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(i)

A Study of the Thermal Decomposition
of some Styrene Copolymers

A thesis

presented for the degree of

DOCTOR OF PHILOSOPHY

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University of St. Andrews

by

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September 1971

United College of St. Salvator
and St. Leonard, St. Andrews



Tm 5966

DECLARATION

I declare that this thesis is my own composition, that the work of which it is a record has been carried out by myself and that it has not been submitted in any previous application for a Higher Degree.

This thesis describes the results of research carried out at the Chemistry Department, United College of St. Salvator and St. Leonard, University of St. Andrews, under the supervision of Dr. J.R. MacCallum since the 1st. October 1968, the date of my admission as a research student.

KENNETH PATERSON

CERTIFICATE

I hereby certify that Kenneth Paterson has spent twelve terms of research work under my supervision, has fulfilled the conditions of Ordinance No.16 (St. Andrews) and is qualified to submit the accompanying thesis in application for the degree of Doctor of Philosophy.

J.R. MacCallum,
Director of Research

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SUMMARY

Information derived from the thermal degradation of polymers may be used to elucidate the mechanisms by which polymers break down under the influence of heat, and also to compare the thermal stability of one polymer with another. In this thesis, the work is concerned with the thermal degradation of a series of hydrocarbon copolymers. The copolymers provide a tailor-made system, whereby the effect of changing chemical structure on thermal stability can be closely examined. The experimental work is in two parts. In the first part the kinetics of degradation are studied by isothermal thermogravimetry and energies of activation and orders of reaction calculated. The second part of the experimental work is concerned with the analysis of the products of degradation from both a qualitative and quantitative aspect. Finally, the results from both experimental parts are discussed in relation to other systems with similar chemical structures and certain conclusions are reached.

CHAPTER 1

INTRODUCTION

Since the late twenties when the first experiments were carried out on the effect of heat on both natural and synthetic polymers, a great deal of work has been done in the field of polymer degradation. It is not the purpose of this introduction to give an account of all the work done so far, as this would prove an enormous task. However, it would seem appropriate to give an outline of the techniques used in this field, and the problems which they can solve.

From the point of view of gaining more knowledge about polymeric materials, thermal degradation is an extremely useful tool. Information on the molecular structure of a polymer e.g. the basic repeat unit, the nature of the chain ends, and the extent of crosslinking between chains can often be ascertained from experiments in which the effect of heat on the polymer is studied. Methods of thermal analysis can indicate the strength of the bonds within and between polymer molecules, and by identifying qualitatively and quantitatively the products of degradation, in conjunction with the kinetics of degradation, a mechanism can often be proposed that accounts for the way in which the polymer decomposes under the influence of heat.

From a commercial standpoint, the behaviour of polymeric materials when subjected to high temperatures is of great importance. Much work is carried out in industrial laboratories to produce polymers which have specific properties that can be exploited commercially. In these circumstances, the work may be of a less fundamental nature, but the correlation between chemical structure and thermal stability is of prime importance in developing new polymer systems that are of interest to both the industrial and academic worker.

In elucidating the mechanism that operates in the thermal degradation of a polymer there are three aspects which can be examined.

1. The way in which the molecular weight of the polymer changes with temperature and extent of degradation.

2. The products that are produced on breakdown of the polymer, from both a qualitative and quantitative aspect.

3. The rate at which the polymer degrades and the activation energies of the processes involved in the degradation.

1. Molecular Weight Changes

Since a polymer comprises a system of molecules of varying chain lengths, it is necessary to define what is meant by the molecular weight of a sample of the polymer. There are two commonly used definitions of molecular weight, the 'number-average' and the 'weight-average' molecular weights. The number average molecular weight \bar{M}_n is obtained by dividing the total weight of all the molecules in a given polymer sample by the total number of molecules and is expressed as:

$$\bar{M}_n = \frac{\sum_1^{\infty} N_i M_i}{\sum_1^{\infty} N_i} = \sum_1^{\infty} n_i M_i$$

where $n_i = \frac{N_i}{\sum_1^{\infty} N_i}$, and is the number fraction of molecules of molecular weight M_i . This molecular weight can be measured by vapour pressure osmometry, membrane osmometry, end-group analysis, ebulliometry, or cryoscopy.

The weight-average molecular weight arises from measurements wherein the contribution from each molecular weight class of molecules is proportional to the weight of the molecule in that class, and is defined as:

$$\bar{M}_w = \frac{\sum_2^{\infty} N_i M_i^2}{\sum_2^{\infty} M_i N_i} = \sum_2^{\infty} w_i M_i$$

where $w_i = N_i / \sum_2^{\infty} N_i$

The methods used in measuring the weight-average molecular weight are light scattering, sedimentation equilibrium and by means of the ultra-centrifuge.

A method much used both for the comparison of molecular weights and for the determination of absolute values of molecular weights has been that based on the relationship between the solution viscosity of a polymer and its molecular weight. It was found that the intrinsic viscosity of a polymer solution $[\eta]$ can be related to the molecular weight M by the relationship:

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

where K and α are constants for a given polymer/solvent system at a fixed temperature. Thus by calibrating a polymer/solvent system using polymer samples of known molecular weight, the molecular weight of an unknown sample can be determined by measuring $[\eta]$. The viscosity measurements provide either a weight-average or number-average molecular weight depending on the molecular weight average used to obtain K and α by calibration.

In recent years the technique of gel-permeation chromatography has become widely used. This method is based on the selective retention of differing sizes of polymer molecules as they flow down a column. Once again, prior calibration is required for any polymer/

solvent system at a specified temperature. The great advantage of this technique is that it can yield directly the distribution of molecular weights in a polymer sample, which is of importance when considering the nature of the polymer prior to thermal degradation and the nature of the break-down products resulting from the degradation.

The study of molecular weight changes in hydrocarbon polymers having a saturated aliphatic backbone with aromatic or aliphatic side groups attached to the main chain, was a technique used by early investigators of polymer degradation. Jellinek^{1,2}, Grassie and Kerr^{3,4}, and Madorsky and co-workers^{5,6,7} pyrolysed polystyrene in vacuo and measured the molecular weight of the polymer at various stages during degradation. The results showed a rapid drop in molecular weight during the first few per cent loss of weight of the sample, followed by a more gradual drop. In a study of the thermal degradation of polyethylene Oakes and Richards⁸ heated samples of the polymer in vacuo and in nitrogen at atmospheric pressure. The molecular weight of the sample again dropped rapidly during the first few per cent loss of weight and then decreased more slowly. On pyrolysing polymethylene, Wall and co-workers⁹ found similar results. McIntyre and co-workers¹⁰ heated several fractionated and non-fractionated samples of polyisobutylene. They again found a rapid drop in molecular weight during the first 10 per cent loss of weight, followed by a gradual drop. It would appear from these results that the polymer chains are undergoing random scission during degradation.

2. Analysis of the Products of Degradation

Since a knowledge of the products produced under the influence of heat is of prime importance in understanding the breakdown of a polymer, the development of techniques to measure qualitatively and

quantitatively the degradation products has been an important part of the work undertaken in the field of polymer degradation. The first work on the pyrolysis of polystyrene by Staudinger and co-workers^{11,12} employed the technique of the separation of liquid products by fractional distillation. Since, by the very nature of this method, large samples of polymer must be used in the reaction, fundamental objections can be raised. A large sample is very likely to give rise to inhomogeneity in temperature within the sample and will also cause secondary reactions to occur among the degradation products due to their inability to diffuse rapidly from the sample.

The breakthrough in the identification of polymer degradation products came with the advent of mass spectrometry, which allowed very small quantities to be dealt with. Polystyrene was one of the first polymers to be investigated by this technique,^{6,7,16,17,18,19,20,21}. In more recent work by Schueddemaige and Hummel²², the same polymer was pyrolysed within a field-ionization mass spectrometer, a relatively new method in the characterisation of high polymers. Other hydrocarbon polymers that have been studied by mass spectrometry include polymethylene⁷, polyethylene^{23,24}, polypropylene^{7,25} and polyisobutylene²³.

The second major tool which has simplified the work of analysis of degradation products has been gas chromatography. By this technique small samples containing the complete range of degradation products can be separated into their component compounds and identified either by their retention times on the column used for separation, or more conveniently by coupling the gas chromatography system to a mass spectrometer. Lehman and Brauer¹⁵ employed gas chromatography to analyse the degradation products of polystyrene and the same polymer was investigated by this technique by Knight¹⁴ and by Kambe and Shibasaki¹³, who also carried out similar experiments on polyethylene²⁶.

The thermal degradation of polymethylene²⁷ and polyisobutylene²⁸ was carried out by Tsuchiya and Sumi with gas chromatography used to separate and identify the products. There is no doubt that the combination of gas chromatography and mass spectrometry in the analysis of polymer degradation products is a powerful tool and the applications of this technique have been investigated by Neher and co-workers²⁹.

In recent years the technique of pyrolysis-gas chromatography has aroused the interest of workers in the field of polymer degradation. As the name suggests, this method combines a simultaneous pyrolysis of the sample with the chromatographic separation of the breakdown products. In practice, the sample is coated on a wire and placed in the carrier gas stream to the column. The temperature of the wire is then raised very rapidly to a pre-determined reading and pyrolysis of the sample takes place. The volatile products of the degradation are then swept onto the column and separation occurs in the normal way. Qualitatively, the technique has some potential for the characterisation of polymeric materials, but there are still problems to overcome if it is to be used as a reliable quantitative method. Levy³⁰ has reviewed the subject of pyrolysis-gas chromatography and Brauer³¹ has discussed the technique as applied to polymer identification.

3. Rates of Degradation and Activation Energies

In the early work on the rates of thermal degradation of polymers and the activation energies of the processes involved, two methods were most frequently used:

1. The measurement of the pressures of the volatile products of degradation.
2. The measurement of the loss of weight of the polymer sample during pyrolysis.

The first method can only be used in cases where the degrading polymer produces measurable amounts of volatile material. Grassie and Melville³² used this technique to study the rate of monomer production during the thermal degradation of poly (methacrylate). The technique consisted of pyrolysing the polymer in a vacuum system and measuring the pressure of the evolved monomer by means of a Pirani gauge. Prior calibration of the system was achieved by introducing monomer into the apparatus at various rates controlled by a needle valve, collecting it in a liquid air trap, and finally distilling it into a calibrated capillary where it was measured. Using the same apparatus, Grassie and Kerr^{3,4} studied the rates of degradation of polystyrene, and by a similar method Brown and Wall³³ investigated the production of monomer from poly(α -methyl styrene).

The second method mentioned for evaluating rates of degradation and hence activation energies was the study of the loss of weight of the polymer and this is still the most important technique today. In his work on the rates of thermal degradation of polystyrene, poly (α -methyl styrene) and polyethylene, Jellinek² used a quartz-spring balance to follow the weight loss. The apparatus, contained within a vacuum system, consisted of a furnace into which the polymer sample could be lowered, and a calibrated quartz-beam which responded to the loss of weight of the sample. The movement of the beam was observed by a telescope. The rates of degradation of the three polymers were measured at various temperatures and activation energies deduced by plotting the logarithms of the rate constants as functions of the absolute temperature, as given by the Arrhenius equation:

$$k = Ae^{-E/RT}$$

where E is the activation energy

k is the rate constant

A is the pre-exponential constant

R is the gas constant

Madorsky^{5,35} developed a helical tungsten spring microbalance for his work on the rates of degradation by the loss-of-weight method. This consisted again of an electric furnace that surrounded the polymer sample in an evacuated system. The weight-loss of the sample was measured by observing the movement of a vertical tungsten spring that had been previously calibrated. Measurements of the rates of degradation of polystyrene⁵ samples were made using this microbalance and similar experiments were carried out on poly(α -methyl styrene)^{19,36}, polyethylene⁷, polypropylene⁷ and polyisobutylene⁷, and some co-polymers of ethylene and propylene³⁷.

A major step forward in the measurement of weight-loss of polymer samples during pyrolysis, was the development of the electronic microbalance that automatically recorded weight loss and also temperature. Some of the earliest work on polymer degradation using an electronic microbalance was carried out by Madorsky¹⁹ on poly(α -methyl styrene), polymethylene and branched polyethylene. McIntyre and co-workers¹⁰ used a similar instrument to study polyisobutylene.

The availability of commercial microbalances, in some cases incorporating both vacuum and furnace facilities led, during the sixties, to a great expansion in the field of polymer degradation. It was decided that the name 'thermogravimetry' (TG) be used to describe the technique of measuring the weight loss of a sample as a function of temperature, and the potential of the method as a means of evaluating the kinetics of polymer degradation soon became apparent. An innovation on earlier weight-loss methods was the introduction of

furnaces that permitted polymer samples to be heated at linearly increasing temperature rates. This overcame the experimental difficulty of minimizing the time taken for a polymer sample to reach the selected temperature during degradation under isothermal conditions, a serious problem at higher temperatures. Many authors have discussed the application of thermogravimetry to the study of polymers and their decomposition kinetics. Doyle³⁸ was among the first workers to look at the stability of polymers by thermogravimetry, and Chiu³⁹ has reviewed the applications of thermogravimetry to the study of high polymers. The kinetics of polymer degradation have been investigated by, among others, Anderson⁴⁰, Flynn and Wall^{41,42}, Friedman⁴³, Florentine and Schroeder⁴⁴, Mickelson and Einhorn⁴⁵ and Osawa⁴⁶, who investigated the thermal degradation of polypropylene in air and in vacuo. Igarashi and Kambe⁴⁷ have described a thermogravimetric study of polyethylene using an automatic recording thermobalance, and similar studies on a series of hydrocarbon condensation co-polymers, of the type investigated in this thesis, have been described recently by MacCallum and co-workers⁴⁸.

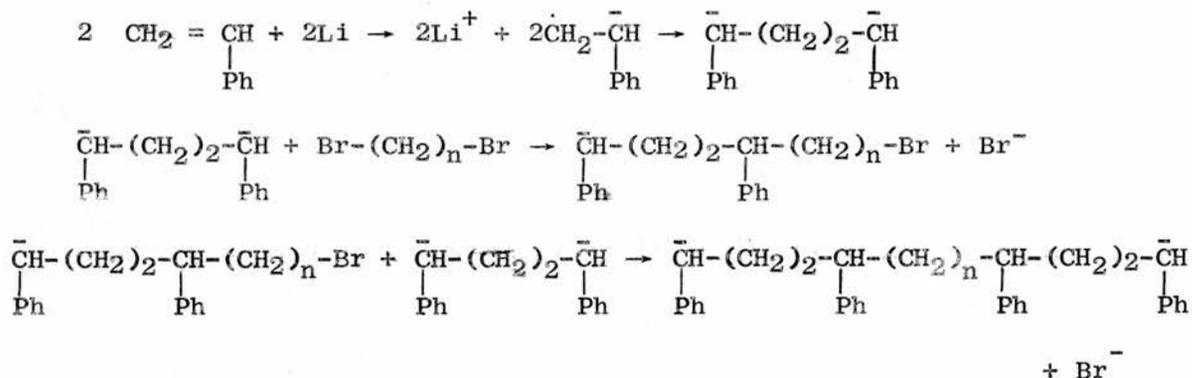
The early work on polymer pyrolysis necessitated separate experiments for the analysis of the products of degradation and the kinetics of degradation. With increasing sophistication in instrumentation it became possible to combine both of these aspects of the work, and in 1968 Chiu¹⁹ described a system of coupled thermogravimetry and gas chromatography for polymer characterisation. This has been followed by Chang and Mead⁵⁰ who in a recent paper described a system incorporating a thermogravimetric analyser, gas chromatograph and high resolution mass spectrometer.

CHAPTER 2

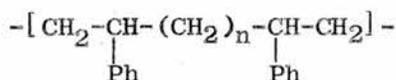
EXPERIMENTAL

1. Synthesis of the Copolymers

The copolymers studied in the work in this thesis were originally prepared by Richards and co-workers⁵¹ who devised a new technique for the synthesis of regular copolymers based on the 'living' polymer method of polymerisation developed by Szwarc.^{52,53} The method involved the production of an initiating dianion ($\bar{M}-M^-$) from a vinyl monomer (M) by the reaction of an alkali metal or alkali metal alloy. Subsequent reaction with a dihalide (X-R-X) yielded regular copolymers with the repeat unit $-(M-R-M)-$. The copolymers under consideration in this thesis were prepared using styrene as the vinyl monomer, lithium as the alkali metal, and a homologous series of dihalides of the type $Br-(CH_2)_n-Br$ where $n = 1, 2, 3, 4$ and 5 . The reaction can be formulated as:



The reaction thus produces a polymer with the repeat unit:



Dr. D.H. Richards kindly made a gift of these and other similar copolymers to this laboratory in order that work could be carried out on their thermal degradation.

As part of the work in this thesis it was decided to repeat the synthesis of the $n = 5$ copolymer using the materials and method described in the paper⁵¹ mentioned previously.

(i) Purification of materials

Styrene monomer was shaken with sodium hydroxide to remove the stabiliser and then washed several times with distilled water. It was dried by standing over molecular sieves and magnesium sulphate, before being distilled under vacuum.

The 1,5-dibromopentane was dried over molecular sieves and purified by vacuum distillation.

Lithium used in the preparation was washed in petroleum ether and then ethanol.

The solvent, tetrahydrofuran, was purified by the addition of lithium aluminium hydride and finally distillation. Sodium wire was added to the tetrahydrofuran to ensure that it remained dry.

(ii) Experimental Method

The lithium metal (0.8 mol) in the form of small pieces was added to the tetrahydrofuran (500ml), while it was being stirred under nitrogen, in a one-litre three necked round bottom flask. After a few minutes a mixture of styrene (0.4 mol) and 1,5-dibromopentane (0.2 mol) in tetrahydrofuran (20ml) was added. The reaction was allowed to proceed for about four hours during which time the solution became opaque due to the formation of lithium bromide. The temperature of the reaction was not rigorously controlled but an ice-water bath was kept around the flask, and the temperature inside the flask did not exceed 30°C. After four hours the excess lithium was removed from the flask and the solution filtered. About half the solution by volume was placed in a dropping funnel and allowed to drip slowly into a beaker containing 2 litres of methanol. The methanol was agitated by a vibrating stirrer. The polymer that precipitated out was filtered off and found to be very 'sticky' and difficult to dry. It was decided to see if the precipitation could be improved by cooling the methanol in an ice bath. The second

fraction from the reaction solution was then treated in the same way as the first except that the methanol was now chilled. This time, the polymer precipitated out in the form of a fine white powder which could be easily dried. The polymer from both fractions was dissolved in chloroform and the precipitation procedure in cold methanol repeated three times. After filtration the polymer was dried for two days in a vacuum oven at room temperature. The weight of dried polymer was 51.5% of the theoretical yield.

The remaining copolymers with $n=1,2,3$ and 4 , which had been given to the laboratory, were each dissolved in chloroform, precipitated in methanol and dried at room temperature in the vacuum oven.

2. Characterisation of the Copolymers

(i) Microanalysis

A microanalysis was performed on each copolymer to determine the carbon and hydrogen content. The results of the analyses are shown in Table 1.

Table 1

Copolymer	Theoretical Composition		Results of Analyses	
	% C	% H	% C	% H
n = 1	91.89	8.11	91.75	8.39
n = 2	91.53	8.47	91.12	8.02
n = 3	91.20	8.80	89.78	9.07
n = 4	90.91	9.09	89.49	9.36
n = 5	90.65	9.35	90.05	9.63

Since the theoretical compositions of the copolymers are very similar to each other, and the error in the analysis for each element is 0.3%, the microanalyses do not yield much information

on the characterisation of each copolymer. They do however show that the sum of the carbon and hydrogen percentages in each case is very close to 100%, indicating that very little residual chloroform or methanol can be present.

(ii) Infra-red Spectroscopy

The infra-red spectra of the copolymers were recorded on a Perkin-Elmer 257 grating infra-red spectrophotometer. A film of each copolymer on a potassium bromide disc was obtained by evaporating off the solvent from solutions of the copolymers in spectroscopic carbon tetrachloride. The spectra were all very similar to the spectrum of polystyrene except for the relative intensities of the peaks, which change as the proportion of methylene groups change.

In order to determine whether the assumption of a repeat unit of the form $-\text{[CH}_2\text{-CHPh-(CH}_2\text{)}_n\text{-CHPh-CH}_2\text{]}-$ was a valid one, Richards and co-workers⁵⁴ recorded the infra-red spectra of the copolymers with $n = 1, 2, 3, 4, 5, 6$ and 10 at three different solution concentrations in carbon tetrachloride. Using a Perkin-Elmer 337 grating Spectrophotometer, peak heights were measured at 1500, 2925 and 3025cm^{-1} . These frequencies corresponded to C = C skeletal in-plane vibrations, CH_2 stretching and = C-H stretching frequencies respectively. The absorbances were found to obey Beer's Law, and after correction for the different aromatic and aliphatic content of the copolymers as predicted by the repeat unit shown previously, the logarithms of the relative extinction coefficients were plotted as a function of n .

It was found that the relative extinction coefficients of the two aromatic absorptions i.e. at 1500 and 3025cm^{-1} remained constant and independent of n . This was also true for the CH_2 stretching absorption at 2925cm^{-1} except in the case of $n = 2$ where the relative

extinction coefficient showed a significant drop from the other values of n . This discrepancy in the case of the $n = 2$ copolymer will be dealt with after the ^1H n.m.r. spectra have been described. For the remaining copolymers in the series $n = 1$ to 5 however, the quantitative analysis of the infra-red spectra seems to support the initial assumption for the repeat unit $-\text{[CH}_2\text{-CHPh-(CH}_2\text{)}_n\text{-CHPh-CH}_2\text{]}-$.

(iii) Nuclear magnetic resonance spectroscopy

^1H n.m.r. spectra were obtained in this laboratory using a Perkin-Elmer R10 60 MHz spectrometer. Spectroscopic carbon tetrachloride was used as the solvent and chemical shifts were measured with respect to tetramethylsilane as an internal standard. A similar instrument was used by Richards et al.⁵⁴ in their work on the copolymers. In addition to carbon tetrachloride, they also used carbon disulphide as a solvent, and again tetramethylsilane was used as an internal standard.

The ^1H n.m.r. spectra of the copolymers are shown in Figure 1. Each spectrum has the same general characteristics of an aromatic region due to the phenyl protons at about 3τ and a region due to the aliphatic protons between 7 and 9τ . The characterisation of each copolymer should be possible by measuring the ratio of the aliphatic to aromatic protons and comparing the results with the theoretical values based on the assumption of the repeat unit described previously. This ratio was calculated for each copolymer and is shown in Table 2, together with the theoretical values and the experimental results obtained by Richards and co-workers.⁵¹

60 MHz ^1H n.m.r. spectra of the copolymers

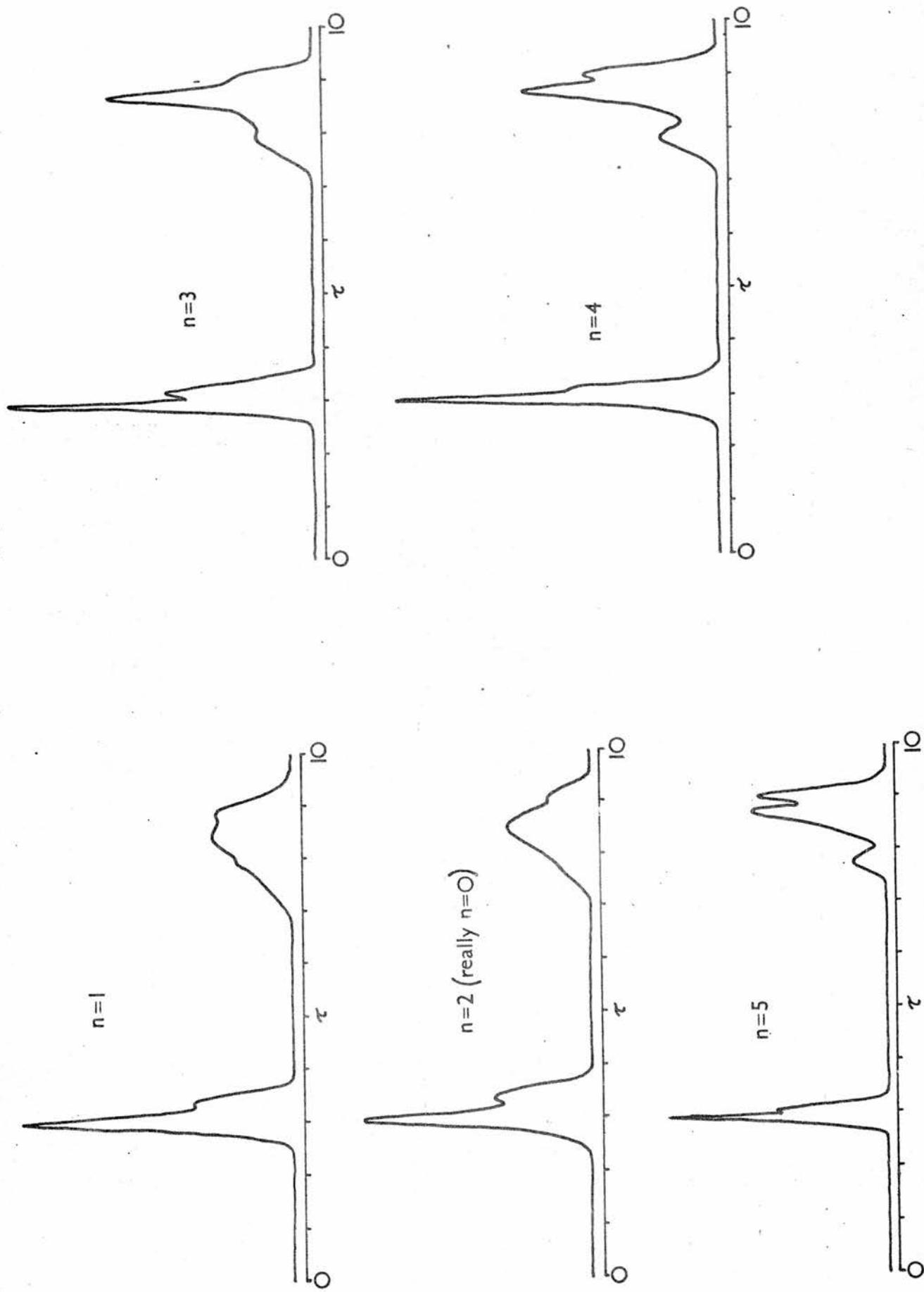


Figure 1.

