Leeming, William B.H. (1973) *Thermal and photolytic degradation of polypropylene.* PhD thesis.

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THERMAL AND PHOTOLYTIC DEGRADATION OF POLYPROPYLENE

A thesis submitted to the University of Glasgow for the
degree of Doctor of Philosophy in the Faculty of Science.

By

William B. H. Leeming, B.Sc.(Glas)

Supervisor
Prof. N. Grassie

Chemistry Department
September 1973.

ACKNOWLEDGMENTS

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

I wish to express my sincere gratitude to Professor N. Grassie for suggesting the problem and for his advice, encouragement and supervision throughout the course of the work.

My thanks are due to all my colleagues in the Macromolecular Chemistry Group for many stimulating discussions and to Mr. J. Gorman for technical assistance.

I would also like to thank my wife, Janet for typing the manuscript.

During this period of research, I was in receipt of a grant from the Science Research Council.

September 1973. William B.H. Leeming

William B.H. Leeming

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THERMAL AND PHOTOLYTIC DEGRADATION OF POLYPROPYLENE

SUMMARY

This thesis describes an investigation into some aspects of the thermal and photolytic degradation reactions of isotactic polypropylene (PP) in vacuo. In addition, with regard to the increasing commercial importance of polymer blends, the thermal and photo - interactions of PP with a number of other polymers were examined.

The vacuum photolysis of PP was examined throughout the temperature range $20^\circ - 354^\circ C$; 2537 Å UV radiation was employed. Photodegradation involves bond cleavage to produce polymer radicals. The subsequent reactions of these macroradicals have been shown to be markedly dependent upon temperature. At ambient temperatures, there exists a competition between crosslinking and scission reactions in which the former is favoured. However, at temperatures approaching the crystalline melting point of the polymer (ca. $167^\circ C$), chain scission predominates. At still higher temperatures, photolysis yields a broad spectrum of hydrocarbon fragments which is similar both in nature and distribution to that resulting from thermal degradation in the range $300 - 354^\circ C$. This is also the case for photodegradation at temperatures below the threshold for thermal volatilisation of the polymer (ca. $300^\circ C$). Experimental evidence suggests that the two modes of degradation are similar ; i.e. random scission of carbon - carbon bonds, producing polymer radicals which then undergo mutual disproportionation or hydrogen abstraction reactions. Indeed,

the major effect of photolysis at any particular temperature in the range 300° - 354°C is to accelerate the thermal reaction occurring at that temperature. In such a photothermal degradation, energy is supplied to the polymer in two distinct forms ; however, once absorbed by the polymer, the origin of the energy loses its significance.

An investigation into some of the factors which may affect the photolysis of PP reveals that photodegradation at ambient temperatures is sensitised by certain metal containing impurities such as titanium dioxide (catalyst residue) and ferric oxide (from production machinery). However, the rate of photolysis has been shown to have relatively little morphological dependence.

The thermal degradation of PP - poly(methyl methacrylate) blends indicates the occurrence of some kind of interaction between the two polymers. Degrading PMMA appreciably accelerates the decomposition of PP and is itself stabilised under programmed heating conditions. Observations may be rationalised in terms of the interaction of a radical species from degrading PMMA with PP macromolecules, causing chain scission of PP and ultimately volatilisation. Contrary to expectations, results indicate that this radical species may be polymeric in nature. Photolysis of PMMA - PP blends apparently effects a polymer interaction probably involving grafting of short chain PMMA radicals to a PP backbone. The behaviour of PP - PMMA mixtures were compared with that of several other polymer blends containing PP as the common polymer. The mode of degradation of each polymer blended has been shown to influence the nature of the interaction with PP.

CHAPTER ONE

INTRODUCTION

1.1 General Introduction.

The degradative processes induced in a polymeric material by its environment will ultimately determine its useful lifetime in that environment. The term "degradation" has been used to cover a variety of processes, mainly physical deterioration or chemical modification. Although only minor chemical changes may be involved in many polymer degradations, these changes will be significant if they bring about modifications in polymer structure which can affect the physical properties and hence their commercial applications. Degradation can be caused by physical means such as heat, light, ultrasonics, high energy radiation and mechanical stress; by chemical means such as oxidation and hydrolysis; or even by exposure to certain bacteria. However, the most common types of degradation reactions studied are those caused by the three basic agencies to which all polymers are subjected either during fabrication or during their subsequent useful life, namely, heat, light and oxygen, alone or in combination. Most early degradation studies were carried out in order to determine the chemical structure of polymer molecules, e.g., the pyrolysis of natural rubber in 1860 (1) and the thermal degradation of polystyrene in 1935 (2). However it has also proved possible to utilise controlled degradations to improve certain properties of a polymer. e.g., in the manufacture of polypropylene resins, molecular weight can be controlled in this manner. The future may also hold possibilities for controlled degradation in the disposal of plastic waste.

There has been a passive interest in the photodegradation of polymers since the early days of commercial plastics when the visible and ultra - violet components of sunlight were observed to be involved in deteriorative ageing or weathering. However little progress was possible in the understanding of these decomposition reactions until the nature of polymers themselves was more clearly understood. It was not until the 1950's that this interest was revived and many serious investigations were carried out. Among these were the first detailed photodegradation studies on poly (methyl methacrylate) by Cowley and Melville (3).

1.2 Practical Considerations in Polymer Photolysis.

In most work mercury vapour lamps have been used as the source of ultra - violet radiation. Low pressure lamps provide a convenient, relatively monochromatic, low intensity source of 2537 Å radiation. Medium pressure lamps provide radiation at a number of wavelengths in the 2200 - 4000 Å region, and a desired wavelenth can be readily be isolated by the use of filters. High pressure lamps give high intensity radiation over a continuum of wavelengths in the same region. These and other ultra - violet radiation sources have been described in detail (4,5). Intensities of radiation from these sources can be varied by the use of screens, by varying the distance of the sample from the source, or by placing filters between the sample and the source. Determination of the intensity of the incident radiation can be made by conventional uranyl oxalate actinometry, (4,6,7), by the more rapid ferrioxalate method (5,8,9), or in other ways (4,5,10).

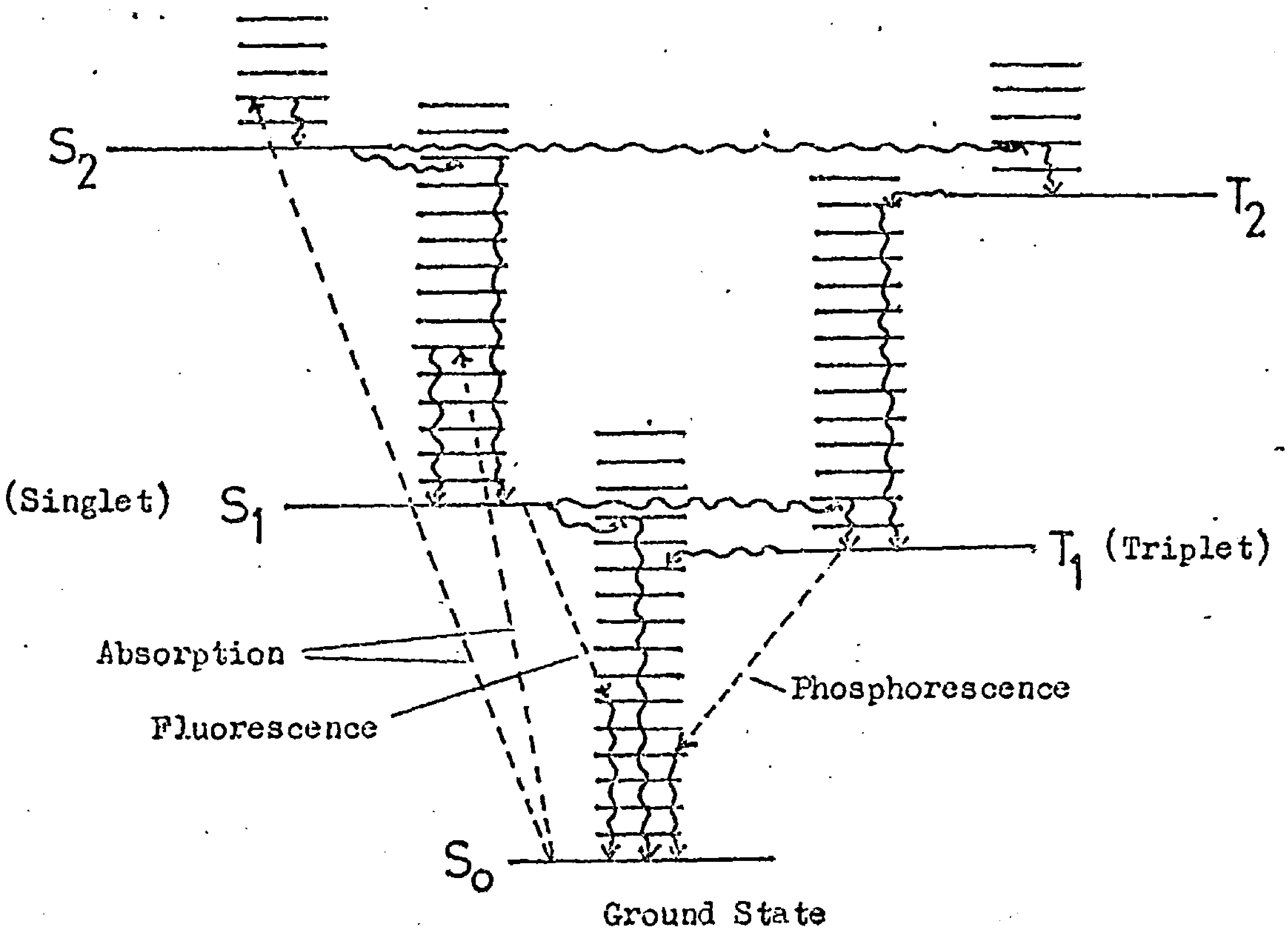
Photodegradations can be studied in solution or with bulk polymers in the form of films or powders. Quartz cells are commonly used as reaction vessels.

1.3 Theoretical Considerations in Polymer Photolysis.

Absorption of ultra - violet photons by a polymer results in free radical reactions which ultimately lead to main chain scission, cross-linking, unsaturation, and the formation of small molecule fragments. It is of fundamental importance to consider the events occuring between energy absorption and bond dissociation.

Most organic molecules lie in a singlet ground state and absorption of a photon raises the molecule to an excited singlet state. The molecule may revert to the ground state by emission of a photon(fluorescence) or by radiationless transitions and the generation of heat. In some instances intersystem crossing can take place, and the molecule will find itself in an excited tripletlevel of lower energy. Again, the reversion to the ground state may be accompanied by photon emission(phosphorescence)or heat. If the molecule has sufficient energy in the excited state, either singlet or triplet, dissociation or rearrangement may take place. Reversion to the ground state may also be accompanied by transfer of energy between the excited molecule and a second molecule. These processes are depicted in FIGURE 1.1.

Photolytic processes can be placed in two separate categories - primary and secondary. A primary process involves the immediate effect of light on the absorbing molecule e.g. deactivation by



Absorption $S_0 + h\nu \longrightarrow S_1$

Fluorescence $S_1 \longrightarrow S_0 + h\nu^1$

Internal Conversion $S_1 \longrightarrow S_0$

Intersystem Crossing $S_1 \longrightarrow T_1$

$T_1 \longrightarrow S_0$

Phosphorescence $T_1 \longrightarrow S_0 + h\nu^{11}$

Dotted Lines = Radiative Transitions

Wavy Lines = Radiationless Processes

FIGURE 1.1 Electronic transitions and photophysical processes in a typical organic molecule by means of fluorescence, heat emission, energy transfer etc., or destruction by transformation of the starting material into new compounds. Secondary processes are the reactions of the molecules, atoms, or radicals produced by the primary process. In a secondary process one of several things may occur :

a) collision between excited molecules and other molecules may result in energy transfer causing chemical reaction.

b) atoms or radicals produced in the primary process may react to give stable products.

or,

c) the excited molecules may react directly with other molecules in the system to form products.

If the energy of excitation is greater than, or equal to, the bond dissociation energy of the weakest link in a molecule, then cleavage may occur. 2537 Å radiation is equivalent to 113 kcal/mole, more than enough energy to break a carbon - carbon bond. It is important to remember that, because the absorbed energy may be transferred, the site at which the ultra - violet energy is absorbed is not necessarily the same as that at which bond rupture may take place. Chain scission and crosslinking are the two principle reactions involving the polymer backbone which may take place when polymers are exposed to ultra - violet radiation.

The reactions occuring in a polymeric system undergoing photolysis may be classified as <u>direct</u> or <u>indirect</u>. A direct reaction is the consequence of absorption of a photon by the polymer causing bond homolysis and the formation of degradation products.

$$P_{n+m} + h\nu \longrightarrow P_{n+m}^{*}$$

$$P_{n+m}^{*} \longrightarrow P_{n}^{\bullet} + P_{m}^{\bullet} \longrightarrow \text{products.}$$

In indirect reactions, "foreign" molecules - polymeric or small molecule impurities - or even other functional groups in the same polymer become involved. It should be noted that relatively few rigorously purified polymers have been investigated and the substances studied should perhaps be called polymer - containing systems. These impurities can be similarly excited and undergo reactions to form free radicals. These excited molecules or fragments may eventually interact with the polymer to give products similar to those arising from the direct reaction. The reverse is also possible. Excited polymer or polymer radicals may interact with the "foreign" molecules. All of these indirect processes can lead to degradation and may involve (a) energy transfer or (b) free radical processes :

(a) $P_{n+m} + S^{*} \rightleftharpoons S + P_{n+m}^{*}$

(b) $P_{n+m} + S^{\bullet} \rightleftharpoons S + P_{n+m}^{\bullet}$

A simple example of an indirect reaction is the effect of atmospheric oxygen on polymer photolysis. In regard to chain scission, oxygen can play the role of an apparent inhibitor (poly(methyl methacrylate)), accelerator (polystyrene), or seemingly be without influence (poly(αmethyl styrene)). Other examples are the influence of sensitisers on the crosslinking of polyolefins (11) and the effect of residual solvents in polymer films (12).

1.4 Classification of Degradation Reaction Types.

Degradation reactions, whether thermal or photolytic, have been broadly classified as chain scission, crosslinking and side group rearrangement or elimination reactions.

Chain Scission

These reactions are characterised by breakdown of the polymer chain backbone, resulting in production of chain fragments. Under certain conditions the ultimate products may be monomer or substances closely related to it with the residue retaining the chemical characteristics of the parent material, in that monomer units are still recognisable.

(a) Initiation

The first of two possible mechanisms involves random initiation in which chain scission occurs at random points along the chain leaving radicals which tend to be large compared to a monomer unit. Examples of this type of initiation are to be found in the room temperature photodegradation of poly(methyl methacrylate) (13) and the thermal degradation of polyethylene (14).

The second mechanism involves end - initiation and occurs particularly in polymers containing unsaturated end groups. The result is the formation of a long chain polymer radical and an end group radical, both of which may be active in the subsequent degradation. The high temperature photodegradation of poly(methyl methacrylate) (3) is a typical reaction in which end initiation is thought to take place.

Poly(methyl methacrylate) is interesting in that both of these modes of initiation also manifest themselves in its thermal degradation. At lower temperatures radicals are produced from scission at chain ends and at higher temperatures from scission of main chain carbon - carbon bonds.

(b) Propogation

Two extremes of behaviour can be observed. Firstly, following initiation, a rapid decrease in molecular weight occurs without evolution of monomer. Volatiles other than monomer may be evolved, however. Most room temperature photodegradations are of this type.

The second extreme type of behaviour can be regarded as a reverse polymerisation. After initiation, degradation proceeds by an unzipping process to produce large amounts of monomer. Examples of complete unzipping include the thermal degradation of poly(methyl methacrylate) and the photodegradation of poly(methyl isopropenyl ketone) at 150°C (15).

Many polymers, however, exhibit intermediate degradation patterns in which appreciable amounts of both monomer and higher chain fragments are formed.

Crosslinking

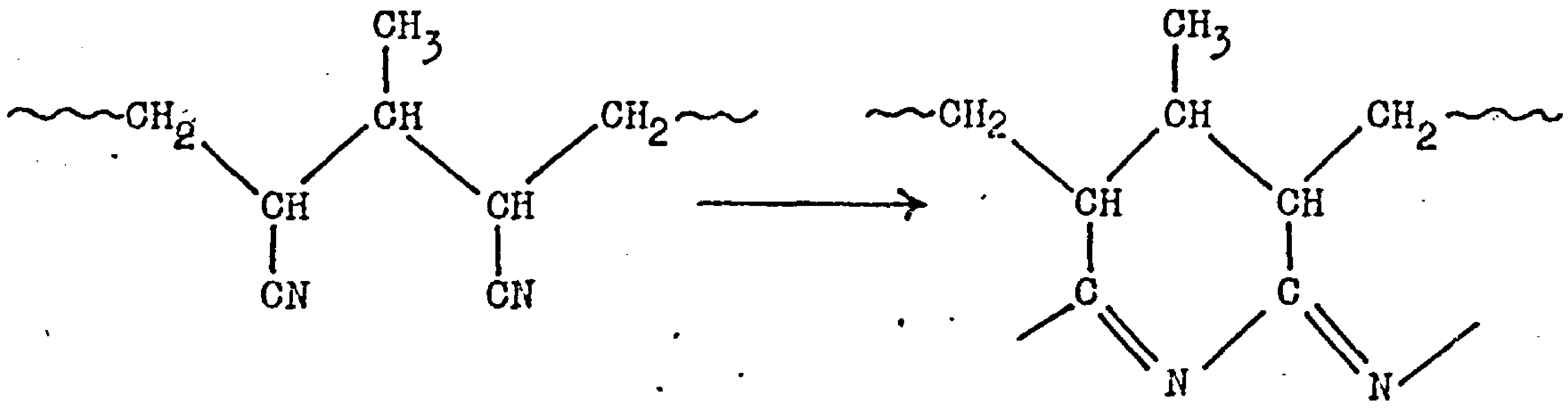
Under some circumstances ultra - violet radiation can cause crosslinking, the formation of intermolecular covalent links which lead to a three - dimensional network and ultimate insolubility of the polymer. Crosslinking is more commonly induced by high energy radiation as in the commercial production of crosslinked poly - ethylene (16). Other methods include thermosetting, in the case of many resins, and incorporation of impurities into the polymer structure to give chemical crosslinking.

Crosslinking may be largely due to reactions of polymer radicals resulting from cleavage of side groups from the main chain. The crosslinking may be by polymer radical combination or by addition to an unsaturated site in another chain. The structure of a polymer determines, to a large extent, whether or not crosslinking takes place. For example, exposure of polystyrene to ultra - violet radiation will readily cause crosslinking (17). Polystyrene has hydrogen atoms alpha to the pendant benzene rings which can be readily transferred and the resultant polymer radicals are resonance stabilised. Combination with other polymer radicals occurs, resulting eventually in a three - dimensional network. However, poly(αmethyl styrene) will only undergo irradiation crosslinking in the presence of sensitisers (18). The methyl groups alpha to the pendant benzene rings prevent formation of stabilised radicals and scission takes place rather than crosslinking. A similar comparison may be made between poly(methyl acrylate) and poly(methyl methacrylate) (19).

Side Group Reactions

a) Rearrangement

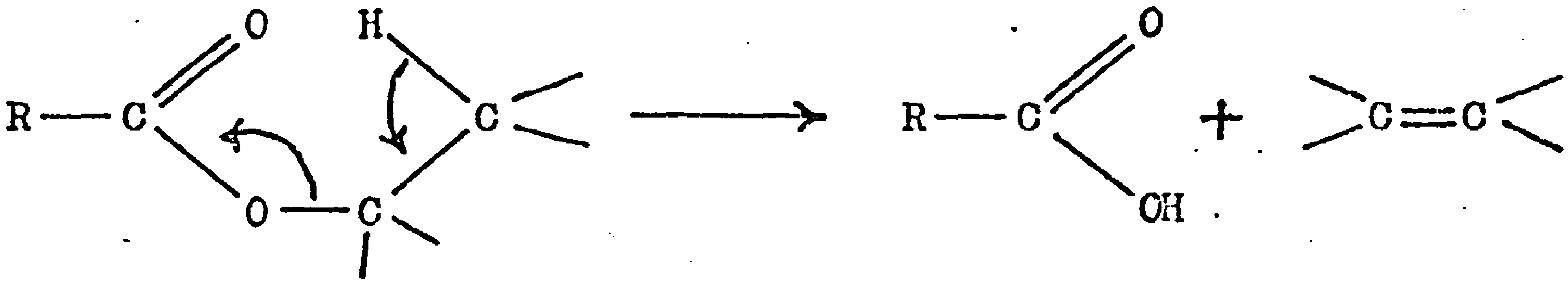
An important example of side group rearrangement is the formation of conjugated carbon - nitrogen sequences during the thermal treatment of polymethacrylonitrile (20,21).



This type of reaction is associated with the development of colour in nitrile containing polymers.

b) Elimination

Elimination involves a chemical change in a side group which results in the formation of a non volatile residue and elimination of a volatile product. The most common reaction of this type is ester decomposition in which the ester splits into an acid and an olefin.



For this elimination to proceed the ester must possess a hydrogen atom on the β carbon of the alkyl group. A typical example is the thermal degradation of poly(t - butyl methacrylate) which yields isobutene as the volatile fragment leaving methacrylic acid in the polymer chain (22).

1.5 Review of Polypropylene Degradation

I Thermal

In view of the fact that in polyproylene every other carbon atom in the chain is tertiary, all the carbon - carbon bonds tend to be appreciably weaker than those in polyethylene which has, in general, only a relatively few tertiary carbon atoms due to the presence of occasional methyl or ethyl substituents. It is perhaps not surprising, therefore, that polypropylene is somewhat more prone to thermal degradation than is polyethylene.

In polypropylene, a reduction of molecular weight sets in at about 230°C but breakdown to volatile products is insignificant below 300°C (23). With the onset of degradation, the weight average molecular weight drops much more rapidly than the number average molecular weight and as a consequence the ratio M_w/M_n, which is fairly high in the original polypropylene, approaches the value of two, the theoretical limit for a random molecular weight distribution (24). This sharp initial fall in molecular weight coupled with the presence of a wide spectrum of hydrocarbon degradation products led to the hypothesis that the reaction proceeds by random splitting of the polymer chain as a result of radical transfer reactions.

Madorsky and Strains (25), using mass spectrometry, and Moiseev, Khloplyankina et al., Bailey et al., and Van Schoden and Evenhius (26 - 30) using gas chromatography have all attempted to determine the volatile degradation products of polypropylene in order to explain the mechanism of decomposition. More recently, a very comprehensive analysis, including separation of saturated and unsaturated hydrocarbons was published by Tsuchiya and Sumi (31). Hydrocarbon products with 1 - 12 carbon atoms were analysed by gas chromatography and a mechanism proposed (FIGURE 1.2).

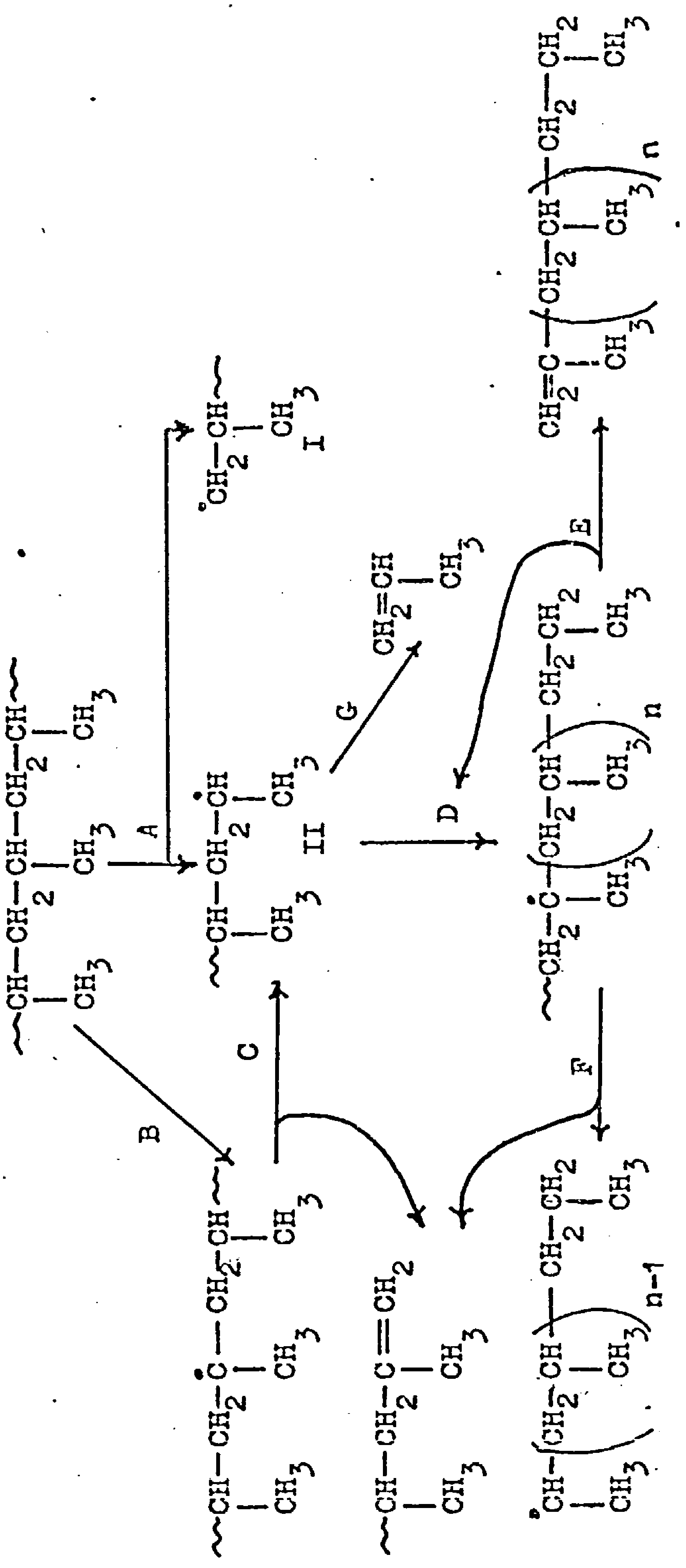
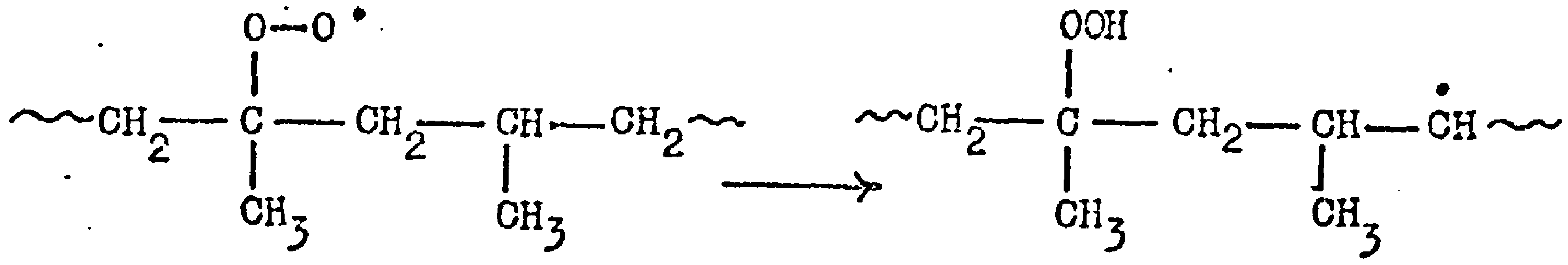


FIGURE 1.2 The Thermal Decomposition of Polypropylene

The initiation (A) occurs by random scission of the main chain, yielding two types of radicals; primary (I) and secondary (II). The production of radical (II) is more favourable than the production of radical (I) during the decomposition because the former is also produced by intermolecular and intramolecular radical transfer to tertiary carbon followed by β - scission (B,C,Dand E). Intramolecular radical transfer and propogation (G) reactions can account for the production of most volatiles. The experimental results indicate that radical transfer takes place mainly at the tertiary carbons and that transfer to the third and fourth carbons of the polypropylene chain is important. This latter possibility had not been considered in previous studies. Since radical transfer to the tertiary carbons increases the amount of radical (II) as comparedwith radical (I). the amounts of products formed from radical (II) were much greater than those for radical (I).

II Thermal Oxidation

It is generally accepted that the branched chain autoxidation of polyolefins is characterised by an induction period during which hydroperoxides are produced (32). The decomposition of these hydroperoxides is commonly recognised as the process responsible for the ensuing rapid oxidation. Hydroperoxidation may be initiated by reactions between metallic and hydroperoxide impurities (33) or perhaps between molecular oxygen and the substrate (34). The exact nature of initiation is not yet understood. Beachell and Beck (35) demonstrated that hydroperoxide groups are mainly situated at tertiary carbon atoms. Hydroperoxidation is terminated primarily by disproportionation of peroxy radicals (36) or by the reaction,



$$\sim CH_2-\underset{CH_3}{\overset{O-O^\bullet}{C}}-CH_2-\underset{CH_3}{CH}-CH_2\sim \longrightarrow \sim CH_2-\underset{CH_3}{\overset{OOH}{C}}-CH_2-\underset{CH_3}{CH}-\dot{C}H\sim$$

Three factors are known to influence the length of the induction period and the rate of oxidation of polypropylene; the temperature at which the oxidation is carried out, the oxygen pressure, and the bulk of the sample. An increase in temperature shortens the duration of the induction period and increases the rate of oxidation (37). An increase in oxygen pressure has a similar effect (37). Boss and Chien (38) have shown that oxidation of solid polypropylene is limited by oxygen diffusion to a depth of 25 mil from the surface. In order to eliminate diffusion effects and thus study the kinetics of the reaction more effectively, Abu - Isa (37) carried out investigations in thin films (0.3 - 0.7mil) of polypropylene. As expected, the rate of oxidation was found to be much more rapid than with thicker films.

Chien et al. (39) have demonstrated that more than 90 % of the hydroperoxide groups, formed during the induction period, are intramolecularly hydrogen bonded and are present in sequences of length two and greater. This affords strong support to the occurence, in the propogation steps of polypropylene autoxidation, of back - biting hydrogen abstraction by the peroxy radical via a six - membered transition state. A very thorough investigation has been made of the non - volatile products of thermal oxidation (40). Functional groups, two of which are formed per chain scission, comprise γ - lactone (17%), aldehyde (21%), ketone (21%), acid (25%), and ester (16%). The presence of γ - lactone is another indication of the importance of intramolecular back - biting.

The thermal decomposition of polypropylene hydroperoxide consists of two separate reactions (41). The first consumes up to 90% of the total hydroperoxide and consists of homolytic decomposition of the hydroperoxide groups. The second involves decomposition of β - hydroxy hydroperoxide structures formed as a by - product of the first reaction. The chemiluminescence observed during the oxidation of polypropylene has been shown to be a function of the hydroperoxide rather than the peroxy radical concentration (42).

The overall autoxidation of polypropylene may be represented by the following sequence :

$$(1) \qquad ROOH \xrightarrow{k_i} RO^{\bullet} + {}^{\bullet}OH$$

$$(2) \qquad RO^{\bullet} + RH \xrightarrow{k_1} ROH + R^{\bullet}$$

$$(3) \qquad {}^{\bullet}OH + RH \xrightarrow{k_2} H_2O + R^{\bullet}$$

$$(4) \qquad R^{\bullet} + O_2 \xrightarrow{k_3} RO_2^{\bullet}$$

$$(5) \qquad RO_2^{\bullet} + RH \xrightarrow{k_p} ROOH + R^{\bullet}$$

$$(6) \qquad 2RO_2^{\bullet} \xrightarrow{k_t} O_2 + \text{products.}$$

Another method of overcoming diffusion effects is to study the reaction in solution. The thermal oxidations of polypropylene in trichlorobenzene (43,44) and in benzene (45) have been investigated in order to provide further insight into the autoxidation mechanism. The effects of both initiation and inhibiting additives on the mechanism of thermal oxidation of polypropylene are also of considerable interest (46,47,48).

III Photooxidation

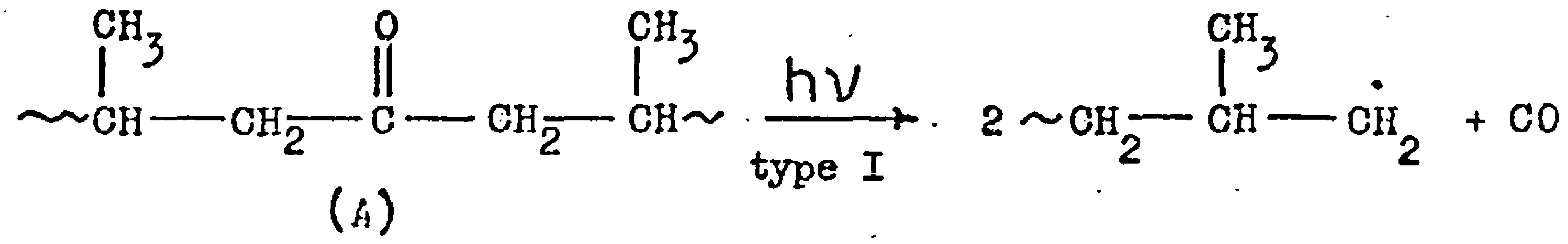
"Pure" saturated polyolefins such as polypropylene are not expected to show on ultra - violet absorption beyond 2000 Å (49) and consequently should be indefinately stable to the sunlight transmitted by the atmosphere (wavelengths greater than 2900 Å). However commercial polypropylene undergoes rapid chemical and physical deterioration on exposure to sunlight (50). This is generally attributed to chromophoric impurities such as hydro - peroxide and carbonyl groups which are introduced into the polymeric backbone by thermal oxidation during the extrusion and moulding processes (50). Transition metal residues of Ziegler – Natta catalysts (50) and polymer - oxygen charge - transfer complexes (51) have also been proposed as possible sources of initiation in the photodegradation of polypropylene.

A series of publications by Carlsson, Kato and Wiles (52,53, 54, 55) has contributed much to our present understanding of the photooxidation of polypropylene. Employing wavelengths greater than 3000 Å in air, these workers showed that the photooxidation of polypropylene film involves, at least in part, the conventional free - radical autoxidation chain process (41), to give hydro - peroxides as initial products. In addition, a host of carbonyl compounds is also formed, probably by secondary processes (52). The rate of photooxidation is also found to increase with the tacticity of the polymer sample (55). However, this effect is believed to be due to the occurrence of a stereo - dependent step (or steps) in the oxidative chain, and not due to differences in sample morphology.

As outlined above, commercial polypropylene which is normally processed in air at temperatures greater than 200°C will have substantial amounts of hydroperoxide and carbonyl impurities. Since these are thought to be a possible source of instability of polypropylene to near ultra - violet radiation, Carlsson and co - workers studied the vacuum photolyses of polypropylene ketones and polypropylene hydroperoxide.

