A THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

THE THERMAL DECOMPOSITION OF SOME POLYSILOXANES

BY

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To my mother and father who have
waited patiently for this production.

PREFACE

The work described in this thesis was carried out by the author at the University of Glasgow, in the Department of Physical Chemistry, which is under the supervision of Professor G. A. Sim.

Work described in Chapter 4 on poly(methylphenylsiloxane) was carried out in conjunction with Mr. Kenneth Francey, B.Sc.

I should like to express my sincere gratitude to my supervisor Professor N. Grassie for suggesting the topic of this thesis and for his interest, advice and encouragement throughout the course of the work.

I acknowledge the assistance given by members of the Department particularly my colleagues in the Macromolecular Chemistry group for helpful discussion and suggestions. To the various members of the Departmental technical staff I also extend my thanks.

I am also grateful to the United States Air Force for the award of a scholarship during the tenure of which this work was carried out.

Finally I should like to thank Miss Marion Murray and Mrs. J. Mackinnon for typing the manuscript.

IAN G. MACFARLANE.

SUMMARY

There is an ever increasing demand for polymers and copolymers having high thermal and oxidative stability. Since the silicone industry began in 1931, silicone polymers have provided for a wide range of industrial needs as thermally stable oils, rubbers and resins. In recent years research has been carried out by a number of workers into the mechanism of breakdown processes in these materials in an attempt to bridge the gap between empirical knowledge and scientific understanding. The present work is aimed at supplementing information in the literature on the thermal breakdown of some linear polysiloxanes containing methyl or methyl and phenyl side groups.

Brief notes on the history of silicones, on common nomenclature and on some aspects of the physical chemistry of silicon and its compounds are given in Chapter 1 and these are followed by a comprehensive review of the literature dealing with work related to the title of this thesis.

Chapter 2 includes a list of sources for the chemicals used in this work, gives details of polymerisation techniques and summarises the apparatus and experimental techniques employed in this study. The first part deals with the thermal analysis techniques and the second part describes the techniques used to identify the degradation products both qualitatively and quantitatively.

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The thermal degradation of poly(dimethylsiloxane) is discussed in Chapter 3. The main products are cyclic siloxanes containing up to eighteen or more dimethylsiloxane units. The cyclic trimer, hexamethylcyclotrisiloxane is the major product. Methane is a product from samples degraded in the presence of base.

In Chapter 4 the preparation and thermal properties of poly(methylphenylsiloxane) are discussed. The two isomeric forms of the cyclic siloxane trimer and the four forms of the cyclic tetramer have been shown to be the major products of degradation. Benzene is also formed.

Several attempts to prepare high molecular weight samples of poly(diphenylsiloxane) are described in Chapter 5. These attempts were not successful.

In Chapter 6 some preliminary studies on copolymers of poly(dimethyldiphenylsiloxane) are described. Although benzene is produced there is evidence that some diphenyl units remain intact and are incorporated into siloxane ring compounds which appear as degradation products.

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CHAPTER 1

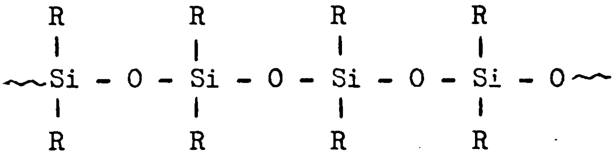
INTRODUCTION

1.1 GENERAL INTRODUCTION (Refs. 1, 2, 4, 5, 6, 7, 8, 12, 14, 17, 18, 19, 20, 21, 22, 23, 40.)

The importance of silicones to modern industry is a fact demanding no more proof than the simple statement that they find application in almost all industries from steel to food. During the past 30 years the organosilicon industry has evolved from a one man research project to a world-wide industry touching many phases of our social and economic material demands. This hybrid organic-inorganic field came into existence just following the development of concepts related to structure of macromolecular substances with purely organic origins.

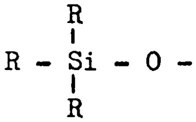
The chemical constitution of the silicones can be represented broadly by the generic formula (Ref. 1) $\left[R_a \; Si \; O_{4-a} \right]_n$ where n is large and α can be varied from 0 to 4.

This gives for $\alpha = 2$ the linear polysiloxane chain



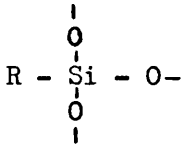
$$\begin{array}{ccccccccc} & R & & R & & R & & R & \\ & | & & | & & | & & | & \\ \sim\sim & Si & - O - & Si & - O - & Si & - O - & Si & - O \sim\sim \\ & | & & | & & | & & | & \\ & R & & R & & R & & R & \end{array}$$

$\alpha = 3$ the monofunctional species



$$\begin{array}{ccc} & R & \\ & | & \\ R - & Si & - O - \\ & | & \\ & R & \end{array}$$

$\alpha = 1$ the trifunctional species



$$\begin{array}{ccc} & | & \\ & O & \\ & | & \\ R - & Si & - O- \\ & | & \\ & O & \\ & | & \end{array}$$

The pendant groups can be almost any organic radical, large or small, with or without functional organic groups. By careful selection of the kinds and ratios of the different organic radicals, the appearance and feel of many wholly organic polymers can be imitated.

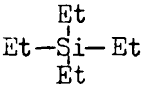
A great deal of effort has been made by government agencies and industry in various countries to produce silicone based polymers with improved properties as well as polymers with backbones based on other elements. To date there has been no real breakthrough to a more practical thermally stable silicone than those based on the methyl (CH_3-) and phenyl (C_6H_5-) substituents which comprise the current commercial materials (Ref. 2). Carborane containing silicones do have unusually high thermal stability but for general use are prohibitively expensive. Boron-nitrogen polymers (phosphazines) appear to have a commercially brighter future than was thought possible a number of years ago (Ref. 3) but at the moment do not compete favourably with silicones.

A recent conclusion (Ref. 2) is that for maximum resistance to thermal or oxidative stress an organic radical which cannot unsaturate on heating is necessary. Thus, if the properties of interest relate specifically to thermal and oxidative stability with moderate flexibility and moderate heat resistance, the industrial organosilicon field quickly narrows to the two above mentioned groups attached to the silicon atom.

It may be of interest to mention that there is no example of a naturally occurring compound in which there is a carbon-silicon bond as in the silicones.

1.2 THE HISTORY OF SILICONE POLYMERS

The history of silicone polymers is reviewed in several comprehensive texts (Refs. 1, 4, 5, 6, 7, 9). The principal landmarks are briefly as follows:

In 1863 Friedel and Crafts reported the synthesis of tetraethylsilane  $\mathrm{Et{-}\overset{Et}{\underset{Et}{Si}}{-}Et}$ and by 1900 about 27 compounds had been reported. Thereafter the major contribution to our knowledge of organosilicon chemistry was made by Professor F. S. Kipping working at University College, Nottingham. Between 1899 and 1944 Kipping published 54 papers (mainly in the Journal of the Chemical Society). They were interested in organosilicon compounds basically from the point of view of organic chemistry. That is, they sought the isolation and characterisation of pure compounds.

Kipping described as "uninviting" the unidentified oils and glue-like substances (silicone polymers) which were often formed in his reactions and in which he took little interest. Reviewing the greater part of his life's work in a lecture in 1937 Kipping foresaw no great technical usefulness for the silicone polymers and certainly made no attempt to develop them.

From about 1931 onwards, interests which were basically industrial, used the ground work of Kipping to develop the polysiloxanes as commercial materials. Interest soon became positively focussed on the dimethyl-siloxanes as heat resistant fluids, resins and rubbers and in 1943 the Dow Corning Corporation was formed for their production in the U.S.A. They were later joined in the U.S.A. by the General Electric Company (1947) and Union Carbide and Carbon Co. (1955), while in the United Kingdom production was started/

started by Albright & Wilson in 1954 under licence from Dow Corning and in 1955 by I.C.I. under licence from the General Electric Company.

1.3 SILICONES AND THE FUTURE

The future importance of any branch of science is never easy to predict but from the standpoint of conservation of natural resources it is interesting that the synthesis of dimethylsiloxanes requires no petroleum feed-stock unlike the great majority of the commercial polymeric materials as they are prepared at the present time. Man's supply of petroleum is not infinite and with the increasing hunger for these useful, natural hydrocarbon, products their cost will inevitably increase. On the other hand, of the raw materials for the production of silicones, SiO_2 is infinite in relation to man's existence on the earth, and methanol can be made from the reduction of carbon monoxide (CO) with hydrogen (H_2).

The production of silicones relies heavily on electrical energy. In the future this will probably come from atomic energy (fission or fusion) or directly from the sun by the use of giant solar cells.

1.4 NOMENCLATURE

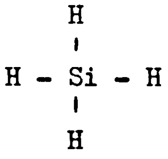
In/

In the early history of silicon compounds (Ref. 9) nomenclature analogous to that of carbon compounds was used. Thus the term silicone, first used by Wohler in 1857 and later by Kipping, was used to denote the silicon analogue of the ketone group in organic chemistry. The term (which was never a suitable one) has been taken over as a trade name by industry to describe species of the empirical formula R_2SiO and no longer plays a part in systematic nomenclature. Despite not being defined scientifically it still serves a useful purpose in categorising organosilicon compounds in general, especially those containing Si-O-Si bonds.

In 1946 the American Chemical Society approved a series of 19 rules, based on an earlier report (Ref. 10), for the naming of organosilicon compounds. Later the I.U.P.A.C. adopted the rules with minor alterations (Ref. 11). These rules have formed the basis for the present system of naming silicones but other nomenclature rules (Ref. 12), which conflict in parts with the I.U.P.A.C. convention, are also used in the literature (Refs. 7, 14).

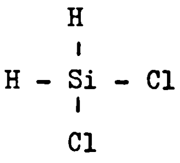
Generally the naming of simpler organosilicon compounds in this thesis will be according to the I.U.P.A.C. rules.

The root compound in silicone chemistry is silane (SiH_4), a name originally suggested by Alfred Stock (Ref. 13). Silicon containing monomers are named as silane derivatives



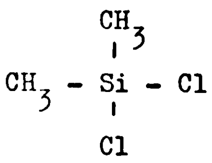
$$\begin{array}{c} H \\ | \\ H - Si - H \\ | \\ H \end{array}$$

silane



$$\begin{array}{c} H \\ | \\ H - Si - Cl \\ | \\ Cl \end{array}$$

dichlorosilane



$$\begin{array}{c} CH_3 \\ | \\ CH_3 - Si - Cl \\ | \\ Cl \end{array}$$

dichlorodimethylsilane

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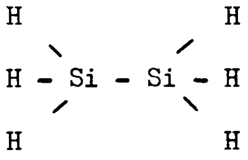
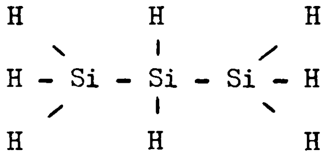
The silanic hydrogen bond is not named explicitly but it is assumed that any bonds left over after substituent groups are named are hydrogenated. Oligomers of silane are named disilane, trisilane and so on

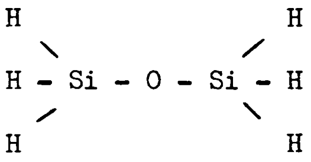


disilane

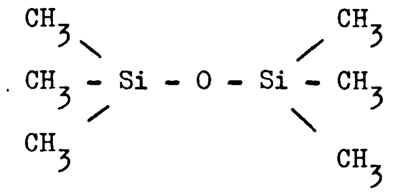


trisilane

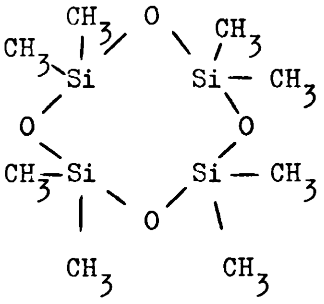
Species consisting of alternating silicon and oxygen atoms are called siloxanes. The prefix designates the number of silicon atoms in the molecule. Substituted siloxanes are named in the same manner as silanes,



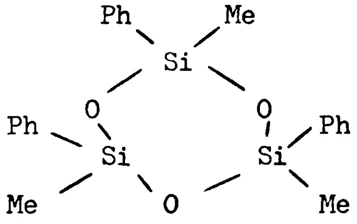
disiloxane



hexamethyldisiloxane



octamethylcyclotetrasiloxane



1,3,5- trimethyl, 1,3,5-triphenyl-cyclotrisiloxane

Three numbering systems appear in the literature which identify the three silicon atoms in a cyclic siloxane trimer as 1,3,5; 2,4,6; 1,2,3 respectively. 1,3,5 (used above) is favoured by I.U.P.A.C. and the American Chemical Society (Ref. 11) whilst 2,4,6 is favoured by Eaborn (Ref. 12), Smith (Ref. 14) and also by the Chemical Society (Ref. 15).

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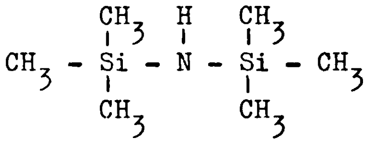
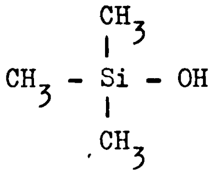
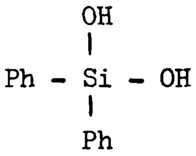
In a manner analogous to the siloxanes, species of alternating silicon and nitrogen are called silazanes:


$CH_3-Si(CH_3)_2-NH-Si(CH_3)_2-CH_3$

1,1,1,3,3,3 - hexamethyldisilazane

The silicon analogues to organic alcohols are called silanols:

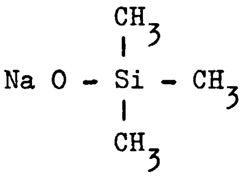

$CH_3-Si(CH_3)_2-OH$


$Ph-Si(OH)(Ph)-OH$

trimethylsilanol

diphenylsilanediol

Metal salts of the silanols are termed silanolates:


$NaO-Si(CH_3)_2-CH_3$

sodium trimethylsilanolate

"Shorthand" Method (Ref. 16)

Sometimes it is convenient to represent siloxane polymers by a widely accepted "shorthand" method first proposed by Hurd (Ref. 16). This method designates the functionality of the monomer building units by letters:

M	monofunctional	R_3 Si O
D	difunctional	R_2 Si O
T	trifunctional	R Si O
Q	quadrifunctional	Si O

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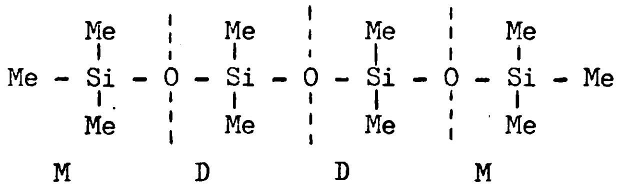
In the fractional subscripts of the formulas, the denominators show that each oxygen atom is shared by two silicon atoms and the numerators indicate the number of oxygen atoms so shared. Unless otherwise stated, the siloxanes are methyl substituted. To illustrate the use of this system, the linear decamethyltetrasiloxane:



$$\mathrm{Me-\underset{Me}{\overset{Me}{Si}}-O-\underset{Me}{\overset{Me}{Si}}-O-\underset{Me}{\overset{Me}{Si}}-O-\underset{Me}{\overset{Me}{Si}}-Me}$$

would simply be written as MD_2M . Octamethylcyclotetrasiloxane would be written as D_4 .

Some siloxane polymers can become so complex, especially where poly-functionality of building units and a variety of substituent groups appear in the same macromolecule, that it is clearer and simpler to write their structural formulae than to attempt to name them.

1.5 FIELDS OF USE

The industrial applications of silicones depend on the constancy of their properties over a wide range of temperature. These properties are typically water repellancy, low surface tension, anti-adhesive properties, and non-toxicity, associated with good thermal and oxidative stability and general resistance to ageing. By altering molecular weight, degree of cross-linking and nature of pendant groups attached to the silicon atoms, silicones can be produced as oils, gums, rubbers or resins - This diversity of properties and physical forms leads to silicones having an unusually large number of uses. Many of these uses are separately relatively/

relatively small but combined explain why silicones production continues to increase.

It is quite impossible to list all the industrial applications of silicones, but a typical sample is presented in Table 1.1.

Table 1.1 Some Typical Uses of Silicones in Industry

Industry	Main Application	Industry	Main Application
Aeronautics Astronautics	Damping Encapsulating, sealing Fire-proof Partitions Gluing, jointing Heat barriers High temperature paints Lubrication Safety Cables	Surgery	Baths for burned patients Misc. tubes and probes Prosthetic parts Sterilising baths
Food	Anti-adherence of moulds and pans Antifoaming Luting of stoppers	Electronics	Damping Encapsulating Impregnating Insulation Lubrication Manufacture of moulds and matrices Protection
Building	Miscellaneous sealings Miscellaneous water repellent treatments	Shipbuilding	Adhesion Bonding Caulking Damping Lubrication Metal protection Sealing Water repellancy
Rubber	Bonding Cable making Calendering Latex processing Lubrication Manufacture of synthetic rubber Mould release agents Moulding Temporary anti-adherence Sealing	Plastics	Anti-adherence of moulds Bonding Calendering Antifoaming during manufacture (polymerisation, washing, etc.) Manufacture of moulds
		Textiles	Fire resistant treatment Water repellancy Protective bedsheets

Silicone rubbers are widely used in many applications where flexibility at extremes of temperature is desired. Although their performance under extreme conditions of temperature is excellent, at normal temperatures their physical properties such as tensile strength, elongation and tear resistance are inferior to those of commercial rubbers.

1.6 THE PHYSICAL CHEMISTRY OF SILICON AND ITS COMPOUNDS

(Refs. 1, 7, 12, 14, 22, 23, 26, 31)

(i) Introduction

An understanding of the basic physical chemistry of silicon and its compounds is fundamental to a study of the degradation of silicones. Although C and Si are found close to each other in the periodic table, they are not as similar to one another as Cl and Br , Li and Na , or Mg and Ca . On the basis of knowledge gained in organic polymer systems alone prediction of the properties of silicones is not usually reliable.

Some fundamental properties of Group IV elements are presented in Table 1.2. Of these properties values for the atomic radius and electronegativity of silicon are clearly unexpected, at least on the basis of naive inter polation. The low electronegativity, in particular is significant; one consequence is that bonds between silicon and elements such as O, N, Cl and F are more ionic than corresponding bonds with carbon. Pauling (Ref. 26) has calculated 23% ionic character for the Si-Cl bond in $SiCl_4$.

It/

It might also be noted that certain bonds are polarised in the reverse of their usual direction; namely $Si^{\delta+} - H^{\delta-}$ as compared with $C^{\delta-} H^{\delta+}$.

Table 1.2 Properties of Group IV Elements

Property	Carbon	Silicon	Germanium	Tin	Lead
Atomic Number	6	14	32	50	82
Atomic Weight	12.01	28.09	72.59	118.69	207.19
Atomic Radius	0.772	1.176	1.225	1.405	1.53
Electronegativity	2.5	1.8	1.8	1.8	1.8
ΔH atomisation, k.cal.					
Relative electron density: atomic number/ atomic rad.^{3}	13.0	8.6	17.4	18.0	22.9

(Ref. 23)

One similarity between silicon and carbon for which many chemists have searched in vain is the double bond with silicon. In spite of many attempts, no-one has ever isolated a Si = C , Si = O or Si = Si containing compound (Ref. 14). The nearest is a claim by Barton and McIntosh (Ref. 24) to have trapped and identified $Me_2 Si = CH_2$ using low temperature infra red spectroscopy. The exact reason for this anomaly has never been convincingly explained, but it may be related to the larger size of the Si atom which would result in less π-orbital overlap.

(ii)/

(ii) Bond Length

Bond lengths between silicon and certain elements (especially oxygen and fluorine) are abnormally short, even when corrected for the electronegativity difference of the atoms (Ref. 25). The Si O Si bond angle in siloxanes (130-150°) is much larger than the COC bond angle in aliphatic ethers (105-115°). Such a situation implies a more complex hybridization at the oxygen atoms than simple p or sp^3 bonds. Another anomaly is that silanols should be weaker acids than carbinols, because silicon (being more electropositive than carbon) should release electrons to the oxygen more freely. The reverse is in fact found. Clearly silicon is involved in some sort of extraordinary bonding. Much has been said about the possibility of $(d-p)\pi$ bonding in compounds and this subject is reviewed by Attridge (Ref. 40), Ebsworth (Ref. 23), Egorochkin (Ref. 28) and Mitchell (Ref. 29).

Reaction intermediates involving increased coordination round silicon cannot be ruled out since penta and even hexacovalent compounds of silicon are known (Ref. 37). Silicon has 5 d-orbitals available for bonding, but, possibly for steric reasons, and in common with the other elements in the second short period, probably never uses more than two of them, so that the coordination number never exceeds six. The best known example of the use of d-orbitals of silicon is probably in the hexafluorosilicate ion, SiF_6^{2-} which has been shown by x-ray crystallographic analysis to have the fluorine atoms arranged octahedrally about the silicon atom.

(iii) Bond Energies

In comparing bond energies it is important to remember that they represent energies involved in homolytic fission whereas in silicone chemistry the normal mode of breakdown is heterolytic fission.

Bond energy values quoted by both Pauling (Ref. 26) and Cottrell (Ref. 31) are listed in Table 1.3. The energy of the Si - C bond falls quite rapidly with an increase in length of the radical (Ref. 30). Thus, the energy of the Si - CH_3 bond is 74 kcal. mol.$^{-1}$; Si - C_2H_5 62 kcal. mol.$^{-1}$; Si - C_3H_7 59 kcal. mol.$^{-1}$ and Si - C_4H_9 54 kcal. mol.$^{-1}$. The exact significance of these figures is not clear but the trend is obvious.

The silicon atom is rather sensitive to changes in hybridisation induced by electronic substituents (Ref. 32). The chemistry of attached groups may therefore change with the nature of the other substituents on the silicon. Correlations of reactivity parameters have been developed (Refs. 33, 34).

Table 1.3 Average Bond Energies for some Linkages of Silicon and Carbon

Bond	Bond Energy		Bond	Bond Energy	
	(a)	(b)		(a)	(b)
Si - Si	42	53	C - Si	69	76
Si - C	69	76	C - C	83	83
Si - H	70	76	C - H	99	99
Si - O	88	108	C - O	84	86
Si - F	129	135	C - F	105	111
Si - Cl	86	91	C - Cl	79	81
Si - Br	69	74	C - Br	66	68
Si - I	51	56	C - I	58	51

(a) T. Cottrell (Ref. 31) (b) L. Pauling (Ref. 26)

(iv) Radical Reactions in Silicon Chemistry

Reactions which have been shown to involve free radicals are not common in silicon chemistry. The addition of Si–H bonds to unsaturated systems is of this sort, and the cracking and polymerisation of the simple hydrides and alkyls are probably also free radical processes, but these do not occur readily except under fairly rigorous conditions. (Refs. 35, 36, 39)

(v) Siliconium Ions

Electron-deficient silicon is an extremely reactive species. Until 1963 the formation of siliconium ions had not been established in any of the reactions of silicon compounds. It is quite clear that many siliconium ions do not form under conditions in which analogous carbonium ions exist (Ref. 7).

(vi) The Electronic Effect of the Si-CH_3 Group

The silicon-carbon bond is surprisingly inert. Its bond energy (see above) is not very high and is very much less than the energies of the Si - O and Si - F bonds; none the less the bonds from silicon to saturated aliphatic groups persist through a variety of chemical reactions, and are moderately stable to such strong reagents as alkali. The reason for this reluctance to react must involve activation energies, since many of the compounds are thermodynamically unstable to substances with which they do not react at room temperature; it is possible that the apparently large activation energies are connected with the absence of lone pairs of electrons, and low-lying excited states in the carbon atom. If the carbon atom attached to silicon is unsaturated the silicon carbon bond is appreciably more reactive.

Eaborn/

Eaborn (Ref. 7) has pointed out that the silicon-carbon bond is chemically rather like the hydrogen-carbon bond. Silicon-carbon bonds may be broken by electrophilic or nucleophilic attack; the former is more effective in removing alkyl groups; and the latter in breaking bonds between silicon and aromatic nuclei.

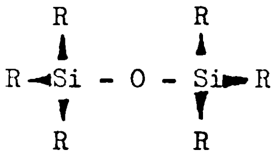
(vii) Linear Polysiloxanes

Linear polysiloxanes possess both inorganic and organic properties (Ref. 1). From the standpoint of physical properties they possess inorganic characteristics due to the high percentage of ionic character in the Si - O bond, and organic characteristics due to the substituent groups and low intermolecular forces resulting from their shielding of the siloxane skeleton. Accordingly, linear polysiloxanes are liquids varying in viscosity and volatility, or sometimes gums or solids due to high molecular weight or crystallinity.

The varying effects of different organic groups are apparent in the range of substituents that have received extensive academic and commercial attention: Me, Ph, H, vinyl, ethyl, stearyl and trifluoropropyl - in about that order. A comparison of the first two in their effect on physical properties of the polymer shows that methyl groups promote fluidity, low viscosity-temperature index, low melting point and high liquid compressibility whereas phenyl groups induce contrasting effects.

Organic groups, R , which are electron donors cause a weakening of the Si - O - Si linkage by increasing polarisation, while R groups which are electron acceptors strengthen the linkage by an increase in the double bond character.

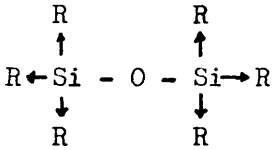
The influence on the Si - C linkage is in the reverse direction (Ref. 39).



R= electron donor

Si - O - Si linkage weakened

Si - C " strengthened



R =electron accepter

Si - O - Si linkage strengthened

Si - C " weakened

The siloxane chain retains a considerable amount of flexability even at low temperatures. NMR (Ref. 38) studies on poly (dimethylsiloxane) have indicated essentially free rotation of the methyl groups at -196°C.

1.7 <u>POLYMER DEGRADATION (GENERAL)</u> (Refs. 41, 42, 43, 44, 46, 47)

(i) Introduction

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

Degradation studies are important in that they can explain the behaviour of polymers under conditions of high temperature, or other modifying influence, and, after a precise knowledge of the degradation mechanism has been obtained, existing polymers can be stablised in a logical way and new polymers "tailored" to meet new or existing requirements.

Such studies also help to elucidate macromolecular structure by providing information on the sequence and arrangement of the repeat units and side-groups in the polymer or co-polymer chain, as well as the nature of chain-ends and of the cross-links between chains. Other information such as the strengths of the various bonds within the macromolecule, the kinetics of the degradation reactions and the effects of varying sample environment on rates and products of degradation can also be gained.

Throughout this thesis the term "polymer degradation" is used in its broadest sense (Ref. 47); that is, to describe all reactions of polymers whether there is a net decrease in molecular weight or not.

(ii) The Mechanisms of Thermal Degradation (General)

Mechanisms of the thermal degradation of polymers normally fall into two distinct categories:

(a) Chain-scission reactions

(b) Substituent reactions

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

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

1.8/

1.8 THERMAL DEGRADATION OF LINEAR POLYSILOXANES

(i) Introduction

One problem which arises in the consideration of inorganic polymers is the chemical difference between them and the more popularly accepted organic polymers (Ref. 45). Polymerisation in organic systems is quite generally kinetically controlled as are the chemical properties of the resultant polymers. On the other hand, inorganic systems are, to the most part, more labile so that equilibrium plays a dominant role in polymerisation reactions as well as in determining quite a few of the chemical and physical properties of the resulting polymers. Primarily because of the fact that equilibrium control predominates, the polymerisation (and degradation) processes in the chemistry of inorganic macromolecules must be viewed in a somewhat different manner (Ref. 45). There are many excellent reviews on the degradation of organic polymers (Refs. 41, 42, 43, 44, 46, 47) but the degradation of inorganic polymers is inadequately dealt with in the literature (Ref. 48).

In organosilicon chemistry, as in any commercially useful branch of industrial chemistry, exaggerated or at times even false claims are not uncommon. Hunter, (Ref. 2), in his review, cites the case of a recent U.S. patent in which a claim was made to have studied approximately 10^5 individual silicon compounds!

(ii) The Composition of Thermal Degradation Products

The composition of thermal degradation products of polydimethylsiloxanes was first studied by Patnode and Wilcock (Ref. 49) who found that in an atmosphere of nitrogen, polydimethylsiloxane decomposes at 350-400°C to form the following percentages of low molecular weight cyclic products:

$[(CH_3)_2SiO]_3$	44
$[(CH_3)_2SiO]_4$	24
$[(CH_3)_2SiO]_5$	9
$[(CH_3)_2SiO]_6$	10
above hexamer	13

Thus, the thermal degradation of polydimethylsiloxanes involves the rupture of the silicon-oxygen bond to form cyclic compounds.

More recently Thomas and Kendrick (Ref. 50) have found the following values for the weight per cent of the thermal degradation products of trimethylsiloxy end-blocked polydimethylsiloxane:

	wt. per cent
$[(CH_3)_2SiO]_3$	43.7
$[(CH_3)_2SiO]_4$	23.5
$[(CH_3)_2SiO]_5$	9.7
$[(CH_3)_2SiO]_6$	10.9
$[(CH_3)_2SiO]_7$	7.2
$[(CH_3)_2SiO]_{8-12}$	5.0
Hexamethyldisiloxane	0.3
Octamethyltrisiloxane	1.0

After 5 hrs. heating in vacuo (420°C) weight loss was complete. There was no evidence of rupture of the Si - C bond.

Rodé and Verkhotin (Ref. 51) have analysed the degradation products of hydroxy end-blocked polydimethylsiloxane as 99 wt. per cent dimethylcyclic trimer.

In/

In the publication of their work on the effects of irradiation on polydimethylsiloxane Tanny and St. Pierre (Ref. 52) have included, for comparision purposes, data on the thermal degradation of this polymer. Without detailing the degradation conditions they present the following figures for the production of cyclics:

	wt. per cent*
$[(CH_3)_2\ Si\ O]_3$	61.0
$[(CH_3)_2\ Si\ O]_4$	30.4
$[(CH_3)_2\ Si\ O]_5$	5.4
$[(CH_3)_2\ Si\ O]_6$	3.2

* originally presented as volume per cent.

Andrianov et. al. (Ref. 53) have predicted, and Aleksandrova et. al. (Ref. 54) have observed, the presence of methane in the degradation products of hydroxyl end-blocked polydimethylsiloxanes. This conflicts with data of other workers (Refs. 50, 51, 58).

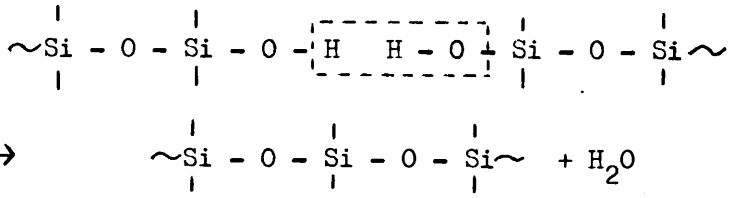
Only a very limited amount of work has been published on the degradation of poly (methyl, phenyl siloxanes) and poly (dimethyl, diphenyl siloxanes) but there is evidence that ring compounds are also favoured in the breakdown of these systems (Ref. 55). Thus, Thomas and Kendrick (Ref. 55) have found the degradation products of a trimethylsilyl end-blocked sample of polymethylphenylsiloxane to be "trans cyclic trimer and various cyclic tetramer isomers". Here there was no evidence of Si - C bond scission.

Investigations/

Investigations of the thermal degradation of heterochain polyorgano siloxanes of regular structure containing aluminium, titanium, and boron atoms has shown that, as with polyorganosiloxanes themselves, the major part of the volatile products responsible for the losses in weight consists of hexamethylcyclotrisiloxane (dimethylcyclic trimer) formed by cleavage of the Si - O bond (Refs. 56, 57).

(iii) Mechanisms of Thermal Degradation

It is a striking fact that the intrinsic viscosity of hydroxyl end-blocked polydimethylsiloxane increases before weight loss starts (Ref. 51). This increase in viscosity has been attributed to an increase in the molecular weight of the polymer as a result of polycondensation involving terminal hydroxyl groups (Ref. 51).

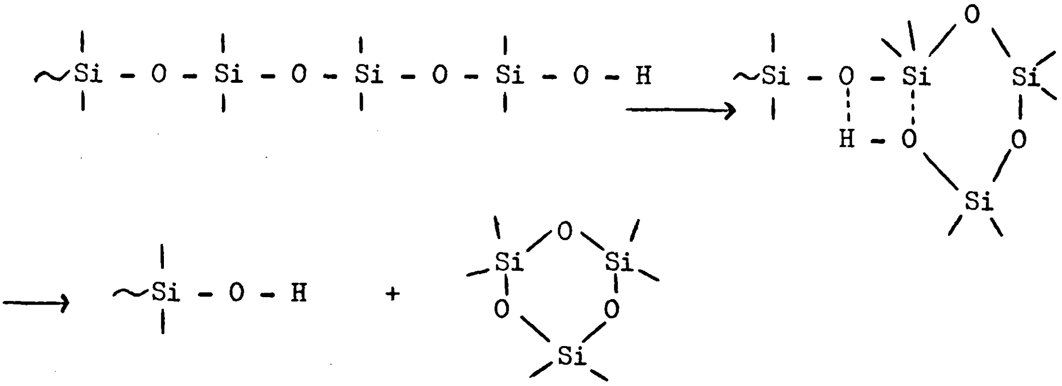


$$\sim Si - O - Si - O - \boxed{H \quad H - O} - Si - O - Si \sim \longrightarrow \sim Si - O - Si - O - Si \sim + H_2O$$

Until quite recently only fragmentary data of a tentative character were available on the mechanism of the thermal decomposition of siloxane polymers and even now the process is by no means clearly understood. A comprehensive study of the thermal degradation of polydimethylsiloxanes by Andrianov et. al. has produced data which the authors claim conflict with that of three works by other authors (Refs. 58, 59, 60). A paper published simultaneously by Aleksandrova et. al. (Ref. 54) includes features which are not wholly consistent with Andrianov's findings.

By/

By saturating a hydroxyl-ended polydimethylsiloxane with water Rode' et. al. have managed to inhibit the molecular weight increase described above and have shown the dependence of the depolymerisation rate constant on the degree of polymerisation to correspond to initiation of this reaction by terminal groups. They therefore propose a mechanism of depolymerisation through hydroxl groups. It is suggested that the high mobility and spiral-like structure of siloxane chains with three silicon atoms in a turn leads to the generation of a transition complex with excited Si --- O and O --- H bonds. Redistribution of the energy of this excited state results in decomposition of the complex splitting off the cyclic product but leaving a hydroxyl group at the end of the siloxane chain.

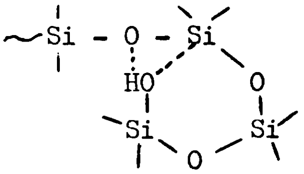


On the basis of bond energy calculations Rode' et. al. (Ref. 51) predict an activation energy of 14 kcal. mol^{-1} for this reaction and claim that experimentally determined values are in good agreement. According to Bridge and Simpson (Ref. 61) with increase in molecular weight, random cleavage of the chain plays an increasingly important part so that the activation energy increases (to 32 kcal. mol^{-1}).

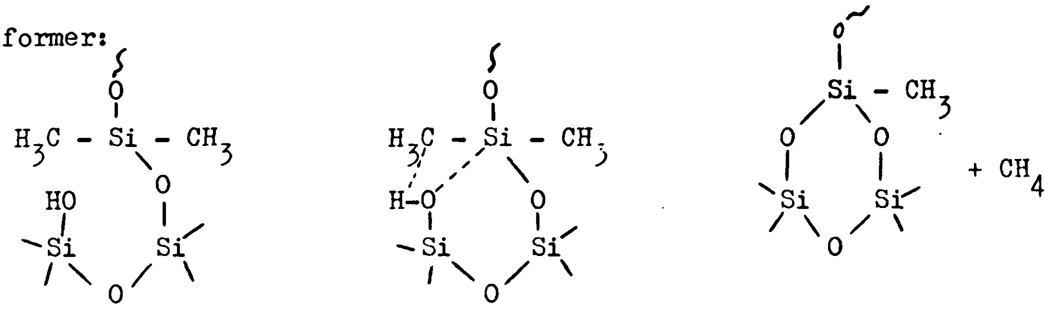
Without/

Without questioning the importance of this mechanism in the degradation of pure polydimethylsiloxane samples Andrianov et. al. (Ref. 53) have criticised Rode' and Verkhoten's work (Ref. 58) on the involvement of hydroxyl chain ends. It is suggested that the data presented by these workers indicates depolymerisation is due to residual sulphuric acid and not hydroxyl groups

The above mechanism differs little, or not at all, from the one proposed earlier by Aleksandrova et. al. (Ref. 54). They report the formation of appreciable amounts of higher cyclics (tetramer, pentamer, etc.) in addition to dimethyl cyclic trimer. The intermediate is pictured as a complex with a pentavalent Si atom and having a hydrogen bond between the hydrogen of Si - OH and the oxygen of the siloxane bond and is drawn thus:

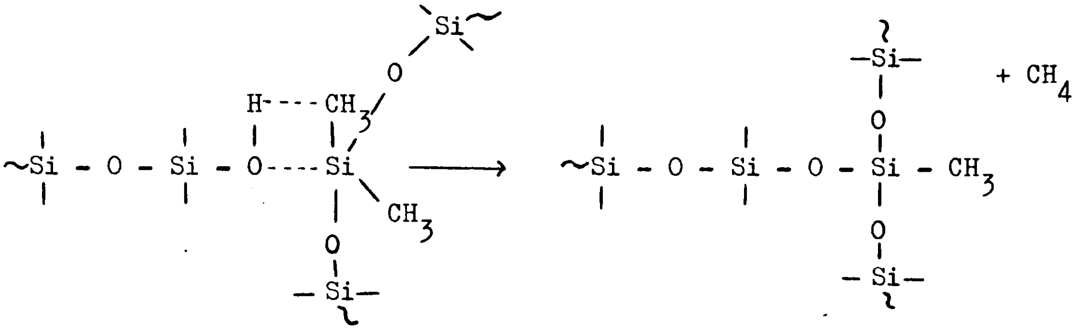


These workers also observe small amounts of methane and to a lesser extent hydrogen and propose the following mechanism, involving chain ends in intramolecular reaction, to account for the former:



The transition here is displacement of the H atom towards the methyl group, a process which the authors describe as being less likely than displacement towards the O atom with its intact electron pair but nevertheless one which is involved. The above mechanism is consistent with the observation that sample solubility is unaffected by heating.

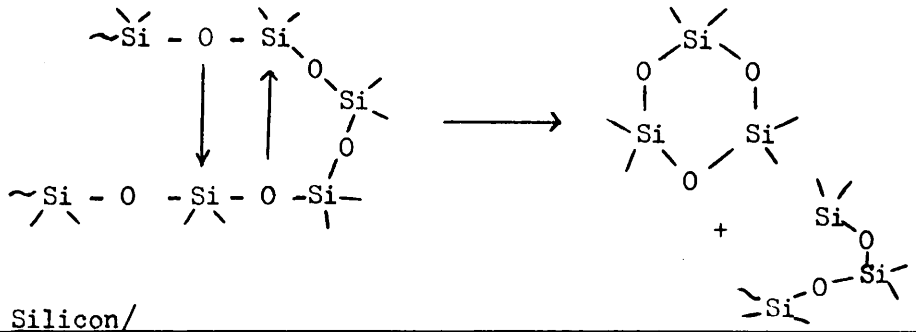
Andrianov et. al., (Ref. 53) working on similar samples, observe Si-C bond scission above 350°C with subsequent loss of sample solubility. It is suggested that the hydroxyl end groups are involved in intermolecular displacement of methyl groups:



It is also suggested by these workers that the depolymerisation process (formation of cyclics) may be affected by water solvating the active centres of depolymerisation.

Examination of the thermal degradation of polydimethylsiloxanes containing various kinds of end groups has shown that the rate of depolymerisation is diminished considerably when the terminal hydroxyls are replaced by methyl groups or by groups containing copper or titanium atoms, although in the latter case other reactions such as cross-linking can occur (Ref. 51).

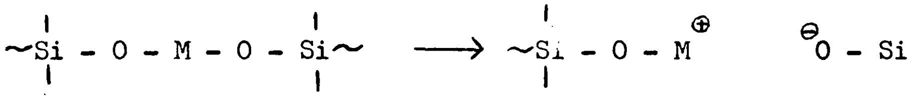
A mechanism has been suggested by Thomas and Kendrick (Ref. 50) for the formation of cyclic products in the breakdown of trimethylsiloxy end-blocked polydimethylsiloxanes in which an intermediate which lowers the energy barrier to the rupture of Si - O bonds is postulated. No experimental evidence is given to support directly the mechanism which is shown below for the formation of the major product hexamethylcyclotrisiloxane (dimethyl cyclic trimer).



Silicon/

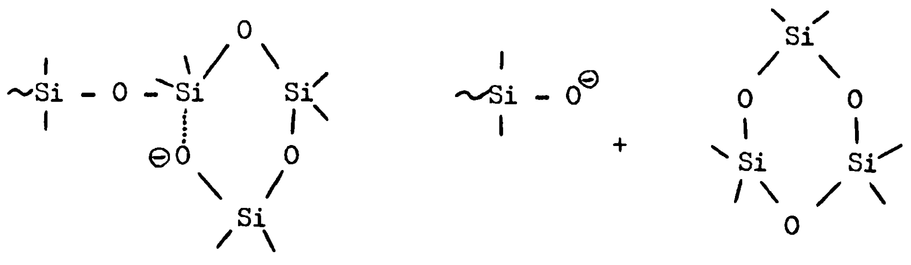
Silicon *d* orbital participation is postulated with subsequent siloxane bond rearrangement leading to the expulsion of a cyclic dimethylsiloxane and the shortening of the residual chain length. The transition state may be formed at any point along the polymer chain, and the process can proceed indefinitely within a chain until the residual linear structure is too short to cyclize readily. This mechanism does not propose the production of ionic species as suggested in an earlier work by Lewis (Ref. 62).

Spectral analysis of Lewis' (Refs. 62, 63) samples showed the presence of metallic impurities (0.05% barium, 0.01% lead, 0.0005% silver, 0.005% aluminium, and 0.001% of magnesium). Since it was thought that the concentration of these species was too small to catalyse the fission of an Si - O bond they were assumed to react with the ends of the chain or to split "abnormal bonds" (e.g. Si - Si or O - O). This involved the formation of so called "live" active centres which accelerated depolymerisation. The polymer molecules were thought to undergo dissociation at the point of incorporation of the impurity atom:



$$\sim\mathrm{Si} - \mathrm{O} - \mathrm{M} - \mathrm{O} - \mathrm{Si}\sim \longrightarrow \sim\mathrm{Si} - \mathrm{O} - \mathrm{M}^{\oplus} \quad {}^{\ominus}\mathrm{O} - \mathrm{Si}$$

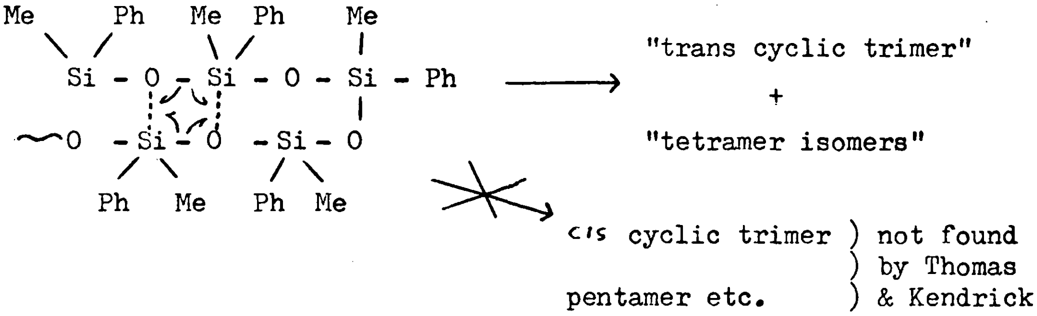
the resulting ions causing depolymerisation with the formation of volatile cyclic products of low molecular weight:



The/

The rate of depolymerisation has been shown to be directly proportional to the square root of the concentration of active centres (Ref. 64). The concept of "abnormal bonds" in the siloxane chain is no longer a popular one and has not featured much in degradation discussions in recent years.

For the degradation of poly (methylphenyl siloxane) with trimethylsiloxy end groups Thomas and Kendrick (Ref. 55) propose a similar mechanism to the one proposed earlier (Ref. 50) for the breakdown of polydimethylsiloxane. In the methyl, phenyl system ring size of products is restricted to trimer (transisomer only) and tetramer. The amount of each is not specified.

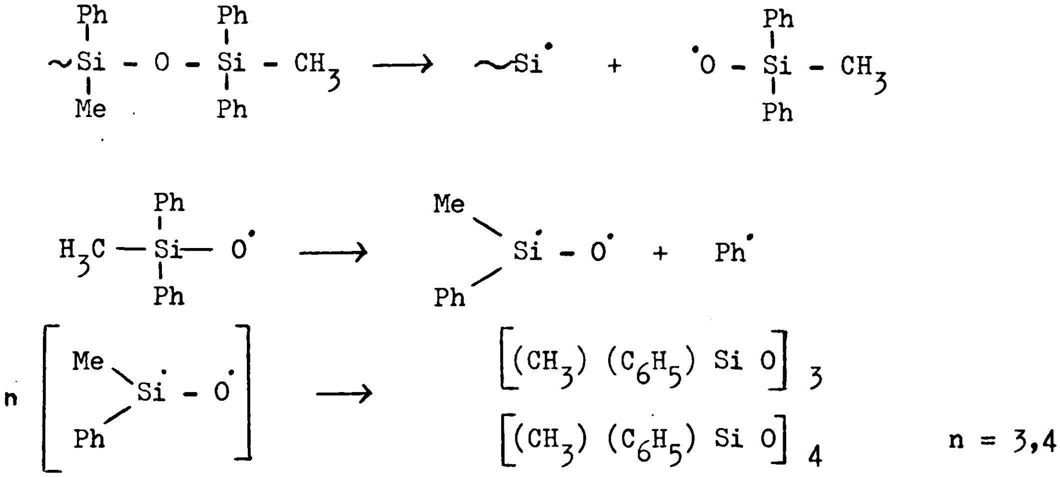


Using polymers with different side groups Thomas and Kendrick provide data to back their suggestion that the activation energy of the breakdown process is mainly a function of the electronic effect of the substituent group attached to silicon, and is probably not influenced to any marked extent by steric conditions. They find poly (methylphenylsiloxane) to have a higher activation energy than predicted and suggest this is due to silicon d -orbital participation in the delocalised π- electron system of the phenyl ring.

Sobolevskii/

Sobolevskii et. al. (Ref. 65) have studied thermally induced changes in oligomethylphenylsiloxanes. They find that in the interval 450-475°C the mechanism of pyrolysis of these species undergoes a change. At temperatures of 425-475°C the main type of thermal change is one of rearrangement resulting in formation of low and high molecular weight compounds. At higher temperatures it is evident that scission of organic radicals from silicon atoms begins to predominate which favours formation of insoluble polymers by a cross-linking process. It is concluded by these workers that elimination of phenyl radicals from the silicon atom at 425-500°C, must be considerably easier than scission of methyl radicals.

The formation of cyclics is thought to go through a radical mechanism where the important reaction is rupture of siloxane bonds, followed by decomposition, rearrangement and recombination of the radicals formed as a result of the primary process (Ref. 65):

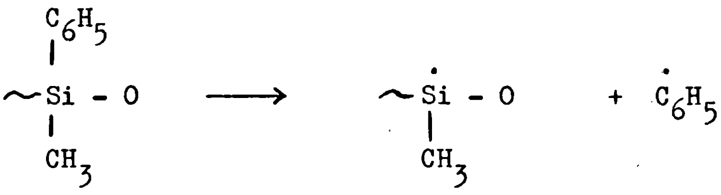


$$\sim\overset{Ph}{\underset{Me}{Si}}-O-\overset{Ph}{\underset{Ph}{Si}}-CH_3 \longrightarrow \sim Si^{\bullet} + {}^{\bullet}O-\overset{Ph}{\underset{Ph}{Si}}-CH_3$$

$$H_3C-\overset{Ph}{\underset{Ph}{Si}}-O^{\bullet} \longrightarrow \begin{matrix}Me\\Ph\end{matrix}\!\!>\dot{Si}-O^{\bullet} + Ph^{\bullet}$$

$$n\left[\begin{matrix}Me\\Ph\end{matrix}\!\!>\dot{Si}-O^{\bullet}\right] \longrightarrow \begin{matrix}\left[(CH_3)\ (C_6H_5)\ Si\ O\right]_3\\ \left[(CH_3)\ (C_6H_5)\ Si\ O\right]_4\end{matrix} \qquad n = 3,4$$

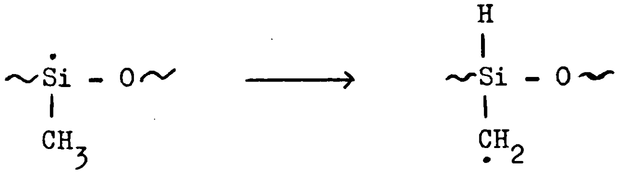
At higher temperatures (475-500°C) direct removal of phenyl groups from the silicon atoms is thought to play an important part:



$$\sim\overset{C_6H_5}{\underset{CH_3}{Si}}-O \longrightarrow \sim\overset{\bullet}{\underset{CH_3}{Si}}-O + {}^{\bullet}C_6H_5$$

This/

This is thought to be followed by rearrangement of the resulting radicals:

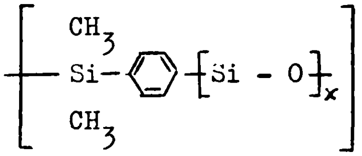


$$\sim\overset{\bullet}{\underset{CH_3}{Si}} - O\sim \longrightarrow \sim\overset{H}{\underset{\overset{\bullet}{C}H_2}{Si}} - O\sim$$

(iv) Effects of Structure on Thermal Stability

It is suggested by Andrianov (Refs. 66, 67) that the spiral structure of polyorganosiloxanes containing 3-6 silicon atoms in a loop of the spiral creates favourable conditions for the formation of rings.

Enlarging the organic radicals attached to the silicon atoms diminishes the tendancy of the polymer chain to form a spiral, so that depolymerisation of diethylsiloxane takes place with greater difficulty and at a higher temperature than that of polydimethylsiloxane (Ref. 67). Polymers containing silphenylene links possess fairly high thermal stability (Ref. 68). Those having the following structure



$$\left[-\underset{CH_3}{\overset{CH_3}{Si}}-C_6H_4-\left[Si - O\right]_x \right]$$

where $x = 1\text{-}4$ are reported to be considerably more thermostable than are ordinary polydimothylsiloxanes. The high thermal stability of these polymers has also been explained as being due to the greater difficulty of breaking the Si-C bond than the Si - O bond in polysiloxanes (Ref. 69).

The/

The introduction of up to 3 mole % of silarylene units into the chain of polydimethylsiloxanes has no significant effect on their thermal stability (Ref. 70). However, there are indications that polymers containing naphthylene bridges in the chain are stable at high temperatures and will yield very strong thermoplastic films (Ref. 71).

The thermal stability of polyorganosiloxanes is substantially influenced also by the three dimensional structure of the polymer. Rupture of one Si - O bond is sufficient for the cleavage of linear macromolecules, but with polymers having a three dimensional structure it is necessary to rupture siloxane bonds at two or even three points. The thermal stability of the latter is therefore greater than that of linear polymers (Ref. 74).

Replacing the methyls in polydimethylsiloxane by phenyl groups considerably improves the heat stability of polyorganosiloxanes (Ref. 72). The enhanced stability is explained (Ref. 74) by the screening effect of the phenyl groups on the siloxane bond. The introduction of one chlorine atom into the phenyl group has no substantial effect on the thermal stability of poly (methylphenylsiloxane), but with two or more chlorine atoms the thermal stability falls.

Soboleveskii and Nazarova (Ref. 75) investigated whether the thermal properties of organosiloxanes are determined by arrangement of methyl and phenyl groups in the chain or by the overall CH_3/C_6H_5 ratio, and concluded that the principal thermal properties of those polymers are almost identical at similar values of the ratio, whether their structure is regular or irregular.

In the light of work by Andrianov et. al. (Refs. 76, 77) on the rearrangement of siloxanes it seems possible that a certain amount of rearrangement could have taken place in the above workers samples.

It is reported (Ref. 78) that the thermal stability of polyorganosiloxanes containing arylene units in the main chain is slightly better than that of the corresponding polymers containing framing aryl groups when the ratio of the groups to the total number of siloxane units is the same.

(v) The Effect of Catalytic Impurities on Thermal Stability

Polydimethylsiloxane, when free from acidic or basic impurities, is stable at relatively high temperatures. In most cases polydimethylsiloxanes are obtained by the anionic polymerisation of cyclic compounds and the presence of catalysts in them is inevitable. Several (Refs. 59, 63, 79) people have shown that the presence of polymerisation catalysts lowers the thermal stability considerably. The thermal stability of polymers is dependent on the type of catalysts used for their preparation.

Authors who have studied this problem recommend three ways of rendering active centres inactive:

(a) extracting the catalyst with water (Ref. 80)
(b) neutralising the residual catalysts (Ref. 81)
(c) Using thermally labile catalysts (Ref. 79).

Of these three methods the first two are not entirely suitable since it is difficult to extract completely or neutralise catalyst concentrations as low as 0.01% in a medium of high viscosity.

In/

In this present study a transient catalyst, tetramethylammonium-hydroxide (TMAH) has been used as a polymerisation catalyst. The decomposition of TMAH which occurs rapidly at about 130°C results in the formation of trimethylamine and methanol:

$$(CH_3)_4\ NOH \longrightarrow (CH_3)_3N + CH_3OH$$

The amine and alcohol do not react with the resulting catalystfree siloxane polymer (Ref. 79).

(vi) <u>Stabilisation of Polyorganosiloxanes</u>

The literature contains references to the possibility of stabilising polyorganosiloxanes, but there is no common approach to this problem.

It has been observed that, when various compounds of metals are introduced into polyorganosiloxanes, the rate of depolymerisation falls considerably. Therefore many authors propose the addition of a great variety of metal compounds. Especially good results are given by compounds of transition metals, among which such salts have been suggested as the acetates and octanoates of iron, (Ref. 82) the naphthenates of lead (Ref. 83), zinc, cobalt, iron and manganese (Ref. 84) and also salts of indium and cerium (Ref. 85). The use has also been proposed of the salts of such rare-earth metals as lanthanum, neodymium, praseodymium, samarium, gadolinium and ytterbium (Ref. 86).

Andrianov (Ref. 67) has put forward the hypothesis that the enhancement of the thermal stability of the polymer by the introduction of heteroatoms into the chain is due to the possibility of forming co-ordinate bonds between the metal atoms and the oxygen of neighbouring chains.

An/

An investigation has been made of the action of metals (tin, antimony, copper, lead, aluminium, nickel, selenium, silver, tellurium, zinc and iron) on the thermal and thermo-oxidative stability of polydimethylsiloxane and polymethylphenylsiloxane. Lead and tellurium accelerate gel formation and the evolution of volatile products, but the other metals have no significant effect (Refs. 72, 87).

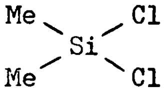
Although quite a wide range of stabilisers have already been proposed for polyorganosiloxanes, the problem of their stabilisation still remains a complicated task. The most effective would obviously be stabilisers combining the properties of an antioxidant with the ability to increase the stability of the main siloxane chain.

1.9 AIM OF THIS WORK

The aim of this work is to prepare and characterise pure samples of high molecular weight linear polysiloxanes having methyl or methyl and phenyl side groups, and to study their thermal degradation in vacuo. The work has concentrated on such features as molecular weight changes during degradation, detailed analysis of volatile products, changes in the involatile residue, influence of molecular weight of starting material, and the effect of end-stopping stabilisers.

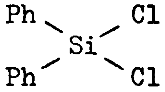
CHAPTER 2

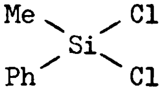
2.1 SOURCES OF REAGENTS EXPERIMENTAL TECHNIQUES

dichlorodimethylsilane  was obtained from two sources

(a) E. Merck Laboratories (Germany). Specification: 99% (GLC.) D_4^{20} 1.074-1.076 or trichloromethylsilane $[Cl_3Si\ Me]$ 0.2% monochlorotrimethylsilane $[Cl\ Si\ Me_3]$ 0.1%

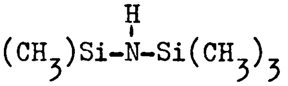
(b) Peninsular Chemical Research (P.C.R.) Inc., Florida, U.S.A. This is repackaged Dow Corning Z-129 silane.

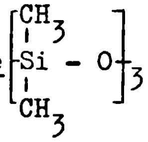
dichlorodiphenylsilane  was obtained from Fluka (Switzerland) and labelled "pure".

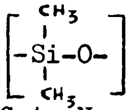
dichloromethylphenylsilane  was obtained from two sources:

(a) Aldrich Chemical Co. Inc. (U.S.A.). Purity determined by I.R.

(b) Midland Silicones (now part of Dow Corning Group) via Hopkin and Williams Chemicals Ltd.

1,1,1,3,3,3, hexamethyldisilazane  $(CH_3)Si-\overset{H}{N}-Si(CH_3)_3$ was obtained from Merck Chem. Co. (Germany)

hexamethylcyclotrisiloxane  $\left[-\underset{CH_3}{\overset{CH_3}{Si}}-O-\right]_3$ was obtained from P.C.R. Laboratories (U.S.A.) Cat. No. 2866

decamethylcyclopentasiloxane  $\left[-\underset{CH_3}{\overset{CH_3}{Si}}-O-\right]$ was obtained from I.C.N. K & K Laboratories (U.S.A.) Cat. No. 2866.

tetramethylammoniumhydroxide /

tetramethylammoniumhydroxide $(CH_3)_4NOH$ was obtained as a 25% aqueous solution from Hopkin and Williams Ltd.

Other reagents and solvents used in this study were, in all cases, of AnalaR grade.

2.2 PREPARATION OF POLYMERS

(i) Introduction

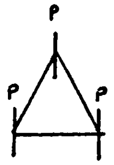
Polysiloxanes were prepared by the hydrolytic conversion of the corresponding dichlorosilane to a mixture of cyclic siloxanes, followed by separation and polymerisation of cyclic trimer or tetramer in presence of tetramethylammoniumhydroxide as catalyst to form the linear polymer.

According to Patnode and Wilcock (Ref. 49) the relative proportions of the compounds formed by the hydrolysis of dimethyldichlorosilane depend upon the condition of hydrolysis but there is a very strong tendancy toward the formation of the cyclic tetramer which is generally formed in the greatest amount. Their method was used with variations on the silane/water ratio. Since the hydrolysis reaction is exothermic, the reaction vessel must be cooled. Water to silane ratios of 2:1 to 5:1 were used without noticably affecting the yield of short chain cyclic polymer. The products of this hydrolysis are principally the cyclic trimer (b.p. 134°C) tetramer (b.p. 175°C) and pentamer (b.p. 210°C) with the tetramer predominating.

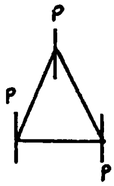
Lewis, (Ref. 88), Young et. al., (Ref. 89), and Hickton et. al., (Ref. 90), suggest methods for the hydrolytic conversion of dichloromethylphenylsilane to a mixture of cyclic siloxanes predominantly cyclic trimer and tetramer.

Here/

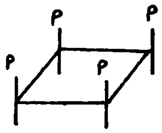
Here, the possibility of forming geometric isomers exists: two trimers and four tetramers. These are conveniently represented as follows, where an edge represents an oxygen atom and a corner represents a silicon atom. Only the phenyl groups are indicated: it is implied that each silicon also has attached to it a methyl group.



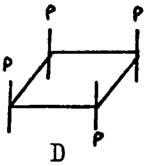
A
(m.p. 99.5°C)



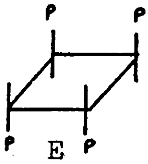
B
(m.p. 44-46°C)



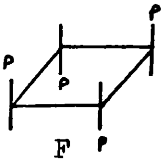
C
(m.p. 64.5°C)



D
(m.p. 55-57°C)



E
(m.p. 99-100°C)



F
(m.p. 74°C)

The separation of these isomers is discussed by the above authors. Isomers A, B and E are relatively easily separated from a mixture of all six isomers by fractional crystallisation but isomers C, D, and F are much less readily separated.

Typical nmr specra of (a) mixture of isomers, and (b) isomer A are given in Fig. 2-1.

Burkhard (Ref. 91) gives a convenient preparation of diphenylsilanediol in high yield from <u>dichlorodiphenylsilane</u> and his method was used for this hydrolysis. The "diol" is stable under room conditions but quantitative conversion to the cyclic siloxane, trimer or tetramer, by adding acid or base respectively to a refluxing solution, is easily effected.

(ii)

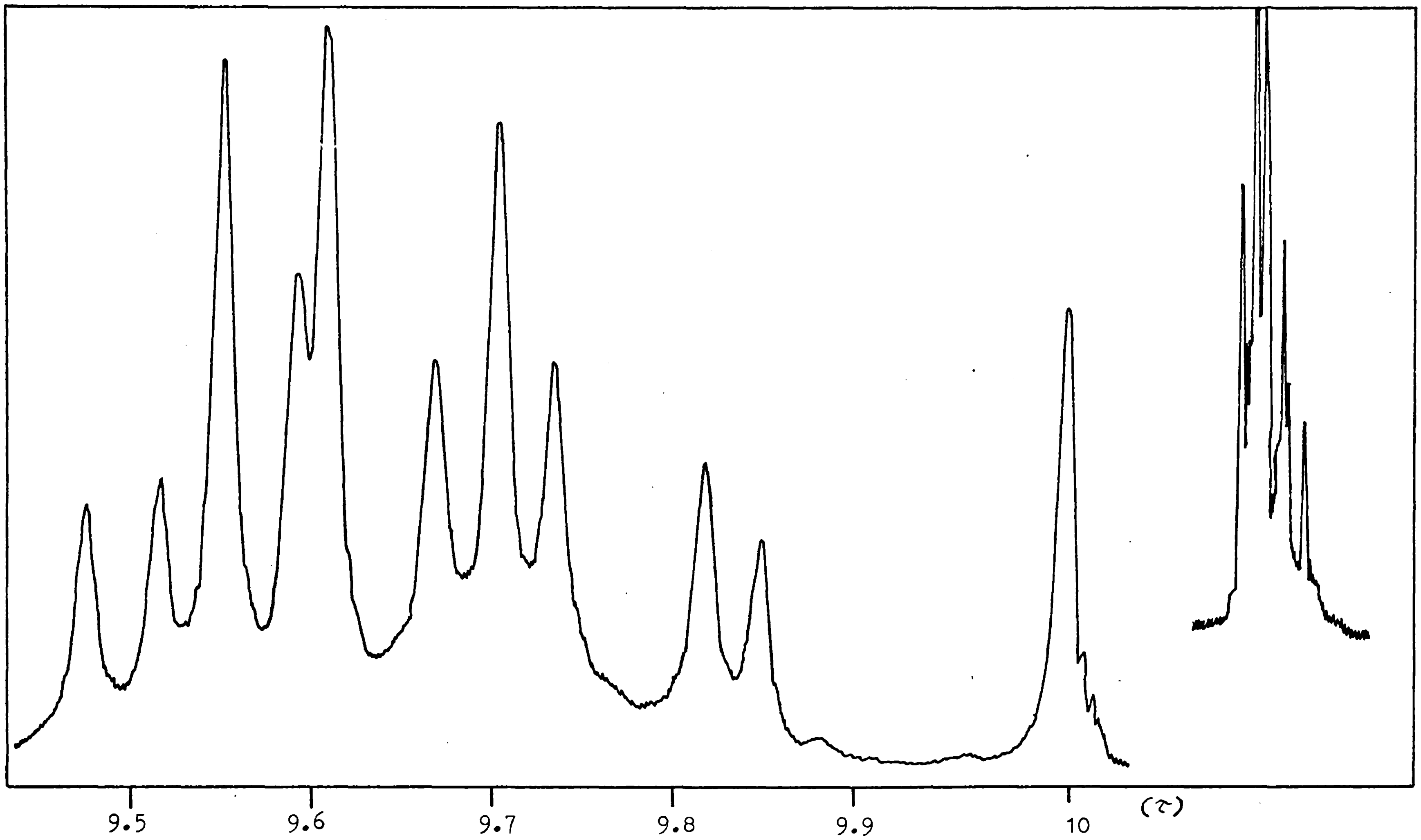


Fig. 2.1(a) Methyl Group Proton Magnetic Resonance Spectrum of a mixture of methyl, phenyl cyclic siloxanes.

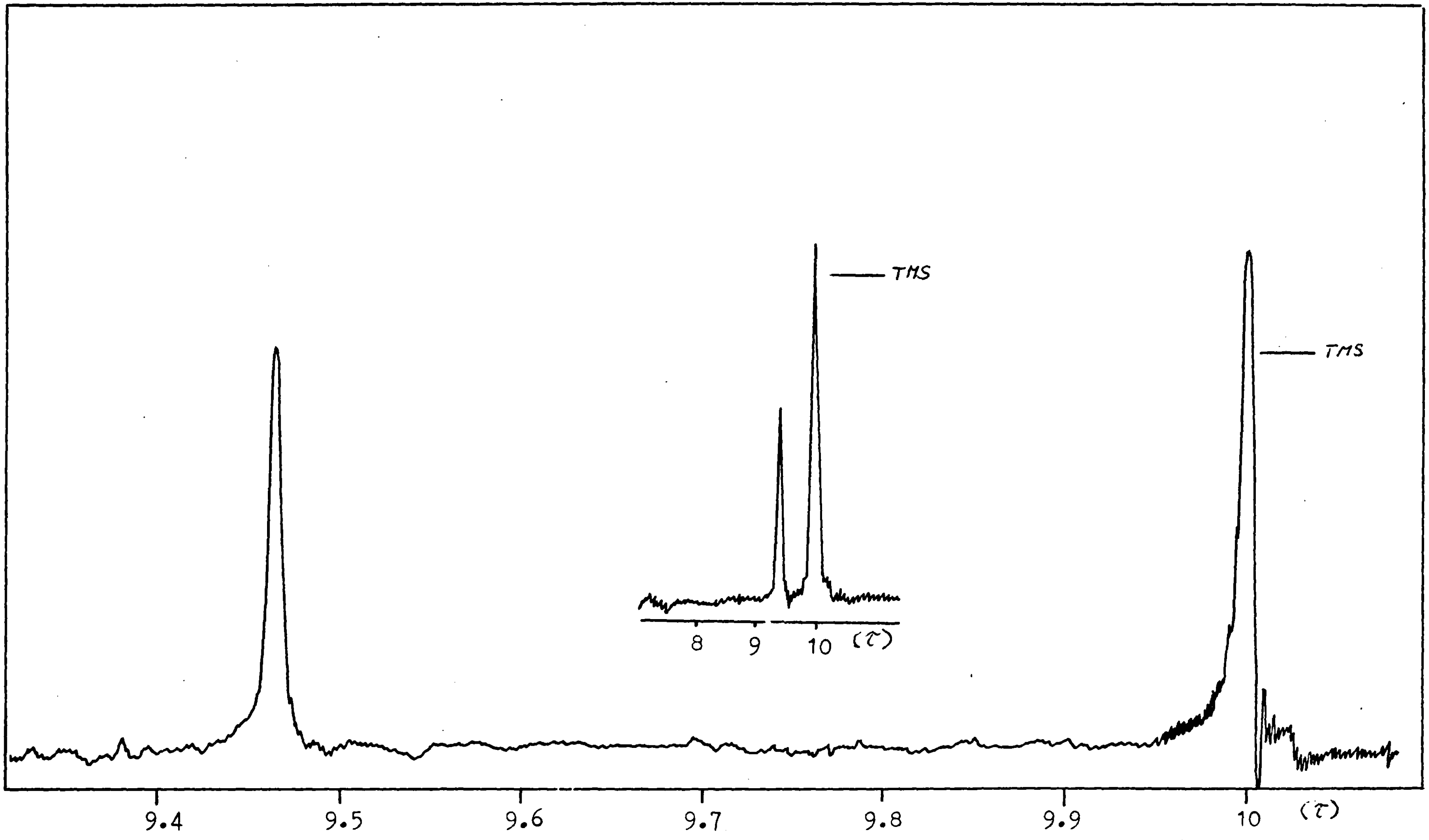


Fig. 2.1(b) Methyl Group Proton Magnetic Resonance Spectrum of methyl, phenyl cyclic siloxane isomer A separated from a mixture of trimers and tetramers.

