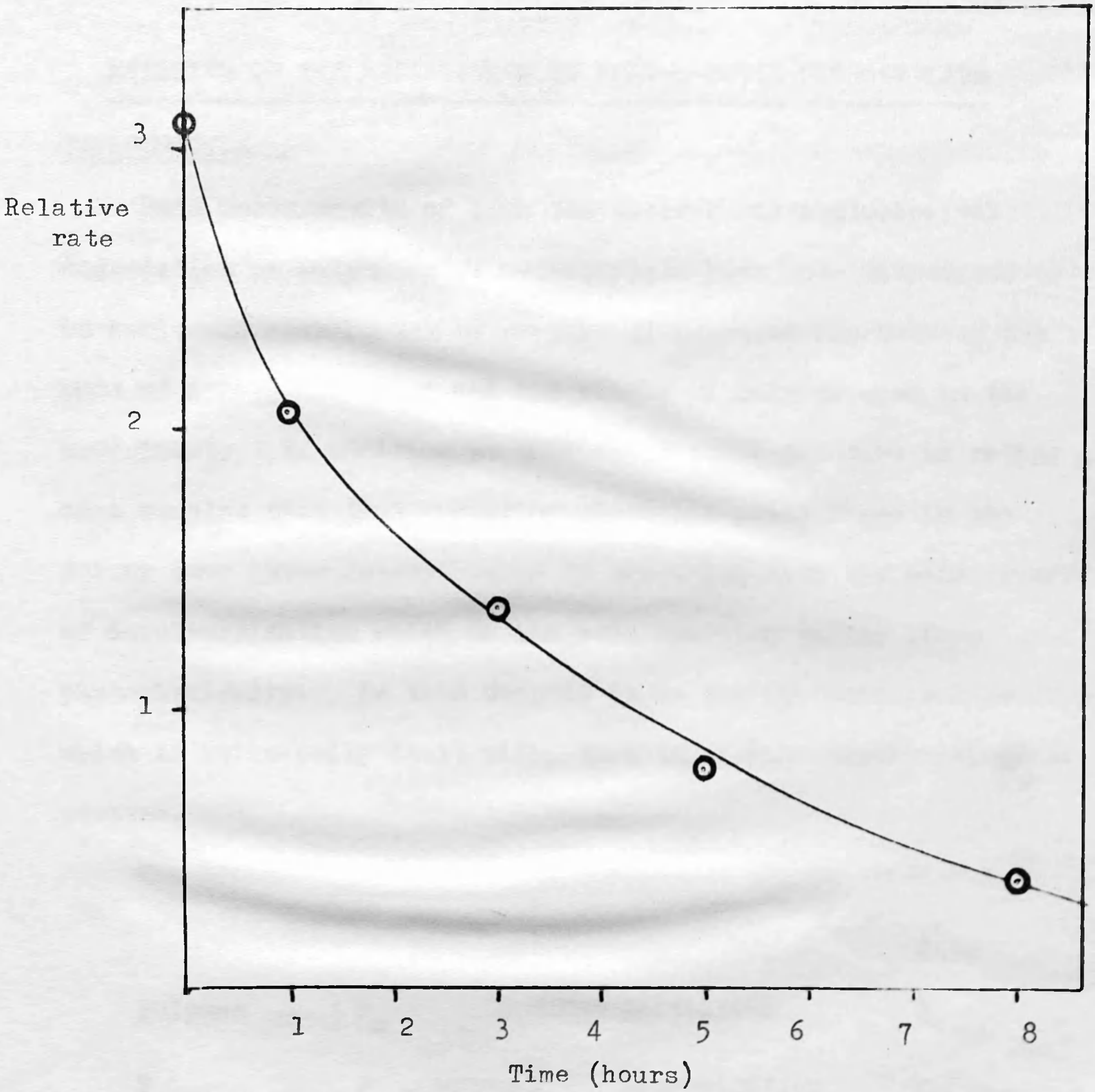


Figure 24. Effect of preheating at 178°C on initial rate of photodepolymerisation of poly-tert-butyl methacrylate..

CHAPTER V

KINETICS OF THE DEGRADATION OF POLY-n-BUTYL METHACRYLATE

INTRODUCTION

Rate measurements of both the thermal and photochemical degradation of poly-n-butyl methacrylate have been discovered to be seriously complicated by an unusual relationship between the rate of depolymerisation and the weight of polymer used in the experiment. In addition to this the thermal reaction is rather more complex than that occurring photochemically since in the former case ester decomposition is competing with the main process of depolymerisation which is the sole reaction taking place photochemically. In this Chapter it is the photochemical reaction which is principally dealt with, that is, a pure depolymerisation process.

The kinetic scheme for such a reaction can be written as[1]

		Rate
Polymer $\longrightarrow P_n$	Initiation	R_i
$P_n \longrightarrow P_{n-1}$ + monomer	Depropagation	$k_d[P]$
$P_r + P_s \longrightarrow$ Stable polymers	Termination	$k_t[P]^2$

in which R_i is the rate of initiation, k_d and k_t the reaction constants for the depropagation and termination steps respectively, and $[P]$ is the concentration of polymer radicals. Since in this particular case under examination the polymer sample is under high vacuum it is assumed that the concentration of monomer within the polymer is low, the diffusion of monomer out of the polymer being rapid, and therefore not rate controlling. The molecular weight and rate evidence in Chapter IV and the close similarity in behaviour of this polymer with polymethyl methacrylate[3] are strong evidence that transfer to polymer does not occur in this system and that the depolymerisation process is predominantly chain-end initiated.

Thus we have:-

Rate of production of monomer $\frac{d[M]}{dt} = k_d[P]$.

Assuming the steady state,

rate of initiation = rate of termination,

that is,

$$R_i = k_t[P]^2 \ .$$

Thus,

$$\frac{d[M]}{dt} = \frac{k_d}{k_t^{\frac{1}{2}}} R_i^{\frac{1}{2}} \underline{\hspace{4cm}} (1)$$

For an end-initiated process,

the rate of initiation = $k_i \Big[\text{Chain-ends} \Big]$.

$$R_i = k_i \frac{K}{Mn}$$

in which K is a constant and Mn the number average molecular weight of the polymer.