Table 2

Copolymer	Aliphatic/Aromatic H ratio		
	Theory	Experimental (a)	Experimental (b)
n = 1	0.82	0.70	0.82
n = 2	1.00	0.65	0.70
n = 3	1.20	1.10	1.18
n = 4	1.40	1.33	1.35
n = 5	1.60	1.60	1.50

(a) Values obtained in this laboratory. (b) Values obtained by Richards et al.⁵¹

The agreement between the theoretical and experimental values is close for all the copolymers except n = 2. The experimental values for n = 2 are very close to the theoretical value of 0.60 to be expected for n = 0, i.e. for the case of head-to-head polystyrene. This evidence supports the results obtained in the quantitative infra-red analysis⁵⁴ of the copolymers. Richards and Scilly⁵⁵ found that whenever a vicinal dihalide was used in the preparation of one of these copolymers, the aliphatic/aromatic H ratio in the ¹H n.m.r. spectrum of the polymer was very close to the value expected from the homopolymer. These results have been interpreted⁵⁵ as indicating that a head-to-head linked homopolymer is produced with elimination of the vicinal dihalide as the equivalent olefin. In the series of copolymers under consideration in this thesis, the copolymer originally designated as n = 2 is thus really head-to-head polystyrene and will be referred to in the remainder of the thesis as n = 0.

On the basis of several readings for each copolymer, Richards et al.⁵⁴ assigned the aliphatic peaks in the ¹H n.m.r. spectra to

the different proton environments present in each repeat unit. Table 3 shows these results with the assigned protons underlined.

Table 3

Peak Number	Average τ value	Assignment
(1)	9.00	-CH ₂ - <u>CH</u> ₂ -CH ₂ -
(2)	8.70	-CH ₂ - <u>CH</u> ₂ -CHPh-
(3)	8.40	-CHPh- <u>CH</u> ₂ -CHPh-
(4)	7.80	-CH ₂ - <u>CH</u> Ph -

These average τ values can be compared with the experimentally measured values for the five copolymers shown in Table 4. The numbers in brackets after the τ values refer to the peak numbers in Table 3.

Table 4

Copolymer	τ value of aliphatic peaks	τ value of aromatic peaks
n = 0	9.0 (2)	3.45
	8.5 (2)	3.0
	7.7 (4)	
n = 1	8.9 (2)	3.33
	8.4 (3)	2.97
	7.9 (4)	
n = 3	9.1 (1)	3.1
	8.75 (2)	2.93
	8.0 (4)	
n = 4	9.0 (1)	3.05
	8.7 (2)	2.93
	7.8 (4)	
n = 5	9.0 (1)	3.05
	8.7 (2)	2.92
	7.75 (4)	

Richards et al⁵⁴ have examined the ^1H n.m.r. spectra of the copolymers, and the features that vary in them as a function of n . In the region of the spectra ascribed to aromatic protons, the smaller peak moves from a value of 3.45τ when $n = 0$, to a shoulder of the main peak at $n = 5$. Bovey et al⁵⁷ have observed two peaks at 3.0 and 3.4τ in the aromatic region of the ^1H n.m.r. spectrum of polystyrene. They have ascribed the former to the meta- and para-hydrogens and the latter to the ortho-hydrogens. The shift to high field in the case of the ortho protons has been explained as a result of the increased shielding experienced when adjacent phenyl groups are orthogonal to one another. In this situation, the ortho protons of one ring lie above the centre of the π -electron clouds of neighbouring rings and the diamagnetic field induced by the ring currents gives rise to a shift to high field.⁵⁸ As n increases in value the two phenyl groups in the repeat unit become further apart from the phenyl groups in neighbouring repeat units and the size of the shift decreases. It has been shown⁵⁴ that when $n \geq 6$ only a single peak is present in the aromatic region of the spectra.

The peak with an average value of 9.0τ , number (1) in Table 3, increases in intensity as n increases and has therefore been assigned⁵⁴ to the configuration $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$. The peak at 8.4τ , number (3) in Table 3, only appears in the case of $n = 1$ and has thus been assigned to the group $-\text{CHPh}-\text{CH}_2-\text{CHPh}-$ as in head-to-tail polystyrene⁵⁷. The assignment of the remaining two peaks in Table 3, numbers (2) and (4), are consistent with the data for similar small molecules.

(iv) Molecular weight data

In their work on the copolymers, Richards and co-workers⁵⁶ reported that the molecular weights of the samples, obtained by

the method described previously, were of the order of 10,000. This value was confirmed by results obtained using gel-permeation chromatography on the samples with $n = 1$ and $n = 5$.

3. Thermogravimetry

The method of measuring the rate of degradation of a polymer sample by 'weight-loss' was described in the introduction. The various techniques that have been used to follow this parameter were also mentioned. Before describing the system used in the work in this thesis, it would be appropriate to look at the various difficulties that occur in measuring the weight and temperature of a sample during thermal degradation, and the steps that can be taken to try and minimise the errors that may arise.

(a) Errors that arise in weighing

(i) Premature loss of sample

If some of the sample is lost due to the ejection of solid or liquid material from the reaction vessel this will obviously have a drastic effect on the weight-loss measurements. In the thermal degradation of polymers, sputtering can lead to anomalous results, while in the pyrolysis of inorganic salts virtually explosive reactions may occur due to the evolution of large quantities of volatile gases. These effects, when not too violent, can be overcome by the use of small samples and conical containers, which are wider at the base than at the top. The covering of samples with a layer of an inert powder has also been used.

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(ii) Chemical attack on the sample vessel

The chemical reaction of the sample vessel with either the sample, or any of the products produced on thermal degradation of the sample, will lead to spurious results. The best methods to prevent this

happening are to use a sample vessel that is resistant to chemical attack under the conditions of the experiment, and to remove any potentially reactive volatile products from the vicinity of the vessel as soon as they are formed. The latter procedure is most usually effected by the use of a vacuum system.

(iii) Buoyancy and Aerodynamic effects

When the thermal degradation of a sample is carried out in a controlled atmosphere serious error can arise due to the 'buoyancy' effect of the gaseous molecules in the atmosphere altering the apparent weight of the sample. Among those who have investigated buoyancy effects are Newkirk⁶⁰, and Lukaszewski⁶¹, while the problems of thermogravimetry carried out in flowing gases have been studied by Sharp and Mortimer.⁶² Buoyancy problems can be overcome by carrying out the thermal degradation at low pressures using a vacuum system. Even in an evacuated system however, errors may arise in sample weighing. Friedman⁶³ has used a vacuum micro-thermobalance to evaluate the errors caused by molecular lift effects while Poulis and Massen⁶⁴ have explained spurious mass changes in vacuum thermogravimetry from the standpoint of Knudsen forces caused by temperature gradients in the balance case.

(iv) Geometry of sample holder and sample size

The sample holder used in the experiments described in this thesis was cylindrical and made of glass. Experiments using this actual thermobalance system with different shaped vessels, showed no significant changes in weight-loss measurements.⁶⁵ A 50mg sample was used for each run on the thermobalance, and again, previous experiments⁶⁵ using 25mg, 50mg, and 75mg samples showed that within the limits chosen, changing the sample weight had no significant effect

on the results. In a review on thermogravimetry, Tourse⁶⁶ has discussed the effect of sample size and container shape on results obtained in weight-loss experiments, and Lukaszewski⁶¹ has recommended a crucible to sample weight ratio of 20:1 for work in controlled atmospheres. The ratio of the crucible to sample weight in the work in this thesis was almost 20:1.

(v) Condensation of volatile material on the weighing system

In almost all types of thermogravimetry this can be a serious source of error. Degradation products that are volatile at the temperature of the pyrolysis but involatile at ambient temperature can condense anywhere on the balance system. Soulen and Mockrin⁶⁷ have attempted to minimise this by enclosing the rise-arm supporting the sample holder in a metal sleeve. In the work in this thesis, the effect of volatile condensation was reduced by cooling the apparatus in the region adjacent to the furnace, by means of a water jacket (see Figure 2). This resulted in most of the degradation products that were involatile at ambient temperature, condensing on the walls of the glass tube and not on the rise-arm of the balance.

(b) Errors concerned with temperature measurement

(i) Due to the atmosphere

As with weight-loss measurements, excessive or variable gas flow rates can lead to errors in the measurement of temperature. The use of a vacuum system again largely overcomes this problem.

(ii) Due to the position of the thermocouple

Doyle⁶⁸ has noted that in modern thermobalances the thermocouple used to measure the temperature is not normally placed within the sample. This immediately raises the difficulty of accurate temperature measurement. Friedman⁶³ has described a system in which

the thermocouple used to measure and control the temperature was spot welded to a pan which was placed so as to be in a zone where the temperature would be equal to that of an empty sample pan. For accurate specimen temperature measurement, Chatfield⁶⁹ placed a noble metal thermocouple in contact with the sample and used the stainless steel split planes and knife edges of the balance mechanism to provide a conducting path from the thermocouple to a potentiometric recorder. In the thermobalance used for the work in this thesis, the thermocouple measures the temperature just above the sample surface (see Figure 2). Previous work in this laboratory⁷⁰ indicates that the temperature read-out from a thermocouple in this position shows little measurable difference from that of a thermocouple placed in an empty sample holder during a dummy run. This of course does not take into account the heat of reaction. Although this may cause inaccuracies in the temperature measurement it was not thought to be a significant factor for such small samples (50mg), and relatively slow reaction rates.

Errors concerned with chart record and speed

Lukaszewski⁷¹ has dealt in some detail with the errors that can arise from such sources as shrinkage in the chart and non-linearity in the chart speed. The former problem can easily be overcome by not starting a run with a new roll of chart paper until it has had time to "dry-out" in the warm air from the electronic circuits in the recording mechanism. Non-linearity in the chart speed can easily be checked by timing with a stop watch.

4 The Apparatus - The Stanton Massflow Balance

The thermobalance used in the work in this thesis was a Stanton Massflow Thermobalance purchased from Stanton Instruments Ltd.,

Copper Mill Lane, London S.W.17. Model number MF-L5. The balance has the following specifications:

Sensitivity: 0.2mg per smallest chart division.

Chart Range: 20mg full scale.

Maximum loading: 200mg.

Maximum rate of weight change: 80mg per minute.

Capacity: 20g.

Maximum furnace temperature: 1000°C.

The vacuum equipment consists of a 5 in. water-cooled baffle valve N.G.N. three-stage oil diffusion pump, backed by a single stage air ballasted N.G.N. rotary pump. There are electromagnetic air/gas admittance valves connected to a 'no-volt' drop-out relay. There are two pressure gauges, a thermomcouple gauge for high pressures ($760-10^{-3}$ torr) and a Penning ionisation gauge for lower pressures ($10^{-2}-10^{-6}$ torr).

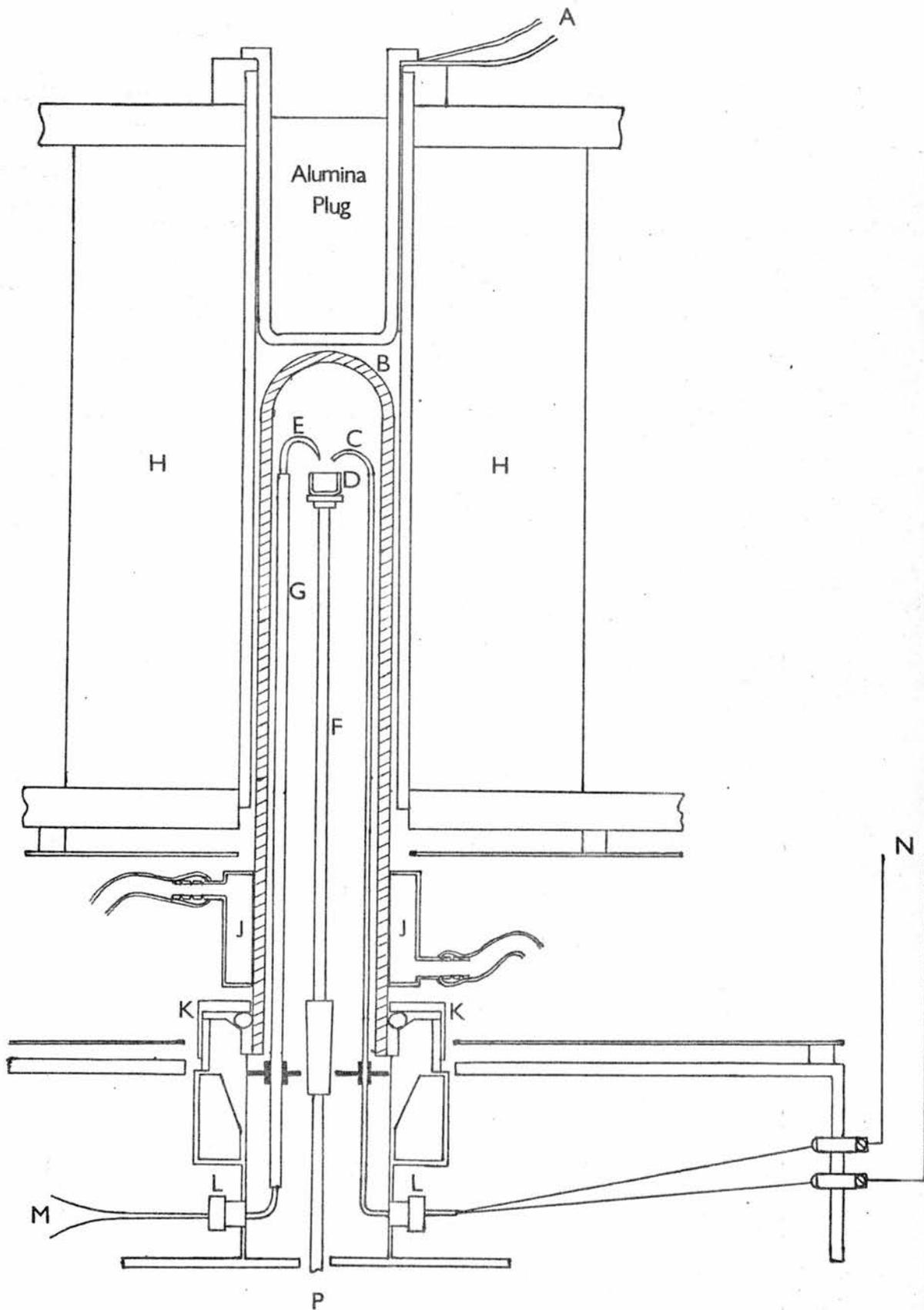
The two figures (Figures 2 and 3) show the furnace and thermocouple arrangement, and the relationship between the inner and outer beams of the weighing system. Figure 2 includes some modifications which will be dealt with after a description of Figures 2 and 3.

Figure 2. The furnace and thermocouple arrangement

- A. Ni-Cr/Ni-Al thermocouple connected to a temperature controller (see modifications to the balance),
- B. 'Pyrex' glass tube,
- C. self-supporting Pt/Pt 13% Rh thermocouple,
- D. glass sample holder,
- E. Ni-Cr/Ni-Al thermocouple,
- F. rise-arm supporting the sample and supported by the balance,
- G. twin-bore quartz tube, insulating support for the Ni-Cr/Ni-Al thermocouple,

Figure 2.

The Stanton Massflow Balance
Furnace and Thermocouple arrangement



- H. nichrome bifilar wound furnace,
- J. water-jacket,
- K. vacuum seal assembly for the glass tube ('O'-ring shown),
- L. vacuum glands leading thermocouple wires from the vacuum to atmospheric pressure,
- M. Ni-Cr/Ni-Al thermocouple wires attached via a cold junction at 0° C to the potentiometer (see modifications to the balance),
- N. Pt/Pt 13% Rh thermocouple wires attached via a cold junction at 0° C to the potentiometer (see modifications to the balance),
- P. compartment containing the inner beam under vacuum.

Figure 3 The inner and outer beams of the weighing system

- Q. inner beam,
- R. a pair of pole-opposed magnets,
- S. outer beam,
- T. air damper,
- U. vanes of the variable capacitor,
- V. rod connecting capacitor plate to the servo motor.

A description of the temperature recording equipment will be given when the modifications to the balance are discussed.

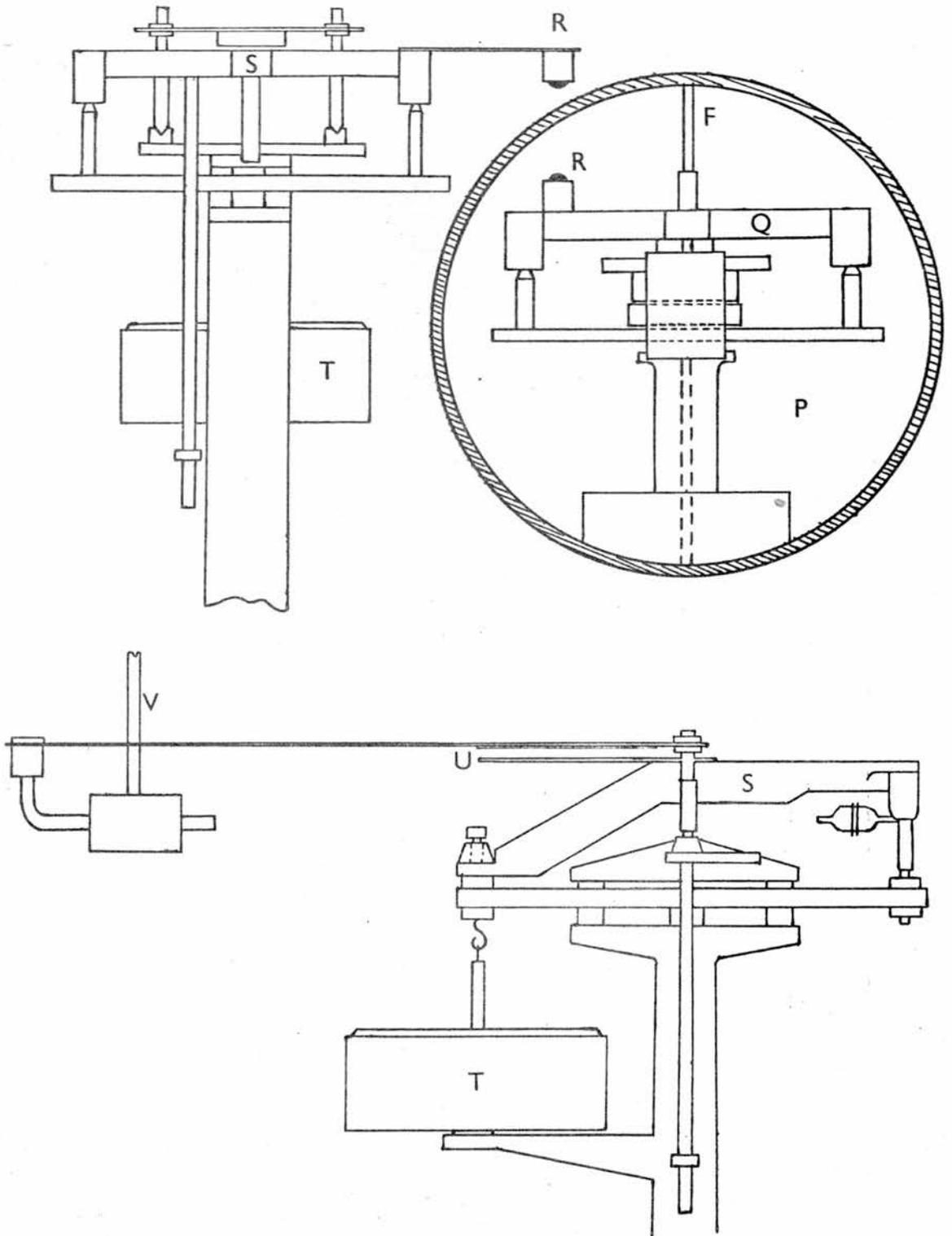
The description⁶⁵ that follows deals with the weighing system of the balance.

The rise arm [F] is carried on the stirrup above the knife-edge of the inner beam [Q]. As the beam operates on a constant load mode, ring weights (20mg each) are added after every 20mg loss of weight (or one complete traverse of the chart scale). The end of the inner beam [Q] carries a small magnet [R] which is in opposition to

Figure 3.

The Stanton Massflow Balance

Inner and Outer Beams of the weighing system



another magnet [R] of the same polarity on the outer beam [S]. The main vacuum chamber (cross hatched shading in Figure 3) comes between the two magnets, but being made of copper, does not affect their operation. The beams are poised to keep the magnetic link in compression.

The outer beam [S] carries one plate of a variable capacitor [U] the other plate of which is connected via a rod [V] to a servo-motor. The electronic chassis (not shown) carries an R.F. bridge circuit which is balanced when the capacitance between the two plates is equal to a preselected value. When there is a weight change, the bridge circuit goes out of balance (through the magnetic link sequence), and energises the servo-motor. The servo-motor then restores capacitative balance through the rod and the lower capacitor plate. Simultaneously the motor moves the recorder pen across the chart. When calibrated correctly, the full scale movement across the chart is 20mg. A micro-switch is attached to the rod, and when the pen reaches the edge of the chart on full scale deflection, another motor system is switched on which places a 20mg weight on the inner beam [Q]. The cycle is then repeated.

5 Modifications to the balance

(i) Changes that affected the weighing system

A cylindrical glass container [D] with the following dimensions was used as the sample vessel: I.D. = 10mm, O.D. = 12.3mm, height = 10mm. It was baked out in vacuum before use, and the base was ground down to a flat surface that provided good frictional contact with the head of the balance rise-arm.

A brass water-jacket [J] was placed around the glass tube below the furnace. This resulted in involatile degradation products

condensing out on the inside of the glass tube and not on the rise-arm or other parts of the balance mechanism where they would have produced a weight gain.

(ii) Modifications to the furnace and thermocouple arrangement

The heating system supplied with the balance, in which the temperature was programmed to rise linearly at about $5.5^{\circ}\text{C}/\text{min.}$, was dispensed with entirely. It was replaced by a 'Transitrol' potentiometric indicating temperature controller, series 12-91B, supplied by Ether Ltd., Caxton Way, Stevenage, Herts. The temperature was monitored by a Ni-Cr/Ni-Al thermocouple ([A] in Figure 2), and could be set in the range $0-500^{\circ}\text{C}$. The thermocouple [A] was fitted between the wall of the furnace and the alumina plug so that the tip of the thermocouple was about 1cm from the bottom of the plug. The original Pt/Pt 13% Rh thermocouple which had occupied the position now taken up by [A] was used as a cold junction for the thermocouple [C] by setting it up in an ice-bath at 0°C . The output voltage from this thermocouple system was monitored by a Pye Universal Decade potentiometer and a solid-state battery galvanometer. This potentiometer was able to record temperatures to an accuracy of 0.2°C .