(ii) Hydrolysis of dichlorodimethylsilane

Distilled water (750ml) in an R.B. flask equipped with magnetic stirrer and thermometer was cooled in an ice/water bath. Dichlorodimethylsilane (Merck) (250ml) in an equal volume of diethylether was added dropwise, the temperature of the reaction mixture being maintained below 20°C. The reaction mixture was vigorously stirred throughout the hydrolysis.

The ether layer, containing the oil formed by hydrolysis, was separated from the excess water, washed several times with a dilute solution of sodium bicarbonate (to remove HCl) and then distilled water, and dried over magnesium sulphate. The liquid was separated by filtration, the ether removed by evaporation, and the oil distilled under reduced pressure to separate the low molecular weight cyclic siloxanes from the non-volatile products of hydrolysis.

The liquid was then distilled through a heavily lagged 10" Vigreux column at ordinary or reduced pressure giving approximately 80ml. of material distilling at 168-173°C/760mm. and redistilled a number of times to give progressively purer cyclic tetramer (b.p. 175°C).

The composition of distillation fractions was checked using GLC and purification continued until there was no evidence of other cyclics under reasonable magnification (purity 99.9%). Typical chromatograms of (a) mixture of cyclics and (b) pure octamethylcyclotetrasiloxane are given in Fig. 2-2.

(iii)/

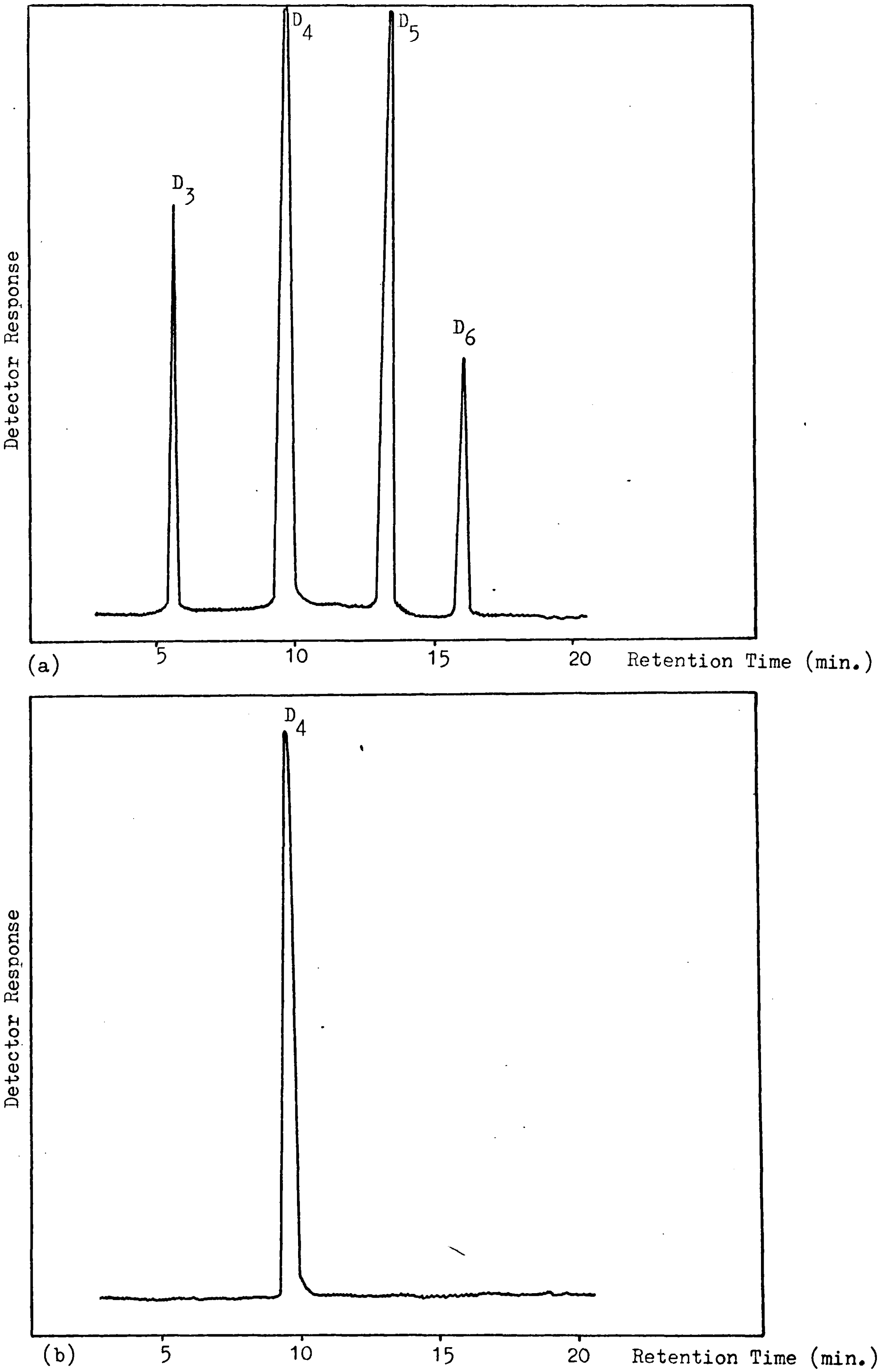


Fig.2.2 GLC Separation of Dimethyl Cyclic Siloxanes

(a) mixture (b) D_4

1% SE 30 25-225°C at 10°/min. after 5 min.

(iii) Hydrolysis of dichloromethylphenylsilane

500g of dichloromethylphenylsilane was diluted with three volumes of ether and this solution added dropwise to an excess of water. The reaction vessel was cooled by an ice/water mixture. The ether layer was separated from the excess water and washed free of chloride with distilled water. After removal of the ether by evaporation, the residue was a clear oil consisting of cyclic trimer and tetramer (9g, 280g respectively) predominantly.

Distillation of this oil under reduced pressure gave distillate boiling at 140°-190°/0.1mm. which was collected in four fractions. The two earlier fractions are predominantly cyclic trimers and the later fractions predominatly cyclic tetramers although each fraction contains some of each of the six isomers. Further heating of the residue gave a fraction (still head temp. 300°/0.1mm.) which was mainly cyclic trimer, presumably formed by the rearrangement of higher cyclics or linear species at temperatures over 400°C.

The separation of cyclosiloxanes was partly effected by adding an equal volume of low boiling petroleum ether to the collected fractions and storing them at -25°C. Within 24 hrs. isomer A began to crystallise from trimer mixtures. After about one week, on removal of isomer A, isomer B began to form slowly.

Only after about 4 weeks did tetramer mixtures yield crystals. First to form were the small amounts of cyclic isomers A and B included in these mixtures, on removal of which tetramer isomer C formed. Attempts to isolate pure samples of isomers D, E and F by crystallisation methods have not been successful.

Adding/

Adding the tetramer mixtures described above to methanol had no desirable effect: Conan et. al. (Ref. 92) report isolation of isomer C by adding a privately obtained "mixture of siloxanes" to methanol.

Proof of identification by m.pt., mass spectrometry, and nmr will be given chapter 4.

(iv) Hydrolysis of dichlordiphenylsilane

200g of dichlorodiphenylsilane dissolved in 77ml of toluene was added dropwise with stirring to a heterogeneous mixture of 77ml of toluene, 161ml of t-amylalcohol and 666ml of water. The solution was maintained below 25°C. After addition of the silane stirring was continued for a further ten minutes. The solution was then filtered and the crystals washed with distilled water until free of acid and air dried. These crystals were shown by I.R. to be practically free of polymeric material. (Fig. 2.3) The infra-red data were in complete agreement with those given by Rochow (Ref. 93) and others (Ref. 94) for diphenylsilanediol.

Further purification was effected by crystallisation from methyl acetate giving needles melting at 148°C (lit 130°-160° depending on method of recrysallisation).

Hexaphenylcyclotrisiloxane

Crystals (10g) of diol obtained by the above process were dissolved in ether and 5ml of conc. HCl were added. The mixture was gently refluxed for about 1-2 hrs. after which the ether was removed and the crystals collected. Flat plates were obtained on recrystallisation from methylacetate m.p. 190°C (lit 190, 188-189°C) and gave the I.R. spectrum of diphenylcyclictrimer.

Octaphenylcyclotetrasiloxane/

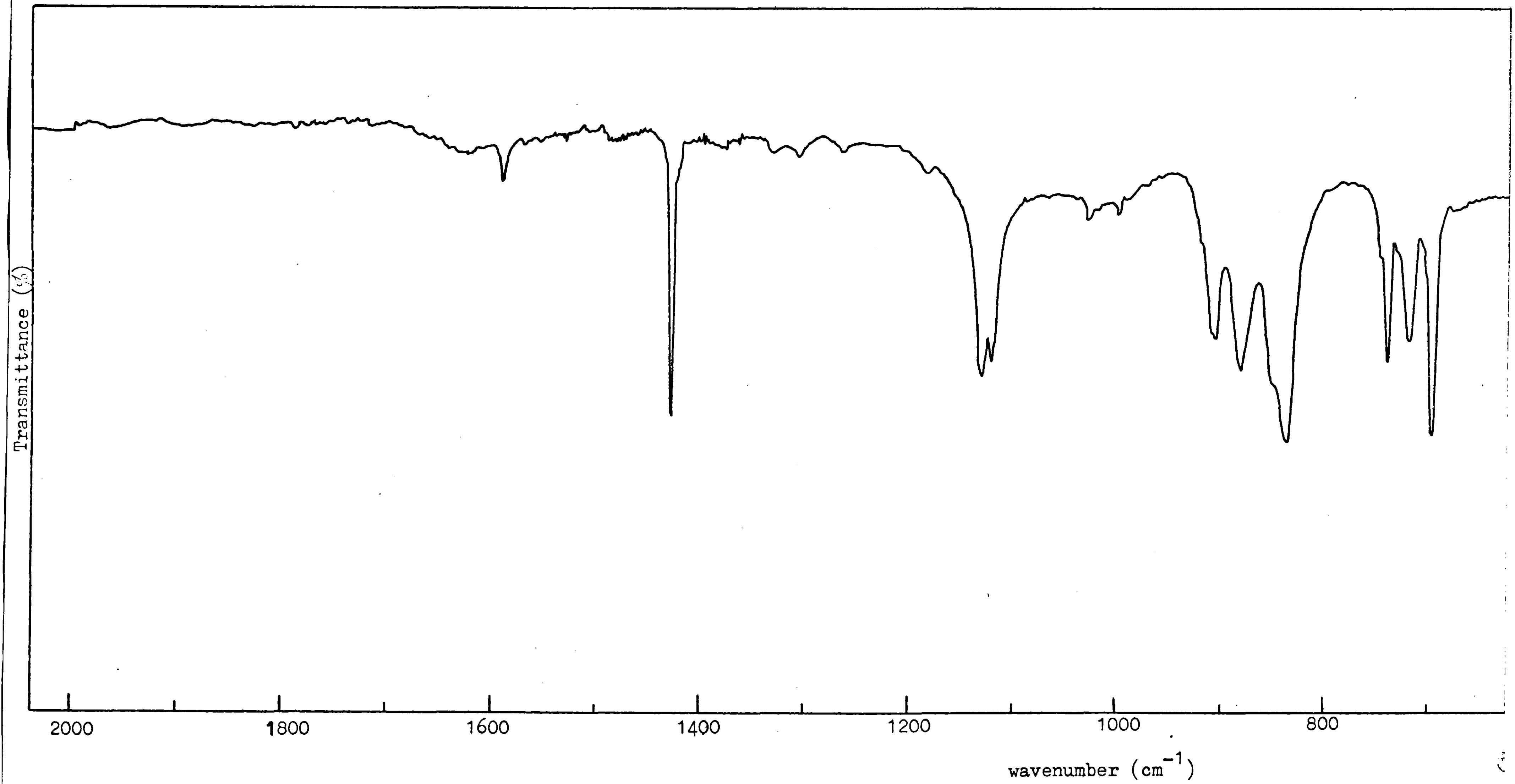


Fig. 2.3 I.R. Spectrum of Diphenylsilanediol.

Octaphenylcyclotetrasiloxane

A drop or two of aqueous caustic soda was added to a boiling solution of diphenyl silane diol in 95% ethanol. On cooling the tetramer, octaphenylcyclotetrasiloxane precipitated. When recrystallised from ethyl acetate needles were obtained melting at 201-202°C.

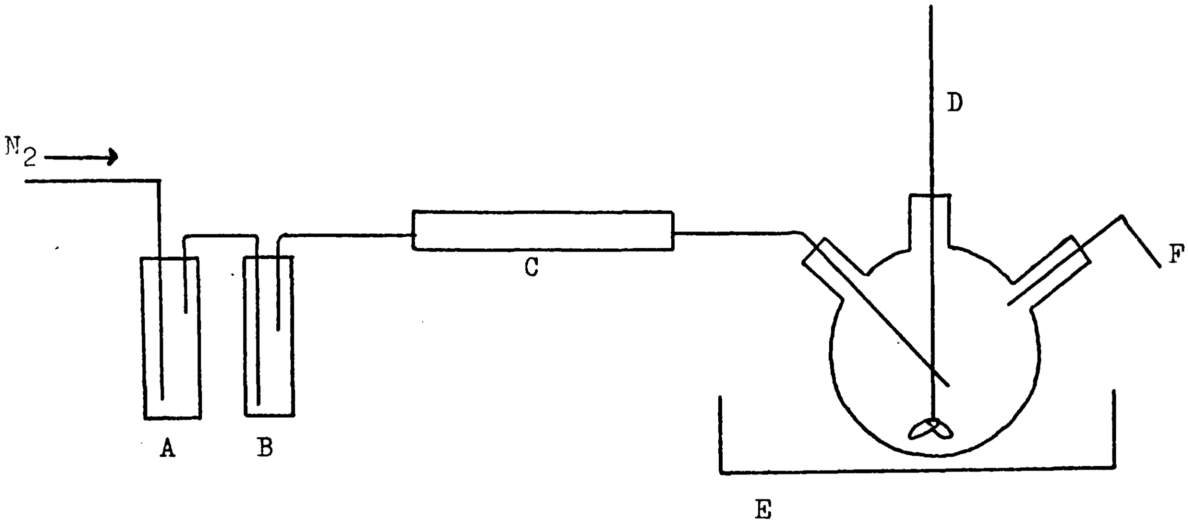
(v) Polymerisation of Cyclic Siloxanes

Unless otherwise described polymerisation of cyclic siloxanes was carried out in bulk under a dynamic stream of nitrogen using tetramethylammonium hydroxide as catalyst. A schematic description of the polymerisation apparatus is given in Fig. 2.4.

Typically, cyclic siloxane (5-20g) was weighed into a three necked R.B. flask, fitted with an inlet for nitrogen (British Oxygen Co. "white spot"), and a mechanical stirrer.

The flask was immersed in a closely controlled thermostatic bath at the required temperature and a vigorous stream of oxygen free nitrogen was flushed through the mixture for approximately 45 minutes to remove all the dissolved oxygen. Initiator (0.001 to 0.1 wt.%), in the form of a dry powder or aqueous solution was added through the third inlet and after a considerable time the reaction vessel was heated to 140°C for 10-15 mins. to destroy the catalyst and then removed from the thermostat. The clear tacky mass which had formed was dissolved in toluene and reprecipitated from methanol. This process succesfully removes residual low molecular weight cyclics. Reprecipitation was repeated a further two times. The polymer was finally dried at 40-45°C (48 hrs.) in a vacuum oven.

The/



A = Solution of Pyrogallol

B = Drying Bottle

C = Drying Tube

D = Mechanical Stirrer

E = Thermostatically Controlled Bath

F = N_2 outlet

Fig. 2.4 Polymerisation under Nitrogen

The preferred polymerisation temperature was 110°C. This allowed the formation of high molecular weight material and also any water present from the addition of catalyst to evaporate.

In all cases the appearance of the polymer was that of a clear tacky gum or viscous liquid depending on molecular weight and phenyl content.

(vi) Preparation of dimethyldiphenylsiloxane copolymers

Copolymers containing both dimethyl and diphenyl units were prepared by polymerising in bulk mixtures of octamethylcyclotetrasiloxane and hexaphenylcyclotrisiloxane or octamethylcyclotetrasiloxane and octaphenylcyclotetrasiloxane in the presence of 0.05 wt% tetramethylammoniumhydroxide using the technique described above.

Details of polymer purification and characterisation are given in chapter 6.

2.3 THERMAL METHODS OF ANALYSIS

(i) Thermogravimetric Analysis (TGA)

For the most part thermogravimetric analyses were carried out using a Du Pont 950 instrument. Samples (10mg) were heated in a platinum sample holder at 10°C/min in a dynamic atmosphere of oxygen free nitrogen ($70 cm^3 min^{-1}$) from ambient to 500°C or 1000°C. The temperature measuring thermocouple was placed 0.1cm from the sample holder.

Since/

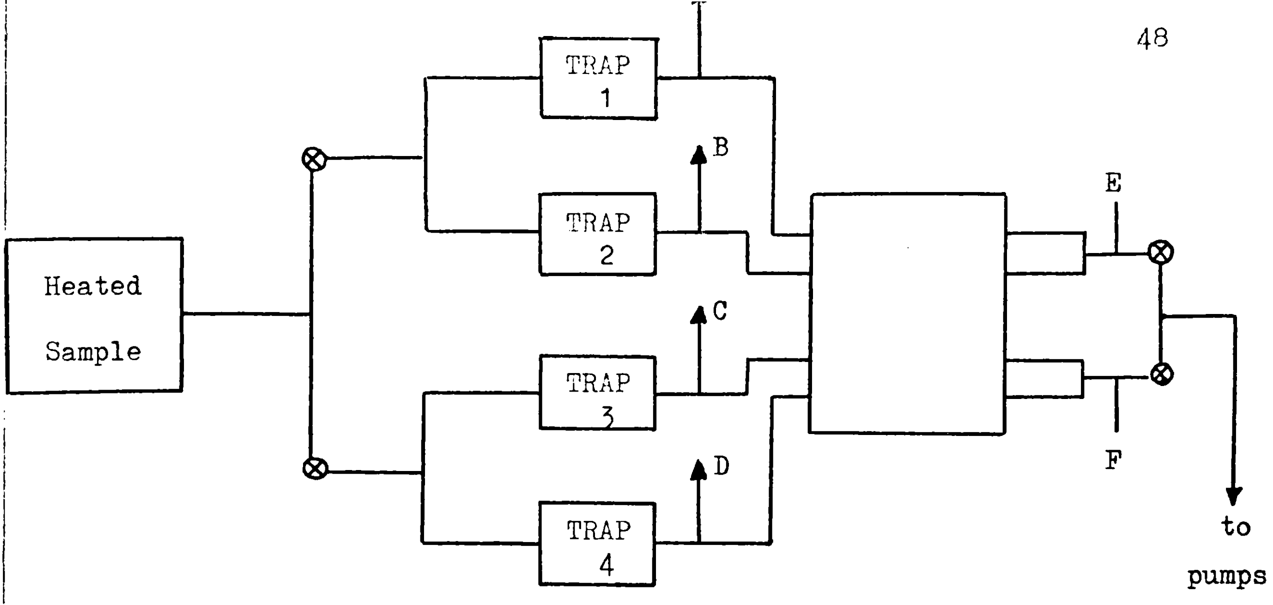
Since it was not possible to obtain a high vaccum with this apparatus a second thermogravimetric analyser (Cahn Instrument Co., California, U.S.A.) was also used. This balance with its Pyrex enclosure is capable of being used for vacuums and controlled-atmosphere operation. Its weighing range is continuously variable up to 1000mg with a sensitivity of 0.1mg.

(ii) Thermal Volatilisation Analysis (T.V.A.)

The thermal degradation of many polymers has been studied using TVA, which has been the subject of a number of publications, (Refs. 95, 96 and 97), and is now a well established technique of thermal analysis. A schematic picture of the general experimental layout used in this study is given in Fig. 2.5.

The polymer sample is heated on the base of a glass tube 6" long, constructed from a Pyrex FG 35 flange. During the experiment the top of the tube and greased flange joint are cooled by a water jacket ("cold ring"). The tube is heated using a Perkin Elmer F11 oven and linear temperature programmer, which enables the sample to be heated isothermally, or linearly from abient temperature up to 500°C at heating rates varying from 1 to 40°C/min. In this study a heating rate of 10°C/min was used throughout. The oven temperature is measured using a chromel-alumel thermocouple, fixed near the base of the tube.

The volatiles are pumped along four geometrically-equivalent routes to a common "back-up" trap at -196°C (Fig. 2.5). The four routes contain traps at the arbitrarily chosen temperatures of 0°, -45°, -75°, and -100°C respectively. Each trap, including the common trap is followed by a Pirani gauge and outputs from these are transmitted via a multihead switch unit to a 12-channel recorder, where they/

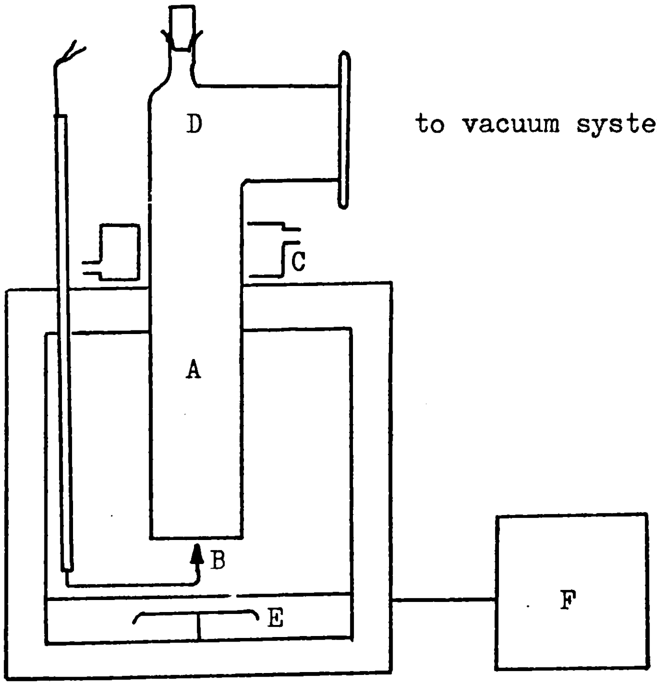


Normal working temperatures (°C): 0, -45, -78, -100

A, B, C, D are Pirani gauge heads

E, F, are sample receiving tubes or I.R. gas cell.

Fig. 2.5(a) Thermal Volatilisation Analyser



A Degradation tube

B Chromel-alumel thermocouple

C "Cooling jacket"

D Removable socket joint

E Oven fan

F Temperature programmer

Fig. 2.5(b) T.V.A. Heating Assembly

they are recorded continuously with oven temperature. Products can be collected for analysis at the points indicated.

It can be shown empirically that the same quanitity of volatiles passes into each of the four routes, but when a trap is reached one or more of the components may be condensed out so that for a mixture of volatiles the Pirani traces are often non-coincident. By means of spectroscopic analysis of the products and a prior knowledge of the behaviour of various substances in the different traps, it is often possible to obtain a useful qualitative picture of the degradation pattern at various temperatures.

Product analysis of TVA fractions

The volatiles fall into two categories:

(a) condensables

(b) non-condensables

The "condensables" are those materials which condense at -196°C in a continuously pumped system and are easily analysed by subsequent distillation into an I.R. gas cell, liquid sample tube or other form of collecting device. "Non-condensables" are collected by "closed-system" degradation and are analysed, after collection in an I.R. gas cell or gas sample tube.

The "cold ring fraction" comprises these products which are volatile at degradation temperatures, but involatile at ambient temperature, and usually consist of short chain fragments. This fraction may be analysed after removal with a tissue moistened with solvent, followed by extraction from the tissue.

The involatile residue may be analysed as a solution or as a solid.

(iii)/

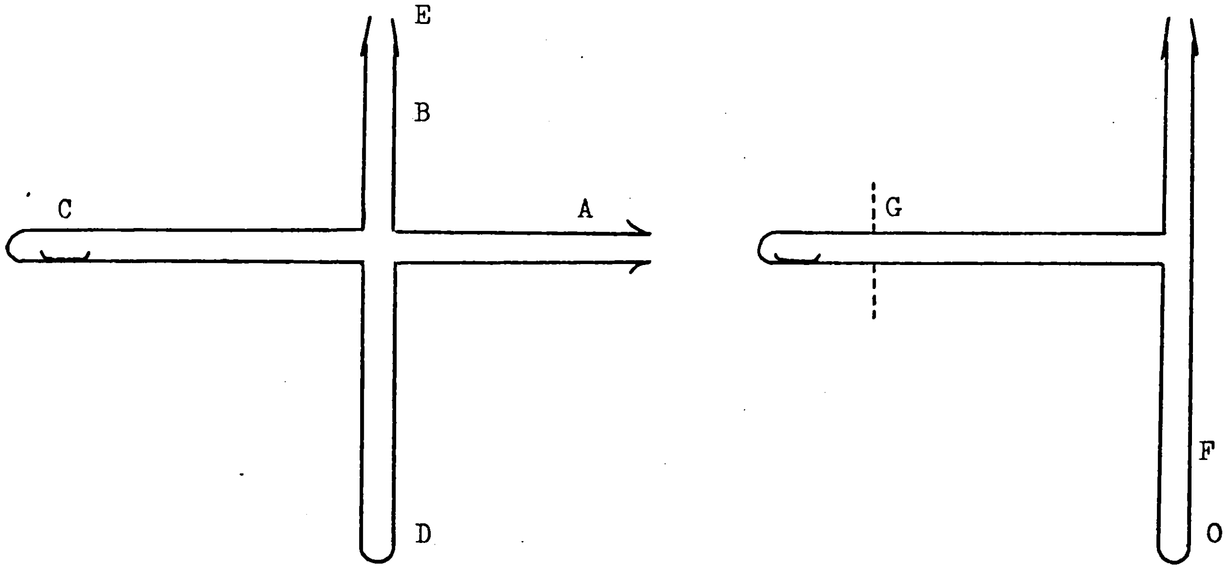
(iii) The "Sealed Tube" Degradation Technique (Refs. 96, 99)

Fig. 2.6 shows a diagram of a sealed tube. Polymer is weighed in a small aluminium boat which is then placed in the tube which is then evacuated (10^{-6}torr) and sealed off at point A. Limb C is then placed in an oven at the required temperature, while limb D is immersed in liquid nitrogen. Degradation products leaving the hot zone condense in limb D. The oven used in this study was a Catterson Smith G31LX Electric Furnace controlled by a Skil 59C/5122 Controller which enabled the temperature to be maintained to ±0.5°C. This temperature was monitored throughout the degradation by a thermocouple sealed into an evacuated tube similar to the one containing the polymer sample and placed symmetrically with respect to it within the furnace. The sample size degraded by this method ranged from 100 to 500 mg.

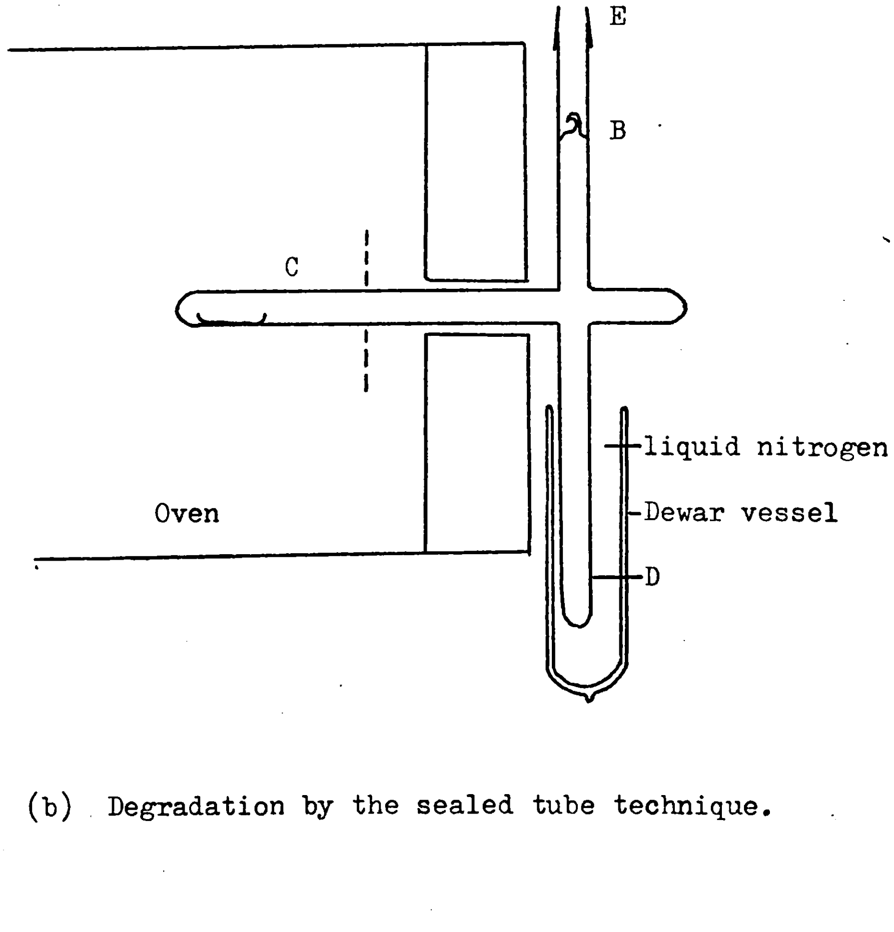
Product Analysis

For the analysis of degradation products the sealed tube containing degraded polymer is normally attached to a vacuum line at E, and the end of limb D in which the liquid products have collected is cooled in an ice-water bath. The break-seal is then broken using a glass covered metal weight, and the gaseous decomposition products are distilled into a suitable receiver cooled in liquid nitrogen. It was established early on that the only products of degradation of samples employed in this technique were low molecular weight cyclic siloxanes and so a simpler procedure was adopted. Limb D, which contains the cyclic products, was immersed in liquid nitrogen to a depth of 2". The tube was then broken at points F and G and tube parts containing degradation products and residue respectively weighed. The cyclic products (all involatile at R.T.P.) were removed by washing with diethyl ether and quantitatively analysed using GLC. When this technique is adopted a simpler sealed tube may be used (Fig. 2.6).

After/



(a) The "Sealed tube"



(b) Degradation by the sealed tube technique.

Fig. 2.6 The Sealed Tube Technique

After degradation, wight loss data were obtained in two ways, first by weighing the sample and second by weighing the volatile products. This was done simply to confirm that polymer was not lost from the reaction area by sputtering. The two sets of data were identical.

(iv) Vacuum Line Degradation System

The work on methylphenylsiloxanes has been carried out on a continuously pumped high vacuum system, a schematic representation of which is given in Fig. 2.7.

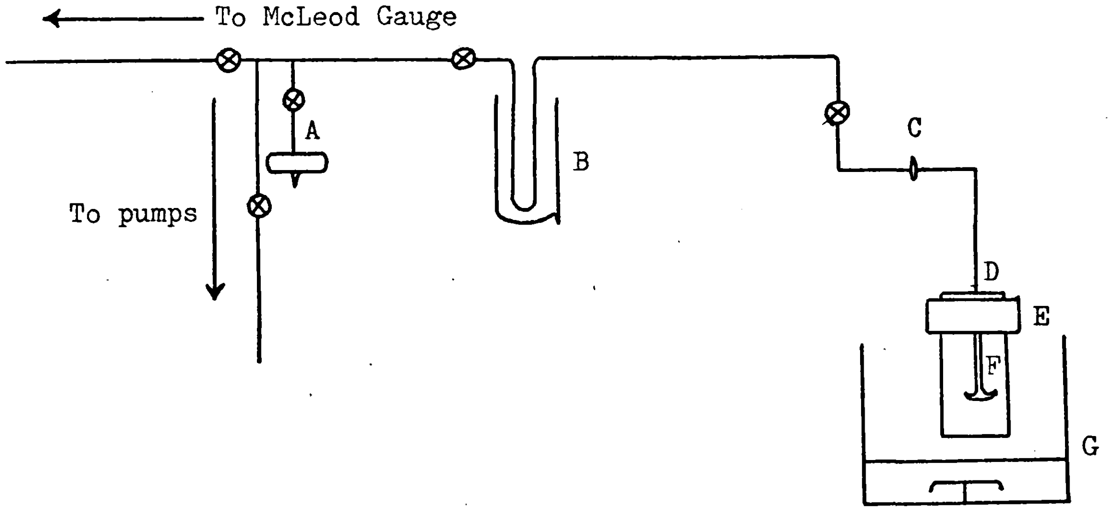
The sample is weighed into a small thin walled glass boat which is then placed at the bottom of the degradation tube. The evacuated tube (10^{-6} torr) is heated using a Perkin Elmer F11 oven equipped with both linear temperature programming and isothermal facilities.

Products of thermal degradation which are sufficiently volatile pass along to the liquid nitrogen trap where they condense. The main products, cyclic siloxanes, collect on the water cooled finger and are later removed by washing the finger with a suitable solvent (carbon tetrachloride, deuterated chloroform, etc.) for further analysis by nmr, GLC and mass spectrometry. The nature of "non-condensable" products may be studied by closing taps and operating the system isolated from the pumping mechanism.

2.4 ANALYTICAL TECHNIQUES

(i) Infra-red Spectroscopy

Qualitative and quantitative spectra were recorded on a Perkin Elmer 257 Grating Spectrophotometer. Polymer samples and residues were run in solution (carbon tetrachloride) or as KBr discs, cold ring fractions in solution, and volatile products examined in the gaseous phase.



A	Gas cell
B	Liquid nitrogen trap
C	S29 Ball and Socket and FG25 flange joints
D	B40 cone and socket joint
E	Water cooled jacket
F	Water cooled finger
G	PE F11 oven

Fig. 2.7 Vacuum Degradation System

(ii) Mass Spectrometry

The mass spectra of various reference siloxane ring compounds were obtained using an AE1 MS12 mass spectrometer operated at 70ev.

(iii) Gas-Liquid Chromatography (GLC)

Gas-liquid chromatographic analyses were carried out using a Perkin Elmer F11 Gas Chromatograph equipped with a flame ionisation detector and linear temperature programmer.

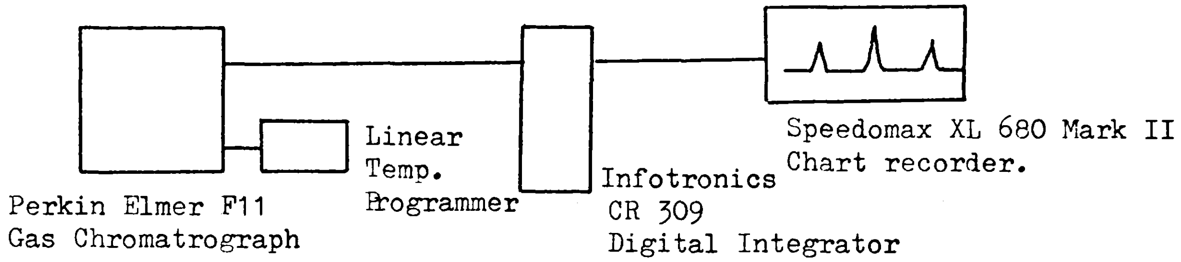
Quantitative analyses were carried out with the aid of an Infotronics 309 Digital Microprocessor after calibration of the flame ionisation detector response as described below. The 309 was connected between the chromatograph output terminals and the strip chart recorder used for displaying the chromatogram (Fig. 2.8). The results obtained by using the Microprocessor are in agreement with those obtained by cutting and weighing peaks.

Two columns have been used for the separation of dimethylsiloxanes, namely 1% OV1 (SE 30) and 20% DC560 on Gas Chrom Q. The separation of methylphenylsiloxanes was carried out using three columns: 1% Dexsil, 1% OV 17, and 1% OV1. Typical chromatograms are shown in relevant chapters. In all cases the column length was 6'.

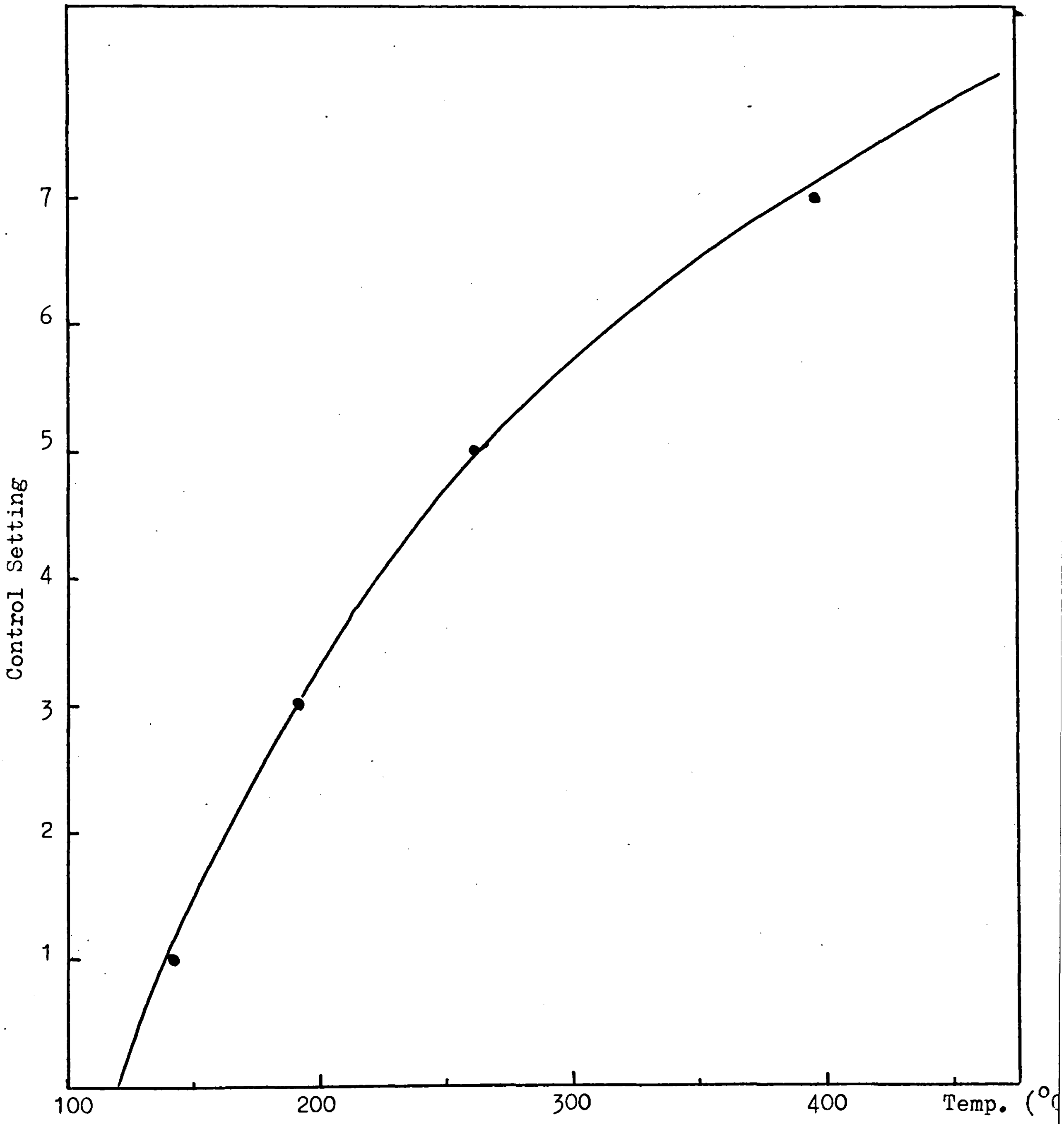
Quantitative Estimation of Dimethyl Cyclic Siloxanes

Quantitative data on cyclic dimethylsiloxane production from polydimethylsiloxanes by GLC, were obtained using the "normalisation method" described by Grant (Ref. 100). This method depends on making the assumption that the chromatogram represents a known proportion of the sample, in this case the whole sample. Here, this is justified by weight loss data and IR analysis.

The/



(a) Experimental layout



(b) Injection Block Temperature for F.11 Chromatogra

Fig. 2.8 Gas Liquid Chromatography

The column was first calibrated with pure components to obtain relative detector response factors. The relative response factor is defined simply as the ratio of the detector response factor to any amount of selected standard component and it is calculated for each component from the peak areas obtained in chromatographing calibration mixtures, and the weights of components in the mixture. In the normalisation method the selected standard is not a specifically added compound but can be any of the components already known to be present in the sample, in this case cyclic dimethyl trimer Relative response factors are calculated by applying the relationship,

$$Rf = \frac{Ai \times Ws}{As \times Wi}$$

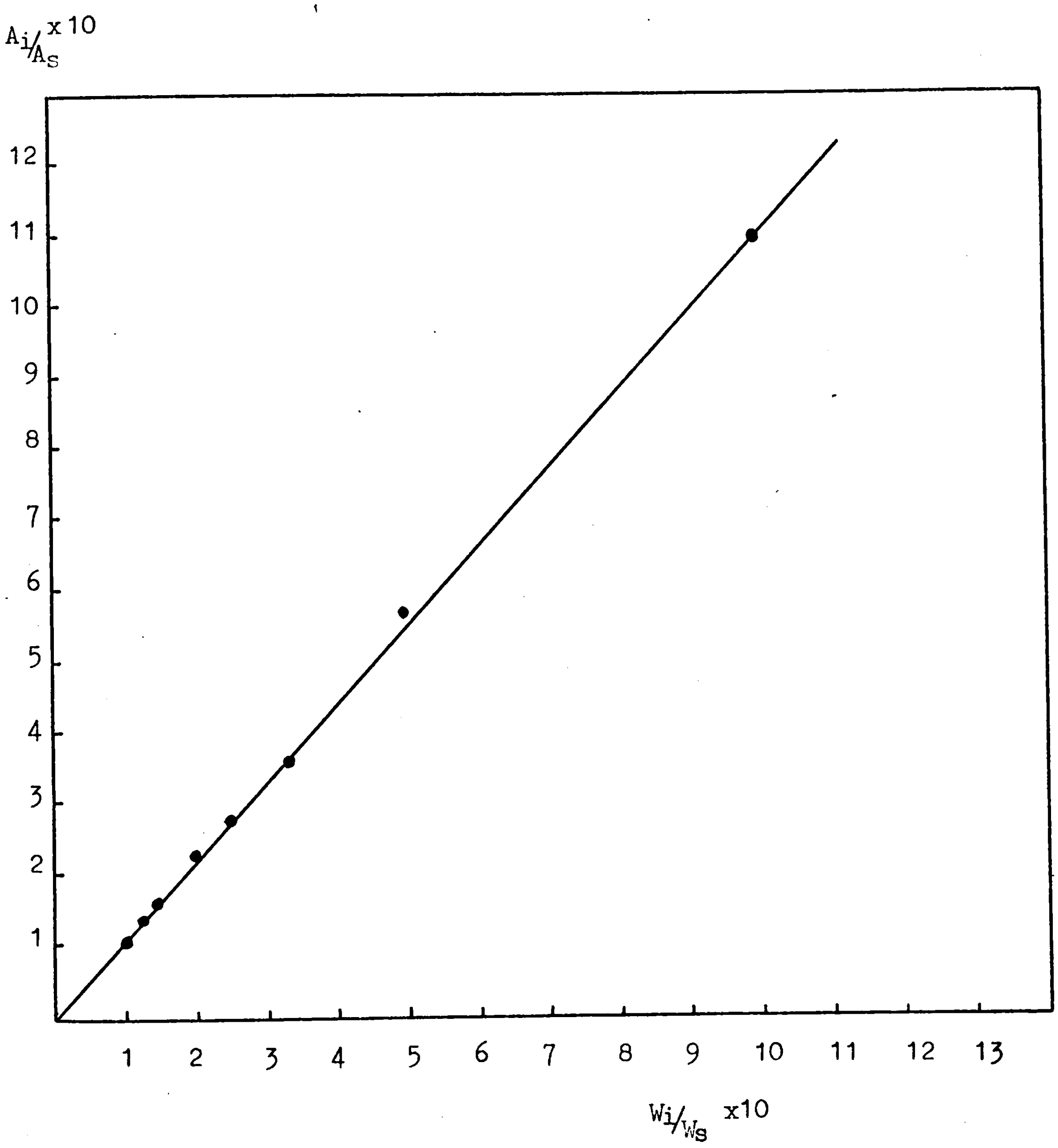
where Rf is the relative response factor
Ws weight of standard
Wi " " component
As peak area of standard
Ai " " " component

The Rf value is given therefore by the gradient, M, of a plot of $(^{Ai}/As)$ versus $^{Wi}/Ws$

Samples of cyclic trimer, tetramer, penamer, and hexamer, purified by repeated fractional distillation, were used to determine relative response factors. The purity of each component as determined by GLC was $\geqslant$ 99.9%. Graphs for determining response factors are given in Fig. 2.9 and values taken from them given in Table 2.1.

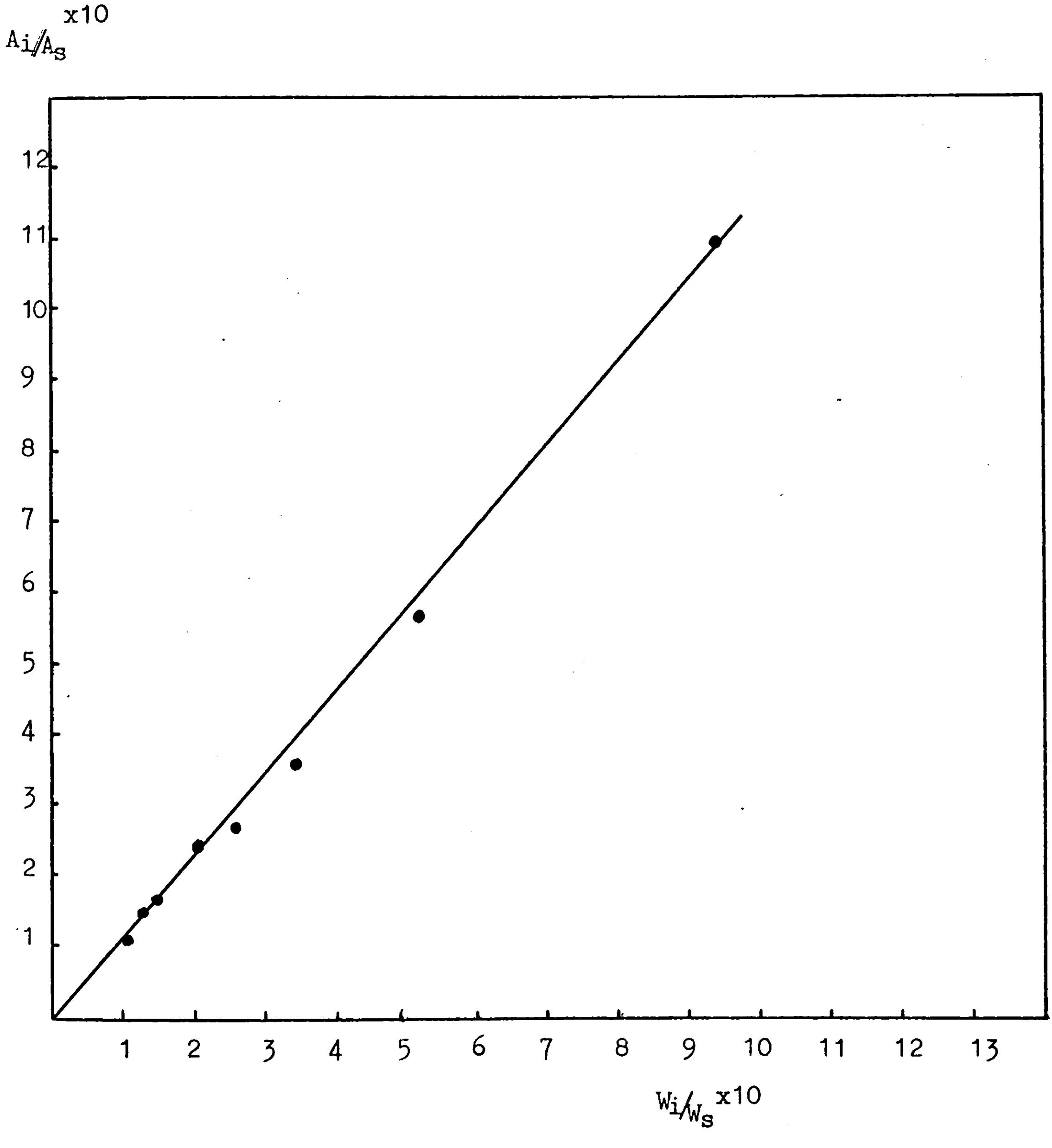
For higher cyclics where pure standards were not available relative response factors have been estimated by extrapolation. The error caused by lack of experimentally determined values will be fairly small since the higher cyclics are present only in low concentrations.

The/



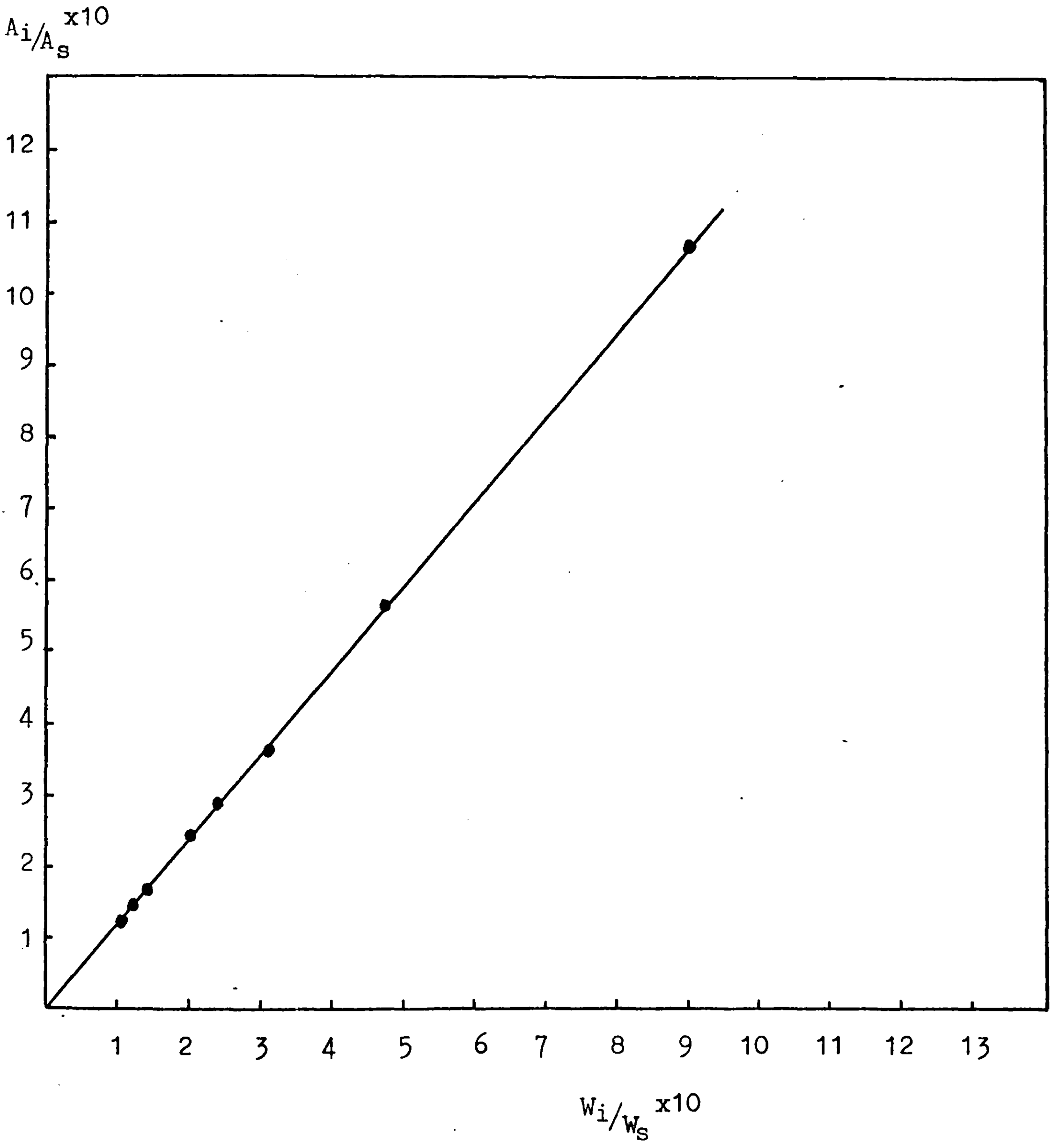
(a) $D_4 : D_3$

Fig. 2.9



(b) $D_5 : D_3$

<u>Fig. 2.9</u>



(c) D6 : D3

Fig. 2.9 Calibration Curves for Flame Ionisation Detector

TABLE 2.1

Gas Chromatographic Detector Response Data

(Relative to dimethyl cyclic trimer)

Oligomer	Relative Response Factor (Rf) = $\frac{A_i/A_s}{W_i/W_s}$
trimer	1.00
tetramer	1.11
pentamer	1.15
hexamer	1.18
heptamer– decamer	1.19 *

* estimated value

The concentration of each component is given by

$$C_i = \frac{Ai/Rf(i)}{(A/Rf)} \times 100$$

(iv) Gas Chromatography - Mass Spectrometry (GCMS)

Confirmation of GLC peak assignments has been made with the aid of an LKB 9000 (LKB Produkter) combined gas chromatograph-mass spectrometer, a schematic diagram of which is given in Fig. 2.10

The mass spectrometer is a single focusing instrument with a fast scanning speed. When a component is observed on the GLC recorder pressing the scan button automatically increases the ionisation voltage to 70 e.v. and a mass spectrum is obtained from the fast UV recorder.

(v) Nuclear Magnetic Resonance Spectrometry (NMR)

Nuclear magnetic spectrometry provides a powerful tool for the compositional and structural analysis of organosilicon compounds, and allows the rapid, specific detection and quantitation of components of virtually inseparable mixtures.

Spectra were obtained using either a Perkin Elmer R10 60 Mcps spectrometer or a Varian HA 100 Mcps spectrometer.

(vi) Ultra-violet Spectroscopy (UV)

Although UV spectroscopy has had extensive use in the study of bonding in organosilicon chemistry it is of limited value for analytical purposes. This situation exists because only a few of the many possible substituent groups on silicon show UV absorption and those that absorb do not show sufficiently distinctive patterns to be of much practical use. Erroneous assignments of UV absorptions have been made for some organosilicon materials, whereas the absorption was actually due to impurities in the samples. (Ref. 19)

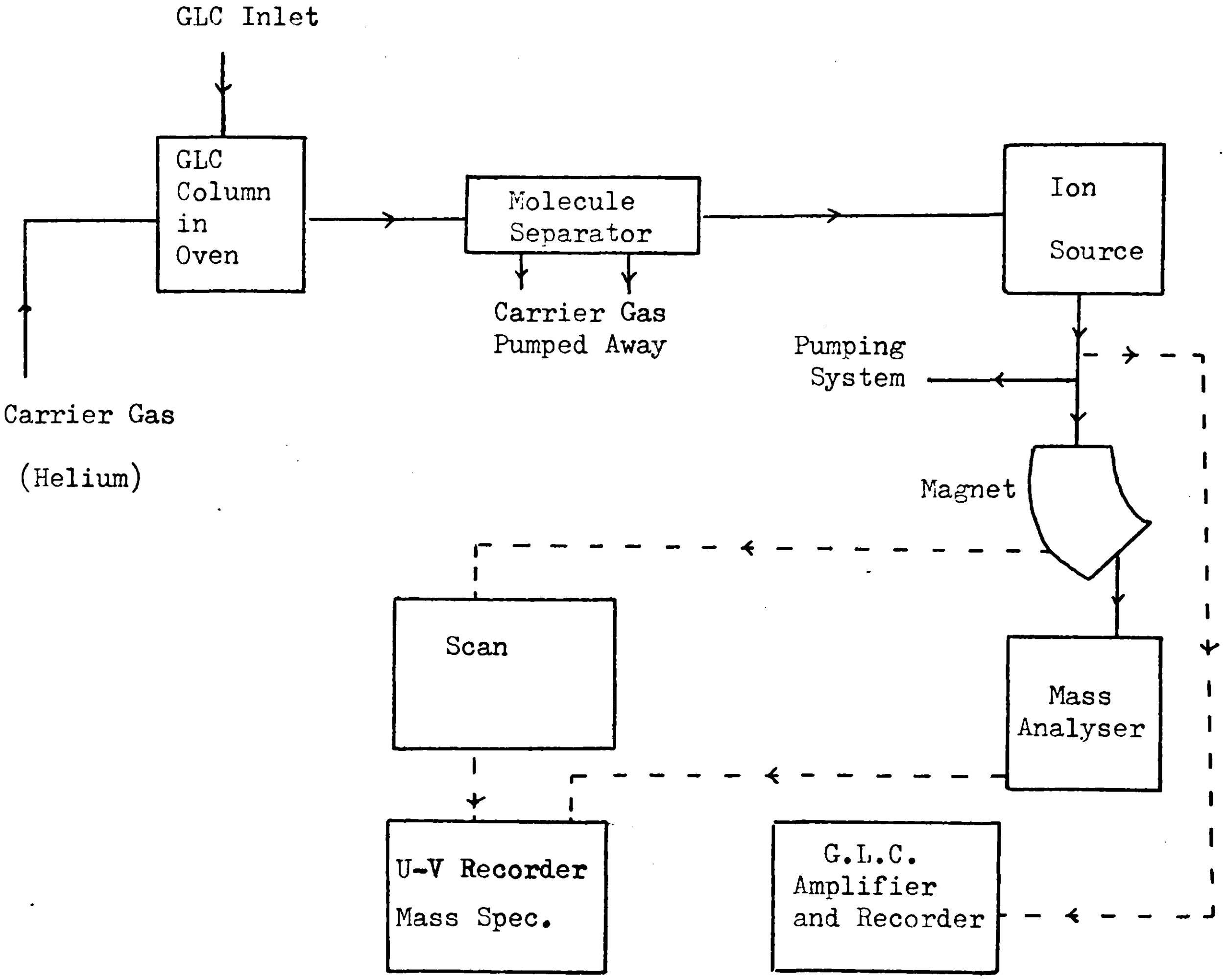


Fig. 2.10 Schematic Diagram of L.K.B 9000 GCMS

In this work the use of uv has been confined to the study of benzene evolution from phenyl containing siloxanes. An SP800 spectrophotometer was used to record spectra. Samples were run in the gaseous phase.

Quantitative Estimation of Benzene

The response of the Unicam SP800 spectrophotometer to known pressures of benzene vapour was measured and a calibration curve (optical density v pressure) was constructed (Fig. 2.11). The pressure of benzene in the gas cell was measured using a McLeod gauge for low pressures and a mercury manometer for higher pressures. Knowing the volume of the system the amount of benzene can easily be calculated.

(vii) Measurement of Molecular Weight

Molecular weights were measured in toluene solution using a Hewlett-Packard 501 High Speed Membrane Osmometer with cellophane 300 membrane. The osmotic plot of a quite typical polydimethylsiloxane sample is illustrated in Fig. 2.12 from which a molecular weight of 258,000 was deduced.

(viii) Gel Permeation Chromatography

The apparatus used is illustrated in Fig. 2.13. The gel, a cross-linked dextran (Sephadex LH20, Pharmacia Ltd.) was contained in a pyrex column (4 x 75cm). Solvent was added from reservoir A above the inlet to the chromatographic column. The solvent was maintained at a constant hydrostatic pressure on the liquid flowing through the column with the aid of a Mariotte flask.

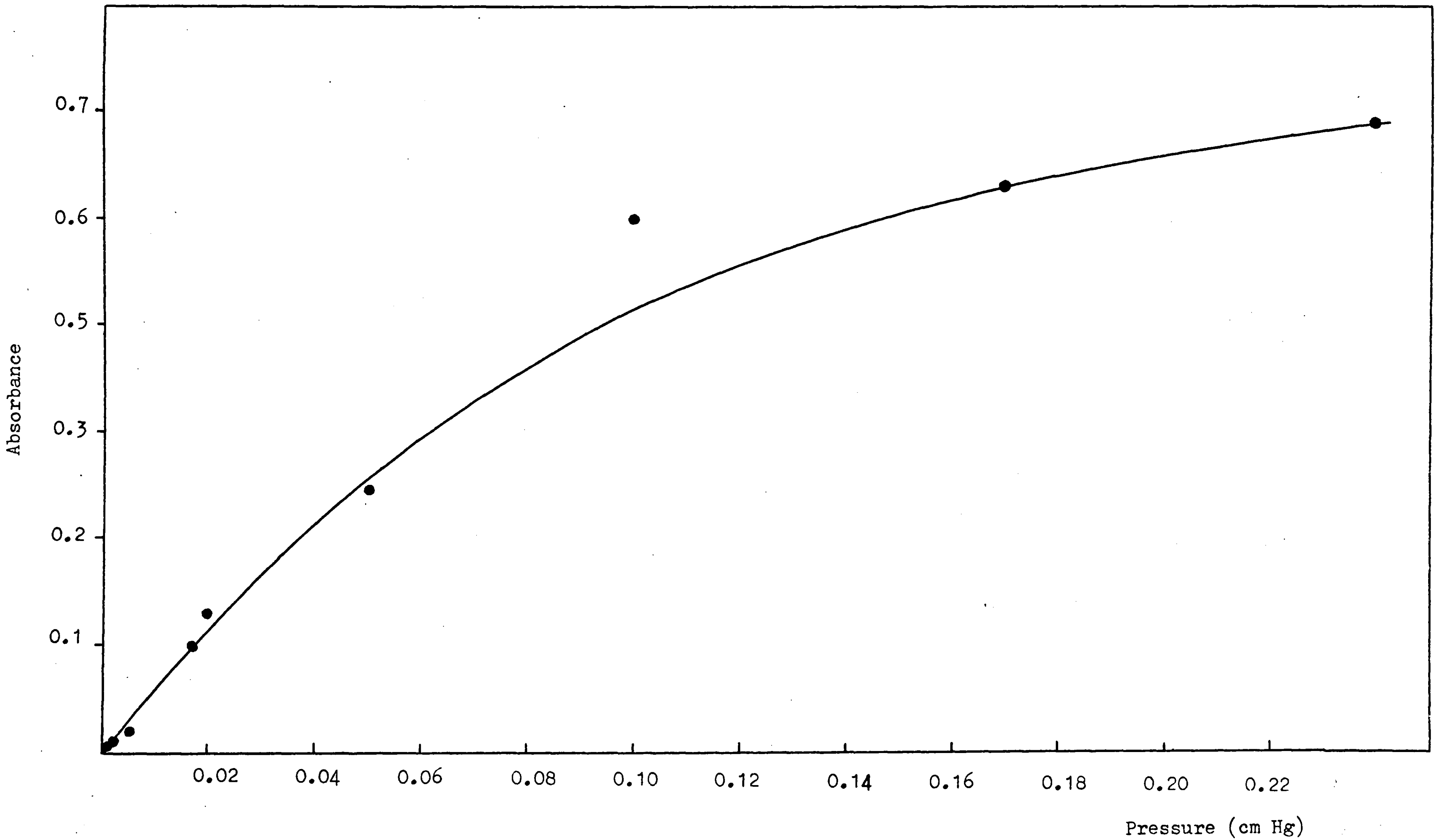


Fig. 2.11(a) UV Calibration Curve for benzene.