Thus equation (1) becomes

$$\frac{d[M]}{dt} = \frac{k_d \ k_i^{\frac{1}{2}}}{k_t^{\frac{1}{2}}} \left[\frac{K}{Mn}\right]^{\frac{1}{2}} \underline{\hspace{4cm}} (2)$$

Thus we find that the initial rate of degradation for a process involving a bimolecular termination step is proportional to the square root of the reciprocal of the molecular weight of the polymer. This relationship was confirmed experimentally by Grassie and Melville[2] in their study of the thermal degradation of polymethyl methacrylate. Also from equation (2) it can be seen that the initial rate of degradation should be proportional to the weight of sample taken, as the molecular weight would be constant for the initial stages of the reaction at least.

SURVEY OF DEPOLYMERISATION THEORIES

Friedman[48] has recently made a useful summary of the expressions obtained for rates of depolymerisation in a number of theoretical treatments of polymer degradation by a number of authors. In general the results are in agreement with the simple treatment above except that Jellinek[49] and Simha and Wall[50] find the rate of evolution of volatile material to be proportional to the square root of the weight of polymer used in the experiment.

All these treatments have assumed the overall radical depolymerisation process to be made up of some or all of the four primary reaction steps, initiation, propagation, transfer and termination, all of which are assumed to be homogeneous. If the overall reaction has no heterogeneous constituents it is self-evident that the overall rate per unit volume should be quite independent of sample size, that is that the rate of evolution of volatile material from a given sample should be directly proportional to the size of the sample in agreement with the results of Friedman's, Boyd's[51], and Gordon's[52] treatments. The half power dependence of rate upon sample size obtained by Jellinek and Simha and Wall must result from some fundamental error in the mathematical treatment.

The error is readily obvious in Jellinek's work. In applying the law of mass action to the expression of the rates of chemical reactions, for example, Rate = Rate constant x $(\text{concentration})^n$, the concentration is expressed quite generally as amount/unit volume. Thus in using number theory and expressing rates in terms of numbers of reacting species, for example, Rate = Rate constant x $(\text{number of molecules})^n$, Jellinek is implying a fixed volume. This is still implied when "number of molecules" is replaced in his treatment by "weight/molecular weight" - weight really means weight/unit volume, that is, density, which is constant.

Thus while Jellinek's final expressions (equations 113 and 115) for the rates of monomer production assuming bimolecular termination both contain the term, $(\text{weight of polymer})^{\frac{1}{2}}$, this does not imply, as he claims, that the rate is proportional to the square root of the amount of polymer used since the term is really constant. Thus the rate per unit volume is independent of sample size or, in other words, the rate of volatilization of a given sample is proportional to the first power of the sample size as found by Friedman, by Boyd and by Gordon and as one would expect in a completely homogeneous process.

Jellinek's error may thus simply be said to have been the application of the Law of Mass Action to numbers of reacting entities, without due regard being paid to the volumes involved.

It has not been possible to pinpoint the corresponding error in Simha and Wall's treatment, possibly because the mathematical argument is not given in sufficient detail. It seems probable, however, that it has arisen in the same way since these workers have also used a number rather than a concentration approach. It is interesting to note that Bywater[47] who implies a concentration unit approach also finds the rate proportional to the square root of the weight of polymer for the bimolecular termination mechanism, although he does not show how he reaches this conclusion.

While the simple approach presented at the beginning of this Chapter is all that is necessary for the comparison of initial rates of depolymerisation, a very much more complicated treatment would be necessary to describe the complete course of the reaction of a single sample. This has been attempted by Gordon[52] whose elegant mathematical approach combines a concentration and statistical treatment. However his application of this approach to the depolymerisation of polymethyl methacrylate is not completely valid.

Thus, using a degradation scheme essentially similar to that set out in the introduction of this Chapter he deduces the following equation for the steady state (equation 8 of reference 52).

$$\frac{k_i \; Mq}{M_o} = k_{t'} M (c + C)^2 \text{\_\_\_\_\_\_\_\_\_\_} (3)$$

in which

k_i = initiation constant,

M = the relative mass of polymer,

q = the reciprocal mean polymer chain length,

M_o = the molecular weight of monomer,

$k_{t'}$ = the disproportionation constant,

C = the concentration of polymer radicals,

c = the concentration of monomer radicals with catalyst fragment.

In this equation the rate of initiation per unit mass, which is equal to $k_i \left[\text{Degradable Chain-ends}\right]$, is represented by $k_i \frac{q}{M_o}$.

Gordon then goes on to deduce equations for the rate of degradation, that is the rate of production of monomer, (equations 17 and 21) from equation 3 on the basis that $\frac{dq}{dt} = 0$. This assumption, which means that the distribution of molecular weights remains constant, will only be correct when all molecules have an equal probability of degrading. Grassie and Melville have shown[2] that only 50% of the molecules in a sample of polymethyl methacrylate are degradable below 250°C and therefore the concentration of degradable ends changes throughout the course of the degradation. It follows that replacement of $\left[\text{Degradable Chain-ends}\right]$ by the reciprocal of the molecular weight and the assumption that $\frac{dq}{dt} = 0$ are not valid for the particular case being considered, except in a comparison of initial rates of degradation.

There has been controversy between Simha[53] and Gordon[54] regarding the development of the kinetics of free radical depolymerisation processes using statistical theory. Apparently the principal difference of opinion arises from the validity of Gordon's assumption that $\frac{dq}{dt}$ can be set equal to zero. Simha in his treatment retains this particular term and arrives at the result that the rate of degradation is proportional to the square root of the weight of polymer taken. A result which appears to be intuitively wrong and which as has already been pointed out may arise from an error similar to that made by Jellinek[49].

The most obvious feature of the many papers which have been published on the kinetics of degradation is the lack of experimental evidence to back the theories postulated. Theory has outstripped the volume of experimental results available and it seems that much practical investigation is required to consolidate or to confound what has been suggested on theoretical grounds. On the practical side, part of the difficulty arises from the fact that a polymer degrading in a vacuum is not a stationary system. The monomer is removed from the polymer, which is usually a fairly viscous liquid, so that the volume is continually changing. In addition to this the molecular weight of the polymer can be changing fairly rapidly so that an accurate measure of concentration becomes almost impossible.

It is clear that these theories which exist for the description of the complete reaction are quite inadequate for application to real systems. The simplified theory given at the beginning of this Chapter and the consequences derived from it can, however, be applied quite rigidly to the comparison of initial rates of reaction and the results and discussion which make up the remainder of the Chapter refer only to such experiments.

POSSIBLE EXPLANATION FOR EXPERIMENTAL RESULTS

Although certain theories exist[49 and 50] which would account for the square root dependence of rate of depolymerisation on weight of polymer sample observed for poly-n-butyl methacrylate it has been shown on pages 105, 106 and 107 how, on deeper examination, these postulates contain a fundamental error which makes the final result untenable.