In order to obtain more sensitive temperature measurements a Ni-Cr/Ni-Al thermocouple [E] was installed, supported near the sample by a twin-bore quartz tube [G]. The wires from this thermocouple were taken out of the vacuum chamber through a vacuum gland [L] sealed with 'Araldite'. Once again this thermocouple was set against a similar thermocouple acting as a cold junction at 0°C and the output voltage from the system was measured by the same potentiometer described previously. Since in the region from $0-500^{\circ}\text{C}$

the output voltage of the Ni-Cr/Ni-Al thermocouple is 20.7 mv. compared with only 4.2 mv. from the Pt/Pt 13% Rh thermocouple the accuracy of temperature measurements is enhanced by using the Ni-Cr/Ni-Al thermocouple.

(iii) Other modifications

The mullite tube supplied with the balance was replaced by a 'Pyrex' glass tube of similar dimensions. This was done primarily in order that the sample could be observed on the rise-arm of the balance prior to the furnace being pulled down.

A liquid air trap was inserted between the oil diffusion pump and the rotary pump to remove undesirable vapours.

6. Operational procedure used with the Stanton Massflow Balance

The following procedure was adopted for each run on the balance and was evolved after consideration of the factors involved in making accurate measurements of both the weight and temperature parameters.

Before each run, the rise-arm [F] and 'Pyrex' glass tube [B] were cleaned thoroughly and dried. 50mg of sample which had been kept under vacuum in a desiccator were placed in the previously weighed sample container [D]. The container and sample were positioned on the rise arm and the glass tube replaced over the rise-arm and thermocouples. The 'O'-ring seal [K] was tightened down, the rotary pump switched on, and the water-jacket [J] slid over the glass tube. As the pressure in the system dropped, the liquid nitrogen trap was filled up, and at a pressure of 0.2 torr the oil diffusion pump was switched on. When the pressure in the system was recorded as 10^{-6} torr on the Penning ionisation gauge, the chart motor was switched on and the balance mechanism released from the 'arrest' position allowing it to move freely on the knife edges. The chart was set to run at 6 in/ hour and the pen recording the weight change of the sample placed in

contact with the chart.

Meanwhile, the thermocouple [A] had been placed against the wall of the furnace [H], which was in the 'up' position above the glass tube. The alumina plug was inserted in the top of the furnace so that the thermocouple fitted tightly between the plug and the furnace wall, but did not protrude below the bottom of the plug. The temperature controller, connected to the terminals on the furnace, was set to the desired temperature and switched on. A digital voltmeter was used to monitor the output of thermocouple [A], allowing the temperature rise of the furnace to be followed. Thermocouples [C] and [E] were connected, via their respective cold junctions (0°C), to the potentiometer.

It was found by experience, that after about an hour had elapsed since the switching on of the furnace and the vacuum system, the temperature of the furnace was steady to within 1 degree and the weight reading shown on the chart was constant. This weight reading (I) was recorded at room temperature and at a pressure of 10^{-6} torr on the Penning ionisation gauge.

The furnace was then pulled down around the glass tube such that it rested on two springs just above the water-jacket [J]. The rise in temperature of the thermocouples [C] and [E] were followed with the potentiometer, while the loss in weight of the sample was automatically followed by the balance. Temperature readings were taken about every minute until isothermal conditions were achieved and were then checked about every 10 minutes. The difference in temperature recorded by thermocouples [C] and [E] was always found to be less than 1 degree while the actual temperature throughout the run was steady to within ± 1 degree.

After about 90% weight-loss of the sample, the balance mechanism was arrested and the furnace raised to the 'up' position and switched off. The balance mechanism was released, and the weight-trace recording allowed to proceed until the glass tube had cooled to room temperature, or until no further change in weight of the sample could be detected. The reading (II) of the weight-trace was then noted, the balance mechanism arrested, and the vacuum released after first switching off the oil diffusion pump and allowing it to cool to room temperature.

The sample container was removed from the rise-arm and reweighed, allowing the weight of the residue to be calculated. The difference between readings (I) and (II), plus the weight of the residue was taken as the true initial weight of the sample, w_0 .

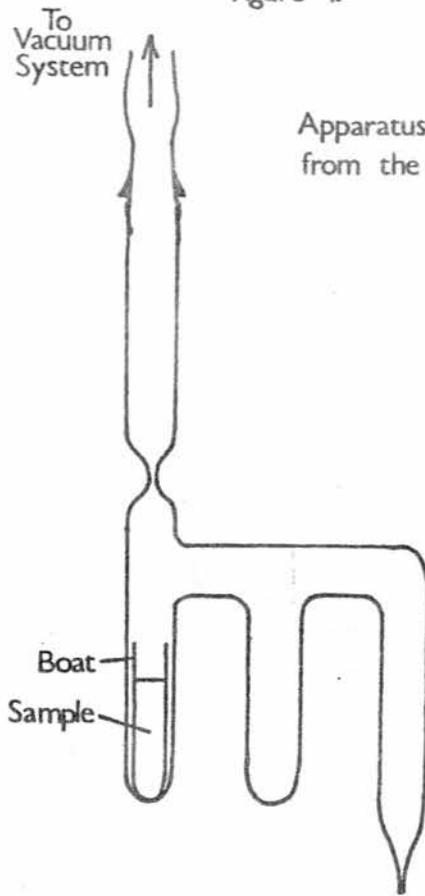
The weight-trace was then taken and the points marked on it corresponding to the following percentage degradation: 10,20,30, 40,50,60,70,80 and 90. At these points the rate of loss of weight was calculated by measuring the slope of the weight-trace. The results obtained from the copolymers with $n = 0,1,3,4$ and 5 are shown in Chapter 3.

7. Thermal degradation of the copolymers in a closed evacuated system, and analysis of the volatile products, liquid at room temperature

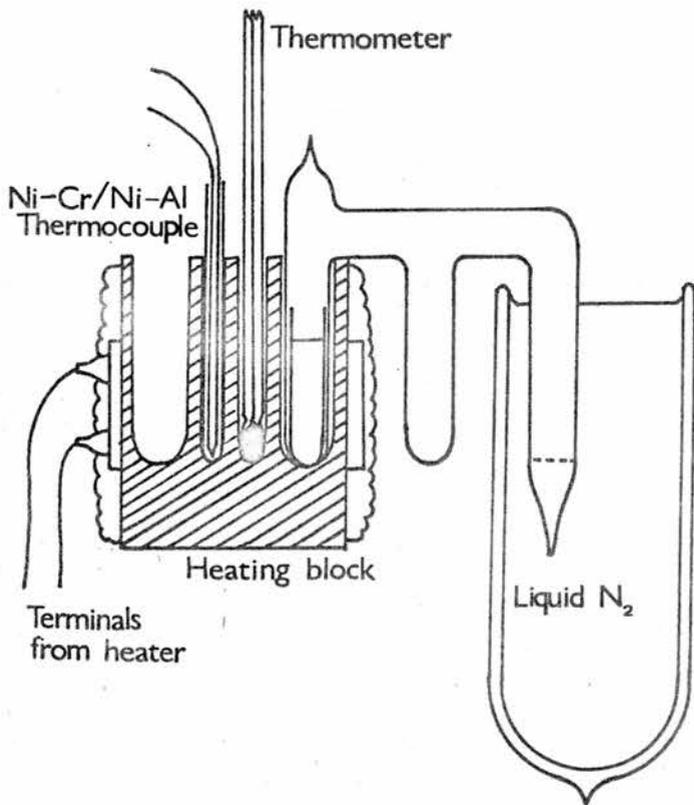
(i) Thermal degradation in a closed evacuated system

The apparatus used in this part of the work was basically a modified inverted 'U' tube of the design used by Jellinek¹ in his work on the thermal degradation of polystyrene. It is shown in Figure 4, and there now follows a description of the apparatus and the experimental method used in this section of the work.

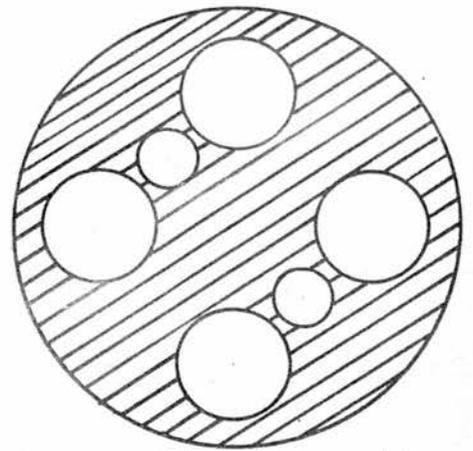
Figure 4.



Apparatus for the collection of volatile products from the thermal degradation of the copolymers



Heating block from above



For each run, an 'h' shaped tube was made from 12mm glass tubing. A central limb was incorporated and a B14 cone attached as shown in Figure 4. The tube was thoroughly washed with a detergent solution, then distilled water, and finally acetone, before being dried in an oven. It was then attached to a vacuum system and checked for any pin holes. Meanwhile, a 'boat' made from 8mm glass tubing was cleaned and dried as described above. The boat was weighed and then to it was added 100mg of a sample of one of the copolymers. The boat and contents were carefully slid into the tube and a constriction made in the tubing. The tube was then reattached to the vacuum system and pumped out to a pressure of 10^{-3} - 10^{-4} mm Hg. To ensure that the inside walls of the tube were free of any contamination, a flame was played over the outside of the tube during evacuation.

The furnace used for the experimental work described here, consisted of a cylindrical block of an aluminium alloy which fitted tightly inside a 100 W band heater. Asbestos tape was wound round the block and heater. Six holes were drilled in the block, four large holes to accommodate tubes of the type described above, and two smaller holes, one of which held a mercury in glass thermometer and the other a glass tube encasing a Ni-Cr/Ni-Al thermocouple. The same temperature controller as described in Part 5 (ii) of this chapter, was connected to the terminals of the band heater with the Ni-Cr/Ni-Al thermocouple again acting as the temperature sensor. The temperature used in all the runs with this heating block was 350°C, and it was found that this temperature could be maintained to within ± 2 degrees.

When the temperature of the heating block was isothermal at 350°C, the constriction in the tube was closed with a flame and

the tube transferred to one of the larger holes in the block. A dewar flask filled with liquid nitrogen was placed around the pointed end of the tube, leaving the middle limb at room temperature. After four hours the tube was withdrawn from the heating block, leaving the pointed end in the liquid nitrogen. Using a hot-air blower any products that were volatile, but had condensed on the walls of the tube before reaching the liquid air trap were distilled over into the pointed end of the tube below the dotted line shown in Figure 4. The tube was then removed from the liquid nitrogen trap, the pointed end wiped dry and the glass cut open along the dotted line. This 'cut-off' section was quickly transferred to a container, sealed, and weighed. The contents of this part of the tube were analysed by gas chromatography as described in the next section. Following analysis, the empty 'cut-off' section was cleaned thoroughly, dried and reweighed, allowing the weight of volatile material collected to be calculated. The other end of the tube containing the sample boat was also cut open and the boat and residue weighed.

(ii) Gas chromatographic analysis of the volatile products, liquid at room temperature

After the 'cut-off' section had been weighed with the liquid fraction inside, the contents were analysed by gas chromatography. The gas chromatograph used in this work was a Griffin and George D6 model, incorporating a Griffin-Martin gas-density balance detector. This detector has a response dependent on the difference in molecular weight of the sample and the carrier gas, in this case nitrogen. The response is also linearly related over a wide range to the concentration of the sample in the carrier gas. By comparison of the ratio of the peak areas of two compounds, the molar ratio of the two

compounds can be determined.

Two modifications were made to improve the system. The first consisted of replacing the injection device supplied by the manufacturer, with a much simpler system that allowed liquid samples to be introduced onto the column by means of a conventional microsyringe. The second change in design was the replacement of the motor driven generator that supplied the detector with a constant current, by an all electronic device with no moving parts that could produce fluctuations in current. The Honeywell 1 mv recorder supplied with the chromatograph was used throughout the work.

After preliminary experimental work on ~~the~~ various parameters that could be altered in the gas chromatographic analysis, the following conditions were decided on, and kept constant for all the analyses.

Sample size: between 1 and 10 μ l, injected with a 10 μ l syringe.

Column: stainless steel, 5mm internal diameter and 2 m long.

Stationery phase and

support material: 10% Apiezon-L (APL) on acid washed 100/120 mesh Celite.

Column temperature : 150^oC.

Carrier gas flow rate: 40ml N₂ per minute.

Chart speed: 12 inches per hour.

In order to quantitatively measure the amounts of the various components present in each sample injected, the detector was calibrated using redistilled sodium dried toluene. Toluene was used because it occurred as a degradation product in the chromatograms of all the copolymers studied, and its peak area could therefore be compared

with the peak areas of the other components in the injection sample. The basis of the relationship between the ratio of the number of moles in two components and the ratio of their respective peak areas is given by the equation⁷²,

$$q = k A \frac{M}{(M-m)}$$

where q = weight of the sample in the carrier gas,

M = molecular weight of the sample,

m = molecular weight of the carrier gas,

A = an integral response (normally the peak area),

k = a constant for a particular instrument.

Rearranging the equation gives,

$$\frac{q}{M} = k \frac{A}{(M-m)}$$

$$k = \frac{q (M-m)}{MA}$$

Hence for the two components (1) and (2), the ratio of the number of moles in each component is given by,

$$\frac{\text{moles (1)}}{\text{moles (2)}} = \frac{A(1) (M(2) - m)}{A(2) (M(1) - m)}$$

Known amounts of toluene were injected onto the column under the conditions given previously. The peak areas were calculated by triangulation, the area being given by,

$$\text{area} = \text{peak height} \times \text{width of the peak at half the height.}$$

Graphs were plotted of moles of toluene versus peak area. The peak areas of the toluene in the chromatograms of the copolymer degradation products were also calculated by the same method as above. By reference to the calibration graphs, the number of moles of toluene in each chromatogram was determined.

In order to compare the peak areas of the degradation products within each chromatogram a Du Pont 310 Curve Resolver was used. This instrument allows the areas of resolved and unresolved peaks in a chromatogram to be compared with one another. Hence the area of each peak in a chromatogram can be expressed either as a percentage of the total area of all the peaks, or it can be compared with the area of any other peak.

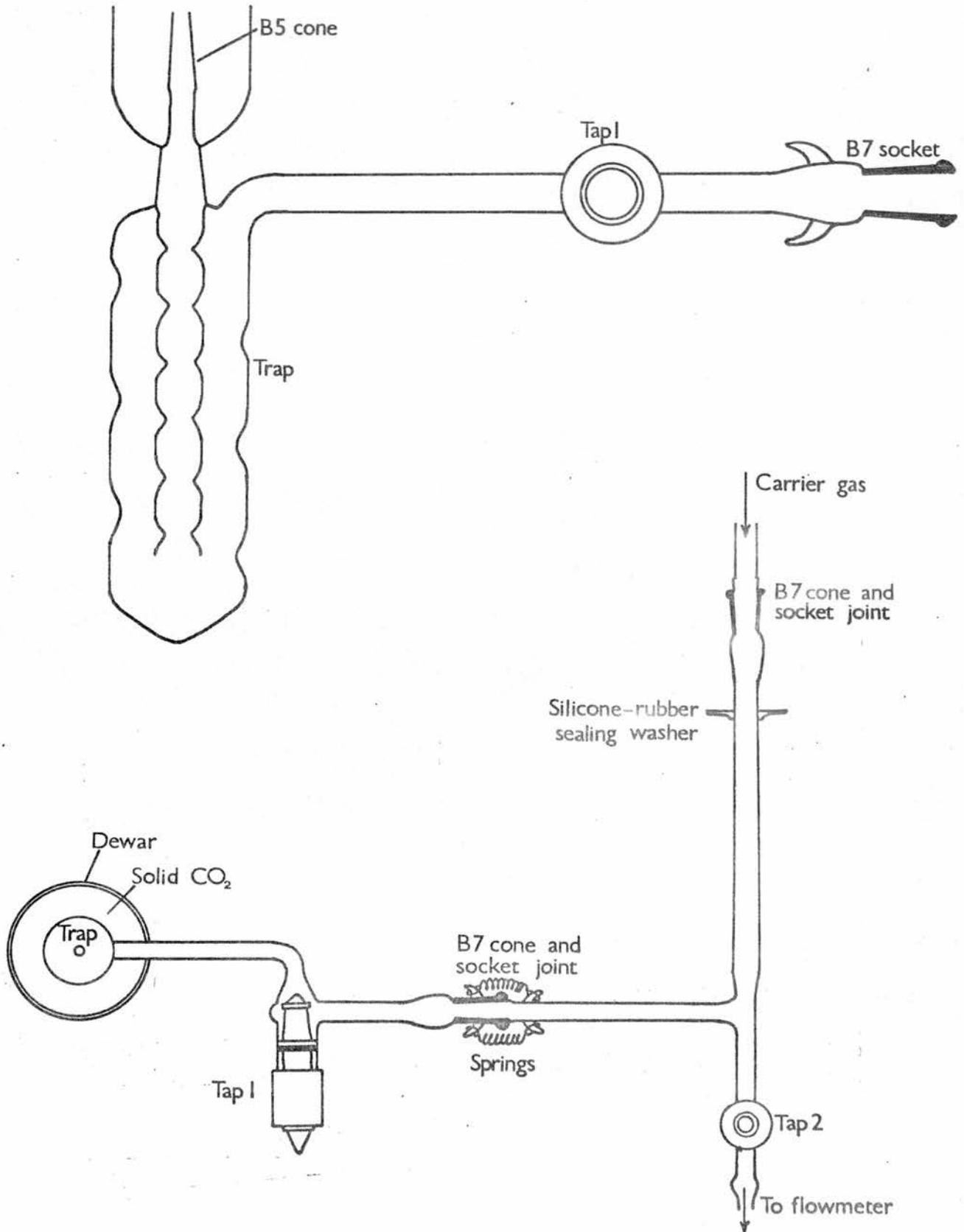
(iii) Analysis by gas chromatography/mass spectrometry

In order to identify components in the chromatograms that proved difficult to identify by their retention times on the column, it was decided to use mass spectrometry as an aid in this work. Since the mass spectrometer available (an AEI MS 902) did not at the time have gas chromatographic facilities attached to it, a trapping device was constructed that could be attached to the chromatograph and after collection of the sample could then be taken to the mass spectrometer. Figure 5 shows this apparatus in detail with a schematic diagram of it in operation.

The trap was based on a design used by the Pye Series 105 preparative gas chromatograph. The central tube in the trap was attached to a B5 cone while the limb on the shoulder of the trap was attached via a greaseless tap (Tap1) to a B7 socket. The other half of the apparatus consisted of a 'T' piece, at one end of which was a B7 socket connecting the apparatus to the outlet of the gas density balance detector. At the other end of this limb was another greaseless tap (Tap 2) with a connection to the flowmeter used to indicate the carrier gas flow rate. A silicone-rubber washer ensured a good seal at the point where the glass tubing passed through the oven wall of the chromatograph. The two pieces of the apparatus were connected via

Figure 5.

Trapping system for the analysis by mass spectrometry
of volatile products from the gas chromatograph



a B7 cone and socket joint held together by two springs. To ensure that material did not condense on the walls of the tubing before reaching the trap, the apparatus was wound in tape that could be electrically heated.

The method of operation was as follows. The trapping section shown in the upper diagram in Figure 5 was attached via the B7 socket to a vacuum system, a B5 cap was used to seal the other open end and the apparatus pumped out to a pressure of 10^{-3} - 10^{-4} torr. Tap 1 was closed, the apparatus removed from the vacuum system and attached to the other half of the apparatus as described above. After being attached to the detector at one end and the flowmeter at the other, the tape was wound around the apparatus and allowed to heat up. With Tap 2 open, the carrier gas flow rate was adjusted in the normal way and a dewar of solid carbon dioxide placed around the trap. The sample was then injected onto the column and the peaks observed on the recorder. On the appearance of the peak selected for trapping, Tap 2 was closed, Tap 1 was opened and the B5 cap removed in order that the carrier gas could escape. When the recorder indicated that the peak was over, Tap 1 was closed and Tap 2 opened again. The tape was removed, the two halves of the apparatus disconnected, and the trapping section taken to the mass spectrometer with the dewar of solid carbon dioxide still around the trap. The B5 cap was removed and the trapping section connected via the B5 cone to the mass spectrometer. The larger outer cone shown in the upper diagram in Figure 5 serves to reduce the pressure differential between the vacuum in the mass spectrometer and atmospheric pressure. With Tap 1 closed and the dewar of solid carbon dioxide still in place the apparatus was evacuated by the mass spectrometer's pumping system.

The valve connecting the apparatus to the mass spectrometer was then closed and the dewar removed, to be replaced by a heater that fitted around the trap. The temperature of the heater was raised to about 100°C and held there. After the trap had warmed up to the temperature of the heater, the valve connecting the apparatus to the mass spectrometer was opened, allowing any volatile material inside the trap to be pumped into the mass spectrometer where it was analysed.

CHAPTER 3

RESULTS

1. Kinetics of degradation by thermogravimetry

Before setting out the theory used to evaluate the results obtained by thermogravimetry, the symbols used in the text will be defined.

They are:

w_0 : the initial weight of the sample.

w : the weight of the sample at any time, t .

C : the conversion (degree of completion or advancement, extent of reaction), such that $(1-C) = w/w_0$.

k : a temperature - dependent rate constant.

A : the pre-exponential factor in the Arrhenius equation.

E : the energy of activation of the decomposition reaction (kJ mol^{-1}).

R : the gas constant ($8.314 \text{ JK}^{-1} \text{ mol}^{-1}$).

T : the temperature, in degrees Kelvin (K)

\ln : \log_e

\log : \log_{10}

p : the order of the reaction

(i) General theory

It is widely assumed,⁴² that for an isothermal case, the rate of conversion, dC/dt is a linear function of a temperature-dependent rate constant, k , and some temperature-independent function of the conversion, C , i.e.,

$$dC/dt = kf(C) \quad [1]$$

The temperature dependence of k , the rate constant, is assumed from the Arrhenius equation,

$$k = A \exp(-E/RT) \quad [2]$$

so that equation [1] becomes

$$dC/dt = A \exp(-E/RT) f(C) \quad [3]$$

Taking logarithms of equation [3] gives,

$$\ln (dC/dt) = \ln A + \ln f(C) - E/RT \quad [4]$$

Thus at constant conversion, C, a plot of $\ln (dC/dt)$ against $1/T$ gives a straight line of slope $-E/R$. Since by definition $(1 - C) = w/w_0$, then,

$$dC/dt = -1/w_0 (dw/dt) \quad [5]$$

and hence,

$$\ln (dC/dt) = \ln (-dw/dt) - \ln w_0 \quad [6]$$

Substituting into equation [4] gives,

$$\ln (-dw/dt) = \ln A + \ln f(C) + \ln w_0 - E/RT \quad [7]$$

Thus at constant conversion, C, and with a constant initial weight w_0 , a plot of $\log (-dw/dt)$ against $1/T$ gives a straight line of slope $-E/2.303R$.

By analogy to simple cases in homogeneous reaction kinetics, the conversion function can be expressed as,⁴²

$$\begin{aligned} f(C) &= (1 - C)^p \quad [8] \\ &= (w/w_0)^p \end{aligned}$$

where p is the order of the reaction. Substituting the above equation into equation [7] gives,

$$\ln (-dw/dt) = \ln A + p[\ln w - \ln w_0] + \ln w_0 - E/RT \quad [9]$$

$$\therefore \ln (-dw/dt) = \ln A + (1 - p) \ln w_0 - E/RT + p \ln w \quad [10]$$

Thus at constant temperature, T, and initial weight, w_0 , a plot of $\log (-dw/dt)$ against $\log w$ gives a straight line of slope p, provided p is constant for all values of w. Further, as w/w_0 tends to unity, the intercept on the $\log (-dw/dt)$ axis will yield the $\log k$ value for each isotherm. A plot of these $\log k$ values against $1/T$ would then give a slope of $-E_0/2.303R$ where E_0 is defined as the initial activation energy.

(ii) Experimental results

In order to test the validity of equation [7], isothermal runs as described in Chapter 2, part 6, were carried out on 50mg samples of the copolymers. The temperature range used was between 591K (318°C) and 653K (380°C), each copolymer being degraded isothermally at four or five temperatures within the given range. Having obtained the weight-loss trace for each run as described previously, the rate of loss of weight (mg/minute) was calculated by measuring the slope of the trace at various values of conversion. The log values of the rate of loss of weight were plotted against the inverse of the absolute temperature, and the plots obtained are shown in Figures 6 to 10.

Allowing an error of ± 1 degree in the temperature of each isothermal run, as found experimentally, straight line plots were obtained. The small letters "a" to "i" indicate the following fractional weight-loss values:

Letter	C	w/w ₀	% Degradation
a	0.1	0.9	10
b	0.2	0.8	20
c	0.3	0.7	30
d	0.4	0.6	40
e	0.5	0.5	50
f	0.6	0.4	60
g	0.7	0.3	70
h	0.8	0.2	80
i	0.9	0.1	90

It was decided not to calculate the $(-dw/dt)$ values for those points

Figure 6.