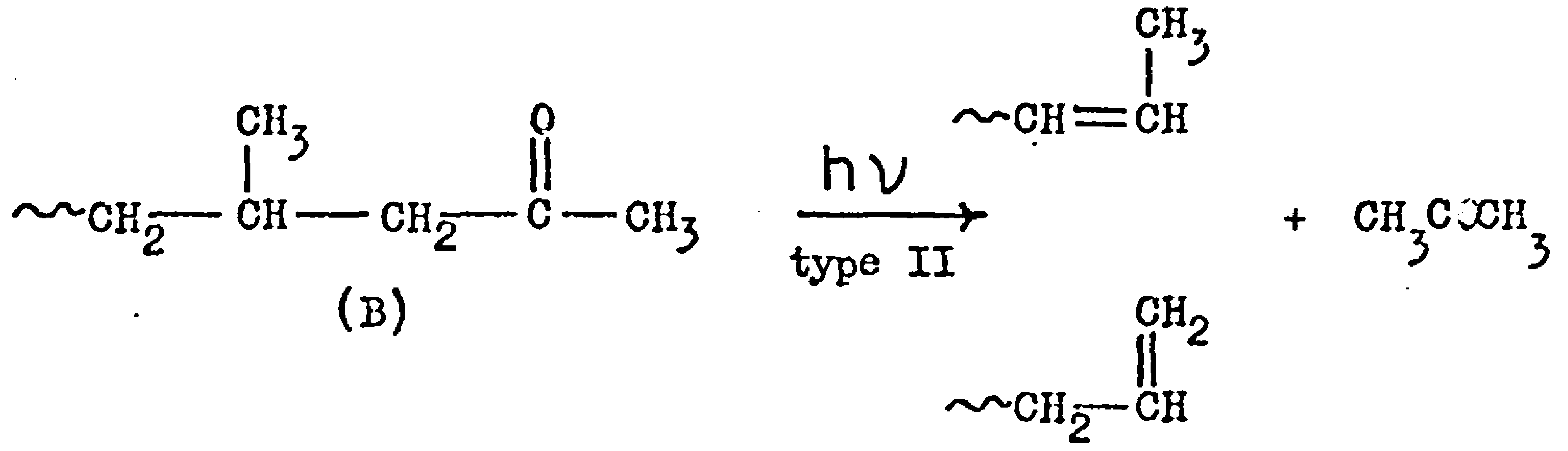
a) Photolysis of Polypropylene ketones. (53)

Air oxidation results principally in two polymeric ketones A and B, in approximately equimolar amounts. (A) is photolysed primarily by a Norrish type I scission to give carbon monoxide and two macroradicals whereas (B) is photolysed by a Norrish type II scission to give acetone and an unsaturated chain end.



$$\sim CH(CH_3)-CH_2-C(=O)-CH_2-CH(CH_3)\sim \ \xrightarrow[\text{type I}]{h\nu}\ 2\sim CH_2-CH(CH_3)-\dot{C}H_2 + CO$$

(A)



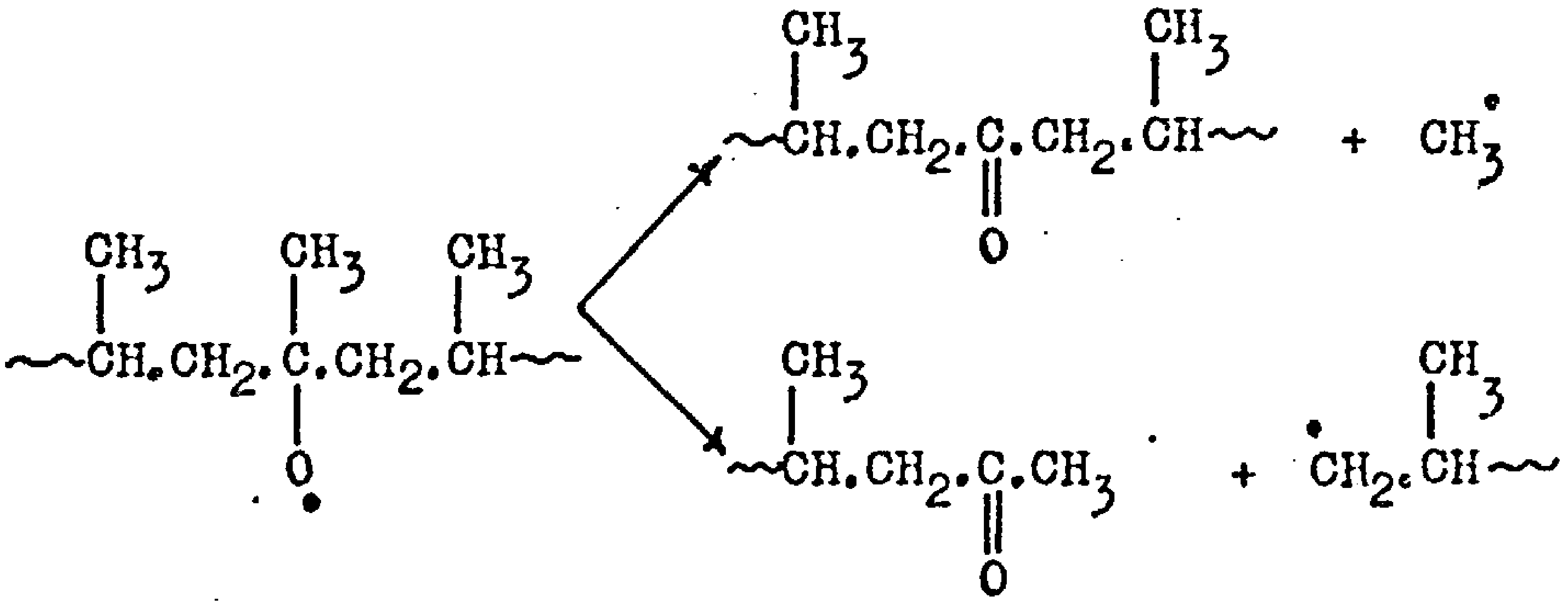
$$\sim CH_2-CH(CH_3)-CH_2-C(=O)-CH_3 \ \xrightarrow[\text{type II}]{h\nu}\ \begin{matrix}\sim CH{=}CH(CH_3)\\ \sim CH_2-CH(=CH_2)\end{matrix} + CH_3COCH_3$$

(B)

Both have quantum yields of approximately 0.08 and are believed to be the source of initiation in the early stages of polypropylene photooxidation. In later stages, however, the photooxidation is probably dominated by other initiation steps, such as hydroperoxide photolysis.

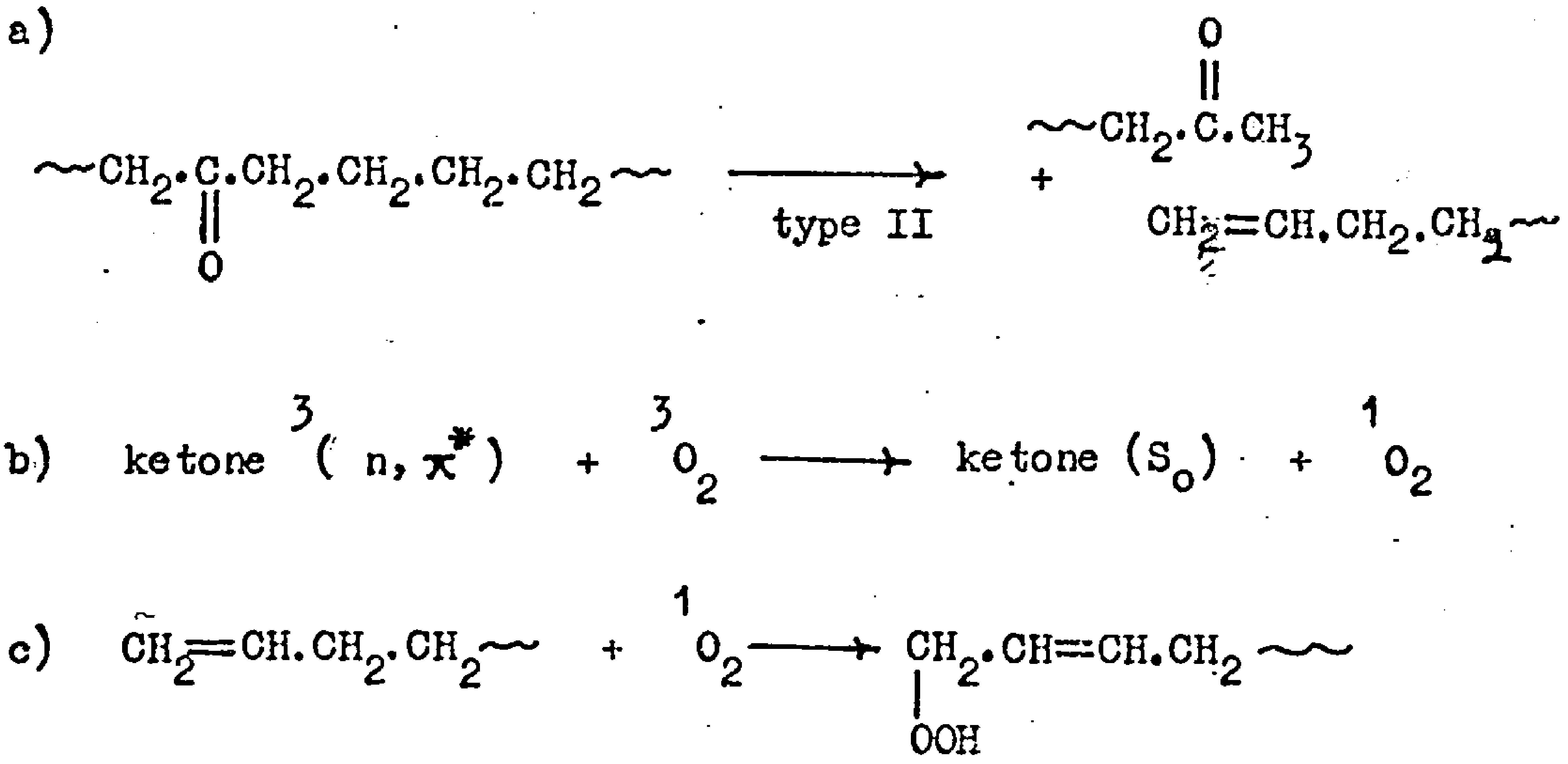
b) Photolysis of Polypropylene Hydroperoxides (54)

The primary photolysis step involves hydroperoxide cleavage into t - alkoxy and hydroxy radicals. The major volatile product is water, resulting from hydrogen abstraction by hydroxy radicals. Little evidence is found for radical induced hydroperoxide decomposition. The t - alkoxy radicals are believed to undergo extensive β scission by two competing processes both of which produce ketonic products.



Carlsson and Wiles (56,57) studied the surface reaction of photooxidation of polypropylene using Attenuated Total Reflection infra - red spectroscopy. They believe that restriction of photooxidation to a thin surface layer is not due to restrictions on diffusion of oxygen but to trace quantities of polymeric carbonyl and hydroperoxide groups present predominantly in the surface layers and formed during processing on the subsequent life of the polymer.

Another method of initiation of polyolefin photooxidation is that proposed by Trozzolo and Winslow (58) involving the participation of electronically excited oxygen molecules. According to the mechanism, singlet oxygen is formed by physical quenching of the n - π^* triplet state of carbonyl groups. By analogy with the solution reactions of singlet oxygen with olefins to form allylic hydroperoxides (59,60), these authors postulated a similar attack by singlet oxygen on vinyl groups within the polymer. The expected proximity of carbonyl and vinyl groups in the polymer is an attractive feature of the mechanism. The mechanism proposed by these workers for the photooxidative degradation of polyethylene is outlined below. It should also apply to polypropylene (50)



a)

$$\sim\sim CH_2.\underset{\underset{O}{\|}}{C}.CH_2.CH_2.CH_2.CH_2\sim\sim \xrightarrow[\text{type II}]{} \sim\sim CH_2.\overset{\overset{O}{\|}}{C}.CH_3 + CH_2{=}CH.CH_2.CH_2\sim\sim$$

b)

$$\text{ketone}\ {}^3(n,\pi^*) + {}^3O_2 \longrightarrow \text{ketone}\ (S_0) + {}^1O_2$$

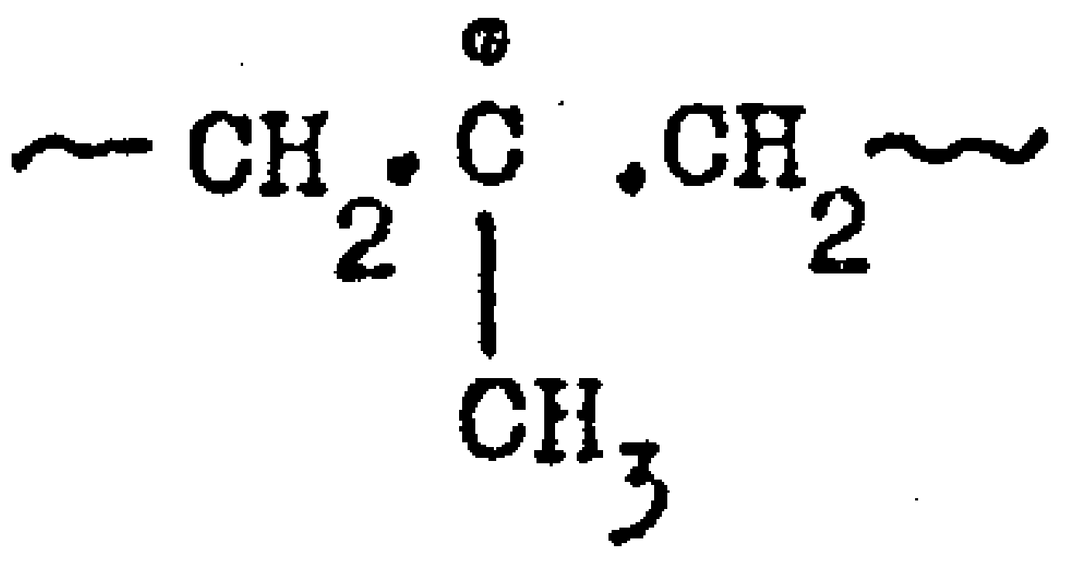
c)

$$CH_2{=}CH.CH_2.CH_2\sim\sim + {}^1O_2 \longrightarrow \underset{\underset{OOH}{|}}{CH_2}.CH{=}CH.CH_2\sim\sim$$

Further photochemical reactions of the hydroperoxide so formed may then take place as previously described.

IV Photolysis in Vacuo

Photodegradation is far more selective than degradation by high energy radiation. This is because the lower energy of the visible and ultra - violet quanta is of the order of the strengths of the bonds in polymer molecules. The quanta of high energy radiation will tend to be much more indiscriminate in their effects.

E.S.R. studies indicate that γ - irradiation of polypropylene, both at 77°K followed by annealing and at ambient temperature, produces alkyl radicals of the type  $\sim\mathrm{CH_2}.\underset{\displaystyle\mathrm{CH_3}}{\underset{|}{\overset{\bullet}{\mathrm{C}}}}.\mathrm{CH_2}\sim$ (61,62,63). These radicals undergo competing crosslinking and scission reactions.

Irradiation of isotactic polypropylene at 77°K with 2537 Å ultra - violet light produces free methyl radicals in addition to the above radicals (64). These methyl radicals could not be detected in atactic polypropylene under identical conditions (65). This was attributed to the ease and rapidity of reaction of methyl radicals formed in the amorphous region compared to those formed in the more diffusion restricting crystalline region.

Hatton and co - workers (66) have reported that unmodified polypropylene film may be crosslinked by ultra - violet radiation only in the presence of some sensitiser (e.g. benzophenone) and with the use of an appropriate bridging molecule (e.g. allyl acrylate). The allyl acrylate penetrates the amorphous regions and this is where crosslinking will occur. Thus atactic polypropylene is more readily crosslinked than isotactic polypropylene where the network consists of heavily crosslinked regions interspersed with non - crosslinked areas. On the other hand, Kujirai et al. (67) claim that ultra - violet irradiation in vacuo can directly crosslink polypropylene film without a bridging molecule. Crosslinking was detected by measuring the gel fraction in a tetrachloroethane solution and also by measuring the degree of swelling in decalin.

However, it should be remembered that polypropylene exhibits no true absorption above 2000 Å and the radicals produced cannot be attributed to the direct photodissociation of C-C and C-H bonds. Some possible chromophoric impurities were discussed earlier in this chapter. Recently, Takeshita et al. (68) have reported that radical formation in the vacuum photolysis of low density polyethylene is due to Norrish type I cleavage of carbonyl group impurities in the polymer chain. They also report that certain aromatic impurities detected in polyethylene can act as photosensitisers.

1.6 Polymer Blends

In the field of commercial polymers, polymer blends have become established materials principally because they are easily adapted to specific needs, and can be modified at any time for improvement in one property at a minimum sacrifice of other properties. Polymer blends may be described as physical mixtures of structurally different polymers and are classified as homogeneous or heterogeneous systems. Homogeneous systems are primarily used to improve processing; heterogeneous systems for imparting toughness; and both are used to lesser extents for reducing the amount of the more expensive material, for introducing thermally reversible crosslinks, and for increasing flame resistance.

The most important of the commercially available polyblends are the impact - resistant styrene and vinyl polymers. The high - impact styrene polymers are blends of polystyrene, or high styrene content styrene - butadiene copolymers, with natural or synthetic rubbers. For impact improvement, poly(vinyl chloride) is blended with butadiene - containing rubbery polymers, some acrylates, ethylene - vinyl acetate copolymers and ABS plastics. Polyethylene and polypropylene are often toughened by addition of butyl rubber.

Considerable interest has therefore been taken in the physical properties of polymer blends, although the chemical properties of such systems have not been the subject of much study. It is well known that the decomposition behaviour of a polymer molecule can be modified considerably by the presence of a second, foreign monomer unit in the chain. It is therefore of interest to observe whether or not polymers degrade differently in the presence of a second polymer. A typical example is the thermal degradation of mixtures of polystyrene and poly(α methyl styrene) (69). Poly (α methyl styrene) is less stable than polystyrene and as it depolymerises to monomer, it produces radicals which can initiate the degradation of polystyrene at temperatures at which it is normally stable.

.7 Aim of this work

Although a great deal of effort has been concentrated on the photooxidation of polypropylene, little has been directed at its photolysis in vacuo. This thesis is concerned with an investigation into the effect of heat and light, alone or in combination on films of isotactic polypropylene. The possible effects of catalyst residues and sample morphology are also considered.

As a consequence of the increasing industrial importance of polyblends, it was deemed worthwhile to investigate the thermal and photo - stabilities of a number of polymer blends containing polypropylene as the common polymer.

CHAPTER TWO

EXPERIMENTAL TECHNIQUES AND APPARATUS

2.1 Source of Polymers

The polymer most widely used in this investigation was a sample of isotactic polypropylene, obtained from Shell as a powder, completely free of additives. A few of its characteristics are listed below:-

Nominal melt index	3.0g/10 min.
Molecular Weight (M_v)	222,300
Crystalline Melting Point	167°C
Tacticity	89 % isotactic

Other polymers used and brief details of their history are given in the appropriate chapters.

2.2 Polymer Form

In photochemical studies of polymers in the solid state, it is recognised that the use of powdered polymer leads to erratic and conflicting results on account of the large number of uncontrollable variables (particle size, layer thickness, surface area of powder, etc) associated with such a system. For this reason, most investigations are conducted on thin films.

Standard methods of preparing transparent polymer films involve melting, pressing, moulding etc. at elevated temperatures in air. However, each suffers from the disadvantage that the polymer may become partially degraded or oxidised during formation of the film. Alternatively, polymer films can be cast from solution by solvent evaporation, a process which normally involves no degradation or oxidation. However, there is no suitable solvent for polypropylene at ambient temperatures and film - casting at elevated temperatures again risks degradation or oxidation.

The method finally adopted involved pressing a polymer powder sample at room temperature into the form of a disc, which was pre - melted and cooled in vacuo prior to use. Approximately 80 mg of powdered polypropylene was placed in a continuously evacuated die and compressed to 20 tons for 4 minutes in a Perkin - Elmer hydraulic press. In this way an opaque polymer disc of radius 1 cm and thickness 230 microns was obtained.

The disc in this form was still unsuitable for photolysis since it was opaque and could be simply be regarded as a more sophisticated form of "powder sample", with many of its uncontrollable variables. This problem was overcome by heating the disc in vacuo, to a temperature slightly above its melting point and allowing it to cool. Great care was taken to ensure the rigorous control of the cooling process since the degree of crystallinity of a sample depends on the rate of cooling from the melt. Indeed, samples of different crystallinities were prepared in this manner. The result of pre - melting a polymer disc was an almost transparent sample suitable for the incidence of ultra - violet radiation.

However for degradations above the melting point of the polymer, pre - melting was of course, not necessary. On melting, a disc becomes transparent and loss of incident light intensity owing to reflection and scattering is minimised.

2.3 Source of Radiation

A Hanovia chromatolite lamp was used as the source of ultra - violet radiation. This lamp employed a low - pressure mercury arc to produce a typical mercury emission spectrum, the intensities of the two resonance lines at 1849 Å and 2537 Å being much greater than those of all the other wavelengths present. The output of this lamp is shown in FIGURE 2.1. The lamp was connected to an L.T.H. Transistorised 1 kVA Voltage Regulator to ensure that any variations in the mains output did not affect the lamp emission.

2.4 Transmission of UV Radiation

Under the experimental conditions employed, it was necessary for the output of the lamp to traverse air, fused silica and a vacuum (inside the cell) before finally impinging on the polymer samples. Thus it is to be expected that the nature of the radiation eventually reaching the polymer disc will be modified to some extent by the absorption characteristics of these media.

a) Transmission by Air

The only component of air capable of absorbing the ultra - violet radiation employed is oxygen, the other constituents being completely transparent in this region of the spectrum. The oxygen absorption spectrum consists of two sets of bands, the one system converging at 2400 Å, and the more important Schumann - Runge system, having a threshold wavelength at 2000 Å and converging towards 1761 Å (70). These two absorptions correspond to two photo - dissociations of oxygen molecules,

$$O_2 + h\nu \longrightarrow O(^3P) + O(^1D)$$

and

$$O_2 + h\nu \longrightarrow 2\,O(^3P).$$

Ozone is produced concurrently according to the equations,

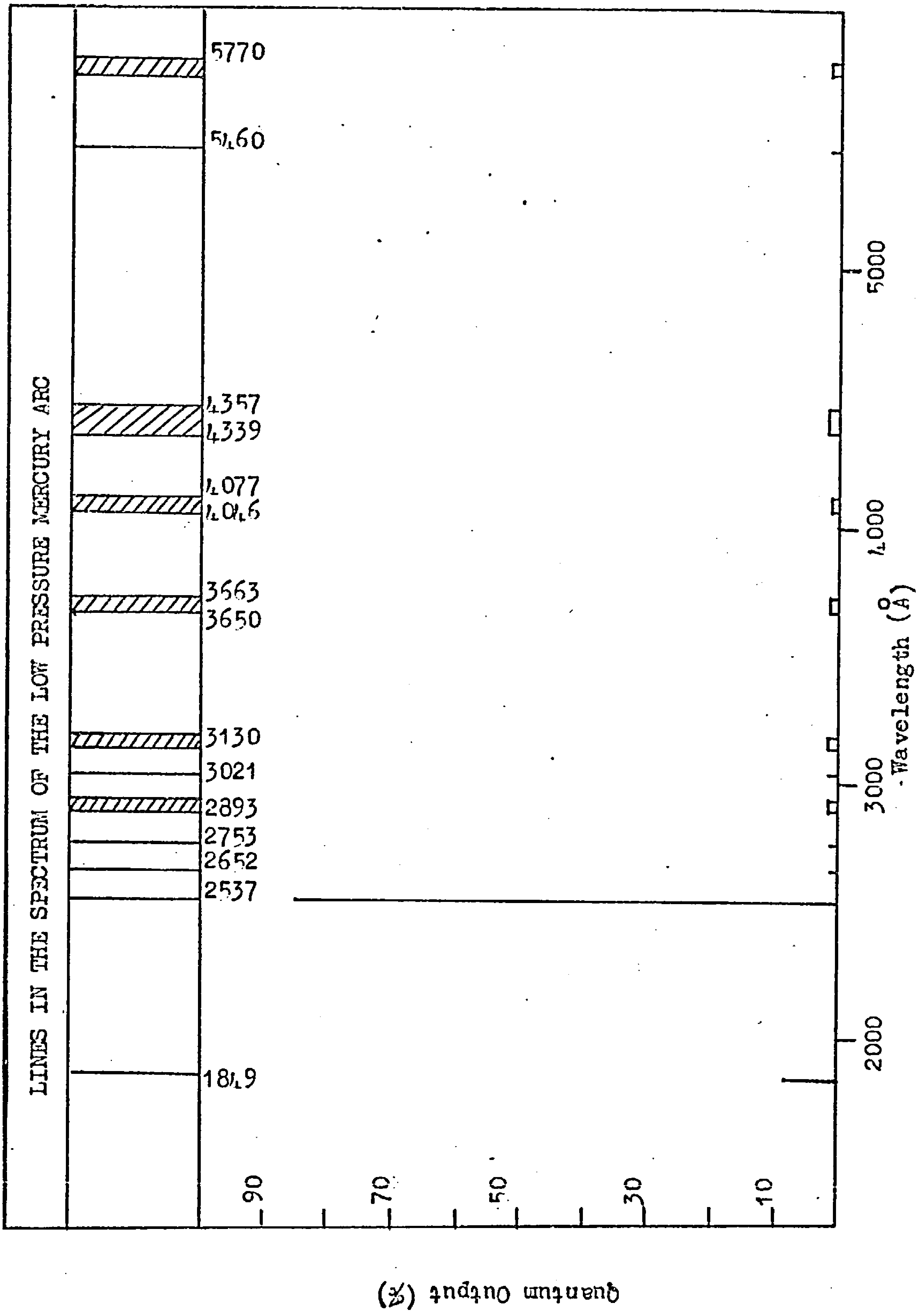


FIGURE 2.1 Output of Hanovia Lamp

$$O(^1D) + O_2 + M \longrightarrow O_3 + M$$

and

$$O(^3P) + O_2 + M \longrightarrow O_3 + M$$

where M is the necessary third body.

It is obvious that only the 1849 Å line has an energy associated with it which exceeds the threshold energy for the disociation of oxygen. It has been indicated (10) that 1 cm of air is sufficient to absorb this line completely.

b) Transmission by Fused Silica

The transmission of fused silica is shown in FIGURE 2.2. It can be seen that, for the wavelength considered, 96 % of the incident light is transmitted.

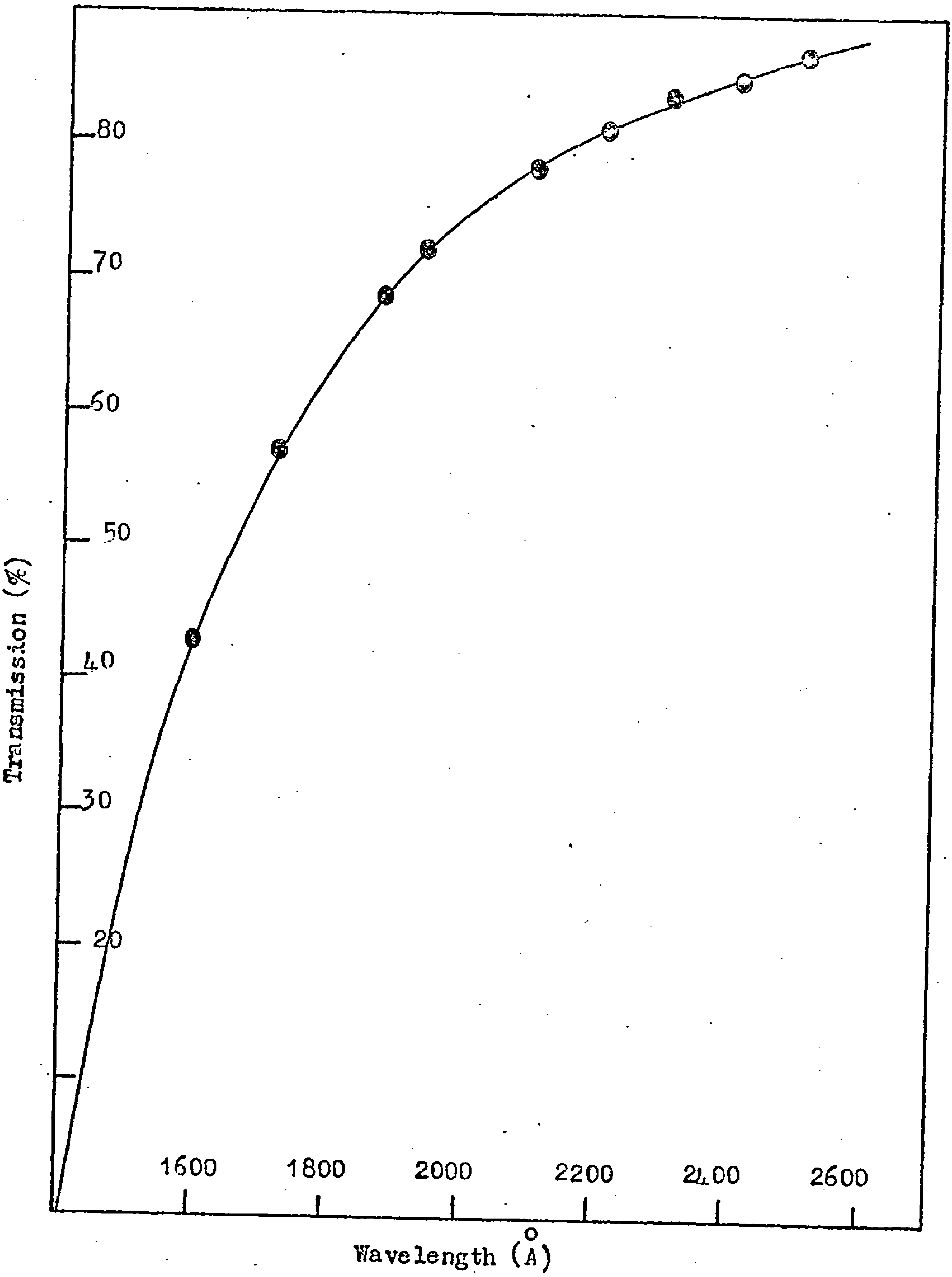
c) Monochromaticity of the Source

It has already been shown that 93 % of the lamp output is composed of the mercury resonance radiation with wavelengths of 1849 Å and 2537 Å, and that, in traversing the arc to polymer path, the intensity of the former is reduced to an extremely low value. The intensity of the latter, however, is only slightly attenuated. Since the intensities of the longer wavelength radiation are negligible compared with that of the 2537 Å, the radiation reaching the polymer sample is virtually monochromatic (2537 Å).

2.5 Determination of the Absolute Numbers of Quanta Produced by the Lamps Employed.

a) Introduction

In order that the results of photolysis may be treated in a quantitative manner and that the results emanating from different



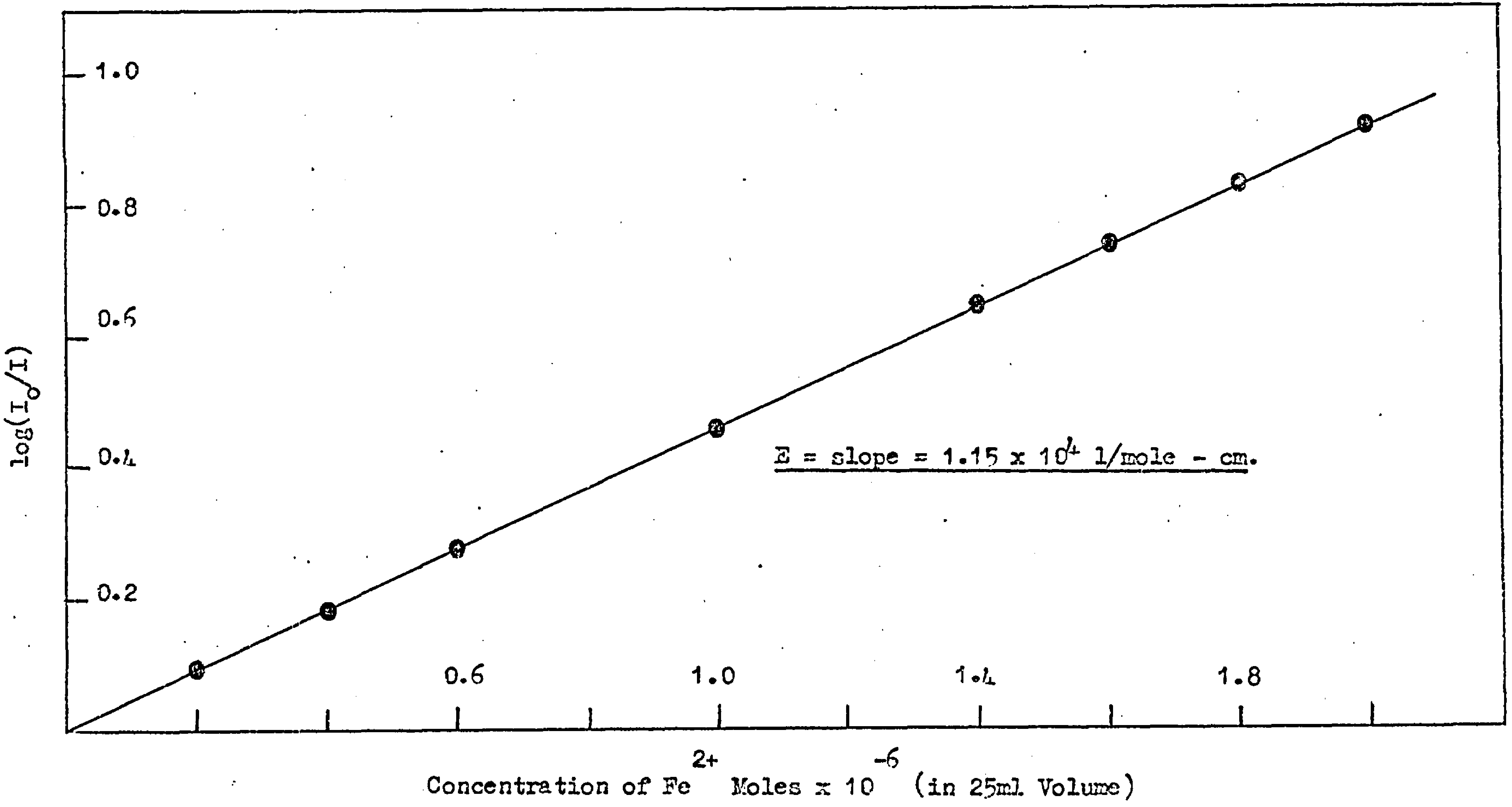
<u>FIGURE 2.2</u> Absorbtion Spectrum of Fused Silica (2mm.)

lamps may be compared quantitatively it is imperative that the absolute number of quanta produced by each source be determined. The method employed in this investigation involved use of the potassium ferrioxalate solution phase chemical actinometer developed by Hatchard and Parker (8) which is simple to use and very sensitive over a wide range of wavelengths. It is based on the fact that when solutions of $K_3Fe(C_2O_4)_3$ in sulphuric acid are irradiated with light of wavelength 2500 - 5770 Å, the iron is reduced to the ferrous state and the oxalate is oxidised. After irradiation, the ferrous iron can be converted into the red coloured 1,10 phenanthroline - Fe^{2+} complex which is highly absorbing and easily analysed.

b) Experimental Procedure

Solid green crystals of $K_3Fe(C_2O_4)_3$ were prepared as described by Hatchard and Parker (8) and Calvert and Pitts (5), the latter giving a fully detailed summary of the procedure. The manipulations and preparation of the ferrioxalate solutions were carried out in a dark room. A standard calibration graph for the analysis of the Fe^{2+} complex was prepared, as shown in FIGURE 2.3, using a Hitachi Perkin Elmer 139 UV - Visible Spectrophotometer.