It has already been shown on pages 103 and 104 how in a completely homogeneous process the rate ought to be proportional to the quantity of polymer. Any other relationship between these two parameters implies some basic modification of the simple scheme presented at the beginning of this Chapter. A number of such modifications have been considered and the consequences thereof will now be considered. In particular those modifications are as follows.

a. Repolymerisation, which might become appreciable if the rate of diffusion of monomer from the molten polymer was slow enough to allow the accumulation of an appreciable concentration of monomer within the polymer.

b. Skin-effect, that is the reaction occurring on the surface layers of polymer only owing to strong absorption of the activating radiation.

c. Absorption of activating radiation by monomer in the gas phase.

d. Heterogeneous effects.

e. Statistical effect.

a. REPOLYMERISATION

It is well established that propagation and depropagation comprise a single reversible process which can be represented by

$$P_n \underset{k_p}{\overset{k_d}{\rightleftharpoons}} P_{n-1} + M$$

so that

$$\frac{d[M]}{dt} = k_d[P] - k_p[P][M_p].$$

in which $[M_p]$ is the concentration of monomer within the polymer mass. In the derivation of equation 1 it was assumed that the concentration of monomer within the degrading polymer is so low that the rate of the reverse process is negligible and can be ignored. The significance of the addition of this step is that the diffusion of monomer from the mass of polymer is slow and that a concentration of monomer builds up within the polymer.

Thus,

$$\frac{d[M]}{dt} = [P](k_d - k_p[M_p])$$

$$= \frac{R_i^{\frac{1}{2}}}{k_t^{\frac{1}{2}}}(k_d - k_p[M_p]) \text{\_\_\_\_\_\_\_\_\_\_} (4)$$

If the second term in the bracket becomes zero we are left with the normal rate equation. There is no obvious way in which such a relationship could lead to the square root dependence of rate upon quantity of polymer. Since $\left[M_p\right]$ is the concentration of monomer within the polymer and $\frac{d[M]}{dt}$ is the rate of escape of monomer from the polymer there will be some relationship between them. If this is a linear relationship, that is

$$\frac{d[M]}{dt} \propto \left[M_p\right]$$

$$\therefore \frac{d[M]}{dt} = K\left[M_p\right]$$

$$\text{then } \frac{d[M]}{dt} = \frac{k_i^{\frac{1}{2}}}{k_t^{\frac{1}{2}}}\left(k_d - k_p\left[M_p\right]\right)$$

$$= \frac{k_i^{\frac{1}{2}}}{k_t^{\frac{1}{2}}}\left(k_d - k_p\ K\ \frac{d[M]}{dt}\right)$$

$$= K_1 - K_2\ \frac{d[M]}{dt}$$

$$\therefore \frac{d[M]}{dt}(1+K_2) = K_1$$

$$\therefore \frac{d[M]}{dt} \quad \frac{K_1}{1+K_2}$$

that is, rate $\propto$ weight of polymer sample.

If the relationship between $\frac{d[M]}{dt}$ and $\left[M_p\right]$ is more complex the development of equation 4 is complicated mathematically and it is still not immediately obvious how a square root relationship of the type sought could be derived from it.

b. SKIN-EFFECT

This is caused by high absorption of the light causing degradation in the surface layers of the polymer with the result that the bulk of depolymerisation takes place at or near the surface of the polymer. The reaction in fact becomes heterogeneous and the problem may be treated in the following way.

Let the intensity of light falling on a layer of polymer at a depth l cms. in the polymer film be I.

By Beer's Law,

$$I = I_o 10^{-ul}$$

in which I_o is the intensity of light falling on the surface and u the extinction coefficient of the polymer. From figure 15 it can be seen that u is approximately equal to 4 for a layer of polymer 0.003 cms. thick.

In equation 1 it has been shown that

the rate of depolymerisation $(R_d) = KR_i^{\frac{1}{2}}$

For a reaction initiated photochemically R_i is proportional to I, the intensity of the radiation.

Thus

$$R_d = KI^{\frac{1}{2}}$$

At the surface

$$R_{d(s)} = KI_o^{\frac{1}{2}}$$

At a layer a depth 0.004 cms. in the polymer film

$$R_{d(l)} = KI^{\frac{1}{2}}$$

$$KI_o^{\frac{1}{2}} 10^{-ul/2}$$

$$KI_o^{\frac{1}{2}} 10^{-2 \times 0.004}$$

$$R_{d(s)} \; 10^{-0.008}$$

$$0.98 \, R_{d(s)}$$

Thus it can be seen that the rate of depolymerisation at a depth 0.004 cms. in the polymer film is almost identical with the rate at the surface. It is only for much thicker films, approximately 0.2 cms., that the rate is reduced by a factor of 2. Therefore under the conditions of the experiments described in this thesis there is no significant effect due to preferential absorption of the activating radiation at the surface layers.

c. ABSORPTION OF ACTIVATING ENERGY BY MONOMER

The absorption of the activating radiation, wave length 2537Å, by monomer vapour would diminish the amount of energy reaching the polymer. The extinction coefficient of the monomer is of the order of 40[54] but under the experimental conditions used, that is a path length of 10 cms. and a maximum pressure of about 1 mm. for the highest rate of degradation, very little radiation would be absorbed by monomer vapour.

d. HETEROGENEOUS EFFECTS

Some experiments were carried out to investigate the possibility of some heterogeneous step, occurring possibly at the surface of the film or at the surfaces in contact with the copper of the tray. Three trays of different diameter were used. The object of using trays of differing diameter was to vary the ratio of film surface area to bulk, and determine whether this had any effect on the rate of reaction and the rate/weight relationship. The radii of the three trays were, 1.6 cms. this is the normal tray used for degradation and is designated 1, 1.3 cms. (m) and 1.0 cm. (s). Table 8 shows the results from a series of measurements using various surface area: bulk ratios. Except in two cases the $\frac{r}{w^{\frac{1}{2}}}$ is substantially constant. The exceptions refer to very thick films, about 0.006 cms., in which one would expect lower rates because of the difficulty of heating the whole mass of polymer evenly. This fall-off in rate takes place for thicknesses of film similar to those for which the fall-off in rate was observed in the photodegradation polymethyl methacrylate[3]. The results of these experiments rule out the possibility of a heterogeneous component in the reaction and still no explanation is forthcoming for the observed rate to weight relationship.