Determination of the activation energy (E)
for the n=5 copolymer

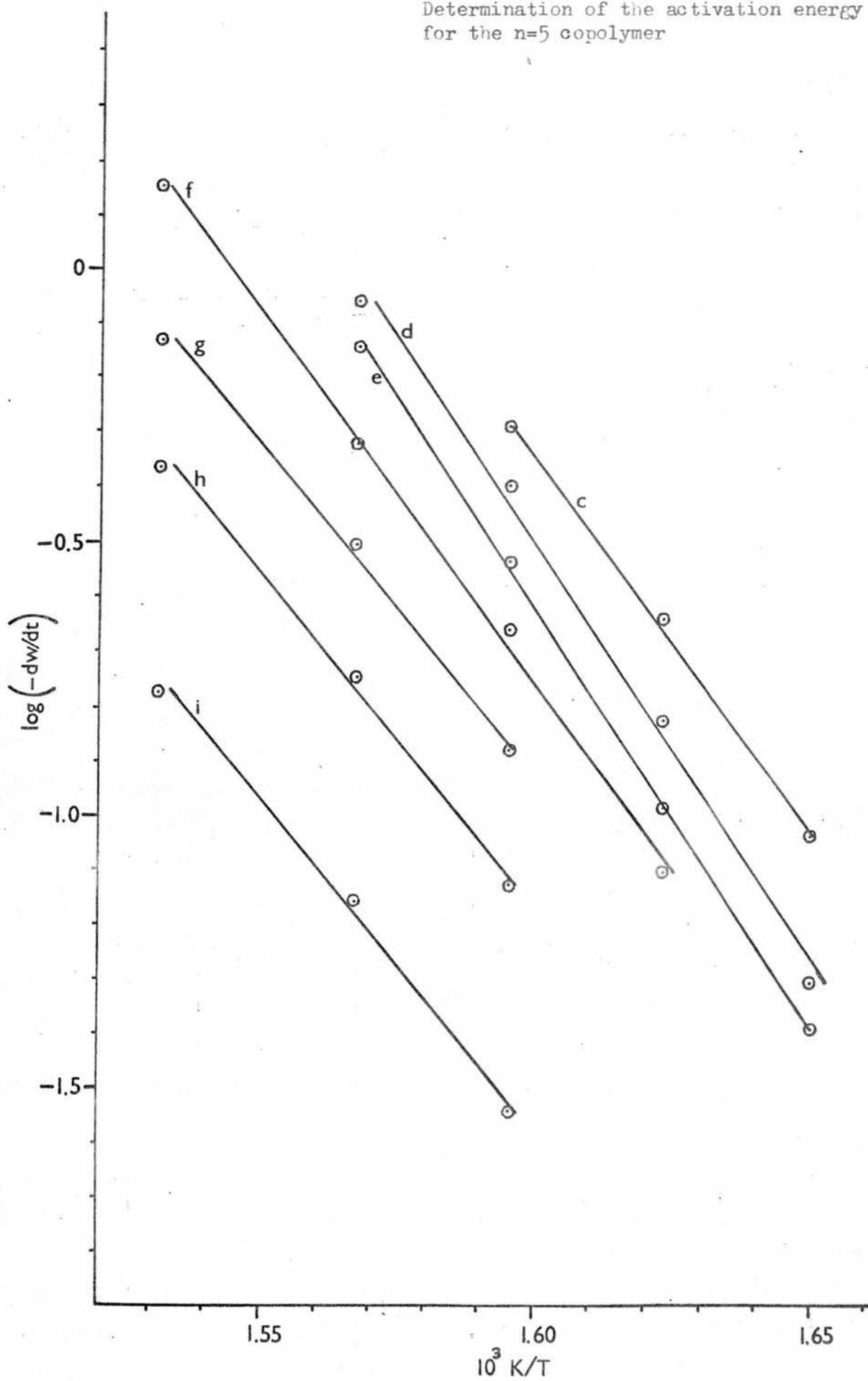


Figure 7.

Determination of the activation energy (E)
for the n=4 copolymer

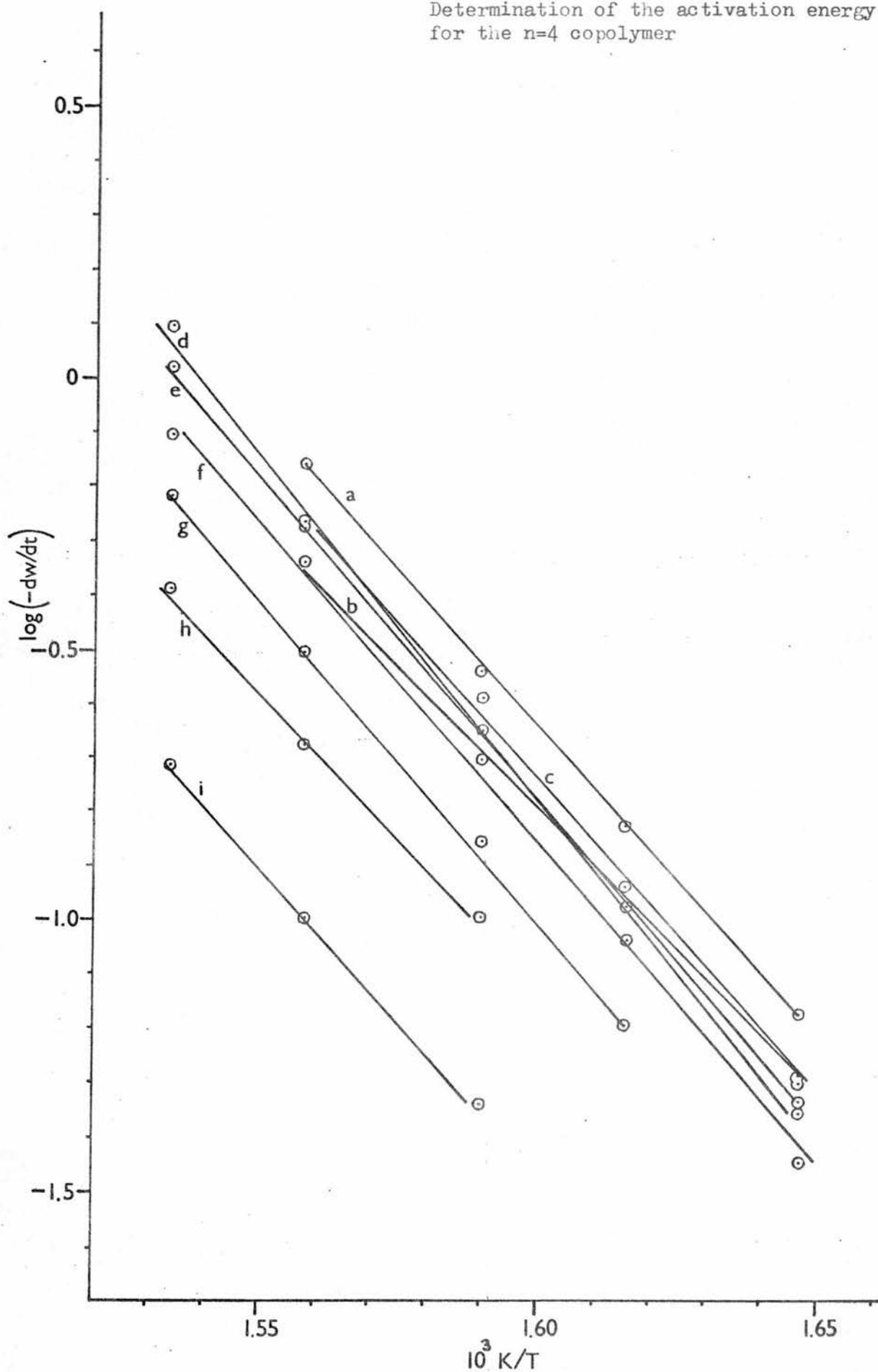


Figure 8.

Determination of the activation energy (E)
for the n=3 copolymer

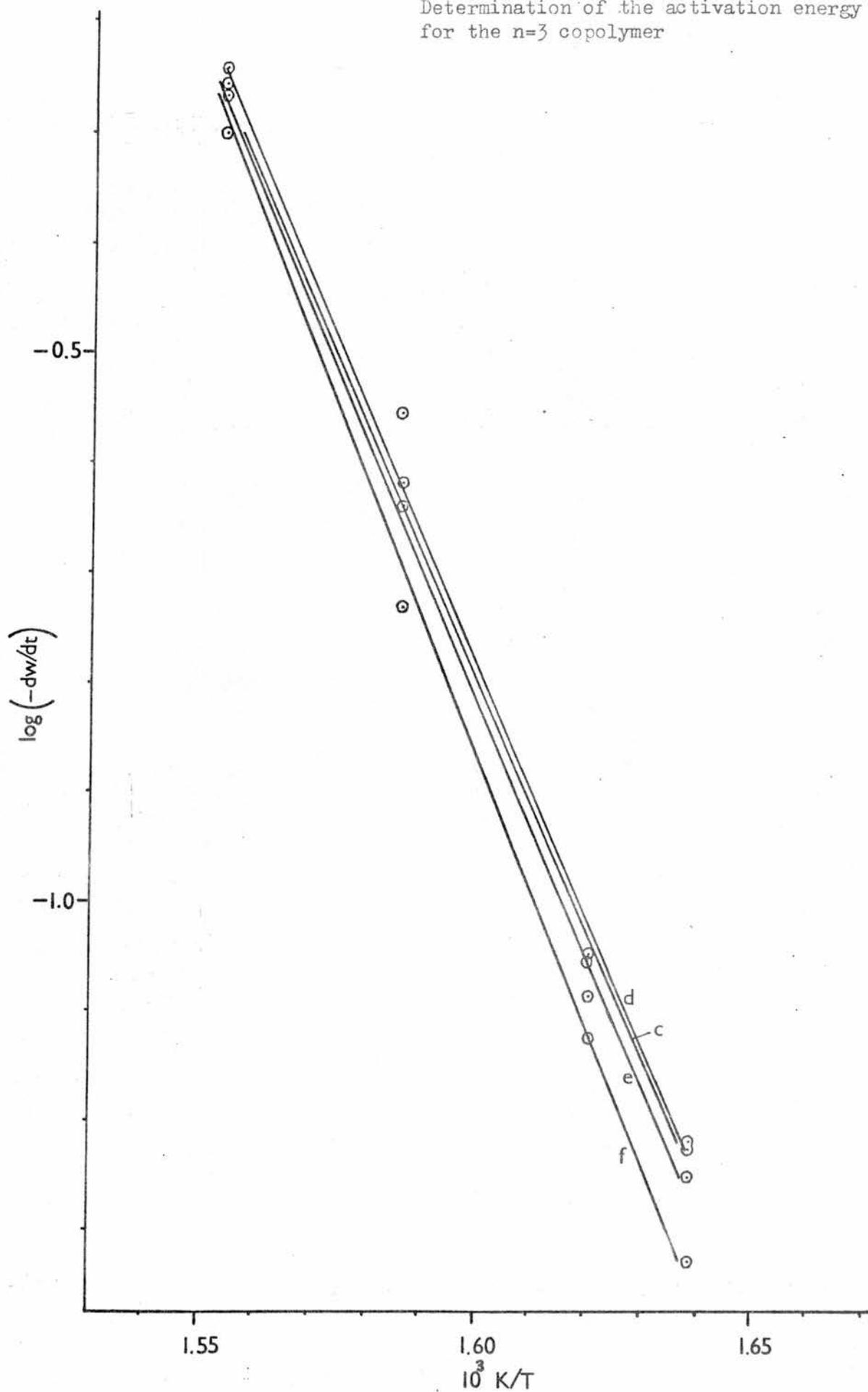


Figure 9.

Determination of the activation energy (E)
for the n=1 copolymer

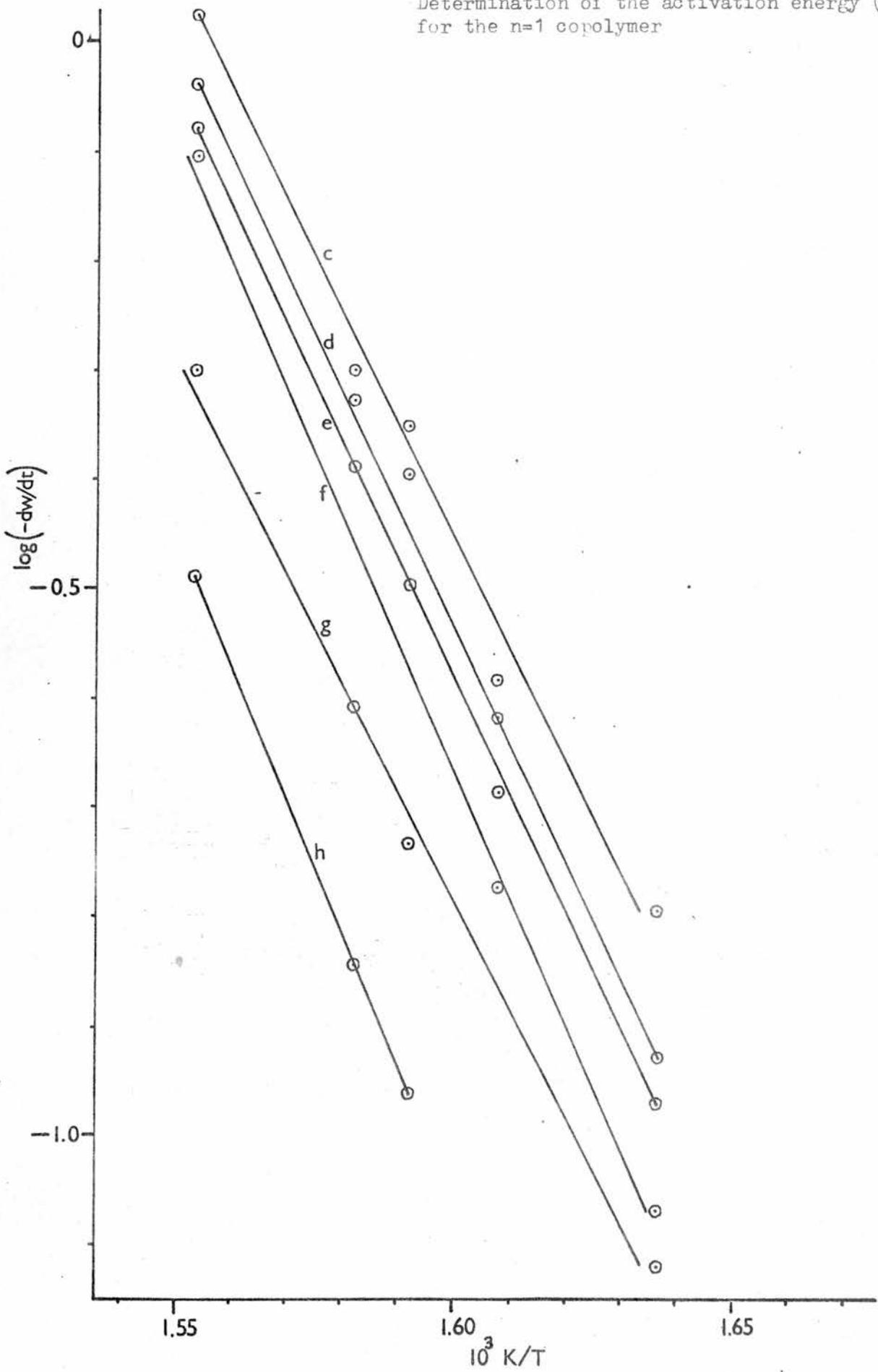
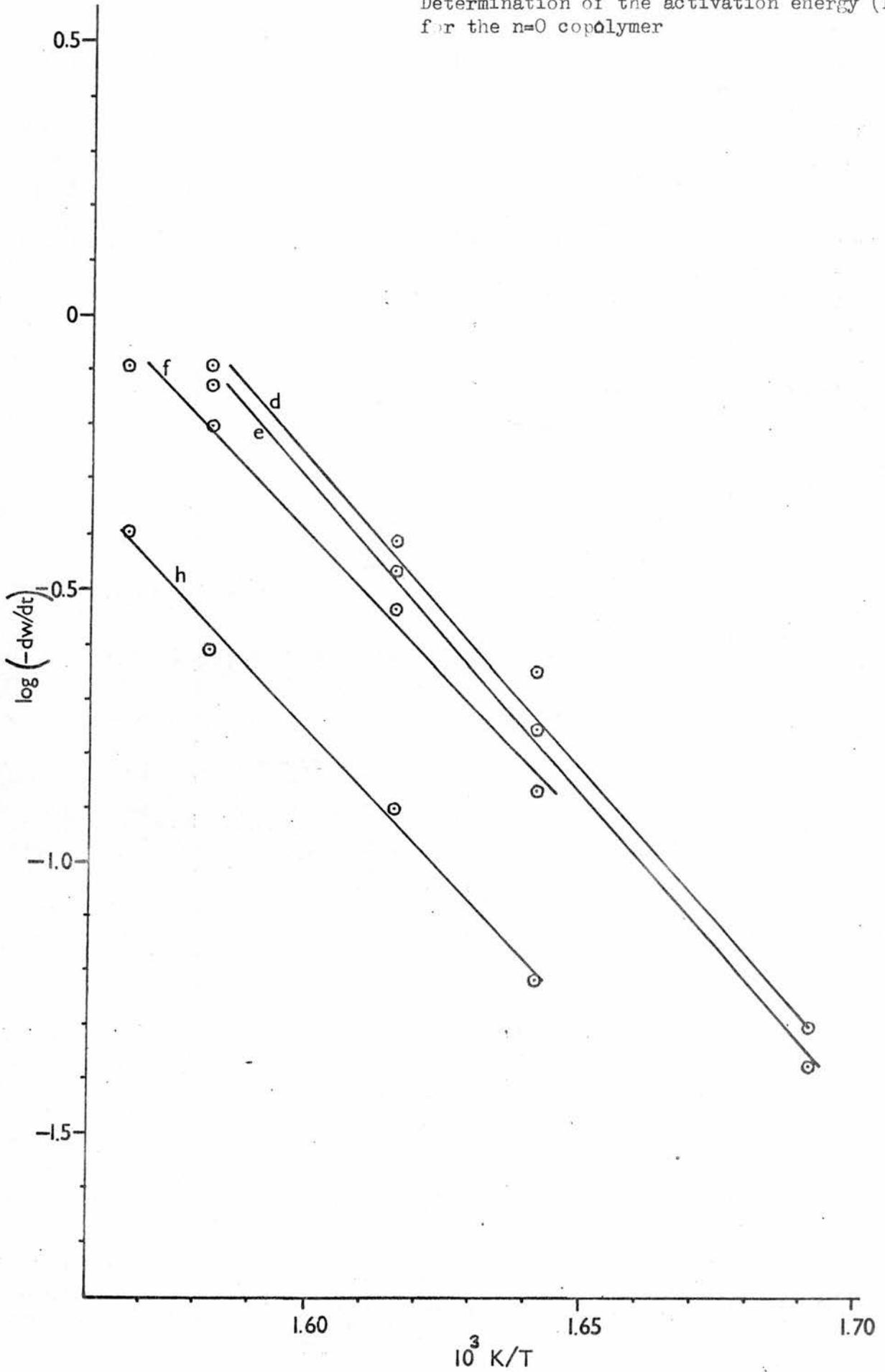


Figure 10.

Determination of the activation energy (E)
for the n=0 copolymer



on the trace at which the rate of loss of weight was either very fast or very slow. It was felt that in both these extreme cases the errors involved in estimating the rates were too high to justify including the values obtained in the results. Thus some of the plots for the extreme values of C are not included in Figures 6 to 10, and in some cases, the values of $\log(-dw/dt)$ are not shown for all the temperatures.

From the slopes of the lines, values of the activation energies (E) at various conversions were calculated, and are shown in Table 5.

Table 5

Activation energies (E) kJ mol^{-1} for the copolymers					
C	n=0	n=1	n=3	n=4	n=5
0.1				219.9	
0.2				200.4	
0.3		193.4	222.7	222.1	295.8
0.4	216.8	203.1	225.4	245.3	292.1
0.5	218.4	203.8	227.6	228.4	291.7
0.6	198.7	225.6	242.3	217.9	262.0
0.7		186.4		229.4	229.9
0.8	201.8	231.9		210.3	232.6
0.9				219.1	233.7

As derived in equation [10], the order of the reaction, p, can be found from a plot of $\log(-dw/dt)$ against $\log w$. From the isothermal weight-loss traces for the n = 0, 1 and 5 copolymers the values of $(-dw/dt)$ were measured after each 1 mg loss in weight for all values of w at which it was felt that the rate of loss of weight could be measured with any certainty. The values of $\log(-dw/dt)$

were plotted against $\log w$ at the various temperatures used in the degradation reactions of the three copolymers, and it was found that straight line plots were obtained. However, in some of the plots, curves were obtained which could be resolved into two or more linear portions. Figures 11 and 12 illustrate this for one copolymer ($n = 5$) at two different temperatures. In Figure 11 the plot of $\log (-dw/dt)$ against $\log w$ is linear between the two conversions, $C = 0.55$ and $C = 0.93$, with a value of $p = 1.5$. In Figure 12 however, two separate straight lines can be drawn from $C = 0.41$ to $C = 0.73$ and from $C = 0.73$ to $C = 0.92$. This gives rise to two gradients, with values of 1.7 and 1.3. The results obtained for these and the other plots mentioned above are shown in Table 6. Since the values of p for each copolymer were not constant at different temperatures or indeed in some cases varied during degradation at the same temperature, it was not possible to determine $\log k$ values from the intercepts

Figure II.

Determination of the order of the reaction (n) for the $n=5$ copolymer at 653 K (380°C).

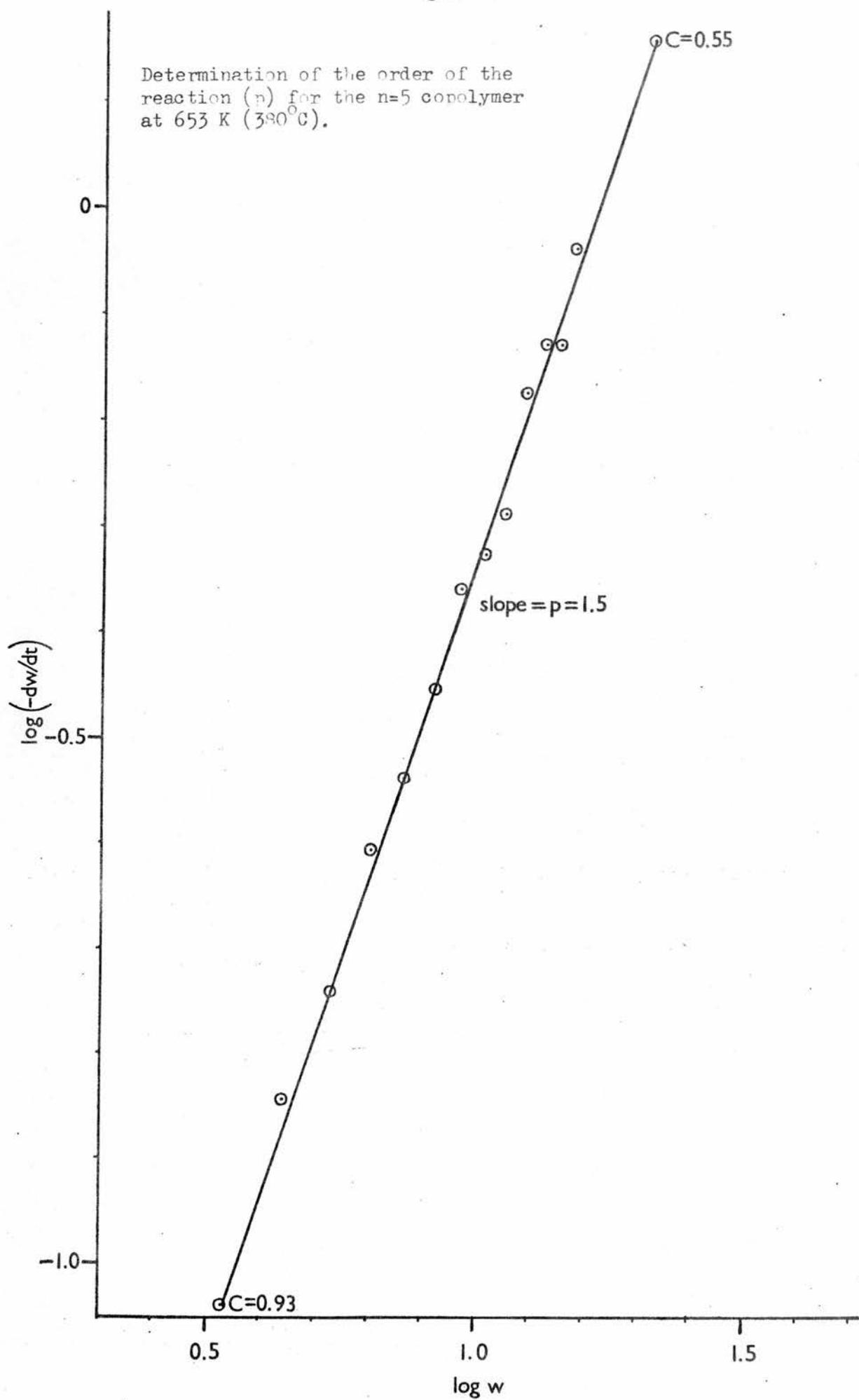


Figure 12.