The light intensity in each of the two photolysis cells was determined by irradiating 15 ml of ferrioxalate solution (V_1) for a period of 60 seconds. After mixing the solution, 10 ml (V_2) was pipetted into a 25 ml volumetric flask (V_3) and the phenanthroline complex prepared along with an identical blank solution using unirradiated ferrioxalate solution. The transmission of the complex



E = slope = 1.15 x 10^4 1/mole - cm.

FIGURE 2.3 Calibration Graph for Ferrous iron (OD at 5100 Å in a 1 cm cell) solution was measured at 5100 Å in a 1 cm cell using the blank solution as a reference.

The number of Fe^{2+} ions formed during the photolysis (nFe^{2+}) was calculated using the formula;

$$n\,Fe^{2+} = \frac{6.023 \times 10^{20} V_1 V_3 \log(I_o/I)}{V_2 L E}$$

where

V_1 = Volume of actinometer solution irradiated (ml)

V_2 = Volume of aliquot taken for analysis (ml)

V_3 = Final volume to which the aliquot V_2 is diluted (ml)

$\log(I_o/I)$ = Measured optical density of the solution at 5100 Å

L = Path length of the spectrophotometer cell used (cm)

E = Experimental value of the molar extinction coefficient of the Fe^{2+} complex as determined from the slope of the calibration plot.

The light itensity incident just inside the silica window of each photolysis cell, I_o^i, was calculated from the equation (5),

$$I_o^i = n\,Fe^{2+}/\Phi_{Fe^{2+}} \cdot t(1 - 10^{-E(A)L}) \text{ quanta / sec.}$$

where

$_{Fe}{}^{2+}$ is the quantum yield of the product Fe^{2+}(equal to 1.25 for the radiation of wavelength 2537 Å)

t = time of exposure

$(1 - I/I_o)$ = $(1 - 10^{-EAL})$ = fraction of incident light absorbed.

Calculated values will be quoted in subsequent chapters.

2.6 Determination of the Peroxide Content of the Polypropylene Sample.

The peroxide concentration was determined using the procedure outlined by Carlsson and Wiles (54). 5mg of the powdered polymer were refluxed with 2.0ml of a sodium iodide solution in isopropyl alcohol (200g/l) after acidification with 7 ml of an acetic acid/ isopropyl alcohol mixture (1 : 10 ratio by volume). At the end of the reflux period, the solution was cooled, diluted to 10 ml with distilled water and the I_3^- formed during peroxide decomposition was determined on a Unicam SP 800 spectrophotometer. The optical density was obtained at 3600 Å in 1 cm cells and the peroxide concentration was estimated from a measured extinction coefficient for I_3^- of 25000 M^{-1} cm^{-1}. A blank solution was refluxed for use as a reference.

This method takes advantage of the oxidative stability of iodide ions in isopropanol (dispensing with the need for a nitrogen atmosphere), and the high sensitivity and convenience of a spectrophotometric method. It has been shown (71) that only a brief reflux (~5 min) is normally required to give a quantitative yield of I_3^- from most hydroperoxides. This procedure allows the estimation of total peroxide levels as low as 1 x 10^{-7} moles in 5 mg sample.

2.7 Determination of Degree of Crystallinity

Polymer molecules with a particular molecular structure (e.g. isotactic polypropylene) aggregate to form crystals, and these, in turn, aggregate to form sperulites. The manner of aggregation of molecules determines the crystal structure and the aggregation of crystals produces the morphological structure (spherulite or single crystal). Polyolefins are only partially crystalline and the determination of the degree of crystallinity (percentage of crystalline material) is of great practical importance. This may be measured by several methods, X - ray diffraction and density measurements being the ones employed in this study.

a) X - Ray Diffraction

X - ray 'powder' photographs were obtained from polymer discs cooled from the melt at different rates. Diffraction curves, of which FIGURE 2.4 is typical, were obtained from these films using a Chromoscan MK II Double - Beam Recording and Integrating Densitometer.

In any attempt to determine the degree of crystallinity of a sample from X - ray diffraction, some measure of the background curve must be obtained. The simplest method of construoting a backgroung curve appeared to be that of Natta and coworkers (72), involving the following steps ;

i) A straight line was drawn to connect the points of the diffraction curve corresponding to $2\Theta = 7^{\circ}$ and $2\Theta = 30^{\circ}$.

ii) The vertical distance $\underline{a}$ from the background maximum to this straight line is determined.

iii) Another point of the background at $2\Theta = 14.8^{\circ}$ was then found at the vertical distance of 0.9a above the straight line.

iv) The background curve was finally finished as a smooth curve passing through the two constructed points and tangential to the diffractogram at the diffraction angles of about 12.5° and 23°, respectively.

The completed background curve is also shown in FIGURE 2.3.

The crystalline fraction (X) was calculated using the equation developed by Woidinger and Hermans (73) ;

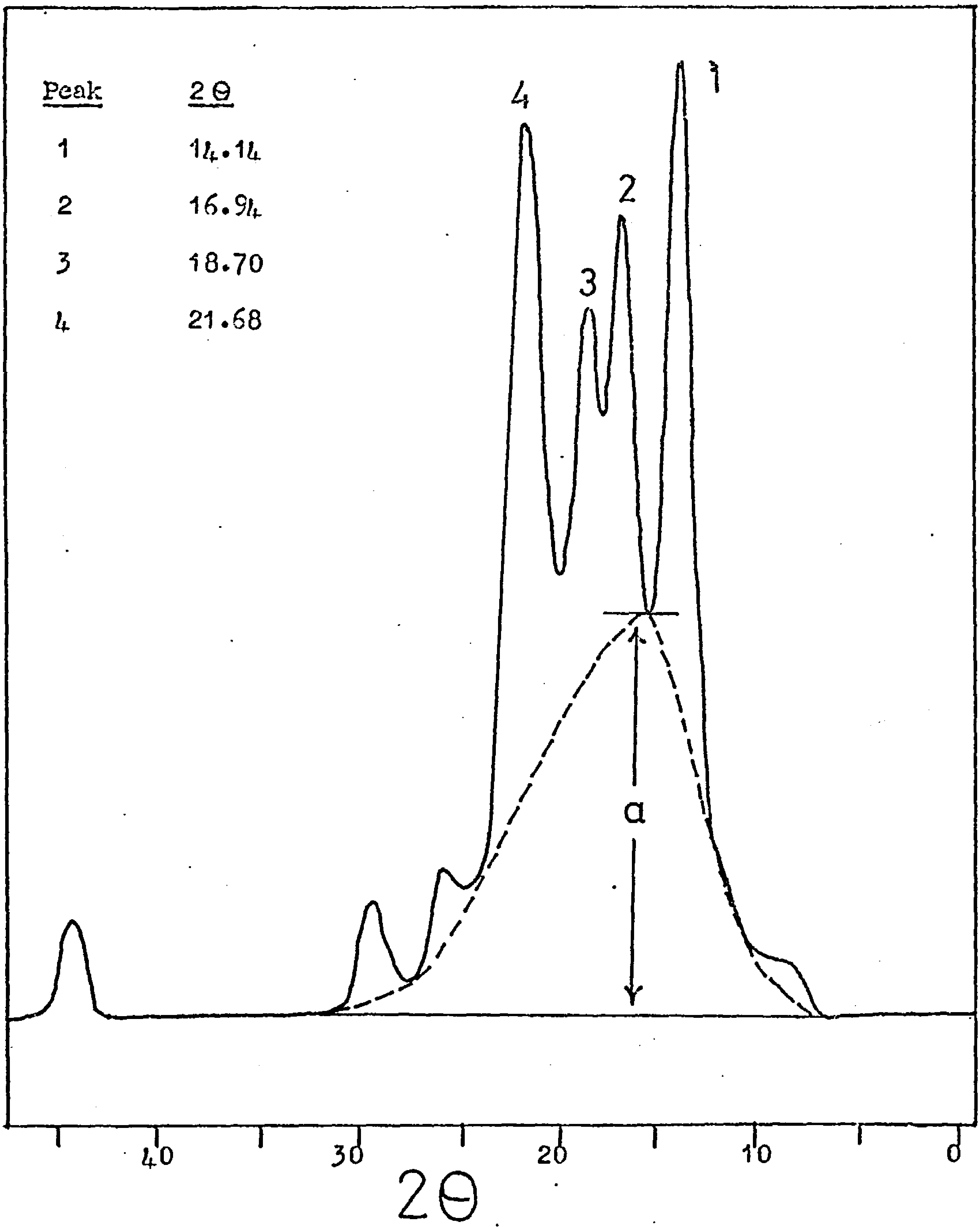


FIGURE 2.4 Typical X - Ray Diffraction Curve for isotactic Polypropylene.

$$O_{cr}/O_{am} = \frac{1200\,X}{925(1 - X)}$$

from which follows,

$$X = \frac{1}{1 + 1.2970\,O_{am}/O_{cr}}$$

where,

O_{cr} = sum of the surfaces of all peaks up to $2\Theta = 50^\circ$ (1200 for a 100 % crystalline samples).

O_{am} = surface of the background above the (almost horizontal) straight line connecting the recorded intensities at $2\Theta = 7^\circ$ and $2\Theta = 30^\circ$. (925 for a 100 % amorphous sample).

b) The Density Method

This method (74) is based on the assumption that the polymer consists of crystalline zones with a theoretical X - ray density (0.936) and amorphous zones with the low density of wholly amorphous atactic polypropylene (0.855). Density values of polypropylene discs cooled from the melt were obtained at 20°C using a density column. The degree of crystallinity of each sample was determined by linear interpolation.

2.8 Thermal Methods of Analysis

a) Thermal Volatilisation Analysis (TVA)

The technique of Thermal Volatilisation Analysis was first described by McNeill (75) and measures the thermal conductivity of the volatile material evolved from a heated polymer sample which is being continuously pumped.

In the basic TVA system, a Pirani gauge is attached to a vacuum line system at a convenient point between the heated sample and the cold trap (- 196°C). The products which leave the hot zone pass through the system and produce a response on the Pirani gauge. If an additional trap, at some temperature between ambient and that of the main trap, is placed before the Pirani gauge, as shown in FIGURE 2.5, then the gauge will now respond only to substances sufficiently volatile to pass through the trap. By varying the first trap temperature in a series of experiments, a considerable amount of information about the nature of the products may be obtained.

The differential condensation TVA apparatus (DCTVA), shown in FIGURE 2.6, was later developed by McNeill (76) and allows the above information to be obtained in a single experiment. This system employs a series of five traps maintained at different temperatures, each followed by a Pirani gauge. The responses from the Pirani gauges are fed into a multi - point recorder so that they are recorded simultaneously. These traces of the responses are a measure of the rate of volatilisation against time. The traces give an indication of the amounts of the various products which are volatile at the various trap temperatures. A separate temperature versus time trace is also recorded so that when a linear temperature programme is used, as in normal practice, any deviations of the heating rate from linearity may be checked.

It has been found that polymers give very characteristic thermograms and much information about stability, reaction mechanisms and the nature of the volatile products can be deduced. Further information can be obtained by analysis of the volatile materials which have condensed in the various traps, the short chain fragments which condense on the walls of the reaction tube outside the

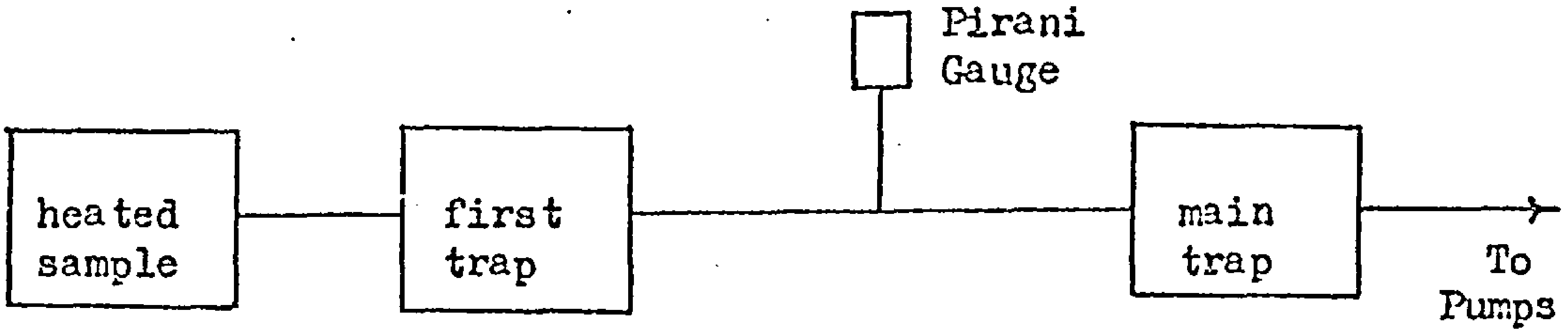
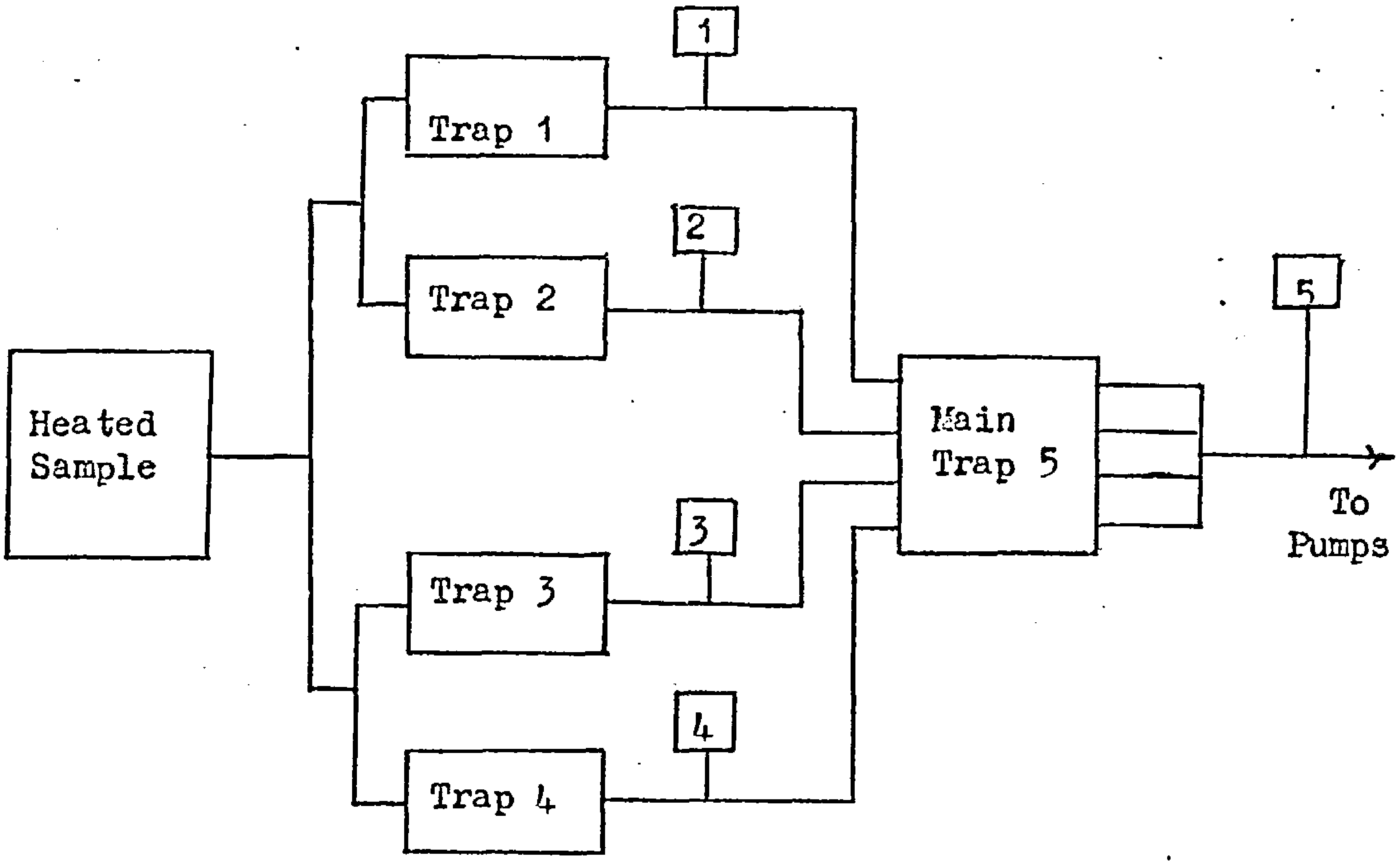


FIGURE 2.5 Basic TVA System



NORMAL WORKING TEMPERATURES :

Trap 1	- 100°C
Trap 2	- 75°C
Trap 3	- 45°C
Trap 4	0°C
Trap 5	- 196°C

1,2,3,4 and 5 = Pirani Gauge Heads

FIGURE 2.6 Schematic Representation of the Four Line Differential Condensation TVA System.

furnace, and the residue.

This technique was found to be particularly useful in investigating the effect of blending polypropylene with other polymers.

b) Thermogravimetry (TG)

Thermogravimetry was carried out using a Du Pont 950 Thermogravimetric Analyser which employs a null type balance in which any weight change in the sample is opposed by an equal restoring force applied to the beam. This restoring force is then a measure of the change in the weight of the sample. The balance can be operated up to 1200°C, either isothermally or by programming at a heating rate of 0.5°C to 30°C per minute.

The main disadvantage of this particular instrument is that it cannot be used under high vacuum conditions. Thus, exact comparison of results with TVA cannot be made.

In this study, a heating rate of 10°C per minute was used to degrade 10 mg samples in an atmosphere of nitrogen.

2.9 Molecular Weight Determination

Molecular weights were measured viscometrically. Although this is a rapid method with relatively few sources of experimental error, it is not absolute like osmometry or light scattering. For linear polymers. solution viscosity is empirically related to molecular weight.

Viscosity can be defined in the following ways (77) ;

Relative Viscosity $$\eta_{rel} = \eta/\eta_o = t/t_o$$

where t_o is the flow time of a reference solvent through a viscometer and t is the flow time through the same viscometer of a dilute solution of polymer in the same reference solvent.

Specific Viscosity $$\eta_{sp} = \eta_{rel} - 1 \equiv \left(t \underset{t}{-} t_o\right)$$

Reduced Viscosity $$\eta_{red} = \eta_{sp/c}$$

where c is the concentration of the polymer solution in g/100 ml.

Inherent Viscosity $$\eta_{inh} = \ln \eta_{rel/c}$$

Intrinsic Viscosity $$[\eta] = \lim_{c \to 0}(\eta_{sp/c}) = \lim_{c \to 0}(\ln \eta_{rel/c})$$

The determination of intrinsic viscosity requires the preparation of dilute solutions of the polymer in a suitable solvent. The viscosities of these solutions are then measured relative to that of the solvent. The intrinsic viscosity is obtained by extrapolating to zero concentration a plot of either inherent viscosity or reduced viscosity versus concentration. However an equation has been developed (78) for determining intrinsic viscosity by a single point determination for dilute solutions ;

$$[\eta] = \left[(2)^{\frac{1}{2}}/c\right](\eta_{sp} - \ln \eta_{rel})^{\frac{1}{2}}$$

A correlation between intrinsic viscosity and molecular weight for linear polymers is achieved through the Mark-Houwink equation (77),

$$[\eta] = K.M^{\alpha}$$

where M is the molecular weight and K and α are constants for a particular polymer - solvent system. The constants K and α are determined by the intercept and slope, respectively, of a log - log plot of intrinsic viscosity and molecular weight. The molecular weights used in such a plot are determined by one of the absolute methods such as light scattering.

In this work, intrinsic viscosities were obtained using an Ubbelohde capillary viscometer, and applying the single - point determination method. Molecular weights were estimated from the intrinsic viscosities of decalin solutions of polypropylene at 135°C using the equation (24),

$$[\eta] = 1.07 \times 10^{-4} M^{0.80}$$

It was considered advisable to use the single - point determination method since it has been reported (79) that polypropylene undergoes severe degradation if maintained in decalin at 135°C for periods upwards of 30 minutes. 1% 2,6 di - t - butyl - p - cresol (Ionol) was added to the decalin as a stabiliser.

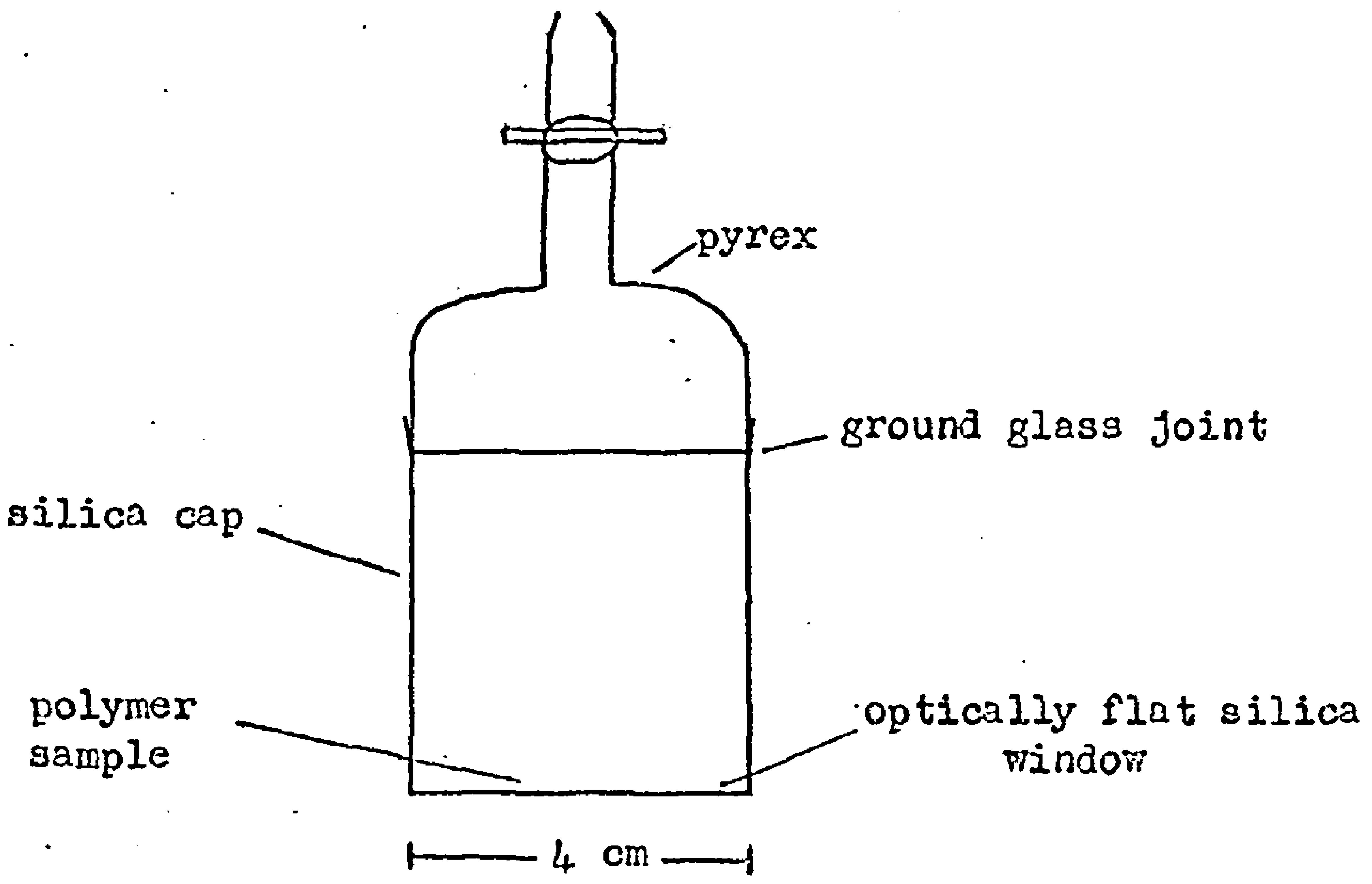
2.10 Degradation Apparatus

a) Photolysis Cells

It is essential that any photochemical reaction be carried out in a vessel which is transparent to the ultra - violet light used. For this reason the caps of the photolysis cells employed were made of silica. The ambient temperature photolysis cell and the photothermal cell are represented in FIGURE 2.7. The two halves of each cell were connected by a ground glass joint. The position of the photothermal cell relative to the rest of the vacuum system is shown in FIGURE 2.8.

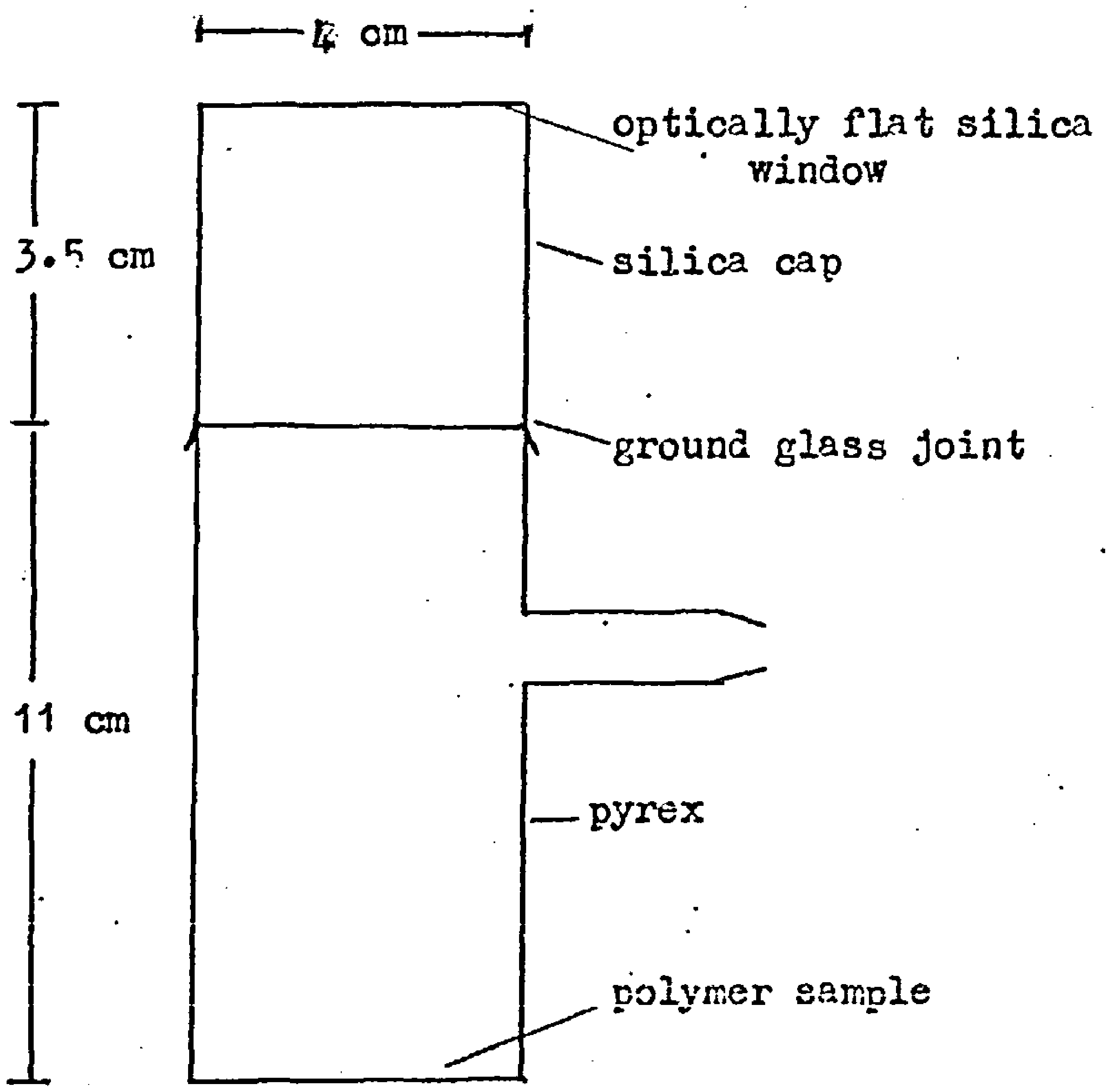
b) Thermal Degradation Cell

Thermal degradations were carried out in the photothermal cell (FIGURE 2.7 (b)) without the incidence of radiation.



Distance from lamp to silica window = 2 cm

a) Ambient Temperature Photolysis Cell



Distance from lamp to silica window = 3 cm

b) Photothermal Degradation Cell

FIGURE 2.7 Degradation Cells

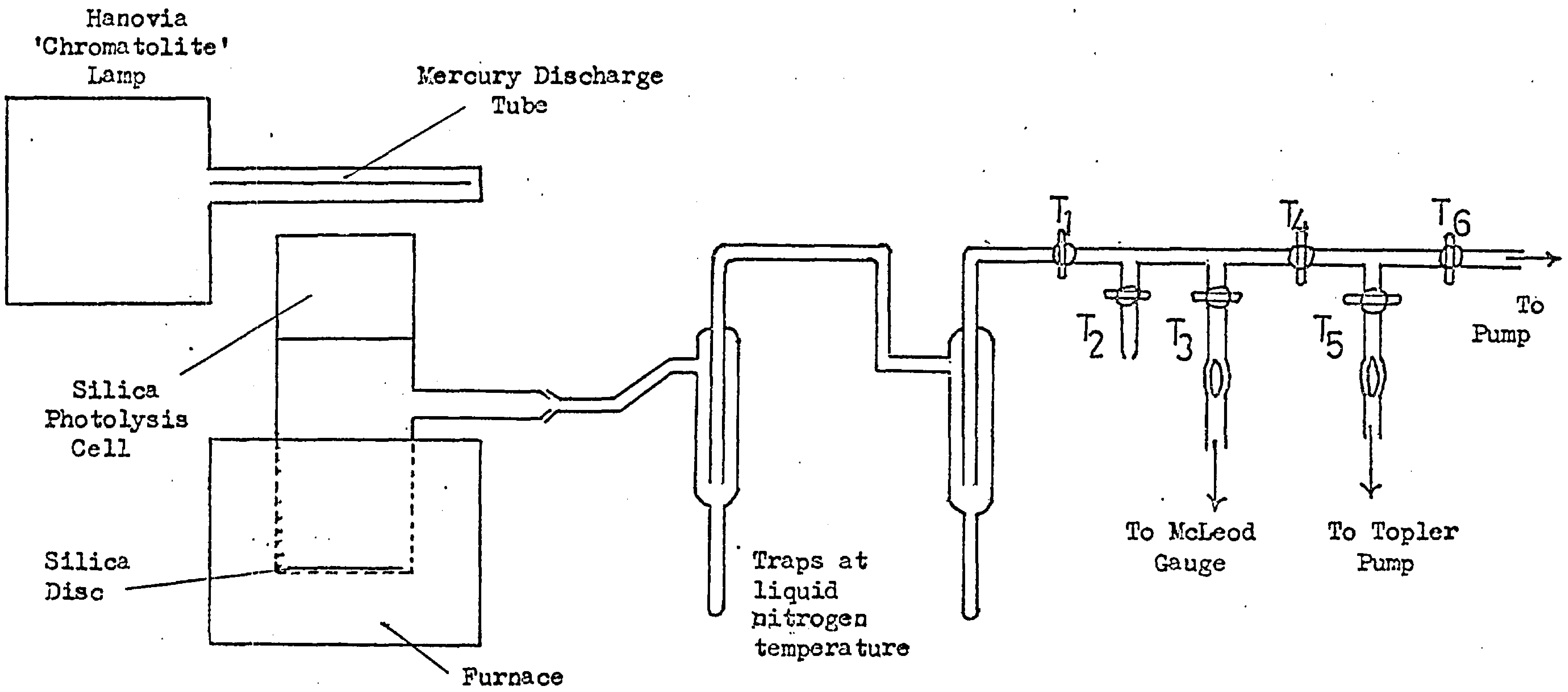


FIGURE 2.8 Photothermal Degradation Apparatus

c) Temperature Control

Degradations, both thermal and photothermal, were conducted over a range of temperatures up to 354°C. The cell was heated to the required temperature by means of a furnace connected to a Sirect Mark II Proportional Temperature Controller in conjunction with a Silicon Controlled Rectifier Unit. Chromel - Alumel thermocouples were used to record the temperature of the furnace and of the silica disc inside the degradation cell. In this way an accurate calibration was obtained (FIGURE 2.9).

2.11 Experimental Procedure

a) Photolysis at Ambient Temperature

Polymer discs (80mgs) were irradiated in the cell illustrated in FIGURE 2.7(a). The lamp was allowed to warm up for 15 minutes prior to exposure of the sample.

b) Photothermal and Thermal Degradation

Polymer discs (80mgs), each supported on a silica disc, were placed in the cell and connected to the vacuum system as shown in FIGURE 2.8. The cell was evacuated, tap T_1 was closed and the two traps immersed in liquid nitrogen. The furnace was then raised and after 10 minutes the sample was adjudged to have reached the required temperature. In photothermal degradations, the sample was exposed to the UV radiation at this point.