TABLE 8

RATE OF PHOTOCHEMICAL DEGRADATION FOR VARIOUS SIZES OF TRAY.

POLYMER USED N.B.2.

Thickness of film cms. x 10^3	Rate (r) mls./min. x 10^3	Weight of polymer mgs. (w)	Tray used	$\frac{\text{rate}}{\text{weight}}$ $\frac{r}{w}$	$\frac{\text{rate}}{(\text{weight})^{\frac{1}{2}}}$ $\frac{r}{(w)^{\frac{1}{2}}}$
4.28	7.1	14.2	s	0.500	1.88
2.94	7.6	16.5	m	0.460	1.87
5.2	7.8	17.6	s	0.443	1.86
6.2	7.8	20.6	s	0.378	1.72
4.4	9.3	24.7	m	0.376	1.88
6.1	10.1	34.3	m	0.294	1.72
4.16	11.0	35.6	l	0.310	1.84

e. STATISTICAL EFFECTS

Turning to the suggestion of Cowley and Melville[3] that the termination process is viscosity controlled in the photo-degradation of polymethyl methacrylate, the evidence is strong that a similar situation exists in the photo-depolymerisation of poly-n-butyl methacrylate. The activation energy of the termination step (see Chapter IV) is very high and comparable to the value found for polymethyl methacrylate[3]. A further manifestation of viscosity control of the termination step can be seen from table 9 which shows that the initial rate of degradation of a series of polymers increases with increasing molecular weight. It has been shown in Chapter IV

TABLE 19

COMPARISON OF RELATIVE RATES OF PHOTODEPOLYMERISATION OF SOME POLY-n-BUTYL METHACRYLATES

Polymer	Preparation	Relative Rate
N.B.1.	Bulk	5.75
N.B.2.	Bulk	4.45
N.B.4.	Transfer in benzene	2.16
N.B.6.	Transfer in benzene	3.52

that the initiator fragment seems to be the centre of initiation, thus a strict comparison of initial rates of degradation can only be made between polymers N.B.1 and N.B.2 which were both prepared by polymerisation in bulk. From equation 2 the initial rate of degradation should be inversely proportional to the square root of the molecular weight of polymer. However N.B.1 (M.W. 1.1×10^6) degrades faster than N.B.2 (M.W. 0.46×10^6). This is explained by the increase in molecular weight being more than offset by a decrease in k_t, the termination rate constant, due to the termination reaction becoming more difficult because of the increase of melt viscosity with increasing molecular weight.

In a recent communication North and Reed[55] have shown how the termination rate constant of the free-radical polymerisation of methyl methacrylate is inversely dependent upon the viscosity of the medium in which the reaction is occurring. They go on to suggest that the rate determining step of the termination process is segmental diffusion of the radical chain-ends out of the coiled polymer chain, and that the termination reaction is diffusion controlled even at zero conversion. The idea of diffusion control seems even more likely to occur in the depolymerisation reaction since the molten polymer in which it takes place has an even higher viscosity than the polymerising monomer.

Cowley and Melville found that for polymethyl methacrylate the life time of a degrading radical (5 - 10 seconds) is similar to the diffusion time of monomer from the molten polymer.

Since the time taken for a polymerising radical to unzip is comparable with the time taken for monomer or monomer sized radicals to diffuse from the degrading polymer it seems possible that the concentration of monomer sized radicals may be fairly large relative to the concentration of degrading long chain radicals. Since the monomer sized radicals must be relatively mobile the termination process may occur predominantly between a large and a small radical rather than between two immobile large radicals. This amounts to suggesting that the termination process is controlled by translational diffusion of the polymer radicals, not segmental diffusion which is the rate determining process in polymerisation.

In a polymer sample such as that used in the degradation experiments described in this thesis the actual number of radicals will be extremely low (approximately $10^{12 - 13}$). If the concentration is so low that the mean free path of radicals between collisions is of the order of the dimensions of the polymer sample the rate of reaction of pairs of radicals will no longer be strictly proportional to the square of the concentration of radicals but will tend to be proportional to the square of the total number of radicals in the system. Thus the rate of termination derived for the conventional concentration units must be corrected by multiplying by a factor kn, in which k is a constant and n is the number of radicals in the system. n can be replaced by weight of sample (w) divided by molecular weight of sample (M.W.). Applying the steady state assumption to the simple kinetic scheme already suggested but amending the termination step as shown we have

$$[P] = \frac{R_i^{\frac{1}{2}}\,k^{\frac{1}{2}}}{k_t^{\frac{1}{2}}}\left(\frac{M.W.}{W}\right)^{\frac{1}{2}}$$

which gives

$$\frac{d[M]}{dt} = k_p\,\frac{R_i^{\frac{1}{2}}}{k_t^{\frac{1}{2}}}\,k^{\frac{1}{2}}\;\frac{(M.W.)^{\frac{1}{2}}}{w^{\frac{1}{2}}}$$

The left hand side of this equation represents the rate per unit weight and it can be seen how the measured rateper polymer sample becomes proportional to the square root of the weight of the sample.

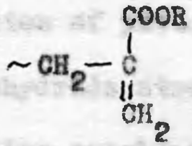
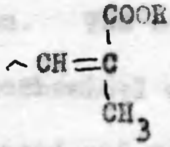
The above treatment implies that the normal statistical mechanics used to describe reaction kinetics are not applicable to a degrading polymer under the conditions described in this thesis. However it must be borne in mind that statistical methods are applicable to systems of large numbers of particles. Although this explanation may seem somewhat improbable it must be emphasised that a degrading polymer is a very unusual system. Not only is it very difficult to obtain an exact measure of concentration of polymer, or polymer radicals, but the concentrations themselves tend to be very low as a result of the very high molecular weights which macromolecules can have.

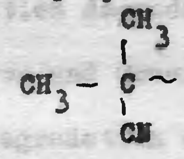
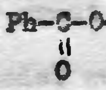
CHAPTER VI

GENERAL DISCUSSION

The object of this final Chapter is to summarise the work described in the preceeding Chapters of this thesis with a view to finding some generalisations which may be useful in further degradation studies.