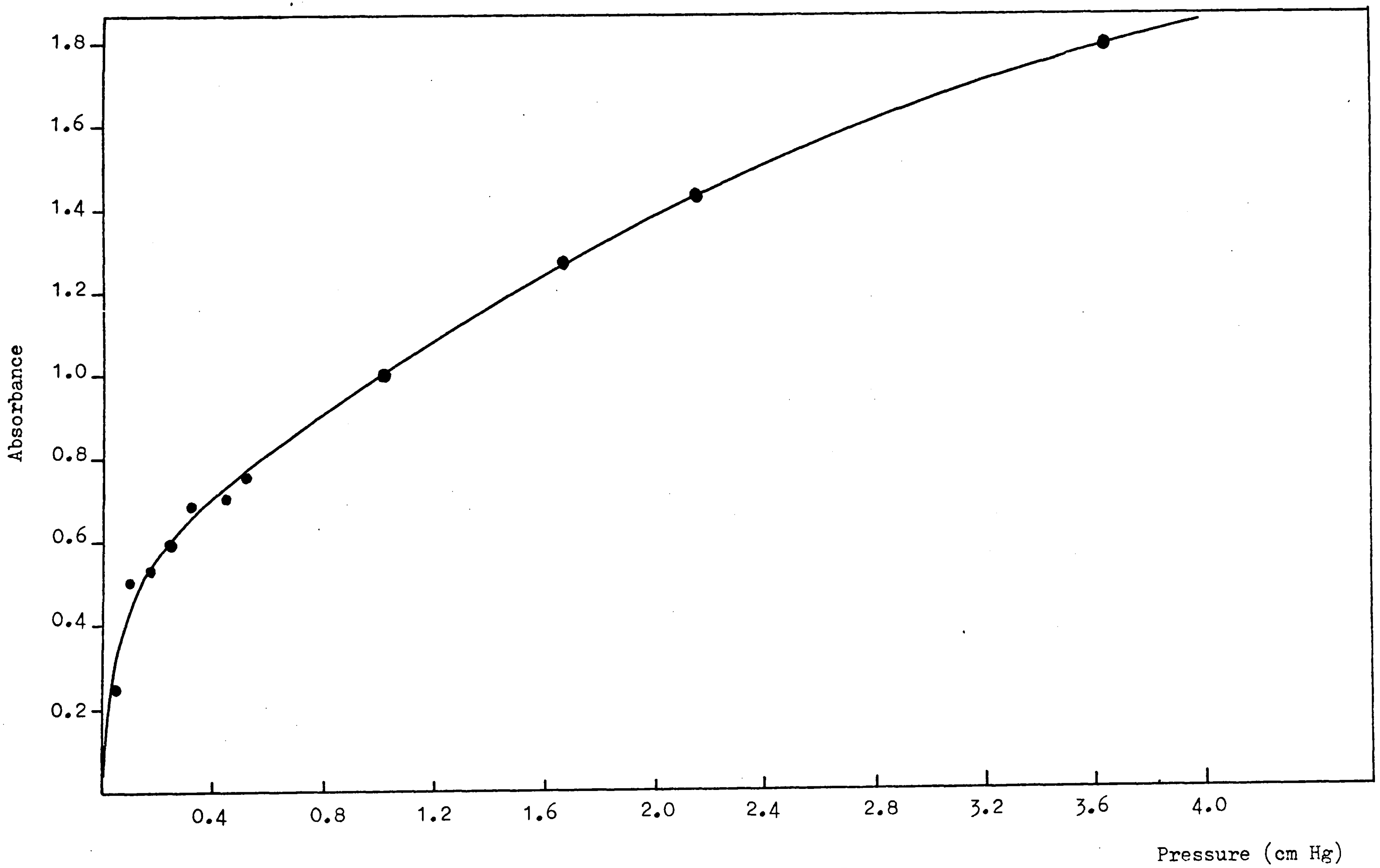
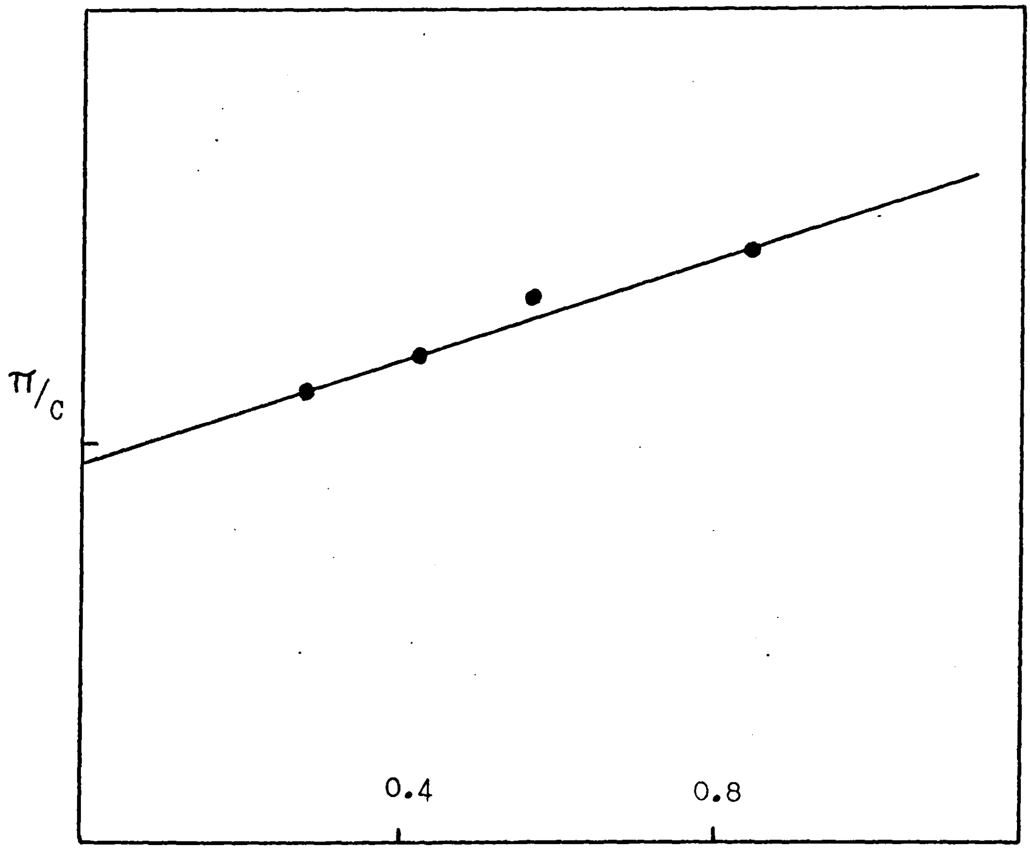


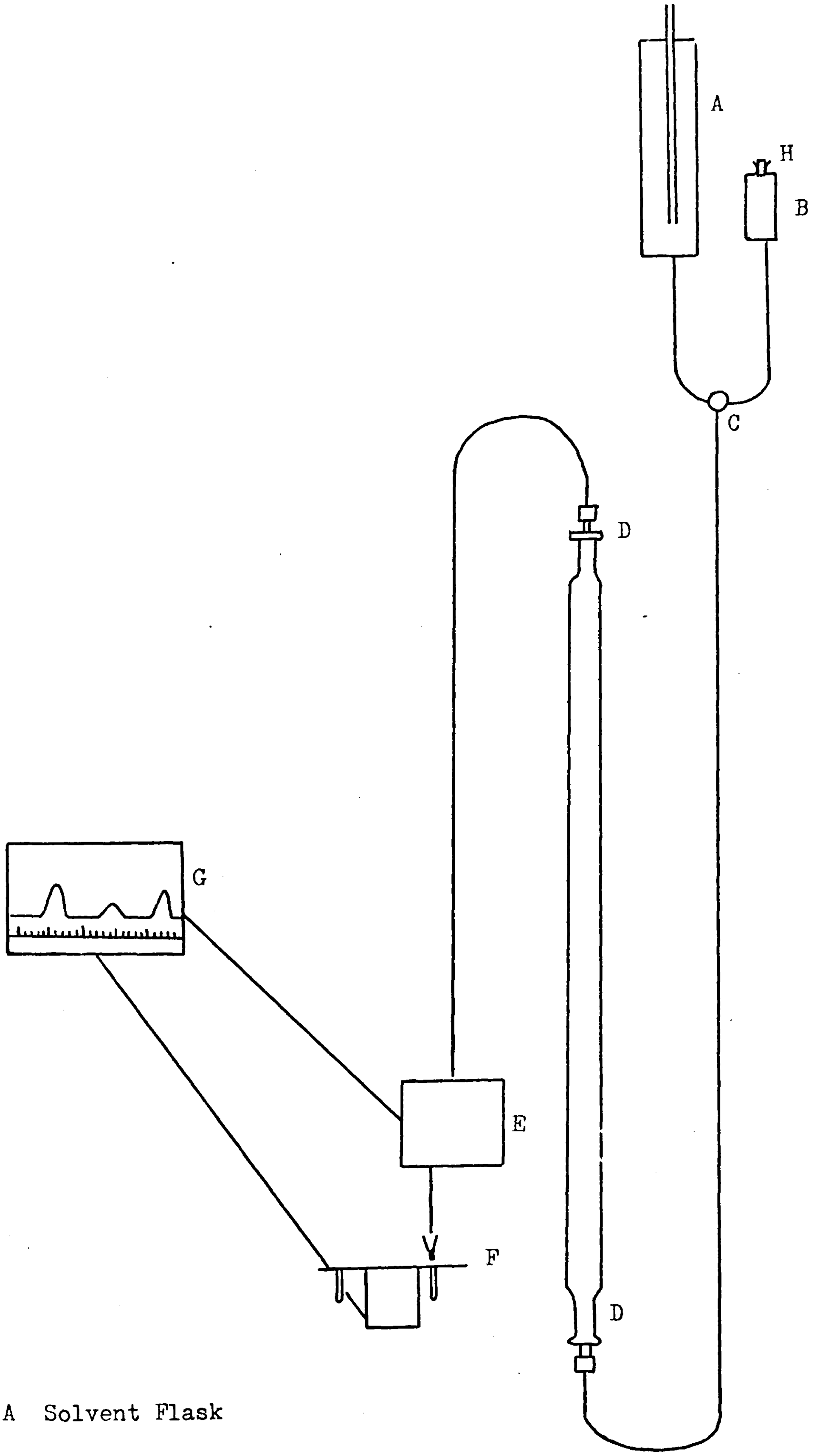
Fig. 2.11(b) UV Calibration Curve for Benzene.



polydimethylsiloxane $(\pi/c)_o = 0.98$

Mn = 258,000

Fig. 2.12 A Typical Osmotic Plot



A Solvent Flask

B Sample Flask

C Three-way Stopcock (Teflon)

D Column ends (Teflon)

E U.V. Detector

F Fraction Collector

G Chart Recorder

H Sample Flask Stopper

Fig. 2.13 Gel Permeation Apparatus

Upward flow elution was preferred because the solvent (chloroform) is denser than the swollen gel. Flow in the elution step is produced simply by a difference in hydrostatic pressure. The solvent resistant column ends (Pharmacia) ensured that except for the nylon sieves and a small metal ring, in the column ends all surfaces in contact with the solvent were of Pyrex glass or polytetrafluoroethylene.

Injection of sample was achieved by closing the teflon three way stopcock C, removing stopper H and allowing the solution to run off. Stopcock C was then reopened to solvent, and stopper H replaced. The column is designed with a very small mixing chamber (less than 0.1% of the total column volume). Eluate from the column passed through a LKB 4701A UV detector and was collected in 10ml fractions by the automatic fraction collector.

CHAPTER 3

3.1 INTRODUCTION POLY(DIMETHYLSILOXANE)

The major features of the recent literature on the degradation of poly(dimethylsiloxane) have been given in Chapter 1. It is clear that while a number of workers have studied this polymer and while information is available on the nature of the products of its thermal break-down there are several features which are not wholly understood. The production of methane from hydroxyl-ended polymers is one such feature and has only been dealt with qualitatively. The involvement of chain ends in the degradation process is somewhat better understood but controversy has arisen over proposed mechanisms.

Using techniques described in Chapter 2 a number of samples of poly(dimethylsiloxane) (pdms) of differing molecular weights have been prepared and thermally degraded. Polymer preparation and molecular weight data are given in Table 3.1. One sample, polymer F, has been used for the major part of the work on molecular weight changes. An attempt has been made to end-block two of the polymers, polymer D and polymer F, using hexamethyldisilazane, in a bid to study the involvement of hydroxyl end-groups in the degradation process.

Products from the degradation of pdms have been analysed using ir, glc and mass spectrometry. The applicability of ir to almost any type of sample, combined with the extraordinarily reproducible group frequencies found with the silicones, make it one of the most useful tools for analysis of monomers and polymers. The ir spectra of silicones are unusual in that the intensity of the absorption bands lying beyond 7 microns is 5 to 10 times greater than is normal with most organic compounds. (Ref. 101).

Linear/

Linear or cyclic species containing eight or fewer units can be characterised by the shape and position of the Si - O stretching frequencies. (Ref. 102).

Because of the very low intermolecular forces in the dimethylsiloxanes, exceptionally high molecular weight species will pass through standard glc columns. Thus, rings up to D_{20} have been observed in this study. It is likely that a refinement of the instrumental conditions would allow even larger rings to be analysed. The sensitivity of this technique coupled with its unrivalled separation ability make it indispensable for the study of the breakdown products of silicones. (Refs. 103-106).

Although mass spectra of the lower dimethylcyclicsiloxanes appear in the literature there is a lack of detailed information on the break-down patterns of higher cyclics. Thus, reference spectra for D_3, D_4, D_5 and D_6 are given by VandenHeuval (Ref. 107) and a brief comment on the break-down of higher cyclics is given by Smith (Ref. 14). This work includes spectra of a number of the higher cyclics.

3.2 PREPARATION OF POLYMERS

The cyclic tetramer used to prepare polymers E and F was of exceptionally high purity as determined by glc. The tetramer used to prepare polymers A, B, C and D contained small amounts (0.5 - 1.5 wt%) of D_3 and D_5. These species polymerise to the same product as cyclic tetramer and are therefore not contaminants in the usual sense. The conditions for polymerisation are given in Table 3.1.

TABLE 3.1

Preparation of Poly(dimethylsiloxanes)

Polymer	Tetramer	Temp. (°C)	Catalyst	Mn
A	+D_3, D_5*	115	few drops of 25% aqueous solution	258,000
B	"	110-130	dry 0.02%	94,500
C	"	108-110	" 0.1%	141,000
D	"	97-98	" 0.02%	183,000
E	pure	100	" 0.01%	269,000
F	"	115	aqueous solution 0.015%	111,500
G	end-blocked sample of polymer D			
H	end-blocked sample of polymer F			

* $D_3 + D_5$ 1.5%

The reaction is known to be first order with respect to tetramer and $\frac{1}{2}$ order with respect to catalyst. (Ref. 108).

The polymers are completely soluble in a number of organic solvents, including benzene, toluene, chloroform and carbon tetrachloride, but are insoluble in the lower alcohols. Characterisation by ir spectroscopy (Fig. 3.1) shows the Si-O-Si stretching made at 1000 - 1100 cm^{-1} and Si-CH_3 absorption at 1260 cm^{-1}.

The possibility that the polymers contain branched structures is remote for several reasons. Branched structure can occur in the polymerisation of siloxanes only if trifunctional units are present in the reaction mixture or cleavage of a Si-C bond occurs during the reaction. The purification of the starting material precludes the former and the latter is known not to occur under the conditions used. (Ref. 51). There is thus no experimental evidence of branched structure in these samples.

3.3 DESTRUCTION OF RESIDUAL CATALYST

The destruction of residual catalyst was achieved by heating samples at 135°C for 10-20 minutes. The catalyst, tetramethylammoniumhydroxide, breaks down at this temperature to form trimethylamine and methanol, neither of which affects the stability of the polymer. (Ref. 79).

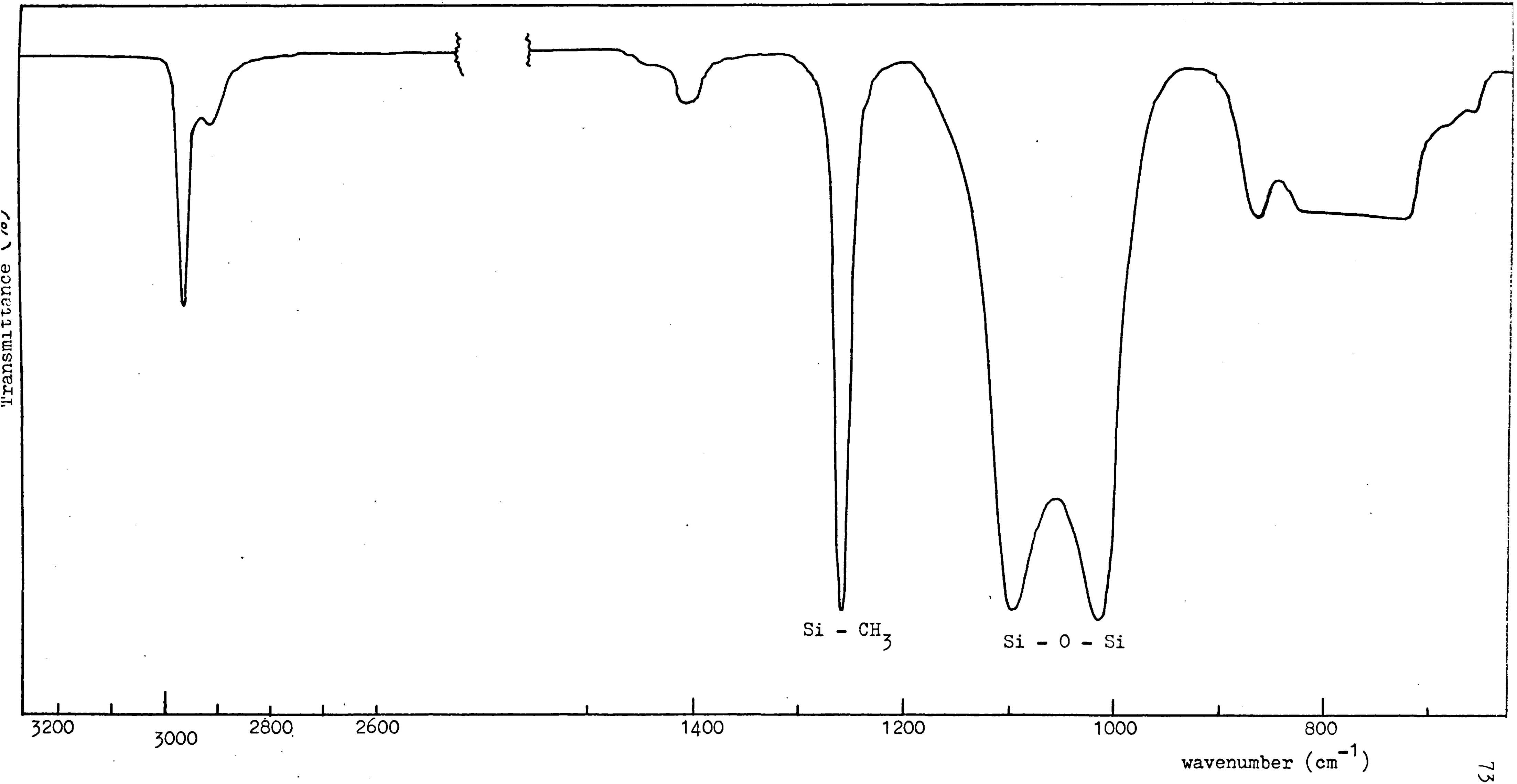


Fig. 3.1 IR Spectrum of poly(dimethylsiloxane)

Solvent CCl_4

Cellpath 0.5 mm.

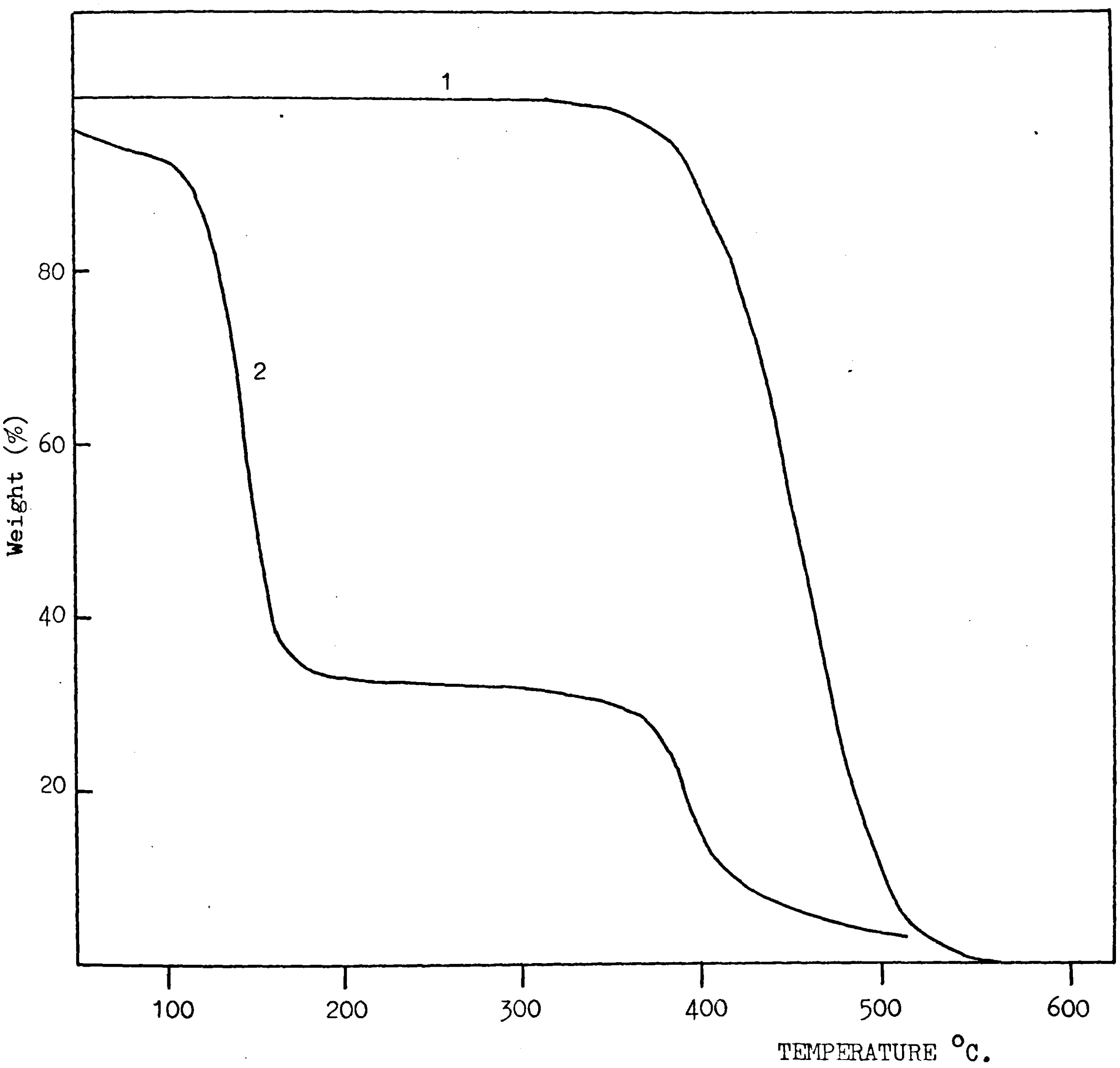


Fig. 3.2 TGA Curves for 1) Polymer F

2) Polymer F + aqueous TMAH

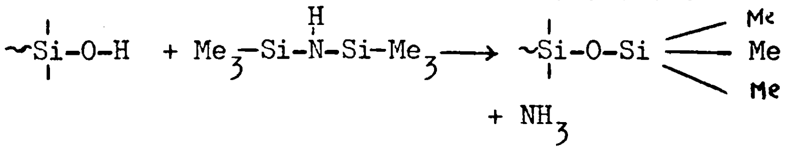
$$(CH_3)_4\ NOH \longrightarrow (CH_3)N + CH_3OH$$

The effectiveness of this process can be judged from a programmed TGA run of a polymer sample with excess catalyst (Fig. 3.2). Catalyst, in the form of a 25% aqueous solution of TMAH, was added to a pure sample of polymer F. The sample looses weight initially due to the evaporation of water from the catalyst solution, followed by a further weight loss due to depolymerisation catalysed by the transient catalyst. When the temperature rises sufficiently to degrade the catalyst the weight loss ceases and the sample shows normal behaviour for the latter part of the programme.

3.4 END-BLOCKING OF PDMS

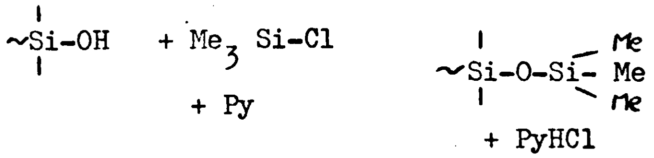
The literature describes two basic methods of preparing polymer samples with trimethylsiloxy end groups. In the first, a mixture containing cyclic species together with a predetermined amount of hexamethyldisiloxane is polymerised in the usual manner. The dimer equilibrates with the polymerising cyclic tetramer to form the desired end-blocked product. (Refs. 109, 110, 114 and 115).

In the second the polymer is prepared with -OH end groups which are then reacted with an end-blocking agent such as a) 1,1,1,3,3,3, hexamethyldisilazane



$$\sim\overset{|}{\underset{|}{Si}}-O-H + Me_3-Si-\overset{H}{N}-Si-Me_3 \longrightarrow \sim\overset{|}{\underset{|}{Si}}-O-Si\begin{matrix}Me\\Me\\Me\end{matrix} + NH_3$$

or b) monochlorotrimethylsilane in the presence of pyridine



$$\sim\overset{|}{\underset{|}{Si}}-OH + Me_3\ Si-Cl + Py \qquad \sim\overset{|}{\underset{|}{Si}}-O-Si\begin{matrix}Me\\Me\\Me\end{matrix} + PyHCl$$

Of/

Of these methods experimental conditions for the first process are adequately documented but apart from one paper by a Russian worker (Ref. 111) few workers describe conditions for reaction 2 a). Andrianov (Ref. 53) prefers method 2 b) claiming it to be more successful than 1).

Two attempts at end-blocking using D and F have been made using process 2 a). Polymer D (0.5g) has been end-blocked by refluxing with excess 1,1,1,3,3,3, hexamethyldisilazane (1.2ml) in toluene (20ml) for 24 hrs. to form polymer G. Recovery of the samples was made by reprecipitation from methanol. Polymer F (3g) was refluxed in 20ml of pure 1,1,1,3,3,3, hexamethyldisilazane for 12 hrs. to form polymer H. The excess silazane was evaporated and the polymer dissolved in toluene and reprecipitated from methanol. Neither of the above procedures affected the molecular weight of the polymer.

Dynamic TGA (Fig. 3.3) shows that unreacted disilazane does not affect the degradation behaviour of a catalyst free pdms sample. This trace has been obtained using a sample of polymer F to which an excess of disilazane had been added by soaking for 24 hrs. at room temperature. It is clear from the TGA data that apart from the weight loss due to evaporation of the disilazane, the polymer behaves normally and is unaffected by residual end-blocking agent.

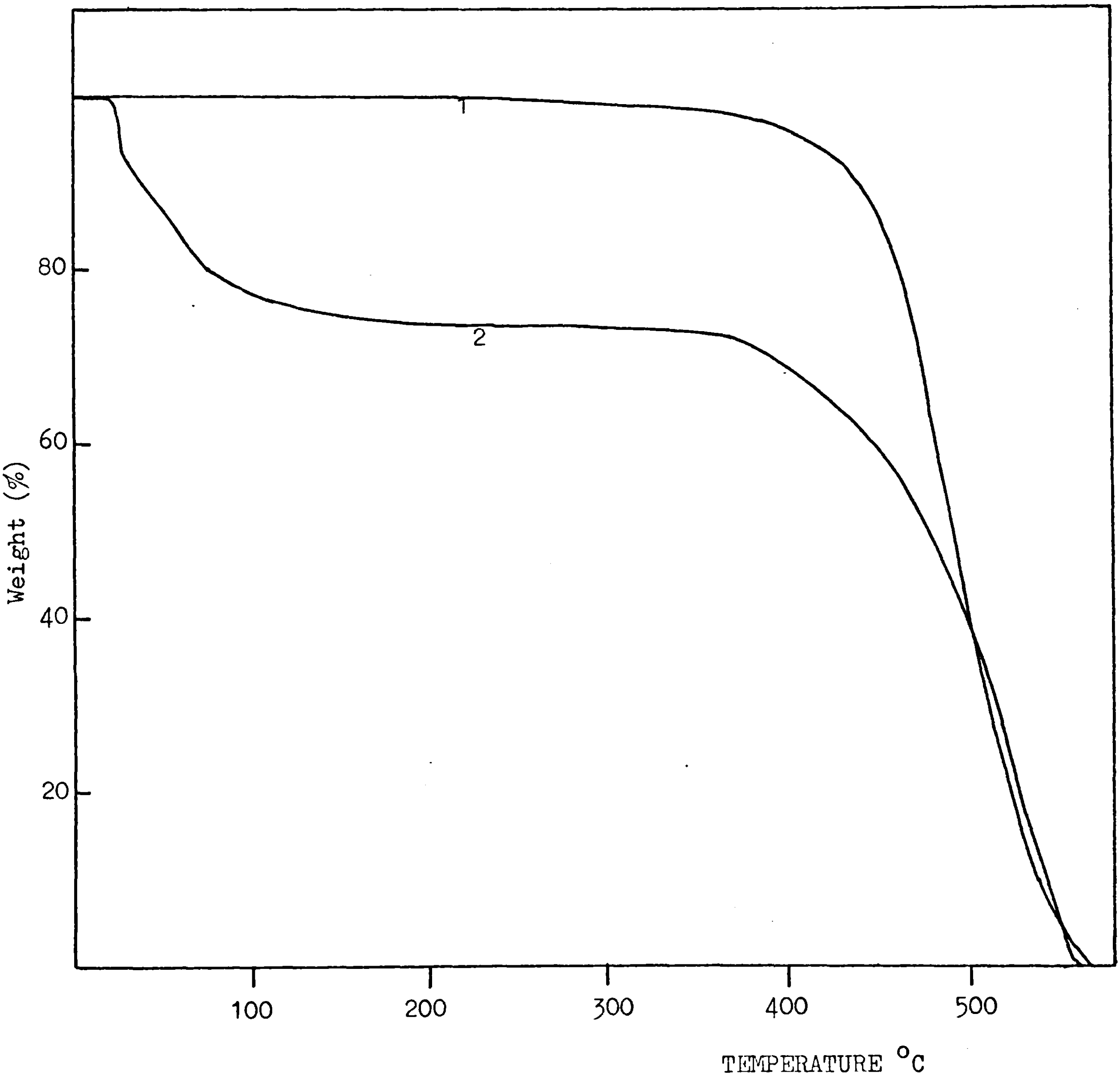


Fig. 3.3 TGA of 1) Polymer H

2) Polymer H + 1,1,1,3,3,3 disilazane (~20 wt.%)

3.5 THERMAL VOLATILISATION STUDIES (TVA)

(i) Introduction

The TVA traces of polyers A-F show similar features and will not be discussed separately in detail. A TVA trace of polymer F is given in Fig. 3.4(a). It shows the evolution of volatile products beginning at about 343°C and reaching a maximum about 443°C. The gaseous products are sufficiently volatile to pass through the two higher temperature traps (0°C and -45°C) but are trapped out at lower temperatures. There is no evidence for non-condensable products such as methane or hydrogen, which would be indicated by a rise in the -196°C trace.

The TVA of polymer H is given in Fig. 3.4(b). It is clear that there has been a substantial degree of stability imparted by the end-blocking process. This provides strong evidence for the involvement of chain ends in the degradation of hydroxyl-ended polymers.

(ii) Analysis of Products

(a) Gaseous products from pure PDMS

Figure 3.5 shows reference spectra of cyclicdimethyltrimer (D_3) and tetramer (D_4), and the gaseous products from the degradation of polymer F. Figure 3.6 shows the products from polymer H. In both cases the cyclic trimer and tetramer account for the complete absorption spectra with the trimer predominating. There is no evidence of any substantial variation in the distribution of these products from the two samples.

(b)/

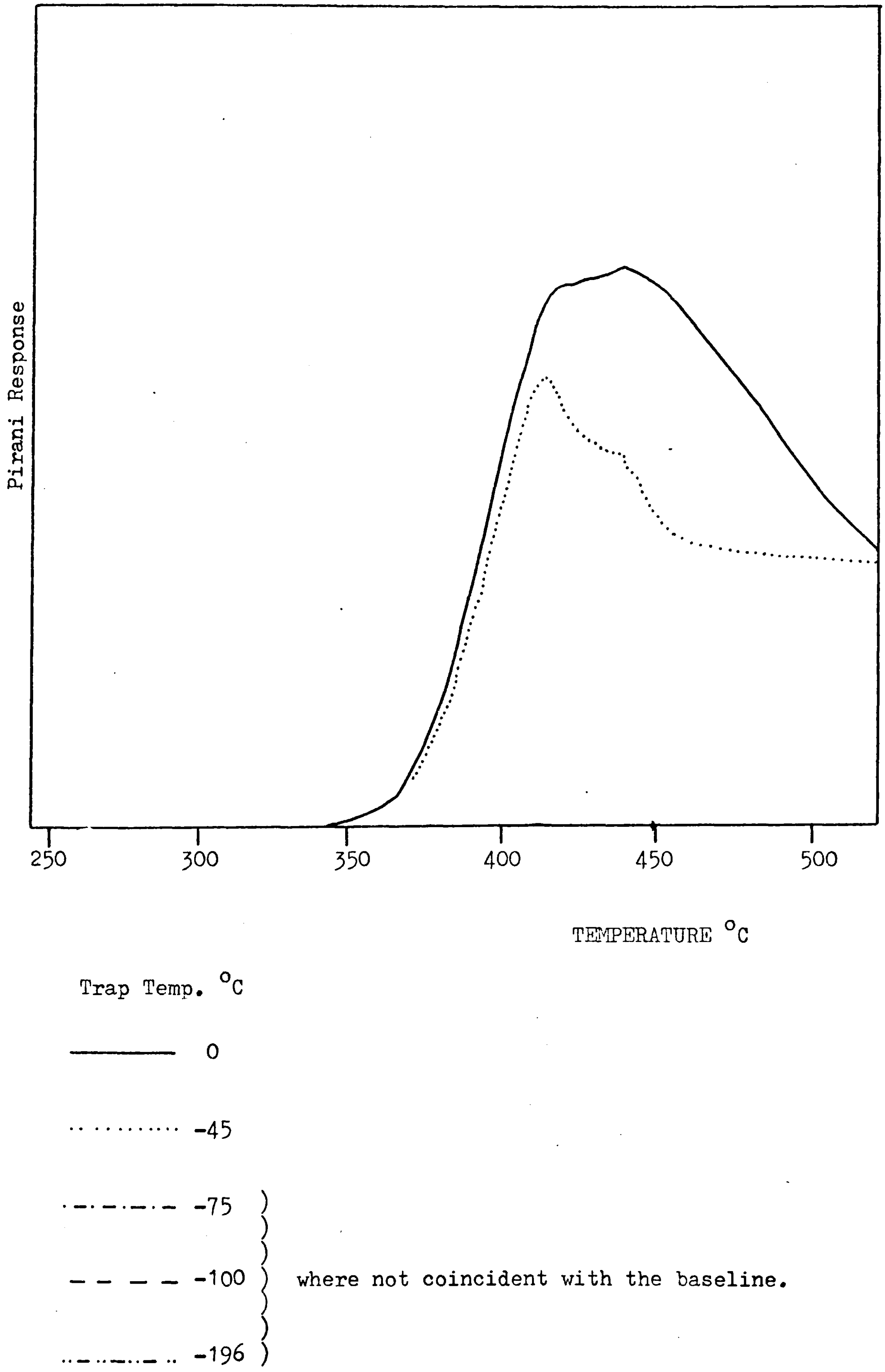


Fig. 3.4 (a) TVA Curve for hydroxyl-ended PDMS.

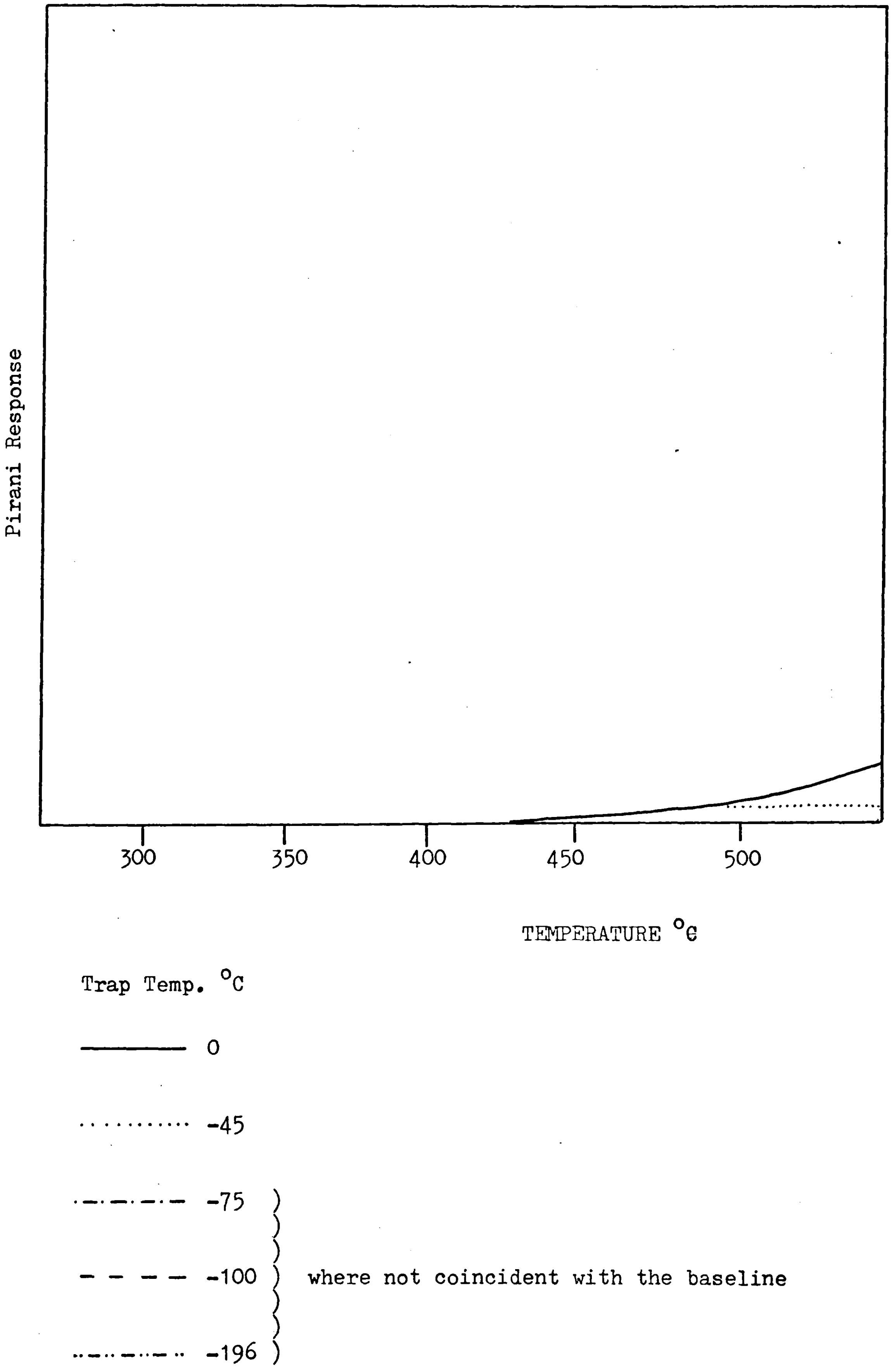


Fig. 3.4(b) TVA curve for polymer H (trimethylsiloxy-ended PDMS).

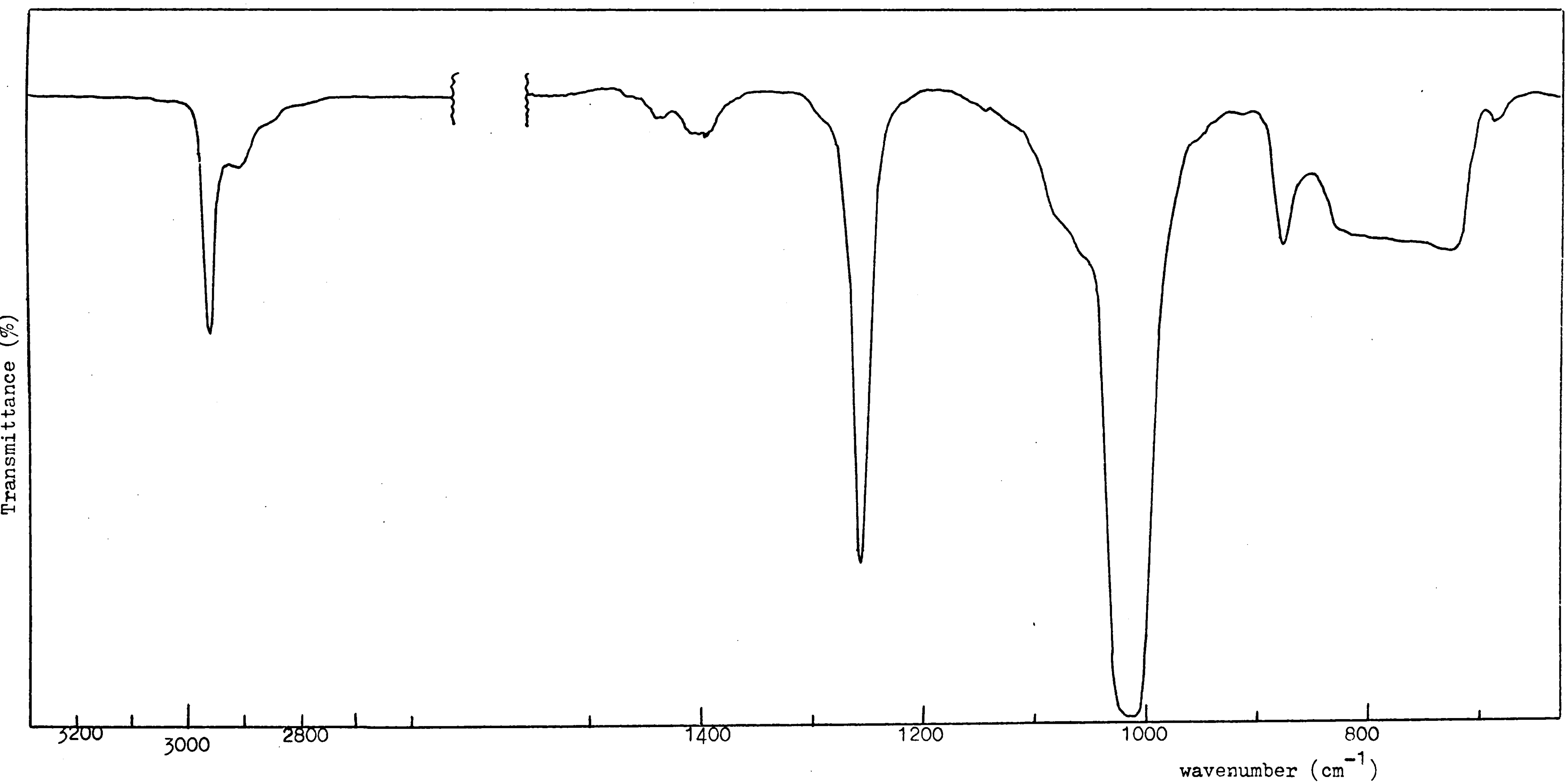


Fig. 3.5 (a) IR Spectrum of hexamethylcyclotrisiloxane (D_3).

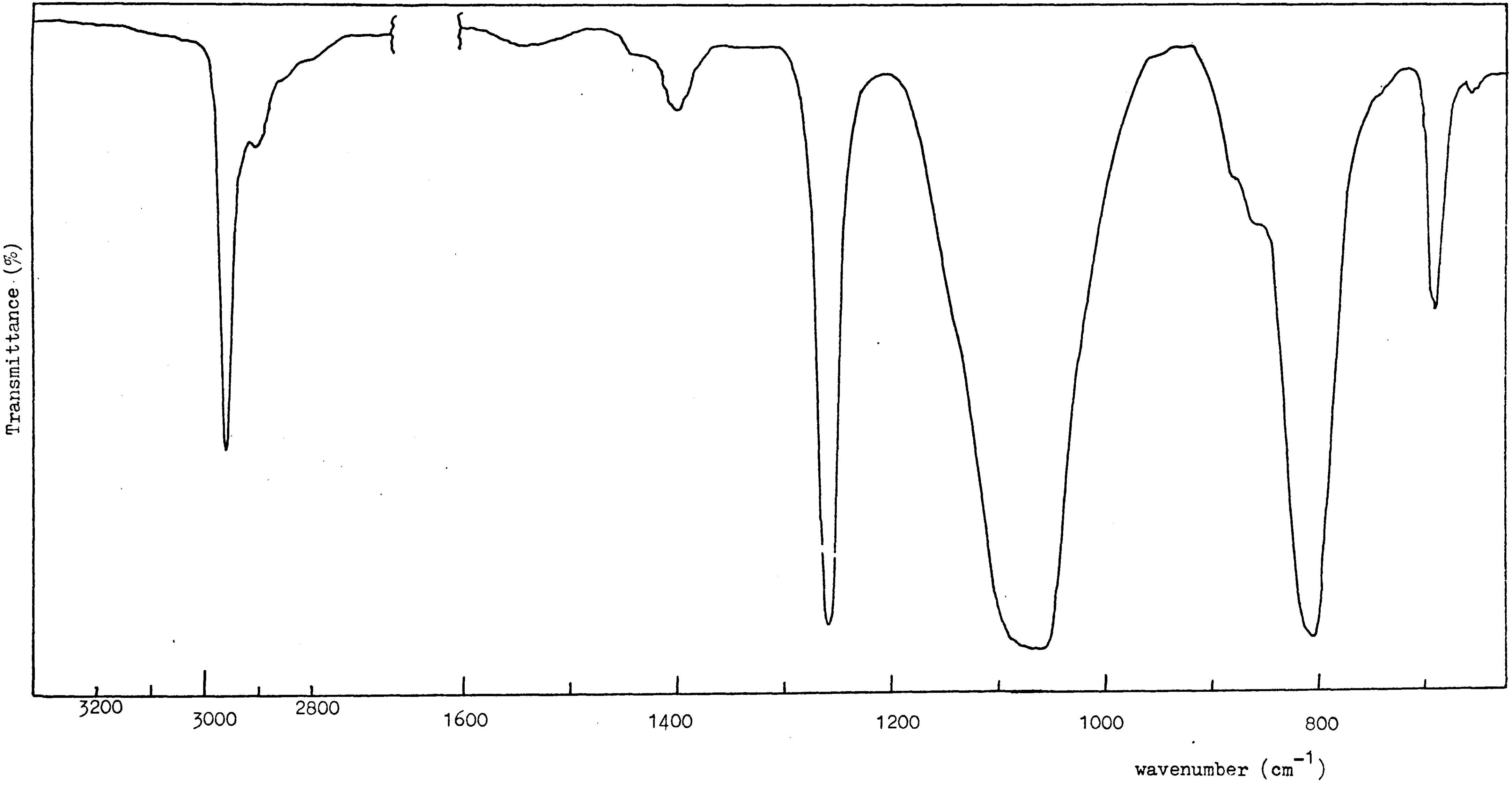


Fig. 3.5 (b) Octamethylcyclotetrasiloxane (D_4).

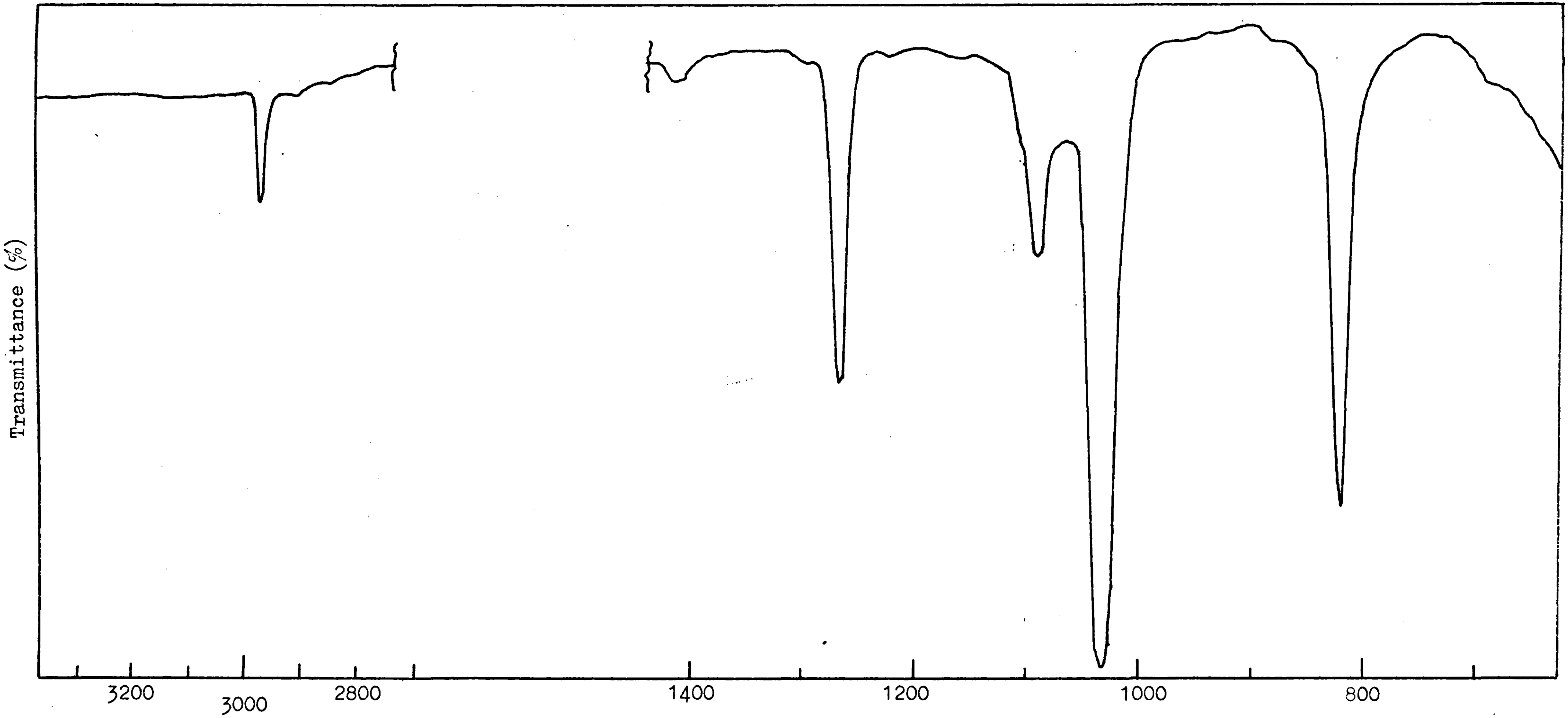


Fig. 3.5 (c) IR Spectrum of gaseous products from TVA of polymer F (hydroxyl-ended PDMS)

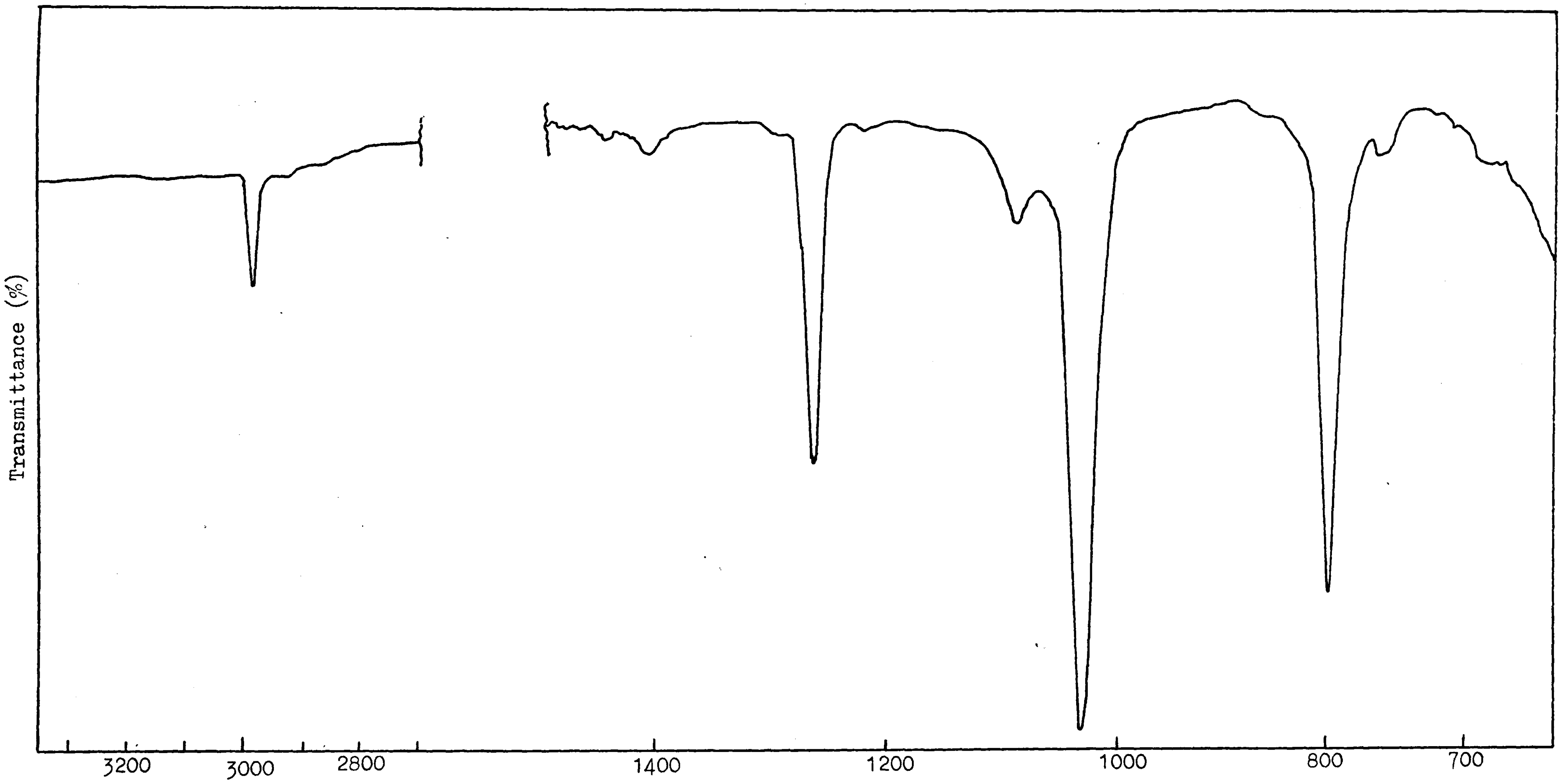


Fig. 3.6 IR Spectrum of gaseous products from TVA of polymer H (trimethylsiloxy-ended PDMS)

(b) Cold ring products from pure PDMS

The ir spectrum of the cold ring is given in Fig. 3.7. This shows the presence of siloxane species only. These species have been shown using GLC and GCMS to be higher cyclics. This work is described under a separate heading.

(c) Residue

The residue which is completely soluble in carbon tetrachloride is a clear rubbery material indistinguishable from the starting material except for an increase in viscosity. Its ir spectrum is illustrated in Fig. 3.8.

(d) Degradation of PDMS + KOH

To investigate the effect of residual basic impurities on the products of the thermal degradation of PDMS a degradation was carried out on a mixture of polymer F with an apprecialbe amount of potassium hydroxide (5-7 wt%). This was repeated using polymer H. The TVA traces are given in Figs. 3-9 and 3-10 respectively.

The most obvious effect of the presence of the base is that a considerable amount of non-condensable material is formed. This has been shown to be predominately methane (Fig. 3.11). The production of methane occurs at temperatures as low as 187°C. The nature of the TVA traces (separation of the lower temperature traces) indicate that smaller amounts of other volatile products are also formed. It is clear that KOH catalyses cleavage of the Si-C bond. The threshold of degradation is, not unexpectedly, much lower (~80°C) than for a pure sample.

Cyclic siloxanes are also formed in the degradation of both samples. In the case of polymer H an unusually large amount of tetramer relative to trimer has been observed in presence of KOH, although for polymer F /

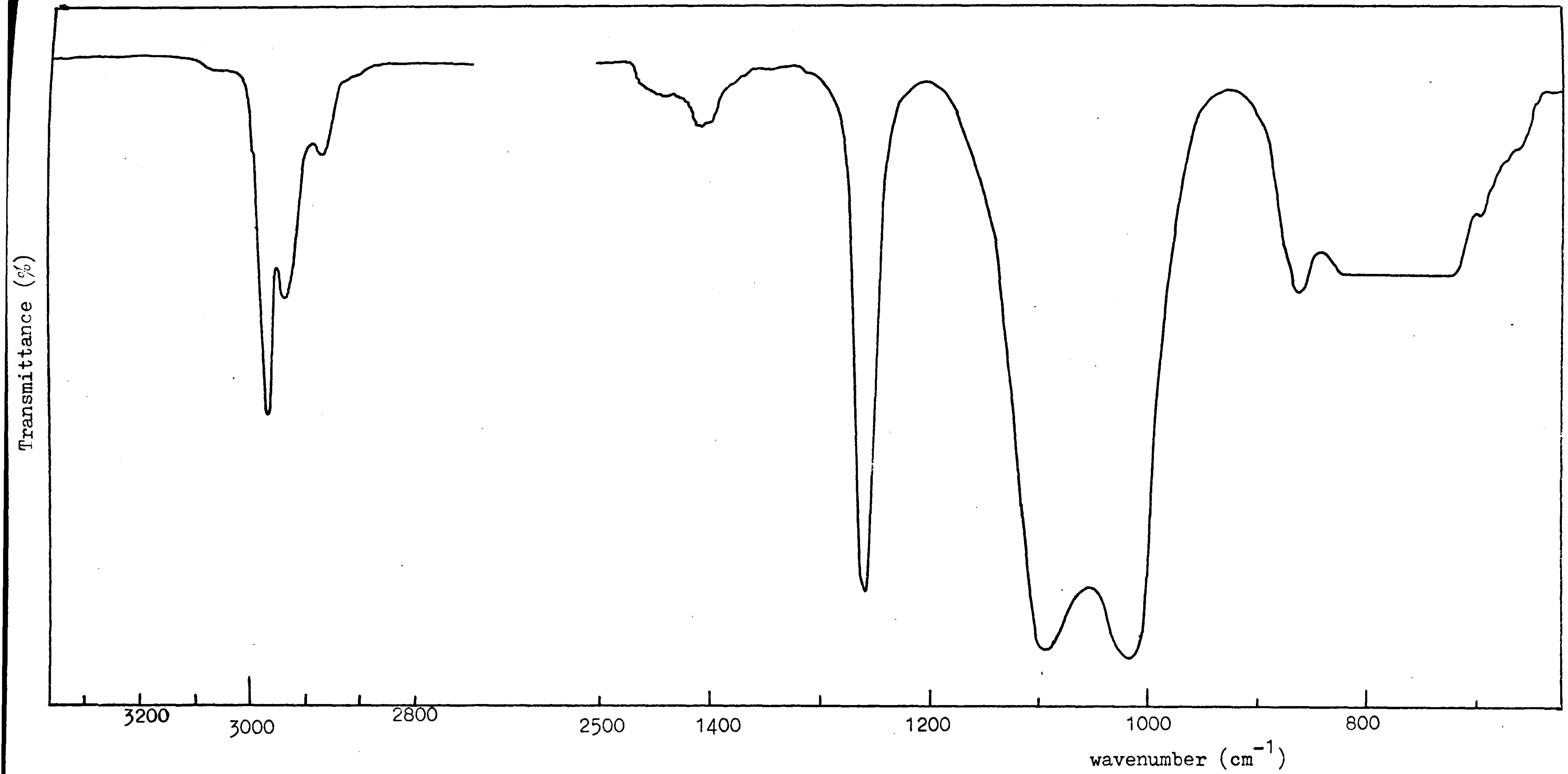


Fig. 3.7 IR of "cold-ring" from TVA of PDMS.

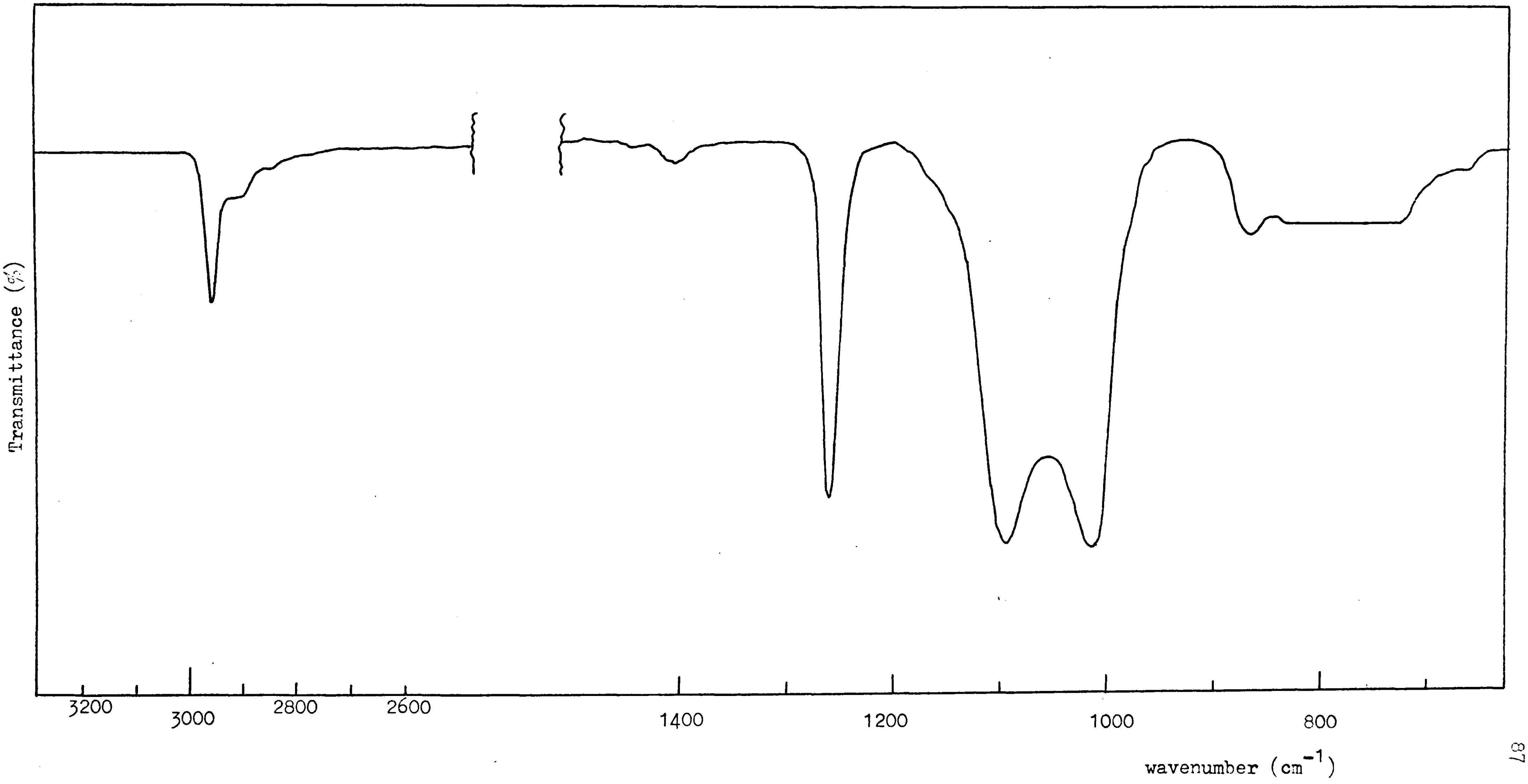


Fig. 3.8 IR Spectrum residue from TVA of PDMS.

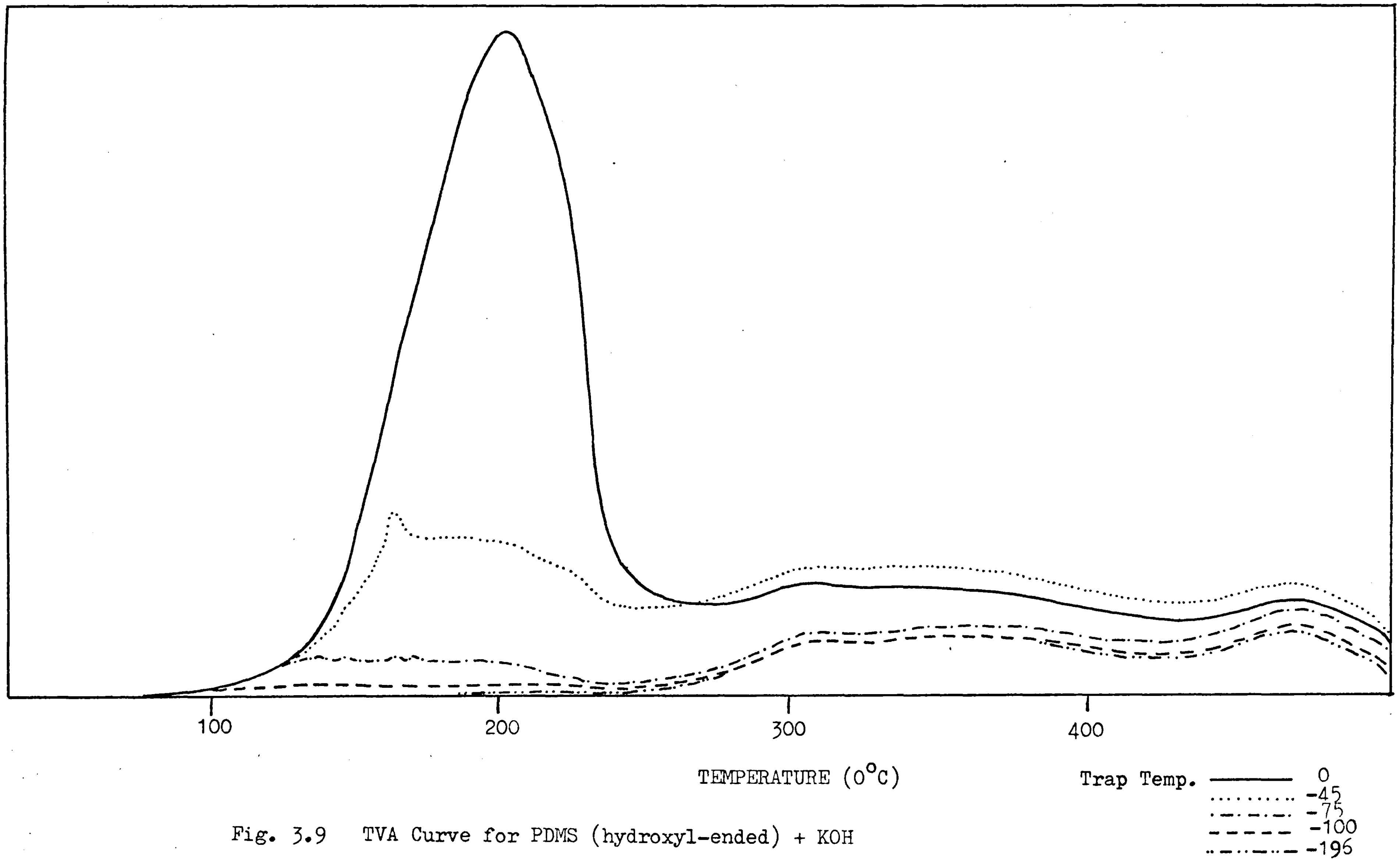


Fig. 3.9 TVA Curve for PDMS (hydroxyl-ended) + KOH

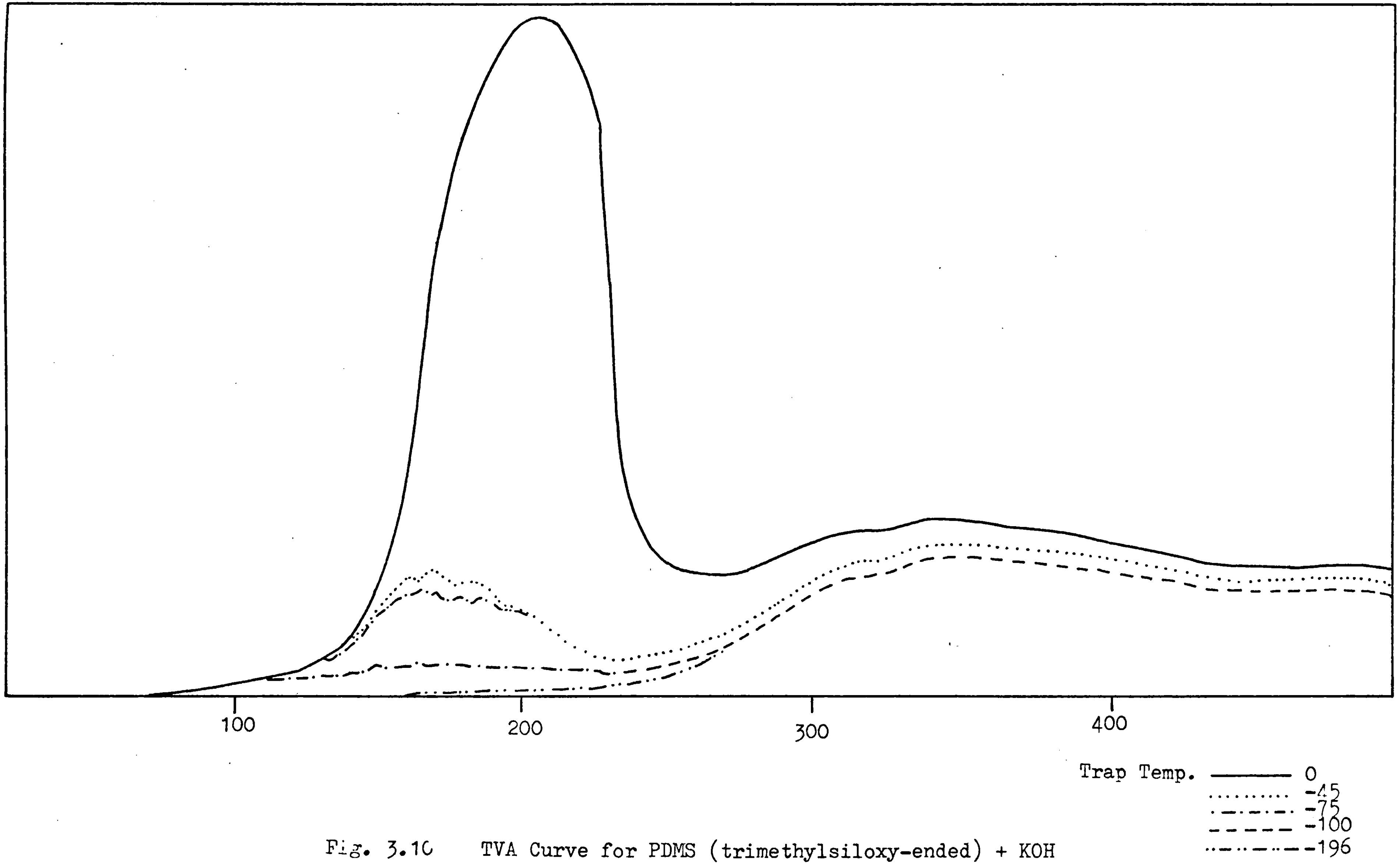


Fig. 3.10 TVA Curve for PDMS (trimethylsiloxy-ended) + KOH

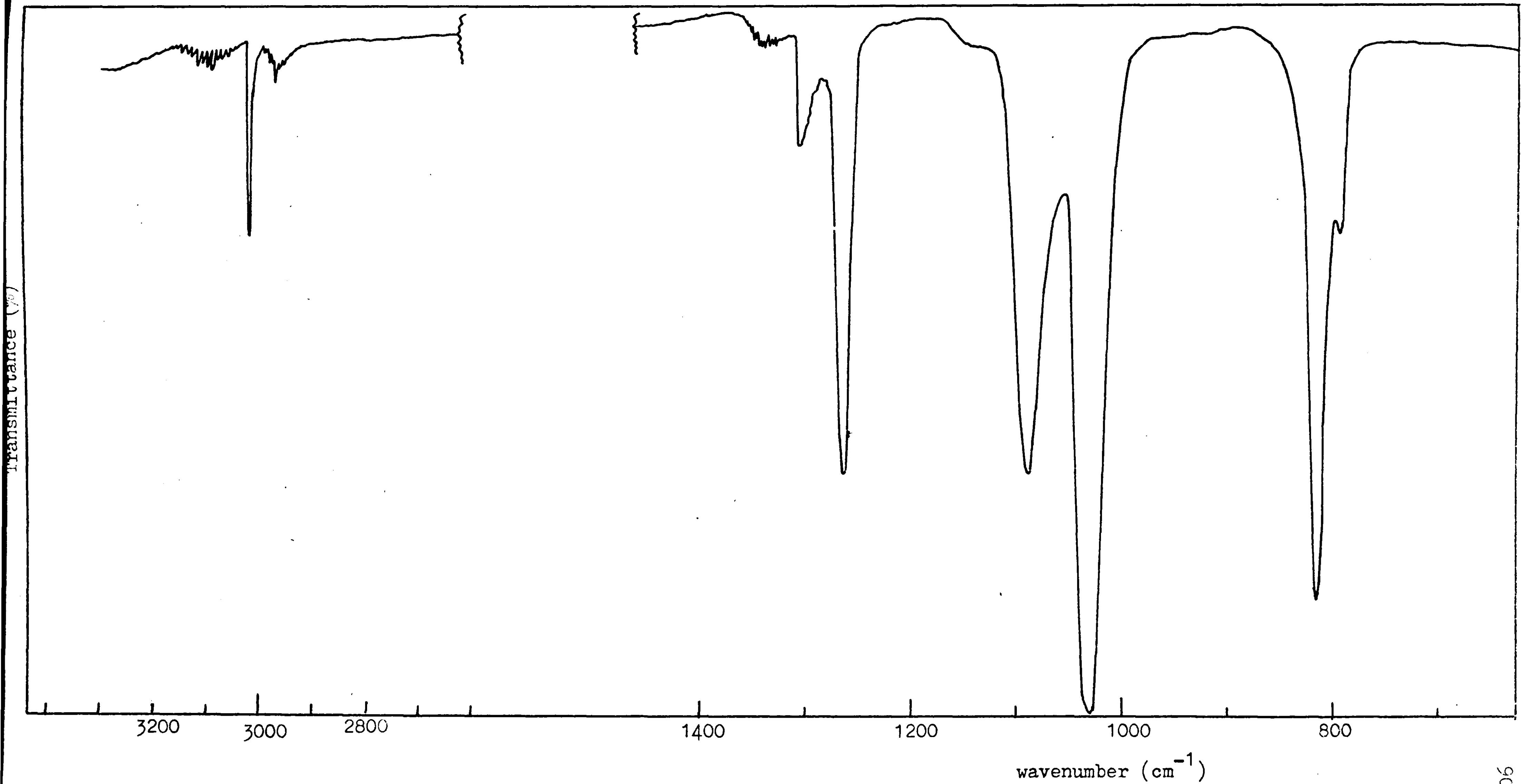


Fig. 3.11 IR of gaseous products from PDMS +KOH 250°C, 50min.

polymer F the distribution is not markedly changed from that for pure PDMS samples.