Degradation products leaving the hot zone condense either on the side of the cell outside the furnace or in the cold traps, depending on their volatility. It has been suggested that, in systems which are not continuously pumped, diffusion of products from the heated sample is inhibited by the increase in pressure in the system, thus causing the occurrence of secondary reactions. It is considered

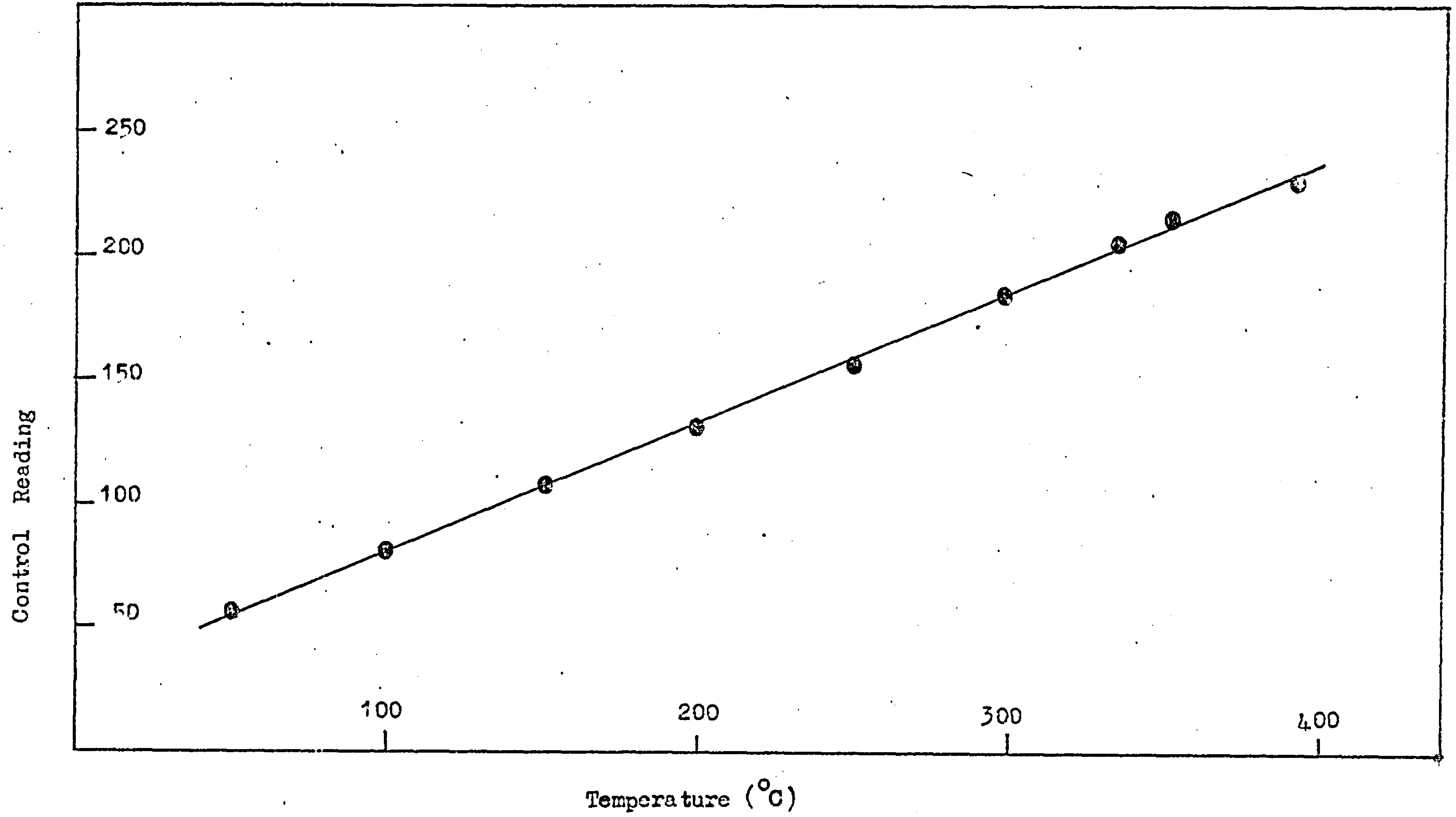


FIGURE 2.9 Calibration of Furnace by Means of Chromel - Alumel Thermocouples

that the system employed in the present study approximates to a continuously evacuated system since only trace amounts of non - condensible materials are produced.

2.12 Product Separation

The degradation products were separated for analysis in the following manner;

a) Permanent gases (those non - condensible at - 196°C) were removed from the apparatus, with cold traps still in position, using a Töpler pump.

b) Products volatile at ambient temperature were then obtained by removing the cold traps and collecting, as before, with a Topler pump. The usual procedure in both cases was to collect the gases in an infra - red gas cell and then, having run a spectrum, to transfer them to a glass sample vessel suitable for MS or GLC analysis.

c) The polymer residue weights were obtained by noting the combined weight of the silica disc and polymer sample before and after degradation.

d) The amounts of short chain polymer fragments (cold ring fraction) were determined by washing out the sides of the cell with warm toluene into pre - weighed sample bottles and removing the solvent under vacuum to constant weight.

2.13 Product Analysis

The polymer degradation products were identified and measured using the techniques and instrumentation outlined below :-

a) Infra - red Spectroscopy

A gas cell of path length 10 cms was used to record the infra - red spectra of gaseous products. The spectra of the cold ring fragments were measured by casting a thin film from warm toluene on a NaCl salt plate using a clean salt plate as a reference. The spectra of the polymer residues were recorded using KBr discs (300mg) containing 3 mg of sample. A bland KBr disc was placed in the reference beam on each occasion.

All spectra were run on a Perkin - Elmer 257 Grating Spectrophotometer and quantitative measurements, where necessary, were carried out using the usual base - line method.

b) UV - Visible Spectrometry

All spectra were obtained on a Unicam SP 800 spectrophotometer.

c) Mass Spectrometry (MS)

An A.E.I.MS 10 Residual Gas Analyser was used to obtain mass spectra of the permanent gases. The spectra of other gaseous volatiles were obtained using an A.E.I.MS 12 Mass Spectrometer.

d) Gas - Liquid Chromatography (GLC)

GLC analysis of the total gaseous volatiles was carried out using a Microtek GC 2000 R Research Gas Chromatograph equipped with dual columns, flame ionisation detector and a linear temperature programmer. A stainless steel column of dimensions 10 ft x $\frac{1}{4}$ in. and packed with 30 - 60 mesh silica gel, was employed. The gas sampling apparatus, which has the advantage of being portable, is shown in FIGURE 2.10. Samples were withdrwn via the rubber septum using a gas syringe and injected into the chromatograph.

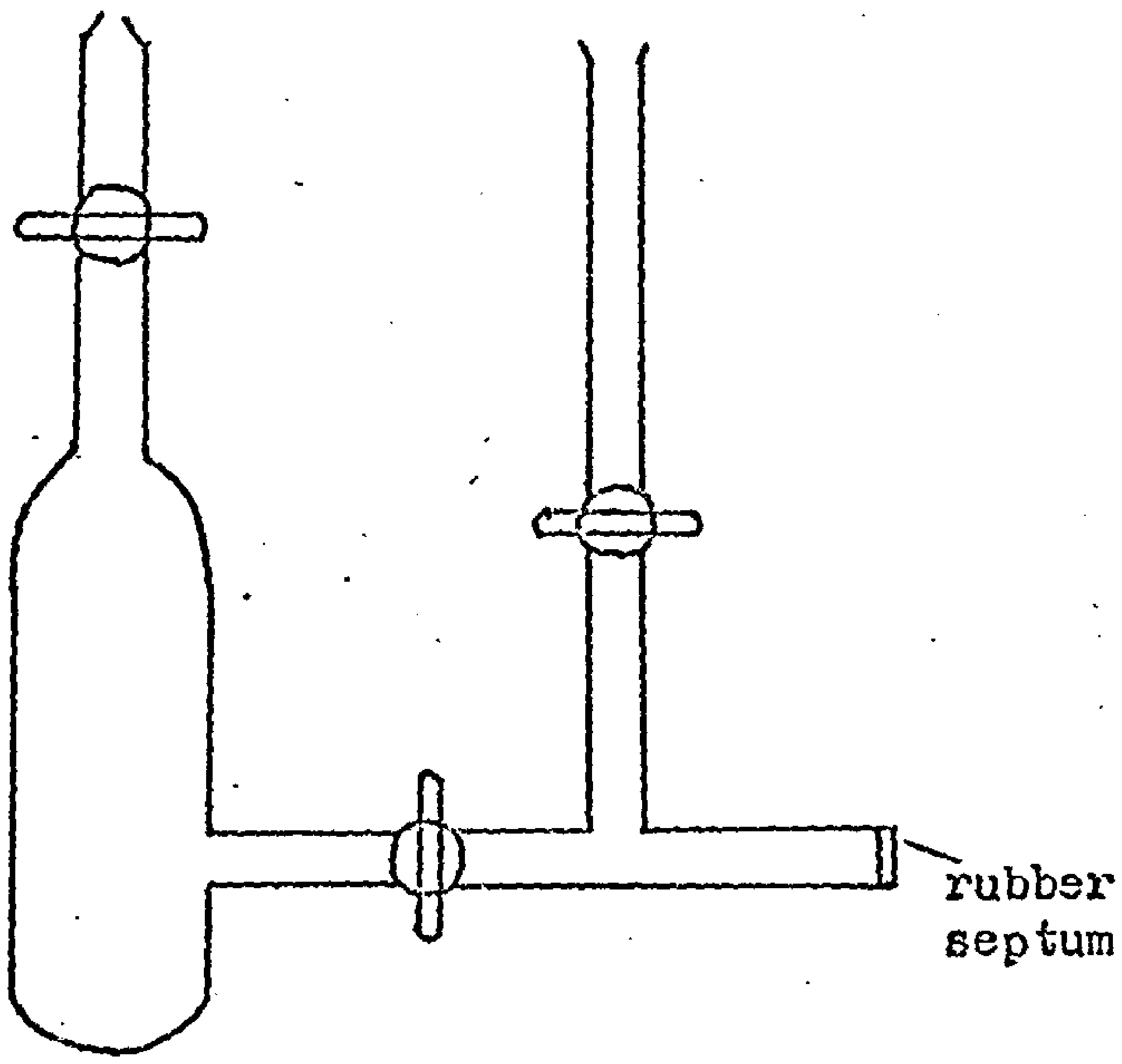


FIGURE 2.10 Gas Sampling Apparatus

CHAPTER THREE

A COMPARISON OF THE THERMAL AND PHOTOTHERMAL DEGRADATIONS OF POLYPROPYLENE.

A series of thermal and photothermal degradations were conducted for times up to 20 hours and over a temperature range of 300° - 354°C. Photodegradations were also carried out, for times up to 100 hours, at temperatures below the threshold temperature for thermal degradation of polypropylene (~300°C) and above its melting point (167°C). Possible differences between the thermal and photothermal degradation reactions were sought through a detailed analysis of volatile products. Experimental conditions and techniques of analysis were as described in Chapter 2. The intensity of the light beam incident on the polymer sample was 2.44×10^{15} quanta/sec.

3.1 Qualitative Comparison of Degradation Products

Before a quantitative study of the degradation products can be contemplated, it is necessary to obtain a qualitative knowledge of each class of component, using more than one technique if possible. Products are classified under the following headings;

a) permanent gases
b) products volatile at 20°C
c) products liquid at 20°C
d) short chain fragments (cold ring fraction)
e) polymer residue

a) Permanent Gases

The techniques of infra - red spectroscopy and mass spectrometry were employed, as described in Chapter 2, to analyse the permanent gases (volatile at - 196°C). FIGURE 3.1 shows the infra - red spectrum of the permanent gas fraction of a polypropylene sample photothermally degraded for 20 hours at 300°C. The only peaks are at 3018 cm^{-1} and 1304 cm^{-1}, and are characteristic of methane.

Mass spectrometric analysis of this same sample indicated the presence of hydrogen (m/e 2) and methane (m/e 15, 16).

Hydrogen and methane were found to constitute the entire permanent gas fraction of every thermal and photothermal degradation reaction studied.

b) Products Volatile at 20°C

The gaseous products volatile at 20°C were collected as described in Chapter 2 and analysed by means of infra - red spectroscopy, GLC and mass spectrometry. They include the small proportion of permanent gases referred to above.

I Infra - red

The spectrum of the total gases produced during the thermal degradation of polypropylene for 8 hours at 354°C is shown in FIGURE 3.2. The spectra resulting from degradations at all temperatures studied within the range 300° - 354°C are similar. The assignments of the various absorptions are listed in TABLE 3.1. These are consistent with a complex mixture of saturated and unsaturated hydrocarbons. Little further information could be obtained from attempts to fractionate the gaseous products.

The spectrum of products from the photolysis of polypropylene

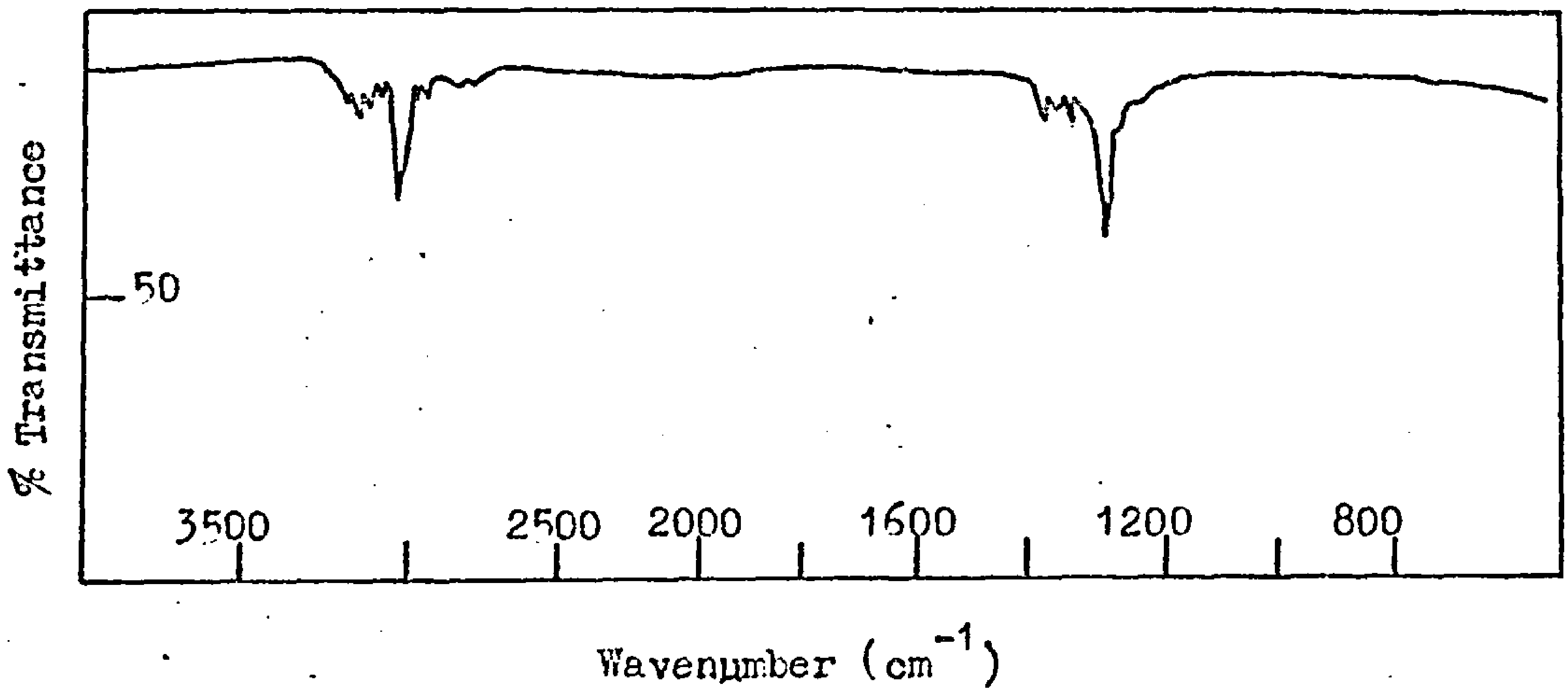


FIGURE 3.1 IR spectrum of the permanent gas fraction of a polypropylene sample photothermally degraded for 20 hours at 300°C.

FIGURE 3.2 Infra - red spectrum of volatiles from the thermal degradation of polypropylene for 8 hours at 354°C.

Wavenumber (cm^{-1})	Intensity	Assignment
3080	m	C-H stretch in C - H
3018	m	C-H stretch in CH_4
2965 2935 2878	s	C-H stretch in $-CH_3$ and $-CH_2-$
1650	m	C=C stretch
1460	s	C-H deformation in $-CH_2-$ and $-C-CH_3$
1380	m	C-H symmetrical deformation in $-CH_3$
1304	vw	C-H deformation in CH_4
988	w	C-H deformation in $RC\underline{H}=CH_2$
910	s	CH_2 deformation in $RCH=C\underline{H}_2$
888	s	CH_2 deformation in $R_2C=CH_2$

s = strong m = medium w = weak vw = very weak

TABLE 3.1 Assignments of the infra - red absorptions shown in FIGURE 3.2.

for 8 hours at 354°C is similar to that of its thermal analogue (FIGURE 3.2) except for an additional absorption, of very small intensity, at 950 cm^{-1}. This extra peak is attributed to a trace quantity of ethylene and is also to be found in all spectra from photodegradations in the range 300°- 354°C.

Photolyses were also carried out below 300°C but above 167°C, the melting point of polypropylene. Two spectra, typical of this range, are represented in FIGURE 3.3. At 200°C, the only identifiable product is methane (3018 and 1304 cm^{-1}), while at 250°C the spectrum is similar to those resulting from photodegradations above 300°C.

Thus it appears that temperature has a marked effect on the production of volatiles in the photolysis of polypropylene, even when thermal degradation is absent.

II Gas Chromatography

Product gases were introduced into the gas chromatograph as described in Chapter 2. FIGURE 3.4 illustrates the trace obtained for the products of photothermal degradation for 16 hours at 354°C. The retention time for each peak was obtained, and standard samples of pure gases were introduced into the column under the same conditions. The peaks in this trace, which is typical of those produced by the products of photolysis at other temperatures in the range studied, are accounted for as in TABLE 3.2.

Traces resulting from the products of thermal degradations in the range 300 - 354°C are similar to that in FIGURE 3.4, save that peak no. 2, attributed to ethylene, is absent. This is in agreement with infra - red evidence.

FIGURE 3.3 I.R. spectra of volatiles from the photolysis of polypropylene

(a) 83 hours at 200°C (b) 90 hours at 250°C.

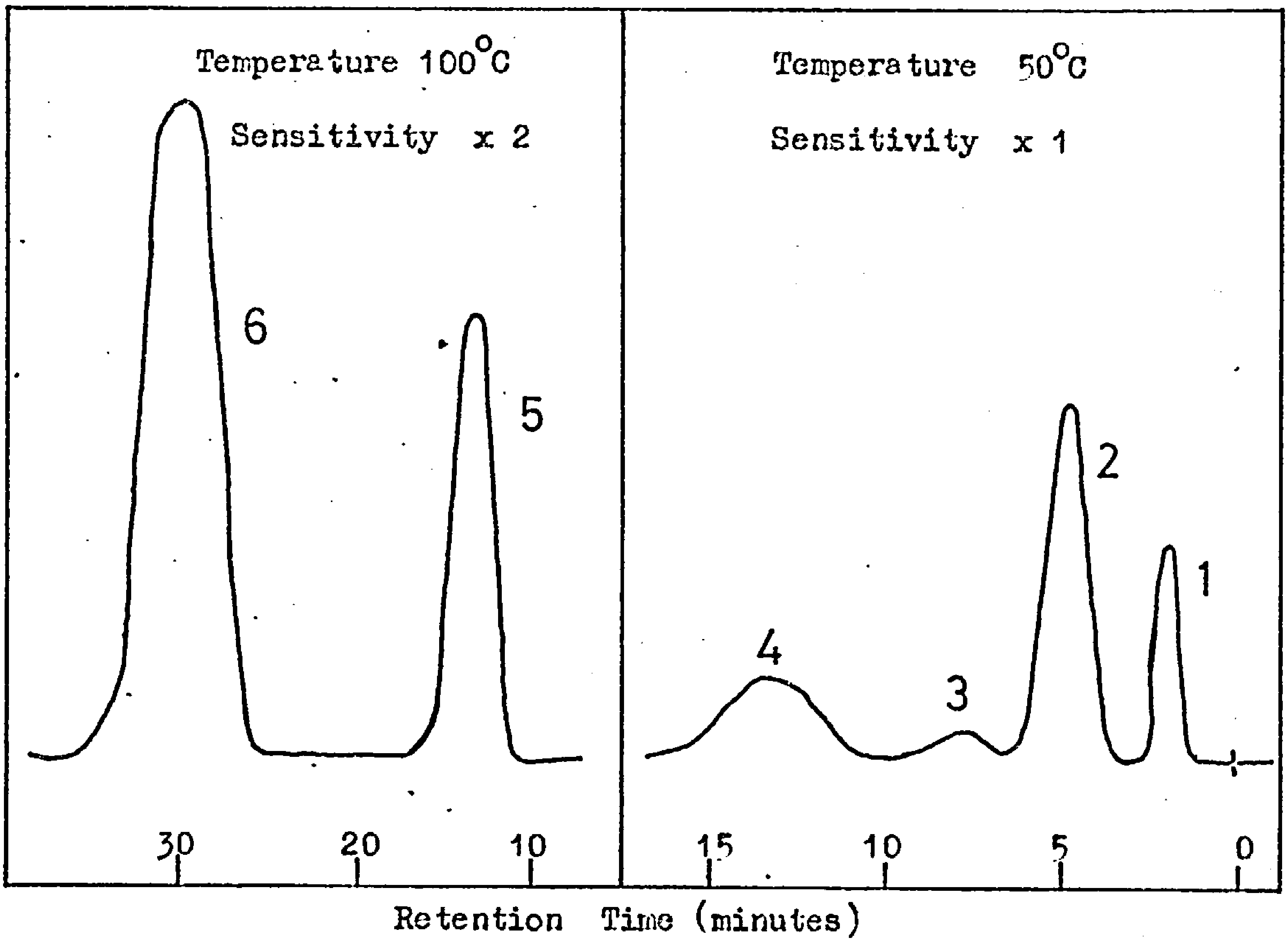


FIGURE 3.4 GLC trace for the products of photothermal degradation for 16 hours at 354°C.

Peak No. in FIGURE 3.4	Gas	Retention Time (minutes)	Temperature (°C)
1	Methane	2.0	50
2	Ethane	4.8	50
3	Ethylene	7.6	50
4	Propane	13.5	50
5	Propene	13.0	100
6	Butene	30.0	100

TABLE 3.2 Assignments of the peaks in the GLC trace represented in FIGURE 3.4.

III Mass Spectrometry

Mass spectra of gaseous products were obtained as described in Chapter 2 and are represented in the form of line diagrams, corrected for background where necessary (FIGURES 3.5, 3.6 and 3.7). The overall features can thus be seen at a glance. The spectrum of any hydrocarbon mixture is complex and consequently difficult to interpret, probably for the following reasons.

Molecular ions formed in a mass spectrometer are odd - electron species. A molecular ion $\boxed{AB}^{+}$, in which portions A and B are connected by a chemical bond, may therefore fragment into a carbonium ion and a radical,

$$\boxed{AB}^{\overset{+}{\circ}} \longrightarrow A^{+} + B^{\bullet} \quad \text{or } A^{\bullet} + B^{+}$$

the most probable cleavages being those which give rise to the most stable carbonium ions and / or radicals. This fragmentation reflects the desire of an odd - electron species to become an even - electron carbonium ion via radical elimination. Thus the molecular ions of molecules containing alkyl side chains frequently decompose by elimination of alkyl radicals rather than by expulsion of saturated neutral hydrocarbon molecules. For example, losses of methyl or ethyl radicals to give $M - CH_3$ and $M - C_2H_5$ ions, are very commonly observed in mass spectra, whereas abundant $M - CH_4$ and $M - C_2H_6$ ions are only infrequently encountered.

Also, fragmentation will occur preferably at sites of branching since the order of stability of carbonium ions is tertiary > secondary > primary. This can be seen by comparing the spectra of two isomeric hydrocarbons, one linear and the other branched. The spectrum of n - nonane is characterised by groups of peaks spaced

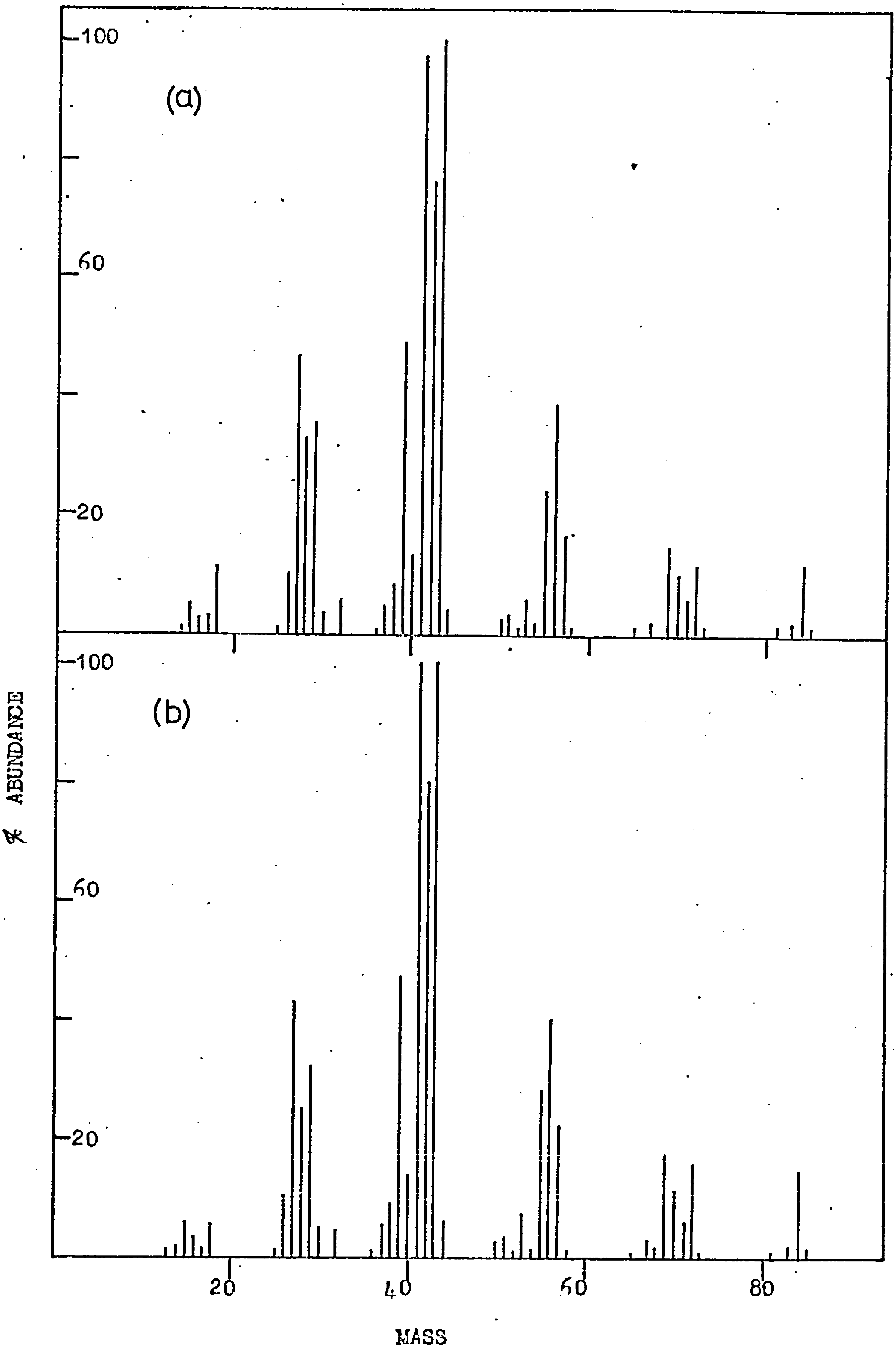


FIGURE 3.5 Mass spectra of products of degradation of polypropylene.

10 % volatilisation at 354°C

(a) Thermal (b) Photothermal

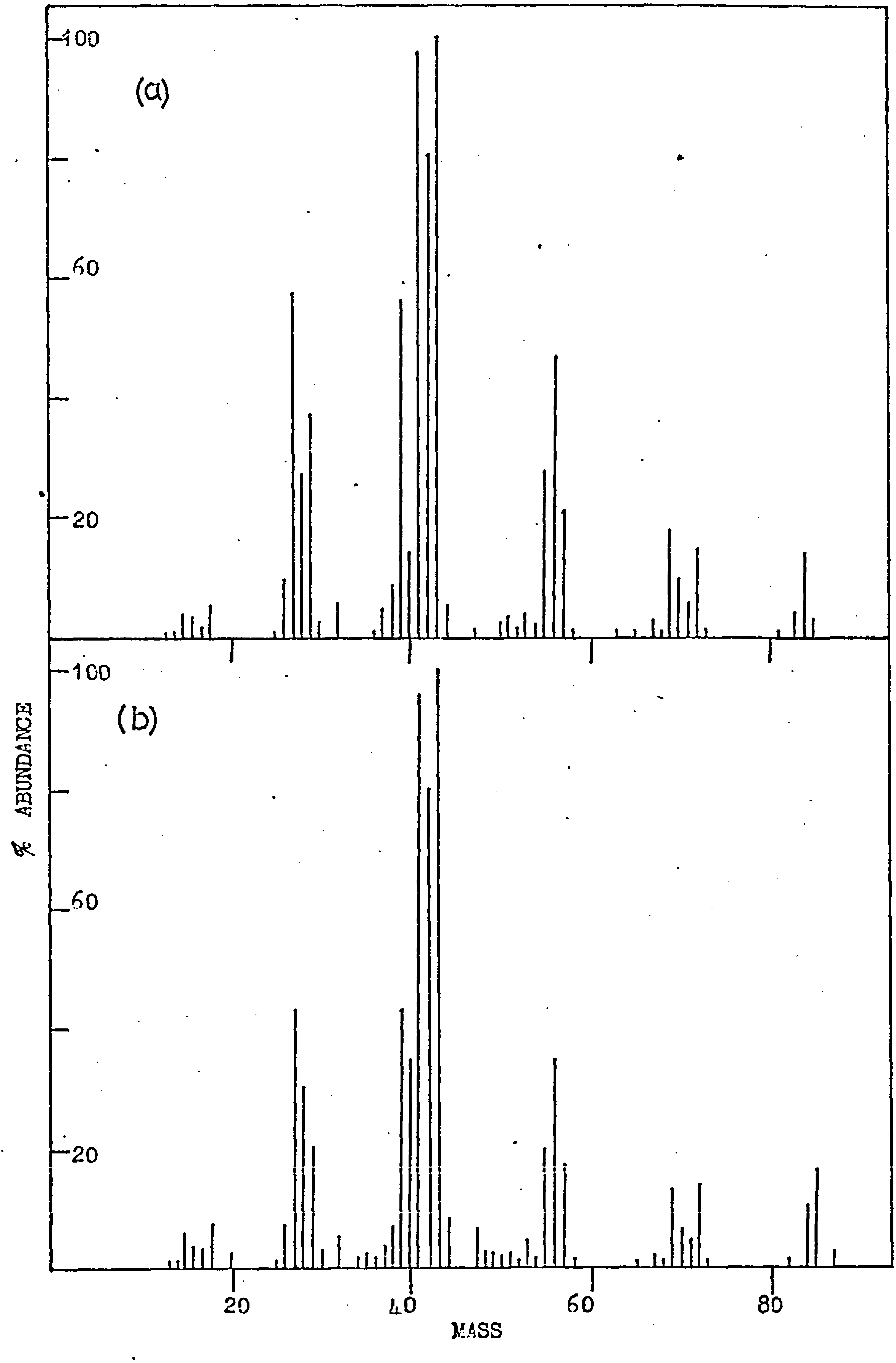


FIGURE 3.6 Mass spectra of products of degradation of polypropylene. 10 % volatilisation at 335°C.

(a) Thermal (b) Photothermal

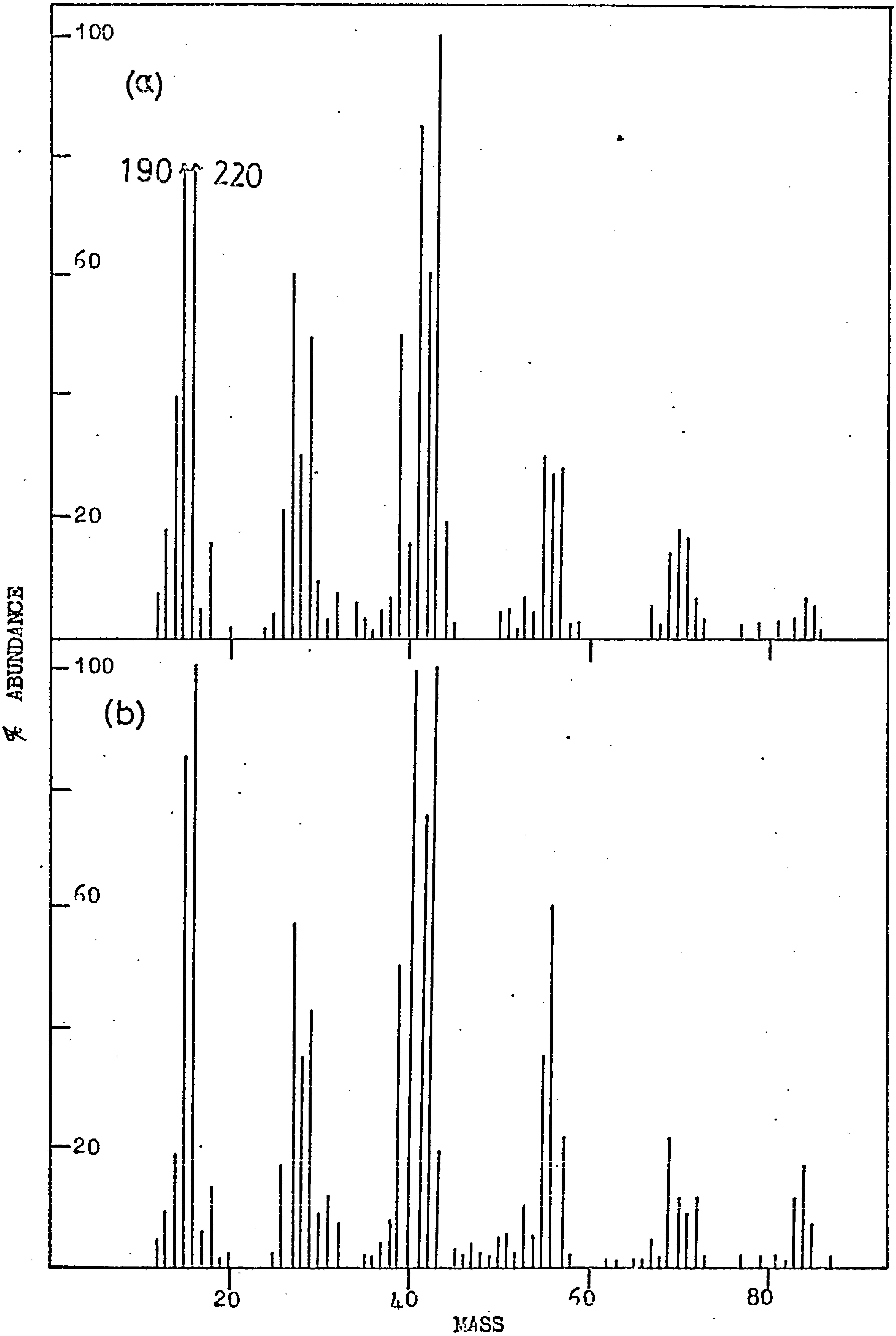
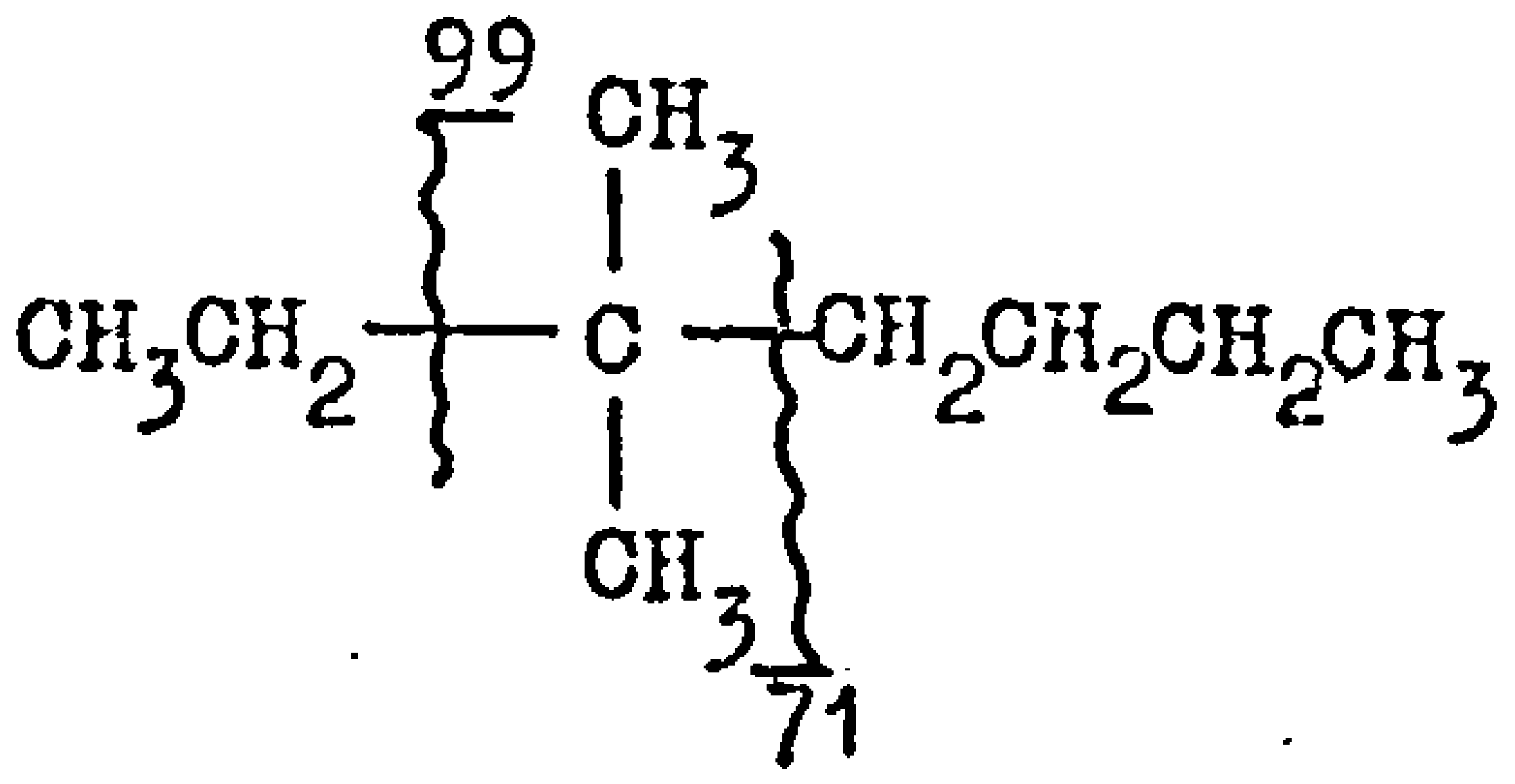


FIGURE 3.7 Mass spectra of products of photodegradation of polypropylene.