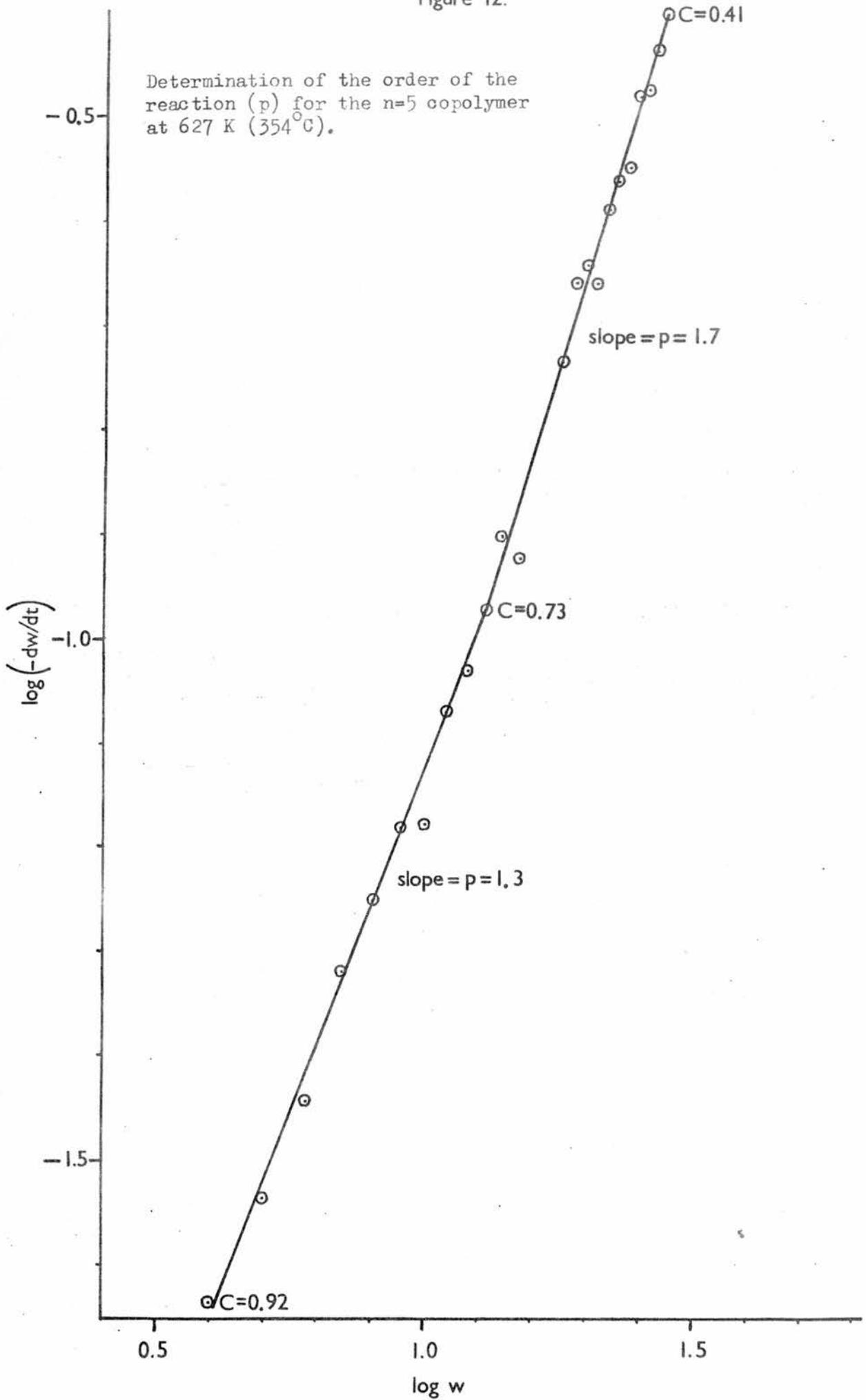


Table 6

Copolymer	Temperature (K)	Conversion (C)	Order of reaction (p)	
n = 0	591	0.07 to 0.31	4.9	
		0.31 to 0.56	1.2	
	609	0.20 to 0.33	3.3	
		0.33 to 0.79	1.1	
	619	0.22 to 0.81	1.0	
	632	0.58 to 0.92	1.4	
	638	0.48 to 0.77	0.9	
		0.77 to 0.93	1.5	
	n = 1	611	0.03 to 0.32	4.5
			0.32 to 0.83	1.2
622		0.15 to 0.19	6.7	
		0.19 to 0.86	1.2	
628		0.54 to 0.86	1.3	
632		0.58 to 0.92	1.2	
644		0.47 to 0.68	1.0	
		0.68 to 0.81	1.1	
		0.82 to 0.95	1.2	
n = 5		606	0.14 to 0.34	2.6
	0.34 to 0.57		1.6	
	615	0.26 to 0.36	3.4	
		0.36 to 0.58	1.9	
	627	0.41 to 0.73	1.7	
		0.73 to 0.92	1.3	
	638	0.34 to 0.78	1.5	
		0.78 to 0.91	1.3	
	653	0.55 to 0.93	1.5	

of the plots. Thus initial activation energies, (E_0) were not determined.

In order to compare the results obtained for the activation energies of the copolymers at various values of C , with those obtained for polystyrene and polyethylene by Madorsky⁵, the following procedure was adopted. Madorsky defined,

$$k_1 = \frac{-dw \cdot 100}{dt \cdot w_0} \quad \% \text{ min}^{-1} \quad [11]$$

and,

$$k_2 = \frac{-dw \cdot 100}{dt \cdot w} \quad \% \text{ min}^{-1} \quad [12]$$

From the plot of $\log k_2$ against the inverse of the absolute temperature, Madorsky obtained straight line relationships, and from the slopes of the lines calculated the activation energies at various values of percentage degradation.

Using the same rate of loss of weight values as before, k_2 was calculated for each value of C and the $\log k_2$ values were then plotted against $1/T$. The results are shown in Figures 13 to 17. Again allowing an error of ± 1 degree in the temperature of each isothermal run, straight line plots were obtained. The small letters beside each line indicate the same values of C as used previously.

From the slopes of the lines, the activation energies were calculated at the various conversions and are shown in Table 7.

Figure 13.

Determination of the activation energy (14)
by the k_2 method, for the n-5 copolymer

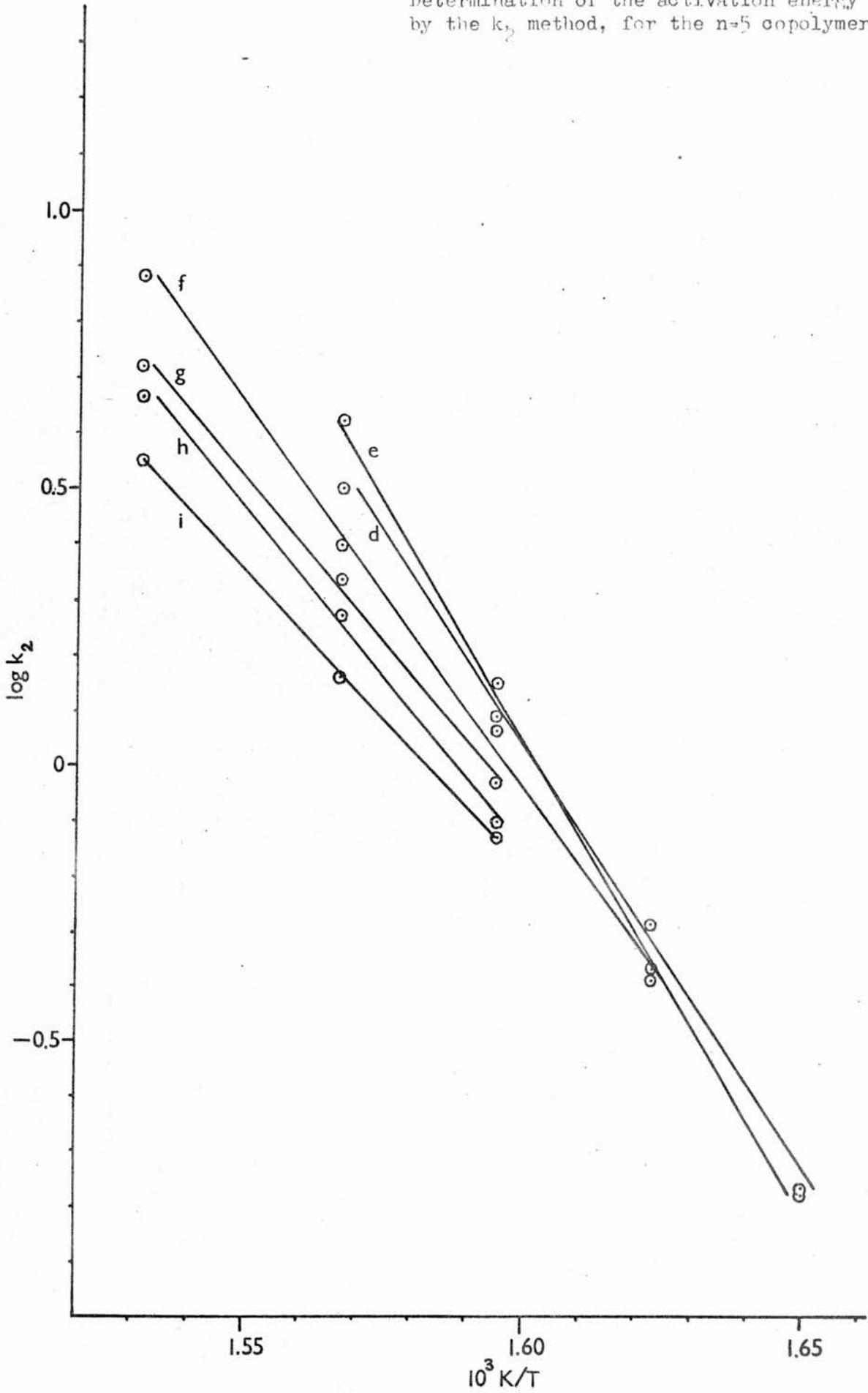


Figure 14.

Determination of the activation energy (E) by the k_2 method, for the n=4 copolymer

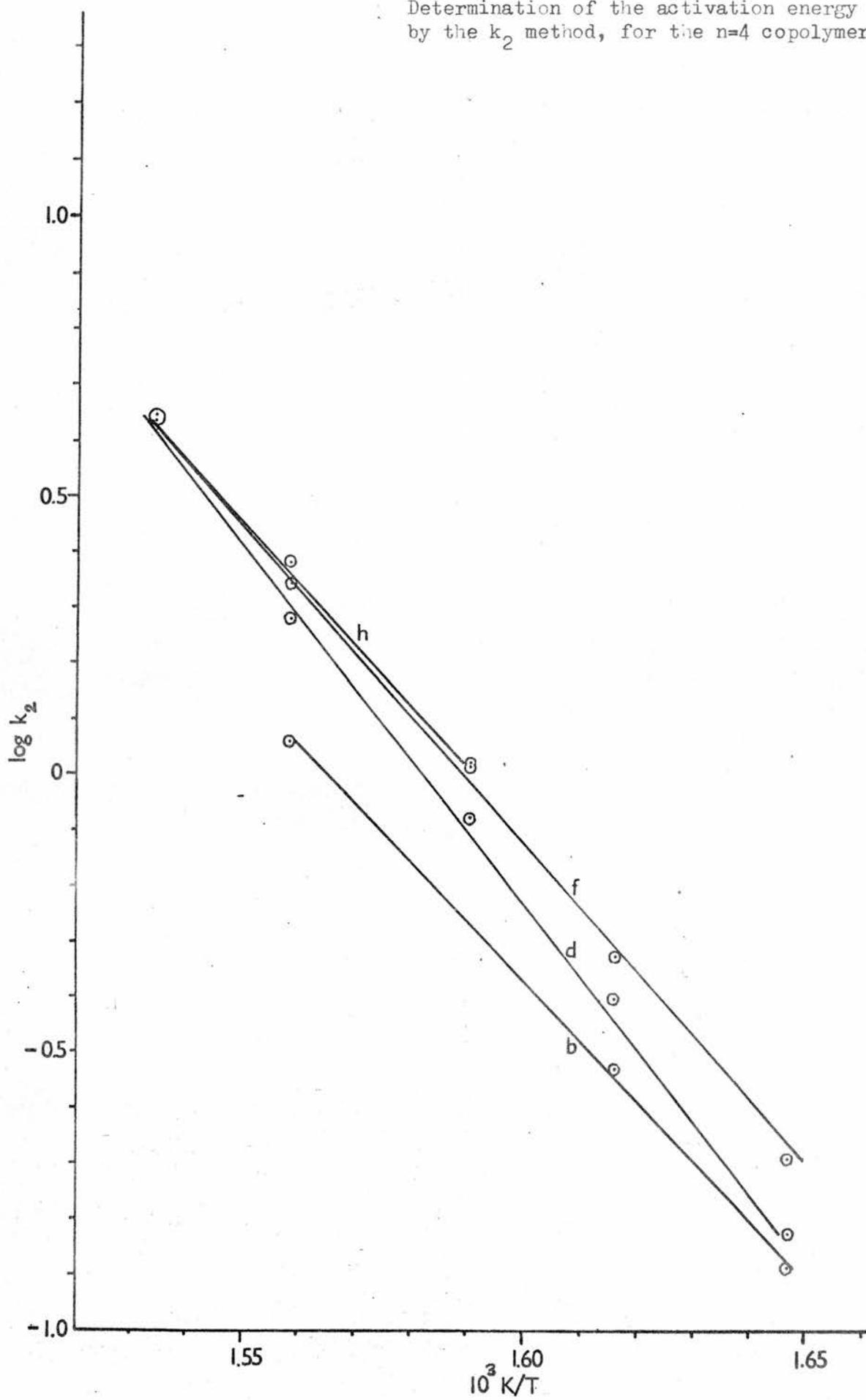


Figure 15.

Determination of the activation energy (E)
by the k_2 method, for the $n=3$ copolymer

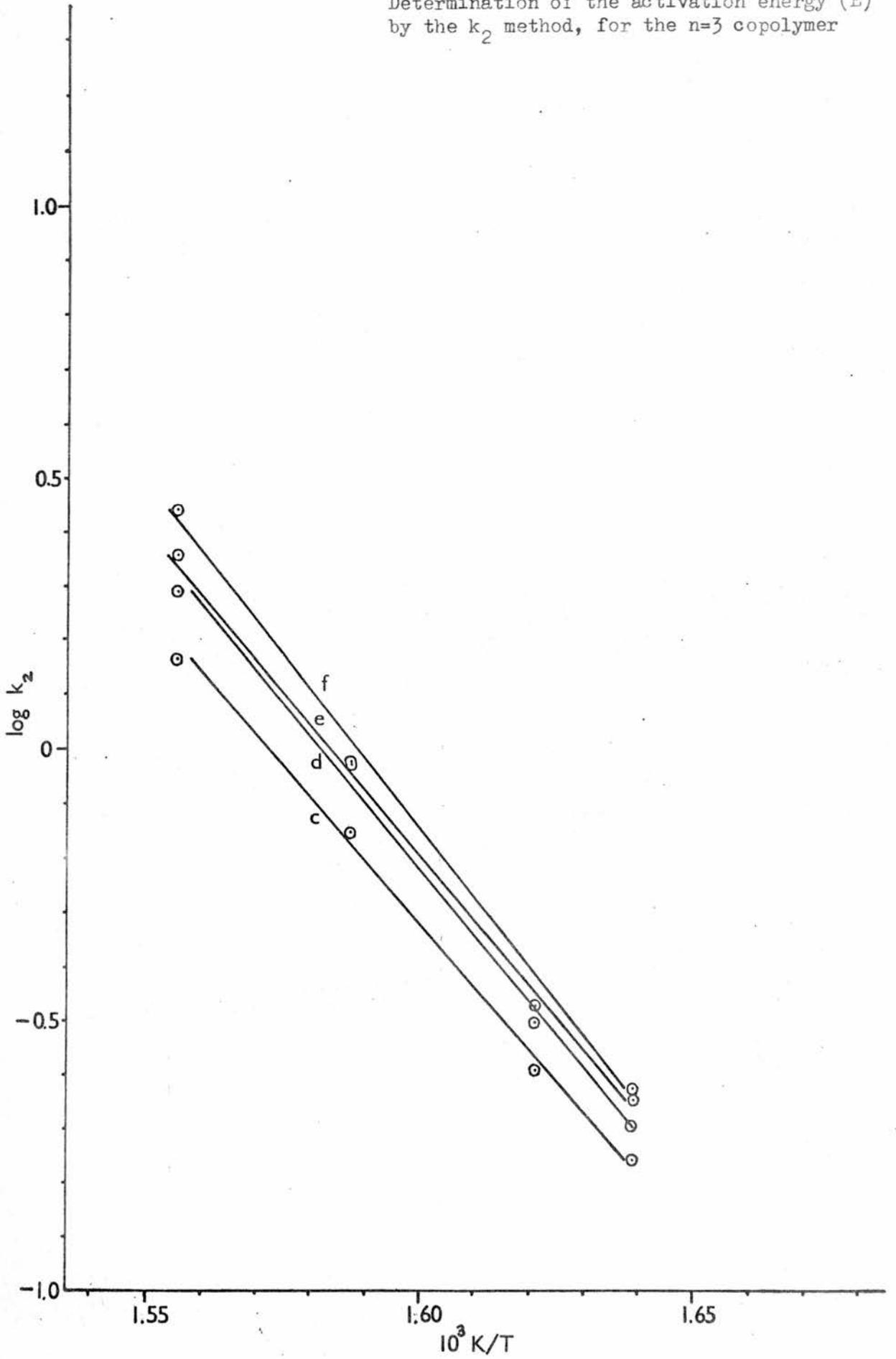


Figure 16.

Determination of the activation energy (E) by the k_2 method, for the $n=1$ copolymer

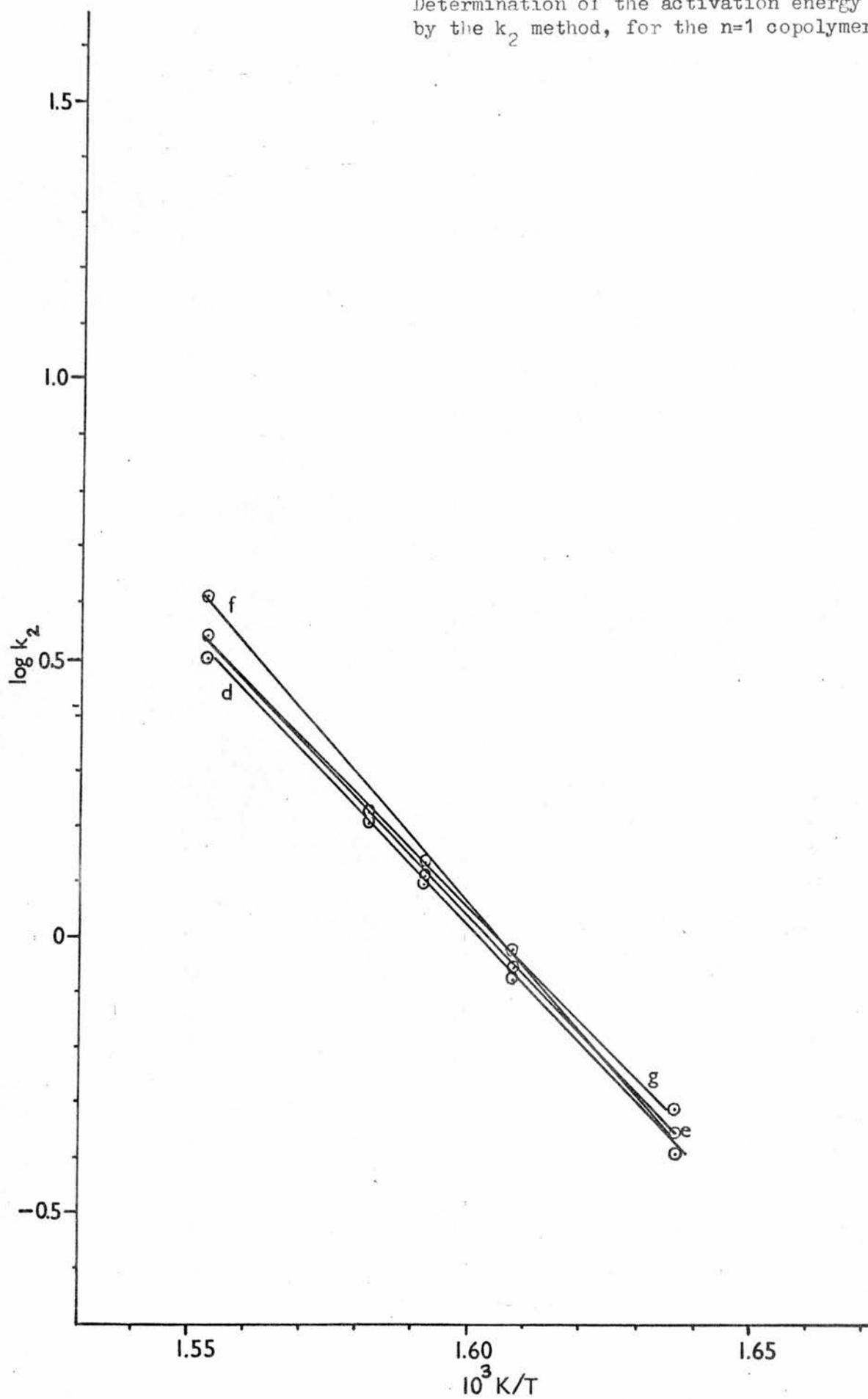


Figure 17.

Determination of the activation energy (E)
by the k_2 method, for the n=0 copolymer

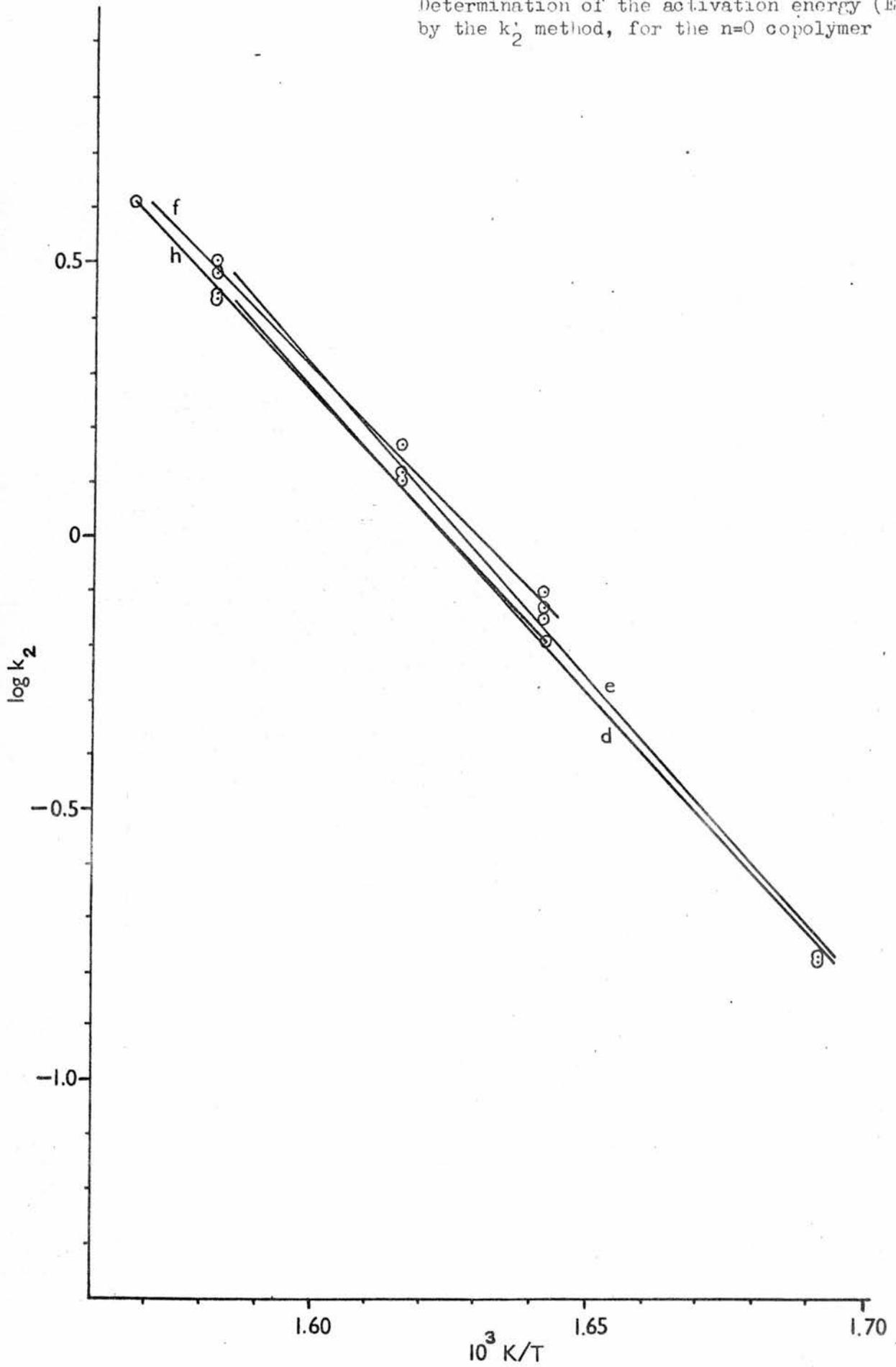


Table 7

Activation energies (E) kJ mol^{-1} for the copolymers by the k_2 method					
C	n = 0	n = 1	n = 3	n = 4	n = 5
0.1				225.5	
0.2				203.6	
0.3		186.7	221.3	226.5	
0.4	211.0	202.8	234.2	247.2	292.8
0.5	218.2	205.2	228.9	233.2	328.7
0.6	195.6	223.0	244.9	217.0	265.9
0.7		196.4		227.2	226.0
0.8	205.6	282.6		214.9	234.2
0.9				214.3	205.6

2. Thermal degradation of the copolymers in sealed tubes.

(i) Analysis of the residues

After removal of the boats from the degradation tubes, the % degradation for each copolymer was calculated from the weight of the residue. A sample of conventional head-to-tail polystyrene was degraded in the same manner and under the same conditions, to provide a comparison with the copolymers. The % degradations are shown in Table 8. For each copolymer four 100mg samples were degraded simultaneously (Tubes 1 to 4), and an average value for the % degradation calculated.