It has been shown that in the thermal degradation of poly-n-butyl methacrylate an ester decomposition reaction interferes with the predominating depolymerisation reaction. It has been postulated that the ester decomposition takes place by a radical mechanism occurring at the ends of depropagating chains giving rise to acid groups in the terminal units. The acid group then reacts with its neighbour first by catalysing another ester decomposition and then by eliminating water with the resulting acid group to give an intramolecular anhydride terminal unit. A mechanism has been suggested for the inhibition of depolymerisation by those cyclic anhydride units. Further evidence for this mechanism has been obtained from a series of degradation experiments involving copolymers of methacrylic acid and n-butyl methacrylate. This inhibition of depolymerisation by cyclic anhydride units incorporated into the polymer chain is very interesting and would seem to suggest an easy route for stabilisation of methacrylate polymers produced industrially. A rather interesting point arose from an examination of the possible modes of initiation of depolymerisation which is end-initiated, namely that the terminal unit formed by disproportionation in methacrylate polymers has the structure


$\sim CH_2-\overset{\overset{COOR}{|}}{C}(=CH_2)$ rather than 
$\sim CH=\overset{\overset{COOR}{|}}{C}-CH_3$ which is the one normally accepted. This idea leads to one possible reason for the difference in behaviour, on heating, of methacrylate and acrylate polymers, since the latter cannot form such a terminal unit.

The photochemical degradation of poly-n-butyl methacrylate has been more intensively studied, primarily because the reaction was found to involve pure depolymerisation. The mechanism of break down is in general very similar to that of polymethyl methacrylate[3], involving a chain reaction, initiated at the ends of the polymer molecules, followed by unzipping of monomer units until mutual termination takes place. One of the main features of the work done was the discovery that the initiator fragments incorporated at the polymer chain end seemed to be the centres of initiation. The catalyst used in the preparation of the polymers was 2, 2'-azoisobutyronitrile, giving the fragment 
$CH_3-C(CH_3)(CN)\sim$ as the terminal unit, whereas benzoyl peroxide, the initiator used by Cowley and Melville in the preparation of the polymethyl methacrylates which they studied, gives either Ph- or 
$Ph-\underset{\underset{O}{\|}}{C}-O-$ at the chain end. These authors found[3] that the fragment from benzoyl peroxide was stable under ultra-violet irradiation. A comparison of stability of initiator fragments to

ultra violet light would provide much valuable information about the sites of photochemical initiation. The stabilising effect of anhydride structures on the photochemical degradation was shown by using copolymers of methacrylic acid and poly-n-butyl methacrylate.

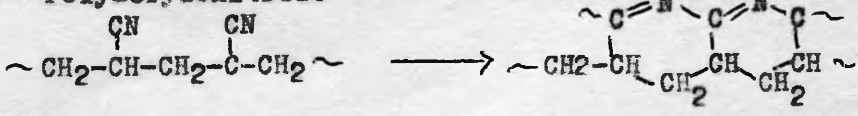
A kinetic analysis of the degradation, both thermal and photochemical, of poly-n-butyl methacrylate was seriously complicated by the measured rate of depolymerisation being proportional to the square root of the weight of polymer sample taken. Possible explanations for this relationship have been dealt with in Chapter V but no completely satisfactory answer was found. Much confusion has existed in the literature on theoretical treatments of polymer degradation, all arising from the fact that the volume of a degrading polymer changes during the course of the reaction and also the molecular weight often changes so that an absolute measure of concentration becomes very difficult if not impossible. It seems probable that the reaction would be much less complicated in solution. Solution degradation has, in fact, been very successfully applied by Cameron and Grassie[56] to the elucidation of the mechanism of the thermal degradation of polystyrene, and it would be of great value in the study of the degradation of the methacrylates.

One point, which is apparent from the work described in this thesis, is the great difference which often exists between the behaviour of model compounds and of polymer. In the thermal degradation of poly-n-butyl methacrylate it is suggested that the ester decomposition proceeds by a radical mechanism in contast to the ester decomposition of corresponding model compounds, which is commonly accepted as involving a molecular mechanism. Ausloos has shown[57] that esters can also be induced to break down into acid and olefine under the influence of ultra violet radiation. However in the photochemical degradation of poly-n-butyl methacrylate no such reaction occurs. Thus care must be taken when comparing results for model compounds and polymers. What is true for a model compound may not be applicable to a macromolecule. Normally the decomposition of model compounds is studied in flow systems in the vapour state and thus the concentration of products is never allowed to become high enough to influence the reaction. For a molten polymer a portion at least of the products may be involatile and is thus retained within the reaction zone. Even for reactions in which the products are volatile a finite time is often required for the volatile fragment to diffuse out of the reaction zone.

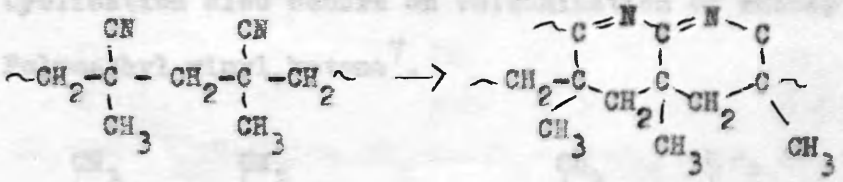
Another point noted from the present work and also from Grant and Grassie's work[10] on poly-tert-butyl methacrylate is the preferential formation of intramolecular cyclic anhydrides, rather than intermolecular linear anhydrides. This fact is deduced from very reliable infra-red measurements. Furthermore the resultant polyanhydride has high thermal stability. An examination of the literature provided many other examples of cylcisation of products on thermal degradation. The undernoted are some illustrations.

INVOLATILE CYCLIC PRODUCT

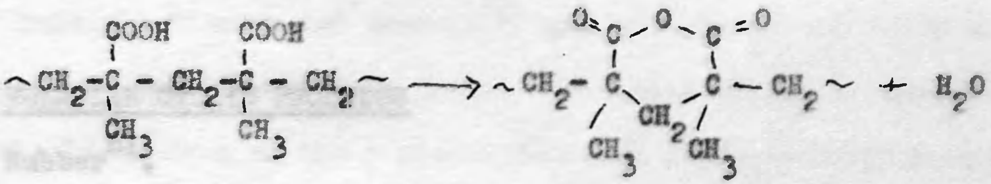
Polyacrylonitrile[14].



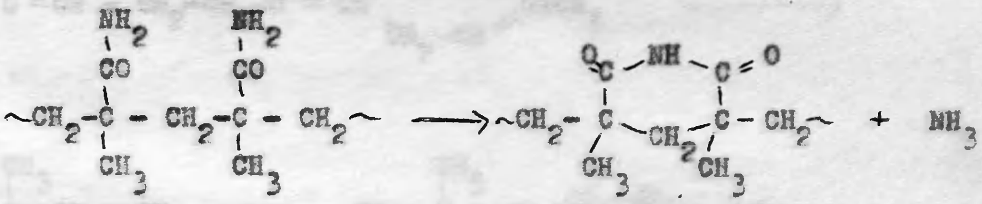
Polymethacrylonitrile[13].