(a) 200°C ; 4 % volatilisation
(b) 250°C ; 10 % volatilisation.

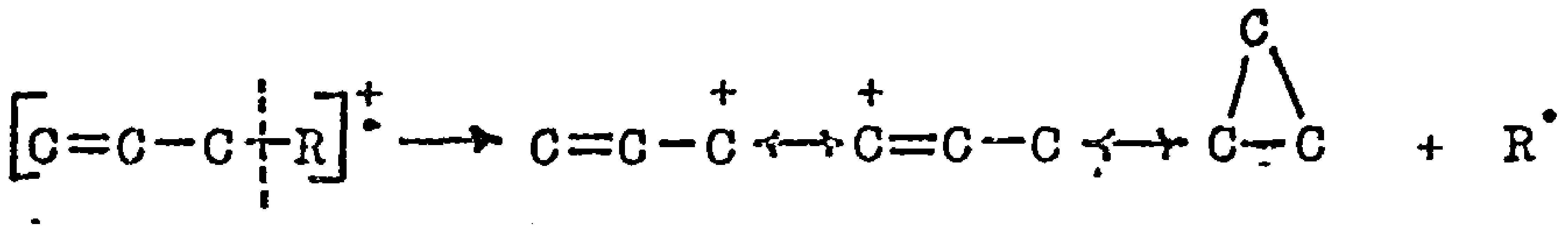
14 mass units apart (corresponding to a difference of CH_2), whose relative abundances decrease fairly regularly with increasing m/e ratio. However in the spectrum of 3,3 dimethylheptane,



$C_5H_{11}^+$ (m/e 71) and $C_7H_{15}^+$ (m/e 99) fragments are enhanced by a factor of about 4 relative to the spectrum of the linear hydrocarbon, since their formation corresponds to the production of tertiary carbonium ions. Moreover, fragmentation is enhanced in branched hydrocarbons and therefore a linear hydrocarbon will exhibit a molecular ion whereas a branched hydrocarbon will not. Thus the spectrum of a mixture of linear hydrocarbons will appear simply as the spectrum of the highest member of the series with the lower members contributing to a distortion of relative abundancies of ions. If that mixture also contains branched material, then the relative abundances of ions is further distorted and the highest peak is not necessarily the molecular ion of the highest molecular weight species present.

Also, in the mass spectra of hydrocarbon mixtures, peaks often occur two mass units below those associated with saturated carbonium ions. These peaks are believed to be due to alkenyl cations, and thus the presence of such peaks cannot be considered as indicative of unsaturated material.

However, when a double bond is present in a molecular ion, fission of the carbon - carbon bond β to the double bond is favoured. The resulting carbonium ion is resonance stabilised ;



By itself, this effect is not sufficient to ensure that the peaks in the mass spectrum corresponding to ions of this type will be characteristic. One reason is that double bonds appear to be able to migrate in the molecular ion, thus rendering the spectra of different olefin isomers very similar.

FIGURE 3.5 is a representation of the mass spectra of the gaseous products resulting from the thermal and photothermal degradations of polypropylene at 354°C. Volatilisation was limited to 10% of the original sample, in both cases. Because of the difficulty of identifying individual components, it was considered sufficient in this study to compare the general features of these spectra. The same overall pattern of a $C_1 - C_6$ hydrocarbon spread is evident in both cases and, furthermore, the distribution and relative abundances of peaks are similar.

FIGURE 3.6 illustrates the mass spectra of the gases produced during the thermal and photothermal degradations at 335°C (10 % volatilisation). The two spectra are very similar and also resemble the spectra in FIGURE 3.5.

FIGURE 3.7 records the mass spectra of polypropylene photodegraded at 200° (4 % volatilisation) and 250°C (10 % volatilisation). Once again, both spectra have the same overall features as those in FIGURE 3.5. However, in FIGURE 3.7, the relative abundances of peaks at m/e 15 and m/e 16 are much greater than in FIGURES 3.5 and 3.6. These two peaks, as well as forming part of the breakdown pattern of higher hydrocarbons, are characteristic of methane. Thus using the mass peak, m/e 43, as a reference, it may be concluded that there is a larger proportion of methane in the hydrocarbon mixture produced during photolyses at temperatures where no thermal degradation occurs. i.e. below 300°C.

The highest major peak in all spectra occurs at m/e 84, corresponding to unsaturated material containing six carbon atoms.

It can be concluded from these results that in the thermal and photothermal degradations of polypropylene in the range 300 - 354°C the products volatile at 20°C include saturated and unsaturated hydrocarbons containing 2 - 6 carbon atoms, in addition to hydrogen and methane. The only notable difference is the production of larger amounts of ethylene in photothermal degradations.

Photodegradation below 300°C results in a similar range of products but there is proportionally more methane in the gaseous hydrocarbon mixture.

c) Products Liquid at 20°C

There were no detectable products which remained liquid at 20°C in any of the degradation reactions. The probable explanation is that materials which might have remained liquid, such as C_5 hydrocarbons and upwards, constituted only a small fraction of the total gas phase and so, under conditions of reduced pressure, were completely volatilised.

d) Short Chain Fragments (cold ring fraction)

The cold ring fraction was volatile at the temperature of degradation, but not sufficiently volatile to pass to the condensation limbs of the degradation apparatus. Consequently, it was deposited on the sides and top silica window of the degradation cell. In photothermal degradations, the fact that cold ring deposited on the silica window was a severe disadvantage of the system since this attenuated the incident radiation so that the effective intensity decreased with time. The short chain fragments were collected for examination as described in Chapter 2.

The cold ring produced in all degradations, both thermal and photothermal, were found to be colourless and relatively insoluble at ambient temperatures. The average molecular weight is probably of the order of 850 (25), corresponding to about 20 propylene units.

The infra - red spectra of the cold ring fractions of every degradation studied were found to be similar. FIGURE 3.8 represents the spectrum of the short chain fragments of a sample of polypropylene thermally degraded for 8 hours at 354°C. The only significant difference from the spectrum of undegraded polypropylene (FIGURE 3.9) is the occurrence of absorptions at 3080 cm^{-1}, 1650 cm^{-1} and 888 cm^{-1} indicating the presence of unsaturation. The peak at 888 cm^{-1} can be attributed to structures of the type $R_1R_2C{=}CH_2$. There is no evidence of unsaturation in the spectrum of undegraded polypropylene (FIGURE 3.9). Peaks above 1000 cm^{-1} are assigned as in TABLE 3.1 and absorptions at 997 cm^{-1}, 973 cm^{-1}, 940 cm^{-1}, 895 cm^{-1}, 840 cm^{-1} and 810 cm^{-1} are accounted for by CH_3 rocking (80).

Because of the large yield of cold ring produced and the rapid decrease in molecular weight with degradation, it is obvious that transfer reactions occur. These are probably both intermolecular and intramolecular and the high average molecular weight of the cold ring suggests that it it is formed in an intermolecular process ;

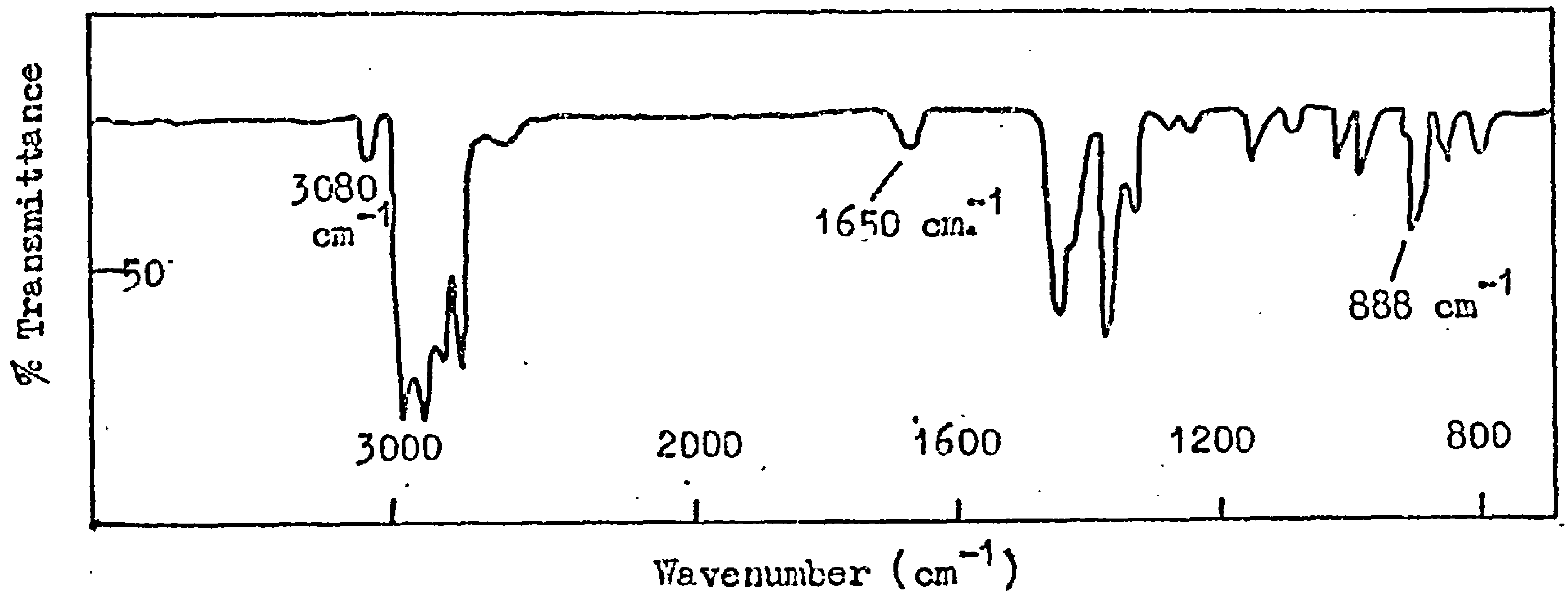


FIGURE 3.8 IR spectrum of cold ring fraction of polypropylene thermally degraded at 354°C for 8 hours.

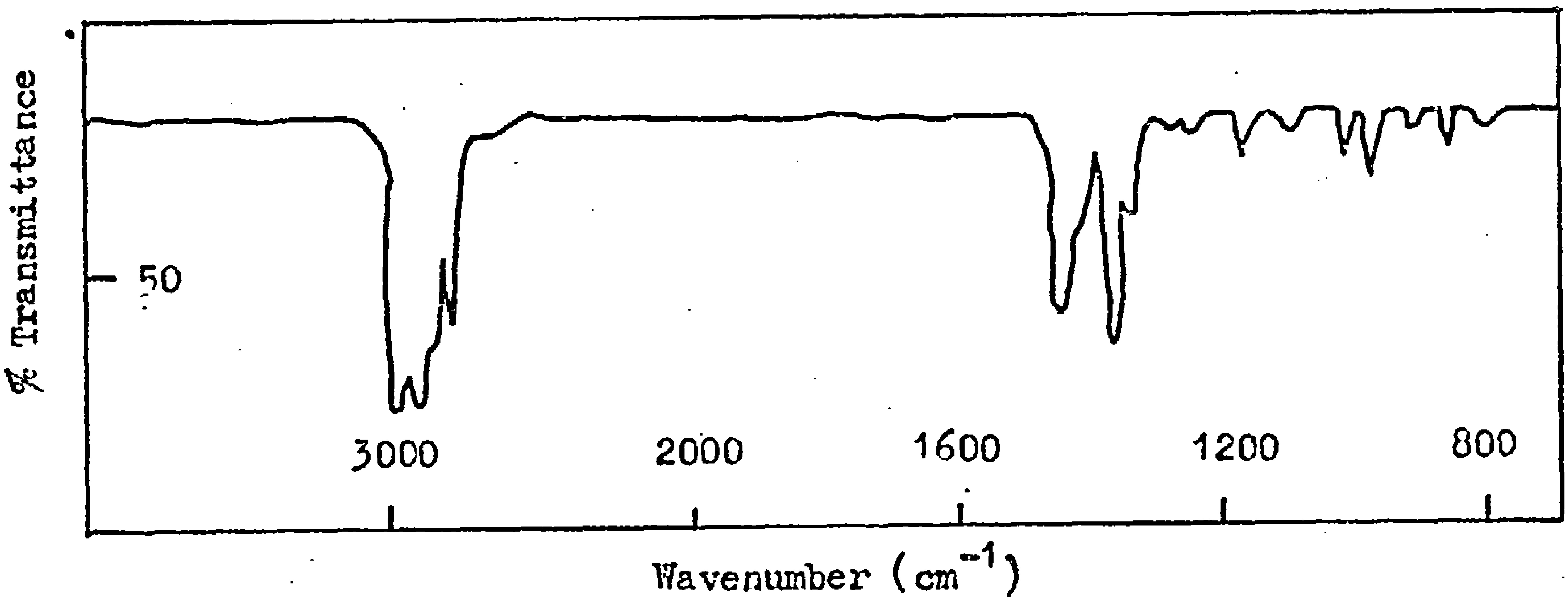


FIGURE 3.9 IR spectrum of undegraded polypropylene.

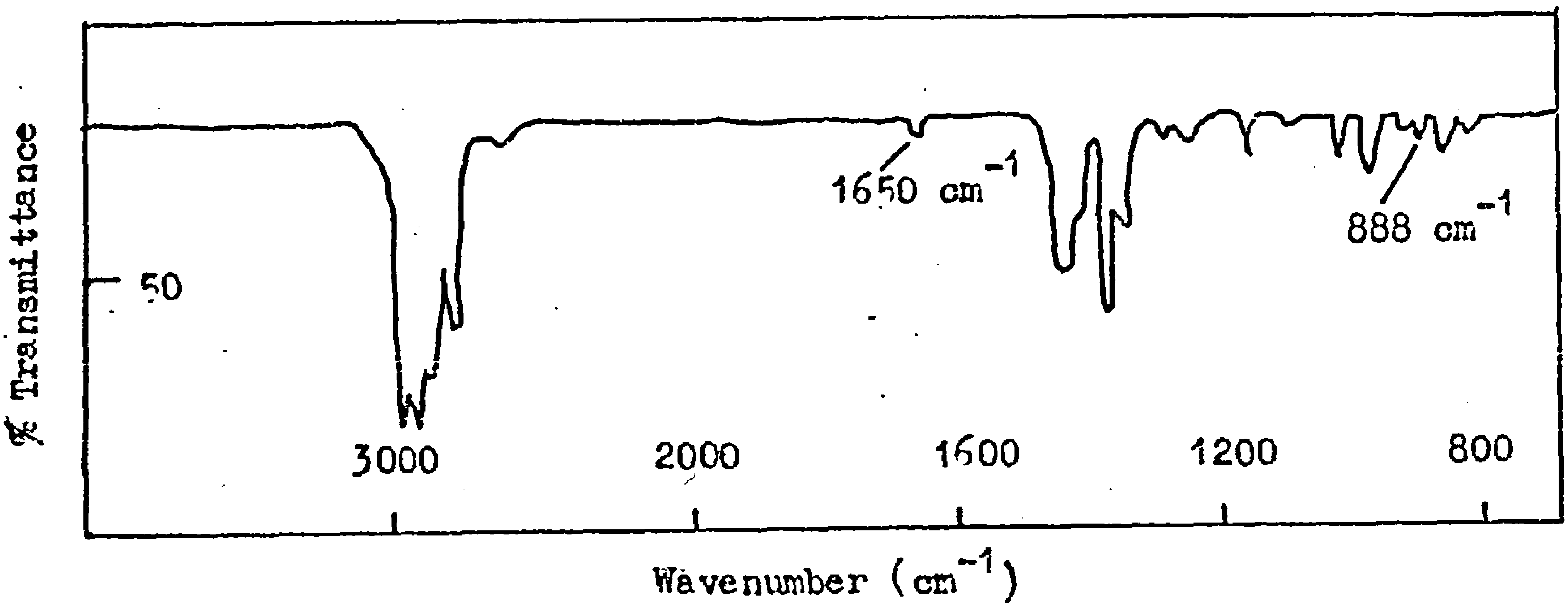
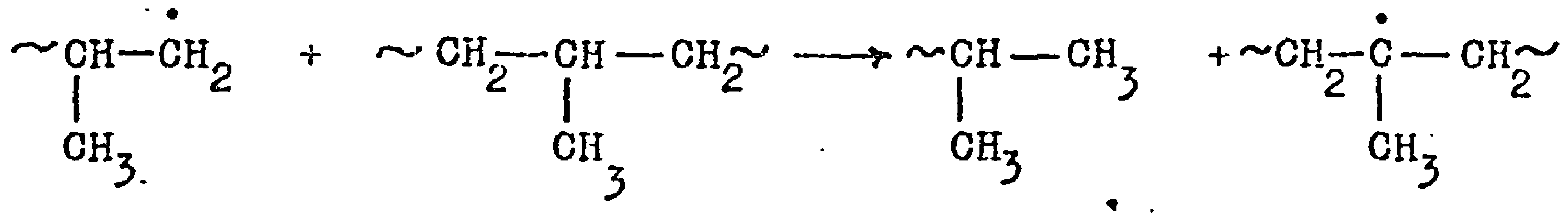
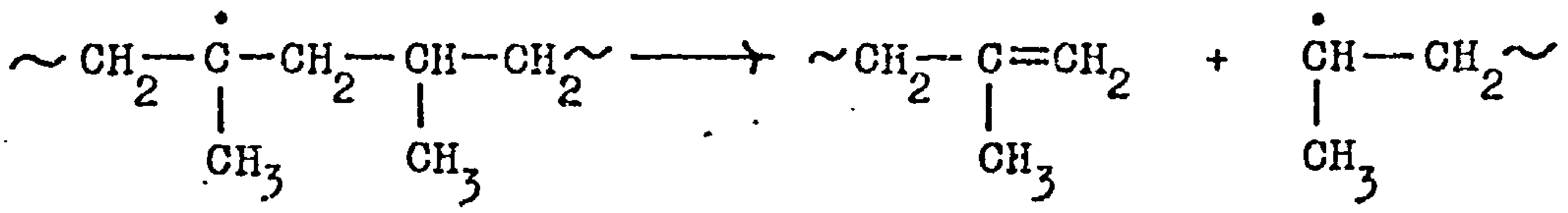


FIGURE 3.10 IR spectrum of residue of polypropylene thermally degraded at 354°C for 8 hours.



$$\sim\underset{CH_3}{\underset{|}{CH}}-\overset{\bullet}{C}H_2 + \sim CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_2\sim \longrightarrow \sim\underset{CH_3}{\underset{|}{CH}}-CH_3 + \sim CH_2-\underset{CH_3}{\underset{|}{\overset{\bullet}{C}}}-CH_2\sim$$

The radical formed by abstraction of the tertiary hydrogen atom may decompose giving an α - olefin and a new radical.



$$\sim CH_2-\underset{CH_3}{\underset{|}{\overset{\bullet}{C}}}-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_2\sim \longrightarrow \sim CH_2-\underset{CH_3}{\underset{|}{C}}=CH_2 + \underset{CH_3}{\underset{|}{\overset{\bullet}{C}H}}-CH_2\sim$$

α - olefins of this type absorb in the infra - red at 888 cm^{-1}.

c) Polymer Residue

The residues from all degradations were brittle, colourless, opaque and insoluble at room temperarure. This made ultra - violet spectroscopic analysis impossible. Infra - red spectra were obtained using the KBr disc technique.

FIGURE 3.10 shows the infra - red spectrum of polypropylene thermally degraded for 8 hours at 354°C. This is typical of the spectra of the residues from all of the thermal and photothermal degradations studied. The peaks at 1650 cm^{-1} and 888 cm^{-1}, present in the chain fragments, are also observed in the residue. Chain end unsaturation is again indicated.

3.2 Quantitative Comparison of Degradation Products

In the previous section, the products of the thermal and photothermal degradations of polypropylene have been compared qualitatively. Where possible, positive identification was made. It is a logical step to complement this information with a more detailed analysis of those products of most interest.

a) Weight loss and shortchain fragments.

Quantitative measurements of weight loss and the cold ring fraction were made as described in Chapter 2. The weights of gaseous volatiles were obtained by difference and are included for completeness.

FIGURES 3.11 - 3.18 (TABLES 3.3 - 3.10) show the results of thermal and photothermal volatilisation at four different temperatures; 300°C, 330°C, 335°C and 354°C. Weight loss is found to increase linearly with time at all temperatures and the rate of photothermal degradation is greater than the rate of thermal degradation at any given temperature.

Graphs of the production of short chain fragments and of gaseous volatiles show the expected corresponding trends. The fact that, in both thermal and photothermal degradations, formation of cold ring exceeds that of gaseous products indicates that hydrogen transfer reactions, probably intermolecular, are very important.

In FIGURE 3.19, the extent of volatilisation in 15 hours for thermal and photothermal degradations is plotted as a function of temperature. It can be seen that at higher temperatures the difference in the extents of volatilisation of thermal and photothermal degradation becomes more pronounced. This is confirmed in FIGURE 3.20 which shows the theoretical effect of irradiation alone as a function of temperature of degradation. At each temperature, the weight loss incurred by thermal degradation is subtracted from that resulting from photothermal degradation. Photodegradation at 200°C and 250°C are included to complete the picture.

For thermal degradation, the plot of the logarithmn of the percentage residue weight as a function of time gives a straight line (FIGURE 3.21) showing that the reaction obeys a first order

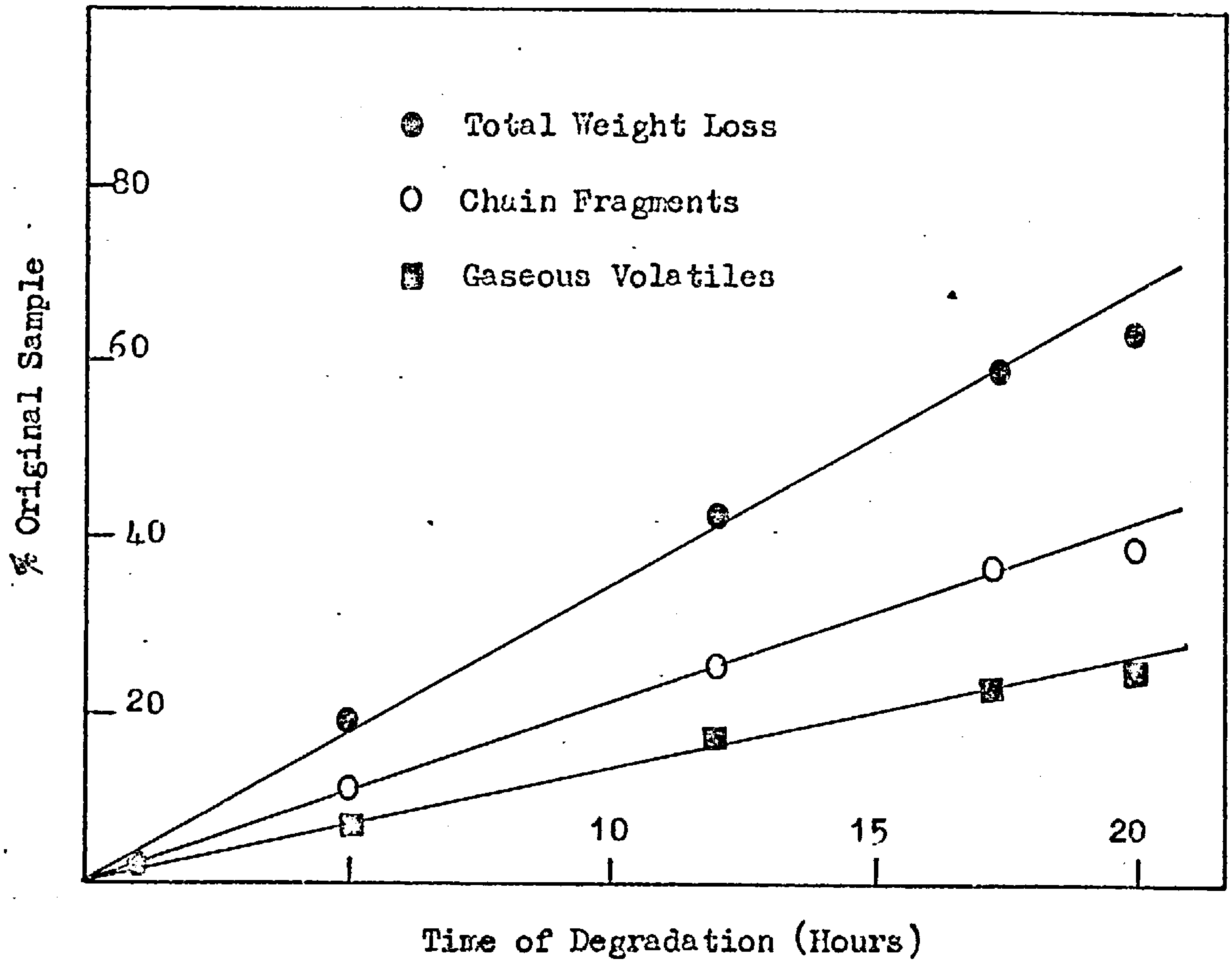


FIGURE 3.11 Thermal volatilisation plots at 354°C.

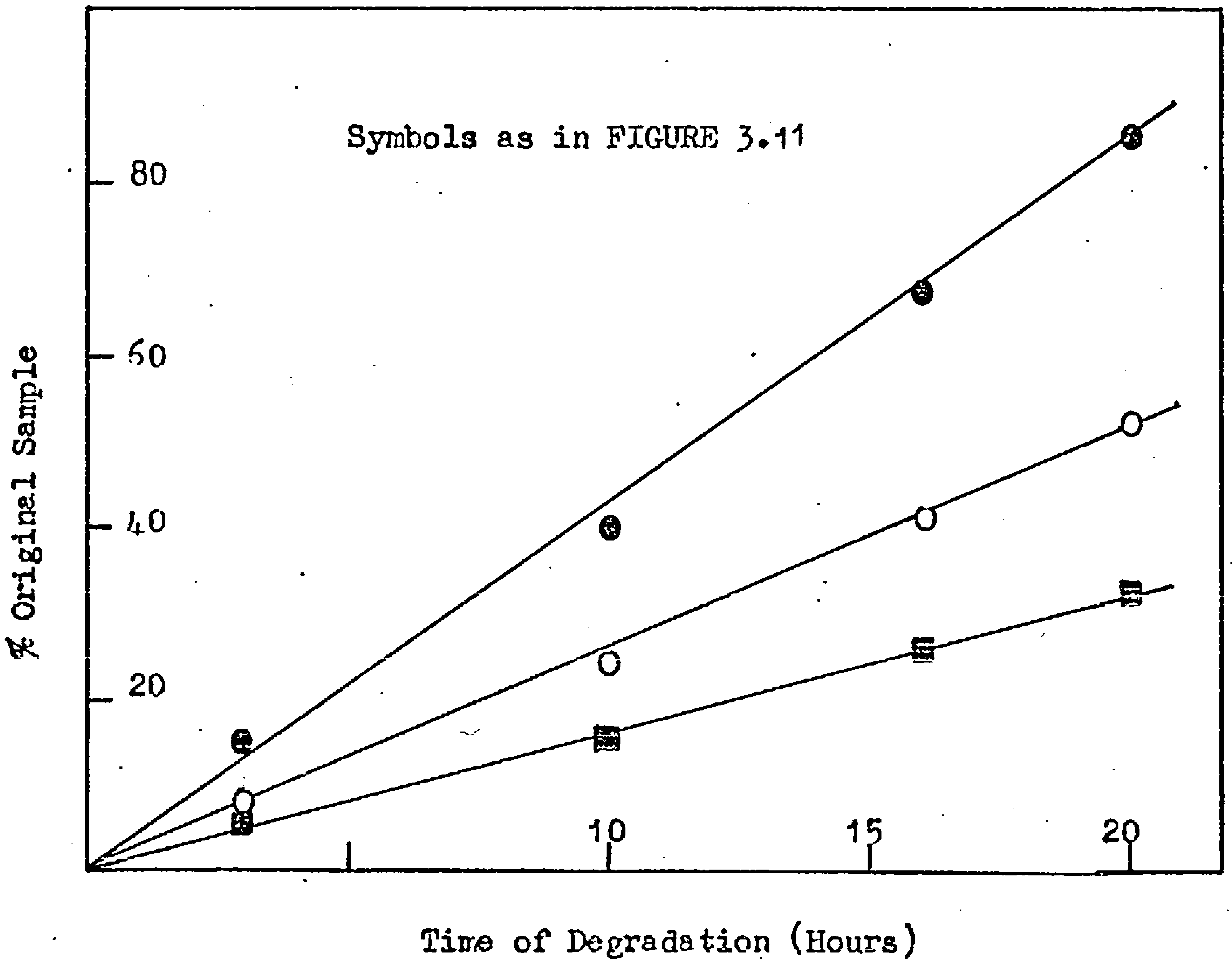


FIGURE 3.12 Photothermal volatilisation plots at 354°C.

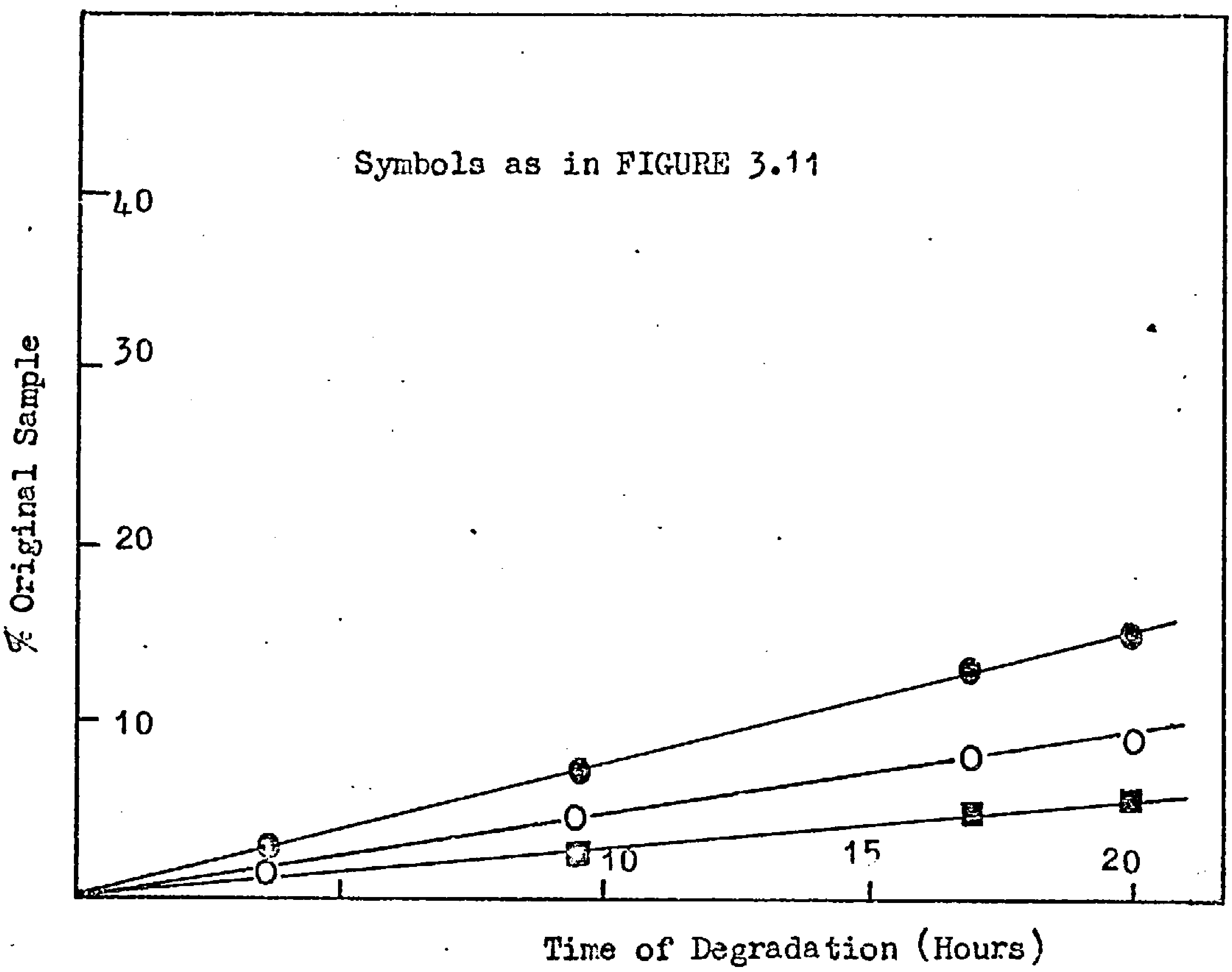


FIGURE 3.13 Thermal volatilisation plots at 335°C.