3.6 TGA

There is a problem associated with reproducibility in the degradation of hydroxyl-ended PDMS samples, a feature first observed by Andrianov et. el. and for which no suitable explanation has been given. Nevertheless, it is possible to observe trends.

The thermograms of polymers A, B, D, and F are given in Fig. 3.12. There is a trend towards higher stability with increasing molecular weight. It is not immediately obvious whether this is a diffusion effect due to the varying sample viscosities, or a genuine indication of the involvement of chain ends in the degradation of hydroxyl-ended species. Polymer H (end-blocked) is more stable than the hydroxyl-ended species (Fig. 3.14). Polymer G shows a lower threshold of degradation than expected (Fig. 3.15). In the light of later work it seems likely that the attempt to end-block this polymer has been unsuccessful.

Two samples, polymer C (141,000) and polymer E (269,000) do not fit the observed trend. Since trace contaminants can have profound effects on the thermal stability of PDMS it may be significant that these samples are both less stable than predicted on the basis of molecular weight. Together with a sample of polymer D (183,000) which unaccountably shows reduced stability from the main sample, polymers C and E show a similar but displaced trend to the one described above (Fig. 3.13).

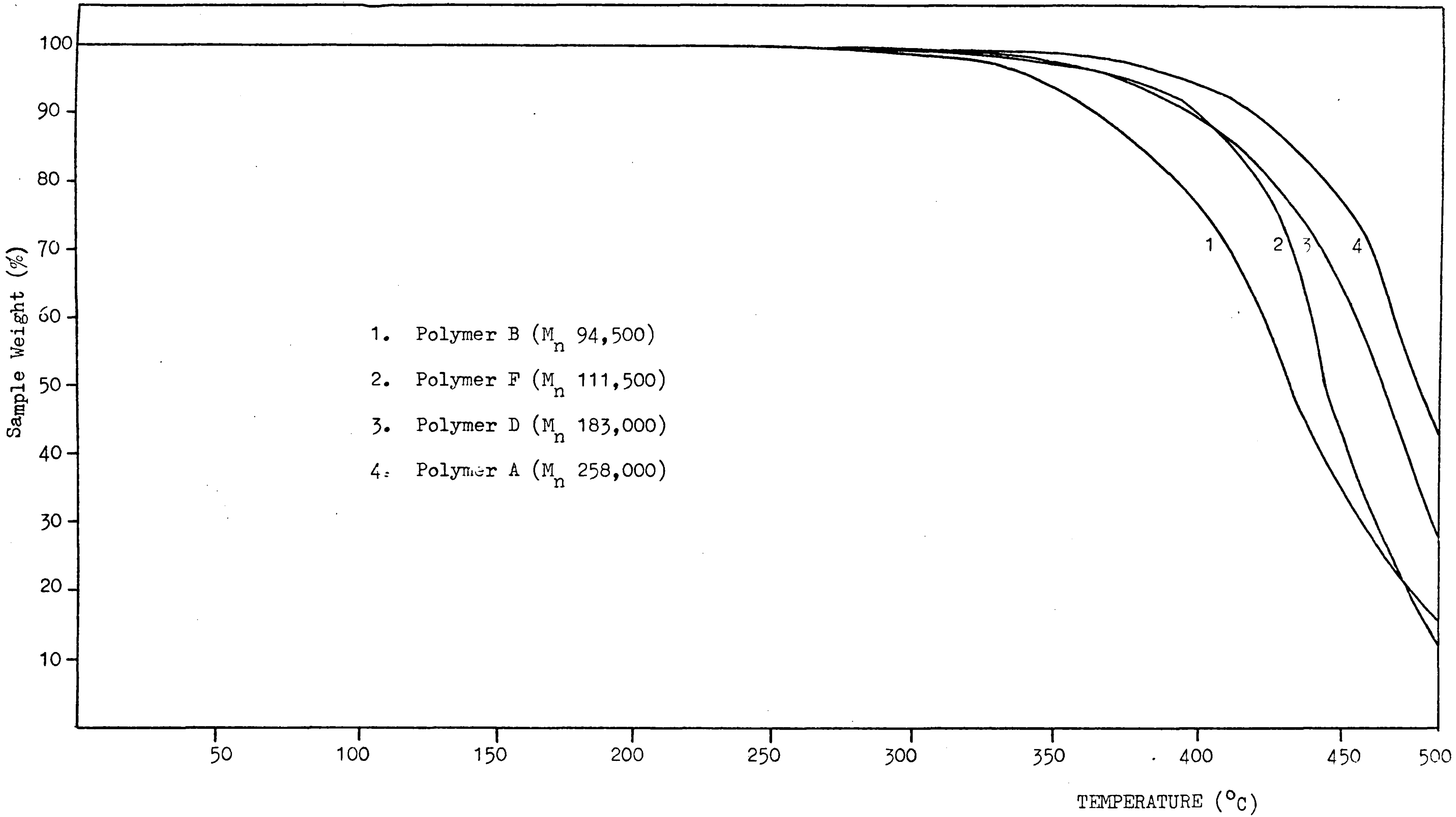


Fig. 3.12 TGA Curves for hydroxyl-ended PDMS

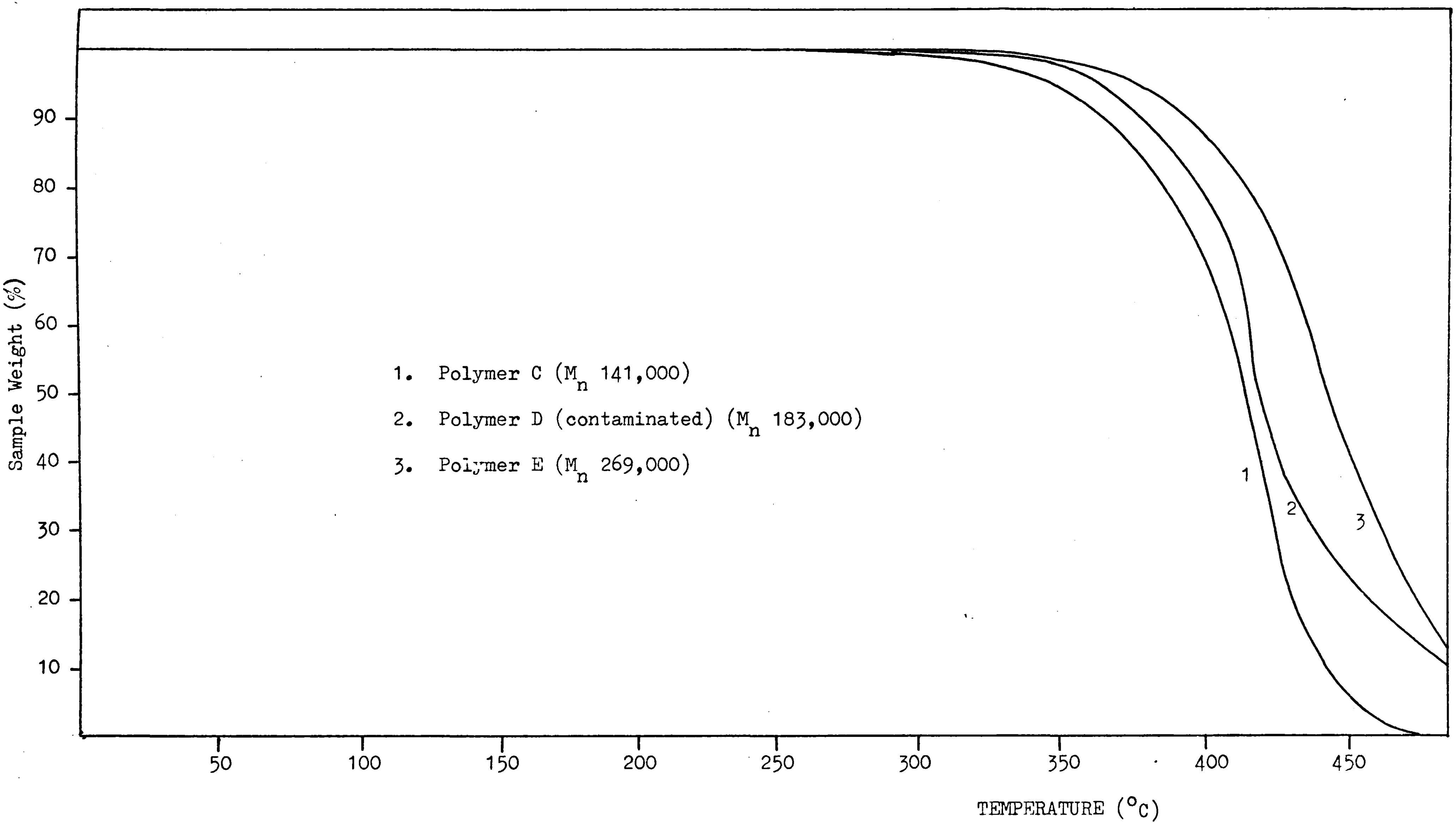


Fig. 3.13 TGA Curves for hydroxyl-ended PDMS

Dynamic N_2 atmosphere, heating rate 10°C/min.

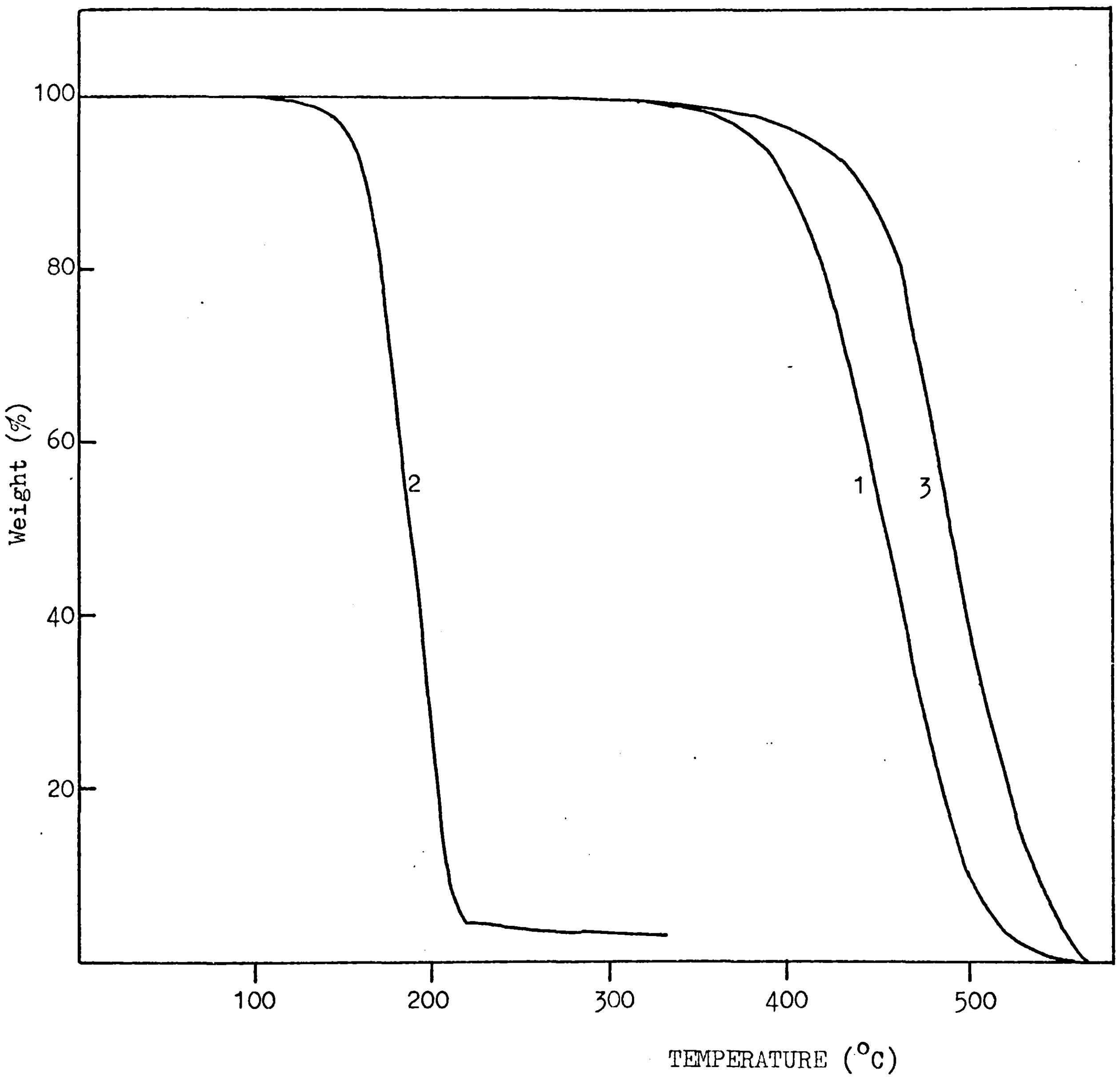


Fig. 3.14 TGA Curves for Polymer F

Dynamic N_2 atmosphere, heating rate 10^{o}C/min.

1. pure polymer F
2. polymer F + KOH
3. trimethylsiloxy-ended polymer F (polymer H)

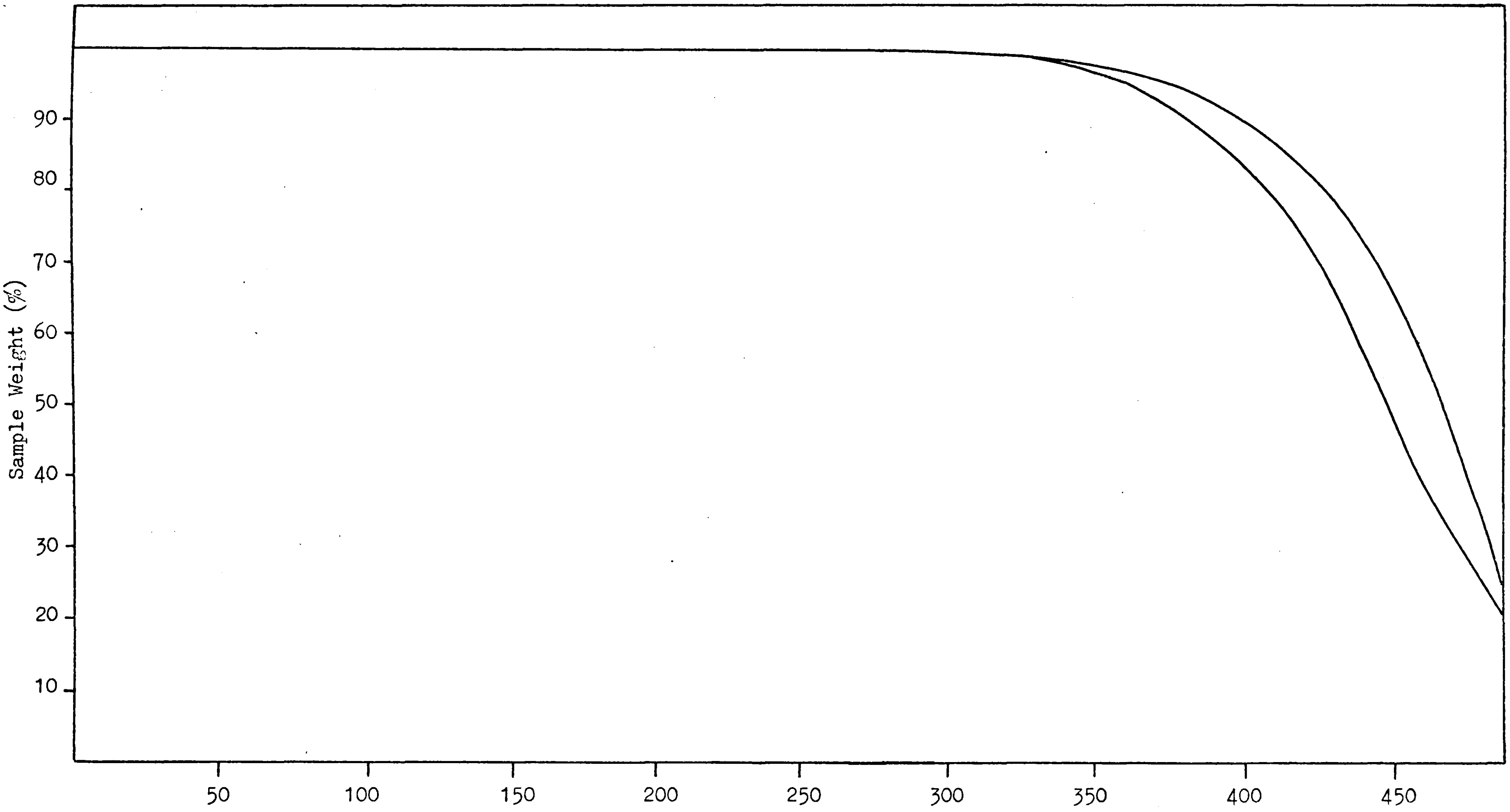


Fig. 3.15 TGA Curves for 1. Polymer D
2. Polymer G (attempted trimethylsiloxy-ended polymer D)

The degradation behaviour of a sample of polymer F with 5wt% KOH is included in Fig. 3.14. The two salient features of this trace are the low threshold of degradation and the fact that the weight loss of the polymer is virtually complete.

3.7 MOLECULAR WEIGHT CHANGES DURING DEGRADATION

Although the literature contains reference to the fact that the molecular weight of PDMS samples having hydroxyl end-groups increases on heating (Ref. 51), this reaction has received very little attention.

The changes in the molecular weight of polymer F on heating isothermally in the sealed tube (see Chapter 2) have been measured using membrane osmometry. Data for seven temperatures, 145°C, 160°C, 200°C, 250°C, 300°C, 335°C and 385°C are listed in Tables 3.2-8 and presented graphically in Figure 3.16.

It can be seen that heating the polymer for prolonged periods at temperatures up to 160°C has no effect on the molecular weight of the hydroxyl-ended species. At 200°C there is a rather ill defined increase after a considerable period of time. This temperature thus represents the threshold for this reaction. At 250°C the molecular weight appears to roughly double in about 42 hrs. and then remain constant. At 300°C the molecular weight reaches a maximum after about 20 hrs. which is followed by a small decrease levelling out at around M_n = 175,000. At 335 and 385°C similar but more pronounced trends occur.

The/

TABLE 3.2

Molecular Weight Changes in Poly(dimethylsiloxane) heated at 145°C

Time (hr.)	Mn
0	111,500
1	111,000
1.25	119,000
2.0	151,000
2.5	106,000
4.0	115,000
6.0	112,000
9.0	121,000
12.0	113,000
15.5	102,000
19.5	81,300
21.0	89,400
24.0	89,700

TABLE 3.3

Molecular Weight Changes in Poly(dimethylsiloxane) heated at 160°C

Time (hr.)	Mn
0	111,500
1	112,000 101,000
2	103,000
3	98,000 94,500
4	100,000
6	97,200
7	95,500
8	111,000
9	90,600
12	113,000
14	113,000
19	91,400 95,800
23	105,000 105,000 116,000
38	101,000 103,000
48	107,000

TABLE 3.4

Molecular Weight Changes in Poly(dimethylsiloxane) heated at 200°C

Time (hr.)	Mn
0	111,500
1	116,000
2	110,000
4	115,000
12	121,000
14	114,000
18	117,000
19	129,000
24	125,000
28	143,000
34	186,000
48	234,000
72	149,000

TABLE 3.5

Molecular Weight Changes in Poly(dimethylsiloxane) heated at 250°C

Time (hr.)	Mn
0	111,500
1	117,000
2	118,000
8	142,000
19	188,000
34	246,000
44	202,000
57	239,000
66	230,000

TABLE 3.6

Molecular Weight Changes in Poly(dimethylsiloxane) heated at 300°C

Time (hr.)	Mn
0	111,500
1	141,000
3	177,000
6	188,000
12	202,000
20	214,000
30	196,000
42	174,000
54	170,000
67	170,000
102	180,000

TABLE 3.7

Molecular Weight Changes in Poly(dimethylsiloxane) heated at 335°C

Time (hr.)	$\bar{M}n$
0	111,500
1	192,000
2	226,000
5	226,000
15	222,000
40	149,000
45	153,000

TABLE 3.8

Molecular Weight Changes in Poly(dimethylsiloxane) heated at 385°C

Time (hr.)	Mn
0	111,500
0.5	191,000
1	204,000
1.5	206,000
4	261,000
6	206,000
8	212,000
10.5	173,000
14.25	144,000
24	143,000

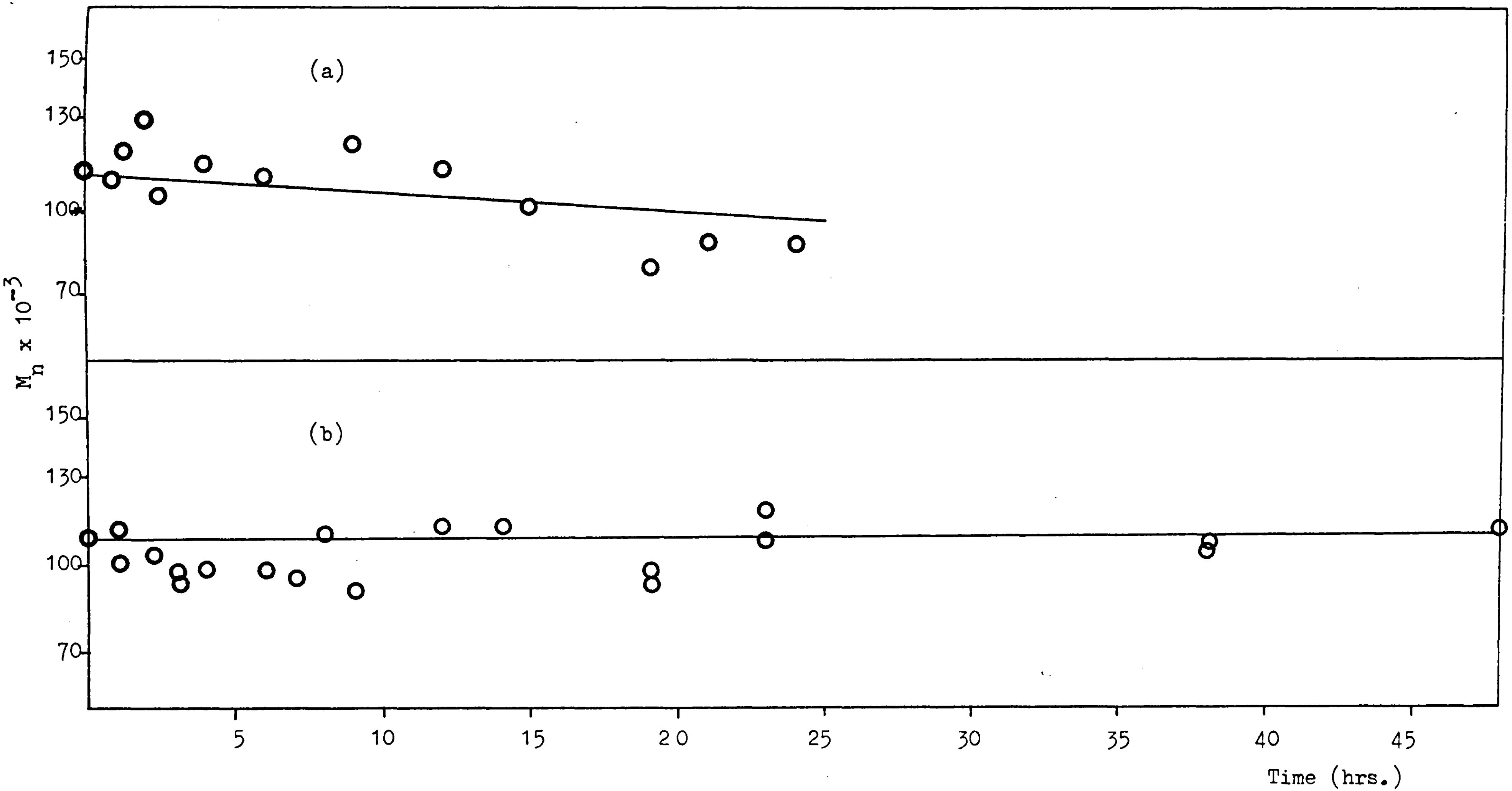


Fig. 3.16 Molecular weight changes in poly(dimethylsiloxane)

(a) 145°C

(b) 160°C

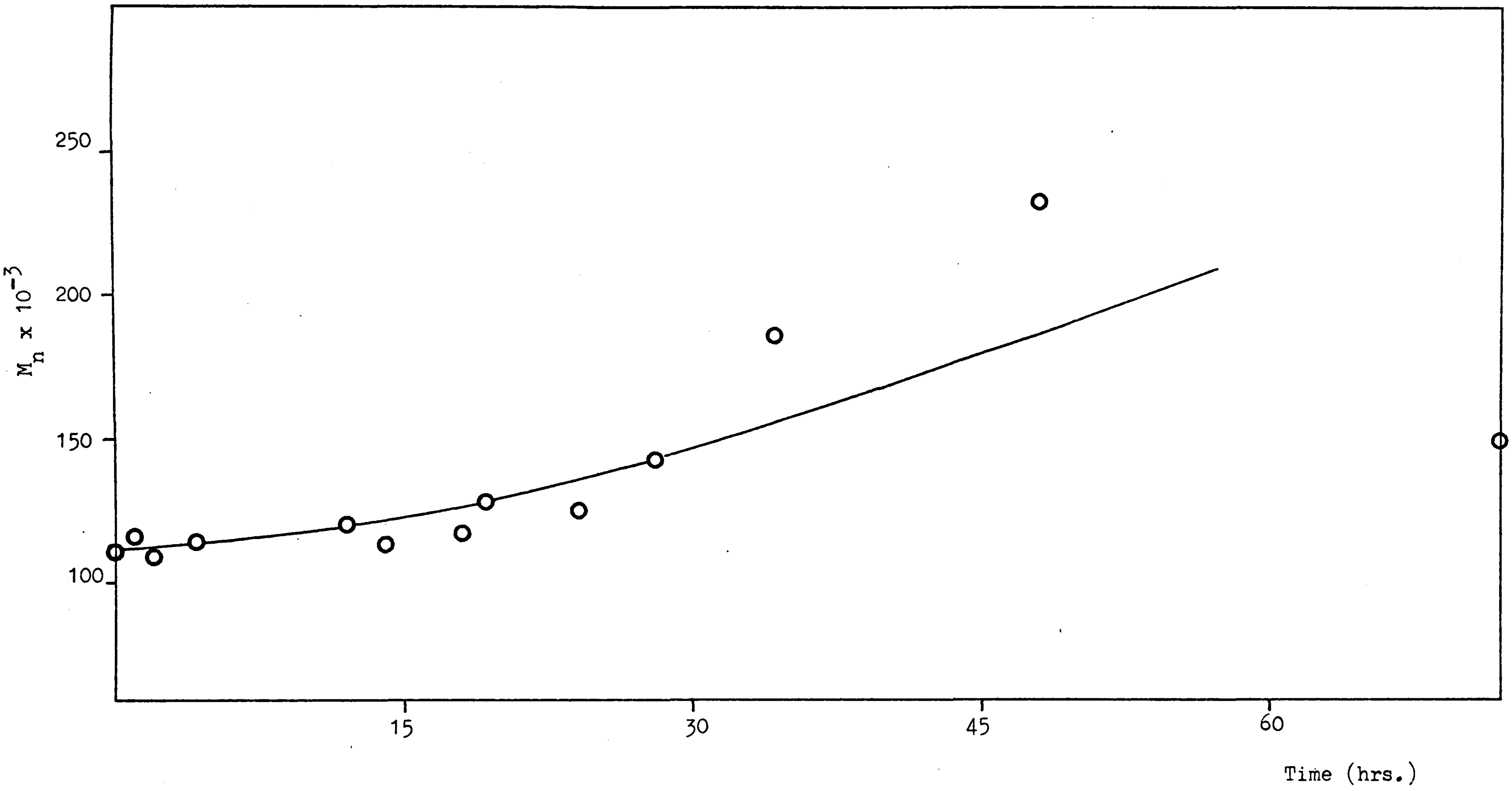


Fig. 3.16(c) 200°C

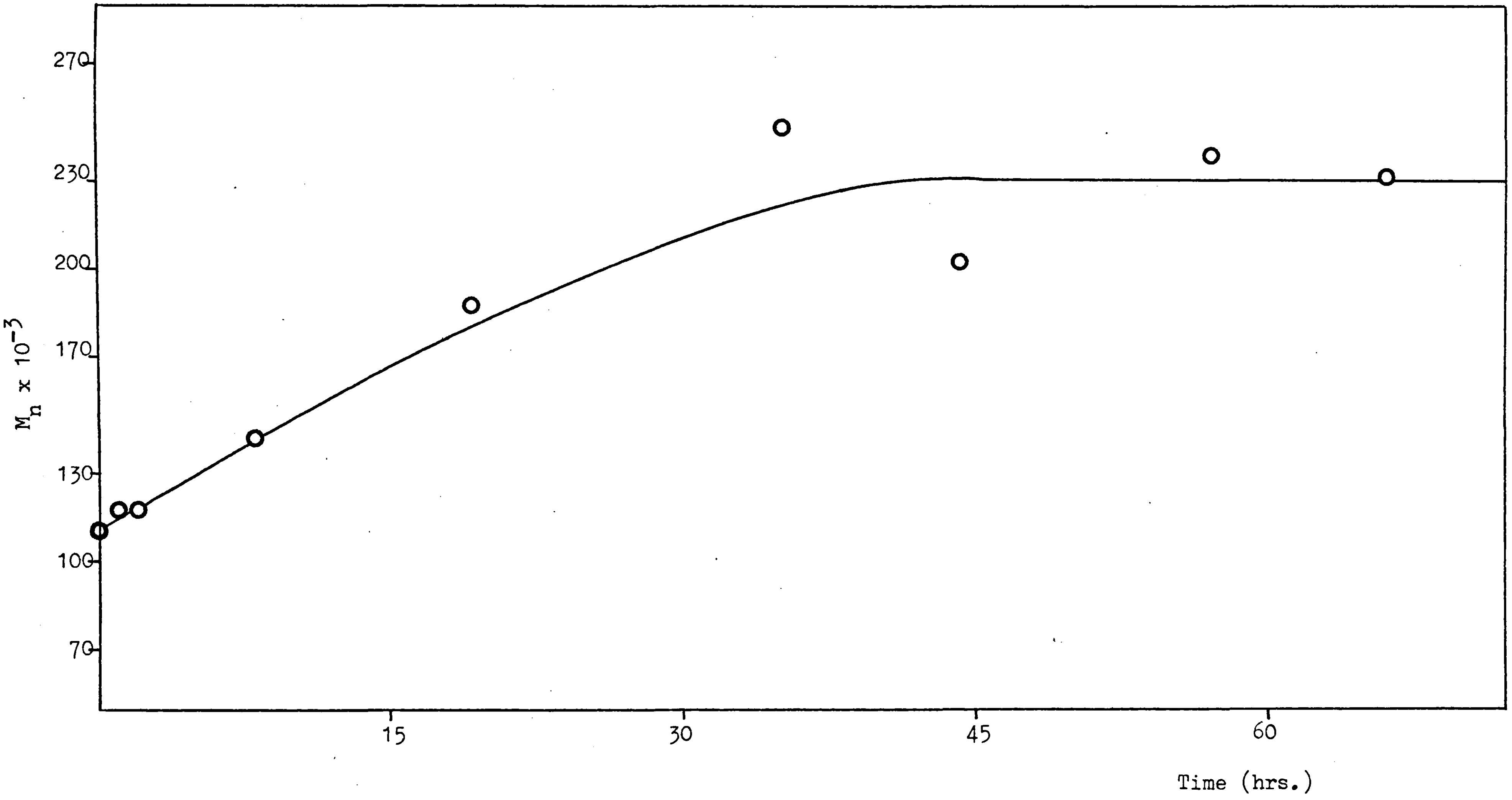


Fig. 3.16(d) 250°C

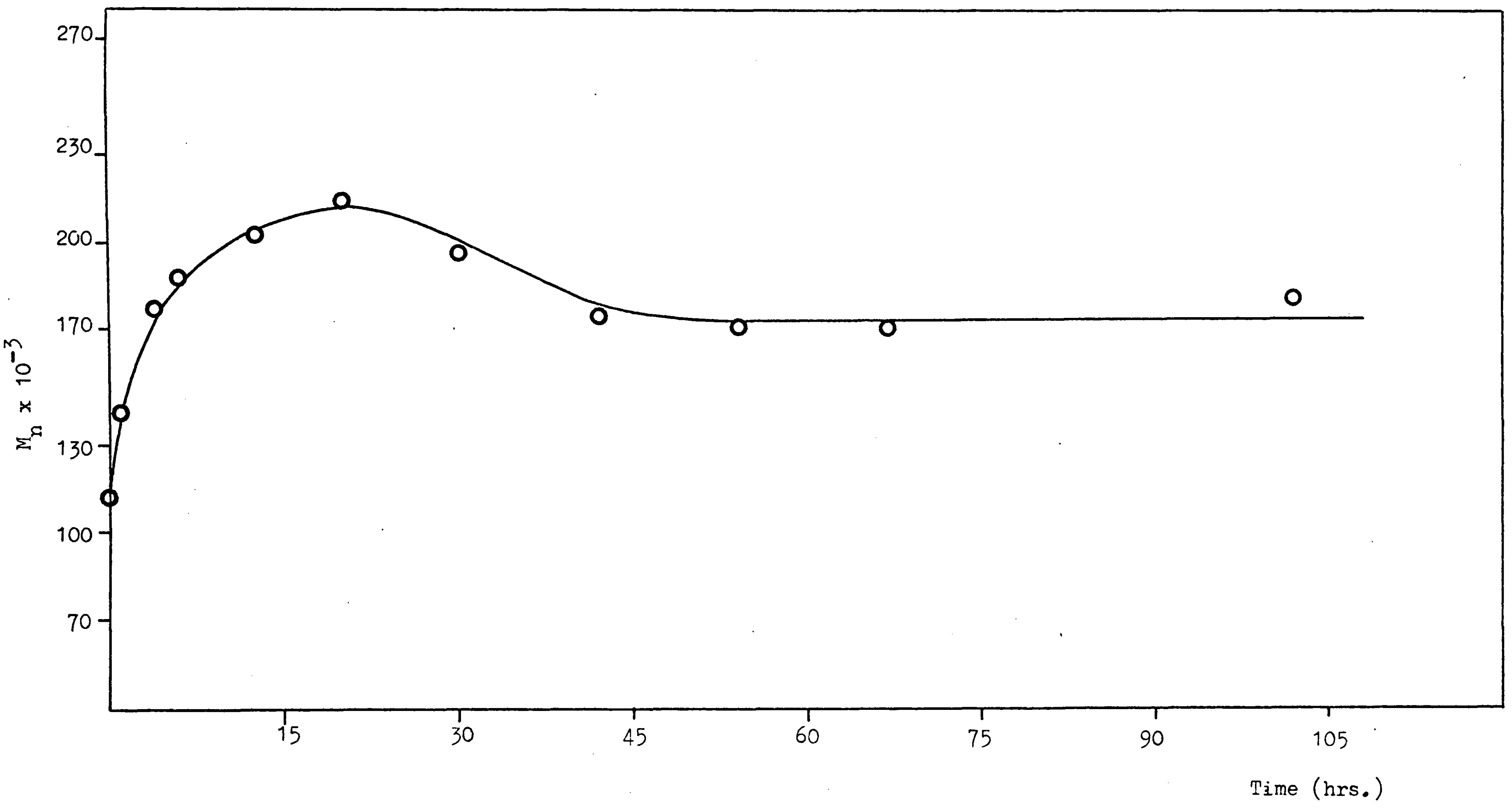


Fig. 3.16(e) 300°C

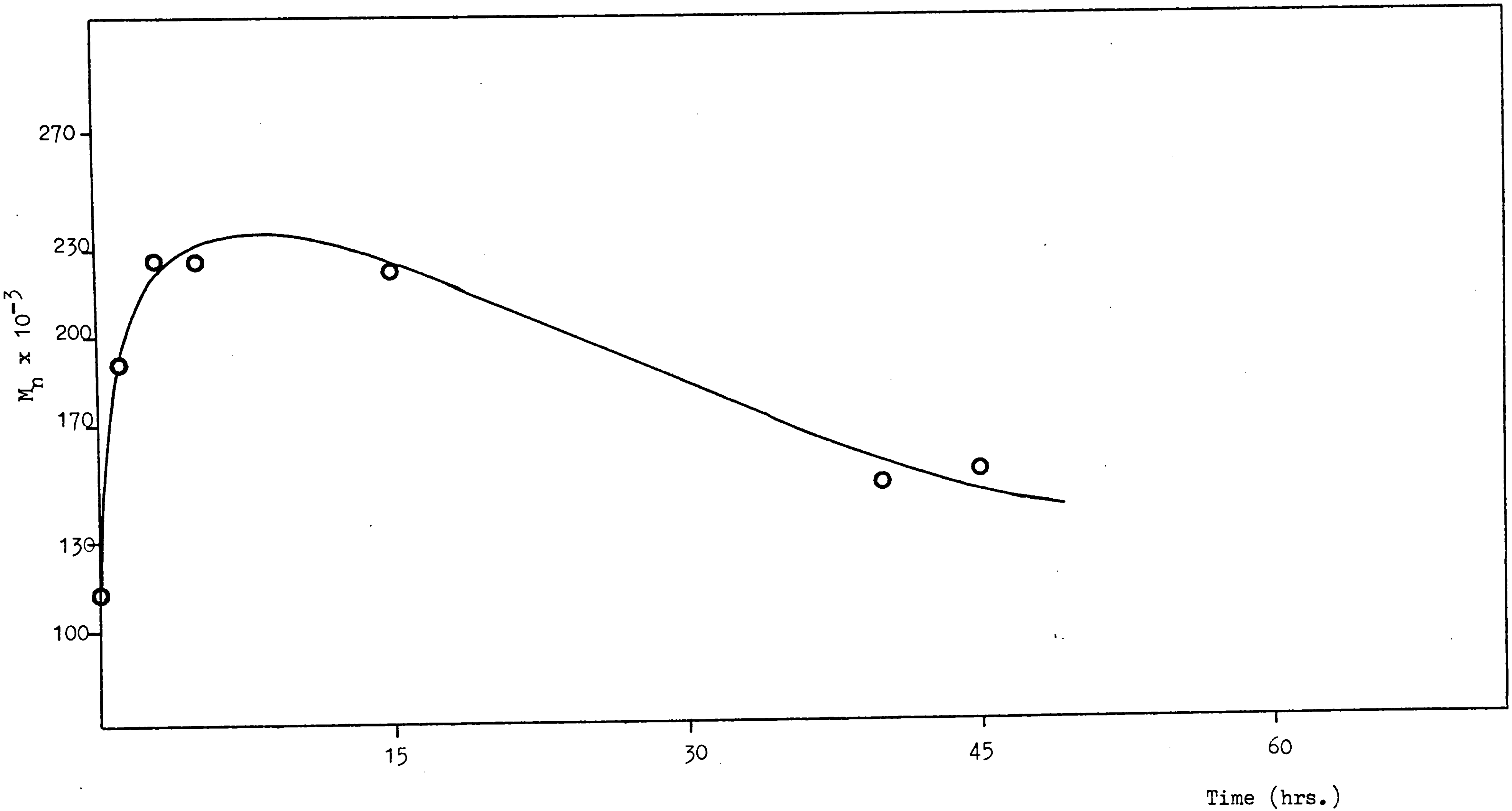


Fig. 3.16(f) 33 °C

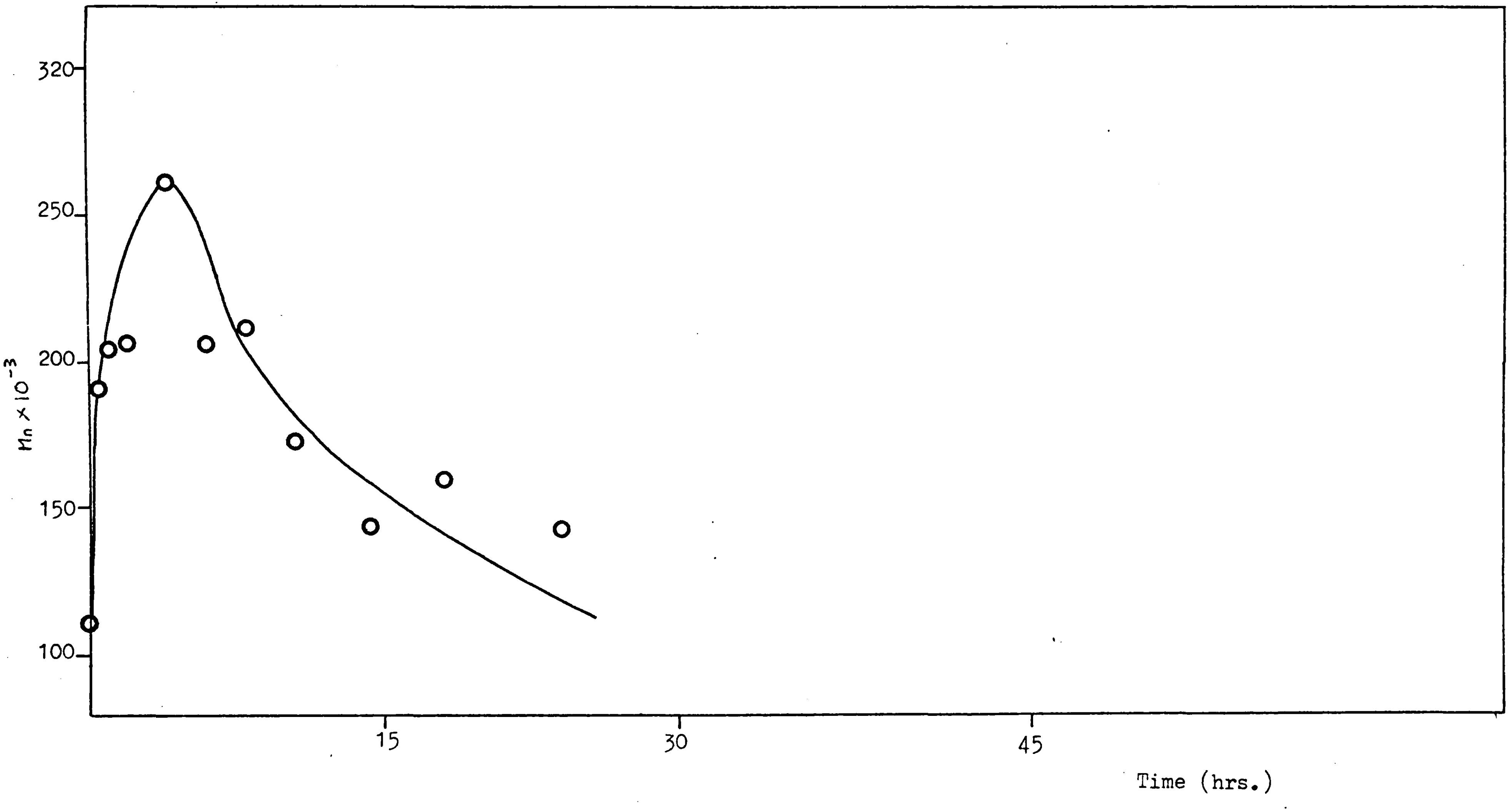


Fig. 3.16(g) 385°C

The weight loss of samples under the sealed tube conditions are illustrated in Fig. 3.17. The rate of weight loss observed in the continuously pumped TGA system is some 30 times greater than that observed using the sealed tube at the same temperature. This is attributed to the thermodynamic control of the reaction kinetics and will be discussed later. In both techniques the rate of weight loss is essentially linear for the major part of the degradation.

3.8 ANALYSIS OF DEGRADATION PRODUCTS

(a) Qualitative Analysis

It has been shown earlier that the complete weight loss of catalyst free PDMS can be accounted for by the presence of low molecular weight siloxane species, with the cyclic trimer predominating. Analysis of the remaining siloxanes has been made using GLC and GCMS.

Up to 18 peaks have been observed using programmed GLC. The retention times suggest that these represent a homologous series and it is on this basis that most workers have made their assignments. Assignments of these peaks have been confirmed using GCMS.

(i) GLC

Details of the GLC analyses using DC 560 on Gas Chrom Q column running at 32°C and at 100°C are presented in Figs. 3.18 and 19, and summarised in Table 3.9. From a comparison of retention times of possible actual products of degradation it is clear that trimer, tetramer, pentamer and hexamer are positively identified. A typical chromatogram of the total products of degradation obtained using a 1% SE 30 column, programmed at 3°/min. from ambient, is illustrated in Fig. 3.20.

(ii)/

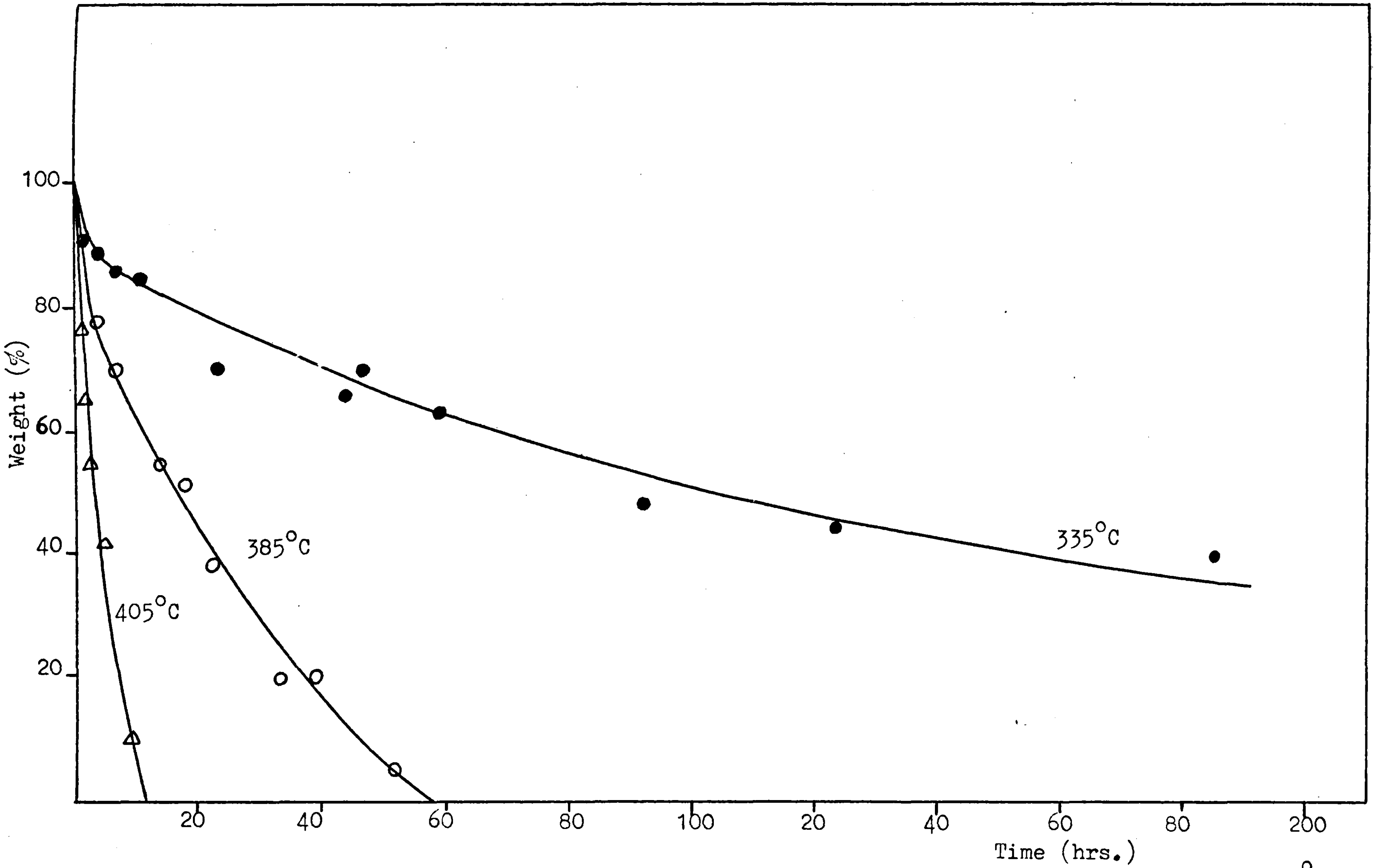


Fig. 3.17 Weight of poly(dimethylsiloxane) (polymer F) as a function of time at various temperatures (sealed tube method).

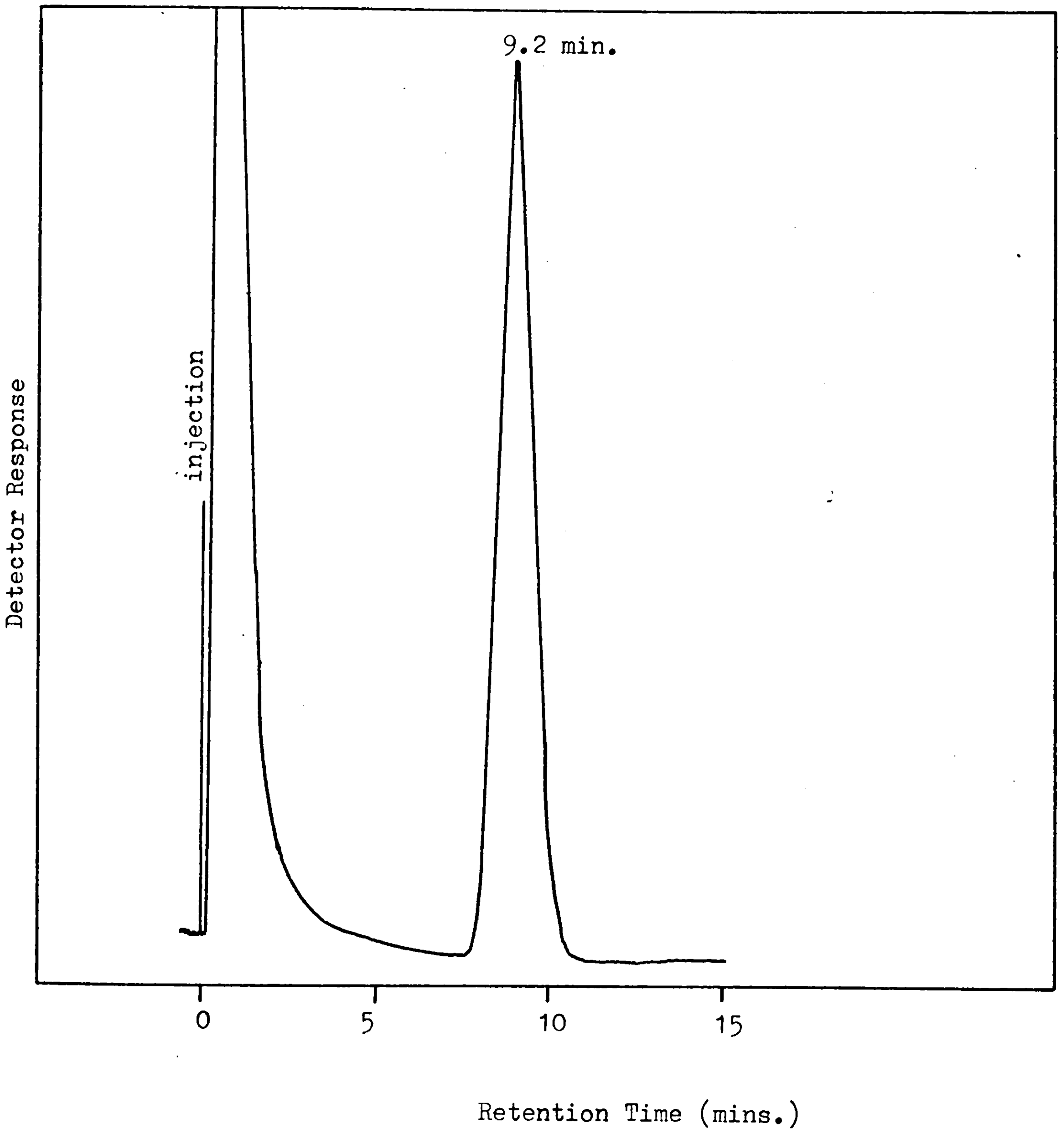


Fig. 3.18 GLC trace of hexamethylcyclotrisiloxane (D_3)

Column DC560 on Gas Chrom Q

Temp. 32°C.

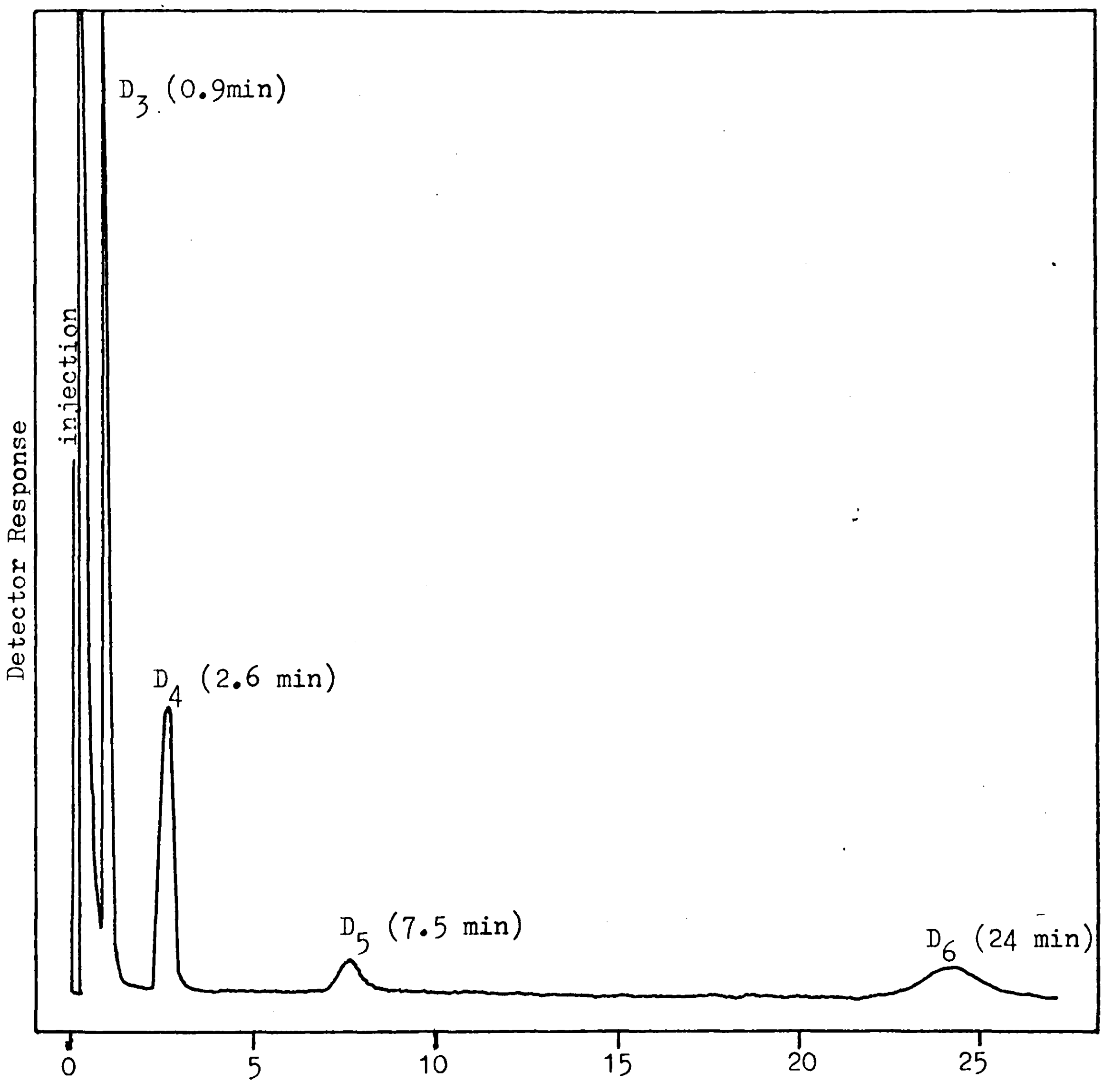


Fig.3.19 GLC trace of hexamethylcyclotrisiloxane (D_3)
octamethylcyclotetrisiloxane (D_4)
decamethylcyclopentasiloxane (D_5)

Column DC560 on Gas Chrom Q

Temp. 100°C.

TABLE 3.9

Comparison of GLC Data for Possible and Actual Products of Thermal Degradation of Poly(dimethylsiloxane)

Sample	Temperature °C	Retention Time, Min
cyclic trimer	32	9.2
products	32	9.0

N.B. Higher Cyclics are retained on the column at 32°C

(cyclic trimer	100	0.9
(cyclic tetramer	100	2.6
(cyclic tetramer	100	2.6
(cyclic pentamer	100	7.45
(cyclic hexamer	100	24.0
products	100	0.9
		2.6
		7.59
products	100	0.9
		2.5
		7.5
		24.0

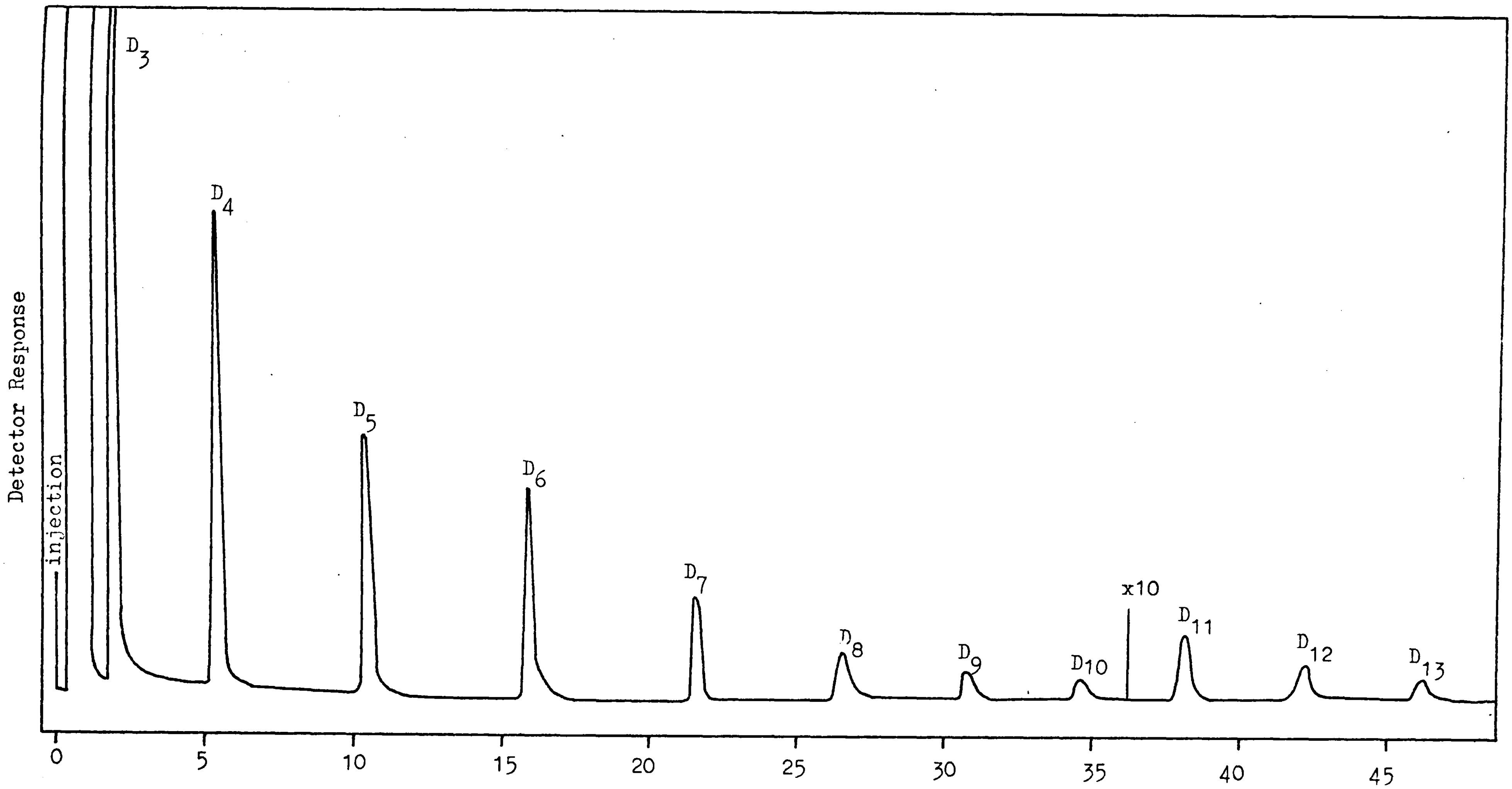


Fig. 3.20 Typical GLC trace of products of degradation of PDMS.

Column 1% SE 30

Programme 5°C/min., ambient -250°C.

(ii) GCMS

Complete mass spectra have been obtained for the D_3 - D_{11} cyclics, which represent more than 99% of the degradation products. The scope of the instrument has allowed fragments of $^m/e \leqslant 840$ to be analysed. Thus lower fragments have also been observed for higher cyclics D_{12-17}. (Fig. 3.21)

Methyl cyclosiloxanes are characterised by an $(M-15)^+$ ion (most organosilicon compounds do not exhibit a molecular ion, or at best only a very weak one) but other features vary with ring size. In both D_3 and D_4 the $(M-15)^+$ ion is the most intense and is represented by peaks at $^m/e$ 207 and 281 respectively. In both cases the second most intense ion is the doubly changed ion corresponding to $(M-30)^{++}$. When the ring size is expanded by a dimethylsiloxy unit to D_5 this doubly charged $(M-30)^{++}$ is no longer present, the base peak is $^m/e$ 73 (elemental composition of Me_3Si), and an intense ion is observed at $^m/e$ 267 corresponding to a 103 mass unit loss. In cyclics larger than D_7 the base peaks remain at $^m/e$ 73 but the $(M-103)^+$ ion disappears or becomes very small.

Vandenheuval (Ref. 107) has proposed a trans annular mechanism to account for the spectra of D_5 and higher cyclics although he represents data for only one such higher cyclic, namely D_6. In the larger cyclics the neutral fragments are large cyclic molecules, D_3, D_4, etc. Thus for a typical higher cyclic, say D_{10}, peaks corresponding to $(M-15)^+$, $(M-15-D_3)^+$, through to $(M-15-D_9)^+$ are observed and account for the major part of the spectrum. The $(M-103)^+$ peak is present but very small.

The/

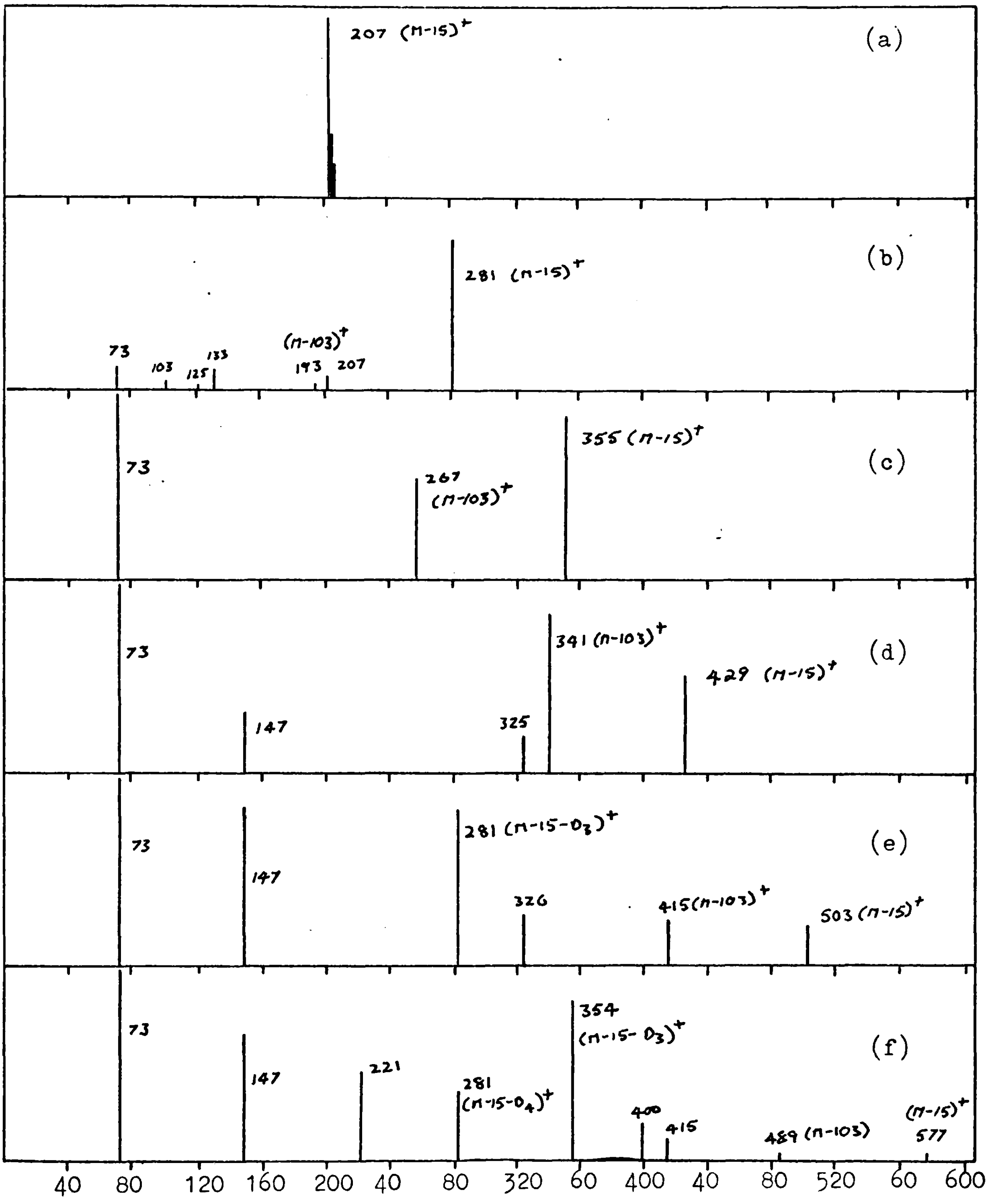


Fig. 3.21 Mass Spectra from GCMS of PDMS products with assignments.