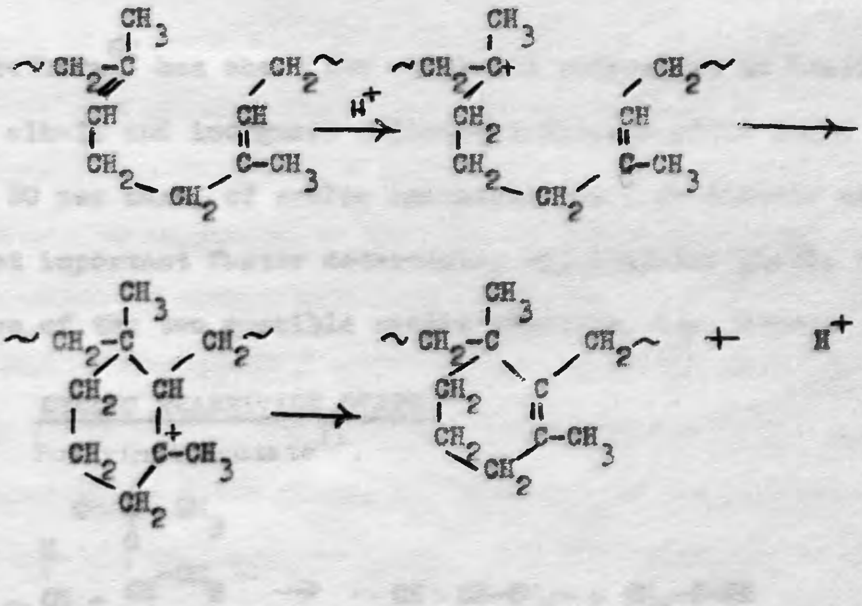
Polymethacrylic acid[29].



Polymethacrylamide[58].

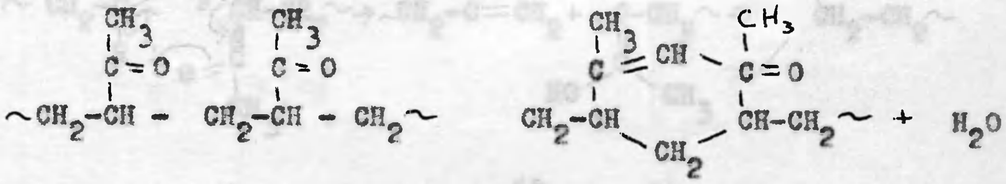


Rubber in presence of a trace of a Friedel Craft catalyst[59].



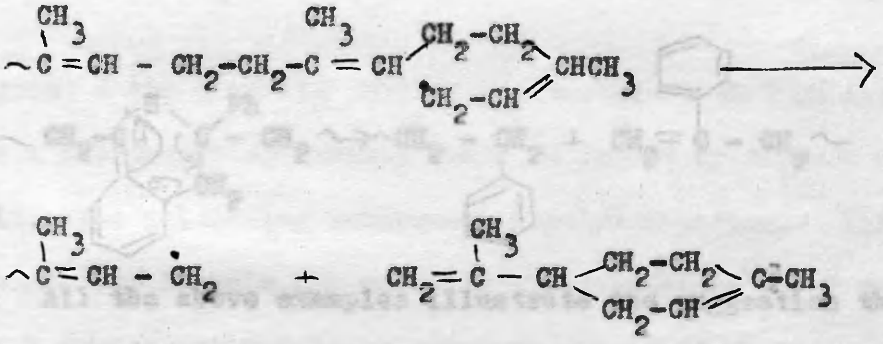
Cyclisation also occurs on vulcanisation of rubber[60].

Polymethyl vinyl ketone[7].



VOLATILE CYCLIC PRODUCTS

Rubber[61].

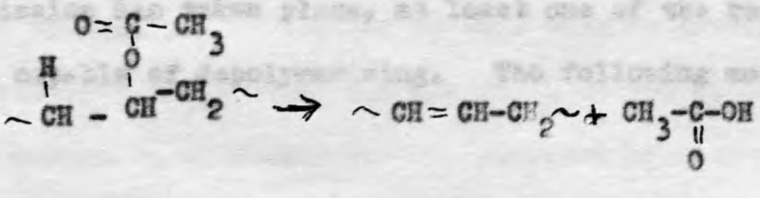


Dipentene

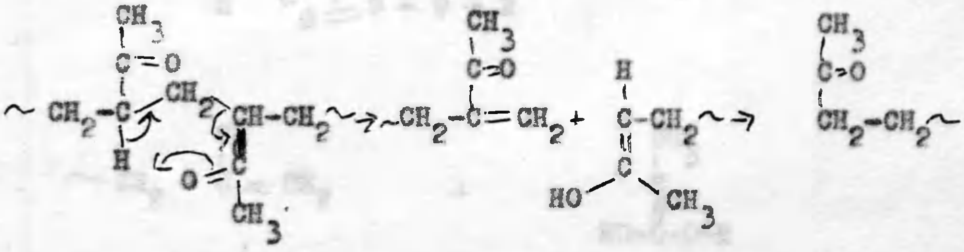
Carothers[62] has shown how aliphatic polyesters on heating in presence of alkali and inorganic chloride catalysts yield large amounts, up to 80 per cent, of cyclic monomeric and / or dimeric esters. The most important factor determining experimental yields is the ring size of the two possible cyclic products, i.e. monomer or dimer.

CYCLIC TRANSITION STATE

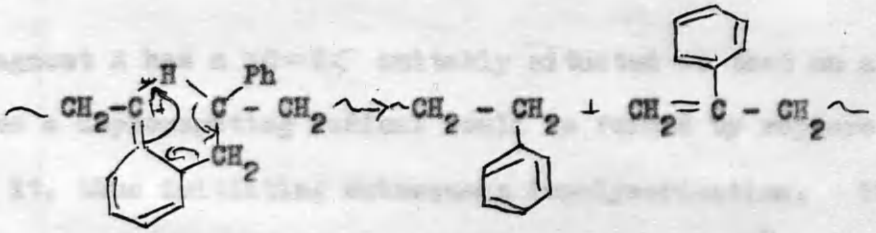
Polyvinyl Acetate[11].