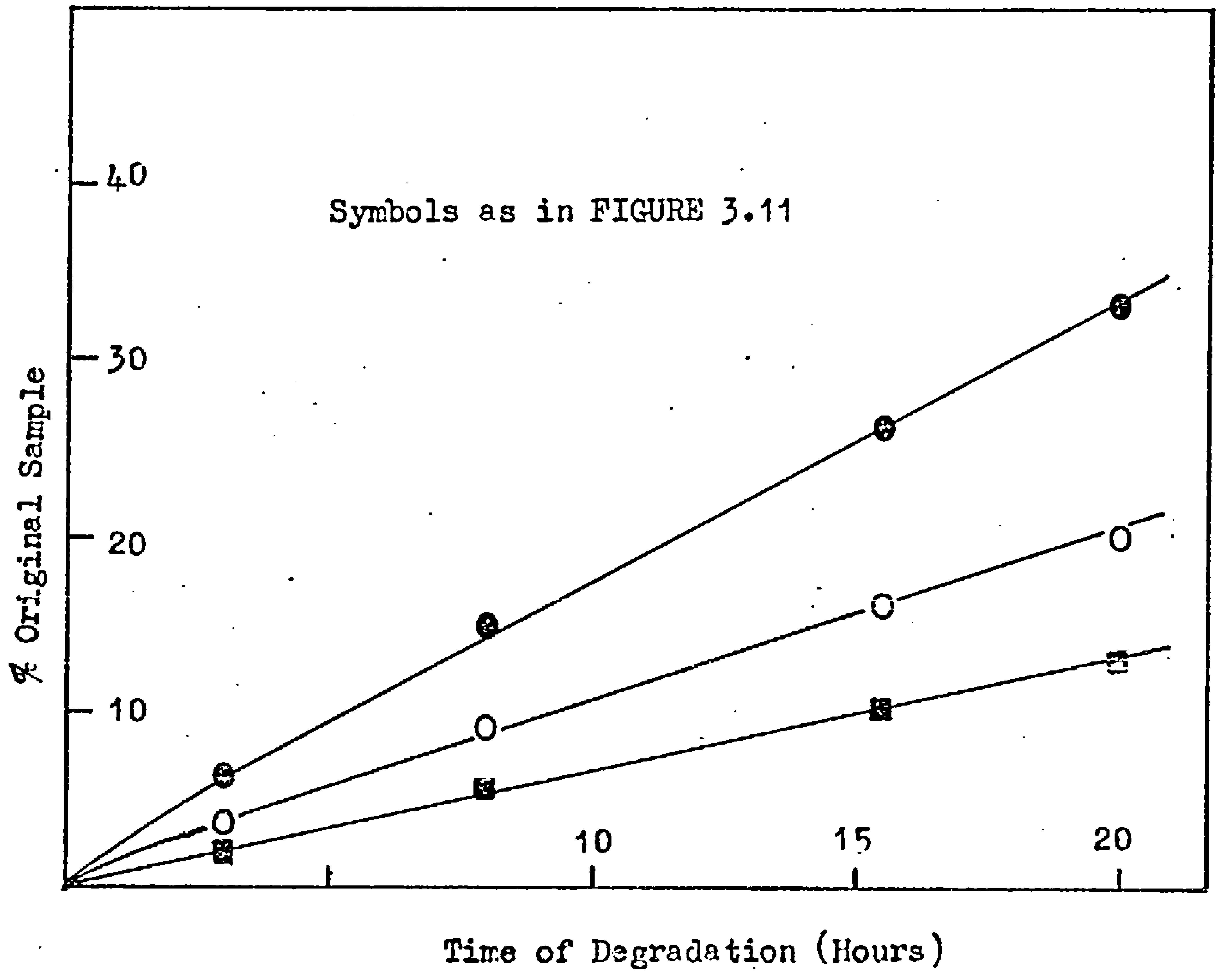


FIGURE 3.14 Photothermal volatilisation plots at 335°C.

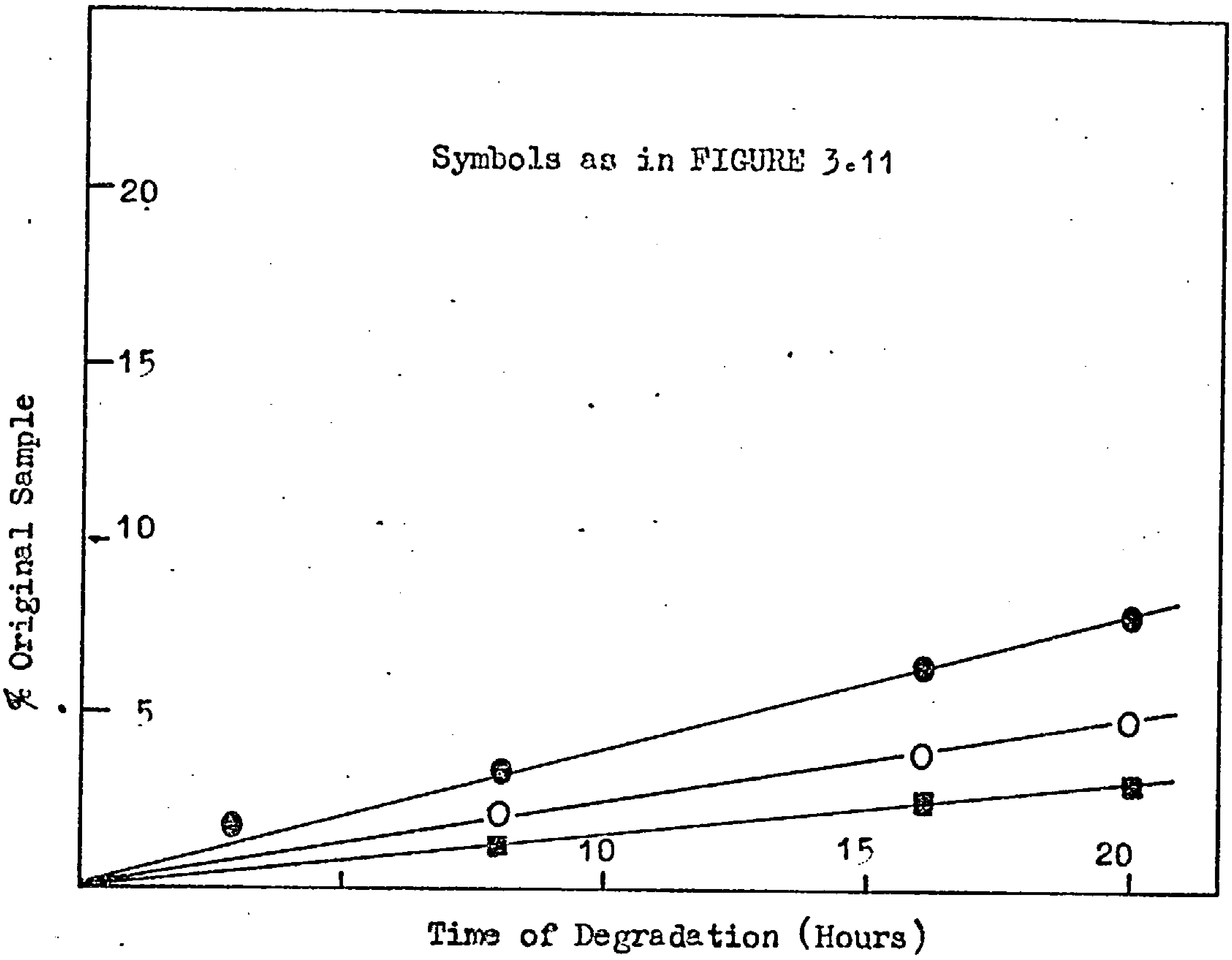


FIGURE 3.15 Thermal volatilisation plots at 330°C.

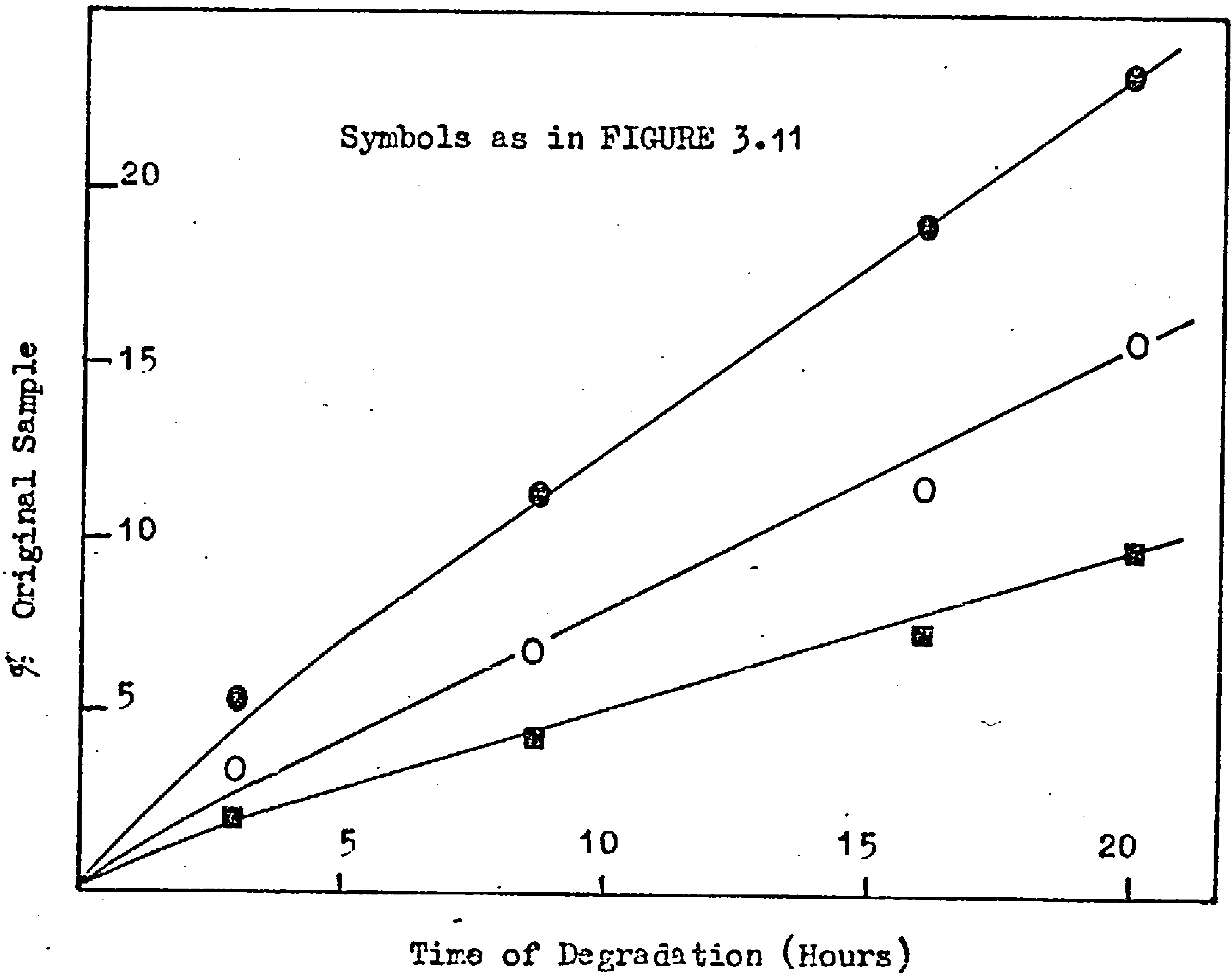


FIGURE 3.16 Photothermal volatilisation plots at 330°C.

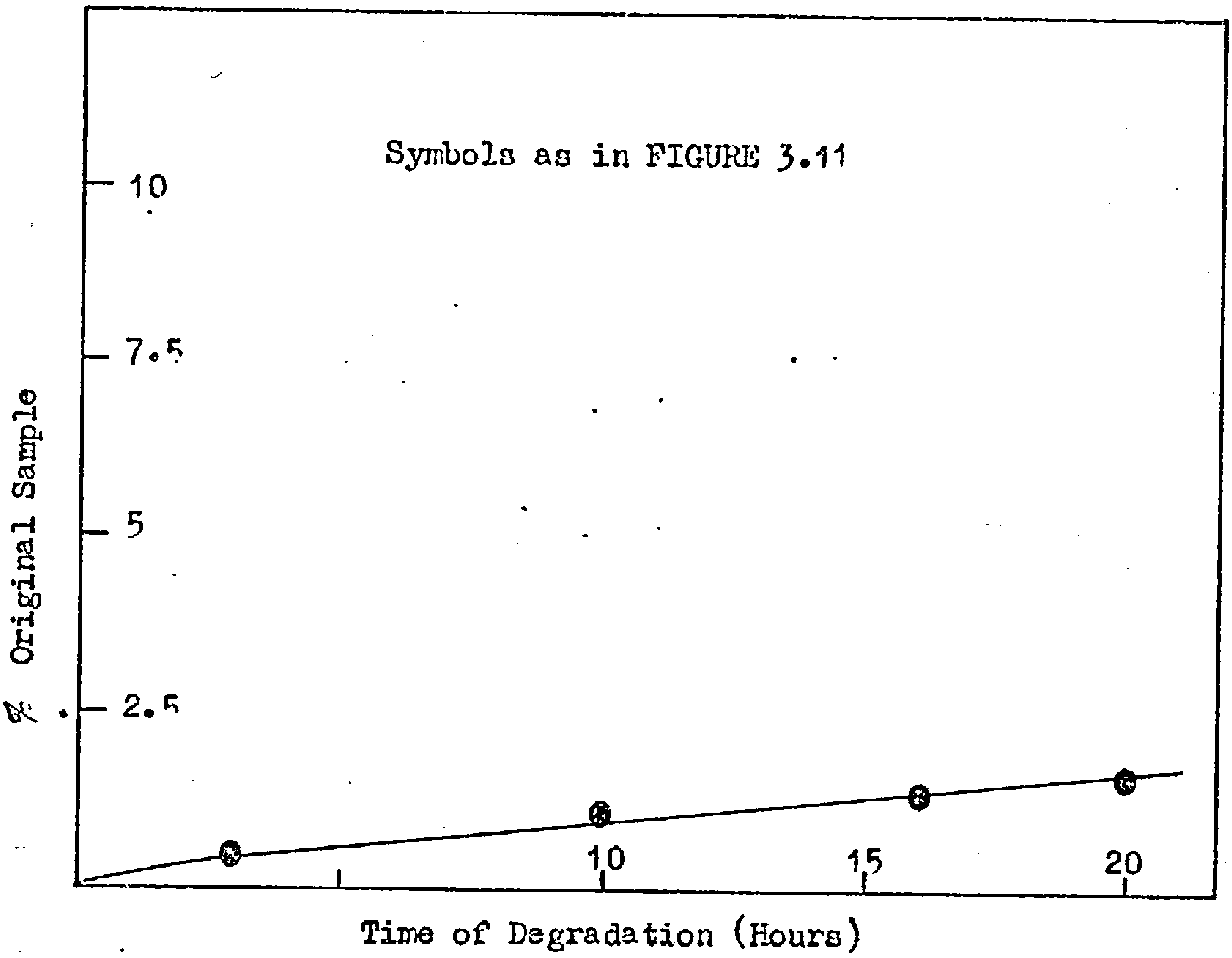


FIGURE 3.17 Thermal volatilisation plot at 300°C.

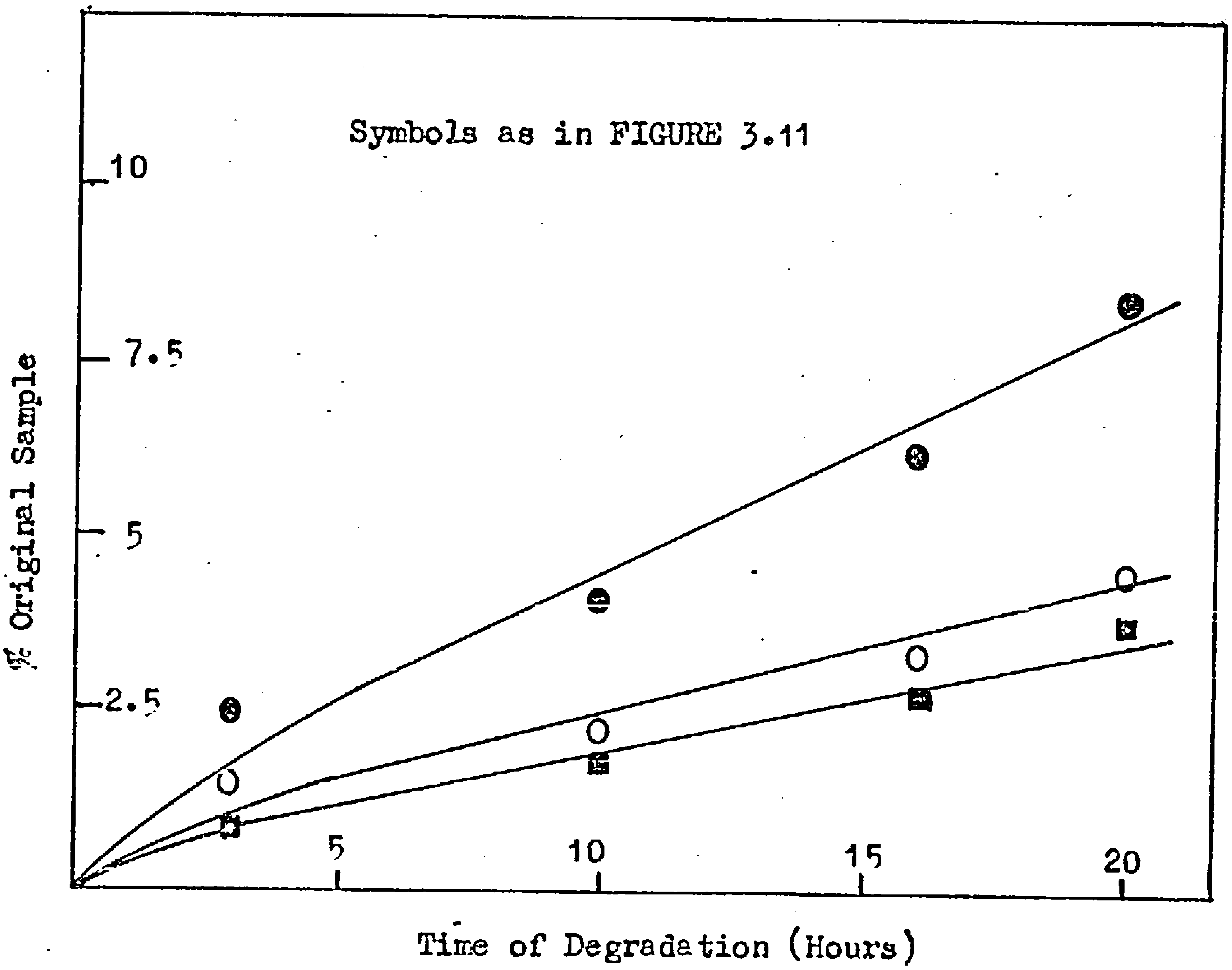


FIGURE 3.18 Photothermal volatilisation plots at 300°C.

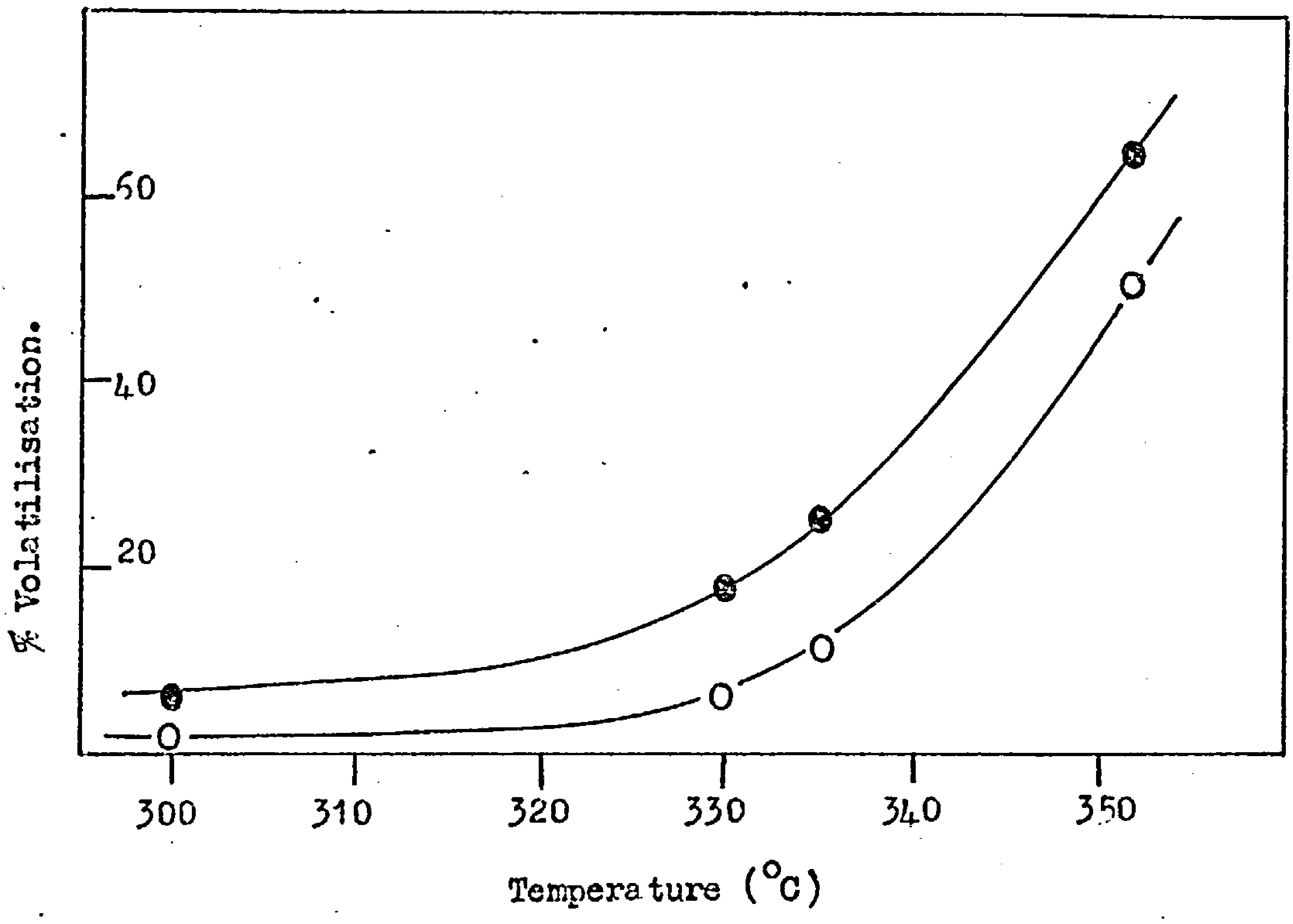


FIGURE 3.19 Extent of volatilisation in 15 hours at various temperatures.

● Photothermal

O Thermal

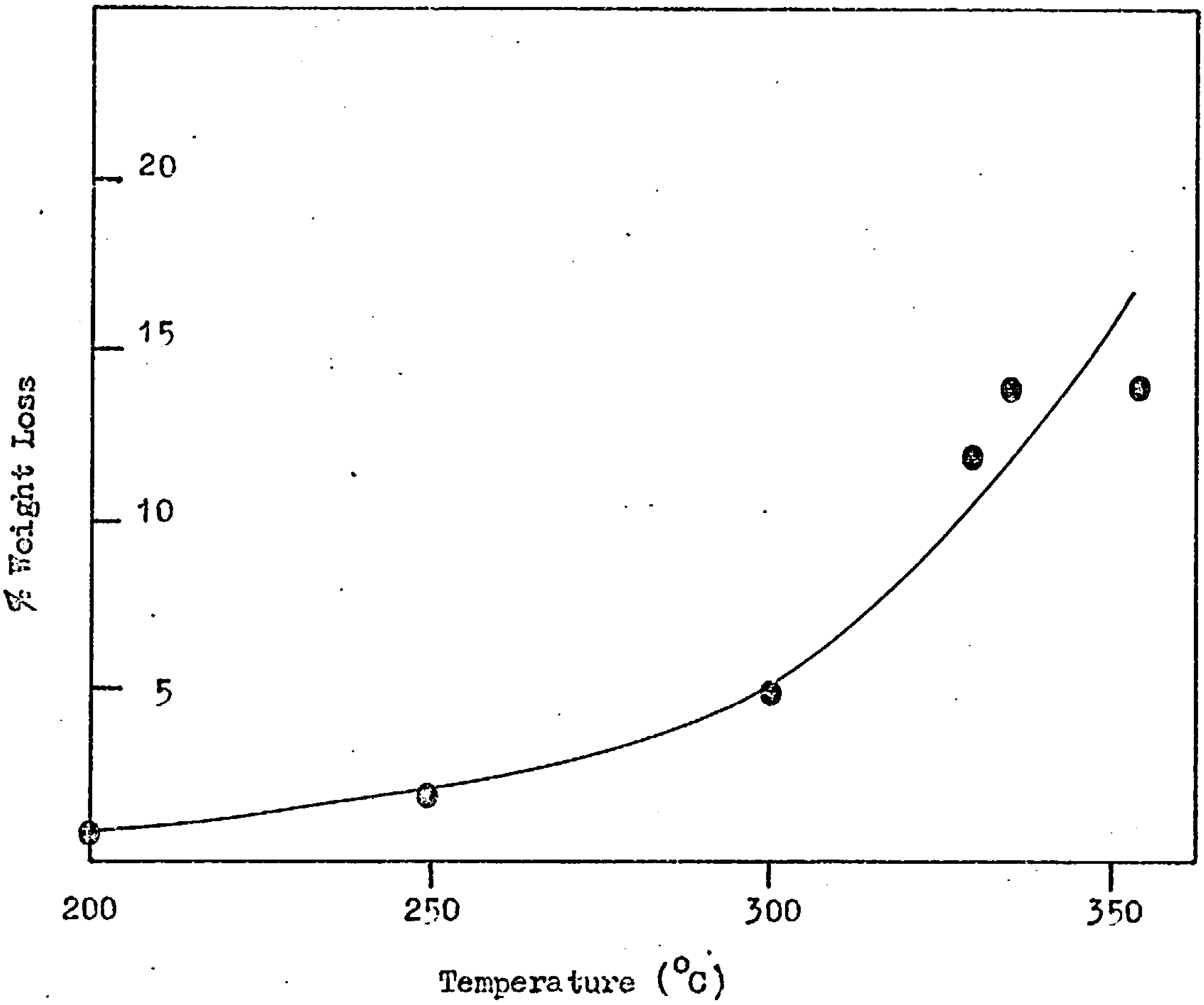


FIGURE 3.20 Theoretical extent of photodegradation in 15 hours as a function of temperature. The degree of thermal volatilisation is subtracted from that of photothermal volatilisation at each temperature.

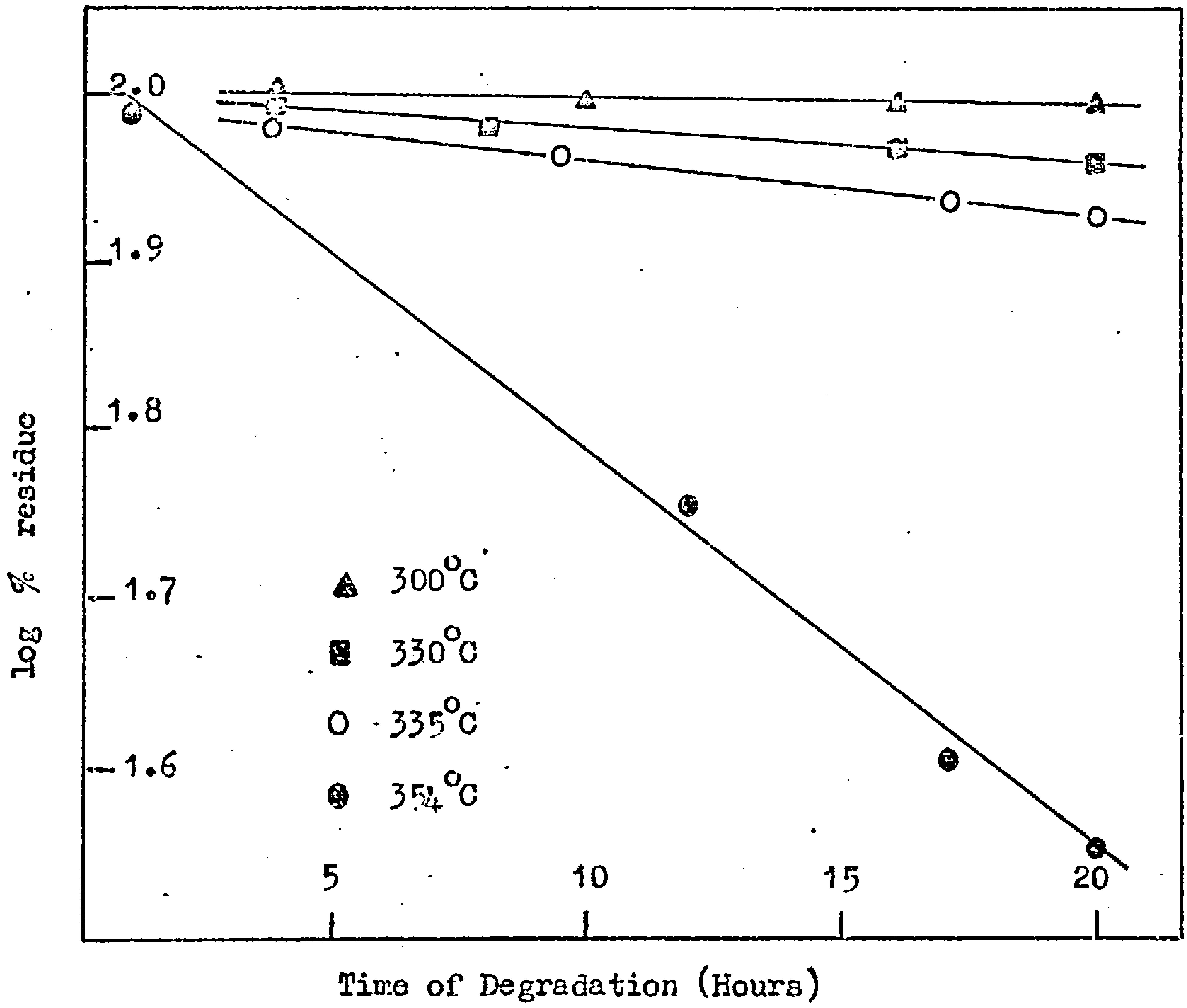


FIGURE 3.21 Plot of log. % residue against time of thermal degradation.

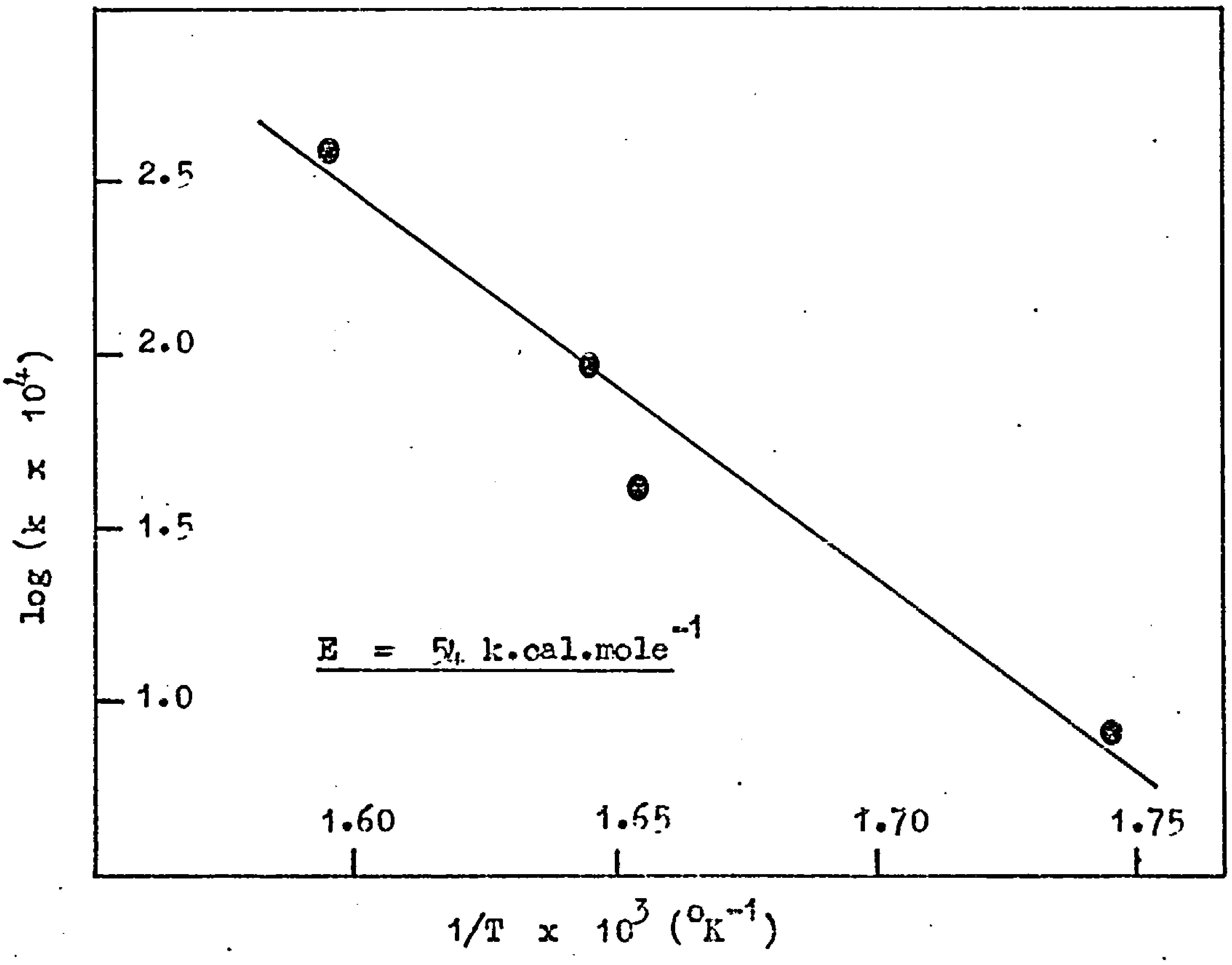


FIGURE 3.22 Activation Energy plot for thermal degradation.