(a) D_3

(b) D_4

(c) D_5

(d) D_6

(e) D_7

(f) D_8

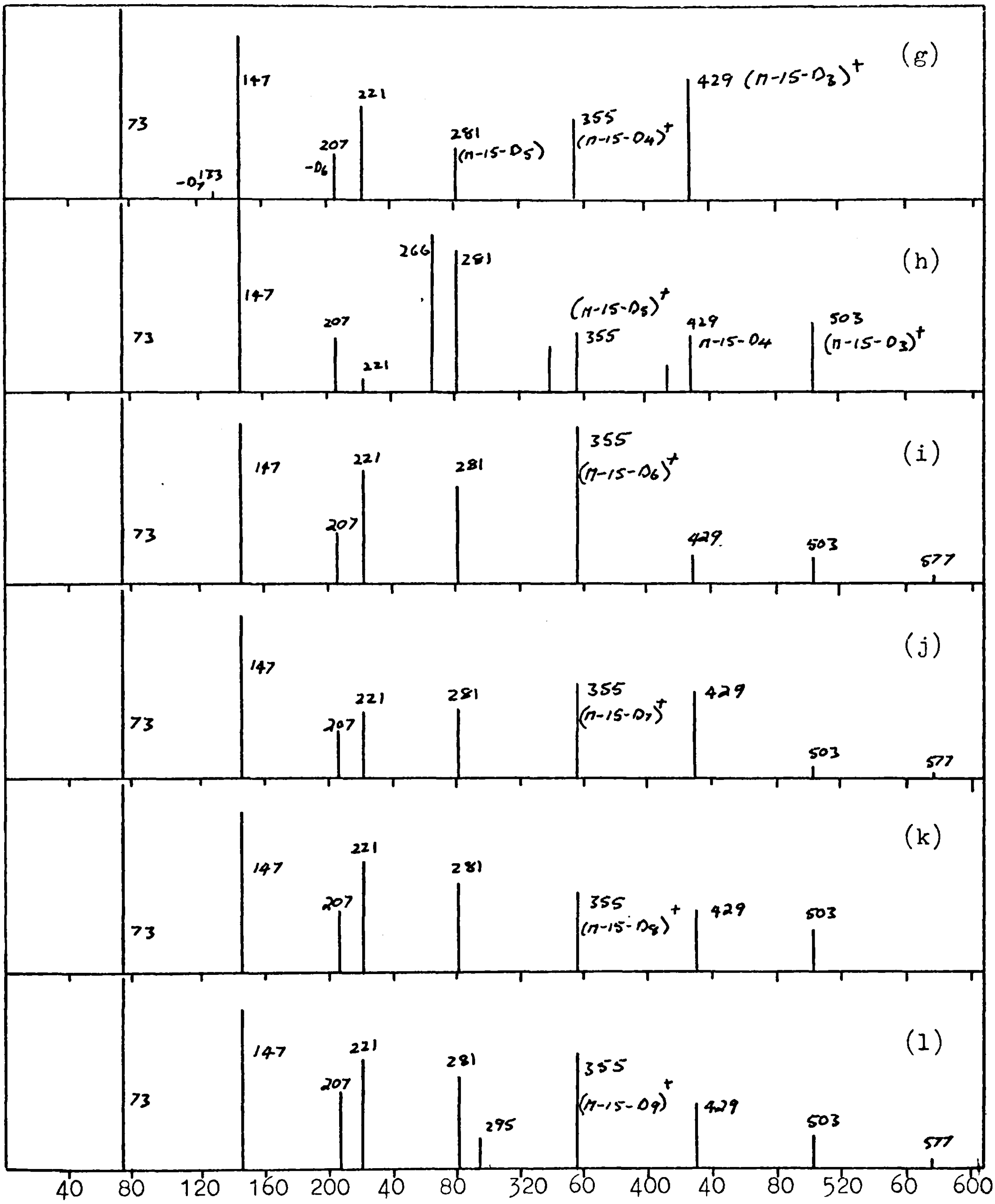


Fig. 3.21 (Cont'd.)

(g) D_9

(h) D_{10}

(i) D_{11}

(j) D_{12}

(k) D_{13}

(l) D_{14}

The instrument detector has allowed the $(M-15)^+$ fragment to be observed for cyclics D_{3-11} and the $(M-15-D_3)^+$ fragment for species up to D_{14}. It seems certain that these latter species will also exhibit an $(M-15)^+$ fragment. The lower parts of the spectra of D_{15-17} contain no salient features. It is clear that the major fragments from these species are lower cyclics.

(b) Quantitative Analysis

Quantitative analysis of the distribution of cyclics at various temperatures have been made using GLC as described in Chapter 2. The results of this work are given in Fig . 3.22 and will be discussed later.

3.9 DEGRADATION OF PDMS IN A LIMITED AMOUNT OF OXYGEN

A sample of polymer E has been degraded in a limited amount of oxygen (~100mm. Hg) at 200°C for 56 hrs. using the sealed tube technique.

Although the reaction in presence of oxygen has not been studied in detail, it is clear that oxygen accelerates production of volatile material, the polymer becomes insoluble and the difference in mechanism is reflected in infra-red spectral changes which take place in the residue.

Portions of the spectra of the original polymer and the soluble fraction after degradation, are illustrated (Fig. 3.22). New absorption appears at 9.42μ in the Si-O stretch region (9-10μ) and the relative intensities of the two maxima in this region of the spectrum of the original polymer have altered.

Infra-red/

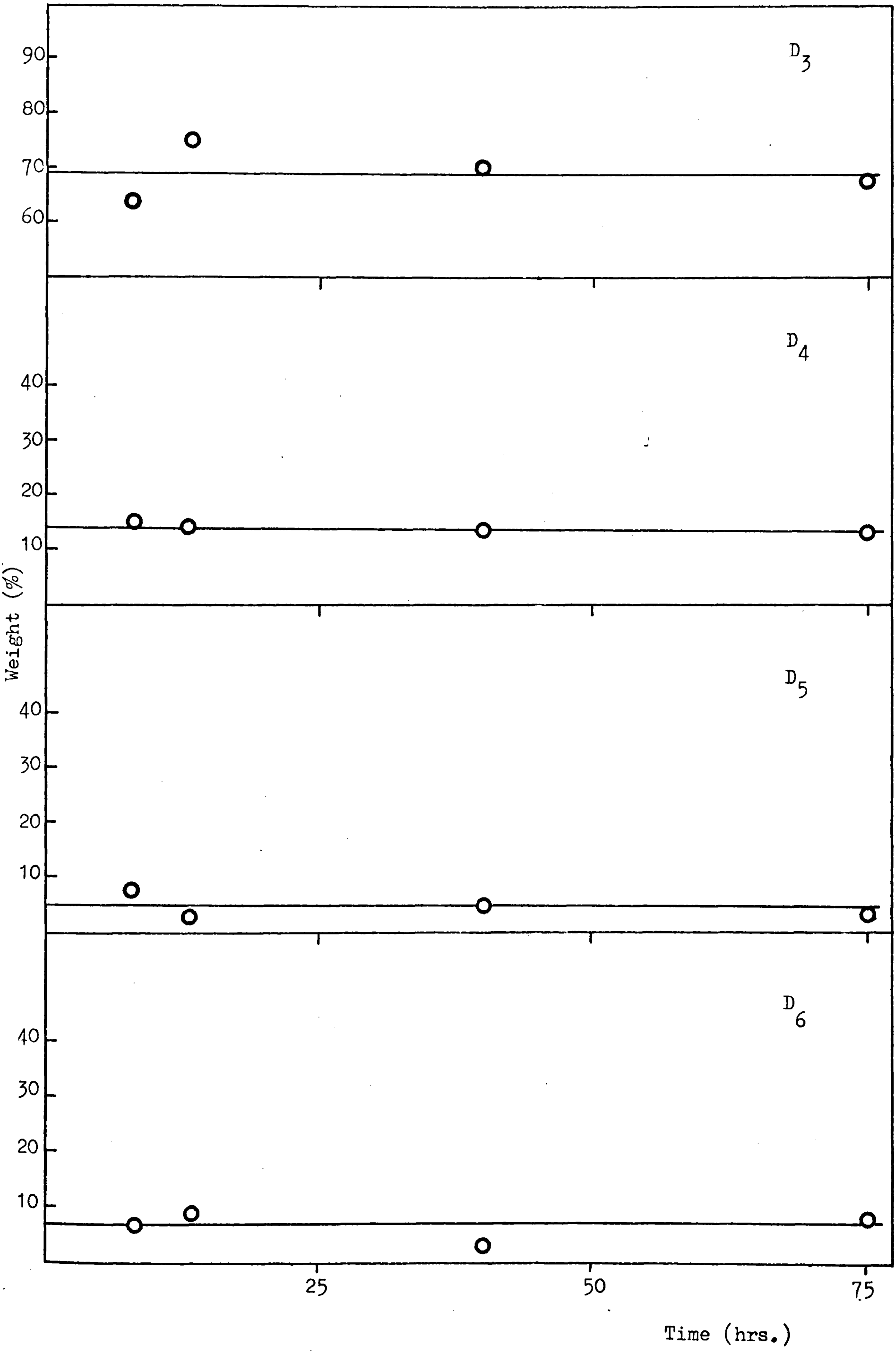


Fig. 3.22 Products of Degradation of Poly(dimethylsiloxane) at various Temperatures a) 275°C.

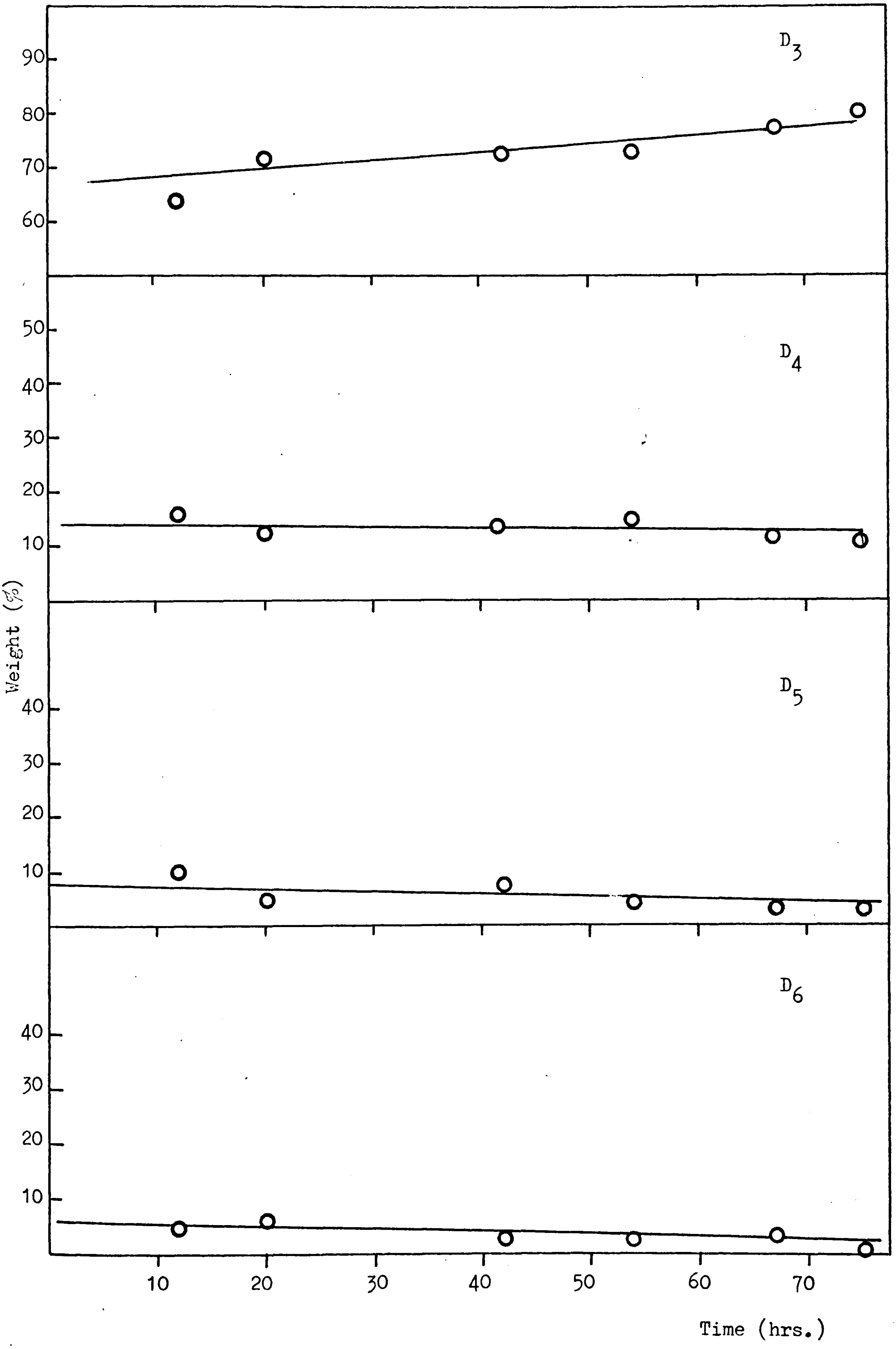


Fig.3.22 (b) 300°C

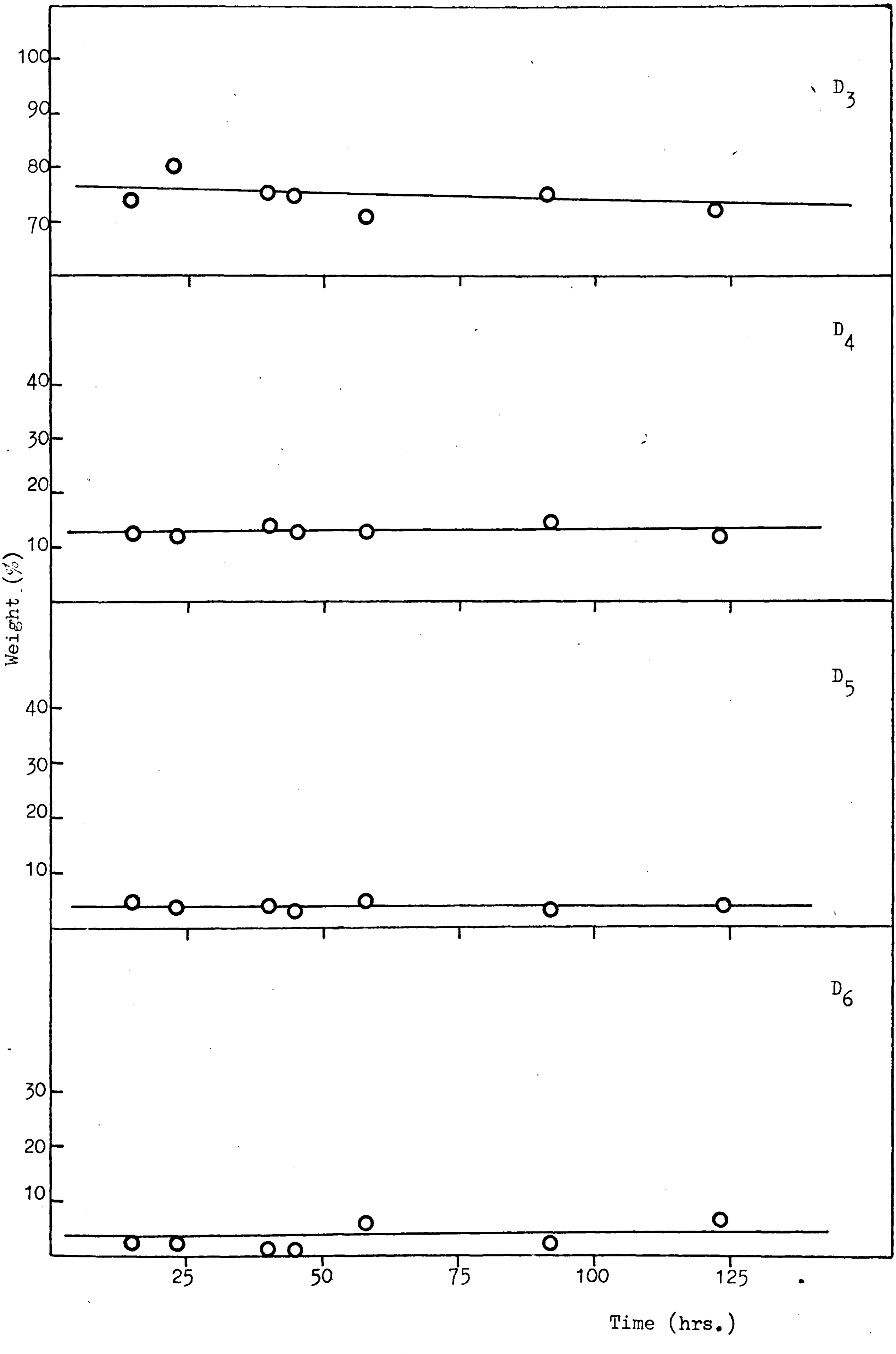


Fig. 3.22 (c) 335°C.

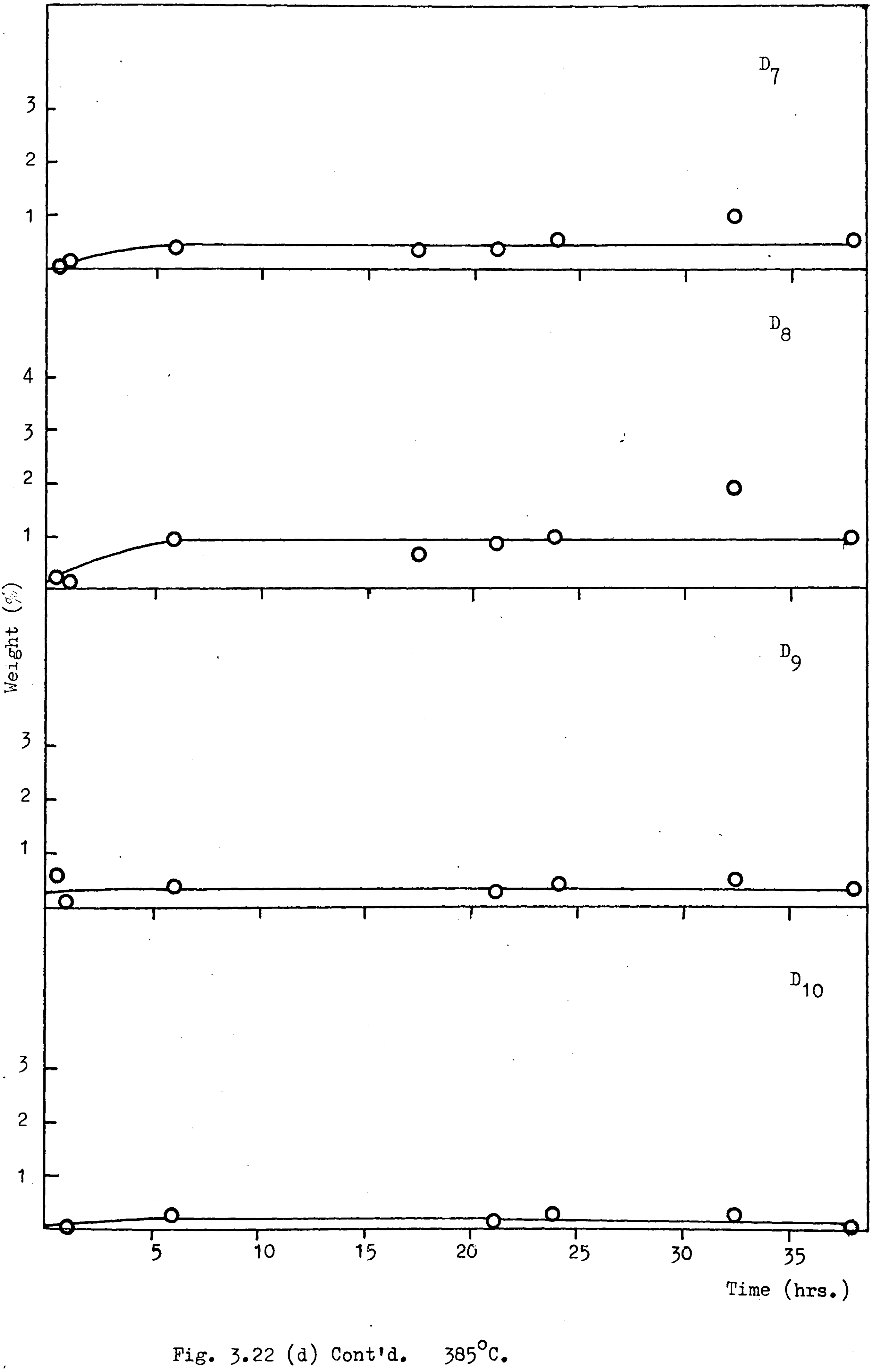


Fig. 3.22 (d) Cont'd. 385°C.

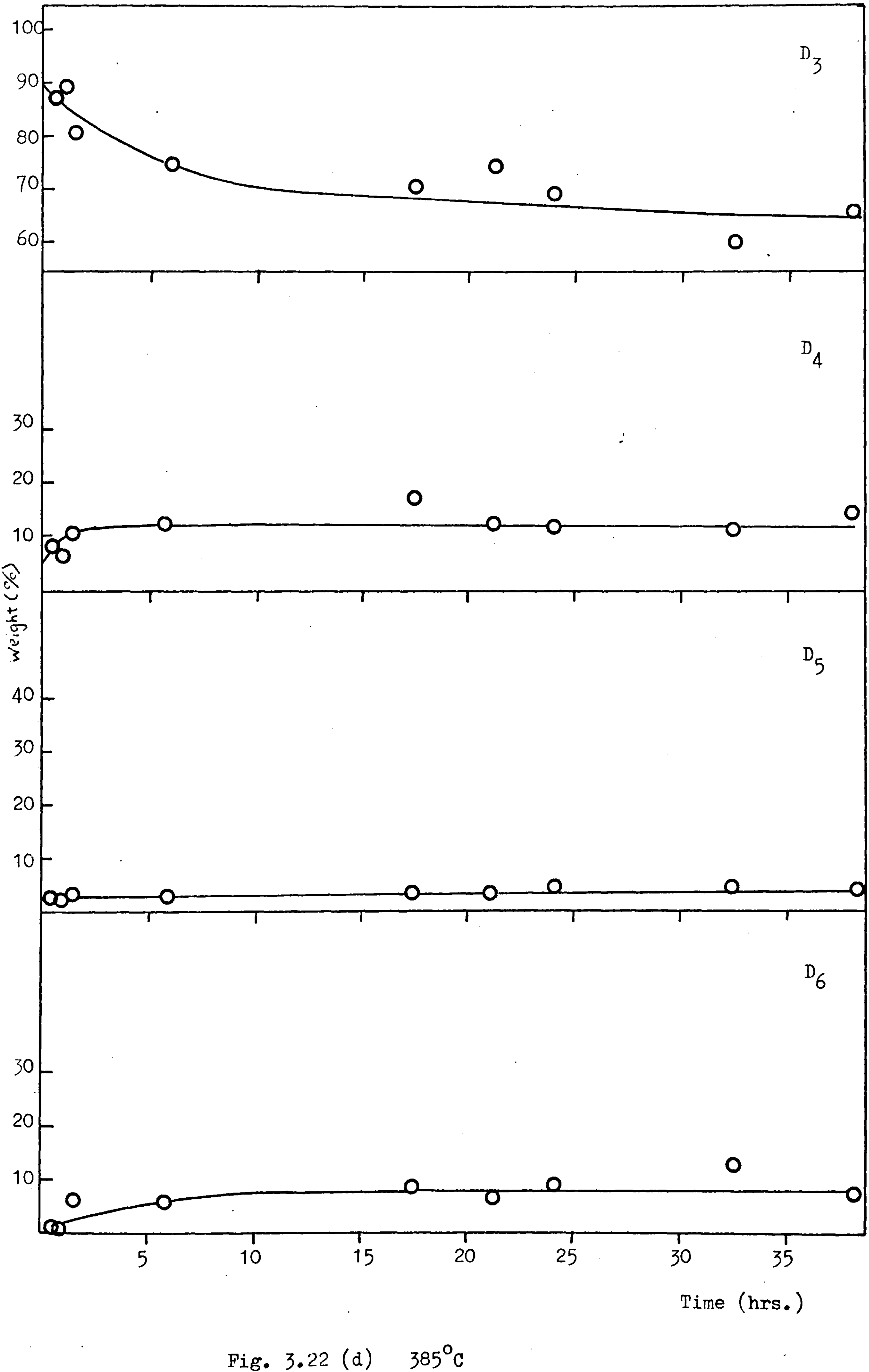


Fig. 3.22 (d) 385°C

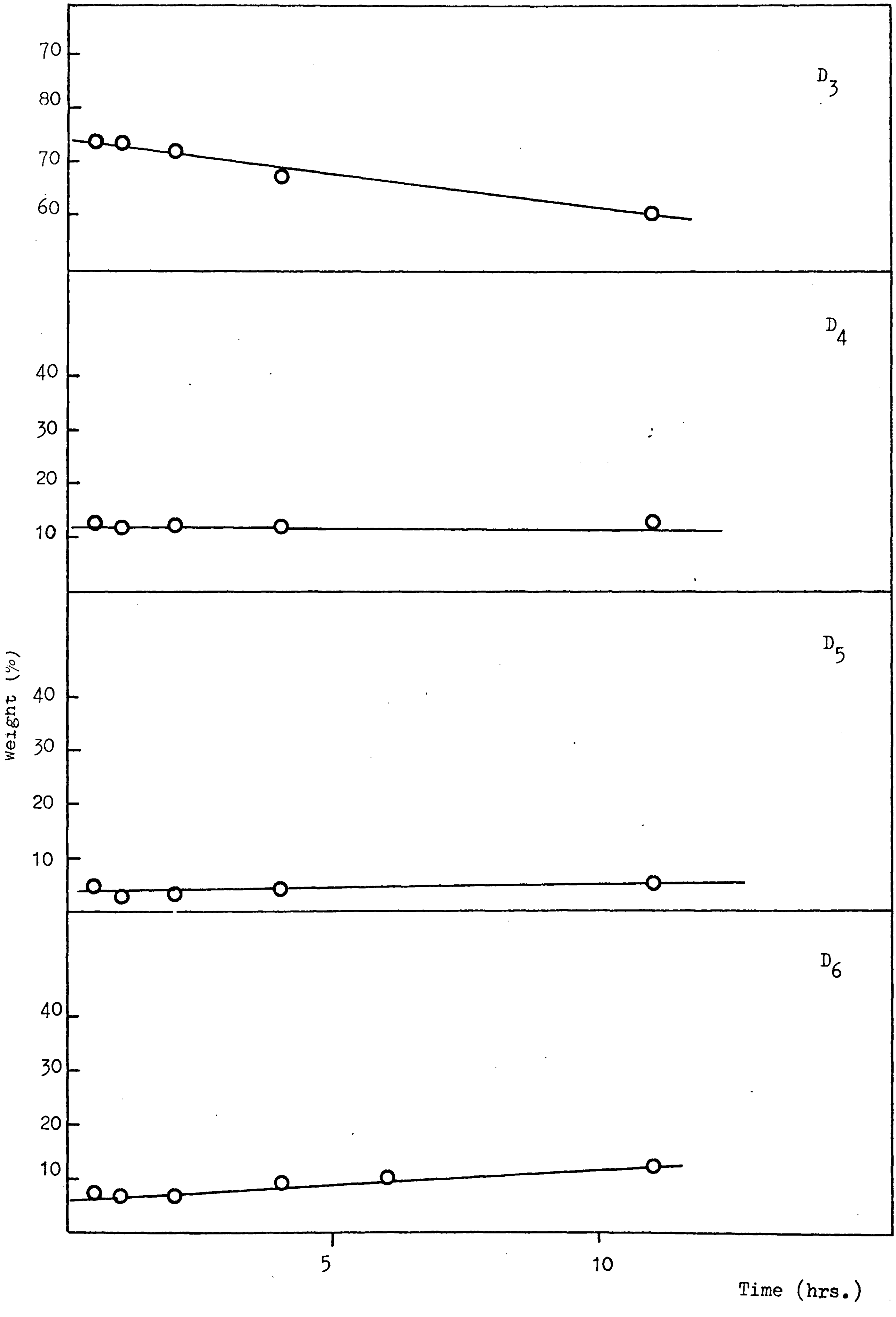


Fig. 3.22 (e) 405°C.

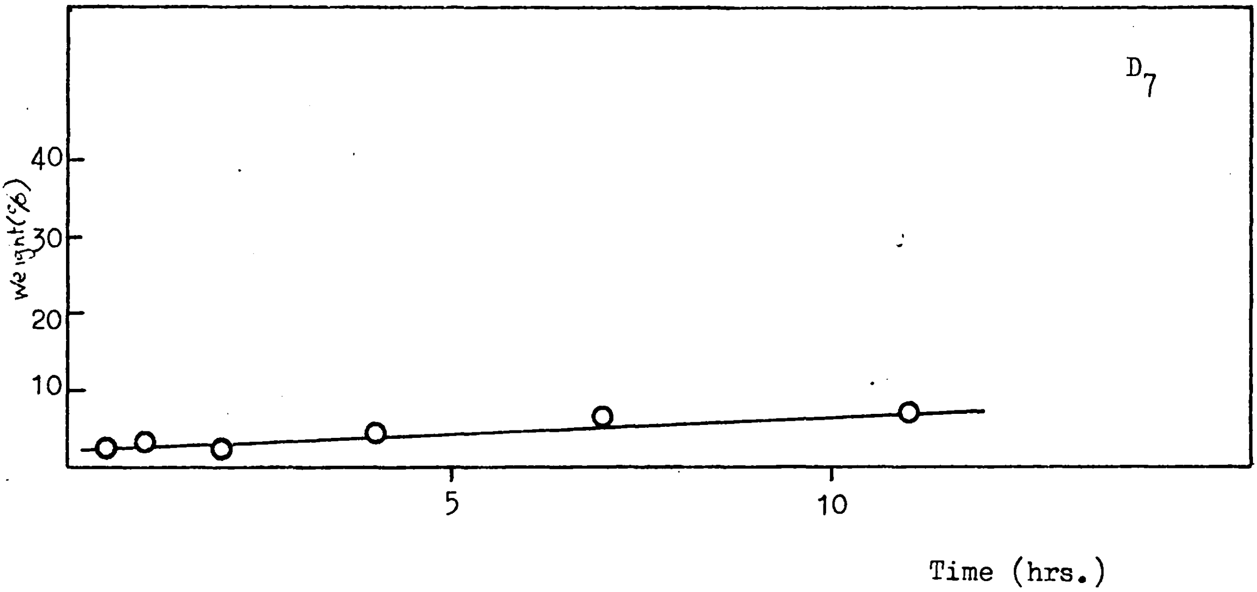


Fig. 3.22 (e) Cont'd. 405°C

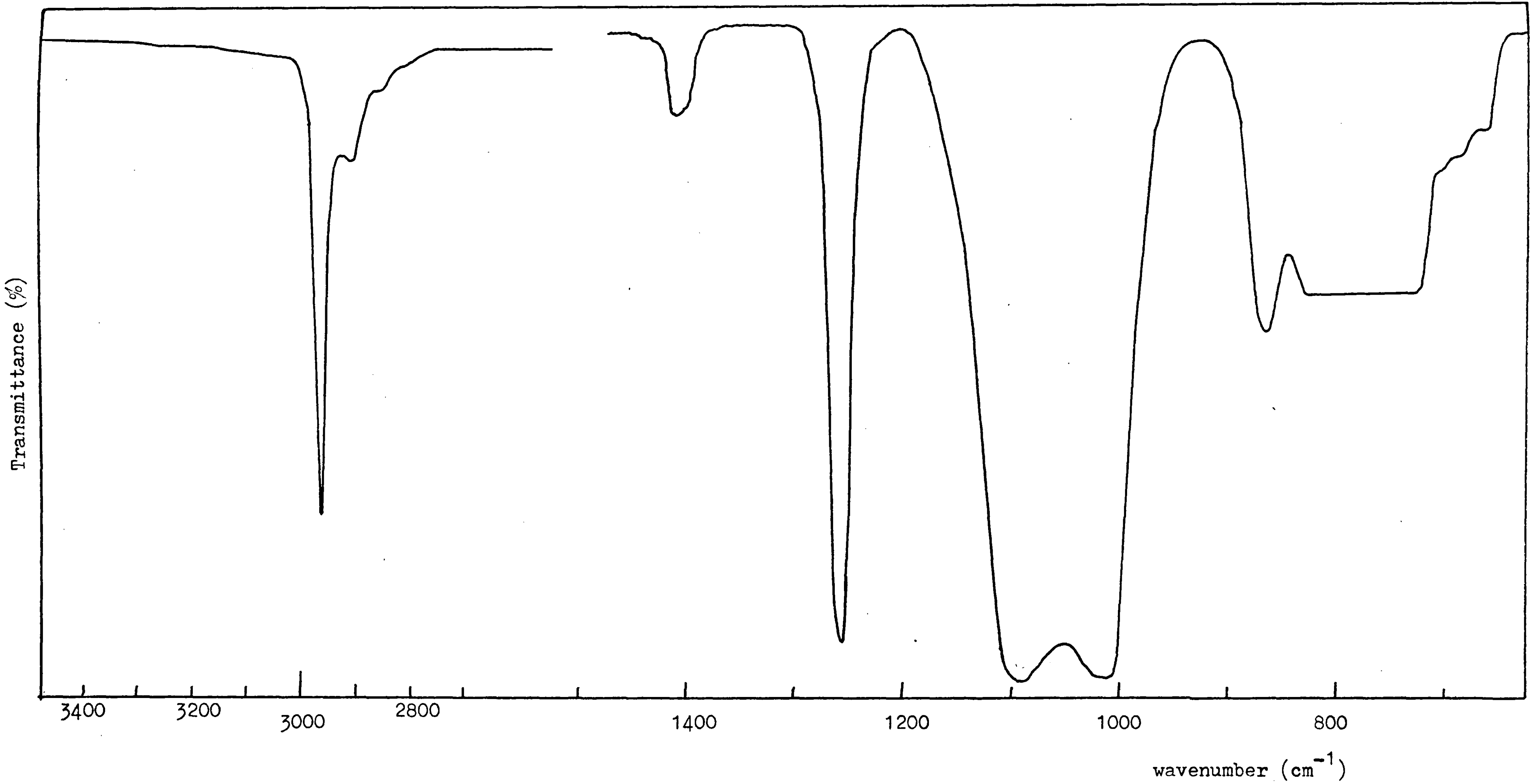


Fig. 3.23 (a) IR Spectrum of PDMS before degradation in limited supply of oxygen.

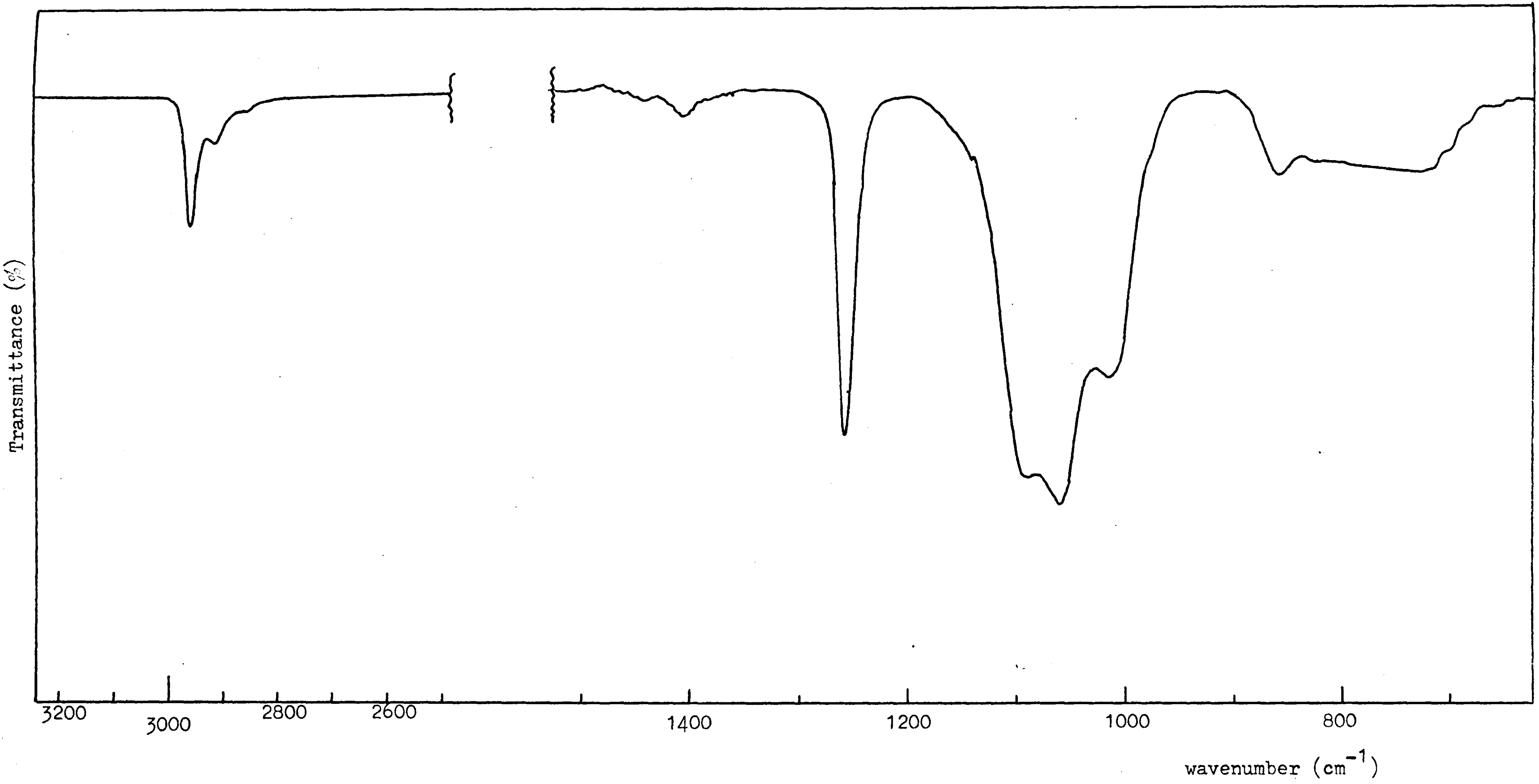
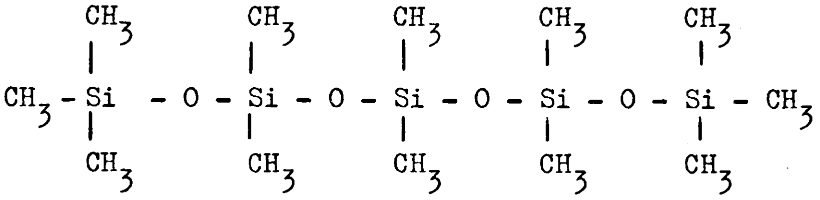


Fig. 3.23 (b) IR Spectrum of PDMS after degradation in limited supply of oxygen.

Infra-red spectra of short chain linear polymers are given by Wright and Hunter (Ref. 102). Absorption at about 9.4μ first appears in dodecamethylpentasiloxane and tends to decrease in longer chain species



$$CH_3-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-CH_3$$

It is unlikely that absorption is due to a molecule of this kind since such a product should be expected to be volatilised from the hot polymer in the above experiment and, in any case, the absorption in question is so very much less intense in these model compounds compared with the degraded material.

On the other hand, Conley (Ref. 112) assigns the region 9.2-9.5μ to the Si-O stretching vibration of Si-O-CH_3. Such an explanation would imply a large concentration of new end groups in the degraded polymer, in turn implying considerable chain scission almost inevitably involving a rather complex mechanism which is not easy to formulate. The most reasonable explanation therefore, of the new absorption at 9.42μ in the degraded polymer is that it is associated with cross-linking. This is an attractive explanation in view of the simultaneous tendency to swell, rather than dissolve completely in carbon tetrachloride.

Wright and Hunter (Ref. 102) show that strong absorptions occur at 9.47μ and 9.36μ respectively in the infra-red spectra of the model branched compounds 3- trimethylsiloxyheptamethyltrisiloxane (A) and 3,3-di(trimethylsiloxy)hexamethyltrisiloxane (B). Their spectra are reproduced in Figs. 3.24.

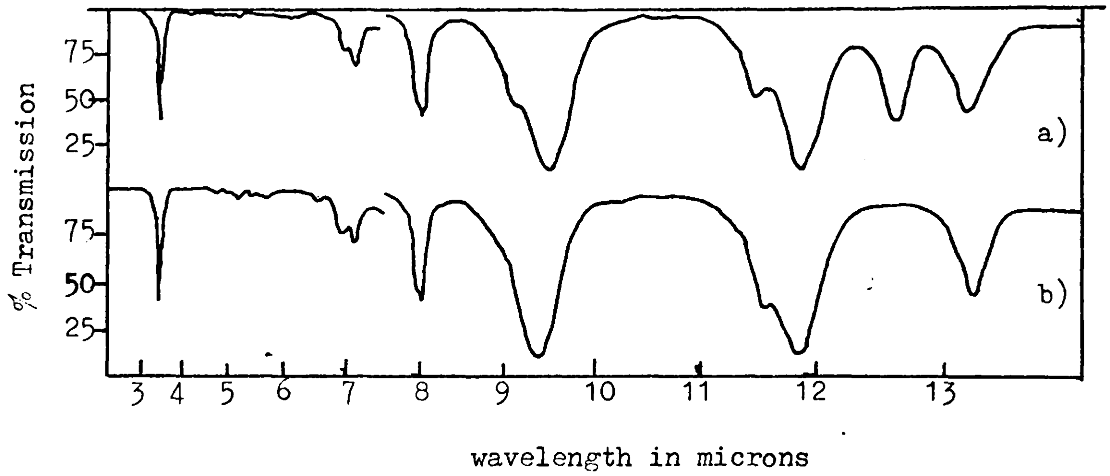


Fig. 3.24 Infrared spectra* of a)3 trimethylsiloxyheptamethyltrisiloxane. b) 3,3 Di-(trimethylsiloxy) hexamethyltrisiloxane.

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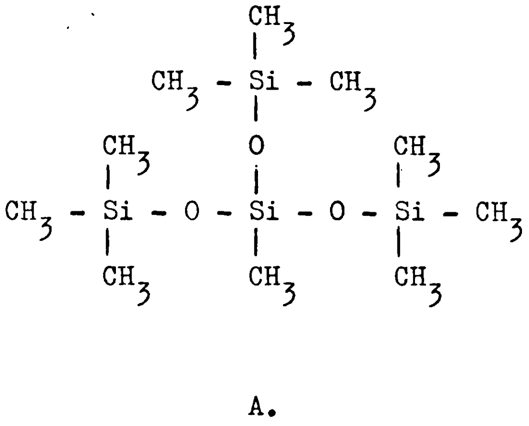
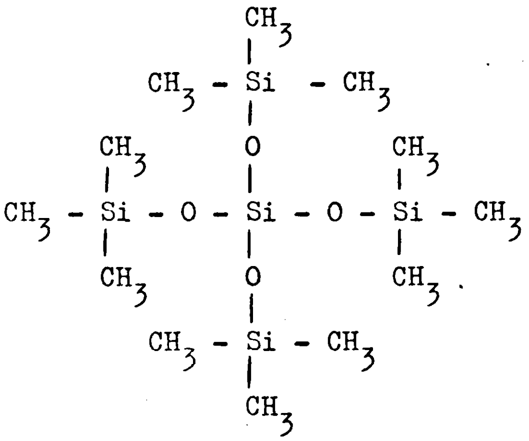
* Reproduced from Ref. 102



A.



B.

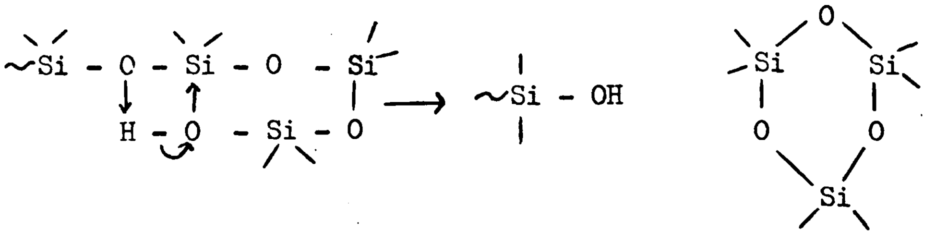
Thus the best explanation of the appearance of the peak at 9.42 in the spectrum of the degraded polymer is that it is due to a cross-linked structure of trifunctional siloxy units. This is consistent with the work of other authors (Ref. 48).

3.10 DISCUSSION

The main features of the mechanism of degradation of poly(dimethylsiloxane) can be discussed in terms of five basic reactions as follows:

(a) Depolymerisation from Chain Ends

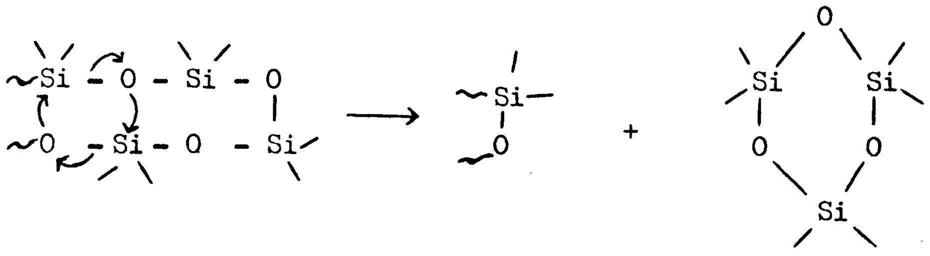
Trimer and larger cyclic products are liberated in a reaction involving a chain termainal intramolecular process which has been formulated (Refs. 51, 54):



(b)/

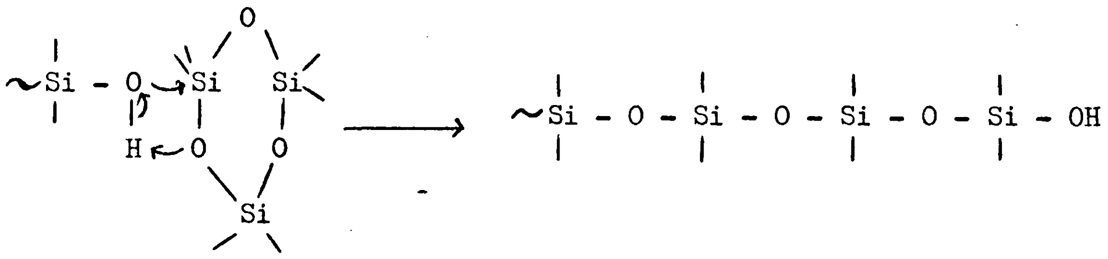
(b) Depolymerisation by Random Elimination

Random elimination of trimer and larger cyclics products may occur without chain scission (Ref. 50).



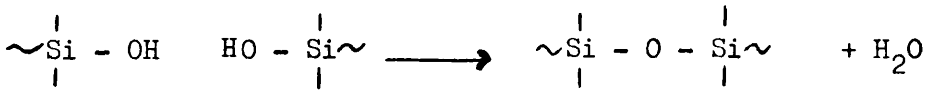
(c) Repolymerisation

Since polymerisation and depolymerisation from hydroxyl terminal structures is believed to be reversible then a build up of degradation products within the hot polymer may lead to repolymerisation.



(d) Intermolecular Condensation of Terminal Hydroxyl Groups

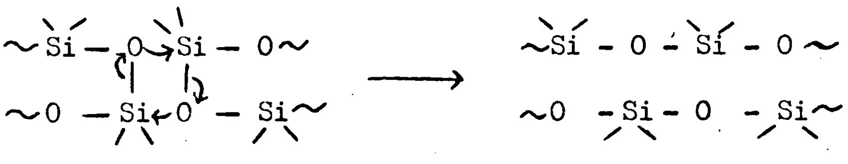
This reaction has been called chain extension and would lead to an increase in molecular weight.



$$\sim Si - OH \quad HO - Si\sim \longrightarrow \sim Si - O - Si\sim \quad + H_2O$$

(e) Intermolecular Rearrangement of Chains

It is believed (Ref. 113) that a reaction between chains with a mechanism similar to that of (b) can occur, resulting in a rearrangement of the polymer chains.



An/

An attempt to gain evidence for reaction (e) using a blend of a hydroxyl-ended poly(dimethylsiloxane) and a hydroxyl-ended poly(methylphenylsiloxane) has proved inconclusive. Degrading a sample of this blend to completion at 450°C gives dimethyl cyclics and methylphenyl cyclics only (analysis by nmr). There is no evidence of mixed cyclics which might be expected if reaction (e) is important. Despite the close relationships between the two polymers the blend is heterogeneous and therefore no final conclusions have been drawn from this result.

Degradation under continuously pumped high vacuum conditions is many times faster (~30) than the reaction carried out using the sealed tube technique. It is believed however that the initial fast rate observed in Fig. 3.17 provides a clue towards the explanation of these different behaviours. Since repolymerisation seems possible as in reaction (c), it is clear that the rate at which degradation products are removed from the degradation polymer will determine the stationary concentration of degradation products within the polymer which will determine, in turn, the amount of repolymerisation and thus the overall net rate of degradation as measured by the rate of weight loss or appearance of degradation products in the cold trap.

The "sealed tube" system is initially evacuated to 10^{-6} torr and for a short period will remain so. On heating, however, there will be a tendency for the pressure to rise significently due to traces of permanent gases either desorbed from the walls of the reaction vessel, trapped initially in the solid polymer or formed in minute amounts in the degradation process. It is suggested that this small rise in pressure is sufficient to inhibit diffusion of degradation products from the degrading polymer to such an extent as to allow much greater extents of repolymerisation (reaction (c)).

This is effectively a "ceiling" temperature effect. The fact that the rates of degradation obtained by both techniques are constant over a large part of the reaction would suggest that the permanent gases are present in the polymer or on the walls of the vessel initially. If they were degradation products one would expect the effect to be progressive so that the reaction in the sealed tube would be increasingly inhibited.

Increase in molecular weight during degradation is commonly due to cross-linking. In such a case the molecular weight should be expected to increase rapidly to infinity. In the present instance the initial increase in molecular weight is strictly limited and fairly constant over a range of temperature. Thus chain extension by condensation of hydroxyl groups seems much more likely than cross-linking. The fact that the molecular weight later decreases after passing through a maximum suggests that the amount of chain extension is limited although the possibility of equilibrium forces playing a prominant role means that classical mechanistic treatment must be applied cautiously.

The marked increase in the stability of polymer H over the hydroxyl ended species is strong evidence that reaction (a) is important in the degradation of the hydroxyl-ended polymers. It is difficult to envisage any other reasoning to account for the increase in stability.

The eventual levelling out of the molecular weight of the polymer sample can be explained by one of two mechanisms. The first suggests that complete molecules are being eliminated from the system rather like the radical depolymerisation reaction which occurs in poly(methylmethacrylate) and related polymers.

The second involves degradation in a stepwise manner according to mechanism (a) keeping pace with the condensation of hydroxyl chain ends in the remaining sample. It has not been possible to distinguish these reactions in this work. Rode' et. al. provide data to suggest that something related to the second of these two mechanism is true and thus claim that whole molecules are not eliminated from the system as predicted by the first mechanism. Andrianov et. al. have suggested these workers are dealing with impure samples. Further extension of this work should be aimed at distinguishing the above processes.

3.11 CONCLUSIONS

1. Cyclics, D_3-D_{17} have been positively identified as products of degradation of poly(dimethylsiloxane) at temperatures up to 450°C. It seems likely that trace amounts (~0.01%) of higher cyclics may also be formed. Cyclic trimer, D_3, is the major product.

2. When heated isothermally at temperatures above 200°C the molecular weight of hydroxyl-ended samples increases. Typically the molecular weight goes through a maximum and eventually levels out. There is no loss of solubility associated with this increase in molecular weight.

3. The distribution of the products of degradation is generally fairly constant with time and temperature although at higher temperatures the production of trimer relative to higher cyclics appears to decrease slightly with time.

4. Cyclic trimer and tetramer are the major products of trimethylsiloxy-ended samples as seen by infra-red analysis.

5. Chain ends play an important part in the degradation of hydroxyl-ended species. Thus, samples end-blocked using 1,1,1,3,3,3, hexamethyldisilazane show increased thermal stability.

6. The production of methane has not been observed during the degradation of catalyst free hydroxyl-ended samples at temperatures below 500°C. On addition of KOH these samples yield methane at temperatures as low as 190°C.

7. Oxygen has a profound effect on the degradation of pdms. After heating at 200°C for 56 hrs. in a limited supply of oxygen there is evidence of cross-linking.

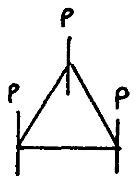
8. Inter-chain rearrangement at temperatures up to 450°C has not been observed for hydroxyl-ended species. There is, however, insufficient evidence for this process to be discounted.

CHAPTER 4

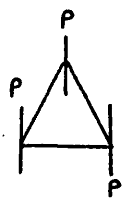
POLY(METHYLPHENYLSILOXANE)

4.1 INTRODUCTION

The literature contains only a relatively small number of papers on the preparation of poly(methylphenylsiloxanes) and even fewer on their thermal degradation. Although a number of workers, including F.S. Kipping, had previously prepared compounds with both methyl and phenyl groups on the same silicon atom, Lewis (Ref. 88) in 1948 was the first to describe the hydrolysis of dichloromethylphenylsilane with subsequent distillation of the product mixture. He showed that the cyclic trimer 1, 3, 5 trimethyl, 1, 3, 5 triphenyl cyclotrisiloxane exists in two forms and proposed that they were stereoisomers with cis and trans configuration. Using an abbreviated structural representation these isomers can be drawn:



cis methylphenyltrimer



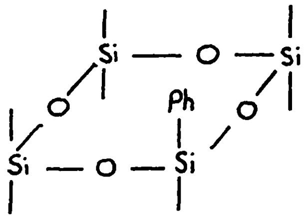
trans methylphenyltrimer

Lewis further proposed that this type of isomerism occurs with the methylphenylcyclic tetramer (1, 3, 5, 7 tetramethyl, 1, 3, 5, 7 tetraphenylcyclotetrasiloxane). In this case four stereoisomers are possible but Lewis was unable to effect any separation.

Also/

Also in 1948 Young et. al. (Ref.89) prepared the methylphenyl trimer and tetramers for their work on the infra-red properties of these and related ring compounds. They were successful in isolating one of the tetramer isomers and quoted its melting point as 99°C.

Daudt and Hyde (Ref. 116) isolated and characterised a number of analogous disiloxanes in 1952, and in 1958 Andrianov and Yakushkina (Ref. 117) prepared a small number of mixed cyclics of which one was heptamethylphenylcyclotetrasiloxane.



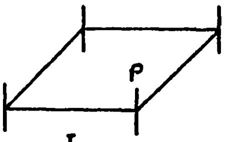
heptamethylphenylcyclotetrasiloxane

These workers later polymerised this compound as well as the tetramer with two methyl, phenyl-substituted silicon atoms hexamethyldiphenylcyclotetrasiloxane (Refs. 118, 119). They found that using an acid catalyst of concentration greater than 2% resulted in cleavage of the Si-Ph bond. Andrianov's cautious approach to the polymerisation of phenyl-containing siloxane rings can be understood from his statement in the introduction to this paper, that "it is well known that cyclic compounds containing phenyl groups on the silicon atom polymerise with difficulty."

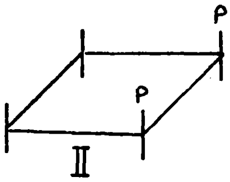
In 1962 Moore and Dewhurst (Ref. 120) applied glc to the separation of the cyclic methyl phenyl isomers. They managed to separate the two trimers effectively but the separation of the tetramers was much less well effected.

Andrianov/

Andrianov et. al. (Ref. 121), in 1965 compared the rate of polymerisation for the following series of cyclic tetramers with varying numbers of phenyl substituents:

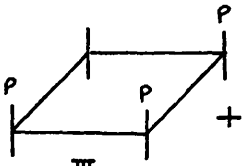


I



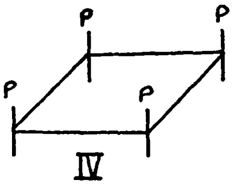
II

+ isomers



III

+ isomers



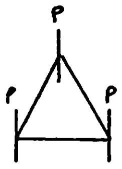
IV

+ isomers

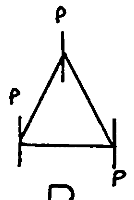
They found that at 150°C, using 0·5% KOH as catalyst, linear high polymers were formed from compounds I-III. It was found that the polymerisation rate decreased with increasing phenyl substitution and that Si-O bond fracture followed by phenyl radical dissociation occurred during polymerisation of compound IV, tetramethyltetraphenylcyclotetrasiloxane.

Later that year Andrianov et. al. (Ref. 122) published more work on the polymerisation of methyl,phenyl siloxane rings. They introduced this paper with the following comment: "It is known that in the presence of potassium hydroxide tetramethyltetraphenylcyclotetrasiloxane polymerises slowly and does not form polymers with high molecular weight." They also showed that the cis trimer is more active in polymerisation than the trans isomer and more active than the tetramer (mixture of isomers).

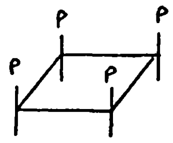
In 1966 Hickton, Holt et. al. (Ref. 123) isolated and characterised all four tetramer stereoisomers, also quoting their melting points.



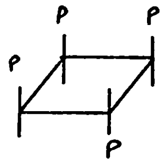
A
(m.p. 99·5°C)



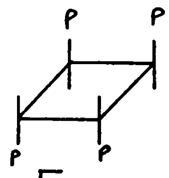
B
(m.p. 44-46°C)



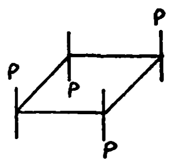
C
(m.p. 64·5°C)



D
(m.p. 55-57°C)



E
(m.p. 99-100°C)



F
(m.p. 74°C)

Their syntheses of the more difficultly separated isomers were elegant but not wholly straightforward or convenient for large scale preparation.

The importance of nmr in the identification and characterisation of these cyclics was made clear by the above work and this technique has become indispensable in the study of these and related compounds. From the study of cyclics these workers moved on to study short chain oligomers in the methyl phenyl series (Ref. 124).

In 1968 Andrianov et al (Ref. 125) applied GPC to the separation of the above cyclics but were unable to resolve the tetramer isomers using this technique. In a study on reactivity in anionic polymerisation carried out in 1969 he and his co-workers reported again that in the polymerisation of the mixed ring, heptamethylphenylcyclotetrasiloxane conversion does not reach the equilibrium value and at 50-70% conversion crosslinking with formation of insoluble polymer occurs. This reaction was carried out at 50°C in the presence of 1·0% DMSO and 0·1% KOH (Ref. 126).

Thomas/

Thomas and Kendrick (Ref. 55), giving no details of preparation, have reported (1970) the thermal degradation products of trimethylsiloxy-ended poly(methylphenylsiloxane) to be D_4 isomers and trans D_3 isomers. They report Si-C bond scission at 400°C.

Andrianov et. al. (Ref. 127), in a paper on the hydrodynamic properties of polymethylphenylsiloxanes report that the change from poly(dimethylsiloxane) to poly(methylphenylsiloxane) by replacing 50% of the methyl groups on the Si atom by phenyl groups, increases the macromolecular rigidity but reduces the parameter "a" in the Mark-Houwink equation. The methylphenyl polymer studied was prepared, by a method described earlier (Ref. 128), from cis trimer at 25°C.

Clearly there is at least a possibility that under certain conditions retention of configuration on polymerisation of pure isomers either trimer or tetramer might result in a polymer structure containing a certain degree of stereoregularity. The exact nature of this regularity would depend on the isomer used and the conditions of polymerisation, but in an extreme case a completely regular structure can be envisaged.

Andrianov (Ref. 129), in 1970, was first to present evidence that such regularity can be achieved. He demonstrated, using nmr, that in the polymerisation of cis methylphenyl trimer, change in the configuration of the monomer does not take place and the polymer has a well defined stereoregular structure. No molecular weight data are given in this paper. The polymerisation was studied at temperatures of 110, 120 and 130°C in the presence of 0·1% of $NaO(Si(CH_3)_2O)_2Na$, and at 50°C in the presence of 0·1% of $(CH_3)_4NO(Si(CH_3)_2O)_2N(CH_3)_4$ in bulk. It was noted that cyclic tetramer/

tetramer was also formed during this reaction.

In a study of the polymerisation kinetics of cis D_3 in benzene solution Andrianov et. al. (Ref. 128) have reported that the reaction is first order for both monomer and catalyst, the activation energy of polymerisation being 24·7k cal mol^{-1}. Again, some cyclic tetramer was also produced.

Sobolevskii et. al. (Ref. 65) have done important work on thermally induced changes in oligomethylphenylsiloxanes in the temperature range 425°C - 500°C. They claim that in the interval 450-475°C, the mechanism of pyrolysis of these oligomers undergoes a change. At temperatures of ~425-475°C the main reaction is regarded as one of rearrangement, resulting in formation of low and high molecular weight organosilicon compounds. At higher temperatures it is evident that scission of organic radicals from silicon atoms begins to predominate, which favours formation of insoluble polymers by crosslinking of the low and high molecular weight products. At 425°C there is production of benzene but at higher temperature hydrogen predominates and small amounts of methane and ethylene are found among the gaseous products. These workers have proposed a mechanism for the thermal breakdown of these oligomers.

In 1974 Williams et. al. (Ref. 130) published a paper containing data on methyl shifts in nmr spectra of siloxane ring compounds containing methyl and phenyl substituent groups. On the basis of this data they have produced a useful shift-structure correlation. They have also reported that there are 97 cyclopolysiloxanes in the trimer, tetramer, and pentamer series containing solely phenyl and methyl groups whose syntheses have not been described!

Conan/

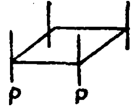
Conan et. Al. (Ref. 92) have found that a mixture of methyl, phenylcyclics obtained privately from a local commercial firm does not polymerise to high molecular weight. However on addition of this mixture to methanol one isomer precipitates (isomer E). This isomer polymerises quite readily to high molecular weight without retention of configuration.

Thus, although the silicones industry has long incorporated phenyl groups into many of its products the field of research into poly(methylphenylsiloxane) polymers and co-polymers is still very much in its infancy.

The high cost, in terms of time and effort, involved in preparing pure samples of suitable cyclics appears to have prevented many workers from pursuing a systematic study of these systems.

The work to be described in this chapter relates to the preparation of a number of atactic linear polymers of different molecular weights and the study of their thermal degradation in vacuo.

4.2 PREPARATION OF CYCLIC METHYL, PHENYL SILOXANES

This preparation has been described in chapter 2. Samples of the two trimers and of one of the tetramers (isomer E ) have been isolated from the products of hydrolysis of dichloromethyl phenylsilane.

Chromatography (GPC & column chromatography) has been applied to the separation of the above mixture without notable success. Separation of trimer from tetramer is possible but less conveniently/

conveniently than by fractional crystallisation. Separation of the tetramer isomers from each other was not effected by this method.

4.3 PREPARATION OF POLYMERS

Using the method described in chapter 2 five polymers have been prepared. The conditions for polymerisation are given in table 4.1.

The polymers are completely soluble in aromatic solvents such as toluene and also in carbon tetrachloride and insoluble in the lower alcohols. Characterisation by ir spectroscopy (fig. 4.1) shows the Si-O-Si stretching mode at 1000-1100 cm^{-1}, $Si-CH_3$ at 1260 cm^{-1} and Si-Ph at 1430 cm^{-1}. The nmr spectra of this series of polymers (fig. 4.2) shows that they are atactic.

4.4 END-BLOCKING OF POLY(METHYLPHENYLSILOXANE)

The most effective method of end-blocking has been to reflux polymer samples (with hydroxyl end-groups) in 1, 1, 1, 3, 3, 3 hexamethyldisilazane for periods of up to 24 hrs. Thus samples of polymers A and D have been end-blocked giving polymers F and G respectively, having trimethylsiloxy ($- Si(CH_3)_3$) end groups.

For high molecular weight material the concentration of end groups is such that direct analysis is difficult, but indirect methods which will be described later indicate that the method has been/

been successful. The molecular weight of samples subjected to this treatment remained unchanged.

Table 4.1 Preparation of Poly(methylphenylsiloxane)s

Polymer	Starting Material	Temp.(°C)	Catalyst	$\bar{M}n$
A	$D_3 + D_4$	120	0·02%	30,000
B	$D_3 + D_4$	115	0·01%	55,700
C	cis D_4	120	0·01%	121,000
D	cis D_4	120	0·02%	200,000
E	cis D_4	120	0·02%	211,000
F	end-blocked sample of polymer A			30,000
G	end-blocked sample of polymer D			200,000

4.5 THERMAL VOLATILISATION ANALYSIS (TVA)

An initial study of the thermal breakdown of this series of polymers has been carried out using TVA. Thus traces of polymer D (hydroxyl end-blocked) and polymer G (trimethylsiloxy end-blocked) are given in figures 4.3 and 4.4 respectively.