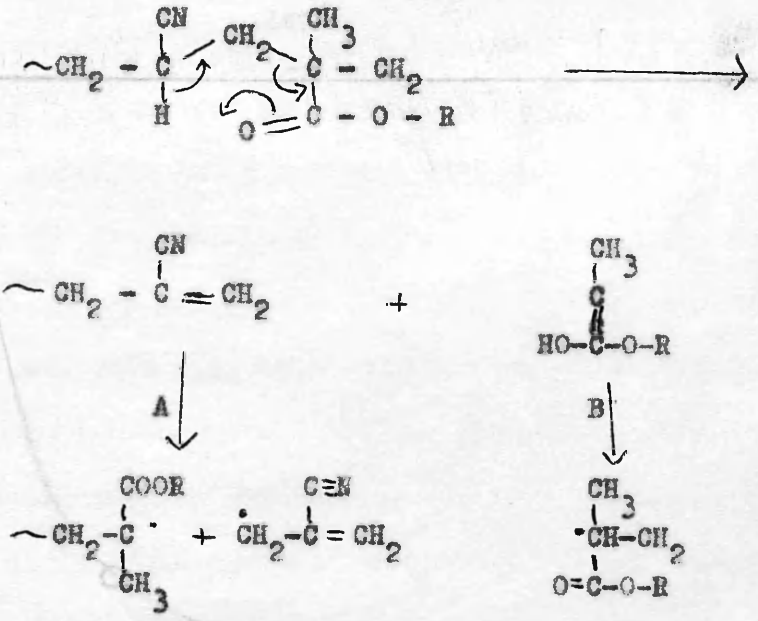
Ultra violet degradation of polymethyl vinyl ketone[6].



Recently Cameron and Grassie[63] have postulated the following mechanism, again involving a cyclic transition state, to account for the break down of their postulated weak links in polystyrene.

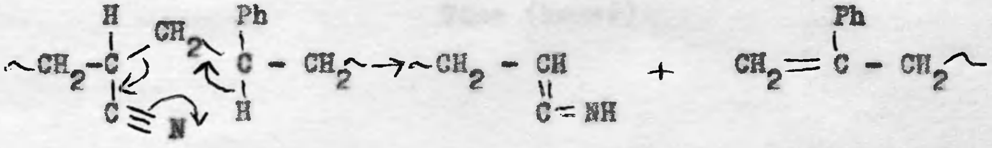


All the above examples illustrate the suggestion that polymer degradation reactions will, if possible, form cyclic products or at least will react through a cyclic transition state, and this may be taken as a guiding principle when elucidating the mechanism of thermal degradation of a polymer. Using this guide a mechanism can now be suggested to explain the observed thermal decomposition behaviour of methyl methacrylate / acrylonitrile copolymers[2]. The methyl methacrylate / acrylonitrile links are found to be thermally the least stable points in the polymer molecule and, once chain scission has taken place, at least one of the resulting chain ends is capable of depolymerising. The following mechanism is suggested,



Fragment A has a $\rangle C=C \langle$ suitably situated so that an allylic radical plus a depropagating radical would be formed by rupture of the bond to it, thus initiating subsequent depolymerisation. This mechanism accounts for Grassie and Melville's observations[2]. B rearranges to give a normal saturated methacrylate end group.

It seems possible that an acrylonitrile unit in a polystyrene chain might also lead to chain scission by a similar type of cyclic mechanism.



Accordingly a copolymer of 150 styrene to 1 acrylonitrile was made by bulk polymerisation at 60°C with no catalyst. The degradation temperature was chosen to be 250°C. Figure 25 shows the change in molecular weight, measured by viscometric methods using

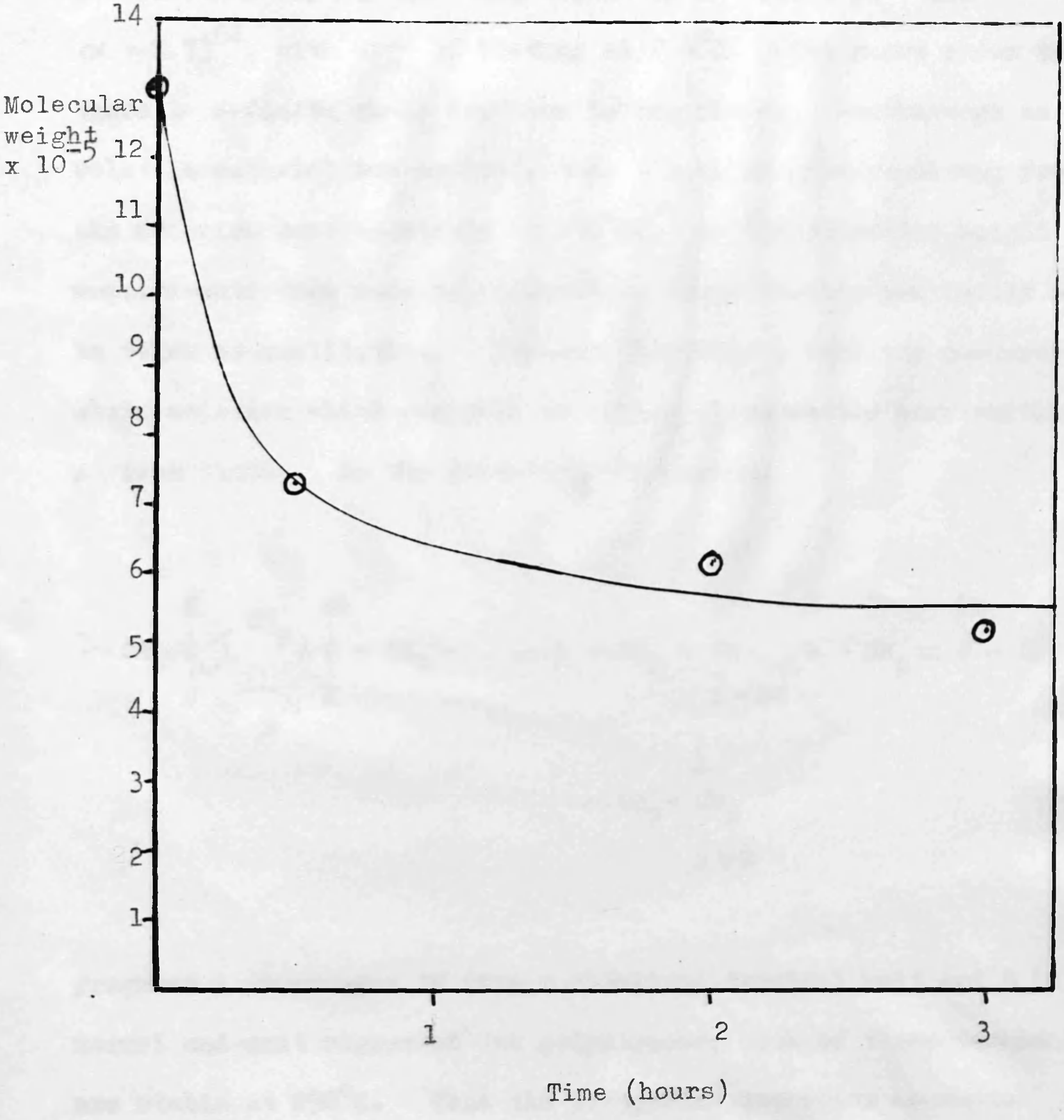
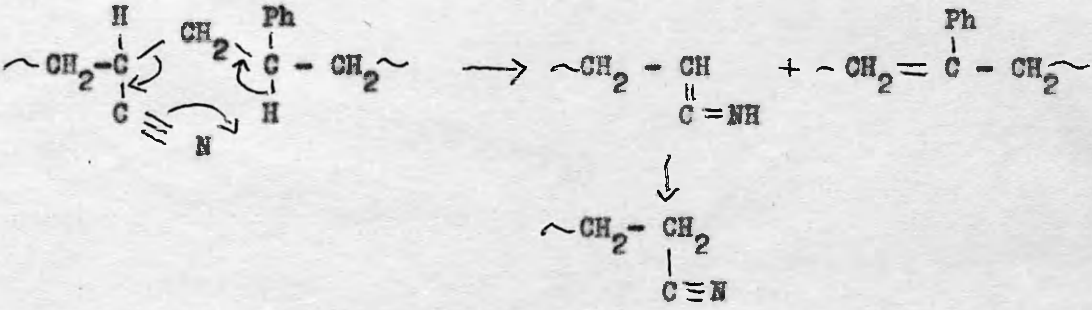