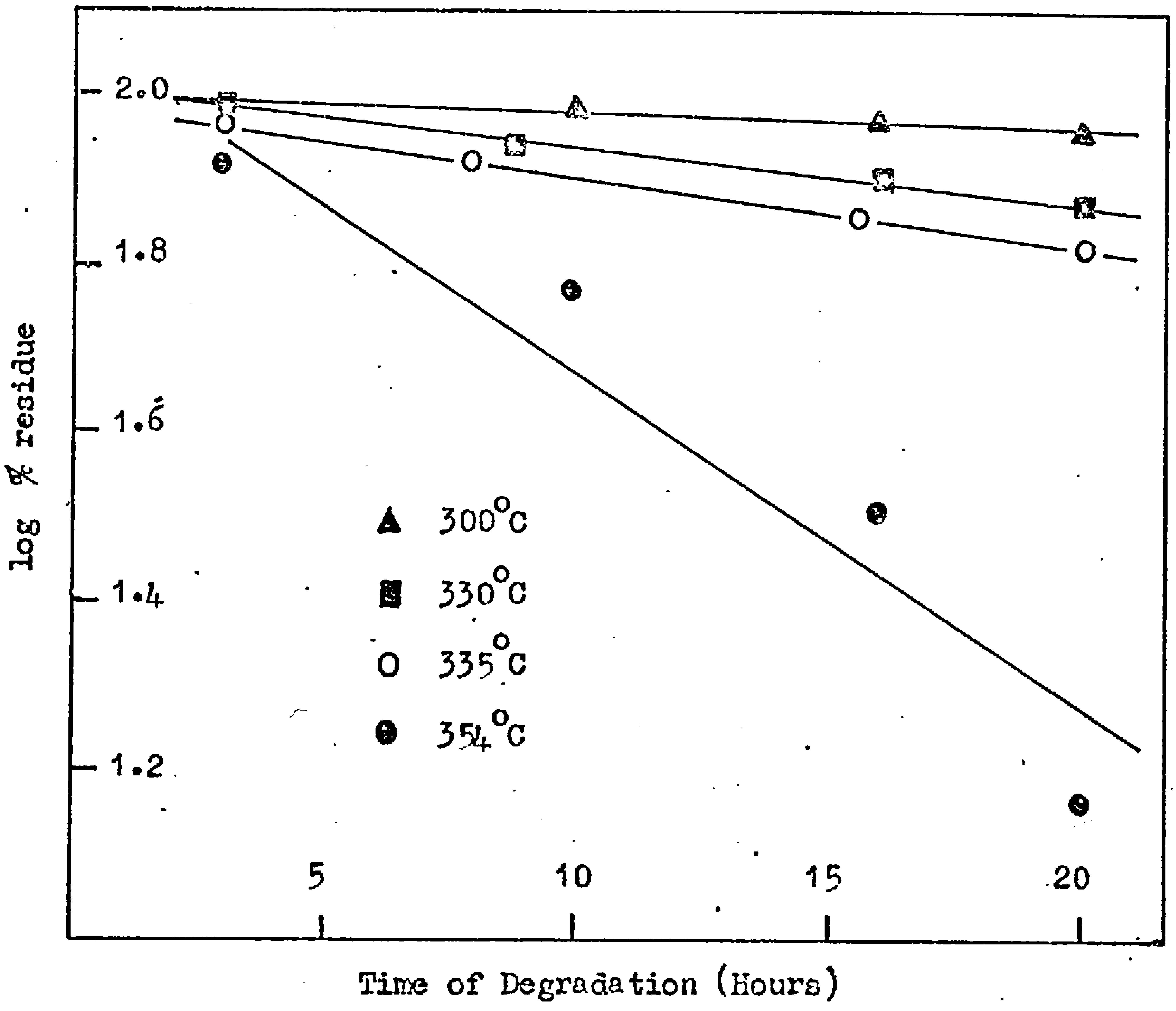


FIGURE 3.23 Plot of log % resiue against time of photothermal degradation.

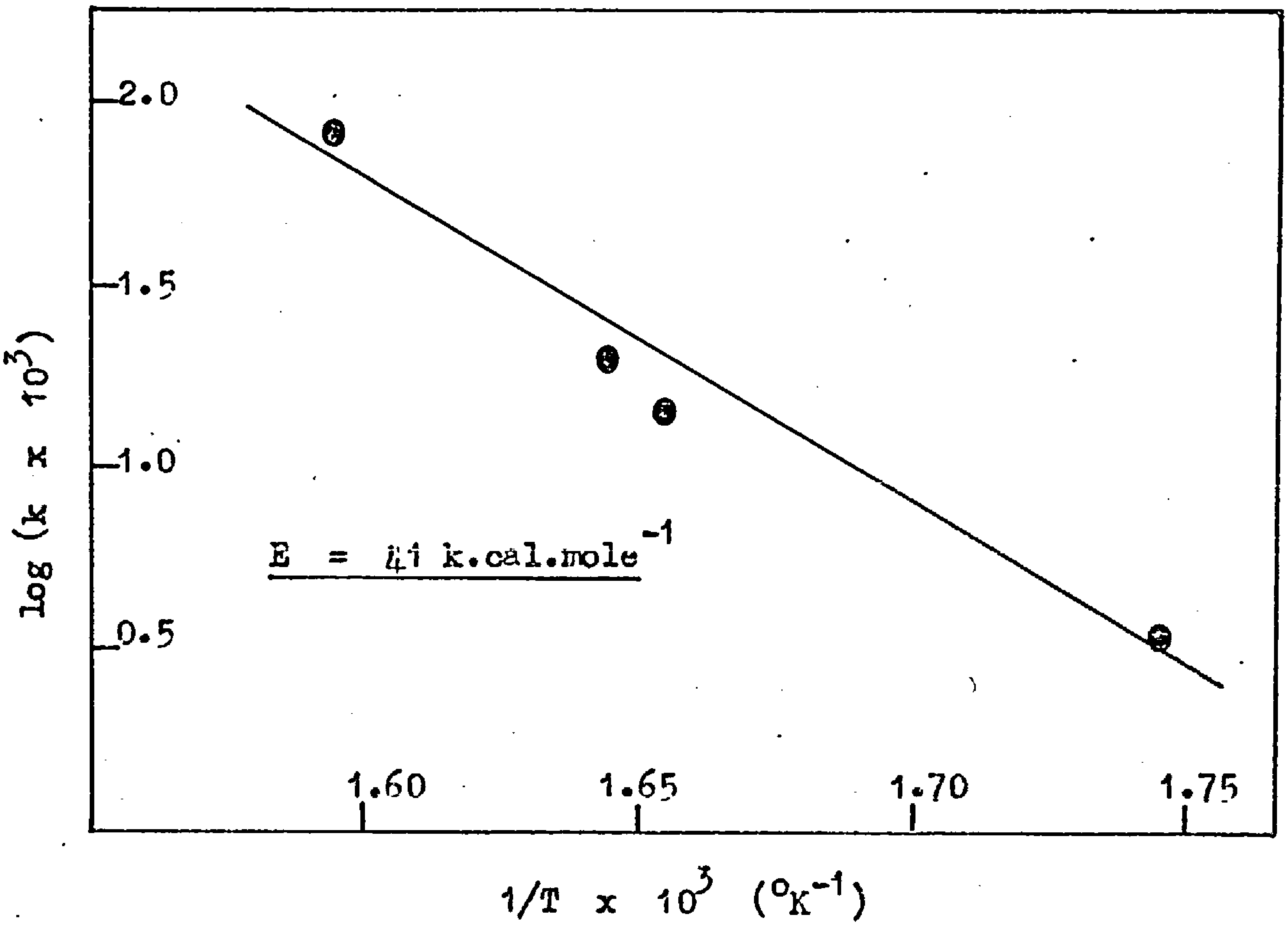


FIGURE 3.24 Activation Energy plot for photothermal degradation.

Time(Hours)	% Original Polymer Sample		
	Weight Loss	Chain Fragments	Gases
1	2.0	-	-
5	19.0	11.6	7.4
12	42.8	25.4	17.4
17.25	59.6	36.7	22.9
20	63.2	38.6	24.6

TABLE 3.3 Thermal Degradation Data at 354°C.

Time(Hours)	% Original Polymer Sample		
	Weight Loss	Chain Fragments	Gases
3	15.0	8.7	6.3
10	40.1	24.3	15.8
16	67.5	41.2	26.3
20	85.5	52.4	33.1

TABLE 3.4 Photothermal Degradation Data at 354°C.

Time (Hours)	% Original Polymer Sample		
	Weight Loss	Chain Fragments	Gases
3.75	3.0	1.8	1.2
9.50	7.2	4.4	2.8
17	13.1	8.0	5.1
20	15.1	9.2	5.9

TABLE 3.5 Thermal Degradation Data at 335°C.

Time(Hours)	% Original Polymer Sample		
	Weight Loss	Chain Fragments	Gases
3	6.5	3.9	2.6
8	15.0	9.3	5.7
15.50	26.5	16.2	10.3
20	33.3	20.3	13.0

<u>TABLE 3.6</u> Photothermal Degradation Data at 335°C.

Time(Hours)	% Original Polymer Sample		
	Weight Loss	Chain Fragments	Gases
3	2.0	-	-
8	3.5	2.2	1.3
16	6.5	3.9	2.6
20	8.0	4.9	3.1

<u>TABLE 3.7</u> Thermal Degradation Data at 330°C.

Time(Hours)	% Original Polymer Sample		
	Weight Loss	Chain Fragments	Gases
3	5.6	3.4	2.2
8.75	11.5	7.1	4.4
16	19.2	11.8	7.4
20	26.0	15.9	10.1

<u>TABLE 3.8</u> Photothermal Degradation Data at 330°C.

Time(Hours)	% Original	Polymer	Sample
	Weight Loss	Chain Fragments	Gases
3	0.05	-	-
10	1.10	-	-
16	1.40	-	-
20	1.60	-	-

TABLE 3.9 Thermal Degradation Data at 300°C.

Time(Hours)	% Original	Polymer	Sample
	Weight Loss	Chain Fragments	Gases
3	2.6	1.6	1.0
10	4.2	2.3	1.9
16	6.3	3.4	2.9
20	8.5	4.6	3.9

TABLE 3.10 Photothermal Degradation Data at 300°C.

Temperature (°C)	% Weight	Loss
	Photothermal	Thermal
200	0.7	-
250	2.0	-
300	6.4	1.4
330	18.0	6.0
335	25.5	11.5
354	65.0	51.0

TABLE 3.11 Extent of Volatilisation in 15 Hours at Various Temperatures.

Temperature (^{o}C)	% Weight Loss (Photothermal minus Thermal)
200	0.7
250	2.0
300	5.0
330	12.0
335	14.0
354	14.0

TABLE 3.12 Theoretical extent of photodegradation in 15 hours at several temperatures. The effect of thermal degradation has been subtracted at each temperature.

Temperature (^{o}C)	Rate Constant (k) x 10^{3} ($Hours^{-1}$)
300	0.65
330	3.71
335	8.44
354	51.56

TABLE 3.12 Rate Constants For Thermal Degradation.

Temperature (^{o}C)	Rate Constant (k) x 10^{2} ($Hours^{-1}$)
300	3.65
330	14.33
335	19.87
354	85.29

TABLE 3.13 Rate Constants For Photothermal Degradation.

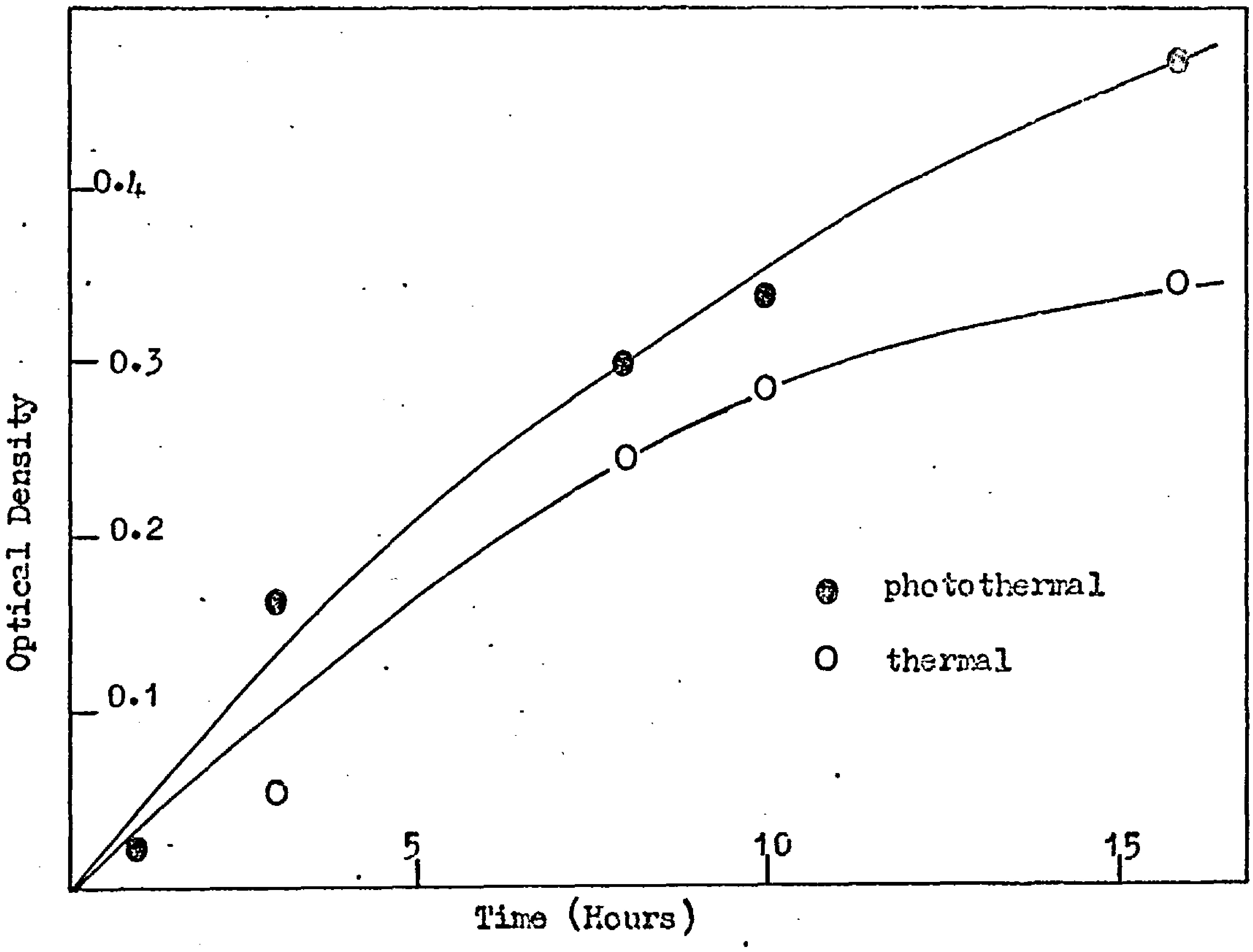
kinetic law. The slopes of such lines represent rate constants of thermal degradation and measurements in the range 300° - 354°C yield an overall activation energy of ca. 54 k.cal.mole^{-1} (FIGURE 3.22). This is in fair agreement with the value of ca. 55 k.cal.mole^{-1} obtained by Moiseev et al (81) for a polypropylene of comparable molecular weight (175,000) degrading in the range 320° - 420°C. Madorsky and Straus (25) obtained a value of ca. 58 k.cal.mole^{-1} for a low molecular weight polypropylene (5000) in the range 336° - 366°C.

Similar plots were drawn for the photothermal degradation of polypropylene (FIGURES 3.23 and3.24) yielding an activation energy of ca. 41 k.cal.mole^{-1}. This value indicates that, under the irradiation conditions employed, the effect of ultra - violet light is to lower the activation energy for the thermal degradation of polypropylene by about 24 %.

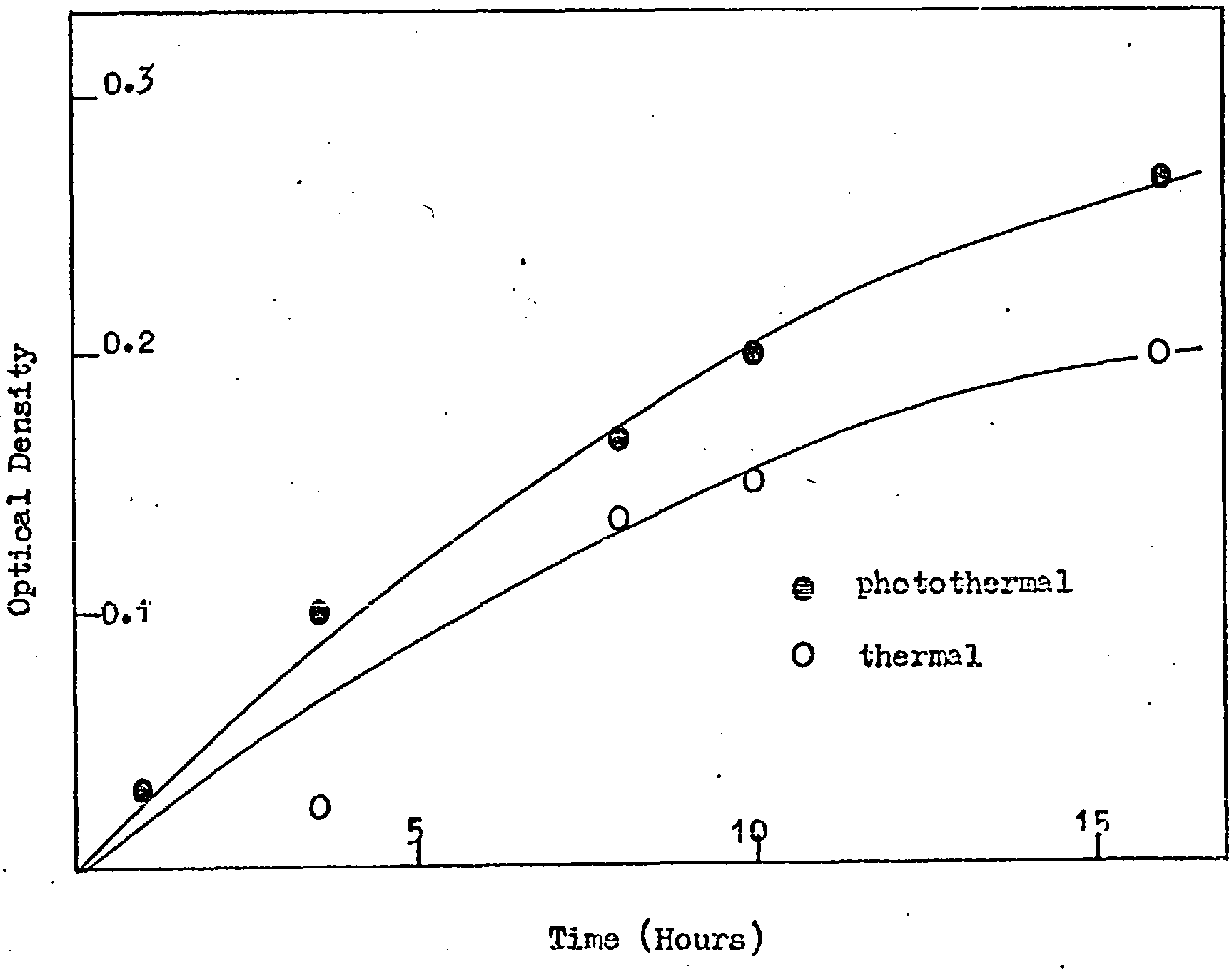
b) Gaseous Volatiles

It is unfortunate that the highly complex nature of the hydrocarbon gases produced prohibits their quantitative analysis. However, in an attempt to examine gas production more closely, a series of degradations, thermal and photothermal, were conducted at 354°C and infra - red spectra recorded of the gaseous products. Optical densities of the salient peaks of each spectrum were measured by the usual baseline method. The absorptions examined are listed in TABLE 3.17 and are assigned as in TABLE 3.1.

FIGURES 3.25 - 3.33 (TABLES 3.14 - 3.16) show the results obtained when the optical density of each peak is plotted as a



<u>FIGURE 3.25</u> Plot of data for peak 3080 cm^{-1} (TABLE 3.14)



<u>FIGURE 3.26</u> Plot of data for peak 1650 cm^{-1} (TABLE 3.14)

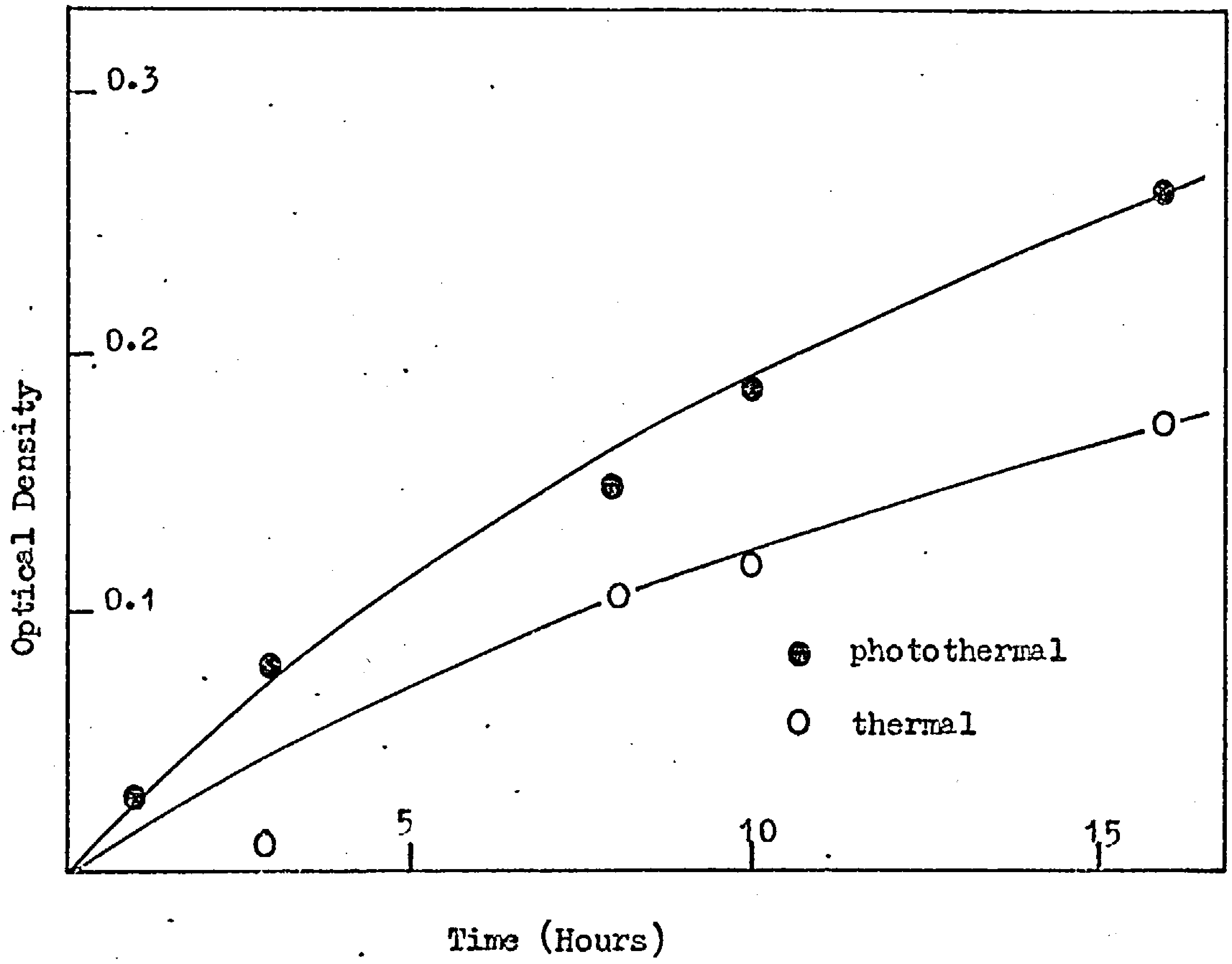


FIGURE 3.27 Plot of data for peak 988 cm^{-1} (TABLE 3.14)

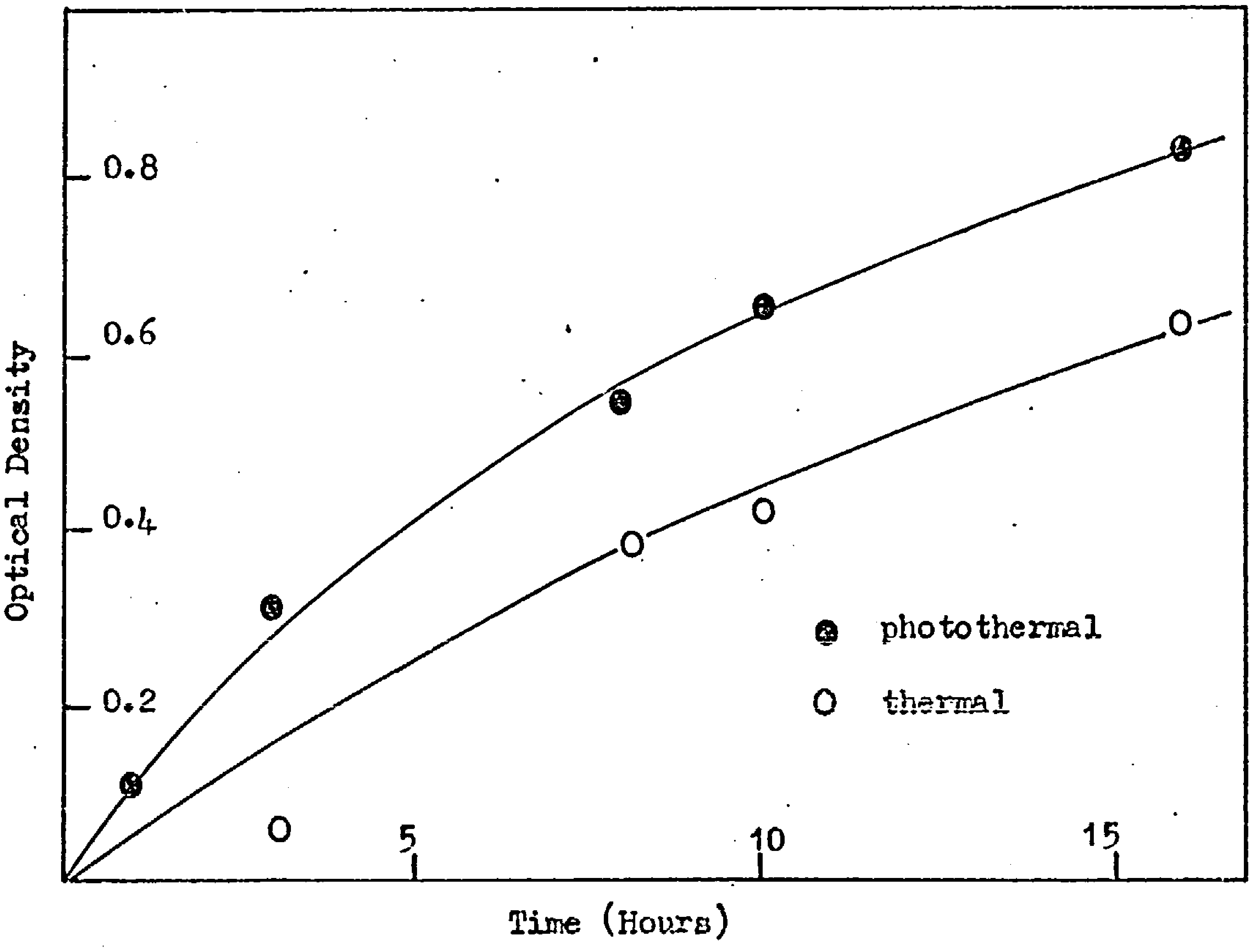


FIGURE 3.28 Plot of data for peak 910 cm^{-1} (TABLE 3.14)

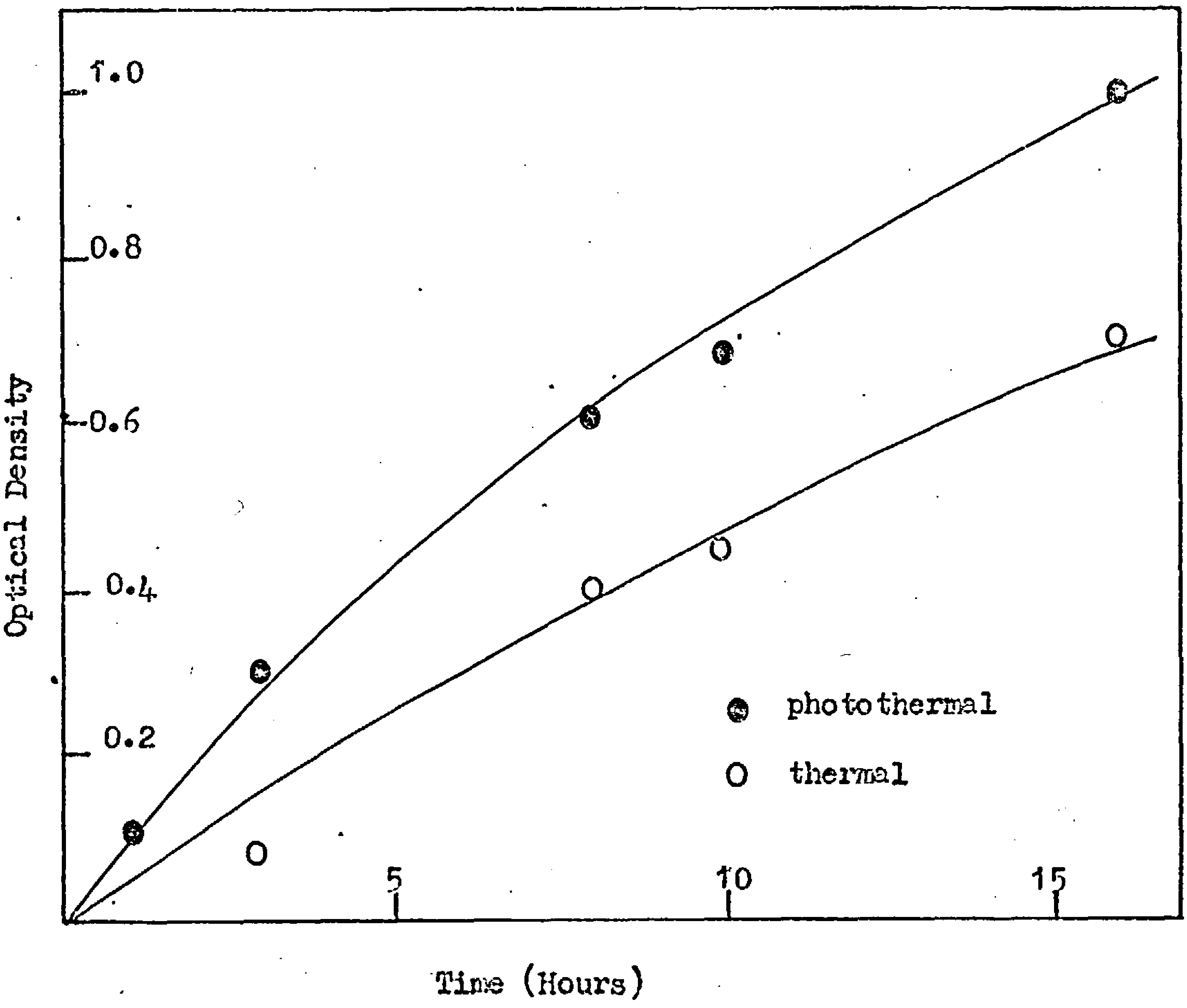


FIGURE 3.29 Plot of data for peak 888 cm^{-1} (TABLE 3.14)

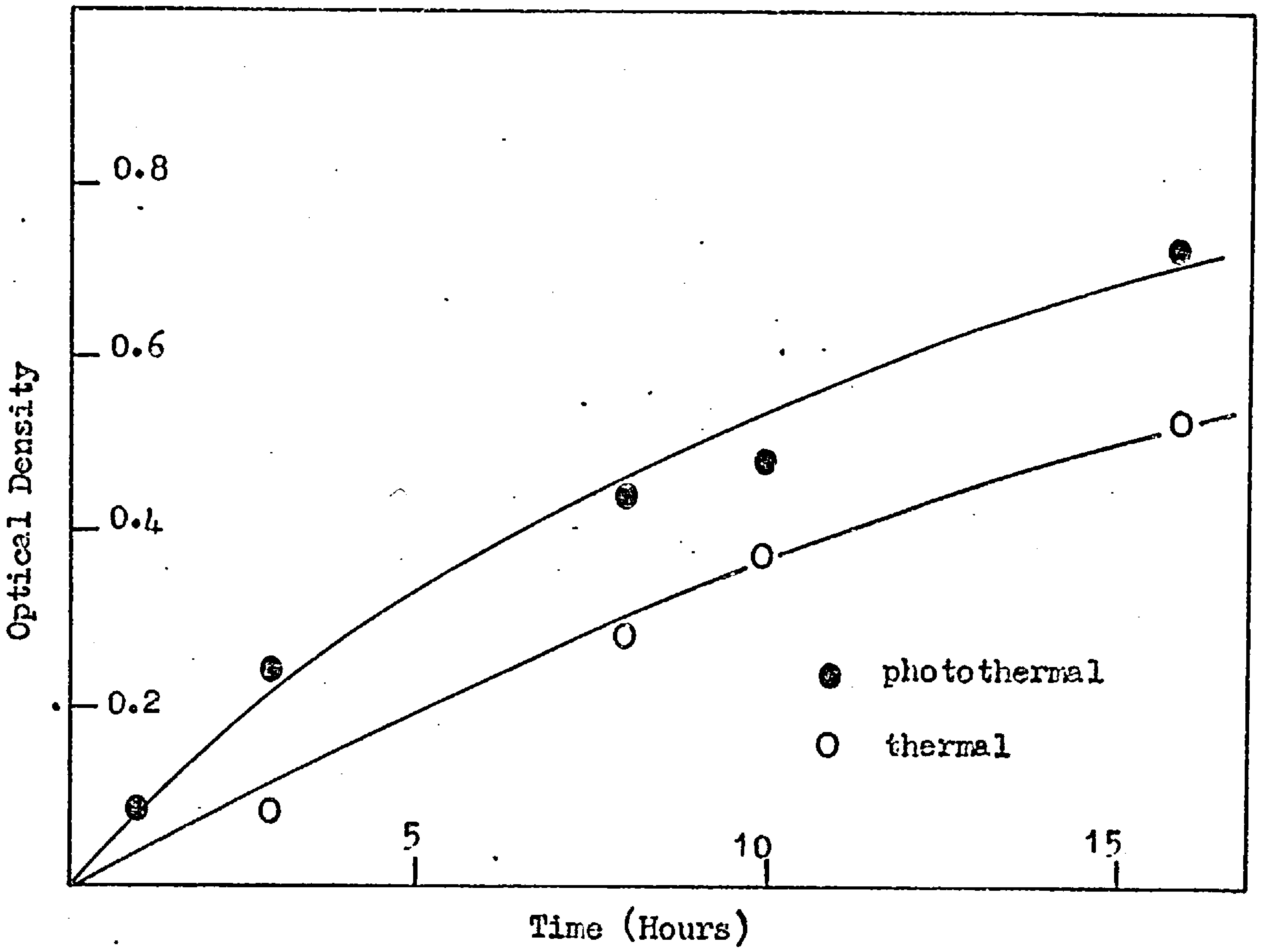


FIGURE 3.30 Plot of data for peak 1460 cm^{-1} (TABLE 3.15)