Infra-red/

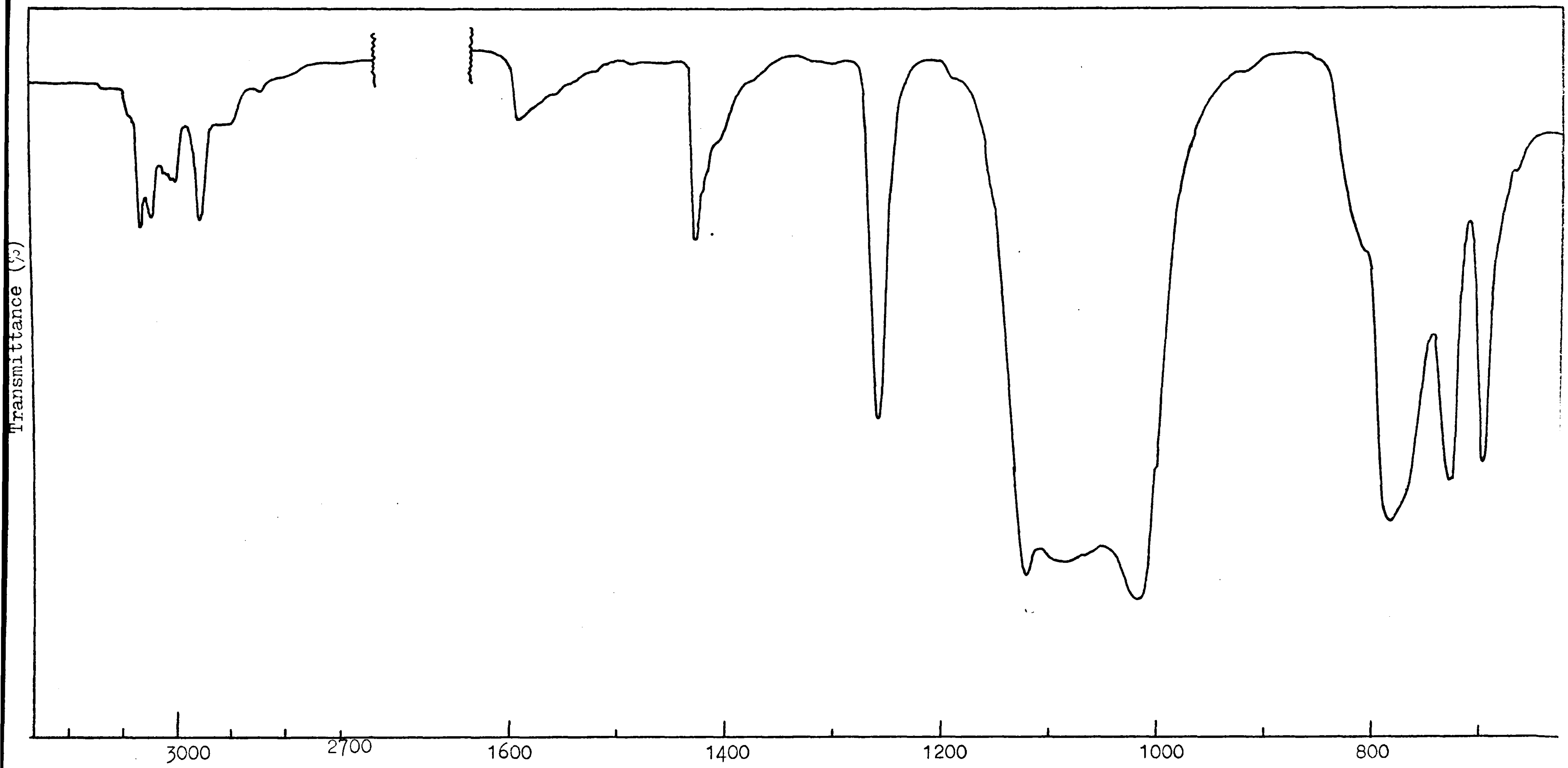


Fig. 4.1 IR Spectrum of poly(methylphenylsiloxane)

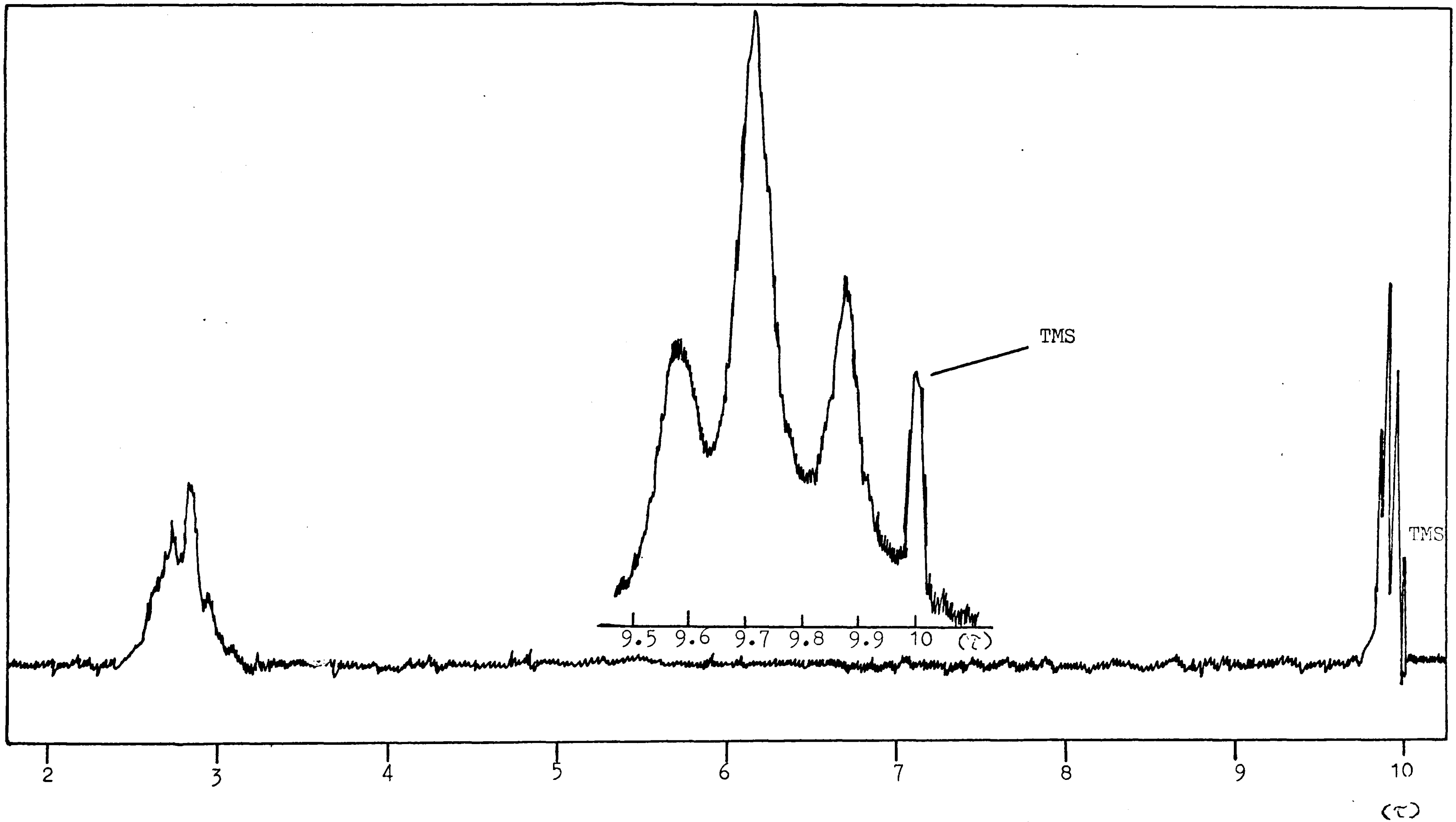


Fig. 4.2 NMR Spectrum of poly(methylphenylsiloxane)

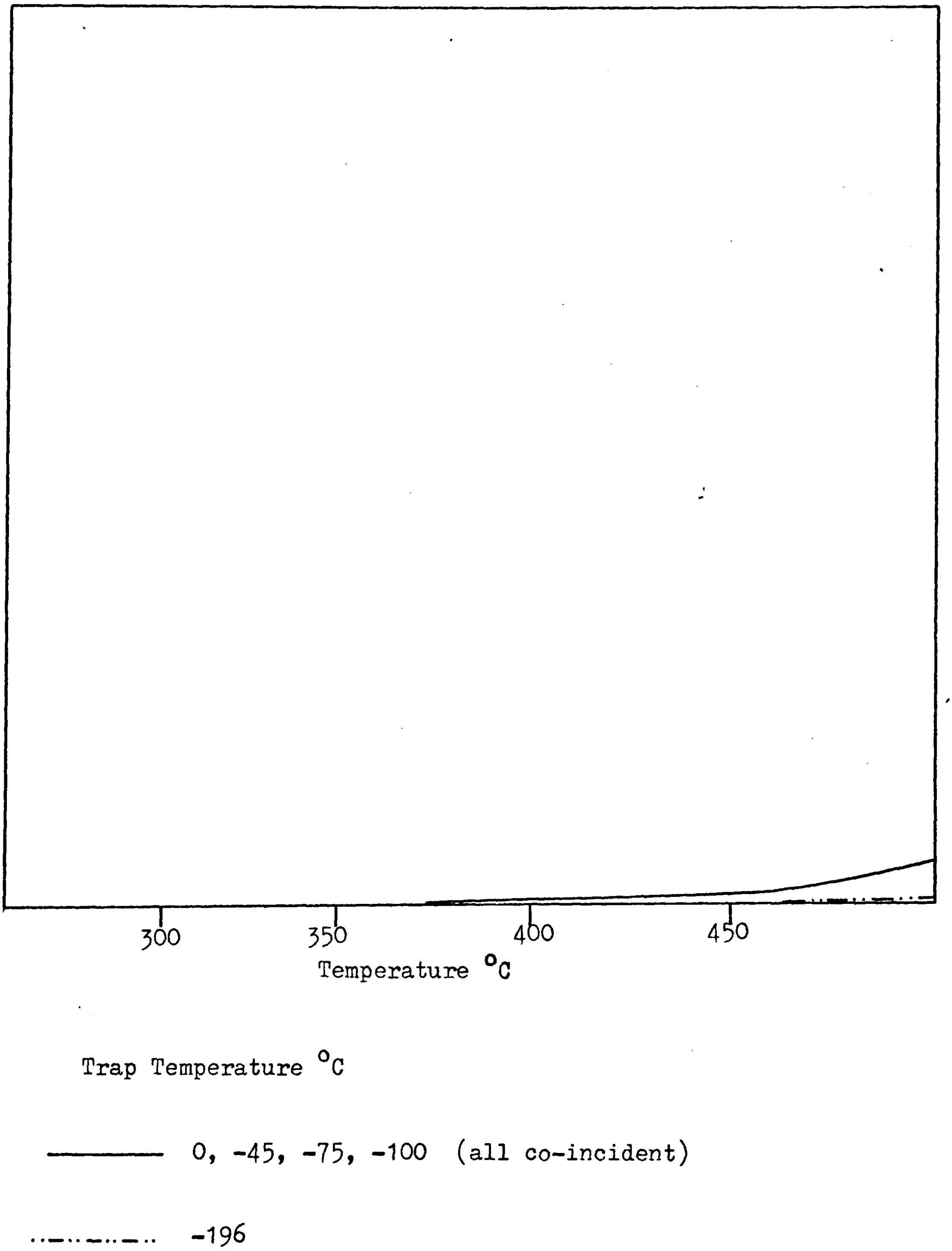


Fig. 4.3 TVA curve for hydroxyl-ended PMPS

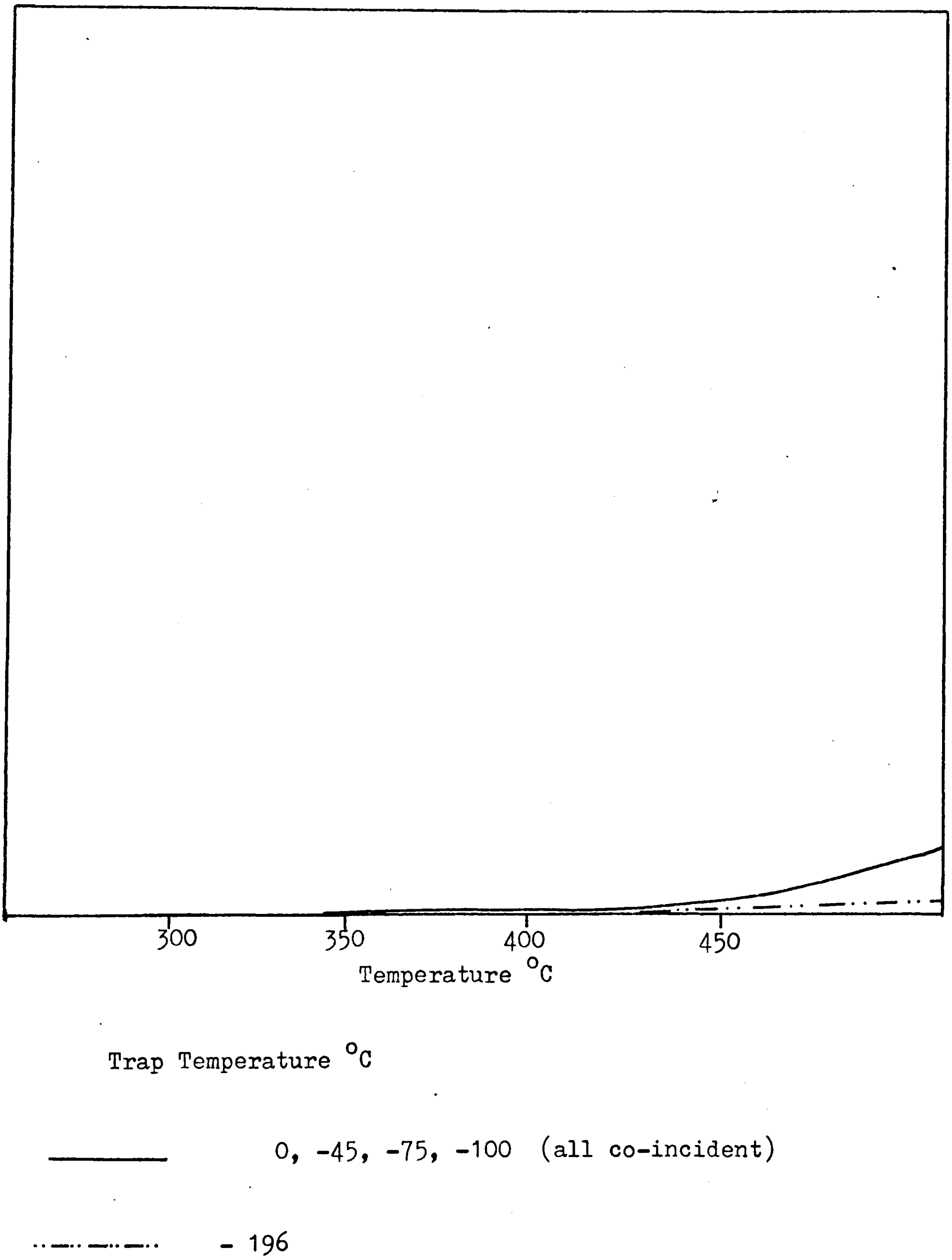


Fig. 4.4 TVA Curve for trimethylsiloxy-ended PMPS.

Infra-red analysis shows that the slight rise at the end of the traces is due to the evolution of benzene. There is no evidence of non-condensable products, such as methane, at temperatures up to 500°C. Table 4.2 contains nmr methyl shifts for possible and actual products collected in the cold ring fraction. Clearly this fraction is composed of cyclic methyl, phenyl trimer and tetramer (all isomers) (nmr fig. 4.5).

Thus, products of thermal degradation of PMPS at temperatures up to 500°C are low molecular weight cyclics (trimer and tetramer) and benzene. Early studies also showed that the polymer becomes insoluble after heating at temperatures as low as 150°C.

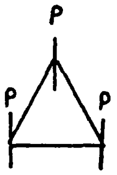
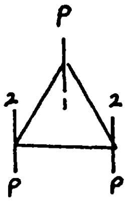
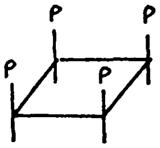
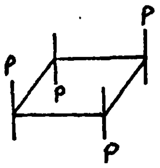
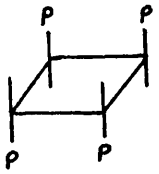
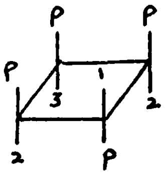
Since the major products of degradation are involatile at room temperature, even under TVA conditions, and therefore do not pass through any of the low temperature traps this technique has not been used extensively to monitor the degradation of this polymer.

4.6 TGA

TGA studies have been carried out under programmed conditions up to 900°C under nitrogen.

The TGA traces of polymers B, C, D and E are given in figure 4.6. For hydroxyl-ended species there is clearly a correlation between initial molecular weight and the weight of residue. A plot of weight of residue (%) from TGA versus initial molecular weight is given in figure 4.8. The trend is towards less residue for higher molecular weight material. It is proposed that this/

TABLE 4.2

Structure of possible Degradation products		Methyl Shift (Ref. 130)	Observed Shift of Thermal Degradation products (τ)	Difference
		9.484	9.488	+0.004
	1	9.622	9.623	+0.001
	2	9.557	9.562	+0.005
		9.519	9.525	+0.006
		9.743	9.743	0.
		9.719	9.721	+0.002
	1	9.852	9.850	-0.002
	2	9.608	9.600	-0.008
	3	9.598	9.592	-0.006

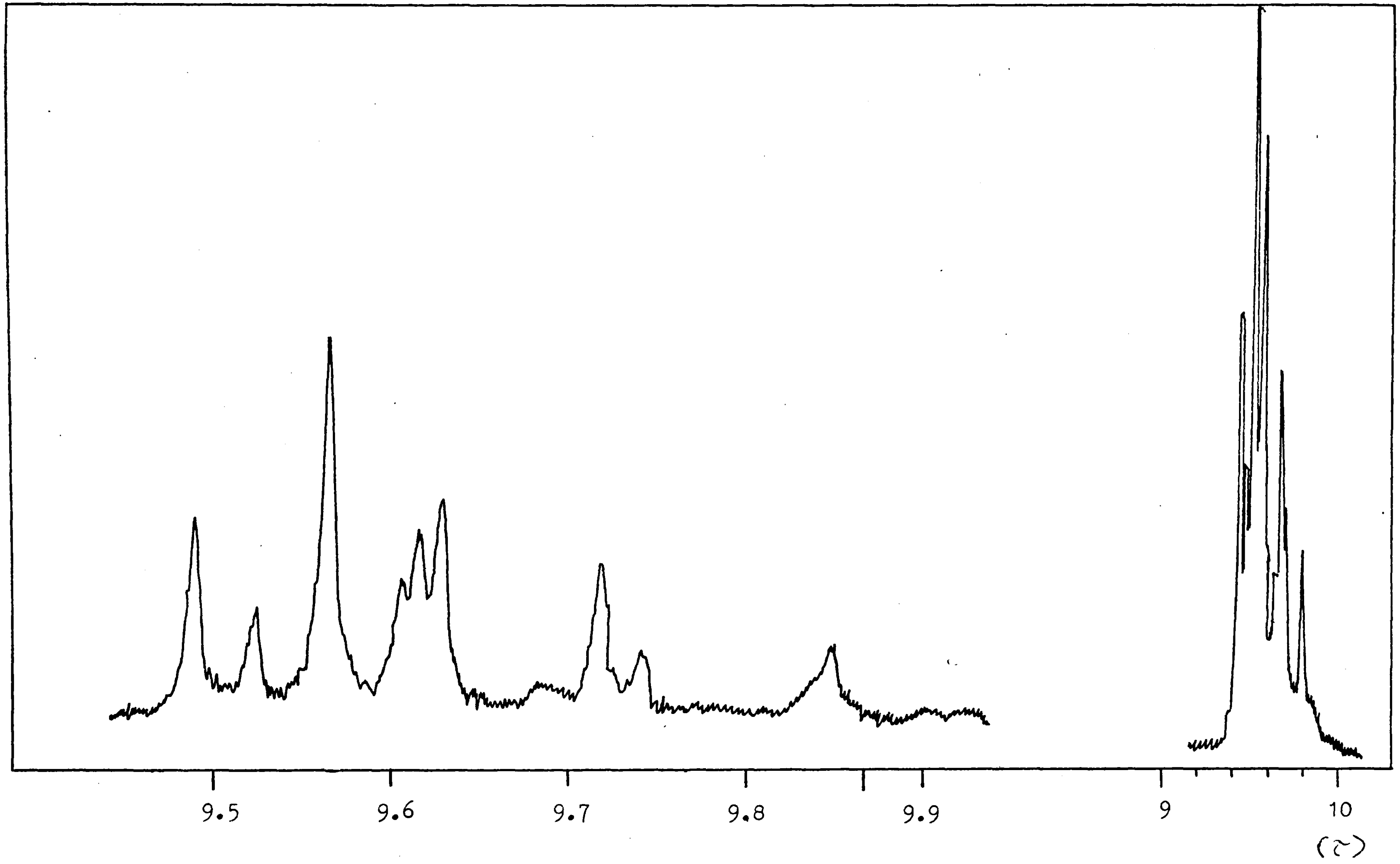


Fig. 4.5 NMR Spectrum of degradation products from poly(methylphenylsiloxane)

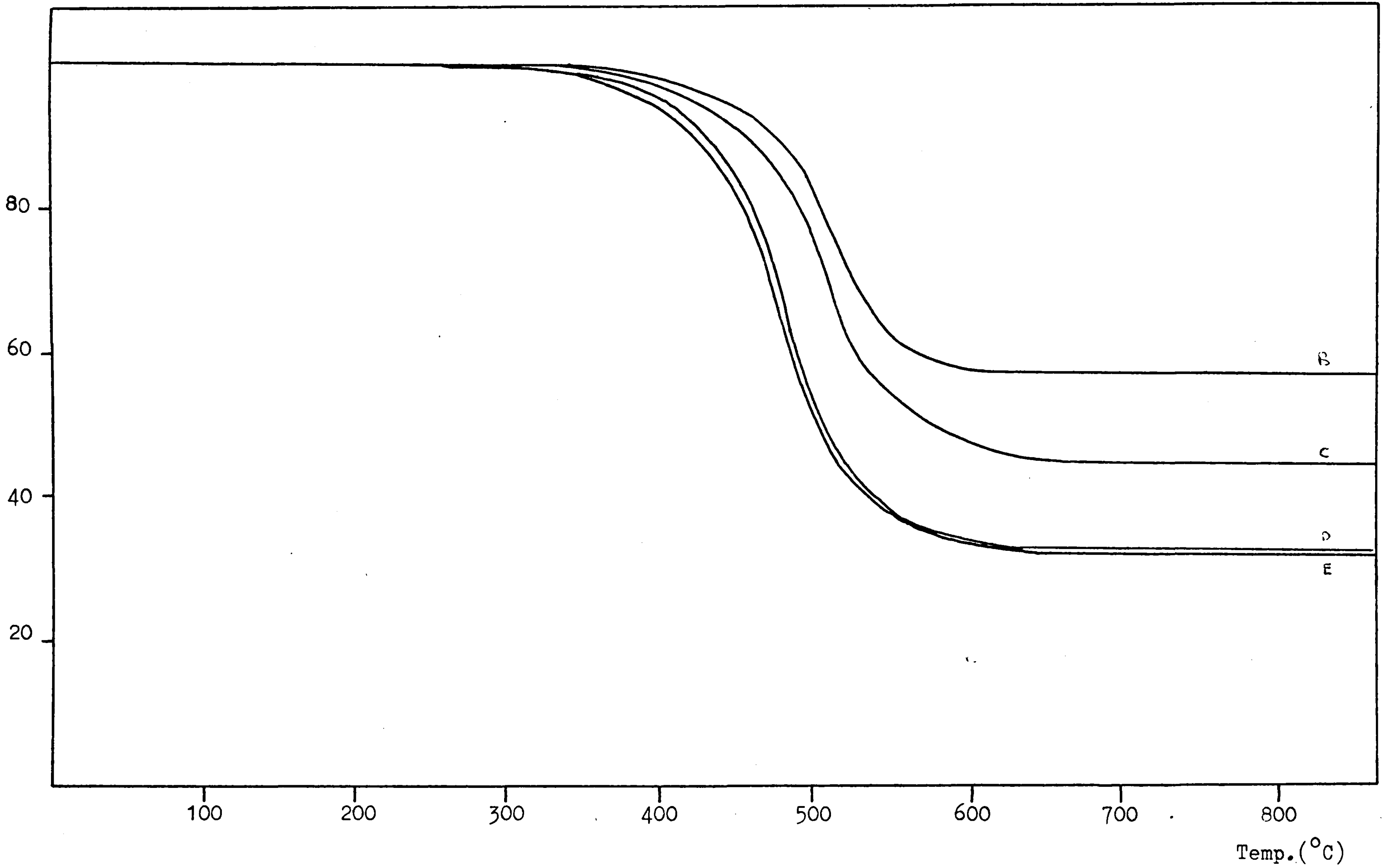


Fig. 4.6 TGA Curves for hydroxyl-ended PMPS.

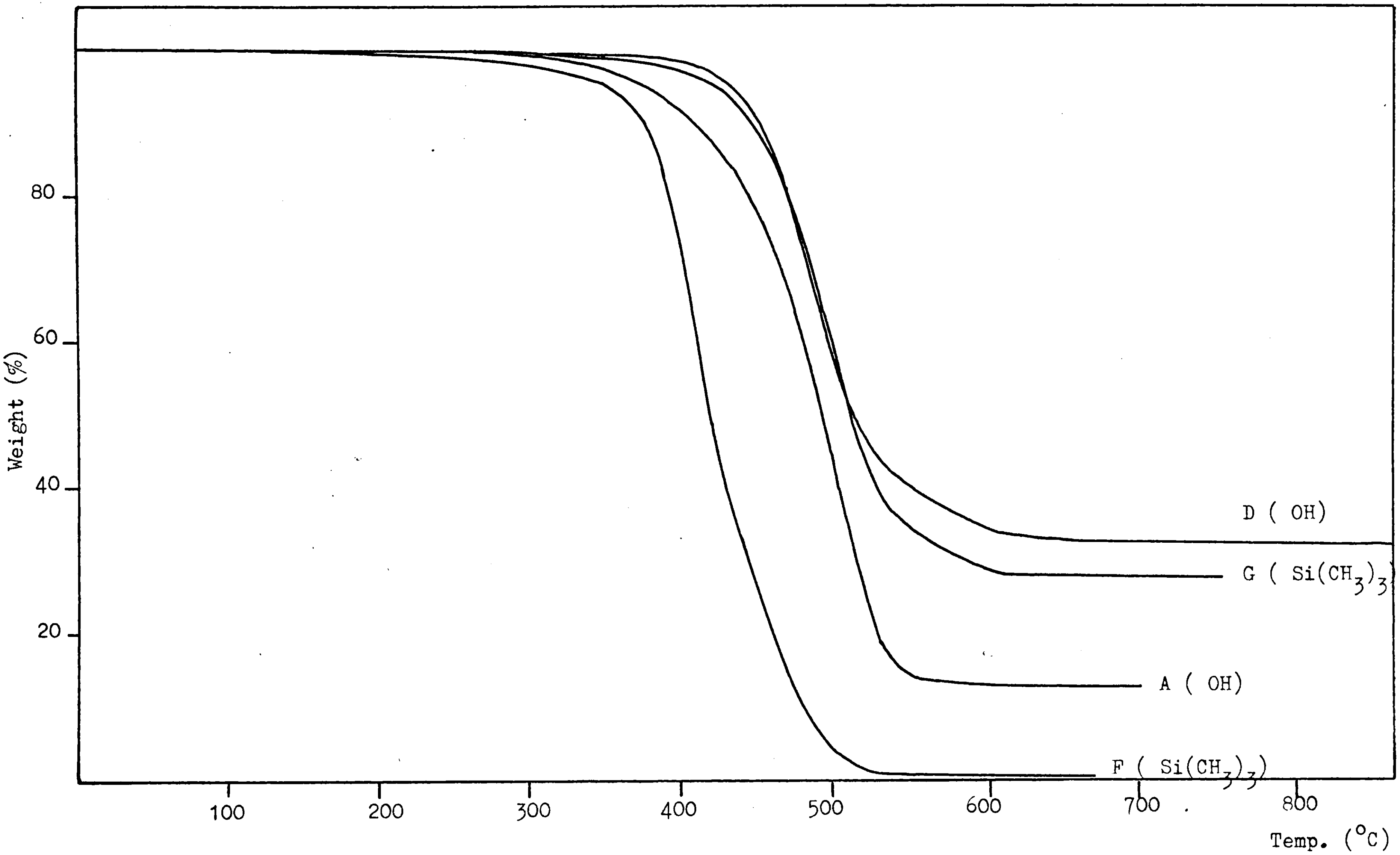


Fig. 4.7 TGA Curves for hydroxyl and trimethylsiloxy-ended PMPS.

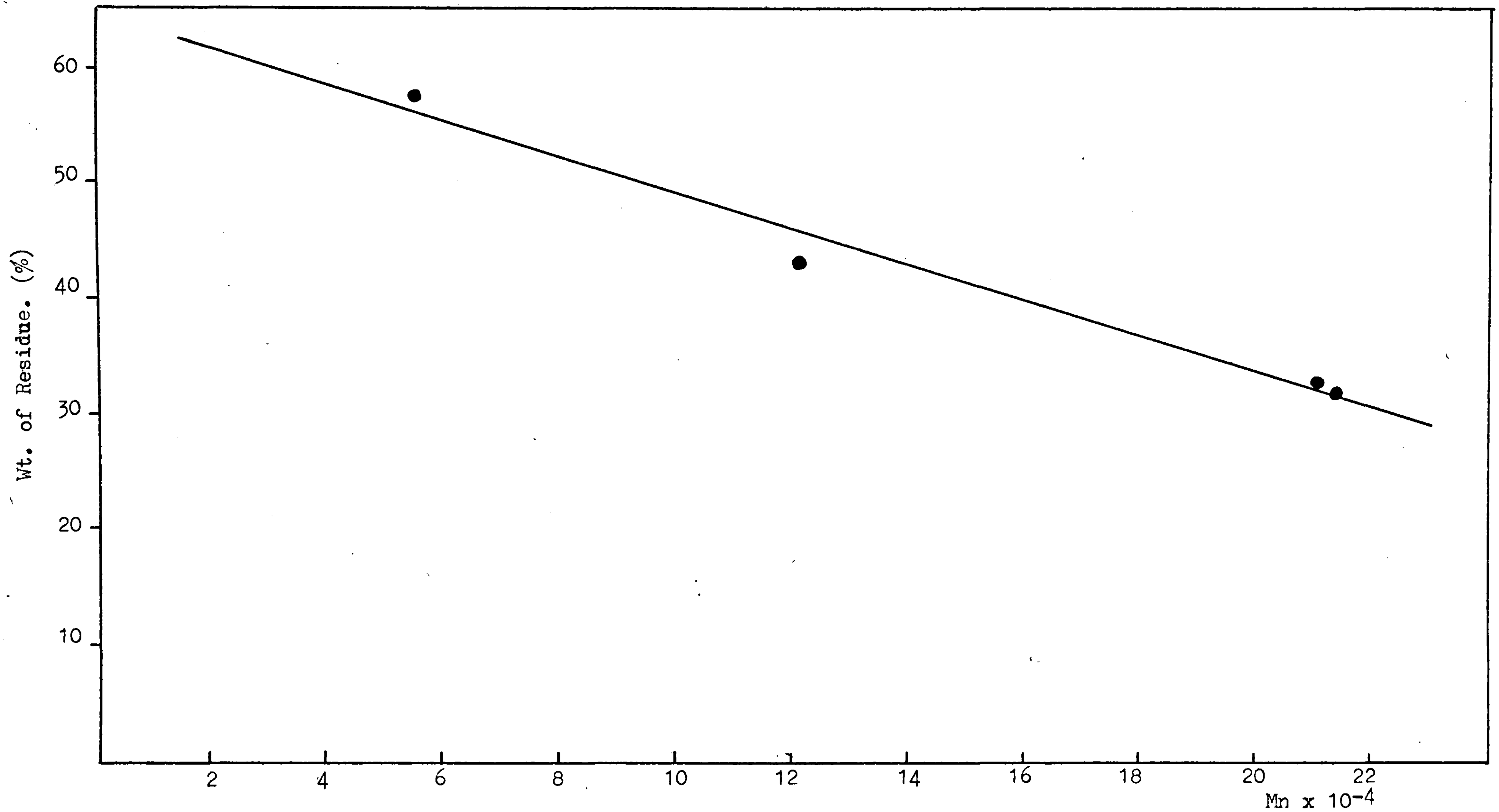


Fig. 4.8 Wt of Residue from TGA(%) versus initial molecular weight for hydroxyl-ended PMPS.

this behaviour is due to involvement of the hydroxyl chain ends in the degradation process. A mechanism for this will be given later.

It is also significant, and consistent with the proposed involvement of chain ends, that end-blocked samples give appreciably smaller residues than hydroxyl-ended samples of similar molecular weight (fig. 4.7).

The lowest molecular weight sample, polymer A, does not fit neatly into the above scheme. It gives substantially less residue than might be expected (fig. 4.7).

4.8 ISOTHERMAL WEIGHT LOSS UNDER VACUUM

Using the continuously pumped high vacuum system described in chapter 2, sample weight loss with time under isothermal heating conditions has been followed for a number of samples, particularly for polymer B (Mn 55, 700) and polymer D (Mn 200,000). Data for three temperatures are given in figures 4.9, 10 and 11. The weight loss for polymers A and F at 400°C are given in figure 4.12.

The data show that at 400°C the low molecular weight sample weight loss is less than the weight loss for the high molecular weight sample. At 450°C and 500°C there is no such clear difference and samples loose weight independently of initial molecular weight. Consistent with the results from TGA polymer F (end-blocked) looses weight at a faster rate than its hydroxyl-ended precursor, polymer A.

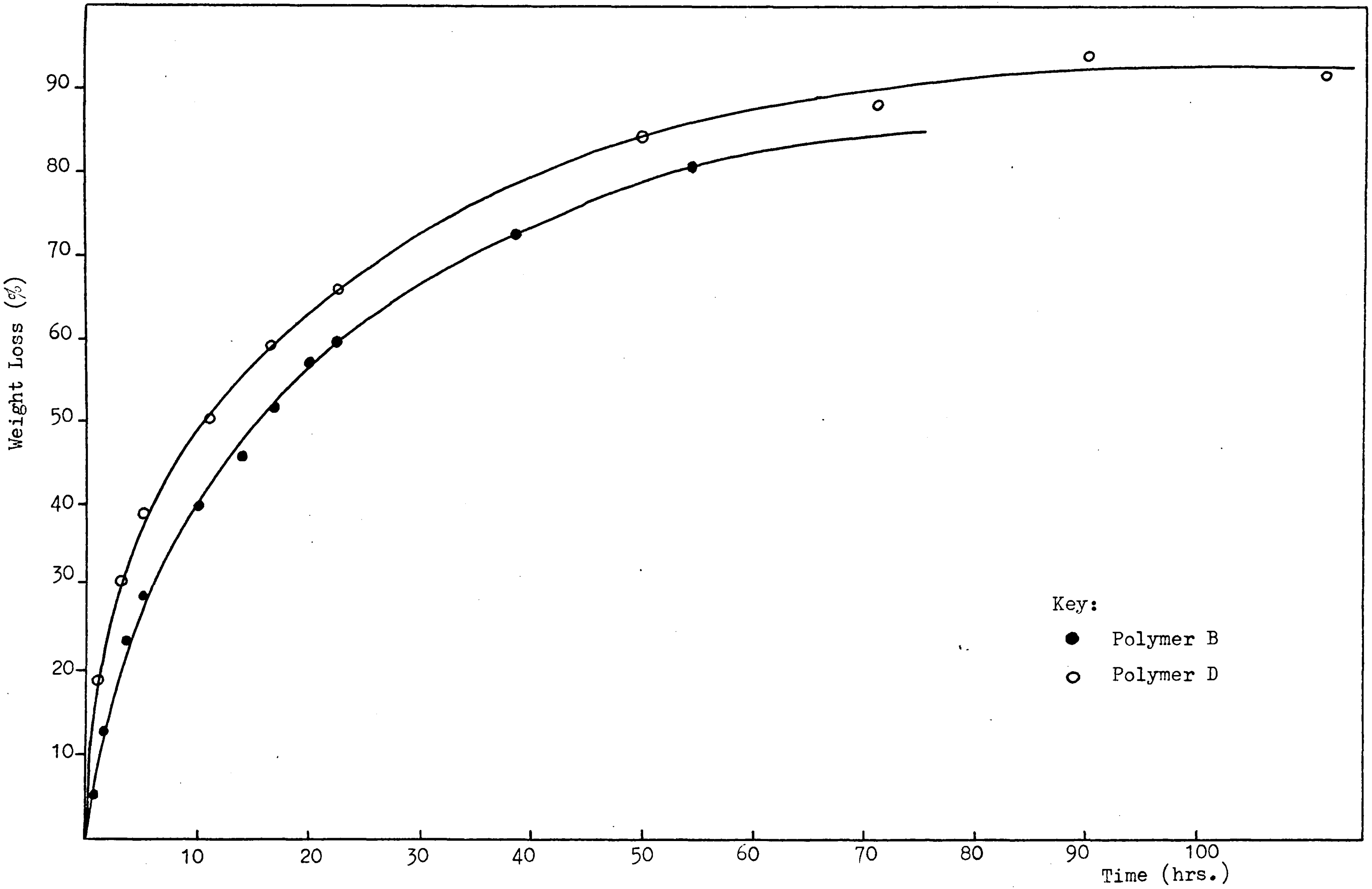


Fig. 4.9 Weight Loss from PMPS at 400°C.

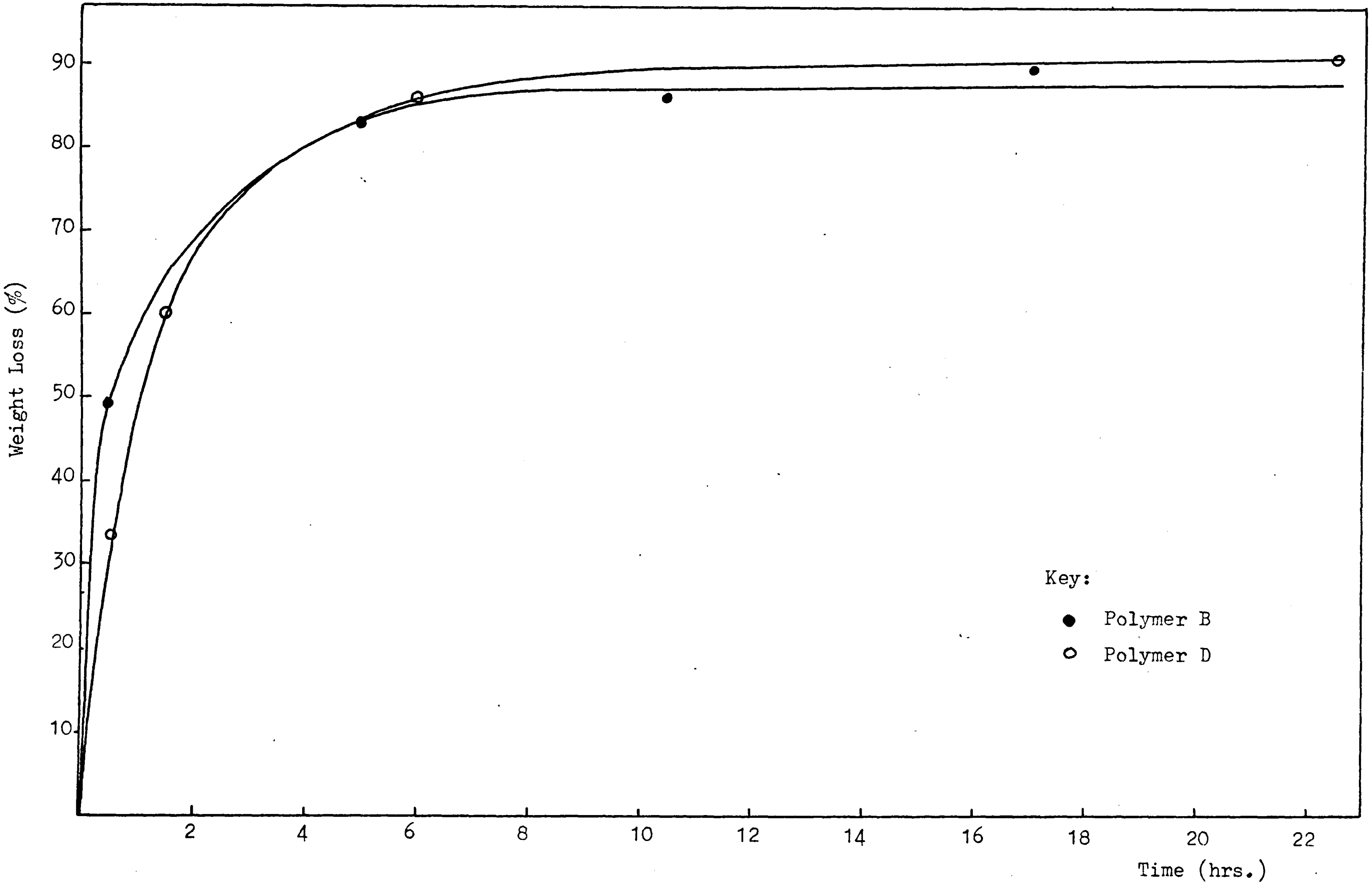


Fig. 4.10 Weight Loss from PMPS at 450°C.

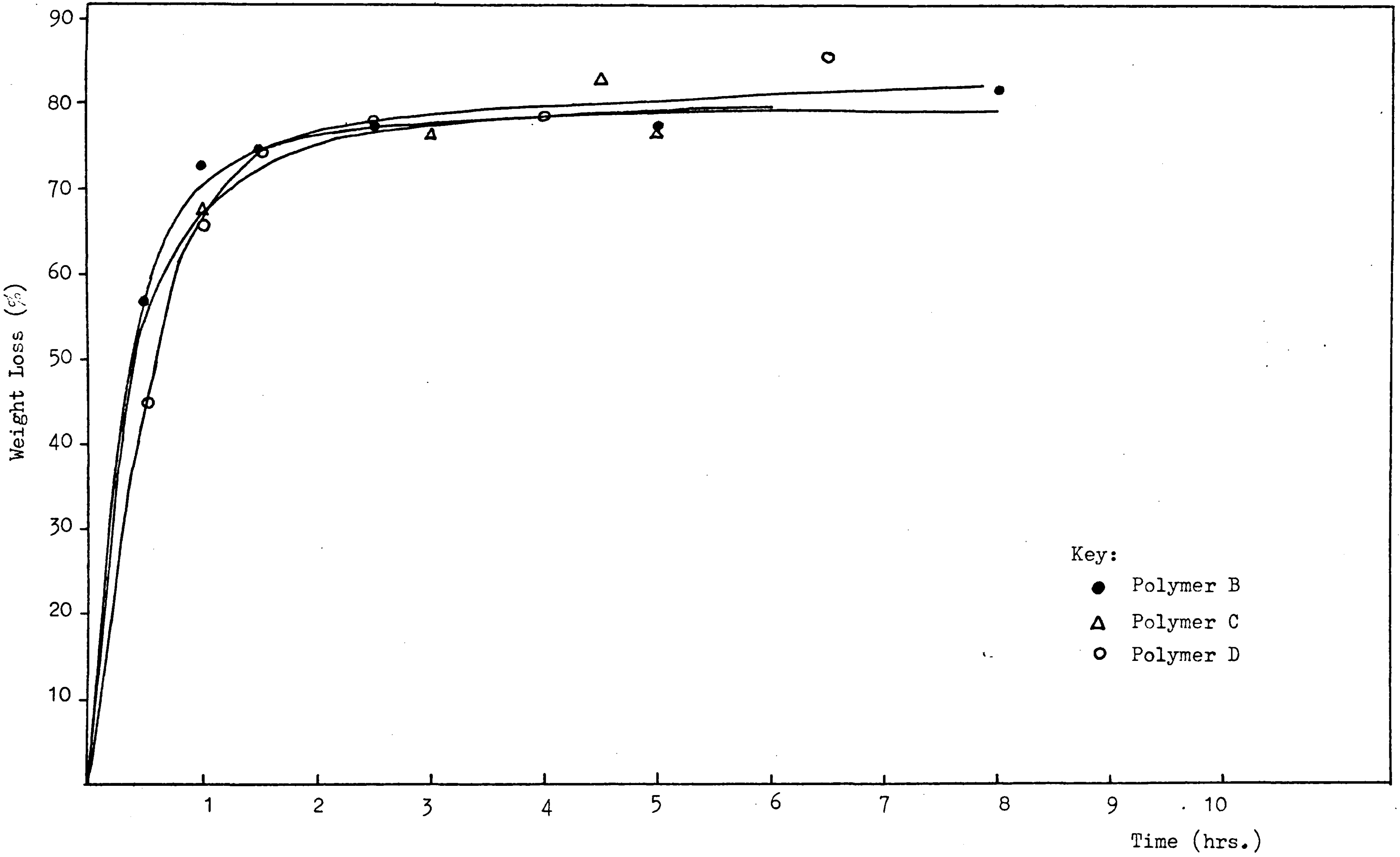


Fig. 4.11 Weight Loss from PMPS at 500°C.

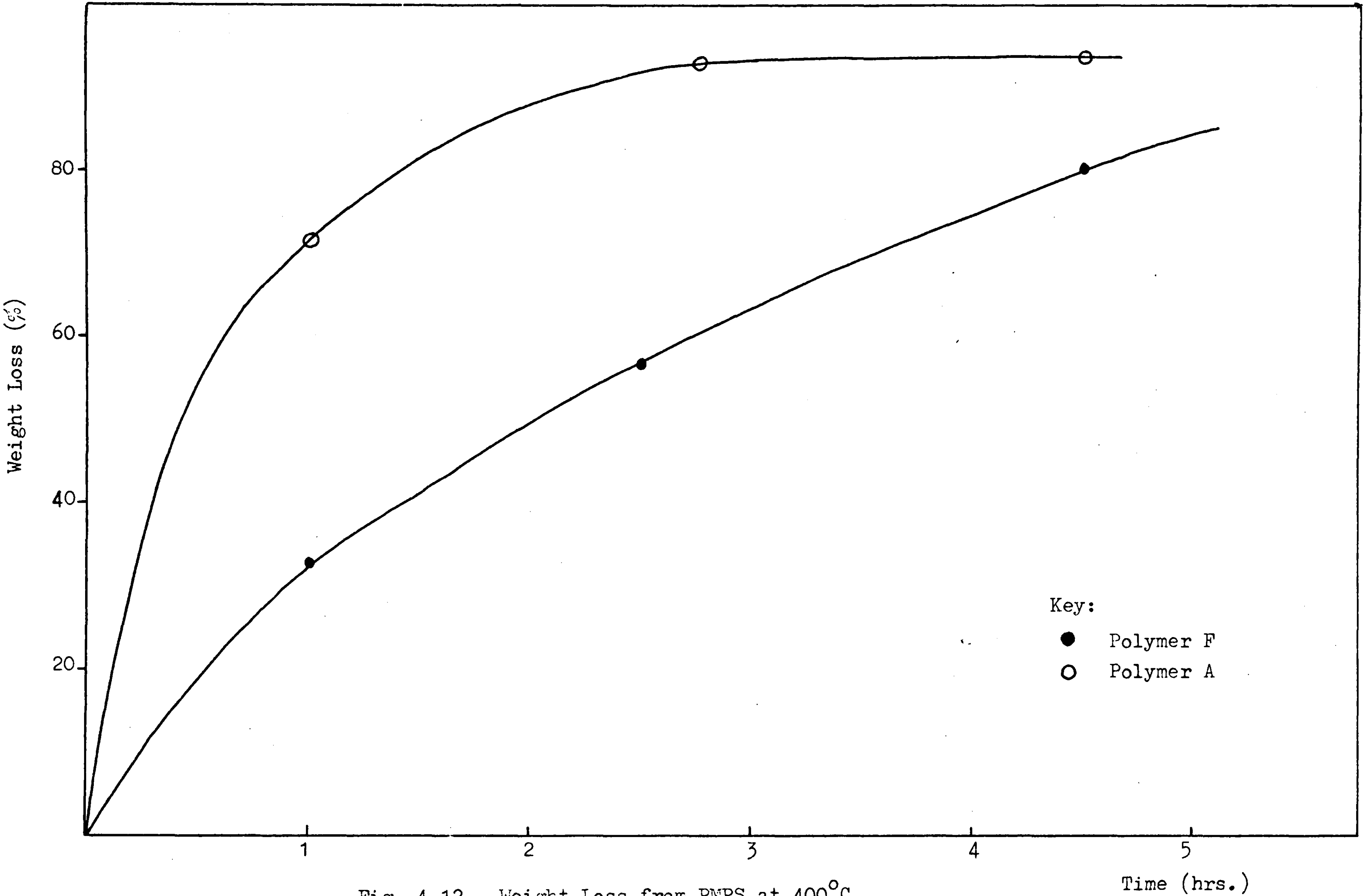


Fig. 4.12 Weight Loss from PMPS at 400°C.

4.9 ANALYSIS OF PRODUCTS

1. The evolution of benzene

Using the continuously pumped high vacuum system evolution of benzene has been monitored.

Data for polymers B, C and D are given in figures 4.13, 14 and 15. At 400°C the lower molecular weight sample evolves more benzene than the higher molecular weight sample. At 450°C and 500°C this trend remains, while the amount of benzene produced increases by factors of approximately 6 and 25 respectively.

2. The "cold-ring" fraction

(a) QUALITATIVE ANALYSIS

i) NMR

NMR affords the most convenient method of analysis for methyl phenyl siloxane rings. The nmr spectrum of a typical mixture of degradation products has been given in figure 4.5. Comparison of the methyl shifts with values obtained for the various methyl phenyl isomeric rings prepared by hydrolysis of dichloromethylphenylsilane, and also with values given by Hickton et. al. shows there to be good agreement (Table 4.2). On the basis of nmr data alone it is evident that both trimer, and all four tetramer isomers, are present.

ii) GLC

Attempts to separate the cyclic methyl phenyl trimer and tetramer isomers have been made using 1% Dexsil, 1% OV17 and 1% OV1 columns with some success. Better separation than appears in the literature/

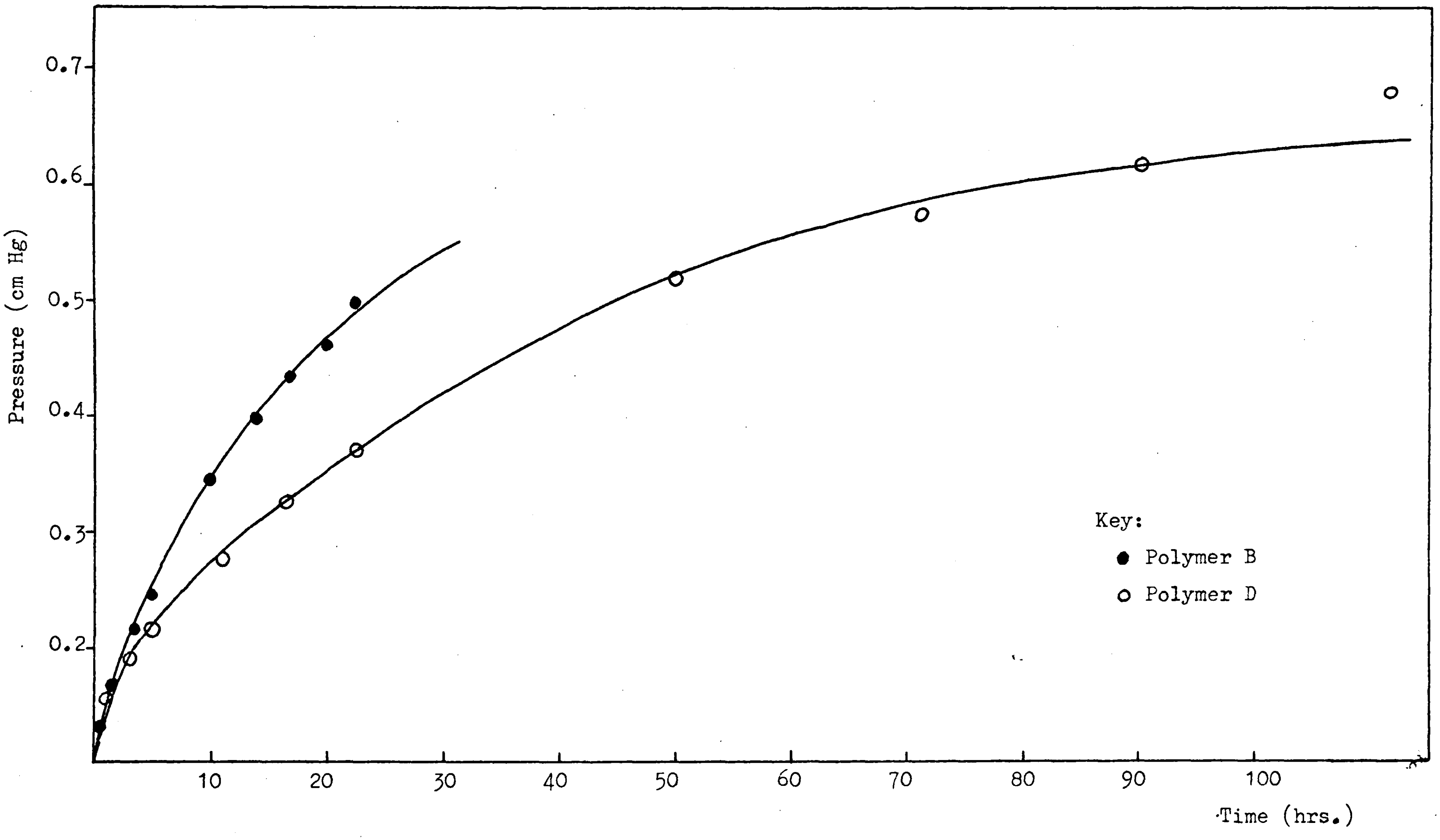


Fig. 4.13 Evolution of Benzene from PMPS at 400°C.

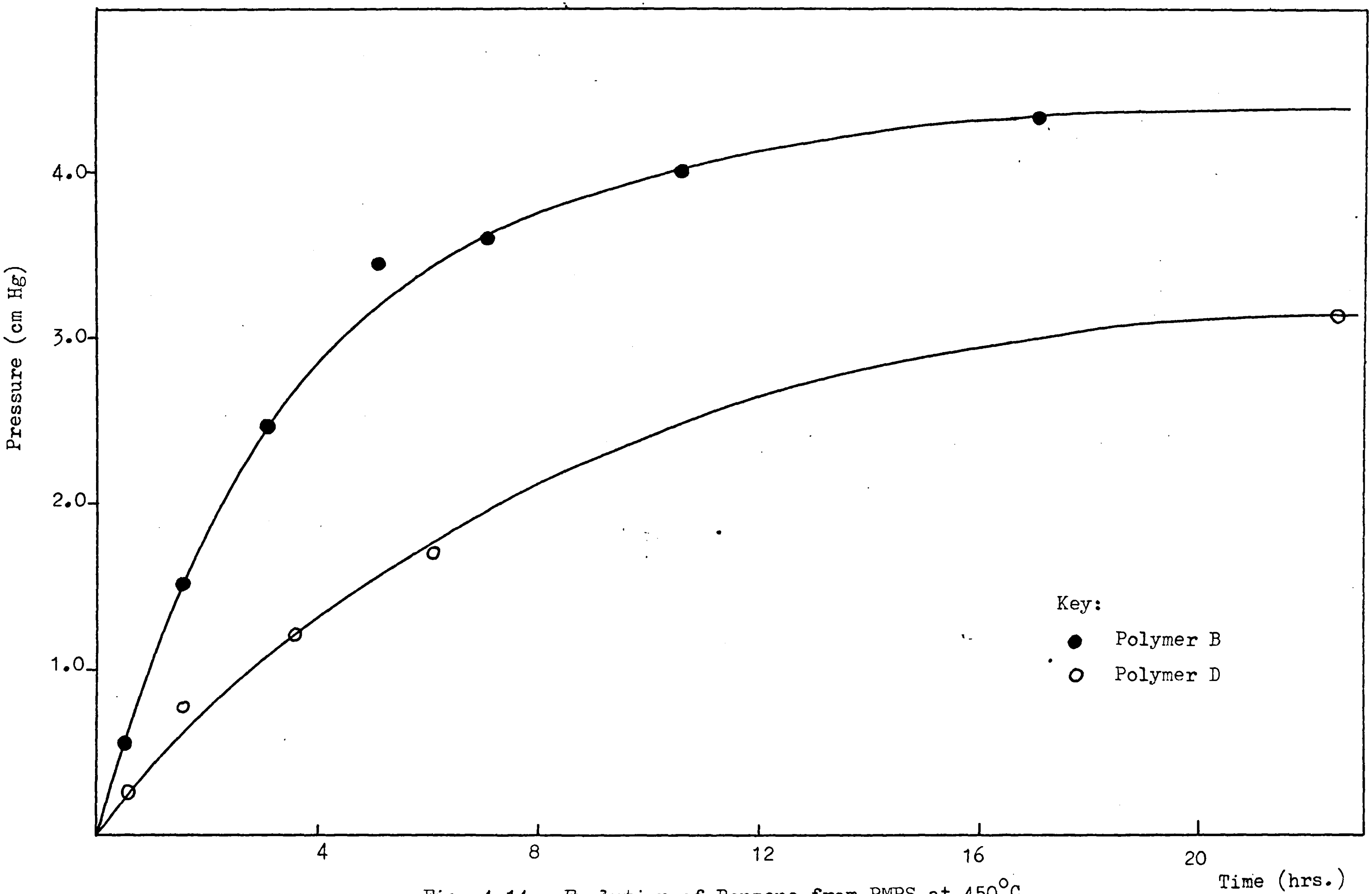


Fig. 4.14 Evolution of Benzene from PMPS at 450°C.

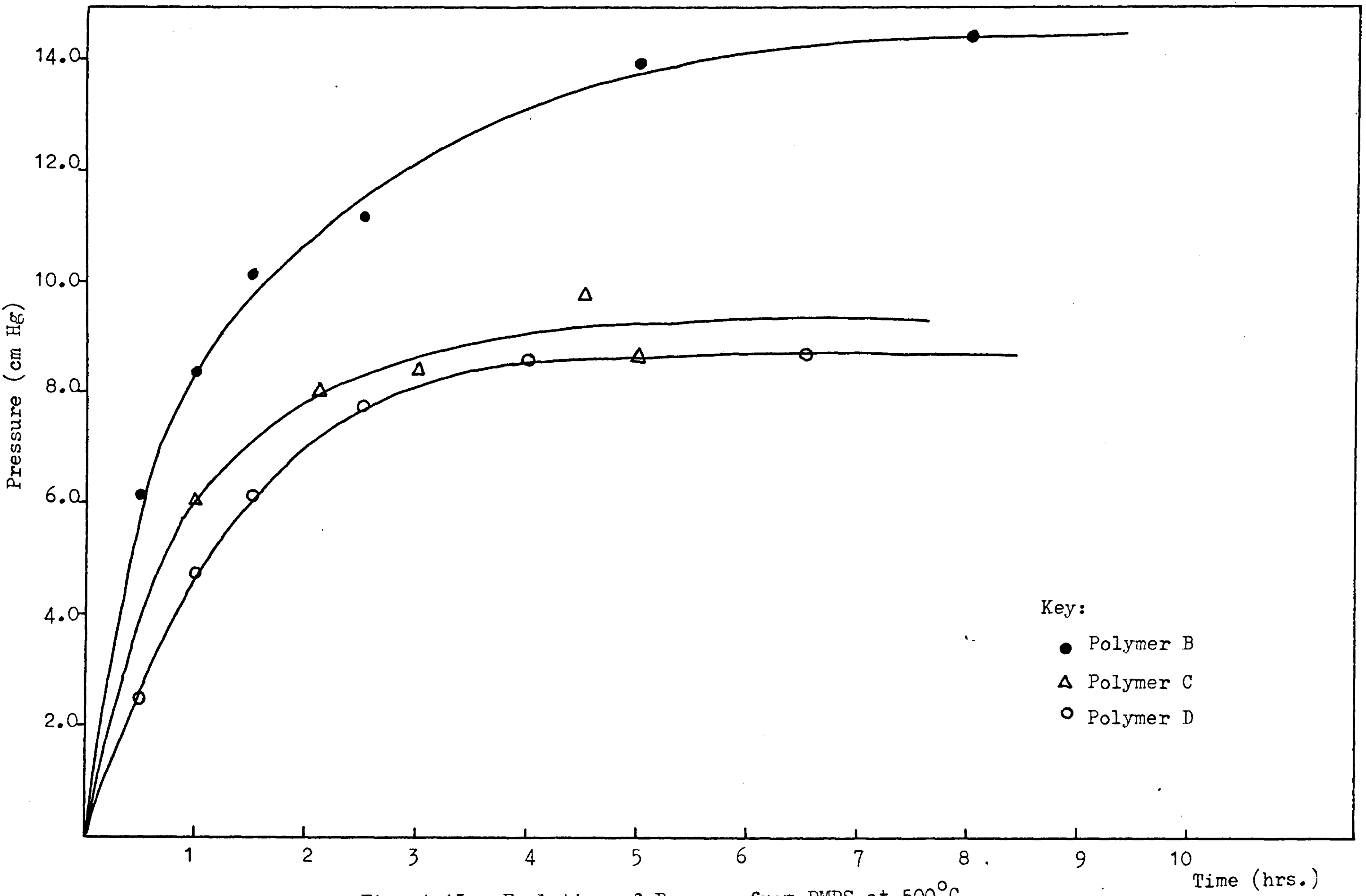


Fig. 4.15 Evolution of Benzene from PMPS at 500°C.

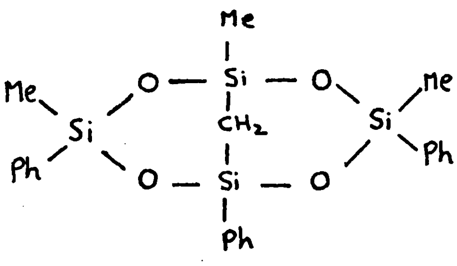
literature has been achieved although complete separation of the tetramer from each other has not been possible. Typical glc traces and conditions are given in figures 4.16, 17 and 18.

The glc trace from the GCMS of the thermal degradation products of PMPS is given in figure 4.19. It can be seen that there are three peaks over and above those assignable to the various trimer and tetramer isomers. These are namely peaks III, VIII, and IX. It has been possible to assign structures using GCMS.

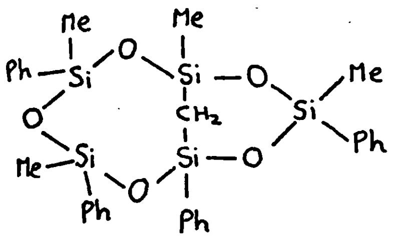
iii) GCMS

GCMS has confirmed the presence of two trimer and four tetramer isomers in the degradation products of PMPS. The mass spectra of peaks I - IX (fig. 4.19) are given in figure 4.20. There is clearly no signicicant difference between the spectra of the various isomers. It is also clear that peak IX is due to cyclic pent amer. This cyclic has not received mention in the literature to date.

Of particular interest are two peaks, III and VIII which come after the trimer and tetramer respectively. The parent ions for these species appear at $^{m}/e$ 466 and $^{m}/e$ 602. It is proposed that these are the M^{+} fragments of the following two structures:



III



VIII

Reasons/

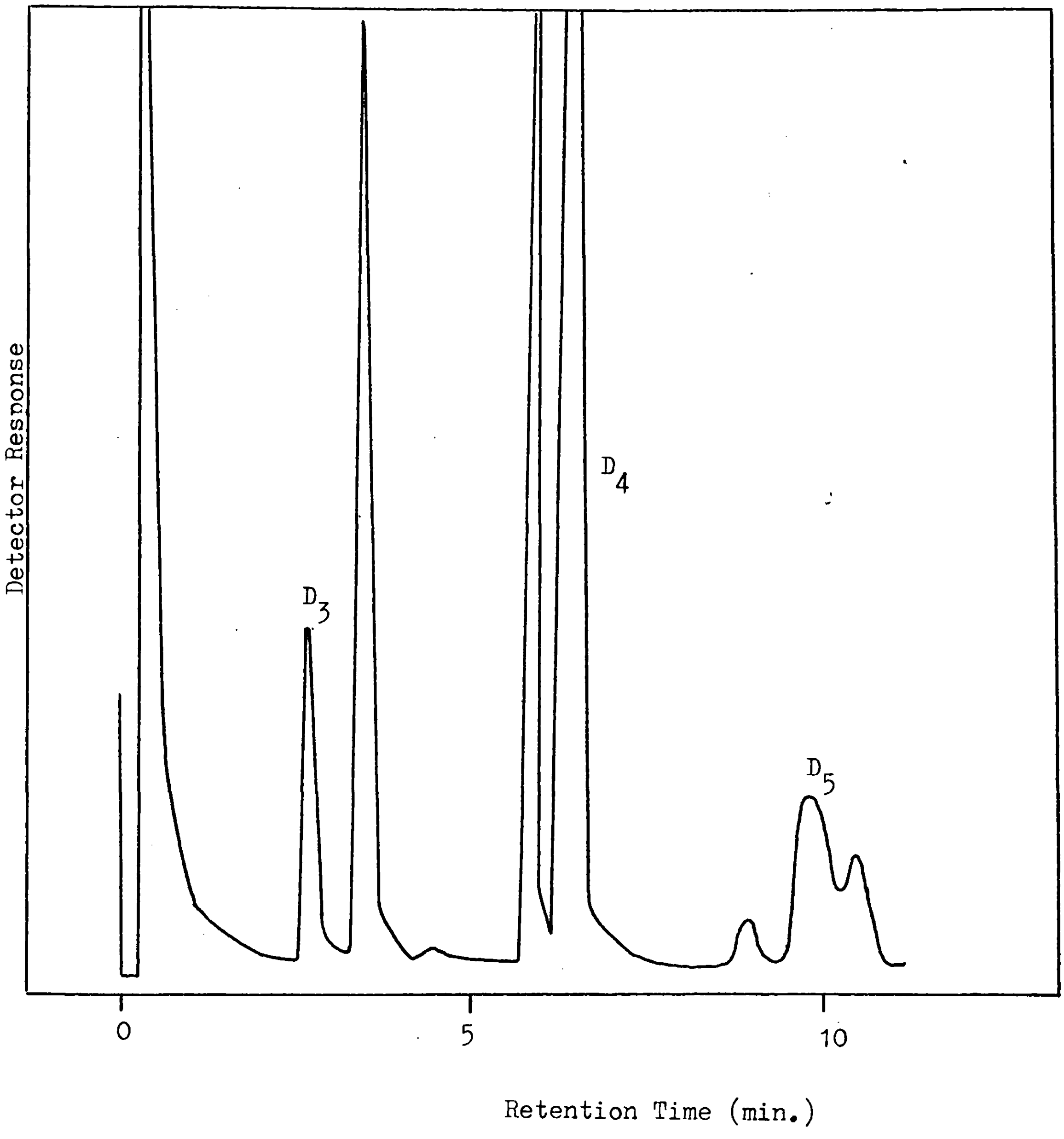


Fig. 4.16 GLC trace for mixture of methyl, phenyl cyclic siloxanes

Column 1% Dexsil

4 min. at 185°C then 8°C $min.^{-1}$

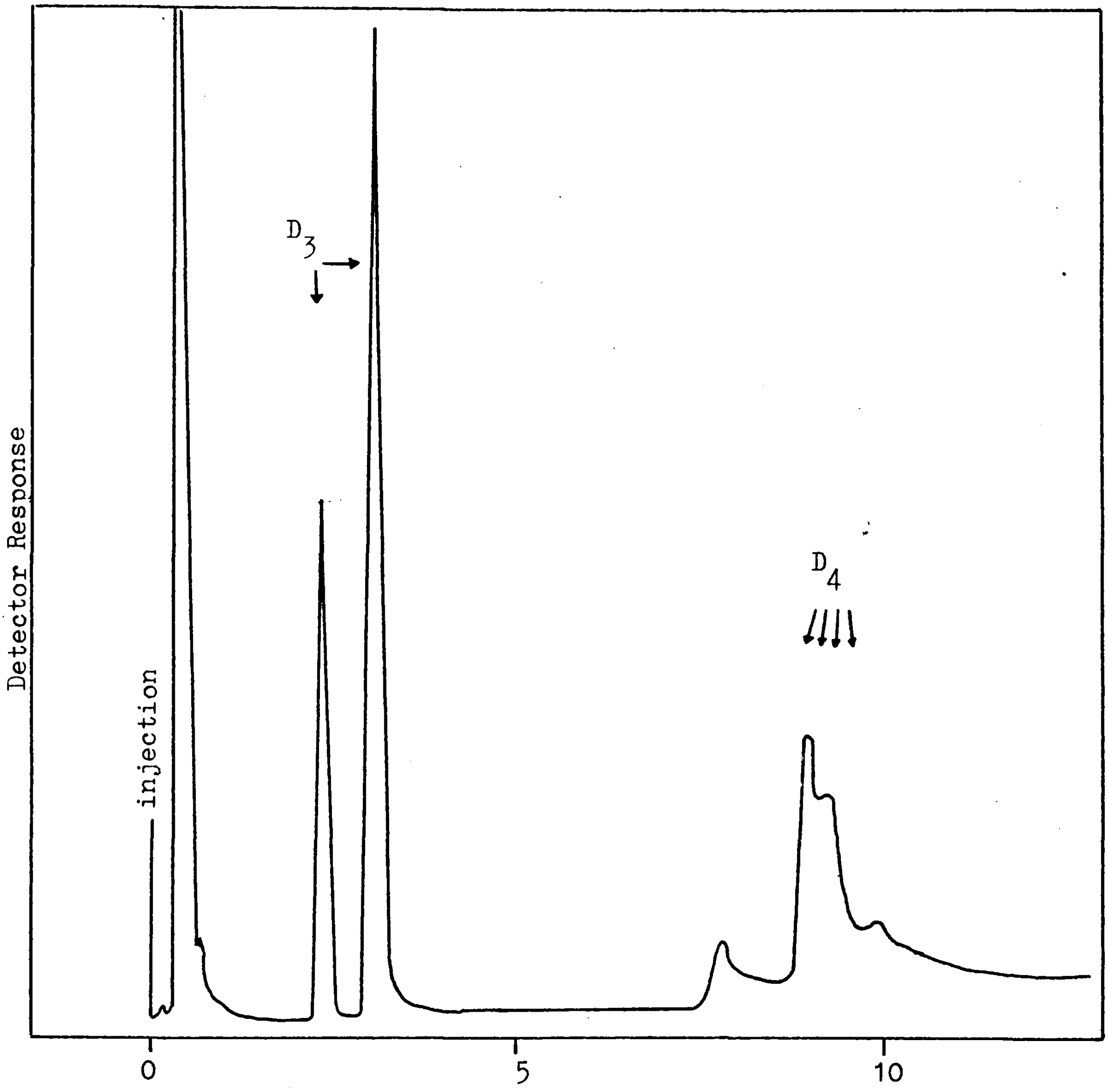


Fig. 4.17 GLC trace for mixture of methyl, phenyl cyclics siloxanes.