Table 8

Copolymer	% Degradation after 4 hours at 623K				
	Tube 1	Tube 2	Tube 3	Tube 4	Average
n = 5	62.3	59.0	62.5	61.6	61.4
n = 4	44.2	45.5	48.1	44.4	45.6
n = 3	55.4	55.0	51.7	53.1	53.8
n = 1	75.7	77.1	73.9	78.8	76.4
n = 0	91.9	95.1	92.9	91.3	92.8
head-to-tail polystyrene	95.6	96.6	94.8	96.2	95.8

^1H n.m.r spectra were obtained for the residues of each copolymer and compared with the spectra of the undegraded material. No significant changes could be detected either in the position of the peaks in the spectra, or in the aliphatic/aromatic H ratios. The I.R. spectra of the residues were also very similar to the spectra of the undegraded copolymers and no extra information could be obtained from them.

(ii) Analysis of the products of degradation

During preliminary experiments on the thermal degradation of the copolymers it was noticed that a viscous straw-coloured liquid collected in that area of the tubes which was at room temperature i.e. between the heating block and the liquid nitrogen trap. In order to remove this material before it reached the trap, a central limb was incorporated in the apparatus (see Figure 4) which succeeded in trapping out this fraction. Two product fractions were thus obtained, a viscous liquid fraction removed by the central limb at room temperature, and a volatile liquid fraction trapped at the temperature of liquid nitrogen.

(a) Volatile fraction, liquid at room temperature

As well as weighing the residues of each copolymer after degradation, the weight of volatiles in the 'cut-off' section was also noted prior to gas chromatographic analysis. The results for each copolymer and for the conventional head-to-tail polystyrene are shown in Table 9. An average over the four tubes is shown in each case, and although the results are of limited quantitative value owing to the difficulty of collecting all the volatile material in the 'cut-off' section, they are of interest when comparing the relative thermal stabilities of the copolymers.

Table 9

Copolymer	Weight of the volatile fraction, liquid at room temperature (mg)				
	Tube 1	Tube 2	Tube 3	Tube 4	Average
n = 5	14.4	15.2	15.8	12.7	14.5
n = 4	10.6	7.4	9.7	11.2	9.7
n = 3	13.9	12.0	11.6	13.2	12.7
n = 1	25.6	30.9	23.7	20.7	25.2
n = 0	37.2	53.2	40.6	35.7	41.7
head-to-tail polystyrene	60.1	64.7	67.0	51.9	60.9

Gas chromatographic analysis of this fraction was carried out as described in Chapter 2, 7 (ii). A reproduction of the chromatogram obtained for each copolymer is shown in Figures 18 to 22, with the chromatogram for head-to-tail polystyrene, obtained under the same conditions, shown in Figure 23. The chromatograms for the n = 3 and n = 0 copolymers were inadvertently run at slightly slower flow rates than the other chromatograms, making direct visual comparison

Gas chromatogram of the volatile products, liquid at room temperature, for the n=5 copolymer.

Figure 18.

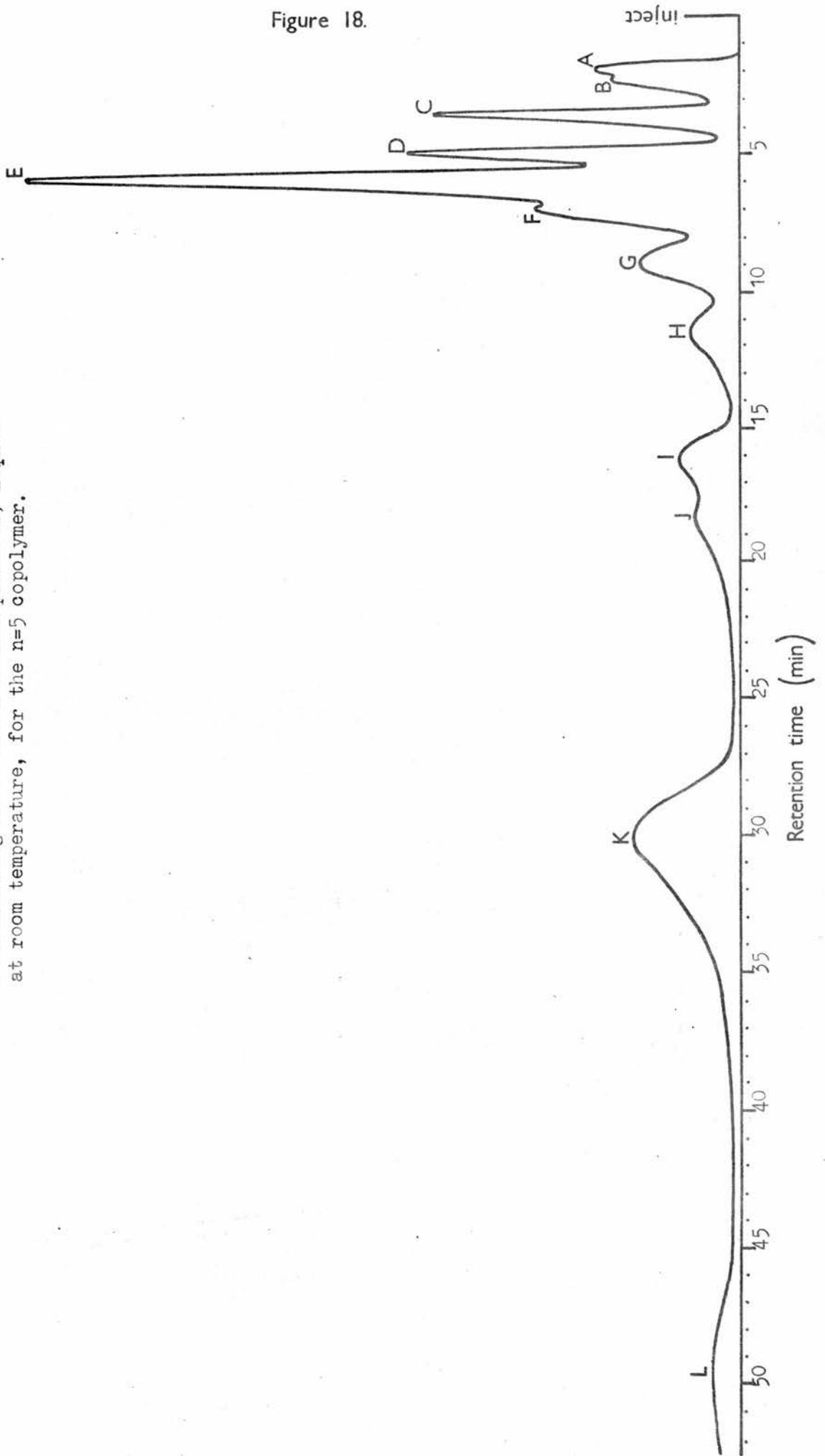


Figure 19.

Gas chromatogram of the volatile products, liquid at room temperature, for the n=4 copolymer.

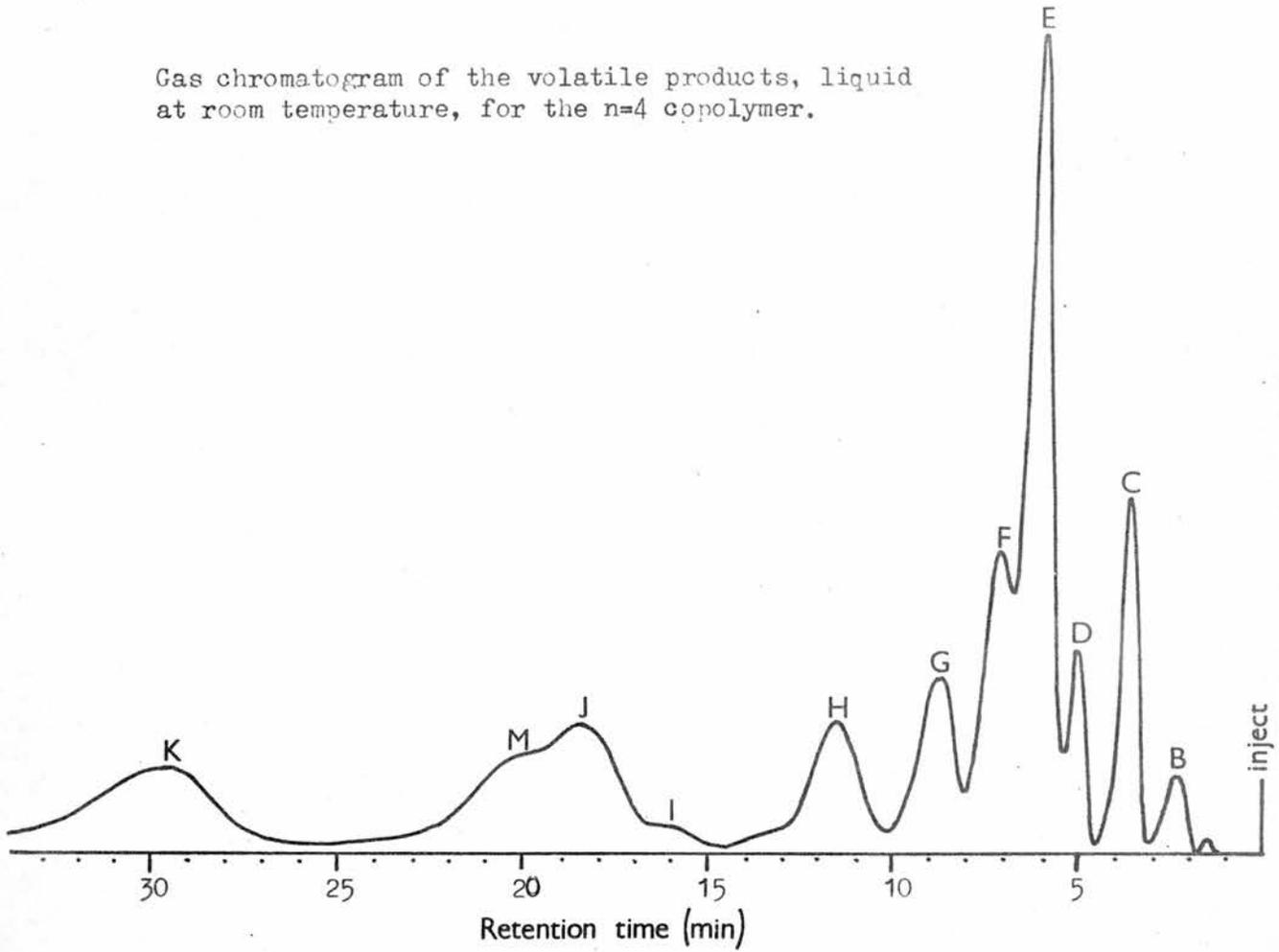


Figure 20.

Gas chromatogram of the volatile products, liquid at room temperature, for the n=3 copolymer.

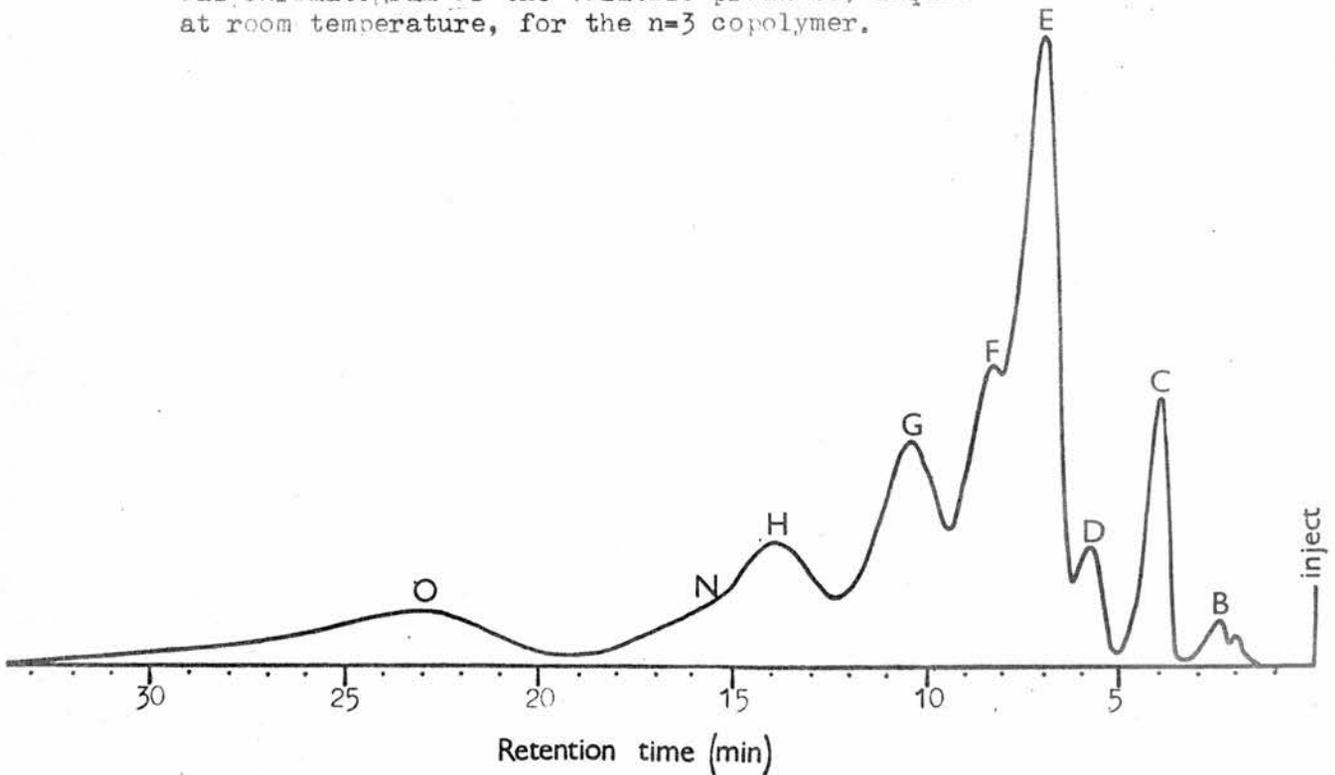


Figure 21.

Gas chromatogram of the volatile products, liquid at room temperature, for the $n=1$ copolymer.

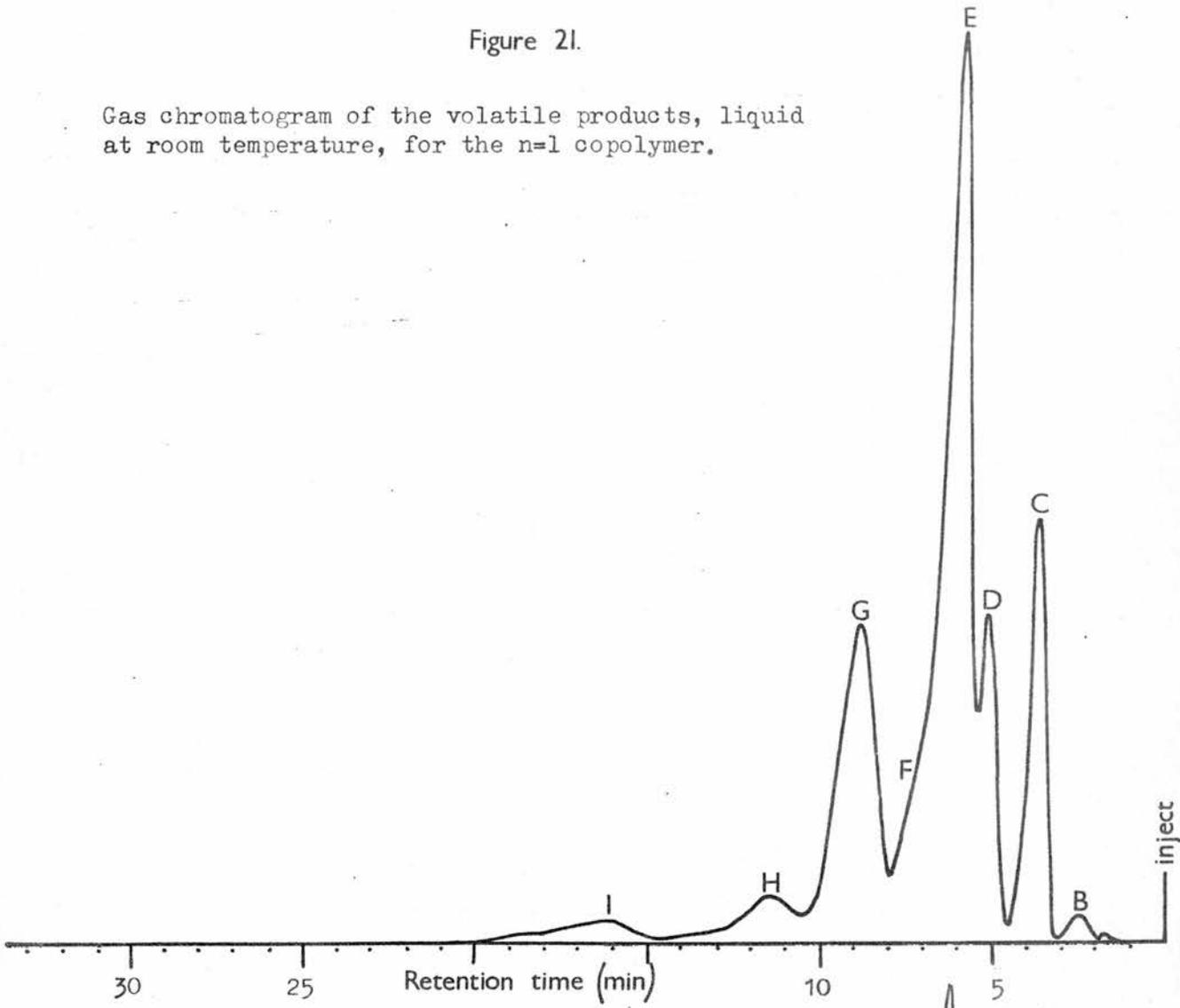


Figure 22.

Gas chromatogram of the volatile products, liquid at room temperature, for the $n=0$ copolymer.

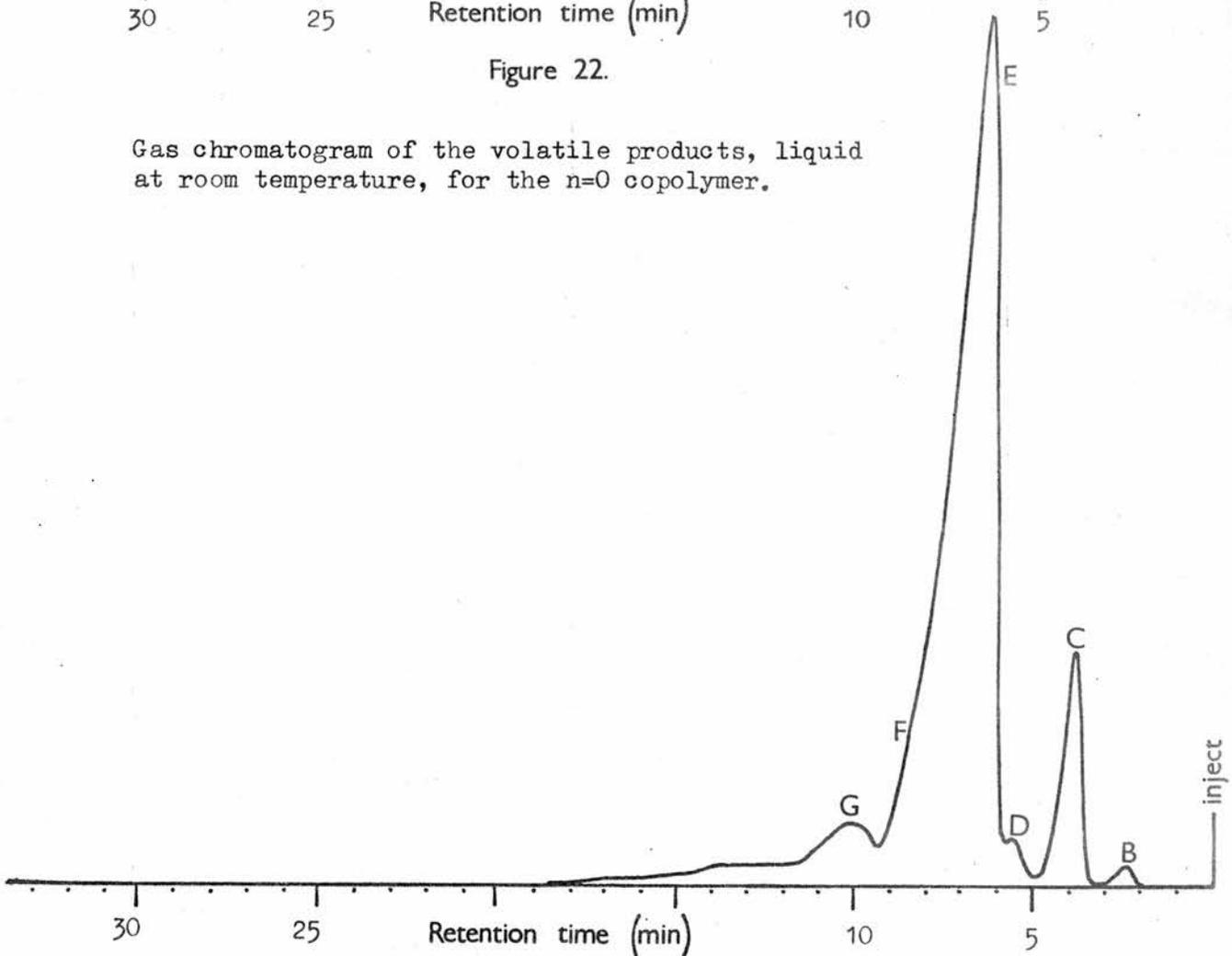
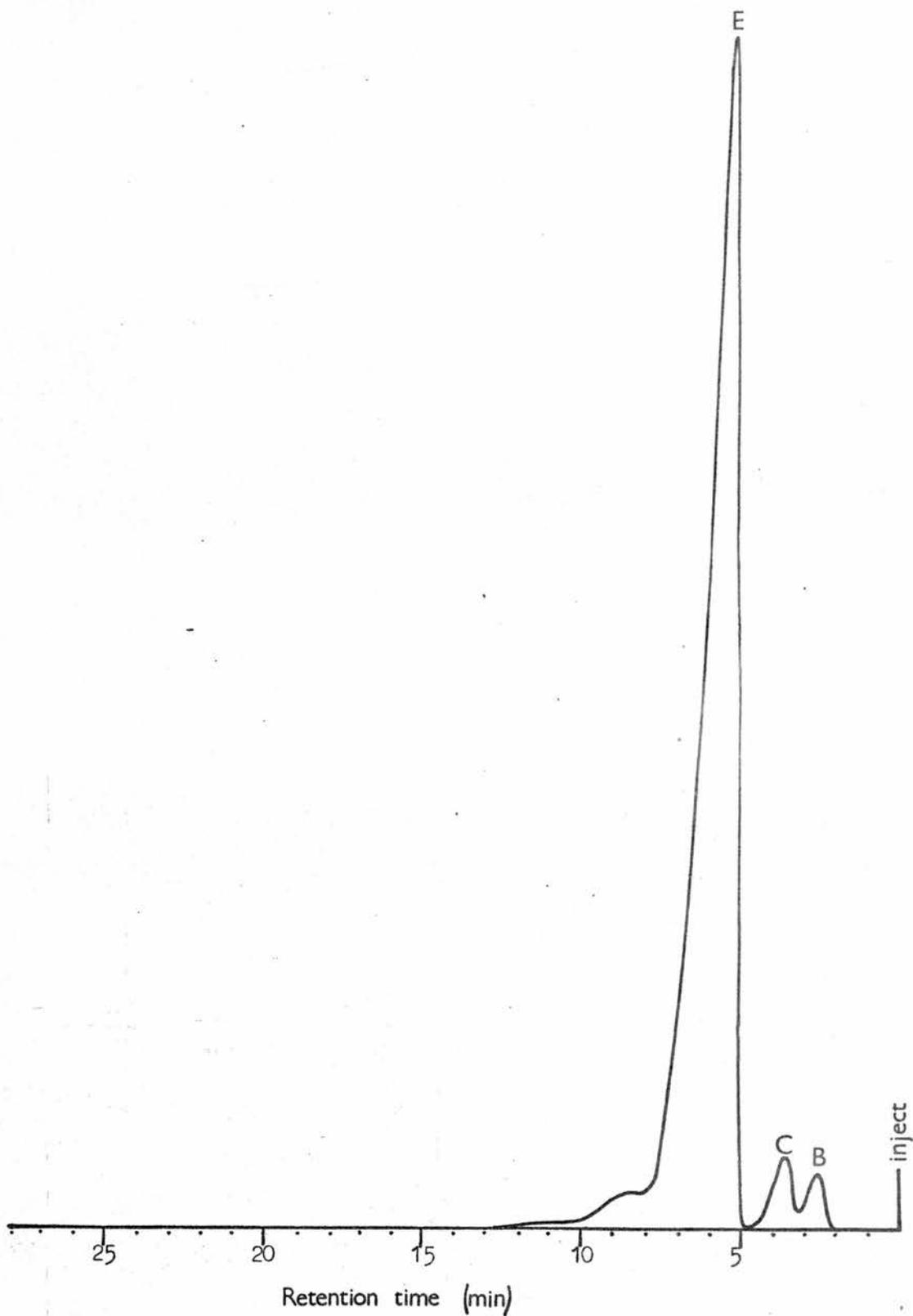


Figure 23.