Figure 25. Effect of heating at 250°C on molecular weight of acrylonitirle/styrene copolymer.

the relationship $[\eta] = KM^{\alpha}$ and values of K 1.13 x 10^{-6} and $\alpha = 0.73$[64], with time of heating at 250°C. The curve shows that there is definite chain scission taking place. Furthermore no volatile material was evolved, thus the chain ends resulting from the scission must be stable at 250°C. As the molecular weight measurements were made by viscometry, these results can really only be taken as qualitative. However they show a definite occurrence of chain scission which can only be taking place at the acrylonitrile/ styrene links. In the postulated mechanism,



fragment A rearranges to give a saturated terminal unit and B is the normal end-unit suggested for polystyrene, both of these terminal units are stable at 250°C. Thus the postulated mechanism accounts satisfactorily for the observed facts.

A further demonstration of the preference of a polymer chain to react intramolecularly is contained in the recent work of Butler[65] and Marvel[66] in which they demonstrate the inter/intramolecular polymerisation of bifunctional monomers. The possibility of achieving such a situation depends on the steric requirements of the reacting groups and also on the configuration of the polymer chain. It would be of great interest and value to undertake a series of studies of "cyclisation" reactions within a group of polymers, for instance various substituted polymethacrylamides to examine the steric effects of various substituents. It would also be of value to take one specific reaction such as ester decomposition and study the effect of polymer chain tacticity on the kinetics of such a reaction.

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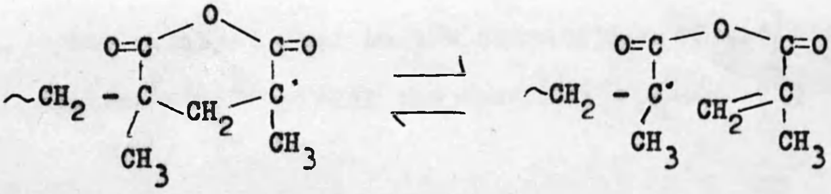
SUMMARY

An investigation of the thermal and photochemical degradation behaviour of poly-n-butyl methacrylate is described in this thesis. The object of the work was to evaluate the velocity coefficients of the various steps in the depolymerisation process with a view to extending kinetic measurements on a depolymerising methacrylate ester as a further method, in addition to polymerisation and copolymerisation, for comparing radical reactivity. The thermal and photochemical depolymerisation of polymethyl methacrylate has already been studied.

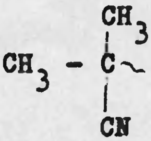
A study of the pyrolysis of poly-n-butyl methacrylate is dealt with. It is shown how the original objective was baulked by the occurrence of an ester decomposition reaction within the n-butyl ester side group. The overall effect of this reaction is to introduce anhydride units into the polymer molecule, which inhibit the depolymerisation process. The following mechanism is proposed for the inhibitive action of the anhydride group.



The extra link to the main polymer chain, via the anhydride function, prevents fast removal of the monomer unit from the vicinity of the depropagating radical and a pseudo equilibrium is set up, preventing further depropagation and stabilising the radical so that it can eventually react with another radical. Further evidence for this mechanism is obtained from a series of degradation experiments involving

copolymers of methacrylic acid and n-butyl methacrylate.

A previous observation that bubbles of gas were evolved during thermal polymerisation of n-butyl methacrylate is followed up and an ester decomposition proceeding by a radical mechanism postulated to account for this reaction. This mechanism is extended to the thermal degradation and tentatively used to account for the large effect which only a few per cent of ester decomposition has on the depolymerisation process.

The photochemical degradation of poly-n-butyl methacrylate is more intensively studied because the reaction is found to involve pure depolymerisation. The mechanism of break down is in general very similar to that of polymethyl methacrylate, involving a chain reaction initiated at the ends of the polymer molecule, followed by unzipping of monomer units until mutual termination takes place. One of the main features of this work is the discovery that the initiator fragments incorporated at the polymer chain end seems to be the centres of initiation. The catalyst used in the preparation of the polymers is 2, 2'- azoisobutyronitrile giving the fragment  $CH_3 - \overset{CH_3}{\underset{CN}{C}}\sim$ as the terminal unit. The stabilising effect of anhydride structures on the photochemical degradation is shown by using copolymers of methacrylic acid and poly-n-butyl methacrylate.

Kinetic analysis of the degradation, both thermal and photochemical, of poly-n-butyl methacrylate is seriously complicated by the measured rate of depolymerisation being proportional to the square root of the weight of polymer sample taken. Possible explanations for this relationship are dealt with, but no completely satisfactory answer can be suggested.