Column 1% OV-17

5 min. at 220°C then 3°C min.$^{-1}$

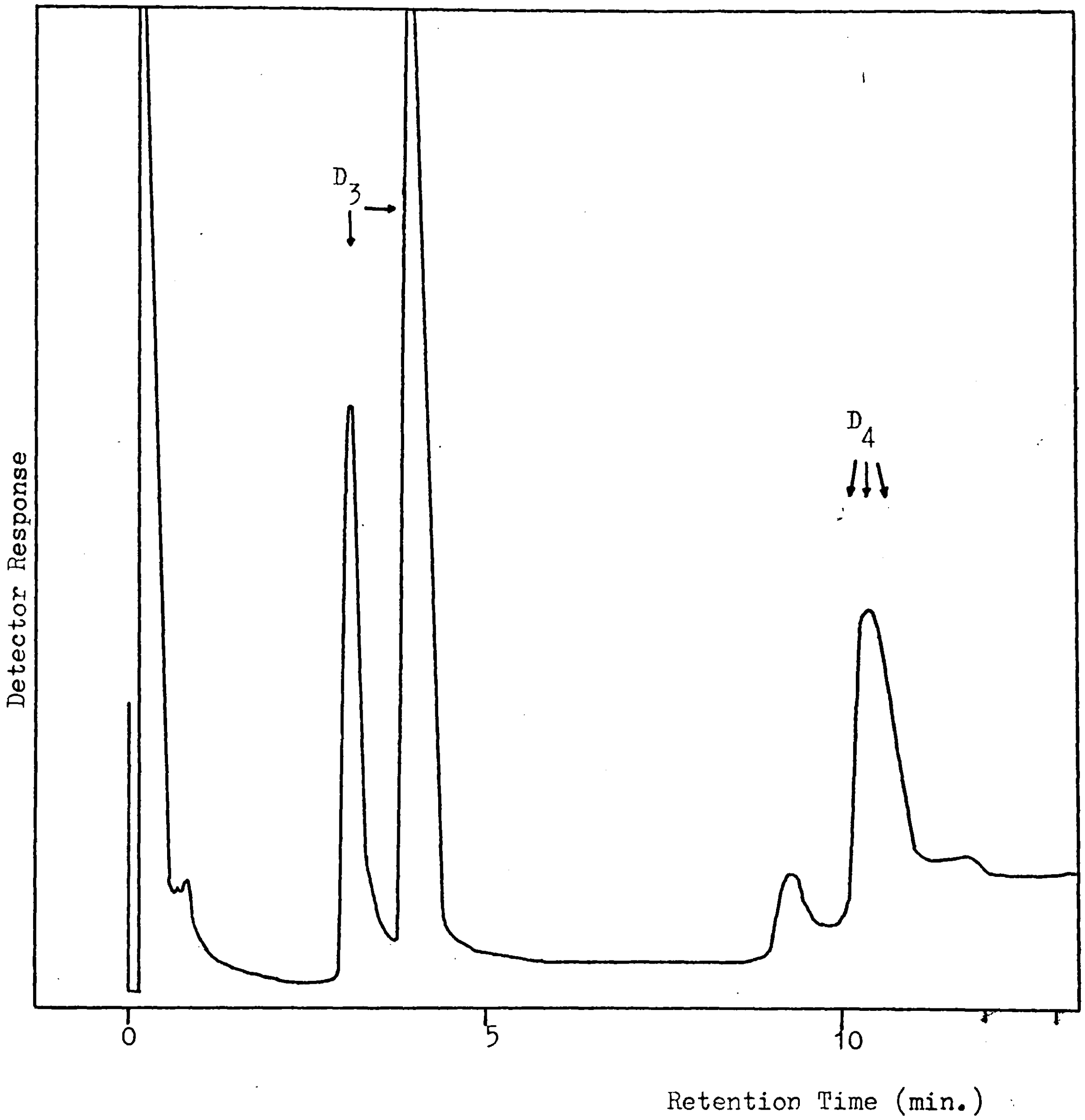


Fig. 4.18 GLC trace for mixture of methyl, phenyl cyclic siloxanes

Column 1% OV-1

5 min. at 200°C then 3°C min.$^{-1}$

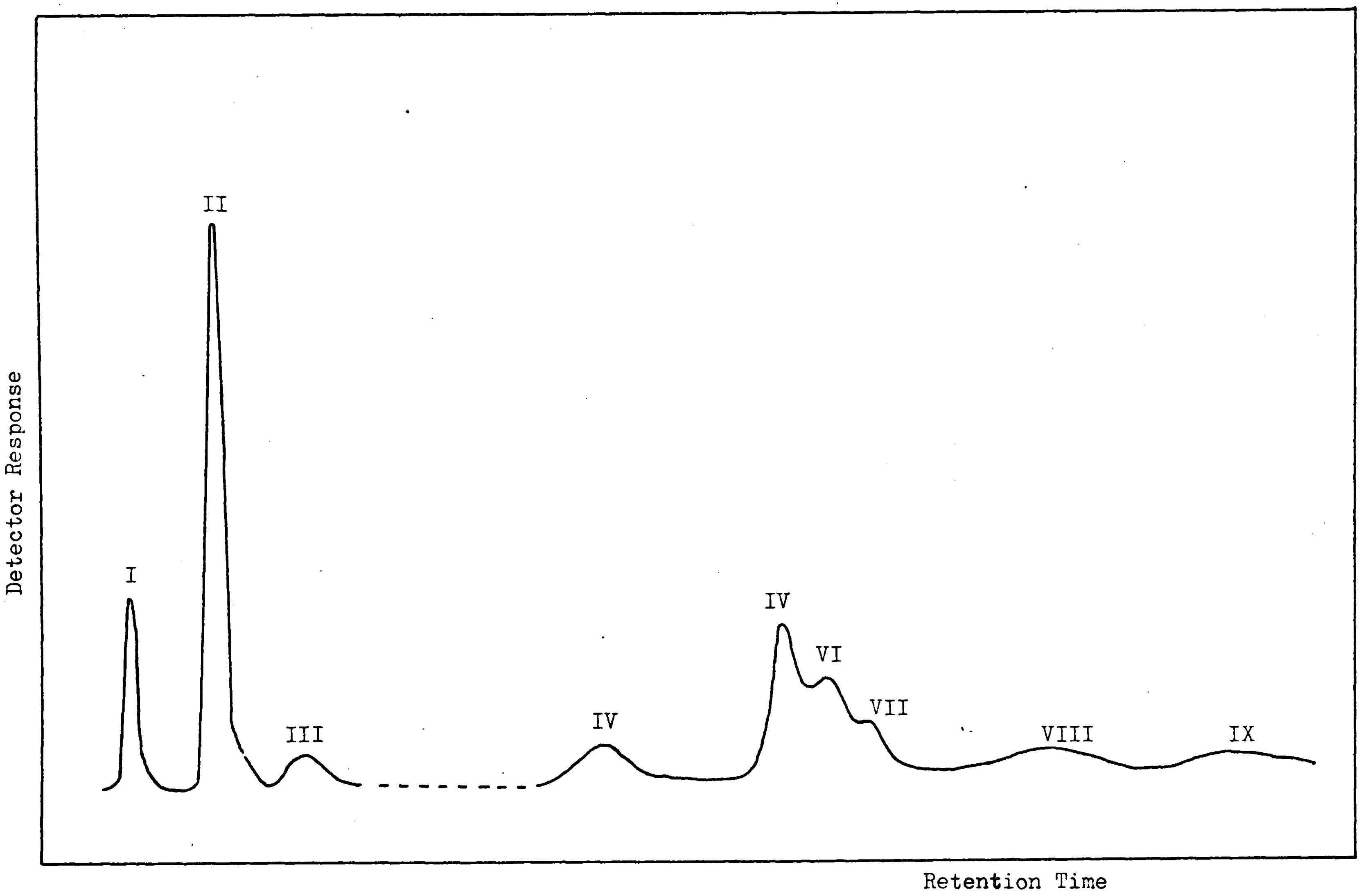
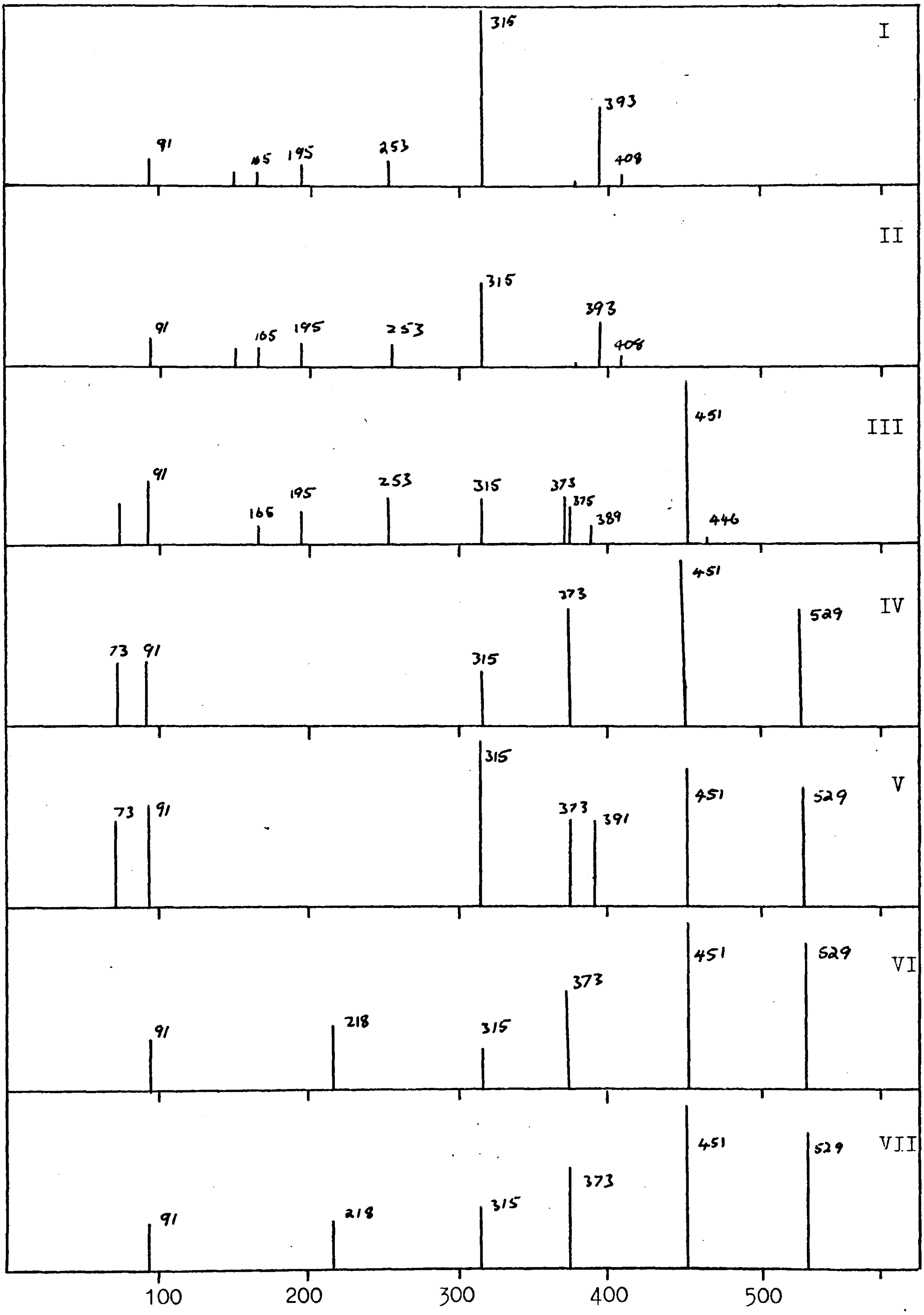


Fig. 4.19(a) GLC trace from GCMS of degradation products of PMPS.


I
91
165
195
253
315
393
408
II
91
165
195
253
315
393
408
III
91
165
195
253
315
373
375
389
451
446
IV
73
91
315
373
451
529
V
73
91
315
373
391
451
529
VI
91
218
315
373
451
529
VII
91
218
315
373
451
529
100
200
300
400
500

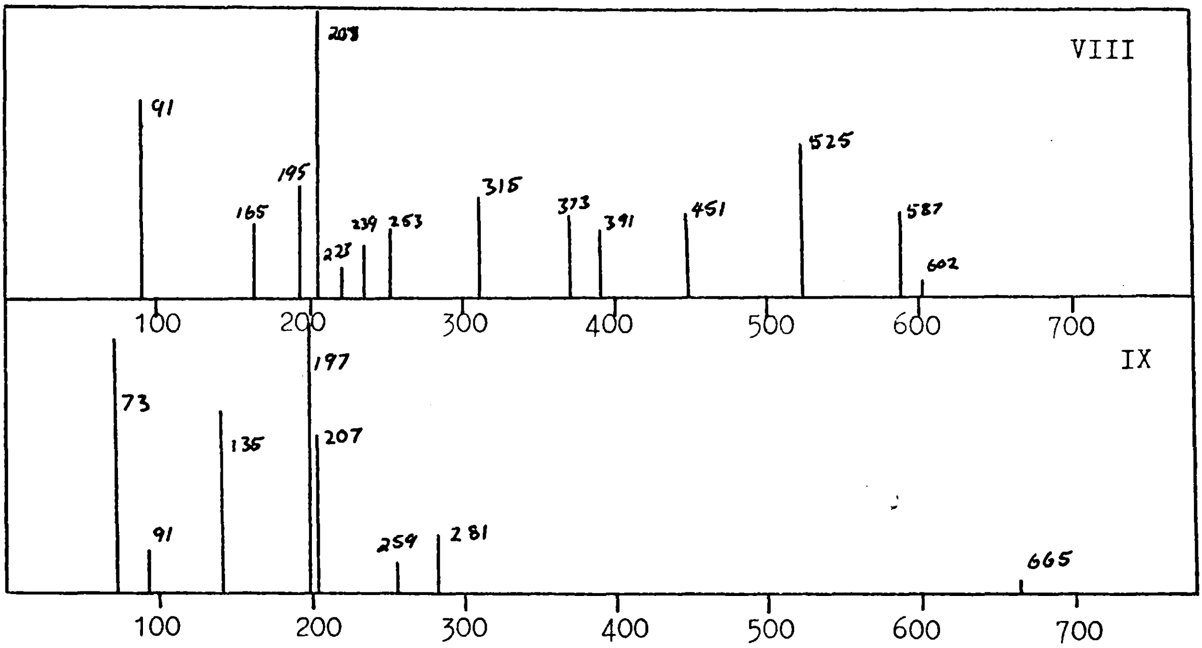


Fig. 4.20 Mass spectra from GCMS of degradation products of PMPS.

Structure Assignment (on basis of reference spectra.)

I	D_3
II	D_3
III	assignment given elsewhere
IV	D_4
V	D_4
VI	D_4
VII	D_4
VIII	assignment given elsewhere
IX	D_5

Reasons for the above assignments will be given below.

(b) QUANTITATIVE ANALYSIS

The relative distribution of products with extent of reaction has not been followed but there are no apparent marked differences in nmr traces taken at several stages of the degradation process. There is also no marked difference in the distribution of products from a hydroxyl-ended polymer from that of one with trimethylsiloxy end-groups. A typical distribution of isomers estimated by integrating nmr peaks is given in figure 4.21.

4.10 DISCUSSION

On the basis of the experimental data presented in the previous sections a mechanism for the degradation of poly(methylphenylsiloxane) is now proposed and discussed. There are several features in the thermal degradation of PMPS which differ from those observed in the PDMS series.

Evidence that the hydroxyl chain-ends affect the degradation of this polymer is given by TGA and other weight loss studies. Surprisingly at first sight, the end-blocking of a polymer with trimethylsiloxy ($-Si(CH_3)_3$) units leads to a sample with lower thermal stability (as measured by weight of residue). It is proposed that the main reaction of the hydroxyl end-groups in the methyl phenyl series is not one of the accelerating depolymerisation, as in PDMS, but of cleavage of a Si-Ph bond according to the following mechanism.

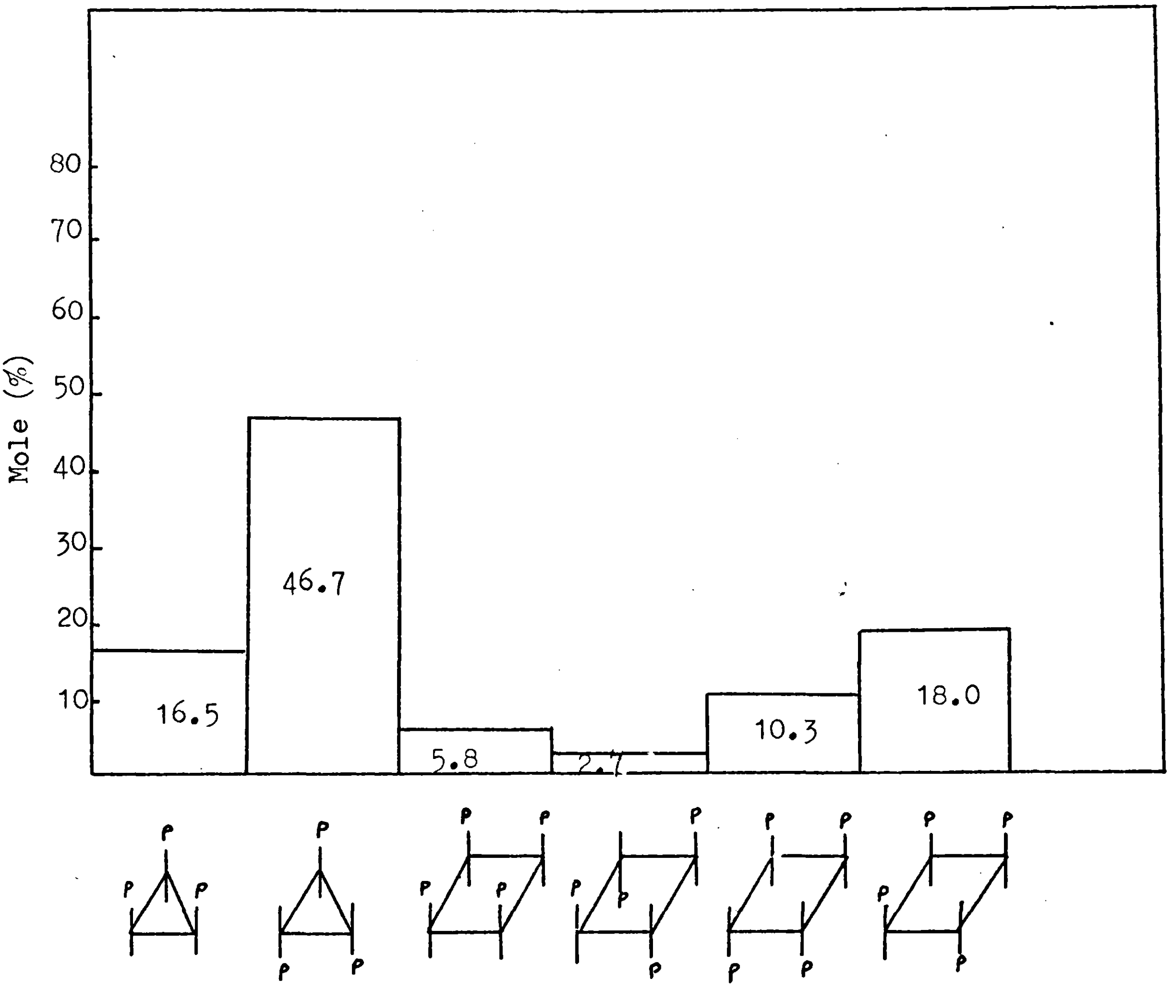
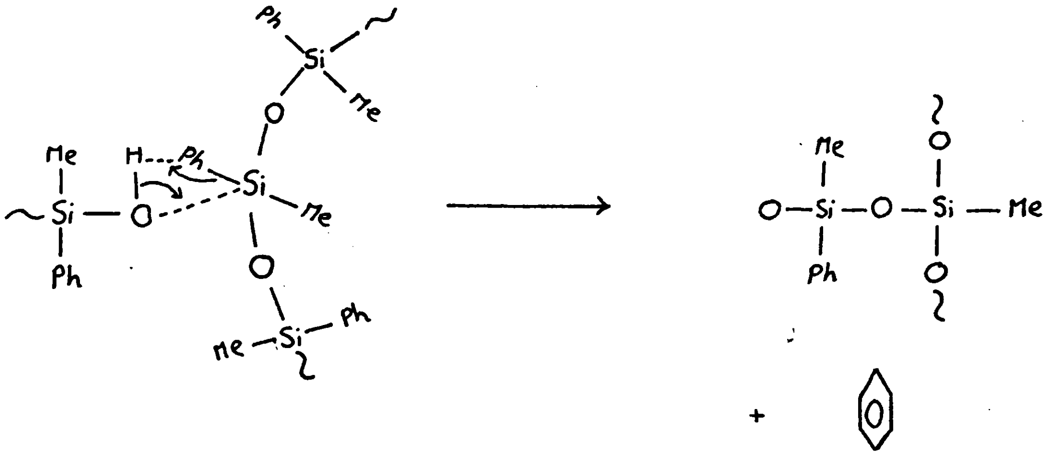
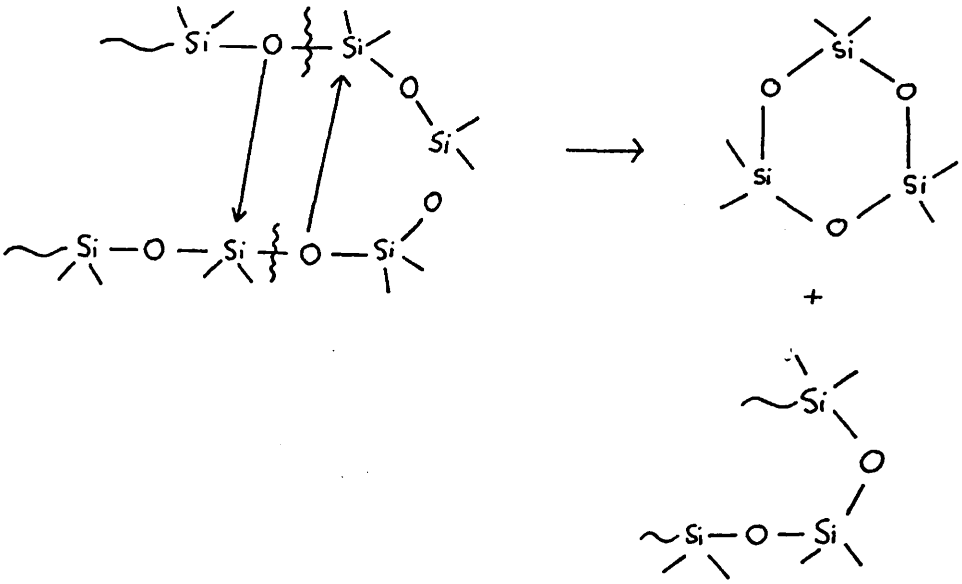


Fig. 4.21 Typical Distribution of Thermal degradation products from PMPS. (Polymer E 500°C 0.5 hrs.)



This mechanism is consistent with the observation that small amounts of benzene are evolved at temperatures below which random cleavage of the Si-Ph bond would be expected. At these lower temperatures the amount of benzene produced is related to the concentration of chain ends (fig. 4.13). This reaction introduces a degree of structurisation into the polymer which will be greater for low molecular weight species than for high molecular weight ones.

With respect to the main depolymerisation reaction, any mechanism for the production of cyclics from the poly siloxanes (apart from postulation of homolytic scission of the Si-O bond) inevitably requires a degree of mobility for the polymer chain. The mechanism presented by Thomas and Kendrick (Ref. 55) is the most straightforward representation for the formation cyclics:



Clearly, this reaction will be inhibited with increasing structurisation of the polymer. In turn this will lead to greater residues from the more structured materials.

The mobility of a polymer end-blocked with trimethylsiloxy units will not be hindered in this manner and under favourable conditions such a polymer can therefore degrade to completion. Thus, trimethylsiloxy end-blocked samples show greater weight loss than similar molecular weight hydroxyl-ended samples under identical heating conditions.

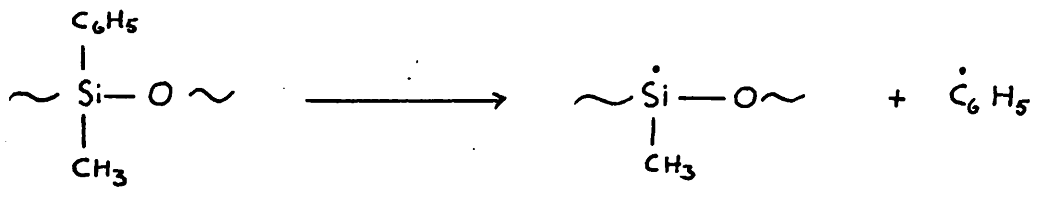
At higher temperatures more benzene is formed than can be accounted for by involvement of chain ends alone. Clearly the Si-Ph bond is being cleaved in a more random process.

This/

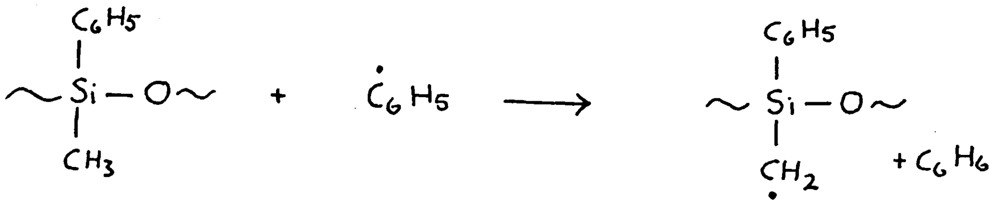
This process should primarily be independent of the initial molecular weight of the polymer. However, secondary factors such as diffusion and chain mobility are often important in determining the course of reactions of this nature, and it is reasonable that at any given temperature the reaction might proceed until such secondary factors prohibit it. Again, at any given temperature this stage will be represented by approximately the same final structure independent of the initial molecular weight of a sample. A low molecular weight sample, might therefore be expected to evolve substantially more benzene than a sample of high molecular weight.

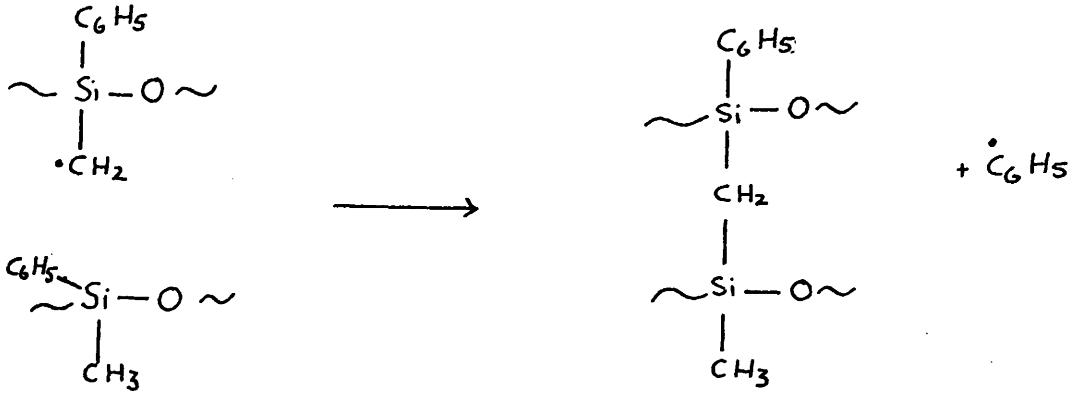
The rate of weight loss should be much less molecular weight dependent, since on the basis of the above argument all samples tend towards the same final structure. Only in the initial stages of degradation will there be substantial viscosity differences which might introduce a molecular weight dependence.

The number of alternative mechanisms for the production of benzene from a polymer system in which there is only a limited source of hydrogen atoms, and in which the postulation of double bond formation is unacceptable (except for C = C), is clearly limited. A free radial mechanism might be written:



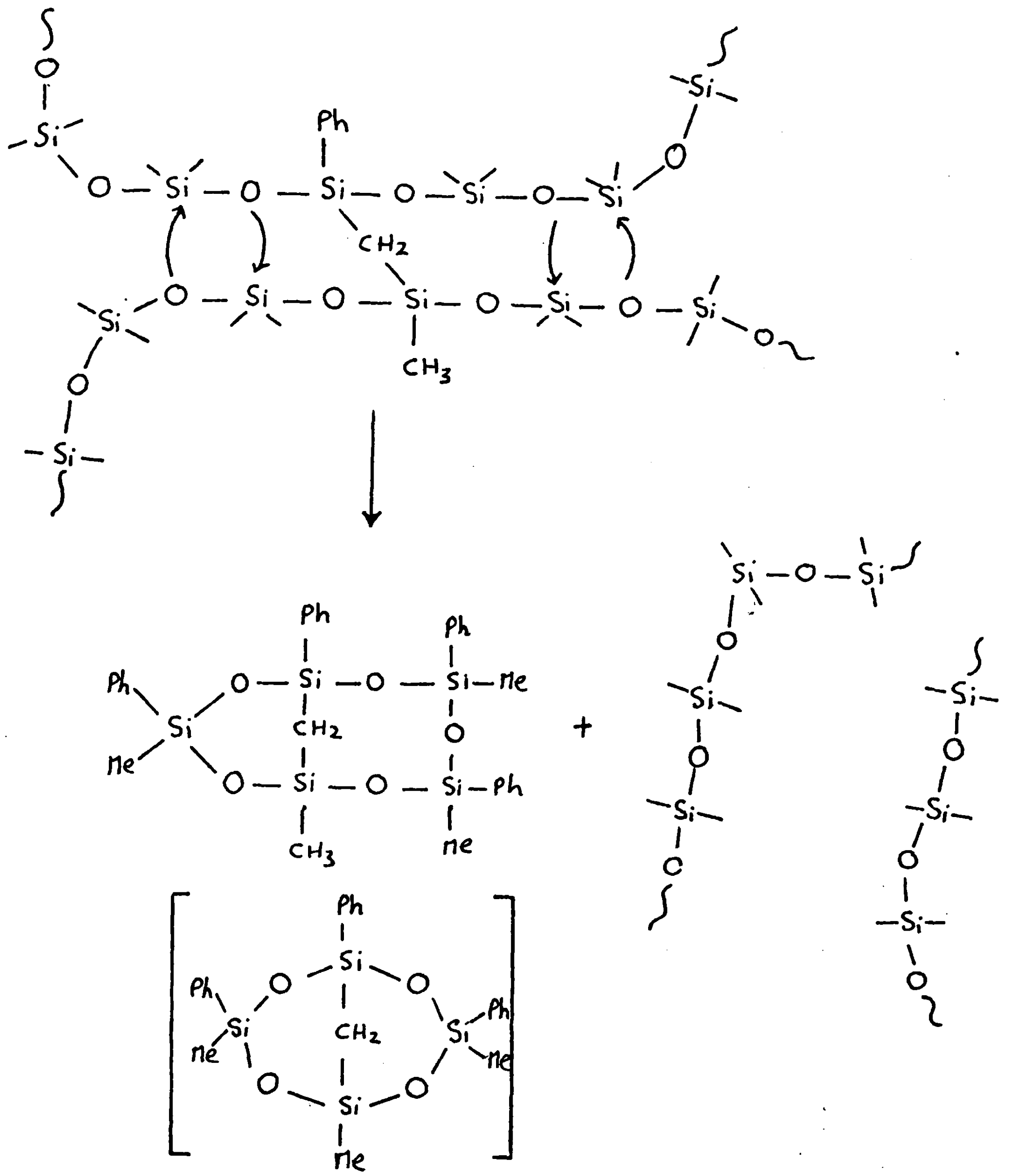
$$\sim \underset{\displaystyle CH_3}{\overset{\displaystyle C_6H_5}{Si}}-O\sim \longrightarrow \sim \underset{\displaystyle CH_3}{\overset{\bullet}{Si}}-O\sim + \overset{\bullet}{C}_6H_5$$





Sobolevskii (Ref. 65) has proposed a similar mechanism for the production of benzene from oligomethylphenylsiloxanes.

If, as shown above, evolution of a benzene molecule results in two chains joined by a methylene bridge then subsequent degradation might be shown thus:



In the glc of the degradation products (fig. 4.19) it was noted that two small peaks appeared over and above those due to the various trimer and tetramer isomers. GCMS has shown that the mass spectra of these species is consistent with their being the two structures drawn above. Clearly, a number of alternative structures can be drawn consistent with the GCMS data, in particular many rearrangements of the above atoms and groups of atoms, but providing a mechanism for their production is not straightforward.

No information on either of these bicyclic compounds is given in the literature.

4.11/

4.11 CONCLUSIONS

1. High molecular weight linear polymers of poly(methylphenylsiloxane) can be prepared from a mixture of cyclic trimer and cyclic tetramer using tetramethylammoniumhydroxide as catalyst.

2. Thermal stability, as measured by rate of weight loss, is substantially greater for poly(methylphenylsiloxane) than for poly(dimethylsiloxane).

3. For hydroxyl-ended species part of this increased stability is associated with slight structurisation of the polymer brought about by reaction of the hydroxyl groups with the Si-Ph bond giving a trifunctional siloxy unit and a molecule of benzene.

4. End-blocking samples with hexamethyldisilazane results in a lowering of thermal stability measured by TGA weight loss. This is due to the increased mobility of these chains over the hydroxyl-ended species which lead to a slightly structured, and therefore more stable, polymer.

5. The major products of degradation of poly(methylphenylsiloxane) are the two isomeric cyclic trimers and the four isomeric cyclic tetramers. A small amount of the cyclic pentamer is formed and benzene is also produced.

6. At temperatures above 400°C benzene is evolved in a random reaction leading to the formation of a methylene bridge between two chains.

7. There is some evidence that the methylene bridge formed when benzene is evolved can be incorporated into the products of thermal degradation as part of two bicyclic species hitherto unreported.

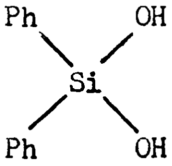
CHAPTER 5

POLY(DIPHENYLSILOXANE)

5.1 INTRODUCTION

From a survey of the literature it appears that co-polymers containing relatively small proportions of phenyl groups can be easily prepared and are indeed prepared for commercial purposes. However, no detailed description of the preparation of pure poly(diphenylsiloxane) could be found.

A convenient preparation of the phenyl diol (diphenylsilanediol) in high yield is given by Burkhard (Ref. 91) as is the subsequent preparation of the cyclic tetramer (and cyclic trimer). As far as polymerisation of the tetramer to the linear polymer is concerned, however, only comments of the following type could be found.



a) Laita and Yelinek (Ref. 131) talk of polymerising a sample of the cyclic tetramer in bulk at approximately 230°C using KOH as catalyst. No details are given.

b) Andrianov et. al. (Ref.132) make the comment that for the polymerisation of dimethylphenylmethyl and dimethyldiphenylcyclosiloxanes in the presence of acid or basic catalysts the m.wt. of the polymers decreases to a considerable extent as the number of phenyl groups in the initial cyclosiloxanes is increased.

c)/

c) Concerning the polymerisation at 150°C of siloxanes with methyl and phenyl substituents in presence of 0·5% of KOH as catalyst, Andrianov and his colleagues (Ref. 121) make the further comment that the rate of polymerisation decreases with increase in the number of phenyl substituents. Thus for heptamethylphenylcyclotetrasiloxane, 50% conversion was achieved in 12 minutes, while for a ring with 4 methyl and 4 phenyl substituents, tetramethyltetraphenylcyclotetrasiloxane, 50% conversion was only achieved after 5200 minutes.

Since the melting point of the cyclic tetramer is 202°C, bulk polymerisation would have to be carried out at an even higher temperature. It was therefore decided to attempt a solution polymerisation at some lower temperature.

In an attempt to polymerise a mixture of phenyl and methyl tetramers Laita and Yelinek (Ref.131) found that at 160°C and using KOH or NaOH as catalyst the phenyl tetramer polymerised first until all was used up after which the methyl tetramer began to polymerise. The methyl tetramer thus acts as an inert solvent. It is unlikely that the complete absence of methyl groups in the phenyl polymer could be guaranteed by this method but it does rather suggest that using another solvent, the ring might be cleaved and polymerisation take place at this temperature and using one of these catalysts.

5.2 ATTEMPTS TO PREPARE POLY(DIPHENYLSILOXANE) IN SOLUTION

With all the above factors in mind experimental work was carried out as follows.

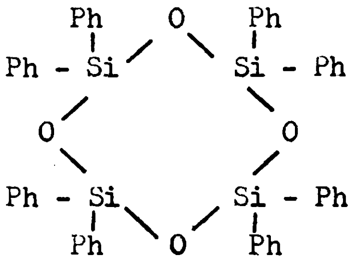
(a)/

(a) Preparation of diphenylsilanediol

Diphenyldichlorosilane was converted to diphenysilanediol using the method of Burkhard (Ref. 91).

The diol was recrystallised from methyl acetate to give white needles (m.pt. 140-143°C). Literature values of melting point are widely variable (133-160°C) and seem to depend upon the method of crystallisation. However, the infra-red spectrum of these crystals is identical with those of Tatlock and Rochow (Ref. 93) and Thompson (Ref. 133).

(b) Preparation of cyclic tetramer (Ref.91)



A few drops of aqueous sodium hydroxide were added to a solution of the diol in boiling 95% absolute alcohol. White crystals separated out. These were recrystallised from warm methyl acetate to give white crystalline plates. The infra-red spectrum indicated that the product was pure tetramer (Ref. 91).

(c) Selection of high boiling solvent for polymerisation

Four solvents which might be suitable for carrying out the polymerisation at 160°C were examined.

i. Nitrobenzene (b.pt. 210°C). This solvent dissolves both diol and phenyl tetramer. On addition of solid KOH at high temperature the nitrobenzene darkens in colour and a deep red/brown solid begins to precipitate. This also happens with aqueous KOH. Aqueous NaOH appears to leave the solvent unaffected. The toxicity of this solvent makes it rather unattractive.

ii. Diphenylether (b.pt. 259°C). Diphenylether dissolves both/

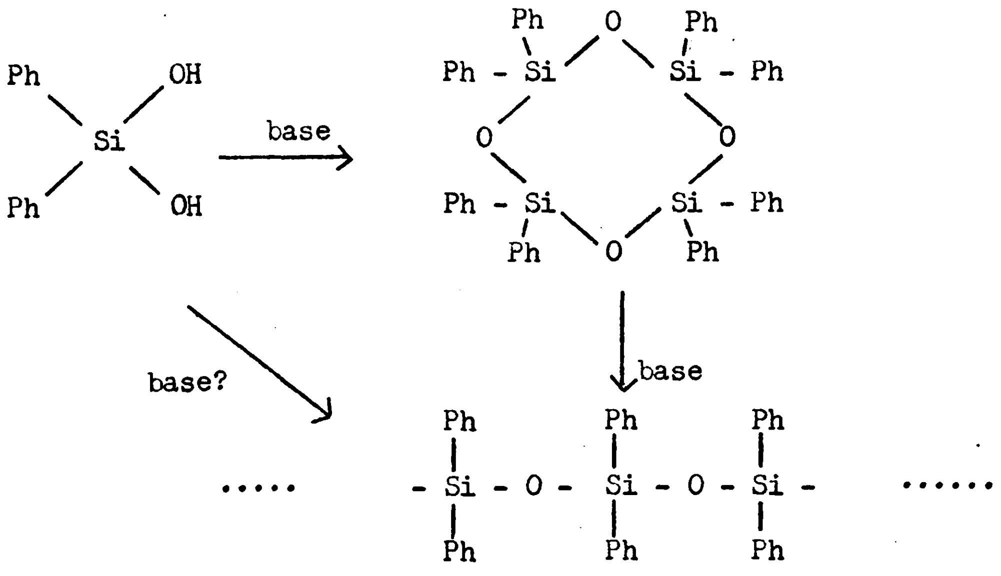
both diol and phenyl tetramer. On additon of solid KOH, the KOH becomes a slurry and the pale yellow of the solvent deepens at high temperatures. The solvent colour also deepens when aqueous NaOH or KOH is added. However, being a solid at room temperature (m.pt. 28°C) this solvent is less easy to work with.

iii. "Digol" (diethylene glycol) (b.pt. 241-248°C). $[O(CH_2\text{-}CH_2OH)_2]$. This solvent dissolves diol but not phenyl tetramer.

iv. "Dimethyldigol" (diethylene glycol dimethylether) $[(CH_3C\text{-}CH_2\text{-}CH_2)_2\cdot O]$ (b.pt. 160-161°C). This solvent dissolves both diol and tetramer and was generally the most suitable of the four.

(d) Attempts to prepare poly(diphenylsiloxane)

Since the catalyst for the conversion of diphenyl silane diol to D_4 and for the polymerisation of the tetramer are the same, it seems possible that polymerisation may be possible directly from the diol.



Thus/

Thus two attempts have been made to polymerise the diol in solution as follows:

1. Diphenylsilanediol (5g) was dissolved in 150 ml. of diethylene glycol dimethylether maintained at 150°C and continuously stirred. 0·5 ml. of an aqueous solution of NaOH (0·005g) was added. After 3 hours the mixture was added to a large volume of water but the white precipitate had an infra-red spectrum identical with that of the cyclic tetramer showing that polymerisation had not occurred.
2. A further attempt was made using a higher concentration of diol (10g in 90g of solvent), a higher catalyst concentration (1 ml. of aqueous NaOH) and a slightly higher temperature (158°C). Once again no polymerisation occurred.

5.3 PREPARATION OF POLY(DIPHENYL SILOXANE) IN BULK

These attempts to prepare poly(diphenylsiloxane) in solution from the diol being unsuccessful, some further attempts were made using the diol and cyclic tetramer in bulk, the latter at higher temperatures. Details are as follows:

A sample of the diol, prepared from diphenyldichlorosilane, as described by Burkhard (Ref. 91), was heated in air at 110°C for 3 days. A viscous gum was formed. The molecular weight of the product was too low for accurate osmotic measurement, but was clearly very much less than 5000.

A big problem in this system is the separation of starting material (effectively cyclic tetramer) from polymeric material.

Work/

Work so far indicates that good solvents for tetramer are equally good for polymeric material so that separation by precipitation is not possible. Also, the tetramer, octaphenylcyclotetrasiloxane, (m.pt. 201-2°C; b.pt. 330-340°C/1mm) cannot be easily removed by evaporation. Laita and Yelinek (Ref. 131) mention this problem but offer no solution.

The i.r. spectrum of the above product, figure 5.1 as far as the phenyl stretch absorptions are concerned, is the same as for cyclic tetramer, but the Si-O-Si stretch area (1000-1100 cm^{-1}) is much broader and less clearly defined, rather like that described by Lady and his colleagues (Ref. 134) who give no indication of the molecular weight of their product and only the briefest mention of how it was prepared.

In order to try to distinguish between the cyclic tetramer and the "polymeric" product some thermal analyses were carried out. Thermal volatilisation analysis (TVA) thermograms were obtained for cyclic tetramer and the "polymer" whose preparation was described above. In neither case were there any products volatile at temperatures up to 0°C. In both cases the sample was completely volatilised to form "cold ring." The infra-red spectrum of the cold ring from the tetramer was identical with that of the original tetramer so that volatilisation was clearly taking place without chemical change.

Thermal gravimetric analysis (TGA) of the "polymer" demonstrated that volatilisation occurred in two steps as shown in figure 5.2. The infra-red spectrum of the "cold ring," shown in figure 5.3, is different to that of the tetramer and of the "polymer" (fig. 5.1). In particular, new peaks appear in the

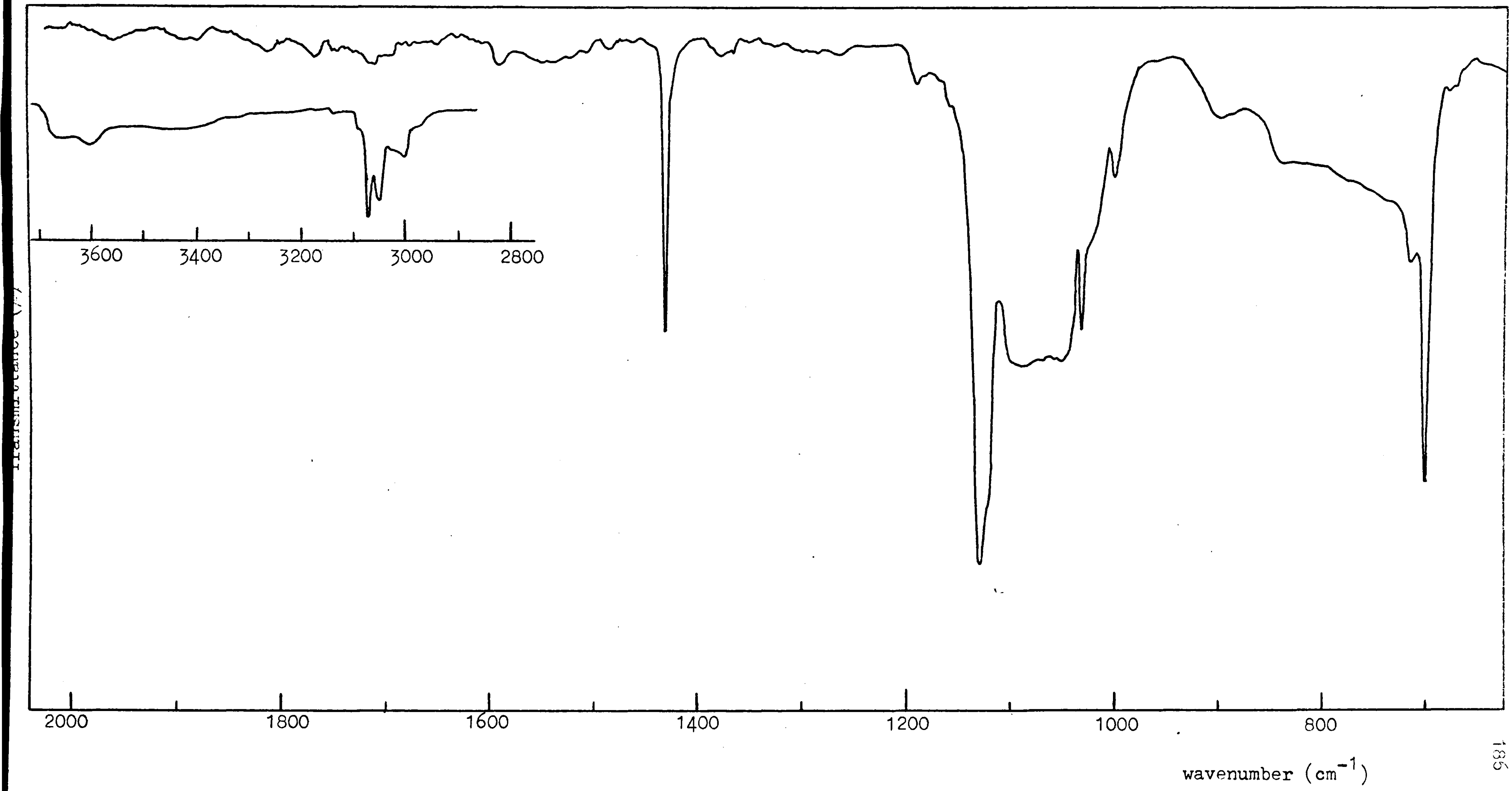


Fig. 5.1(a) IR Spectrum of diphenylsiloxane "polymer".

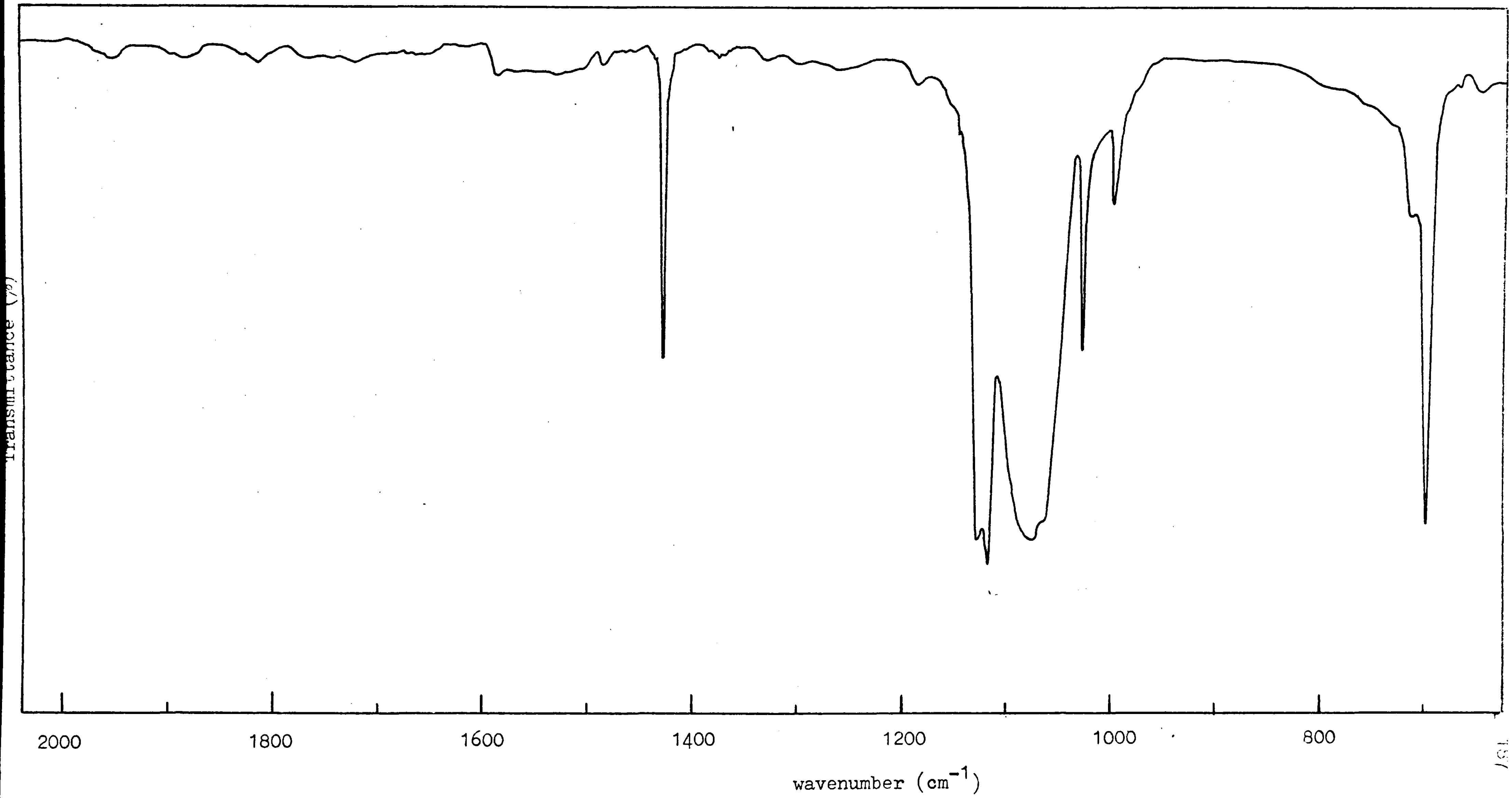


Fig. 5.1 (b) IR spectrum of diphenylsiloxane tetramer

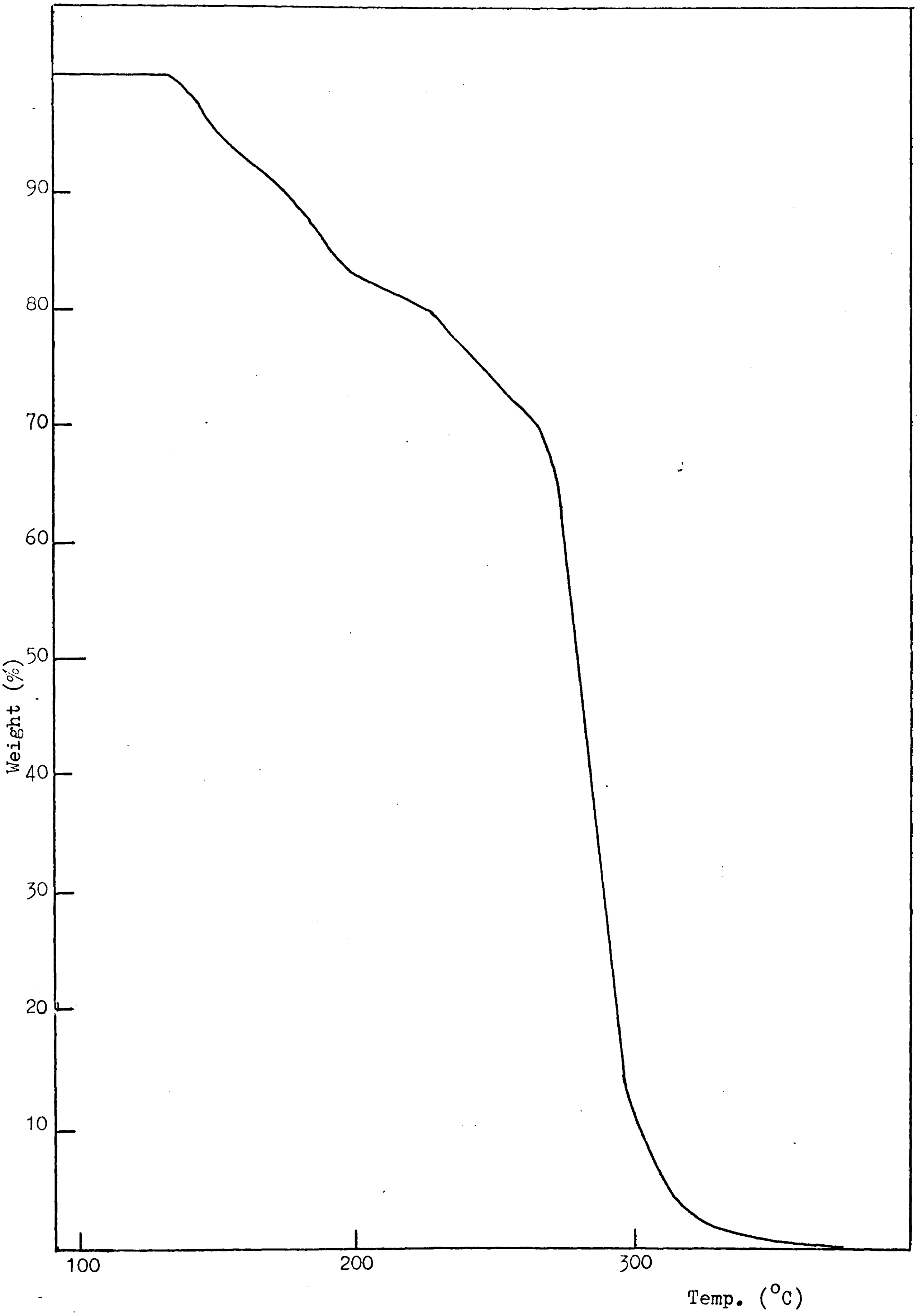


Fig. 5.2 TGA (under vacuum) of diphenylsiloxane "polymer"

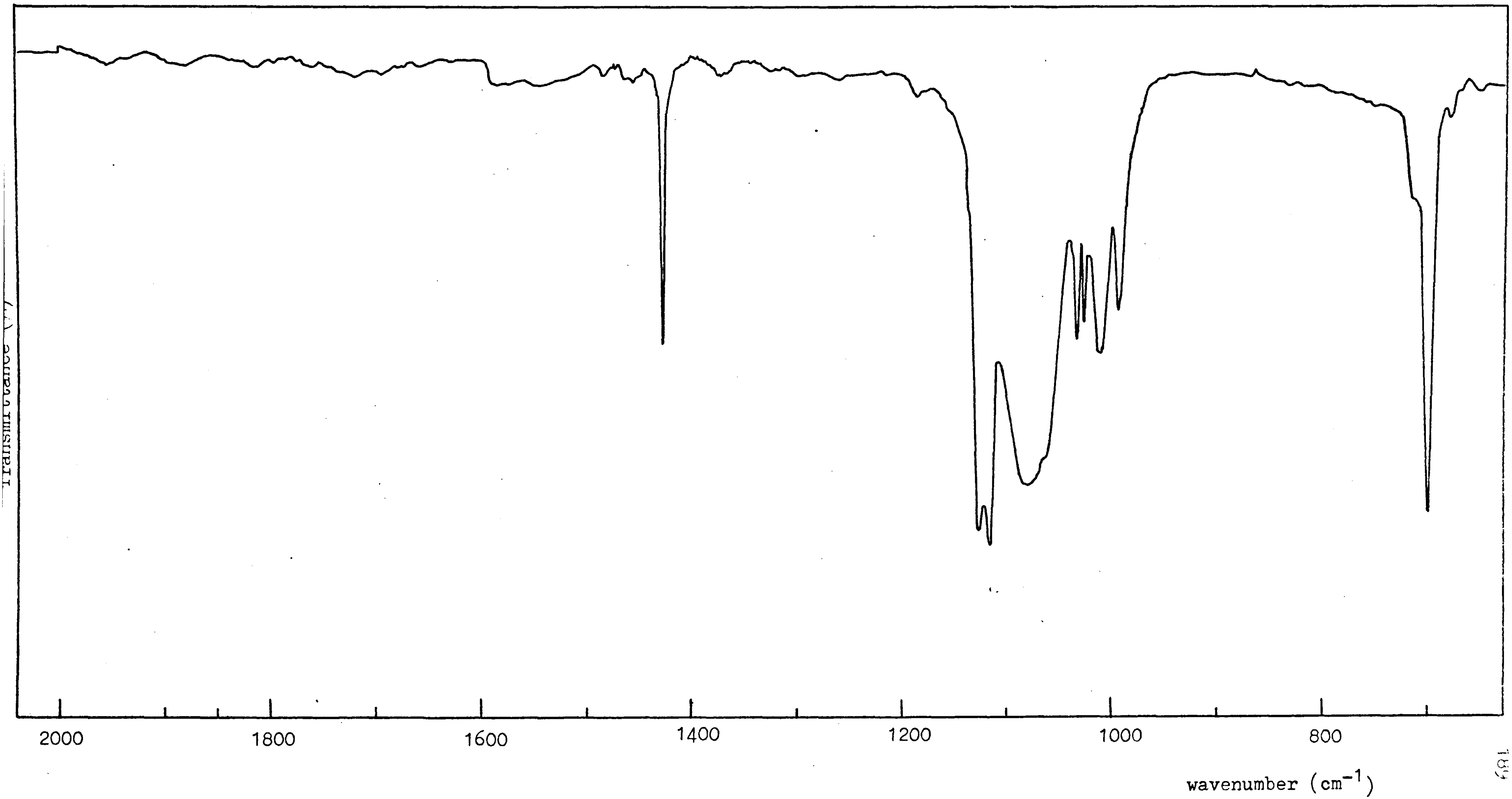


Fig. 5.3 IR Spectrum of cold ring from degradation of diphenylsiloxane "polymer".

Si-O-Si region (1000-1100 cm^{-1}). It is clear that the "polymer" has not volatilised unchaged, which in any case is unlikely since even quite a short chain polymer should be expected to be of low volatility in view of the very low volatility of the tetramer. It is suggested that the TVA and i r. data are evidence that some very short chain polymer was formed in the polymerisation process and that the cold ring is probably a mixture of degradation products, trimer (Refs. 89, 94, 133) and tetramer. This line of investigation was not pursued further in view of the general failure to obtain clear cut polymers with usefully high molecular weights.

Three further attempts to prepare a high molecular weight polymer sample were made using bulk tetramer at 230°C. Details were as follows:

a. 12 hours in static air

b. 24 hours in vacuum

c. 4 days in vacuum

In each case approximately 0·1% of KOH was used as catalyst. The products of all three reactions were deep brown in colour and soluble in CCl_4. Like the previously prepared sample, molecular weights were very low. The Si-O-Si regions (1000-1150) of the infra-red spectra of all three "polymers" are similar to that of the polymer described above.

These experiments thus confirm the impression given by the literature that high molecular weight poly(diphenylsiloxane) is not readily prepared.

CHAPTER 6

POLY(DIMETHYLDIPHENYLSILOXANE)

6.1 INTRODUCTION

Work to be described in this chapter relates to some preliminary studies of the preparation and thermal degradation of copolymers containing dimethyl and diphenyl units, prepared by copolymerising cyclic dimethyl tetramer with cyclic diphenyl trimer or tetramer using potassium hydroxide or tetramethylammonium hydroxide as catalyst.

Gilbert and Kantor (Ref. 79) in their paper on transient catalysts for the polymerisation of organosiloxanes give brief details of the preparation of a copolymer from 10 g of diphenyl tetramer in 95 ml. of dimethyl tetramer using a dimethylsilanolate catalyst. Their copolymer had a viscosity of 5×10^6 centipoises but further details of purification and characterisation are not given.

Merker and Scott (Ref. 135) have given a value of 24·9 as a measure of the relative reactivity of diphenyl trimer to dimethyl trimer at 40°C but this figure was not arrived at by direct reaction of these two species.

One of the main difficulties encountered in a systematic

study/

study of this copolymer system is the separation of residual high boiling cyclics from the polymer. Merker and Scott (Ref. 135) have commented on this problem. They found it necessary to keep the monomer feed low in diphenyl trimer. On the basis of their results they have concluded that reactivity is enhanced by substitution of electronegative (phenyl) groups for methyl groups.

Laita and Jelinek (Ref. 136) have shown that in the anionic copolymerisation of diphenyl tetramer with dimethyl tetramer, a phenomenon analogous to that observed in radical polymerisation is observed, the presence of one monomer inhibiting the polymerisation of the other. The diphenyl tetramer polymerises first and only after its disappearance does the dimethyl tetramer begin to polymerise. Once the diphenyl tetramer has disappeared the dimethyl tetramer polymerises slowly. Andrianov et. al. (Ref. 137) using GPC to analyse the reaction mixture during the early stages of polymerisation have not obtained evidence to support the observations of Laita and Jelinek. They claim that dimethyl units are incorporated during the early stages of the polymerisation reaction.

As late as 1970 Andrianov et. al. (Ref. 138), in a paper on the synthesis and properties of these copolymers, make the comment that "there are no systematic data in the literature relating to the properties of copolymers of the poly(dimethyldiphenylsiloxane) series." In this paper they show that there is an induction period in the copolymerisation of dimethyl tetramer with diphenyl tetramer which increases with the concentration of diphenyl tetramer. At the same time there is a reduction in the molecular weight of the copolymer obtained when equilibrium is reached. They also show that/

that the presence of diphenyl groups in the framework of the siloxane chain changes the properties of the latter substantially. This is explained by the reduction in mobility of the macromolecules because of the bulky diphenyl groups: this leads to an increase in the glass transition temperature, and to the loss of the capacity of the polymer to crystallise if the concentration of the diphenylsiloxane groups is more than 4%.

Again in 1972 Andrianov et. al. (Ref. 139) attempted to apply the Mayo and Lewis method to determine the relative reactivities of dimethyl tetramer and diphenyl tetramer. These workers have described the development of a GPC technique for determining the composition of the reaction mixture at different stages of the process, a measurement which is otherwise difficult. Using this method they find it possible not only to determine the copolymer yield but also to separate high boiling diphenylcyclosiloxanes and octaphenylcyclotetrasiloxane from unreacted octamethylcyclotetrasiloxane.

Investigating the kinetics of copolymerisation they have found that the rate of formation and the equilibrium yield of copolymer were both regularly reduced with increasing concentration of octaphenylcyclotetrasiloxane in the initial mixture. It was observed that with all diphenyl : dimethyl ratios used the polymers formed during the early stages of conversion were enriched with diphenyl units. However, even in the early stages dimethyl tetramer polymerises and dimethylsiloxane units are included in the copolymer chain. Thus in a system containing 20 mole % octaphenylcyclotetrasiloxane the copolymer formed at 13% conversion will already contain 50 mole % of dimethylsiloxane units.

Control experiments run with mixtures containing over 90 mole % of octaphenylcyclotetrasiloxane and similar experiments with pure octaphenylcyclotetrasiloxane showed a complete absence of polymerisation while the mixtures were kept at 160°C for a "lengthy period of time." (Ref. 139).

Andrianov et. al. (Ref. 139) have also shown that in the above copolymerisation chain transfer reactions take place at approximately the same rate as the propagation reactions. This means that the applicability of the Mayo - Lewis (Ref. 141) method, when the latter is used for quantitative determination of the relative reactivities of organocyclosiloxanes in ionic copolymerisation reactions, is limited (Ref. 139).

E.E. Bostick (Ref. 140) has done some work on the preparation of block copolymers of diphenyl and dimethyl units using a lithium silanolate catalyst.

Due to the importance of using only samples with well defined structures in a systematic study of a polymer or copolymer system a proportion of the time devoted to the work described below has been concerned with the construction of a GPC column and ancillary equipment.

6.2 PREPARATION OF COPOLYMERS

An attempt has been made to prepare copolymers of dimethyldiphenylsiloxane from dimethyl tetramer and diphenyl trimer or tetramer using the method described in chapter 2.

Six/

Six copolymers have been prepared using various monomer feed ratios. Details are given in Table 6.1. Attempts to prepare copolymers from mixtures with greater than 30 mole per cent diphenyl units were not successful.

6.3 PURIFICATION AND CHARACTERISATION OF COPOLYMERS

The GPC column described in chapter 2 has provided a successful means of separating diphenyl tetramer and other high boiling low molecular weight cyclics from the copolymers. A typical GPC trace from the mixture formed during preparation of copolymer E is given in figure 6.1. The alternative and more convenient method of separation by reprecipitating the polymer from a solvent-nonsolvent mixture (toluene, methanol) has not proved effective for this separation where the diphenyl tetramer is present in appreciable amounts.

Infra-red examination of copolymers

The infra-red spectra of copolymers of this series are as expected. They show the Si-Ph absorption at 1430 cm^{-1} and Si-Me at 1260 cm^{-1}. The spectra of two of the copolymers are shown in figures 6.2 and 6.3.