Gas chromatogram of the volatile products, liquid at room temperature, for polystyrene (head-to-tail).



a little difficult.

n = 5 copolymer (Figure 18)

The chromatogram of the volatile products of the degradation of the n = 5 copolymer was the first to be analysed. The peaks were labelled A to L, and by the use of standard compounds the following were provisionally identified by their retention times.

Table 10

Peak	Retention time (min)	Assignment
B	2.3	Benzene
C	3.5	Toluene
D	5.0	Ethylbenzene
E	5.9	Styrene
F	7.0	n-Propyl benzene

In order to confirm the above assignments and to help in identifying the remaining peaks in the spectrum the trapping system shown in Figure 5 was used. Each peak in the spectrum (excluding L, which was not identified) was introduced into the mass spectrometer and analysed.

Peaks A and B proved impossible to identify by this technique perhaps due to insufficient amounts of sample for the trapping system. The initial assignments of peaks B,C,D,E and F were confirmed by the mass spectra obtained for the peaks. Peak E was found to consist of a small amount of iso-propylbenzene in addition to styrene.

As can be seen from Figure 18, complete resolution of the peaks in the chromatogram was not achieved. This was due to the compromise that had to be reached between good separation of the peaks and the retention times and therefore the shapes of the peaks. The overlapping of the peaks produced complicated mass spectra containing

not only the spectrum of the component that was being examined, but also the spectra of the components immediately adjacent. Since the components had many common peaks, and were present in different concentrations, the relative intensities of the m/e values proved of limited help in comparing the mass spectrum of each peak with the literature values for known compounds. By concentrating on the major fragments in the mass spectrum of each peak, the following assignments were made on the basis of each fragmentation pattern.

Table 11

Peak	m/e values for the peaks in each spectrum											Assignment
	in descending order of intensity											
G	117	118	91	115	78	51	39	65	116	63	C_3H_5 -	
H	91	92	134	51	65	78	39	77	105	27	C_4H_9 -	
I	117	132	91	115	131						C_4H_7 -	
J	91	92	148	65	105						C_5H_{11} -	
K	91	92	65	105	103	162					C_6H_{13} -	

The quantitative analysis of the chromatogram in Figure 18 was carried out as described in Chapter 2, 7 (ii). The area of peak C (toluene) was compared with the calibration graphs for peak areas of toluene corresponding to known numbers of moles. Using the Du Pont 310 Curve Resolver, the area of each peak was expressed as a fraction of the peak area of toluene, and using the expression derived on Page 32 the number of moles of each compound in the chromatogram was calculated. Since styrene formed the largest single component in the chromatogram, it was given a value of 100 mole % and the other components were expressed relative to this value. Table 11 shows these results expressed as the average values for the four runs.

Table 12

Peak	Retention time (min)	Assignment	mole %
B	2.3	Benzene	9.1
C	3.5	Toluene	50.5
D	5.0	Ethylbenzene	20.0
E	5.9	Styrene	100.0
F	7.0	n-Propylbenzene	4.9
G	8.9	C_3H_5 - 	15.4
H	11.4	C_4H_9 - 	15.7
I	16.1	C_4H_7 - 	23.6
J	18.2	C_5H_{11} - 	6.3
K	29.5	C_6H_{13} - 	41.3

The chromatograms of the remaining copolymers, $n = 4, 3, 1$ and 0 together with the sample of head-to-tail polystyrene were analysed in a similar manner and the results are shown in the following tables. The same letters have been used for peaks that have been given the same assignments.

n = 4 copolymer. (Figure 19)

Table 13

Peak	Retention time (min)	Assignment	mole%
B	2.4	Benzene	11.4
C	3.7	Toluene	41.6
D	5.1	Ethylbenzene	19.5
E	6.0	Styrene	100.0
F	7.1	n-Propylbenzene	10.3
G	8.7	C ₃ H ₅ - 	18.5
H	11.5	C ₄ H ₉ - 	15.3
I	15.8	C ₄ H ₇ - 	6.8
J	18.2	C ₅ H ₁₁ - 	33.7
M	19.9	unidentified	-
K	29.3	C ₆ H ₁₃ - 	22.7

n = 3 copolymer. (Figure 20)

Table 14

Peak	Retention time (min)	Assignment	mole %
B	2.5	Benzene	6.1
C	4.1	Toluene	25.6
D	5.9	Ethylbenzene	8.3
E	7.0	Styrene	100.0
F	8.4	n-Propylbenzene	7.0
G	10.3	C ₃ H ₅ - 	39.3
H	13.9	C ₄ H ₉ - 	19.4
N	15.3	unidentified	-
O	22.7	unidentified	-

n = 1 copolymer. (Figure 21)Table 15

Peak	Retention time (min)	Assignment	mole %
B	2.5	Benzene	2.5
C	3.6	Toluene	34.6
D	5.1	Ethylbenzene	14.2
E	5.7	Styrene	100.0
F	peak masked	n-Propylbenzene	not measured
G	8.8	C ₃ H ₅ - 	24.7
H	11.5	C ₄ H ₉ - 	5.0
I	16.2	C ₄ H ₇ - 	not measured

n = 0 copolymer. (Figure 22)Table 16

Peak	Retention time (min)	Assignment	mole %
B	2.5	Benzene	2.3
C	4.0	Toluene	18.4
D	5.8	Ethylbenzene	2.9
E	6.4	Styrene	100.0
F	peak masked	n-Propylbenzene	16.5
G	10.1	C ₃ H ₅ - 	8.5

head-to-tail polystyrene. (Figure 23)Table 17

Peak	Retention time (min)	Assignment	mole %
B	2.5	Benzene	3.0
C	3.5	Toluene	4.7
E	5.1	Styrene	100.0

(b) Viscous liquid fraction

Very little work was done on this fraction, which was present in various degrees for all the copolymers. It was noticed that when the limb containing this fraction was warmed, the material became appreciably more mobile but on cooling its viscosity increased. ^1H n.m.r. spectra of these fractions did not yield any information that could distinguish them from the original copolymers, but the I.R. spectra, very similar to the spectra of the copolymers, showed new absorptions around 1640 and 990 cm^{-1} . These were very weak in comparison to the other peaks in each spectrum, but they are indicative of the presence of the $\text{>C} = \text{CH}_2$ group. From the spectral information and the high viscosities of these samples it was thought that they were probably low molecular weight oligomers of the copolymers. In order to compare the relative amounts by weight of the viscous and volatile liquid fractions, the average weights of the volatile fractions (Table 9) were expressed as percentages of the total weight lost from the boats during degradation. By subtraction, the percentage of the total weight lost accounted for by the viscous liquid fraction was obtained. The ratio of the viscous liquid fraction to volatile liquid fraction was thus calculated, and the results are shown in Table 18.

Table 18

Copolymer	Average % degradation	Viscous liquid fraction %	Volatile liquid fraction %	Viscous / Volatile liquid / liquid
n = 5	61.4	76.4	23.6	3.2
n = 4	45.6	78.7	21.3	3.7
n = 3	53.8	76.4	23.6	3.2
n = 1	76.4	67.0	33.0	2.0
n = 0	92.8	55.1	44.9	1.2
head-to-tail polystyrene	95.8	36.4	63.6	0.6

CHAPTER 4

DISCUSSION

1. Results obtained by thermogravimetry

In this section of the chapter, the results obtained for the activation energies and orders of reaction in the degradation processes will be examined. An attempt will be made to explain the experimental values with reference to other well investigated systems, and to show the interdependence of such factors as order of reaction and activation energy.

Tables 5 and 7 show the values for the activation energies of the copolymers determined by the two methods, described previously. The range in which (C) has the values 0.4, 0.5 and 0.6 has the most relevance. It was felt, that even if rates of loss of weight could be measured at low conversions, the uncertainty in determining the point at which isothermal conditions were achieved made measurements in this region of dubious validity. Similarly, rate measurements at high values of (C) are of little importance when there is a large uncertainty in calculating the slopes of the weight-loss curves. The values of (E) in the range $C = 0.4$ to 0.6 can be seen to be in good agreement for the two methods of calculation. Within the range of copolymers at a constant value of conversion, the activation energies show a general upward trend from $n = 0$ to $n = 5$. Exceptions to this are shown by the $n = 1$ copolymer at $C = 0.4$ and 0.5 , and also by the $n = 4$ copolymer at $C = 0.6$. These deviations from the general trend will be mentioned later, meanwhile it seems reasonable to draw the conclusion that the activation energies of the copolymers in the range of conversion 0.4 to 0.6 , increase with increasing number of methylene groups in the repeat unit. This conclusion is consistent with the data obtained by Madorsky⁵ in his work on the thermal

degradation of polystyrene and polyethylene, also in vacuo. From a plot of $\log k_2$ versus $1/T$, the activation energies for the two polymers were calculated at $C = 0.5$. Madorsky's results are summarised in Table 19.

Table 19				
Polymer	Molecular weight	w_0 (mg)	Temperature range (K)	Activation energy (E) kJ mol^{-1} at $C = 0.5$
polystyrene	230,000	5→6	608→638	226
polyethylene	20,000	6	658→678	335

As the number of phenyl groups in the chain decreases, from polystyrene to polyethylene, there is a corresponding increase in the value of (E), measured at a conversion of 0.5. Reference to Table 7 shows that although this increase in (E) can be clearly seen when considering the two extreme cases in the series $n = 0$ to 5, there are discrepancies within the series that contradict the general trend. A closer look at the values obtained for the orders of reaction may help to explain these anomalies.

Table 6 shows the orders of reaction (p) obtained from plots of $\log (-dw/dt)$ versus $\log w$, for the copolymers $n = 0, 1$ and 5. The high values of (p) at low conversions are of little significance, again due to the difficulty of measuring initial rates accurately and of knowing at what point isothermal conditions were achieved. The values of (p) at conversions at which the rate of loss of weight could be measured with some certainty lie between 1 and 2, with a general rise in values from $n = 0$ to $n = 5$. The important fact however is that the order of reaction is not constant for a given copolymer over the temperature range used to evaluate activation energies. This behaviour in the order of reaction cannot be accounted for

by experimental error. Figures 11 and 12 show the typically good linear relationships that were found for plots of $\log (-dw/dt)$ versus $\log w$. The changes in (p) imply that the degradation processes that are taking place are functions of both the conversion of the copolymer, and the temperature at which it is being degraded. Thus the rate expressions, measured for the copolymers at different temperatures, reflect the contributions made by various reactions. Since the resulting balance between these reactions may well be temperature dependent, the question arises as to whether the activation energies calculated over a range of isothermal temperatures at different conversions, can be used here to compare the stability of one copolymer with another. The (E) values for the copolymers at $C = 0.5$ would indicate an order of thermal stability:

$$n = 5 > n = 4 > n = 3 > \text{head-to-tail polystyrene} > n = 0 > n = 1$$

As will be seen later, this order of stability is not consistent with the results obtained either from the thermal degradation of the copolymers in sealed tubes or from temperature programmed thermogravimetry.

Reference to Table 6 shows another significant feature in the variation of the order of reaction with respect to conversion, namely that no maximum is observed in the rate of loss of weight curve between about 30 and 50% degradation. This phenomenon has been observed in the thermal degradation of high molecular weight samples of polystyrene.^{3,5} This rate maximum was not observed however in the thermal degradation of low molecular weight samples of polystyrene.^{6,73} Wall and co-workers⁷³ using samples of $\bar{M}_n = 7,000 \pm 1,000$ and $14,000 \pm 1,000$, found that the rates of degradation decreased slowly to between 40 and 50% degradation and then more rapidly, but almost linearly, to about 90% degradation.

2. Results obtained from the degradation of the copolymers in sealed tubes

In this section, the information resulting from the thermal decomposition of the samples in sealed tubes will be assessed. The most important part with a bearing on possible reaction mechanisms for the degradation of the copolymers, is the information derived from the gas chromatographic analysis of the volatile liquid fraction. To begin with however, the three components of each degradation that were examined, namely the residue, viscous liquid fraction, and volatile liquid fraction will be looked at in a little more detail.

As was mentioned in the previous chapter, the residues were chemically very similar to the starting material in each case. Molecular weight changes may well have occurred in the residues, but these were not measured. Table 8 shows the % degradation after 4 hours at 623K for each copolymer, and for the sample of head-to-tail polystyrene. The significance of these results is that using % degradation as a criterion of thermal stability, the order of thermal stability of the samples is:

$n = 4 > n = 3 > n = 5 > n = 1 > n = 0 > \text{head-to-tail polystyrene}$

Reference to Table 9 which shows the weight of the volatile liquid fraction collected for each sample, confirms the same order of thermal stability as above, using this time the weight of volatile material produced as the criterion of stability. In their thermogravimetric study of the same copolymers used here, MacCallum and co-workers⁴⁸ degraded 50mg samples under vacuum at a linear heating rate of 3°/min. From a plot of the temperature at which a conversion (C) was attained versus 'n', the following order of thermal stability was deduced:

$n = 4 > n = 3 > n = 5 > n = 1 > n = 0$

The temperatures at which the $n = 3$ and $n = 5$ copolymers attained the

same conversion were found to be very similar, and indeed in the cases of $C = 0.4$ and 0.5 , the positions of $n = 3$ and $n = 5$ in the above series became reversed. Thus both the results of thermogravimetry at a linear heating rate, and those obtained by measuring the weight of the residue and volatile liquid fraction for a fixed time under isothermal conditions, point to the same order of thermal stability. Reference to the previous section in this chapter, in which an order of thermal stability was worked out based on energies of activation, shows that the two orders of stability are quite different. Since the results from two independent sets of experiments give the same order of thermal stability, namely:

$$n = 4 > n = 3 > n = 5 > n = 1 > n = 0,$$

the order of stability derived from the energies of activation must be regarded with some reservation. This supports the proposal in the previous section that if the energies of activation reflect a balance of reactions that is changing with temperature and conversion, they are not a good guide to comparing the stability of one copolymer with another.

The viscous liquid fraction from the degradation of the copolymers was assumed to consist of low molecular weight oligomers of the copolymers. This was decided as pointed out in Chapter 3 from spectral evidence and the high viscosities of the material. It was not decided whether the evidence of unsaturation in the I.R. spectra of these fractions was due to the presence of double bonds in the oligomers or to traces of more volatile 'small' molecules that had condensed before reaching the liquid nitrogen trap. Table 18 shows the amounts of the viscous and volatile liquid fractions expressed as percentages of the total weight lost from the 'boat' during degradation. The ratio

between the viscous and volatile liquid fractions shown in the last column is interesting, since the value of this ratio indicates the relative amounts of large fragments and 'small' molecules produced by the copolymers during thermal degradation. If this ratio is expressed in decreasing magnitude from left to right the order is:

$$n = 4 > n = 5 \approx n = 3 > n = 1 > n = 0 > \text{head-to-tail polystyrene}$$

This order, with $n = 5$ very similar to $n = 3$, again parallels the results obtained by MacCallum et al⁴⁸ for the order of thermal stability of the copolymers. The conclusion can therefore be reached, that the relative stability, as assessed by thermogravimetry at a constant heating rate, increases with increasing ratio of viscous to volatile liquid fractions. This seems reasonable, since large fragments produced on breakdown of the copolymers will be less volatile than 'small' molecules which can escape more easily from the boat. Since in thermogravimetry only the weight-loss parameter is used as a basis for establishing stability with respect to temperature, the more volatile the degradation products the greater will be the weight-loss and the less thermally stable the sample.

Figures 18 to 22 show the gas chromatograms obtained for the volatile liquid fractions from the thermal degradation of the copolymers. Figure 23 shows the gas chromatogram of the volatile liquid fraction from the thermal degradation of a sample of conventional head-to-tail polystyrene. On preliminary examination, two features in the chromatograms are worthy of note. The first, is that there is a general increase in the complexity of the chromatograms from $n = 0$ (Figure 22) to $n = 5$ (Figure 18). The second, is that on the basis of increasing complexity, the chromatogram of the copolymer designated as $n = 0$, does not fit into the series of chromatograms

between $n = 3$ and $n = 1$. In fact, the chromatogram of the $n = 0$ copolymer is much more similar to the chromatogram of head-to-tail polystyrene, further evidence that this particular member of the series is indeed head-to-head polystyrene and not the copolymer $n = 2$, as might be expected from a synthesis involving a 1,2-dibromo alkane. Tables 12 to 17 show the assignment for each peak identified in the chromatograms, together with the mole percentages based on a value of 100 for styrene. Styrene was chosen since it was present in each chromatogram in by far the largest amount on a mole basis. The pattern that emerges in each chromatogram of the copolymers after toluene, is the occurrence of alkyl benzenes followed by their unsaturated analogues.

The assignments shown in Table 11 based on the mass spectral data are incomplete due to the overlapping of spectra making complete identification almost impossible. As was mentioned in the previous chapter, the number of peaks common to the spectra of alkyl and alkenyl benzenes made the relative intensities of the peaks of little help in assigning each peak to a specific compound. However, certain features in the spectra can be used to make a more positive identification possible, and these will now be looked at for each peak in turn.

The m/e values for Peak G are consistent with the assignment C_3H_5Ph . There are three possible isomers of this compound; 1-Phenylpropene, 2-Phenylpropene and 3-Phenylpropene. From the literature, the first three peaks in the mass spectrum of 2-Phenylpropene are, in decreasing order of intensity, 118, 117 and 103. This certainly does not match the spectrum of Peak G. The remaining two isomers have very similar fragmentation patterns. They are shown below with the m/e values in decreasing order of intensity from left to right.

m/e values

1-Phenylpropene	117	118	91	115	39	51	116	63
3-Phenylpropene	117	118	91	115	39	51	65	78

Comparing these values with those shown for peak G, and allowing for the difficulty of calculating the relative intensities of peaks, it can be seen that the spectrum assigned to C_3H_5Ph is consistent with either of those above, or a mixture of the two.

The m/e values of Peak H have been assigned to C_4H_9Ph . Of the four isomers of this compound, only two have similar fragmentation patterns. Again the m/e values decrease in intensity from left to right.

m/e values

1-Phenylbutane	91	92	134	65	27	39	105	51
1-Methyl-1-phenylpropane	91	92	134	43	65	41	39	51

The absence of the peak at an m/e value of 43 in the spectrum of Peak H and the presence of a peak at an m/e value of 105 suggests that the assignment C_4H_9Ph is probably 1-Phenylbutane.

The m/e values of Peak I are consistent with an assignment of C_4H_7Ph . There are unfortunately, relatively few isomers of this compound that have mass spectra well documented in the literature. All that can really be said about the structure from the mass spectral data is that the compound consists of an aliphatic C_4 chain containing 1 double bond, attached to a phenyl group.

From the m/e values of Peak J, the assignment $C_5H_{11}Ph$ has been made. From the quoted literature values of the mass spectra of the isomers of this compound, the most consistent with the experimental values is the spectrum of 1-phenylpentane. This is shown below,

with decreasing intensity in the m/e values from left to right.

m/e values

1-phenylpentane 91 92 148 65 105 41 39 27

Finally, the assignment $C_6H_{13}Ph$ was made on the basis of m/e values obtained for Peak K. Of the m/e values quoted in the literature for isomers of this compound, the three 'straight-chain' isomers, 1-Phenyl hexane, 2-Phenyl hexane and 3-Phenyl hexane were closest in fragmentation patterns to the experimentally determined values of m/e . Shown below are some literature values of the peaks obtained from the mass spectra of these three isomers, again the m/e values are in decreasing order of intensity from left to right.

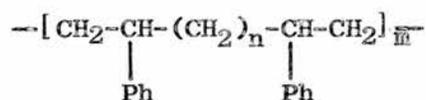
m/e values

1-Phenyl hexane	91	92	162	105	43	65	27	78
2-Phenyl hexane	91	133	162	92	104	27	41	77
3-Phenyl hexane	105	91	162	106	77	79	104	103

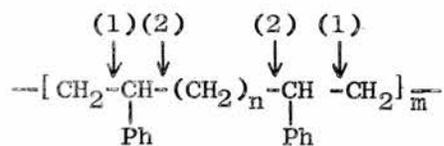
Having identified most of the volatile products, liquid at room temperature, at least in terms of their molecular formulae, it would seem appropriate to attempt to rationalise the results on the basis of possible reaction mechanisms for the thermal degradation of the copolymers. Any reaction mechanism must of course be hypothetical, but by considering routes which are chemically feasible it should be possible to postulate a reasonable reaction scheme. A basic assumption will be made at this point, that the thermal degradation of the copolymers involves the production of radicals by bond scission, and that these radicals then react in a manner that is consistent with the known behaviour for this type of species.

The polymer chain under investigation can be represented,

for all the copolymers, by the general formula:



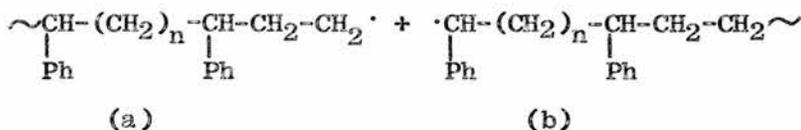
Since in order to break the polymer chain during thermal degradation, cleavage of C-C bonds must occur, a knowledge of the relative strengths of the C-C bonds in the copolymers would be of the greatest importance in deciding where the initial break in a chain might occur. Reference to the bond dissociation energies of C-C bonds in 'small' molecules, shows that the C-C bond in a methylene chain e.g. the central bond in n-butane⁷⁴, has a dissociation energy of 336 kJ mol⁻¹. This value increases to 390 kJ mol⁻¹ for the exocyclic C-C bond in toluene⁷⁵, but drops to a value of 252 kJ mol⁻¹ when the C-C bond is one removed from the phenyl ring as in iso-propylbenzene.⁷⁴ Extending these values to the C-C bond strengths in the polymer chain, it would seem reasonable to say that the weakest bonds will be those designated (1) and (2) in the chain below:



The mechanisms that follow are based on an initial chain scission at either (1) or (2), followed by the reactions of the macroradicals produced by these breaks. Although many different radical reactions may take place after the initial break in the chain, only those that lead to identified products of the degradation reactions will be considered.