These absorptions provide a convenient method for evaluating the methyl : phenyl ratio in this copolymer system. This ratio has been calculated for copolymers A - E using values of 384 and 202 for the molar extinction coefficients for $Si(Me_2)$ and $Si(Ph_2)$ respectively. These values have been obtained using model compounds/

TABLE 6.1

PREPARATION OF POLY(DIMETHYLDIPHENYLSILOXANE) FROM OCTAMETHYLCYCLOTETRASILOXANE AND HEXAPHENYLCYCLOTRISILOXANE OR OCTAPHENYLCYCLOTETRASILOXANE

Polymer	Starting Material		Mole % diphenyl units in monomer feed	Temp.(^{o}C)	Catalyst	Mn	Mole % diphenyl units in copolymer
	dimethyl,	diphenyl					
A	D_4	D_3	2	115	0·01% TMAH	248,000	3·8
B	D_4	D_4	3·5	160	0·03% KOH	452,000	4·9
C	D_4	D_3	5	115	0·05% TMAH	328,000	3·9
D	D_4	D_4	10	160	0·03% KOH	141,000	13·8
E	D_4	D_3	20	120	0·05% TMAH	258,000	17·0
F	D_4	D_3	30	115	0·05% TMAH		

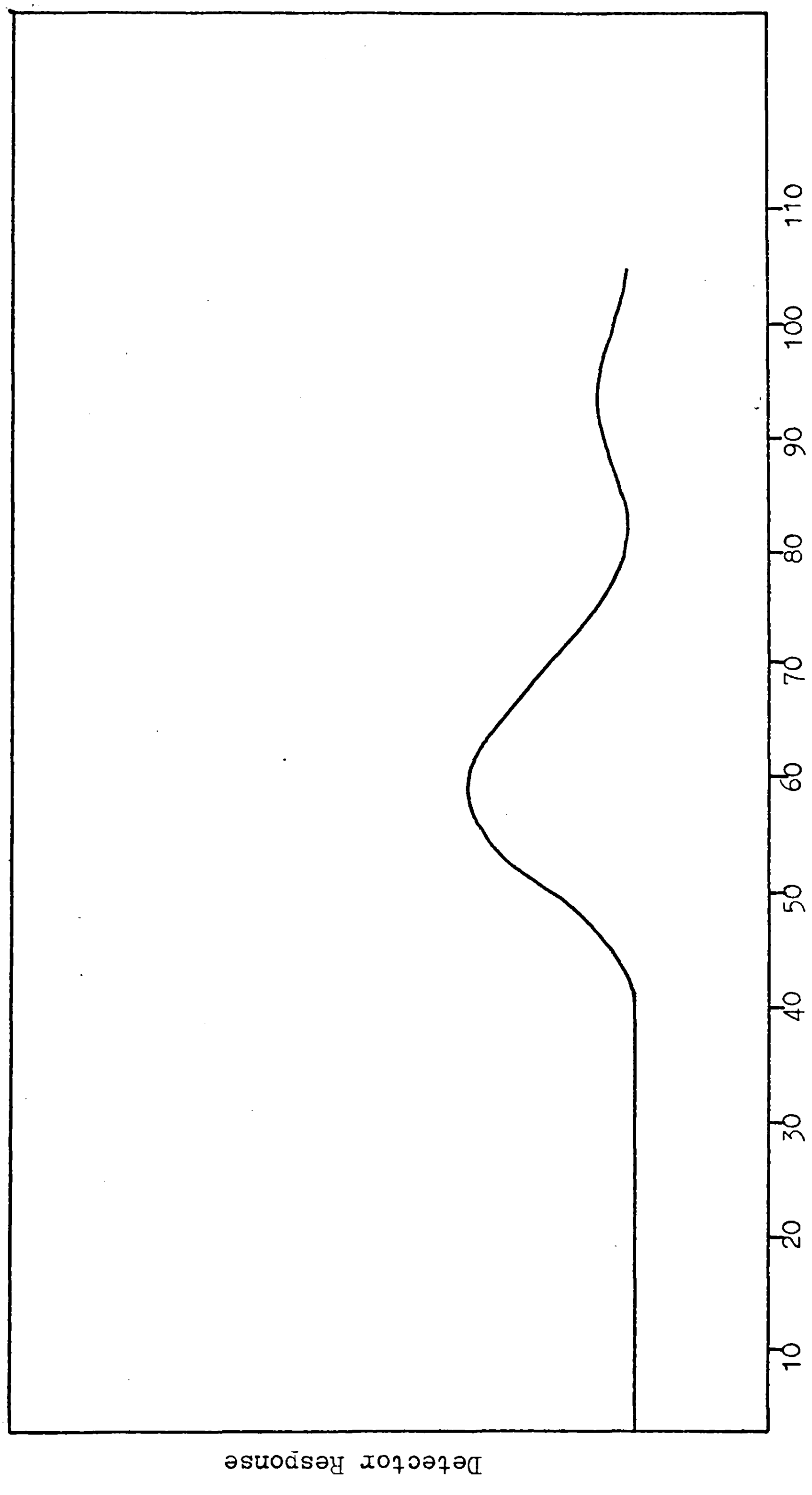


Fig. 6.1 Separation of residual low molecular weight material from copolymer E using GPC.

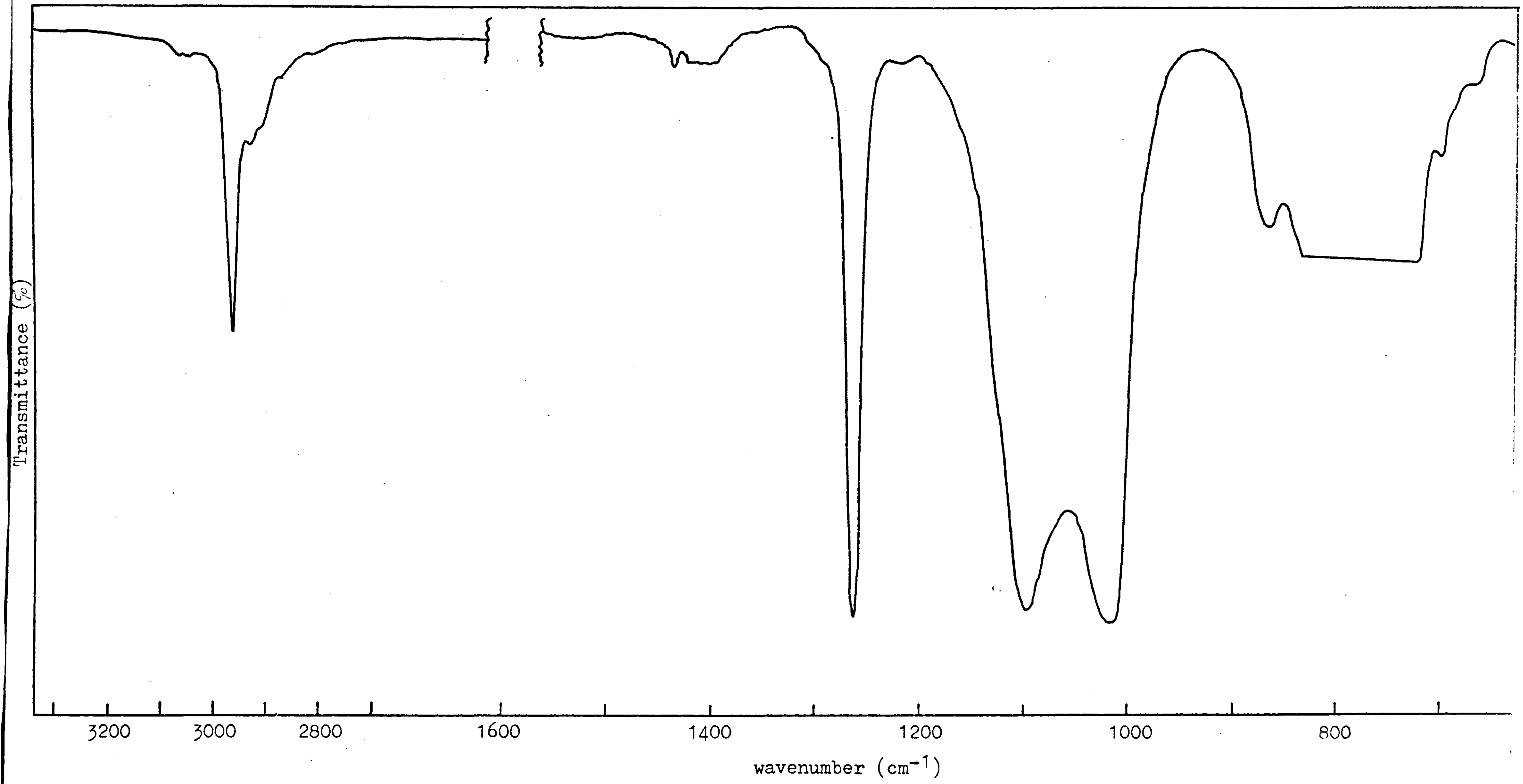


Fig. 6.2 IR Spectrum of copolymer B

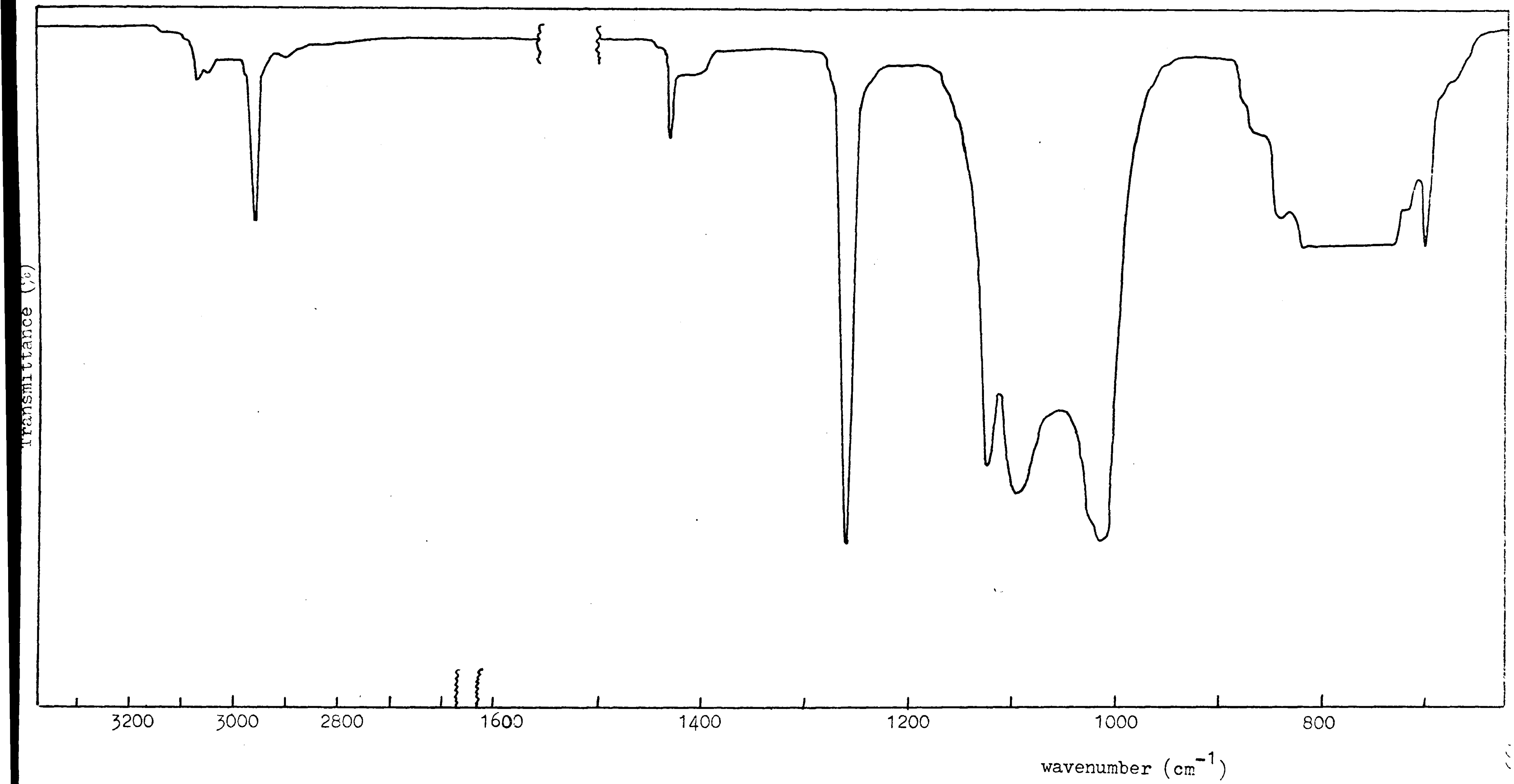


Fig. 6.3 IR Spectrum of copolymer E

compounds (cyclic trimers, tetramer and polydimethylsiloxane, see Table 6.2). It is known that the infra-red characteristics of pendant groups in the silicones vary only slightly in the compound in which they are found. (Ref 14)

6.4 THE EFFECT OF RESIDUAL DIPHENYL TETRAMER ON THE NATURE OF THERMAL DEGRADATION PRODUCTS

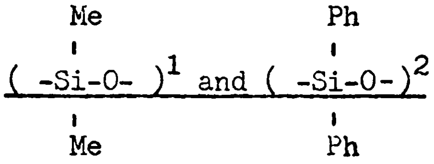
Although GPC separation has been used to characterise the copolymers the amounts of purified samples so far obtained have been insufficient for use in a complete study of the thermal behaviour of this system. The work described below has been carried out using samples which contain some residual diphenyl tetramer. The amounts of residual tetramer in the copolymers prepared from mixtures with low diphenylsiloxane content will be insignificant but copolymers containing relatively large amounts of diphenylsiloxane units are opaque (white) due to the presence of the cyclic tetramer.

There is some evidence that the residual material described above takes little part in the degradation of the polymer. A sample of polydimethylsiloxane together with a substantial amount (30 wt. %) of diphenyl tetramer was degraded at 350°C and gave no cyclics containing both units and no benzene. The nmr spectrum of the cold ring fraction is given in figure 6.4. The methyl protons form a broad singlet at τ 9·938 which probably contains contributions from the methyl groups of a number of dimethyl cyclics (eg. pentamer τ 9·935, hexamer τ 9·938) (Ref. 130). A TGA of this mixture/

mixture (dynamic N_2, temperature programme to 700°C) is indistinguishable from that of pure polymer. There is thus no apparent stabilisation of the polymer due to reaction with the diphenyl siloxane ring.

TABLE 6.2

CALCULATION OF IR EXTINCTION COEFFICIENTS FOR



$$\left(-\overset{\text{Me}}{\underset{\text{Me}}{\text{Si}}}-\text{O}- \right)^1 \text{ and } \left(-\overset{\text{Ph}}{\underset{\text{Ph}}{\text{Si}}}-\text{O}- \right)^2$$

Compound	Concentration (mg/ml)	Absorbance	Molar Extinction Coefficient
dimethyl trimer	4·58	0·241	374
	4·525	0·220	346
dimethyl tetramer	4·58	0·263	408
	4·45	0·250	400
dimethyl pentamer	4·53	0·250	393
	4·47	0·245	390
PDMS	4·57	0·234	378
	5·62	0·298	382
diphenyl trimer	6·09	0·064	198
	6·37	0·07	207

1 1260 cm^{-1}

2 1430 cm^{-1}

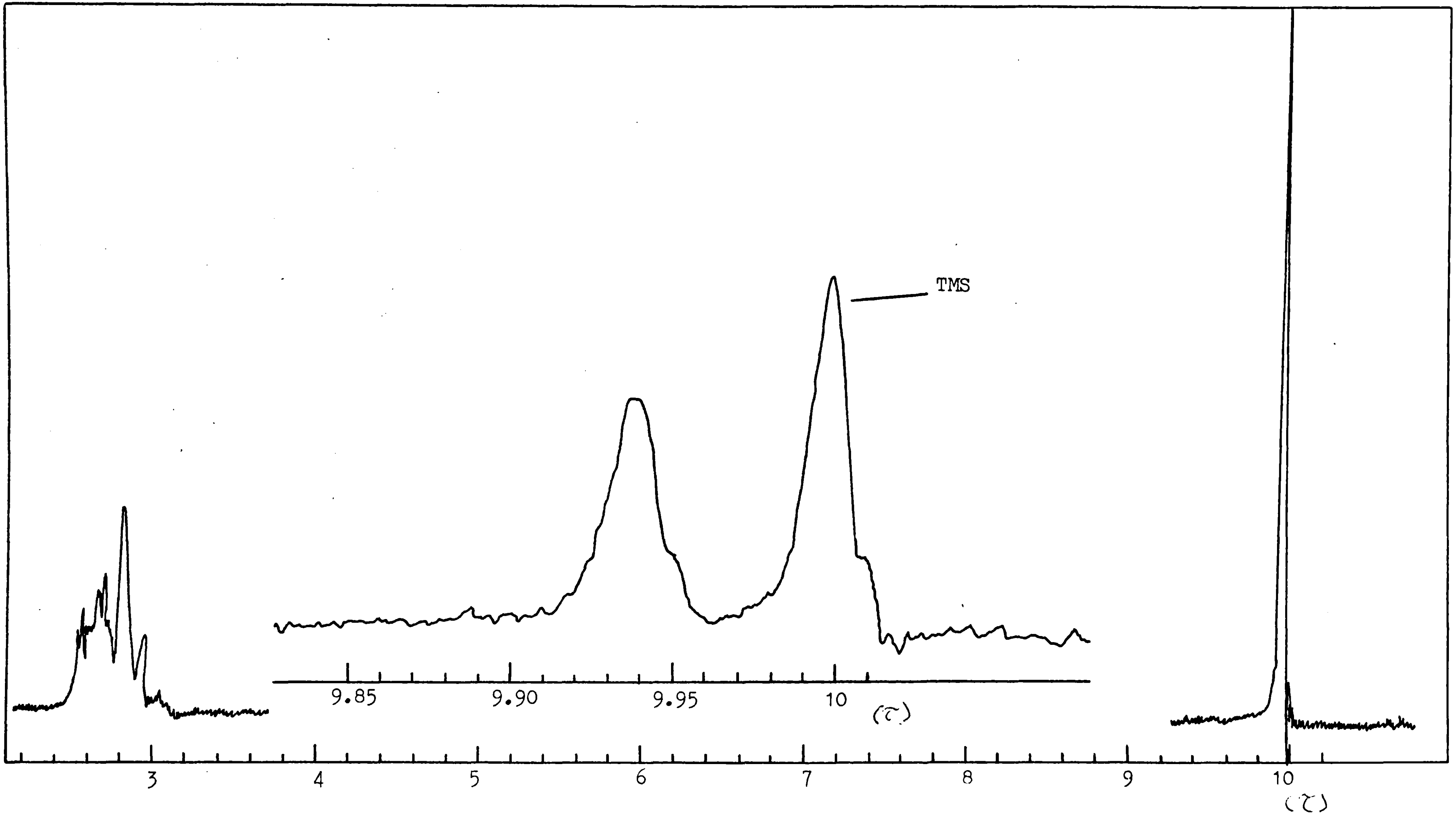


Fig. 6.4 The nmr spectrum (+ expansion of methyl shifts) of the "cold ring" fraction from the thermal degradation of a blend of PDMS and octaphenylcyclotetrasiloxane.

6.5 TGA

TGA traces have been obtained for co-polymers A, C, E and F under programmed conditions up to 900°C under dynamic nitrogen and for copolymers B and D up to 500°C under nitrogen.

The traces for copolymers A, C, E and F are given in figure 6.5. There is clearly some correlation between per cent diphenyl units in the copolymer and the weight of residue. This can be partly understood if formation of residue is a direct result of cleavage of the Si-phenyl bond.

Figure 6.6 and figure 6.7 give TGA curves for copolymers B and D respectively, both of which have been prepared using potassium hydroxide as catalyst. The traces obtained at several stages of purification are included in these figures to illustrate the profound effect that residual catalyst has on the observed degradation characteristics.

6.6 TVA

The TVA traces for copolymers A, B, C, E and F are given in figures 6.8-12. The nature of these traces is different from that from poly(dimethylsiloxane) or poly(methylphenylsiloxane). The production of non-condensable material appears to begin at approximately the same time as the main degradation process although in the degradation of copolymer there is very little evidence of any non-condensable products.

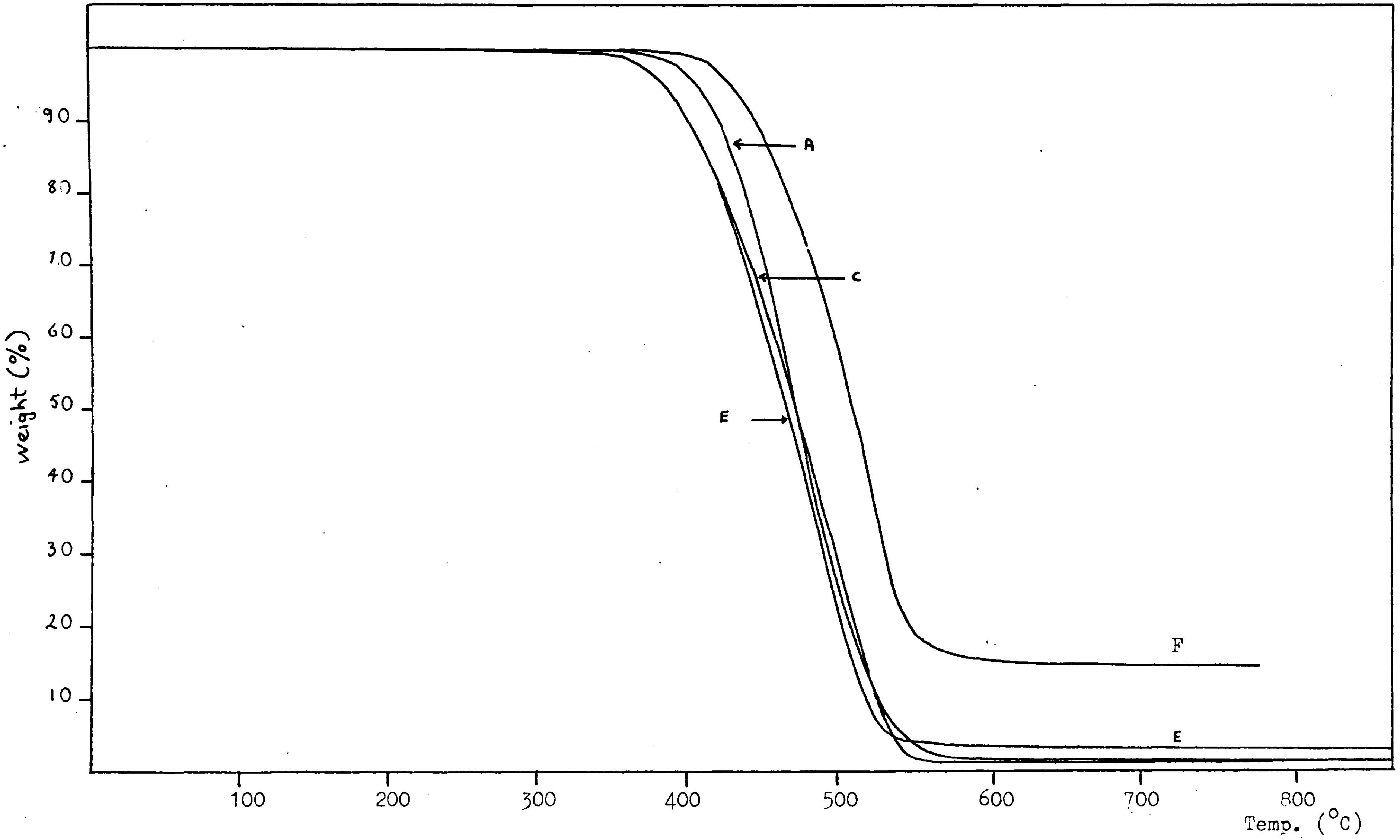


Fig. 6.5 TGA Curves for copolymers A,C, E and F.

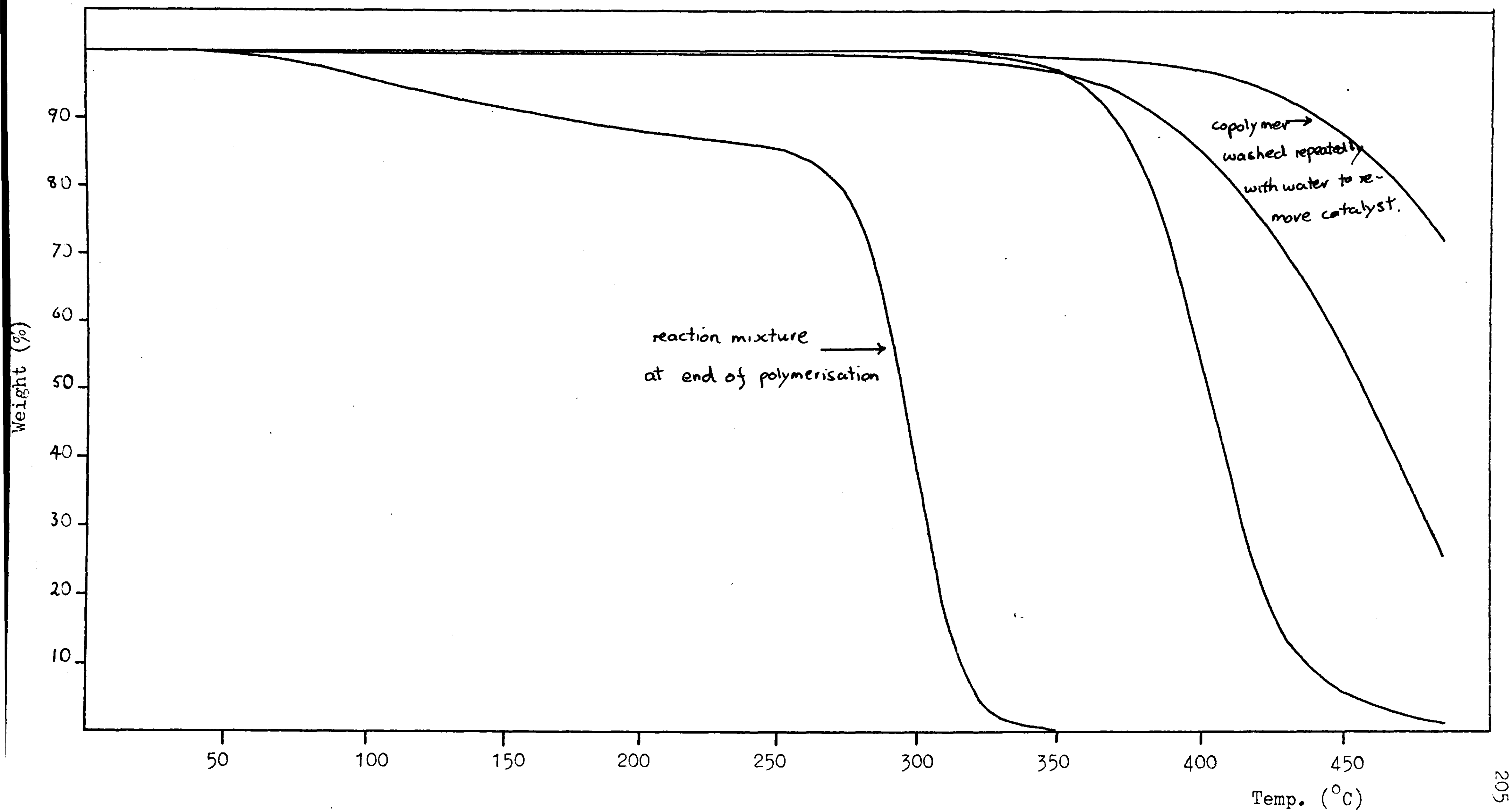


Fig. 6.6 TGA Curves for copolymer B at various stages of purification.

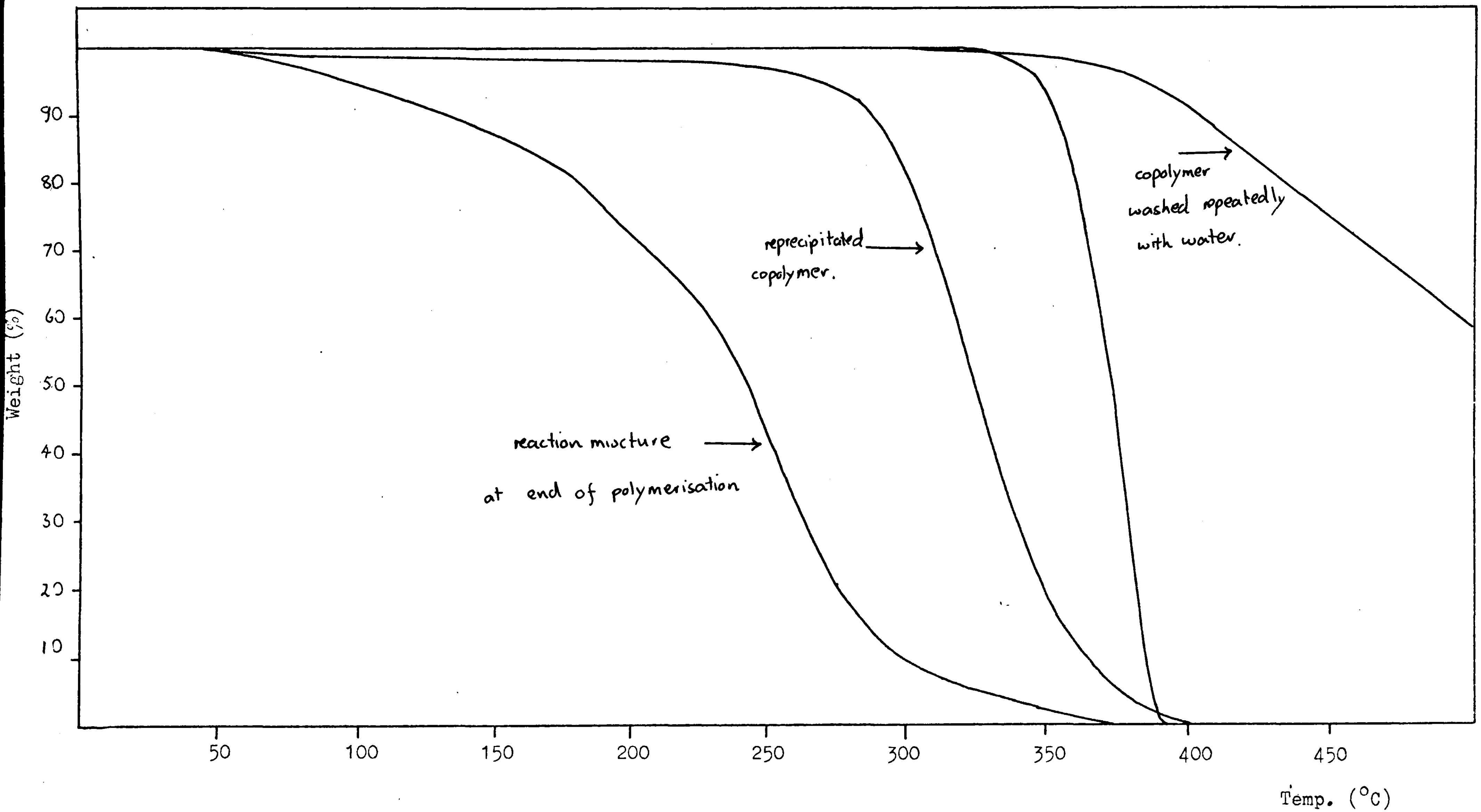


Fig. 6.7 TGA Curves for copolymer D at various stages of purification.

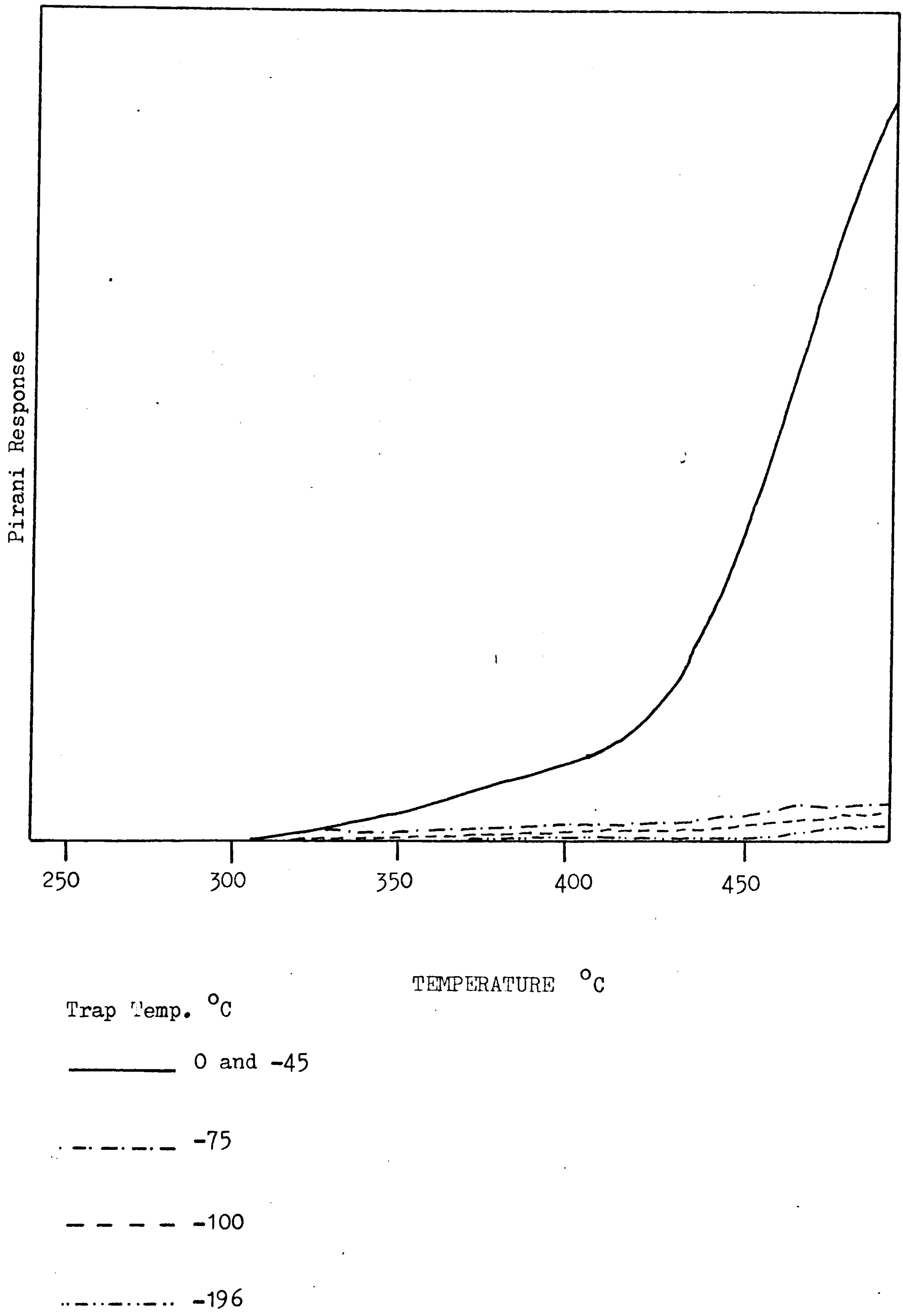


Fig. 6.8 TVA Curve for Copolymer A.

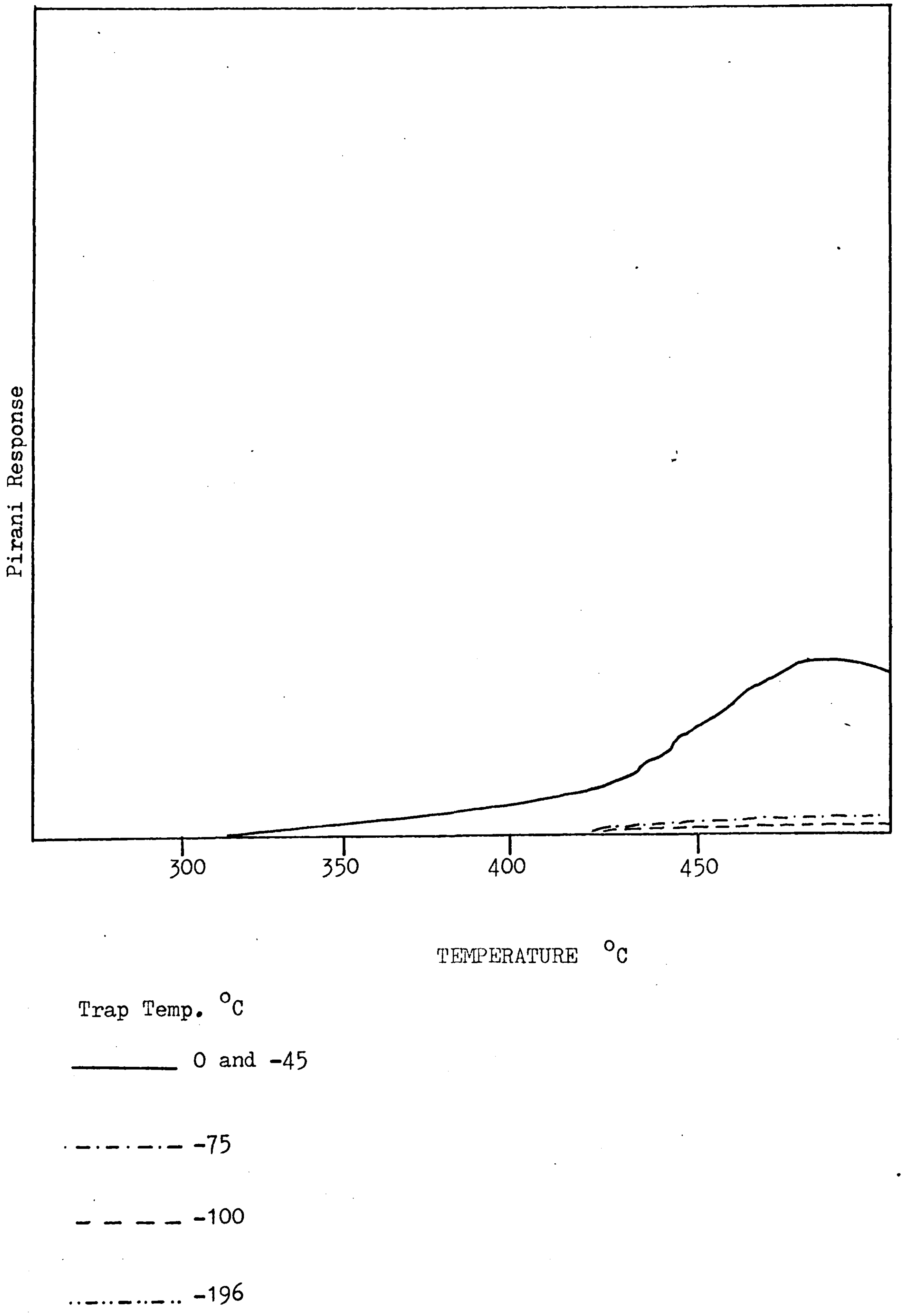


Fig. 6.9 TVA Curve for Copolymer B.

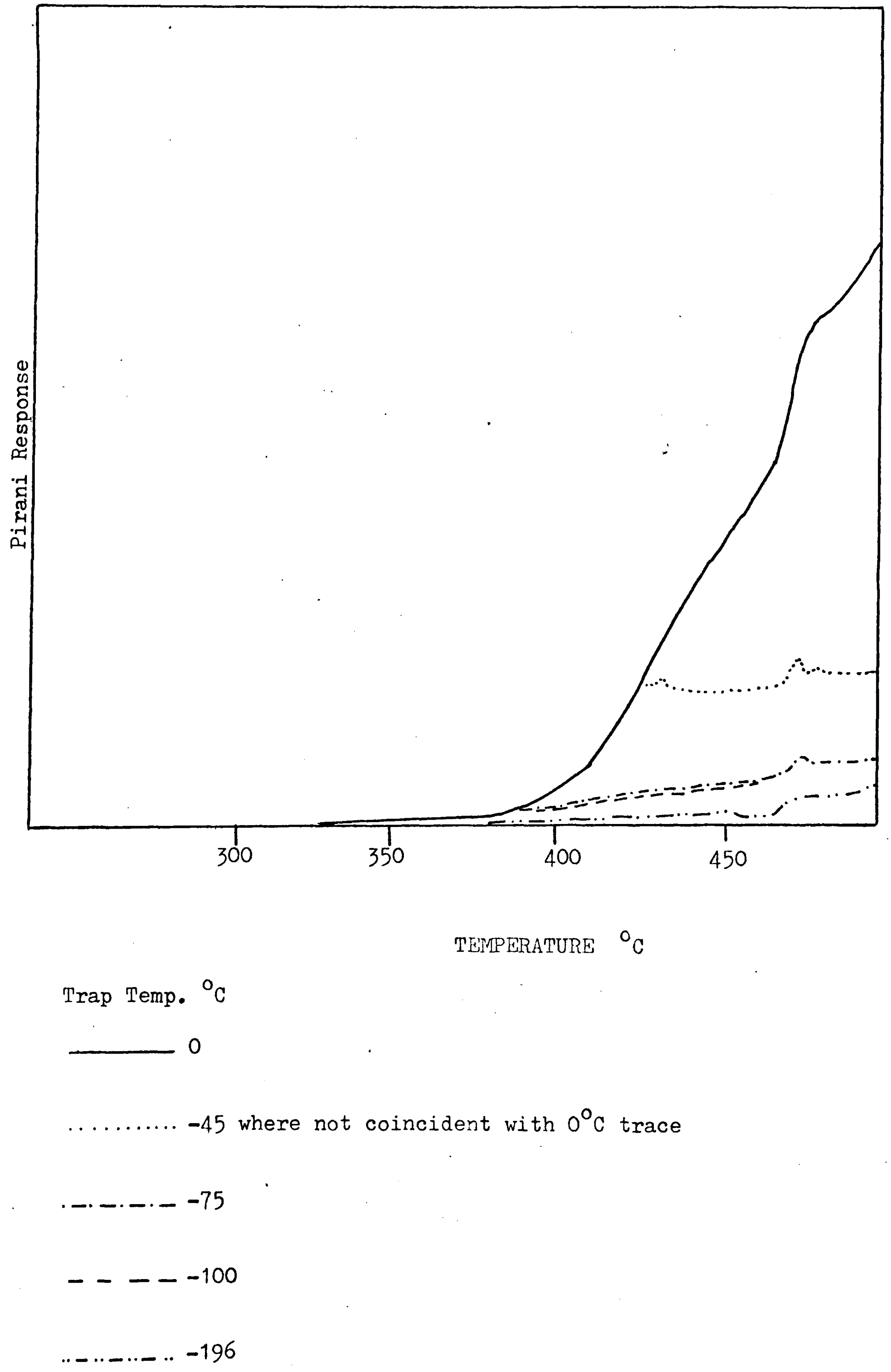


Fig. 6.10 TVA Curve for Copolymer C.

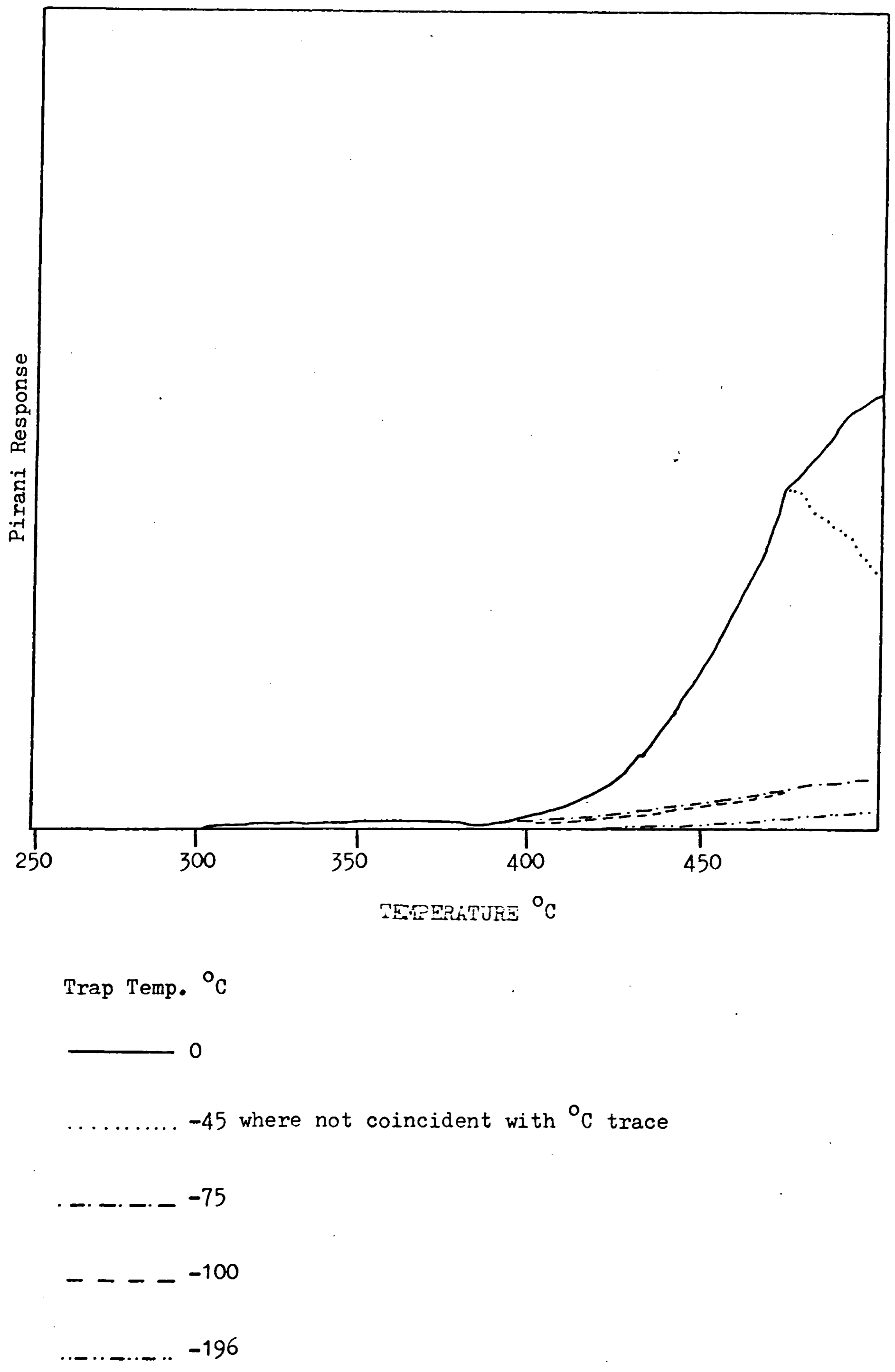


Fig. 6.11 TVA curve for copolymer E.

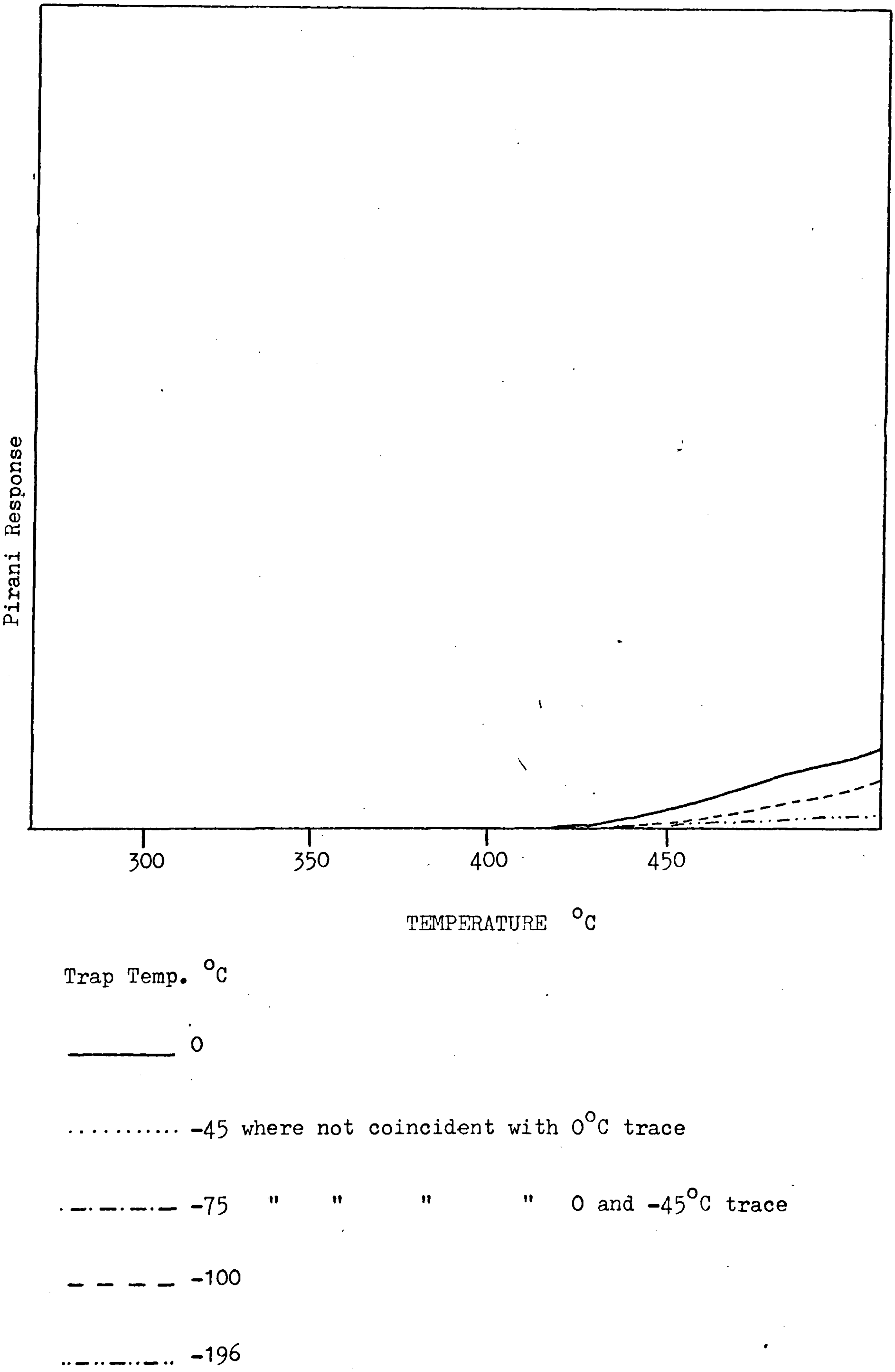


Fig. 6.12 TVA Curve for Copolymer F.

Analysis of products

The products from the degradation of copolymer E which will be described are typical of the series.

The infra-red spectrum of gaseous products from TVA is given in figure 6.13. It is clear, and not wholly unexpected, that cyclic dimethyl trimer and tetramer account for most of the absorption bands. The remaining absorption can be ascribed to gaseous benzene which is formed following cleavage of the Si-phenyl bond.

The infra-red spectrum of the cold ring fraction is given in figure 6.14. It is clear that there is an appreciable phenyl content in this fraction but in the light of the fact that the original sample contained some cyclic diphenyl tetramer, which has been shown to volatilise unchanged, the infra-red spectrum alone cannot give much information about the presence of diphenyl units in the degradation products.

The nmr spectrum of the methyl protons of this fraction is given in figure 6.15. Clearly amongst the degradation products are species with methyl groups in several environments. Table 6.4 gives the nmr shifts observed along with those for some possible products, whose values have been predicted using the equation proposed by Williams et. al. (Ref. 130) and described below.

Williams et. al. (Ref. 130) have shown that the chemical shifts for the methyl groups in methyl, phenyl siloxane rings depend upon the ring size and upon the position and orientation of neighbouring/

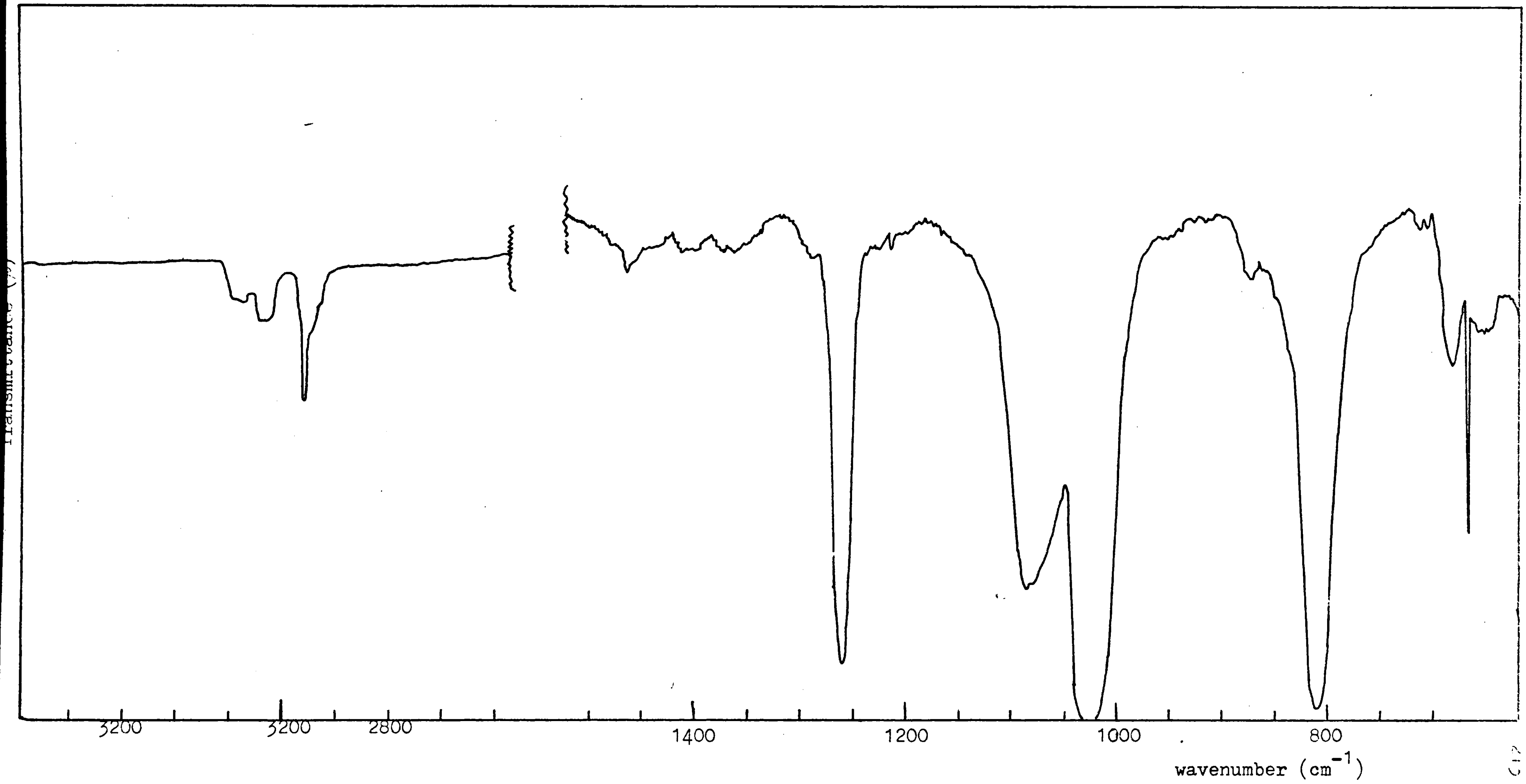


Fig. 6.13 IR Spectrum of gaseous products from TVA of copolymer E

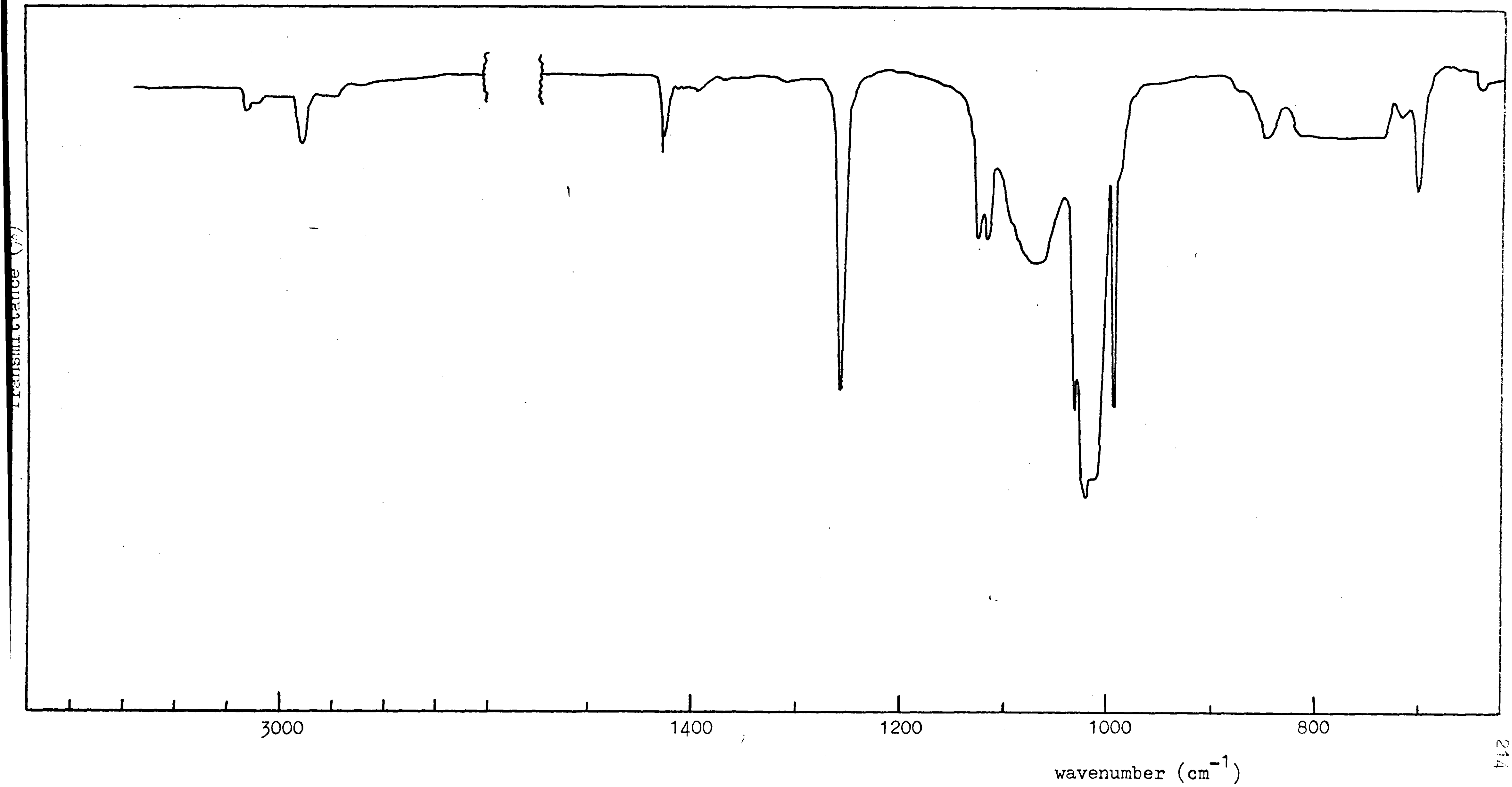


Fig. 6.14 IR of "coldring" fraction from TVA of copol. E.

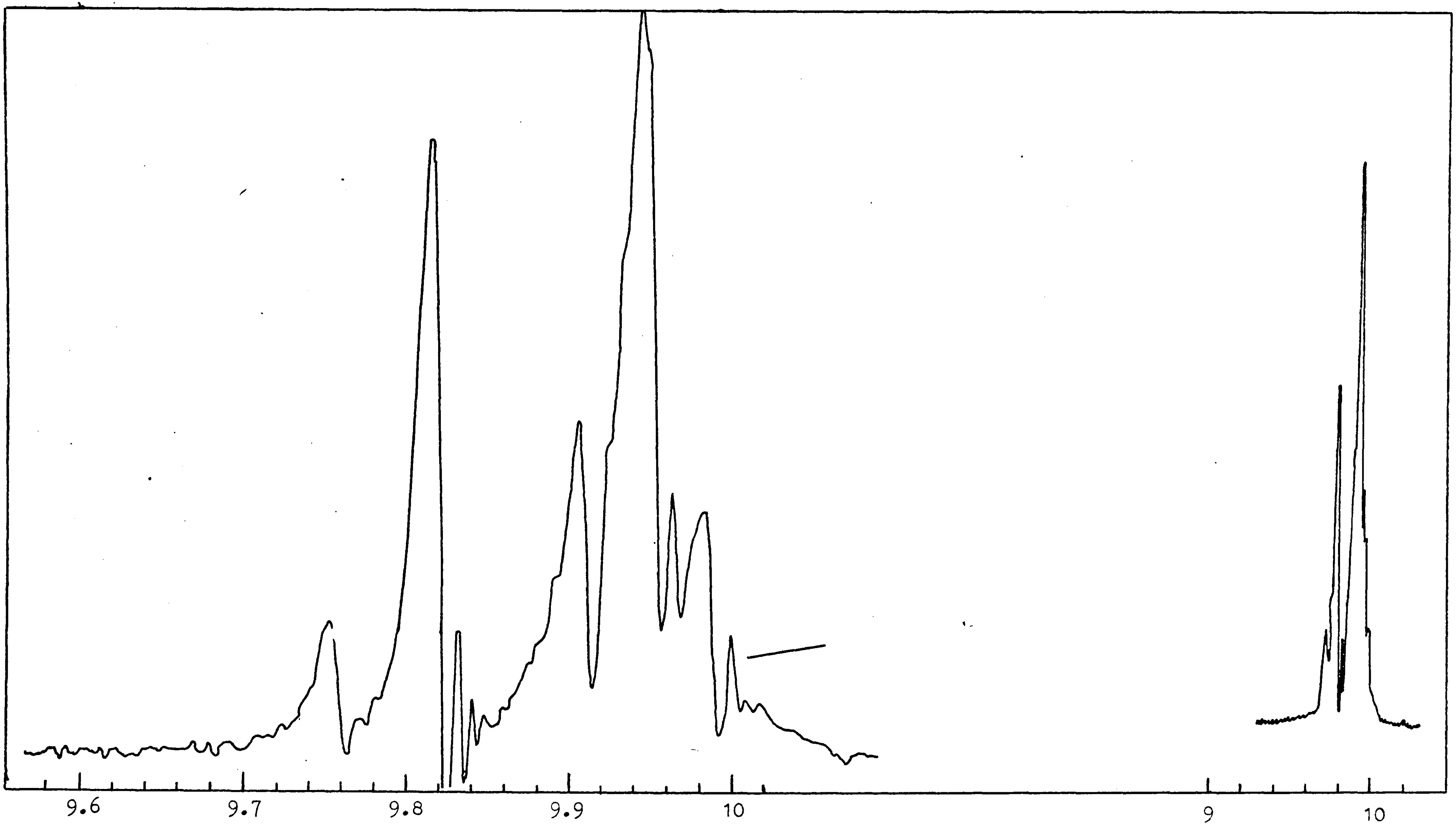


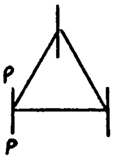
Fig. 6.15 NMR Spectrum (methyl protons) of "cold ring" fraction from TVA of copol. E.

neighbouring pehnyl groups and are expressed by the following equation,

$$\tau = a_0 + a_1x_1 + a_{2c}x_{2c} + a_{2t}x_{2t} + a_{3c}x_{3c} + a_{3t}x_{3t}$$

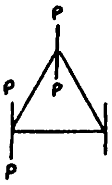
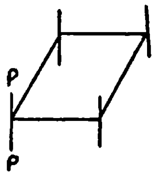
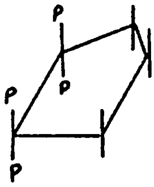
in which a values are regression parameters which depend upon ring size and where x values are structural variables.

Regression parameters (a_1) are given by the authors for cyclic trimer, tetramer and pentamer and are reproduced in part in this thesis, in Table 6.3. Structural variables (x) are specified as follows: x_1 is unity when the silicon which bears the observed methyl group also bears a phenyl group and is zero otherwise; x_{2c}, x_{2t} are the number of adjacent phenyl groups orientated cis and trans respectively to the observed methyl group; x_{3c}, x_{3t} are the number of remote phenyl groups orientated cis and trans, respectively.

Taking tetramethyldiphenylcyclotrisiloxane  as an example, the equation reduces to:

$$\tau = 9{\cdot}878 + (-0{\cdot}240) \times 0 + (-0{\cdot}001) \times 1 + (0{\cdot}077) \times 1 + 0 + 0$$
$$= 9{\cdot}800$$

The main peak at τ 9·939 is most likely due to dimethyl cyclics (e.g. pentamer τ 9·935, hexamer 9·938) (Ref. 123). Clearly from Table 6.4 there is good agreement between the chemical shifts of products and those of predicted structures, and while the nmr assignments require confirmation and support using other analytical techniques there is reason to believe that during degradation some diphenyl units remain intact and are incorporated into such cyclic species as

 ,  ,  and others.

6.7/

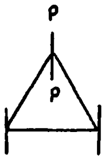
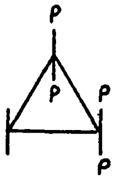
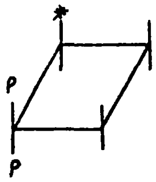
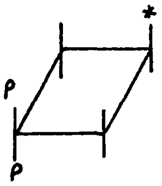
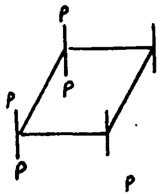
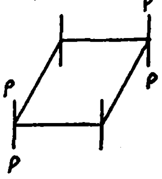
TABLE 6.3

NMR SHIFT-STRUCTURE CORRELATIONS FOR METHYL PROTONS IN METHYL, PHENYL SILOXANE RING COMPOUNDS*

Ring Size	a_o	a_1	a_{2c}	a_{2t}	a_{3c}	a_{3t}
Trimer	9·878	-0·240 ±0·006	-0·001 ±0·004	-0·077 ±0·004		
Tetramer	9·904	-0·224 ±0·005	0·044 ±0·003	-0·069 ±0·003	0·054 ±0·006	-0·031 ±0·006
Pentamer	9·908	-0·277 ±0·010	0·041 ±0·008	-0·056 ±0·008	0·059 ±0·008	-0·008 ±0·008

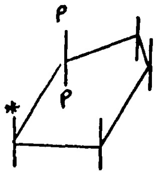
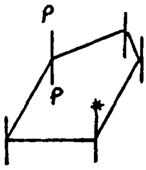
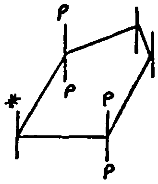
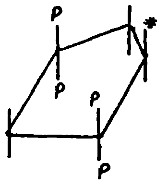
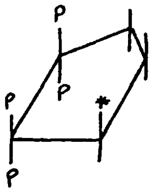
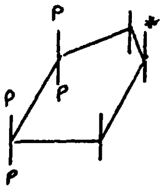
* Reproduced from Ref.130.

TABLE 6.4

Structure of possible Degradation products	Predicted shift* (τ)	Observed shift of Thermal Degradation products (τ)	Difference
	9·800	9·809	+ ·009
	9·722	9·747	+ ·025
	9·879	9·880	+ ·001
	9·927	9·927	0
	9·902	9·900	- ·002
	9·854	9·861(shoulder)	+ ·006
dimethylcyclics[1]			
D_5	9·935	9·940	+ ·005
D_6	9·938		+ ·002

*using method described in Ref. 130

[1] observed shifts

	9·893		
	9·959	9·961	+ ·002
	9·878	9·875(shoulder)	- ·003
	9·944	9·960	+ ·016
	9·944	9·960	+ ·016
	10·010	9·979	- ·031

6.7 SUGGESTIONS FOR FUTURE WORK

Clearly the dimethyldiphenylsiloxane copolymers have not received the same attention in the literature as most comparable organic copolymers. The distribution of diphenyl units in these copolymers does not appear to be well understood although Andrianov's (Ref. 139) work suggests that the high rate of transfer of reactive centre to polymer during polymerisation coupled with equilibrium processes lead to random distribution of the diphenyl units. The indication is that the latter are not, as might be expected, present in blocks of three or four from the trimer or tetramer starting material.

A detailed study of the thermal degradation products of polymers stripped of low molecular weight material is a potentially invaluable method of characterising these copolymers.

There are a small number of papers in the literature on the preparation and polymerisation of cyclic siloxanes containing both dimethyl and diphenyl units e.g. 1,1, diphenylhexamethylcyclotetrasiloxane (Refs. 117, 142). Polymerisation of such compounds offers an alternative approach to the preparation of polymers containing both dimethyl and diphenyl units.

6.8 CONCLUSIONS

1. Copolymers containing dimethyl and diphenyl units up to approximately 30 mole per cent can be prepared by copolymerising octamethylcyclotetrasiloxane with hexaphenylcyclotrisiloxane or/

or octaphenylcyclotetrasiloxane using potassium hydroxide or tetramethylammoniumhydroxide as catalyst.

2. The problems of purification of these copolymers, commented on by several workers, can be overcome using GPC.

3. Preliminary data from TGA and TVA indicate that incorporation of diphenyl units into a dimethylsiloxane polymer leads to a structure of increased thermal stability.

4. At temperatures below 500°C the Si-phenyl bond is cleaved giving benzene as a product.

5. Infra-red study has shown that cyclic dimethyl trimer and tetramer are formed as thermal degradation products.

6. Nmr studies have given an indication that during thermal degradation (TVA) some of the diphenyl siloxane units in the copolymer are incorporated into cyclic siloxane rings giving rings containing both dimethyl and diphenyl siloxane groups.

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