Initial chain scission at (1)

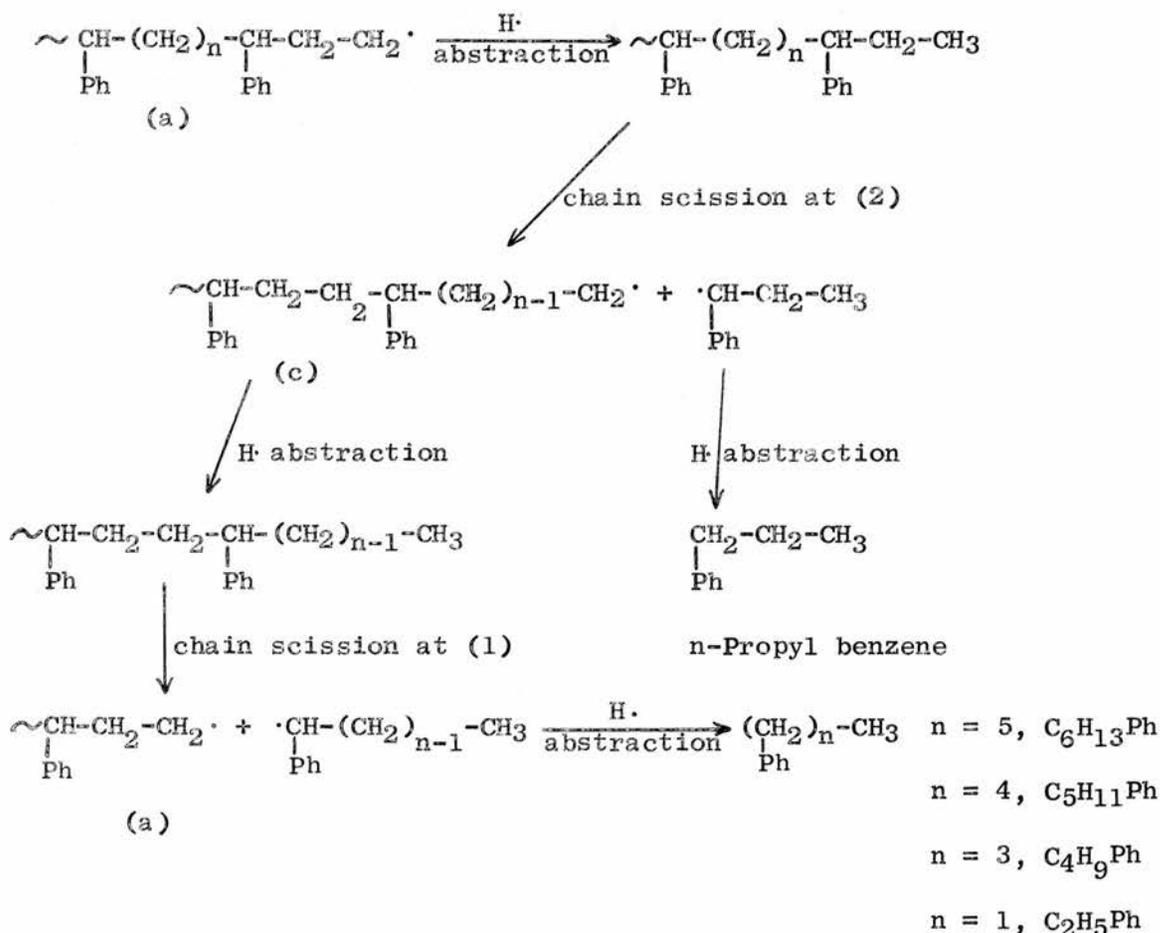
This leads to two macroradicals, (a) and (b):



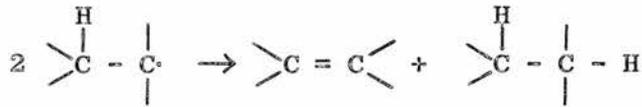
(a) and (b) will be considered separately, (a) being taken first.

Abstraction, or transfer, especially of hydrogen atoms, is a well documented reaction in free radical chemistry, and is known to occur in the thermal degradation of polystyrene.⁷⁶ The following scheme can be postulated involving only chain scission at (1) or (2).

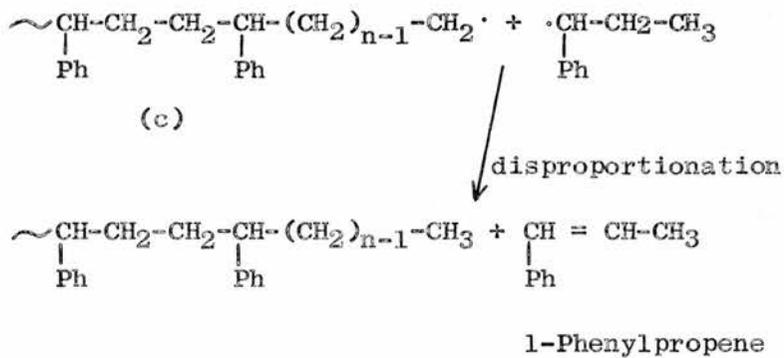
Abstraction of H (transfer), which is involved in the scheme, will be elaborated on later. Starting with (a):



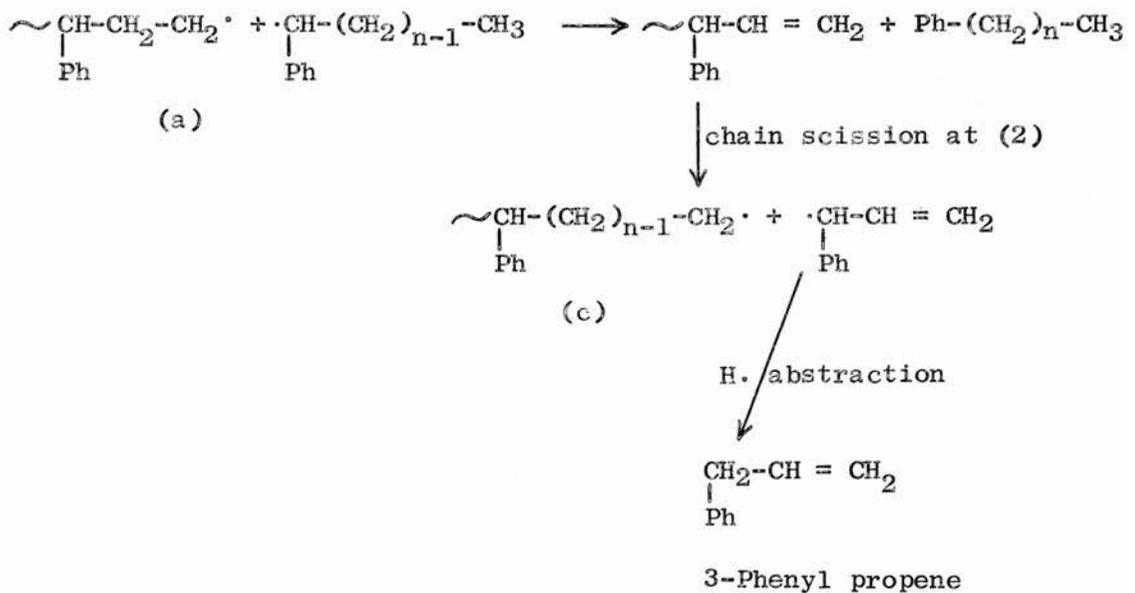
A possible reaction of a pair of radicals when close together is disproportionation i.e.



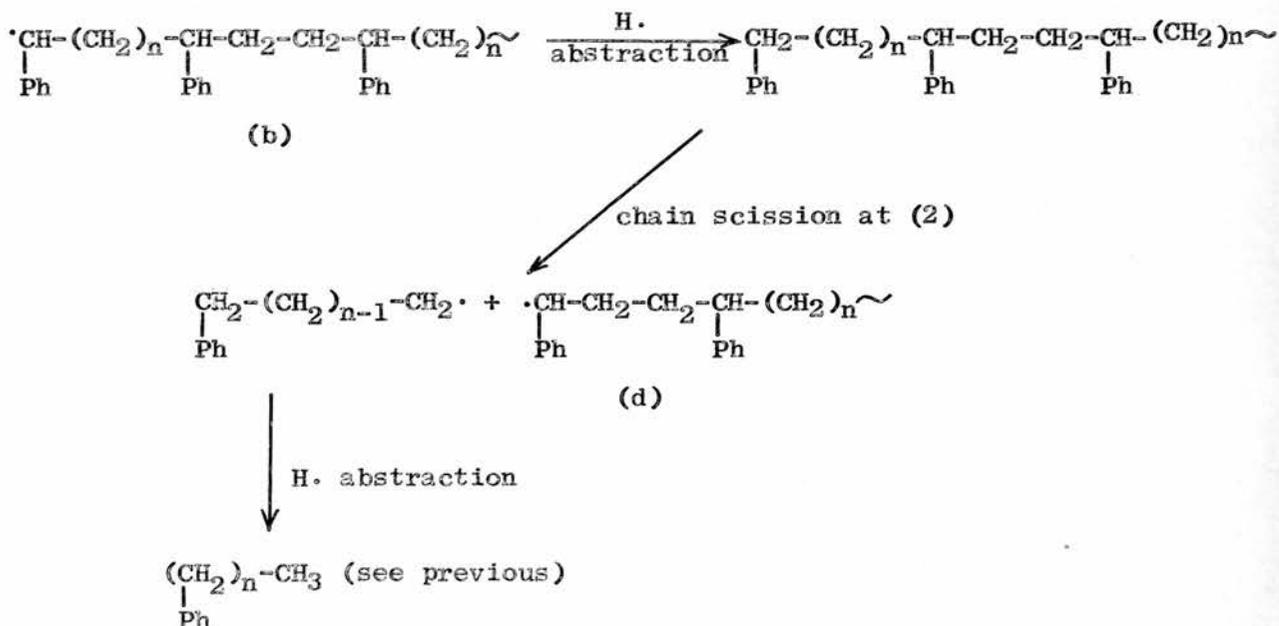
This is energetically favourable, as two new bonds are made for one broken. If we introduce disproportionation into the previous reaction scheme at the particular step:



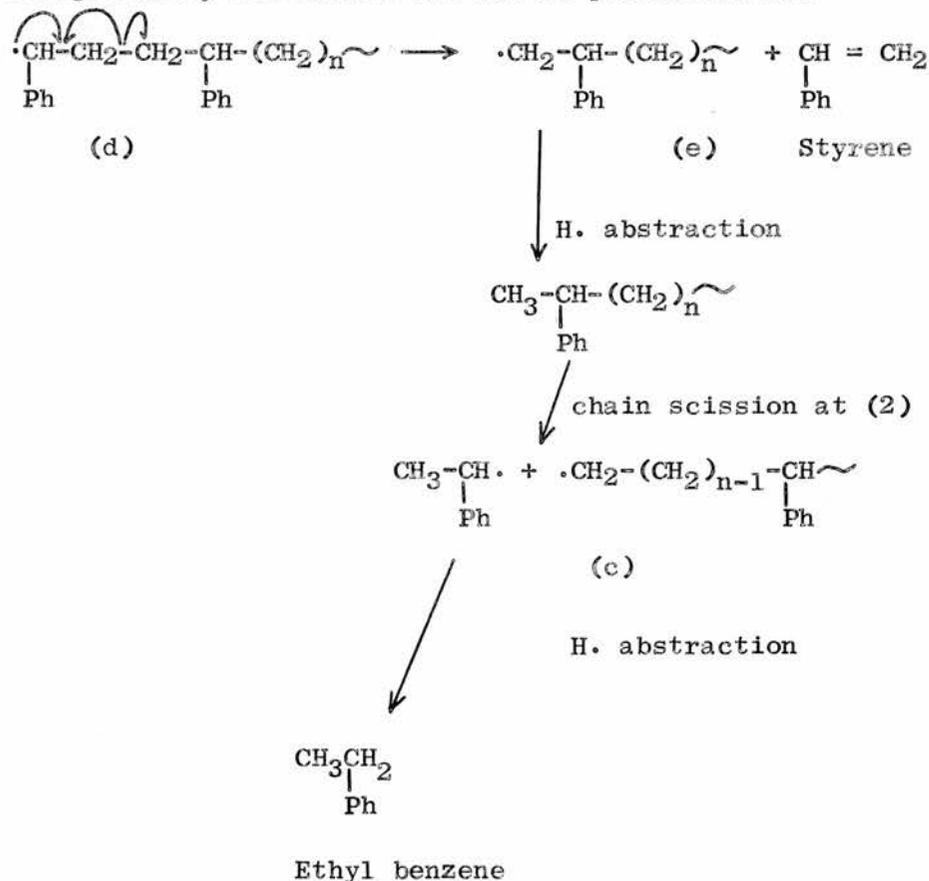
Referring to the last step in the first reaction scheme, and introducing disproportionation as an alternative:



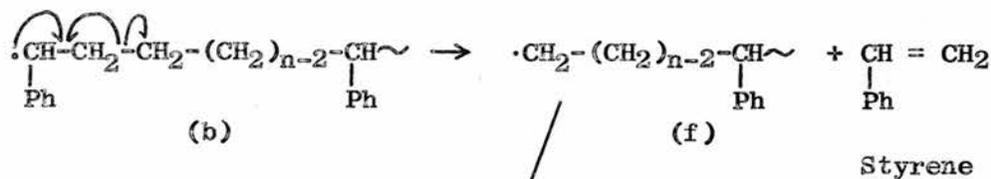
Considering now the macroradical (b), the following mechanism can be postulated:



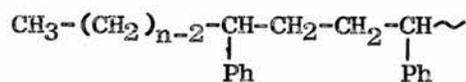
The macroradical (d) has the necessary configuration for the production of a $\text{>C}=\text{C}<$ in conjunction with an aromatic system. This is energetically favourable and can be postulated as:



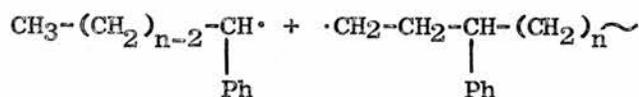
The original macroradical (b) used in the above reaction scheme also has the necessary configuration for the formation of a double bond in conjunction with an aromatic system. This can be visualised as:



H. abstraction

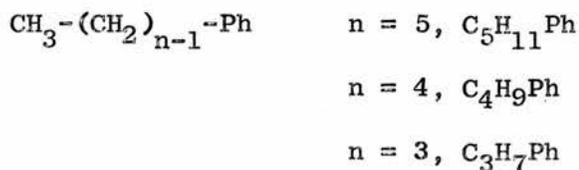


chain scission at (1)



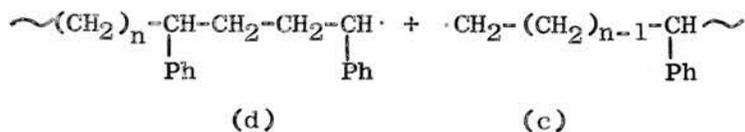
(a)

H. abstraction

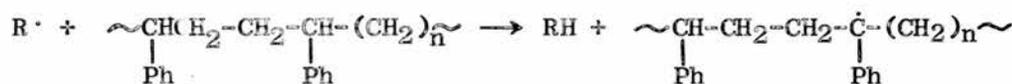


Initial chain scission at (2)

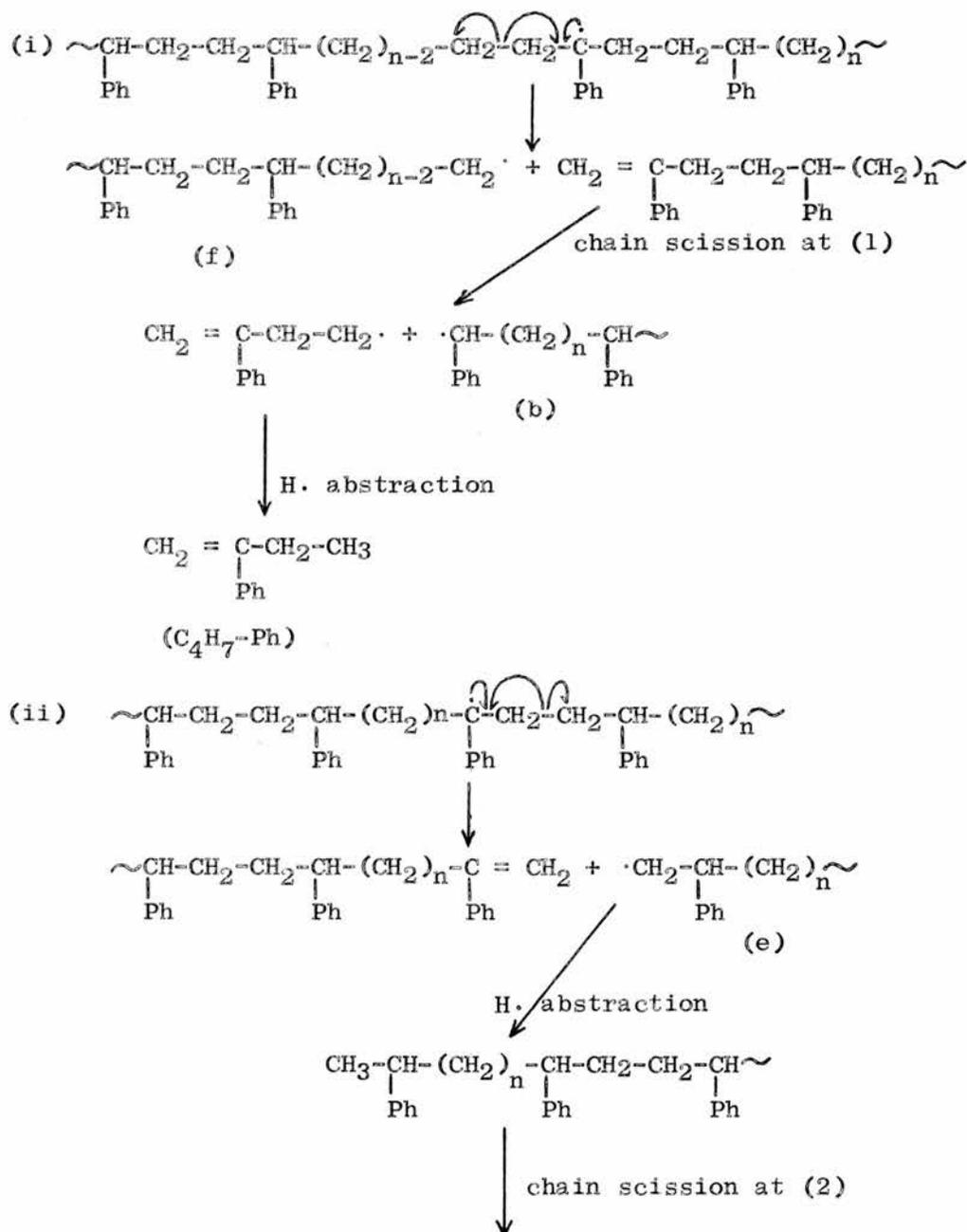
This produces two macroradicals, (c) and (d):

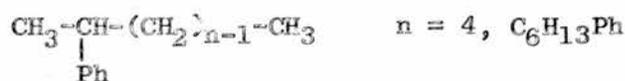


abstract a tertiary hydrogen atom in the following way:

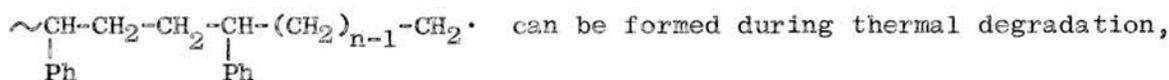


By undergoing chain scission, the macroradical thus produced has the necessary configuration to produce a $\text{>C} = \text{C}<$ bond in conjunction with the aromatic ring. Since the macroradical is not symmetrical about the tertiary carbon atom, two possibilities exist for chain scission. The two possibilities, (i) and (ii), will be looked at separately with a possible mechanism for subsequent reaction:





While the speculative nature of the above mechanisms cannot be over emphasised, they do account in a qualitative way for almost all the components identified in the volatile fraction, liquid at room temperature. No attempt was made to investigate any possible volatile fraction that was gaseous at room temperature, mainly because of experimental limitations. In an analogous system of copolymers having the repeat unit $-\left[\underset{\text{Ph}}{\text{CH}_2}-\underset{\text{Ph}}{\text{C}}(\text{CH}_3)-(\text{CH}_2)_n-\underset{\text{Ph}}{\text{C}}(\text{CH}_3)-\text{CH}_2\right]_m$ the volatile fraction, gaseous at room temperature was found to comprise less than 1% by weight of the total weight loss from the boat.⁷⁷ For this reason, none of the postulated reaction schemes involve the production of purely aliphatic species. However, if radical species of the type



can be formed during thermal degradation, then it is quite possible that saturated and unsaturated aliphatic compounds could arise. The likelihood of non-aromatic species being produced should be greater as the value of 'n' increases. In their work on the thermal decomposition of polymethylene, Tsuchiya and Sumi²⁷ used gas chromatography to analyse the degradation products. From 100mg. samples pyrolysed at isothermal temperatures between 648 and 738K and at a pressure of 10^{-3} torr, they obtained a volatile fraction that produced a chromatogram consisting of a series of double peaks, each doublet being an n-alkane, together with its 1-alkene analogue. Similar gas chromatograms were obtained by Kambe and

and Shibasaki²⁶ in their studies on the thermal degradation of polyethylene.

The proposed reaction schemes, based on simple, well known properties of radical species, account then for most of the components that were identified in the gas chromatograms. By their very complexity, the mechanisms cannot be used to compare the amounts of each component predicted by the reaction schemes, with those calculated from the gas chromatography results. What can be said however, is that if in the copolymers, initial chain scission occurs at (1) or (2), followed by the types of mechanism proposed in the above reaction schemes, then the products consisting of C₁, C₂ and C₃ skeletons attached to a phenyl group, are derived almost exclusively from the unit $\begin{array}{c} \text{-CH-CH}_2\text{-CH}_2\text{-CH-} \\ | \qquad \qquad | \\ \text{Ph} \qquad \qquad \text{Ph} \end{array}$. This should mean that in those copolymers which have higher values of 'n', the relative amounts of the C₁-Ph, C₂-Ph and C₃-Ph species should not change significantly as 'n' changes. Reference to Tables 12 to 16 shows that for the n = 5 and 4 copolymers, the mole %'s of toluene, ethyl benzene and C₃H₅-Ph with reference to styrene, are similar, while for the n = 3, 1 and 0 copolymers the relative amounts of the C₁-Ph, C₂-Ph and C₃-Ph species are similar neither to each other, nor to the n = 5 and 4 copolymers.

The appearance of benzene as a degradation product of the copolymers is perhaps surprising, since as already mentioned the exocyclic C-C bond in an equivalent model compound such as toluene has a dissociation energy of 390 kJ mol⁻¹. In order that benzene be formed during the decomposition of the copolymers, the bond between the phenyl ring and the main chain must break and a

hydrogen atom must be removed from the copolymer chain. Benzene is known to occur as a product in the thermal degradation of polystyrene, but literature values for the relative amount produced differ widely, depending on experimental conditions. Wall⁷⁸ pyrolysed 1 mg samples of polystyrene at 673 K for 20 minutes at a pressure of 10^{-5} torr. Analysis of the degradation products by mass spectrometry showed that benzene was present to the extent of 1.1 mole %, based on a value of 100 mole % for styrene. Later work by Straus and Madorsky²¹, using similar conditions but larger samples (15 - 30 mg), found that benzene occurred in the degradation products to the extent of 5.7 mole % based again on a value of 100 mole % for styrene. Pyrolysis-gas chromatography was used by Lehman and Brauer¹⁵ to analyse the products of degradation of 2-3 mg samples of polystyrene at 698 K. No trace of benzene was found in their chromatograms. Knight¹⁴, using flash-pyrolysis conditions to degrade 1-5 μ g. samples of polystyrene, analysed the products by gas chromatography. Even at elevated temperatures (973K), only traces of benzene were observed. From all these results, it would seem that sample size is a factor in determining how much benzene is produced in the thermal degradation of polystyrene. On this basis therefore the amount of benzene produced from 100 mg samples of the copolymers (2.3 - 11.4 mole %) is more reasonable than might at first appear. The amount of benzene produced in the thermal degradation of the sample of head-to-tail polystyrene (3.0 mole%) must be treated with some reservation as the sample was prepared in a benzene solution. Madorsky⁷⁹ has suggested that the formation of benzene in the thermal degradation of polystyrene takes place either by a concerted mechanism

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