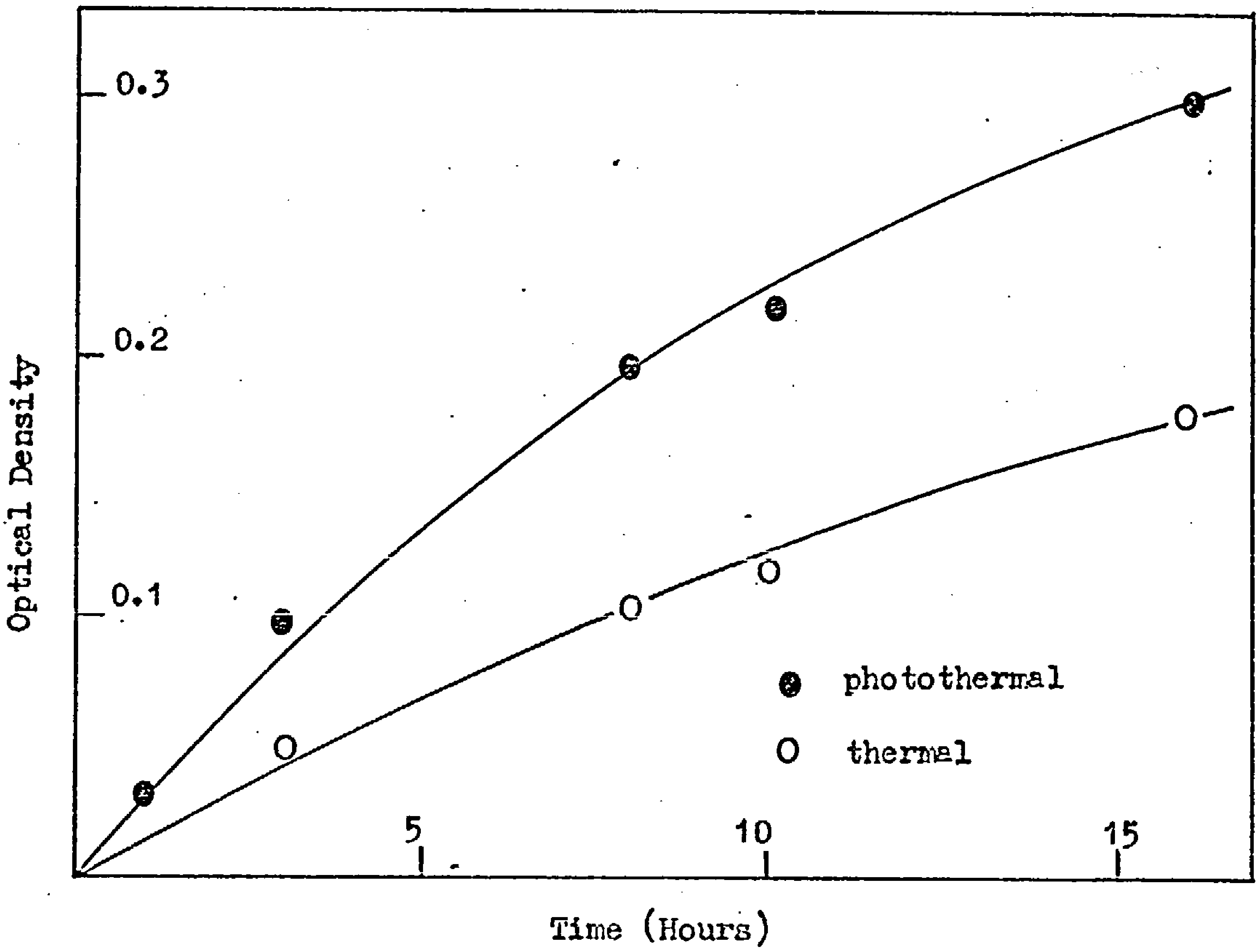
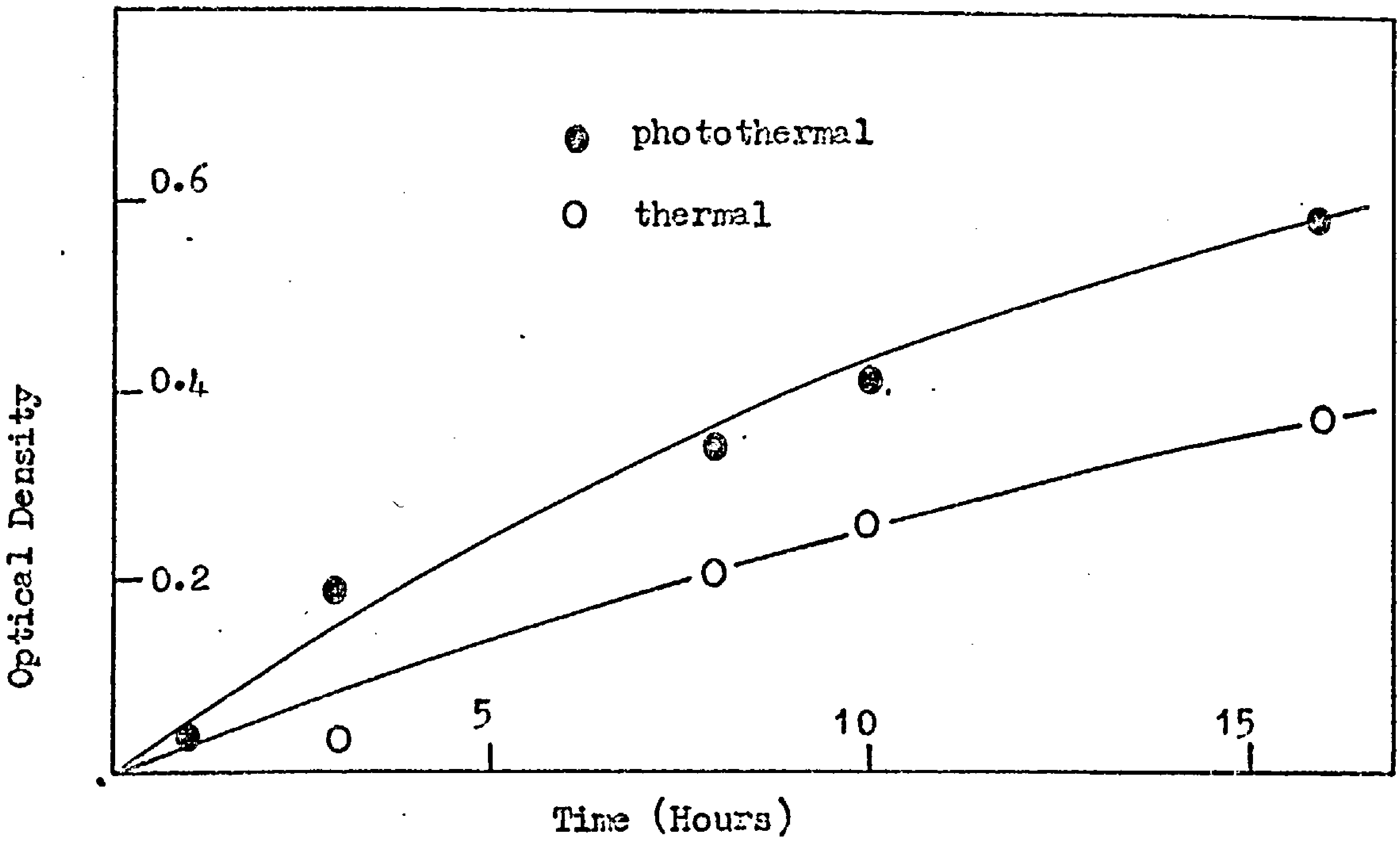
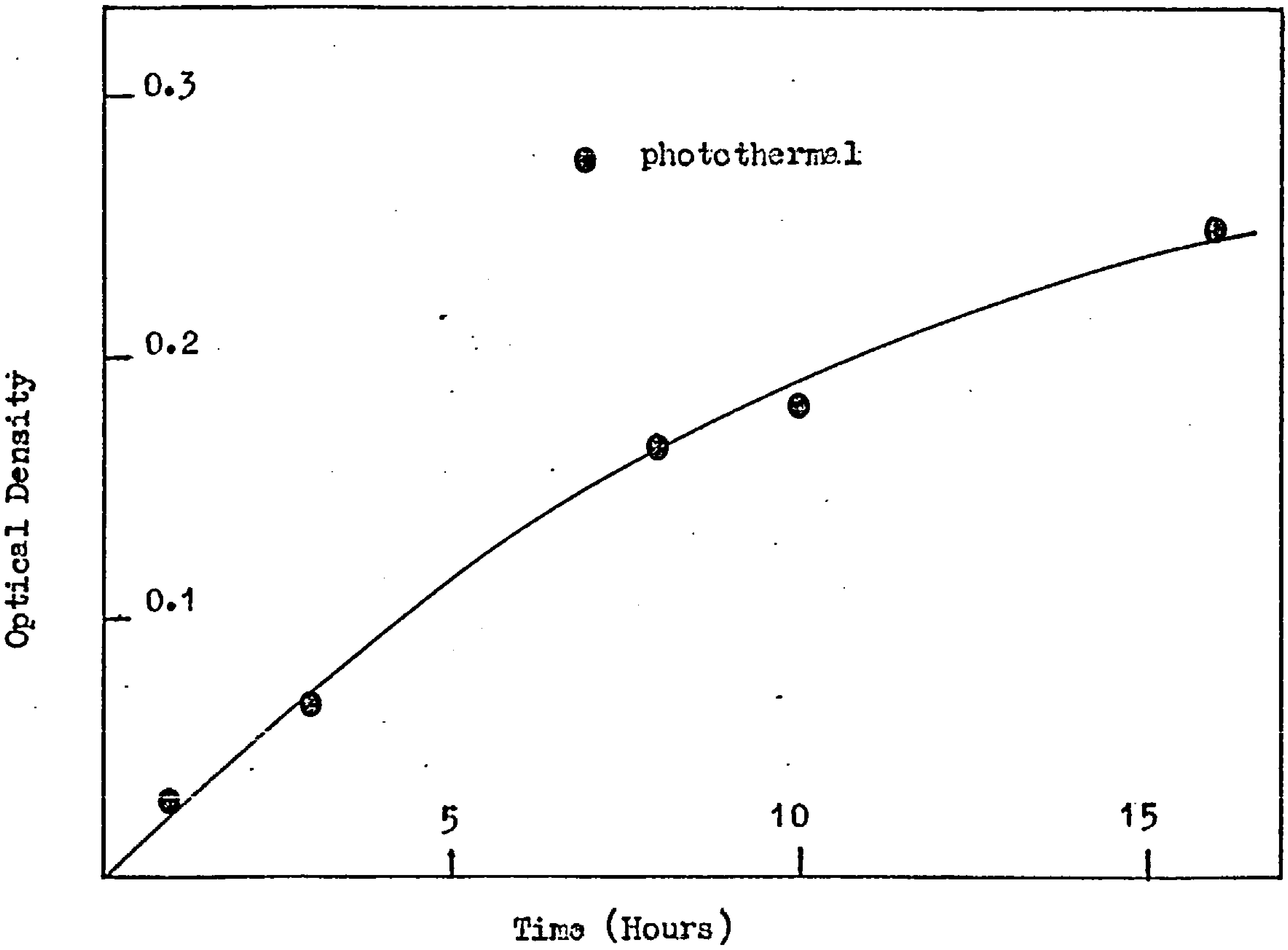


FIGURE 3.31 Plot of data for peak 1380 cm^{-1} (TABLE 3.15).



<u>FIGURE 3.32</u> Plot of data for peak 3018 cm^{-1} (TABLE 3.16)



<u>FIGURE 3.33</u> Plot of data for peak 950 cm^{-1} (TABLE 3.16)

Wavenumber (cm^{-1})	Time (Hours)	Optical Density Thermal	Optical Density Photothermal
3080	1	-	0.024
	3	0.053	0.167
	8	0.249	0.301
	10	0.285	0.341
	16	0.344	0.475
1650	1	-	0.030
	3	0.021	0.097
	8	0.135	0.166
	10	0.152	0.202
	16	0.202	0.271
988	1	-	0.028
	3	0.008	0.079
	8	0.112	0.148
	10	0.121	0.187
	16	0.176	0.267
910	1	-	0.114
	3	0.064	0.321
	8	0.391	0.553
	10	0.423	0.669
	16	0.647	0.847
888	1	-	0.113
	3	0.082	0.309
	8	0.401	0.612
	10	0.448	0.686
	16	0.698	1.056

TABLE 3.14 Optical density as a function of time of degradation for the peaks attributed to unsaturation in the infra - red spectrum of the gaseous degradation products of polypropylene at 354°C.

Wavenumber (cm^{-1})	Time (Hours)	Optical Density	
		Thermal	Photothermal
1460	1	-	0.086
	3	0.084	0.248
	8	0.290	0.458
	10	0.387	0.490
	16	0.530	0.738
1380	1	-	0.033
	3	0.054	0.103
	8	0.103	0.196
	10	0.117	0.221
	16	0.177	0.304

TABLE 3.15 Optical density as a frequency of time of degradation for the peaks attributed to saturated species in the infra - red spectrum of the gaseous degradation products of polypropylene at 354°C.

Wavenumber (cm^{-1})	Time (Hours)	Optical Density	
		Thermal	Photothermal
3018	1	-	0.033
	3	0.024	0.192
	8	0.215	0.342
	10	0.265	0.416
	16	0.371	0.592
950	1	-	0.027
	3	-	0.066
	8	-	0.166
	10	-	0.178
	16	-	0.248

TABLE 3.16 Production of methane (3018 cm^{-1}) and ethylene (950 cm^{-1}) in the thermal and photothermal degradations of polypropylene at 354°C.

Wavenumber (cm^{-1})	Optical Density		O.D. Ratio
	Thermal	Photothermal	Phototherm./Therm.
3080	0.270	0.350	1.30
1650	0.150	0.200	1.33
988	0.120	0.185	1.54
910	0.460	0.660	1.43
888	0.425	0.700	1.64
1460	0.390	0.510	1.31
1380	0.120	0.220	1.83
3018	0.260	0.415	1.60
950	-	0.180	-

<u>TABLE 3.17</u> $OD_{\text{photothermal}} \diagdown OD_{\text{thermal}}$ of the salient peaks in the infra - red spectrum of the gaseous products of polypropylene degraded for 10 hours at 354°C.

function of time of degradation. As expected, photodegradation results in a greater optical density of any given peak than the corresponding thermal degradation.

Only two absorptions can be positively identified; at 3018 cm^{-1} and 950 cm^{-1} corresponding to methane and ethylene respectively. FIGURE 3.32 compares the production of methane in the thermal and photothermal degradations and FIGURE 3.33 shows the photoproduction of ethylene with time. There is no corresponding thermal production of ethylene.

The ratio of OD photothermal to OD thermal for a 10 hour degradation was calculated for each peak in the hope that some indication might be obtained of the relative rates of formation of the materials producing these peaks(TABLE 3.17).

Bearing in mind the accuracies involved, the values obtained are probably, within experimental error, the same.

CHAPTER FOUR

LOW TEMPERATURE PHOTOLYSIS OF POLYPROPYLENE

In Chapter 3 an examination of the high temperature (200° - 354°C) photodegradation of polypropylene and the corresponding thermal degradation were described. This chapter complements that information by describing an investigation of low temperature (20° - 200°C) photolysis of the polymer.

Polymer samples, prepared by pre - melting and cooling at 20°C pressed polymer discs as described in Chapter 2, were irradiated in vacuo for times up to 70 hours, using the apparatus illustrated in FIGURE 2.7 (b). The intensity of the light beam incident on the polymer samples was 2.44×10^{15} quanta/sec. The effects of irradiation were assessed by molecular weight analysis and from weight loss characteristics in subsequent thermal degradation experiments.

4.1 Crystallinity and Sample Form

In the temperature range under consideration, polypropylene, like any other crystalline polyolefin, exhibits varying degrees of crystallinity. FIGURE 4.1 illustrates the decreasing degree of crystallinity with increasing temperature of a sample of isotactic polypropylene (82). At its melting point, the polymer becomes completely amorphous.

In polymer photolysis, it is generally accepted that the more crystalline the sample, the greater will be the amount of scattering and reflection of light and the smaller the amount of

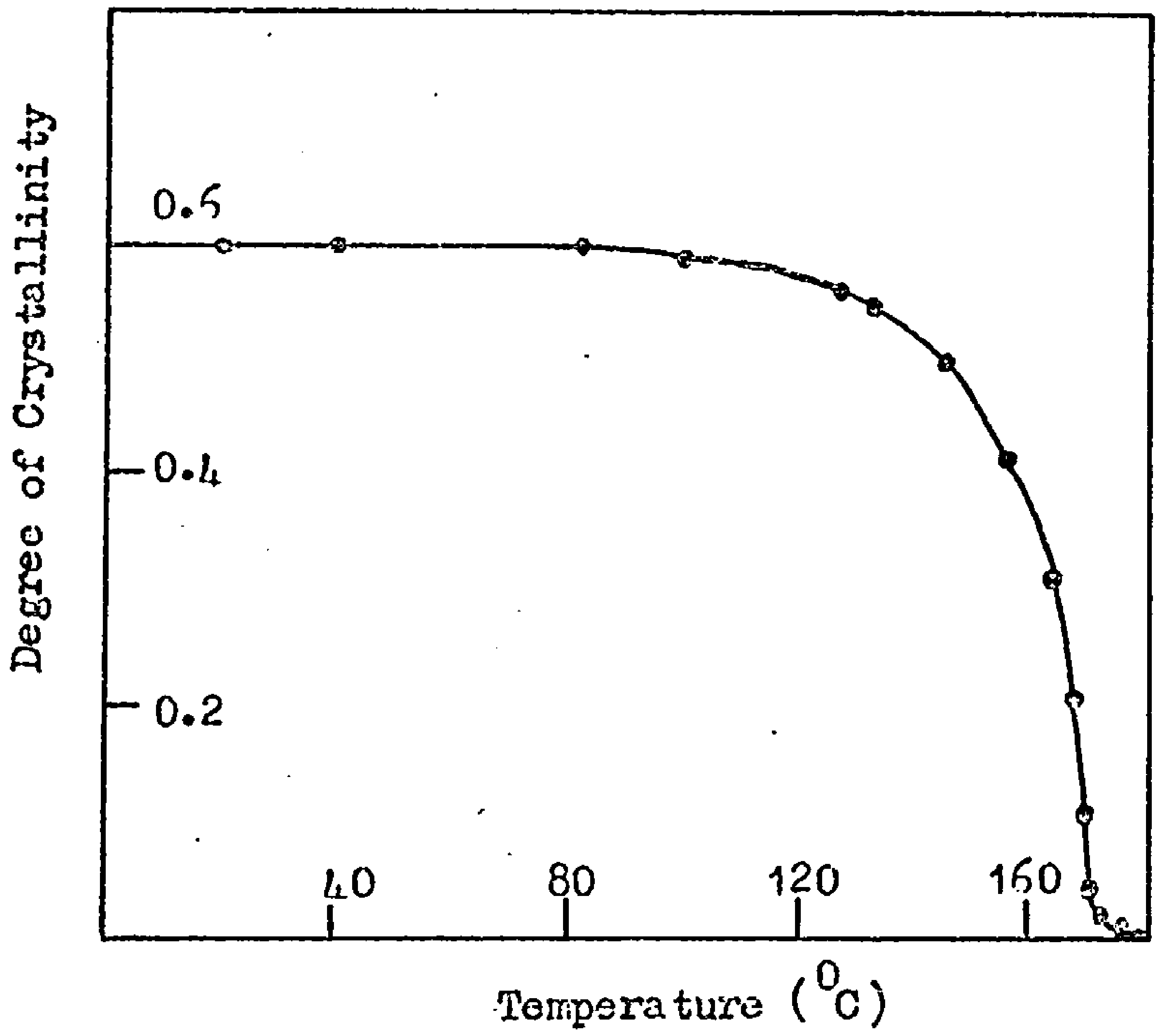


FIGURE 4.1 Degree of crystallinity as a function of temperature for isotactic PP ($\bar{M}_v$ = 640,000)

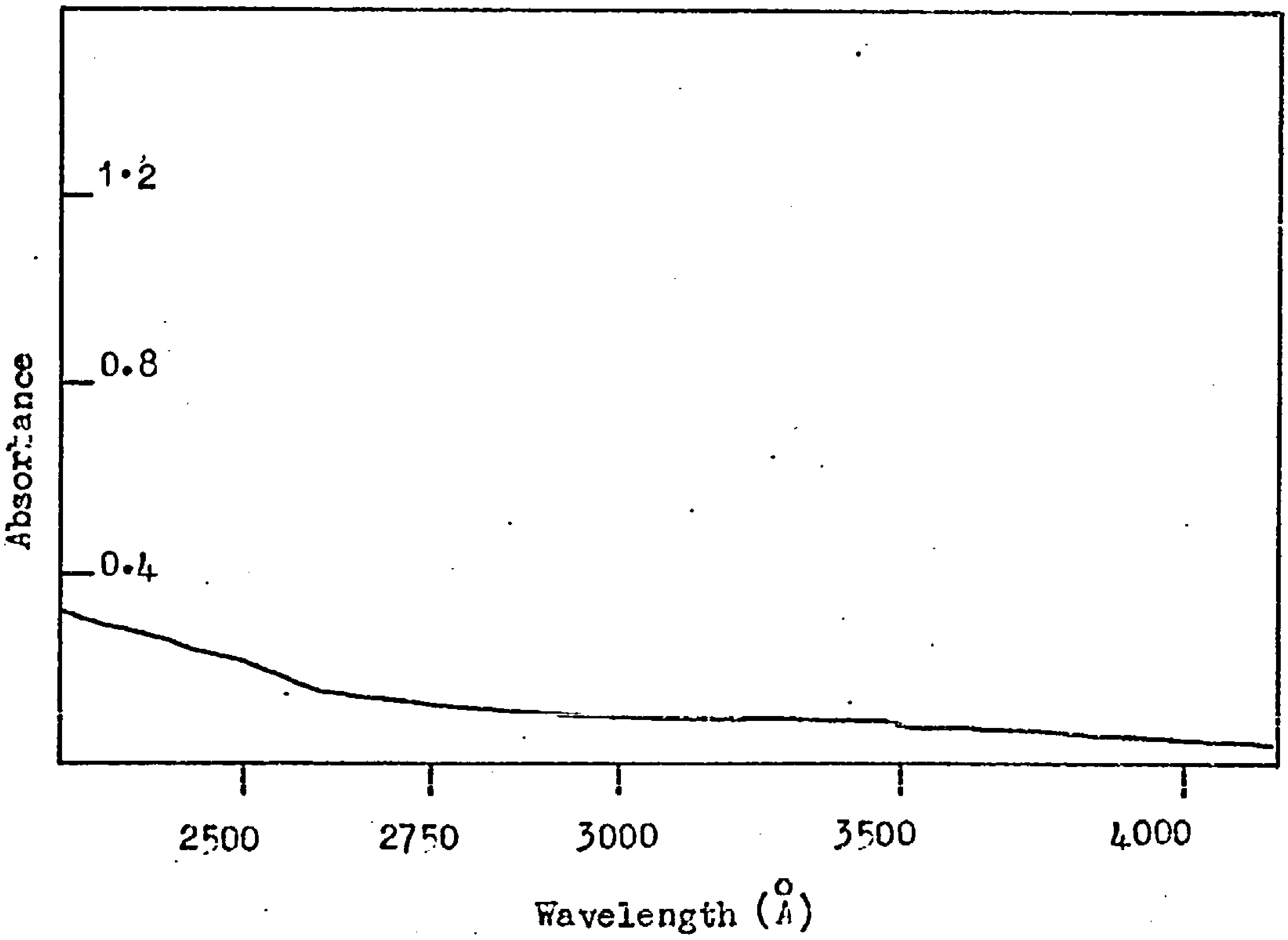


FIGURE 4.2 UV spectrum of a pre - melted PP disc (80mg).

effective incident radiation. Unfortunately, it was not experimentally feasible to determine the extent of scattering at different temperatures and thus compensation for this phenomenon was not possible. The amount of scattering and reflection was, however, determined at 20°C.

4.2 Ultra - Violet Absorption at 20°C

Pure polypropylene should not be expected to absorb in the ultra - violet beyond 2000Å and any such absorption (FIGURE 4.2) must result from chromophoric impurities (50).

The intensity of the light absorbed by a 'polymeric system' is obtained from the difference between the incident and transmitted intensities ; i.e. $I_a = I_o - I_t$. The transmitted intensity, I_t, is given by the equation ;

$$I_t = I_o 10^{-\epsilon c l},$$

where ϵ = the molar extinction coefficient,

c = concentration

and l = thickness of the film.

Since c is a constant for a given polymer, ϵ c can be replaced by Ka, a specific absorption coefficient having units of cm^{-1}. Thus:

$$I_t = I_o 10^{-Ka\, l}.$$

The transmittances at 2537 Å of films of known thickness were measured at 20°C and log (I_o/I_o) was plotted against thickness (FIGURE 4.3). A linear plot resulted which was extrapolated to zero thickness. This gave a loss in transmission of 27.6 % due to light scattered and reflected.

The specific absorption coefficient, Ka, was taken from the slope

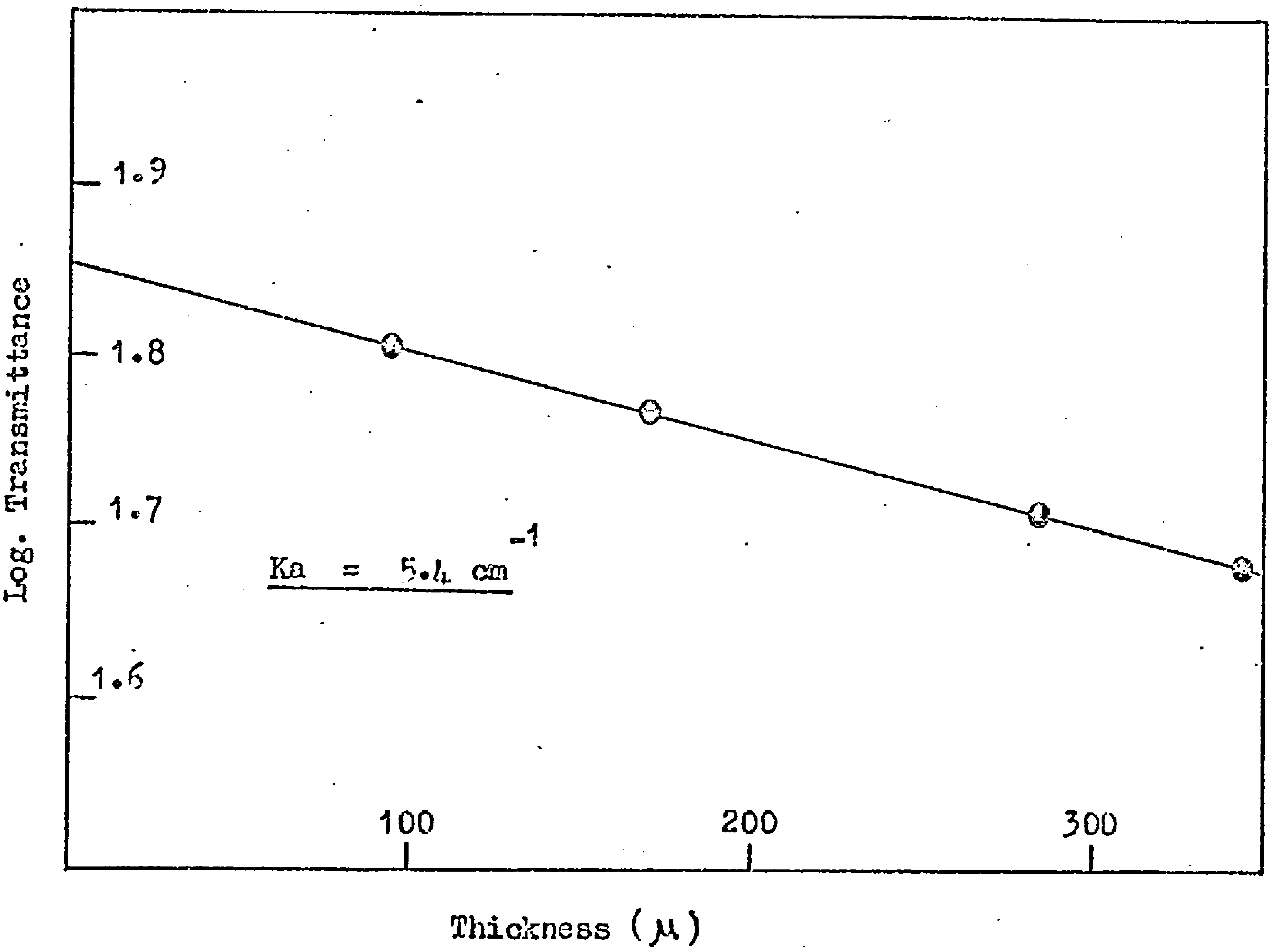


FIGURE 4.3 Relationship between transmittance and disc thickness.

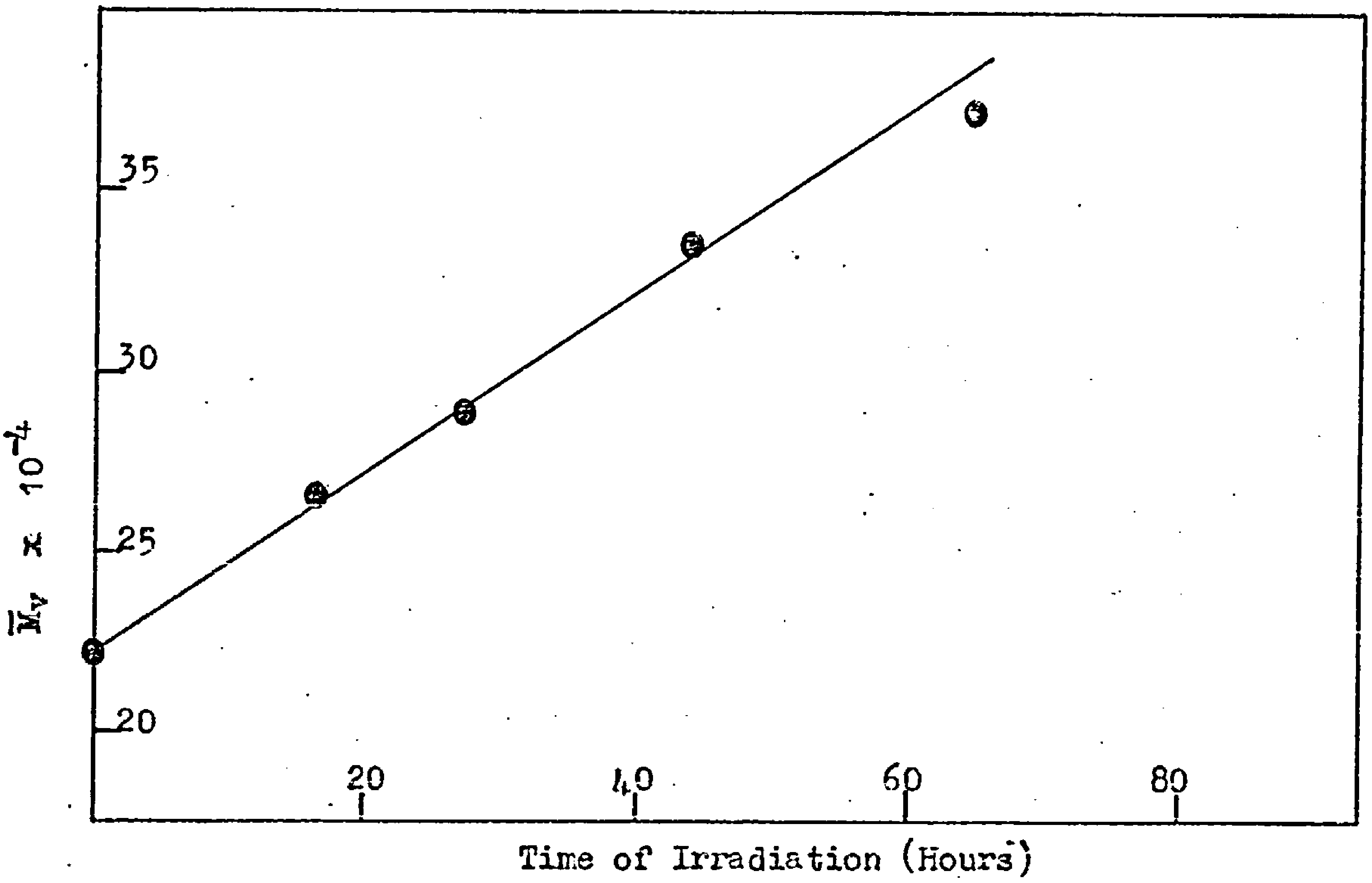


FIGURE 4.4 Molecular Weight as a function of time of irradiation at 20°C.

of the log (I/I_0) versus thickness plot and found to be 5.4 cm^{-1}. This Ka value yields a molar extinction coefficient, ϵ, at 2537 Å of 0.136 l.mole^{-1}.cm^{-1}. This value, of course, will vary with samples of polypropylene of different origin and will clearly depend on the concentration and nature of the chromophoric impurities.

4.3 Changes in Molecular Weight

Viscosity average molecular weights, $\bar{M}_v$, were estimated from the reduced specific viscosities of decalin solutions of polypropylene at 135°C. The theoretical and practical considerations are outlined in Chapter 2.

FIGURES 4.4 and 4.5 illustrate the changes which occur in the molecular weight of polypropylene irradiated in vacuo for various times at 20°C and 200°C respectively. At 20°C, $\bar{M}_v$ increases with time of irradiation while at 200°C, it decreases. It is also evident from FIGURE 4.5 that no thermal degradation occurs at 200°C.

In FIGURE 4.6, the molecular weights of samples irradiated for 41 hours are plotted as a function of temperature of irradiation (20° - 200°C). It is clear that crosslinking predominates over scission at lower temperatures while at higher temperatures (above about 100°C), the reverse is true. It should be noted that at 20°C no weight loss is detected and at 200°C, the maximum temperature, the weight loss after 70 hours irradiation is in the region of 2 %.

4.4 Thermal Degradation of Pre - Irradiated Samples.

In order to obtain preliminary information about the effects of pre - irradiation on the thermal degradation of polypropylene, Thermal Volatilisation Analyses were carried out on samples pre - irradiated for different times in the temperature range 20° - 200°C.

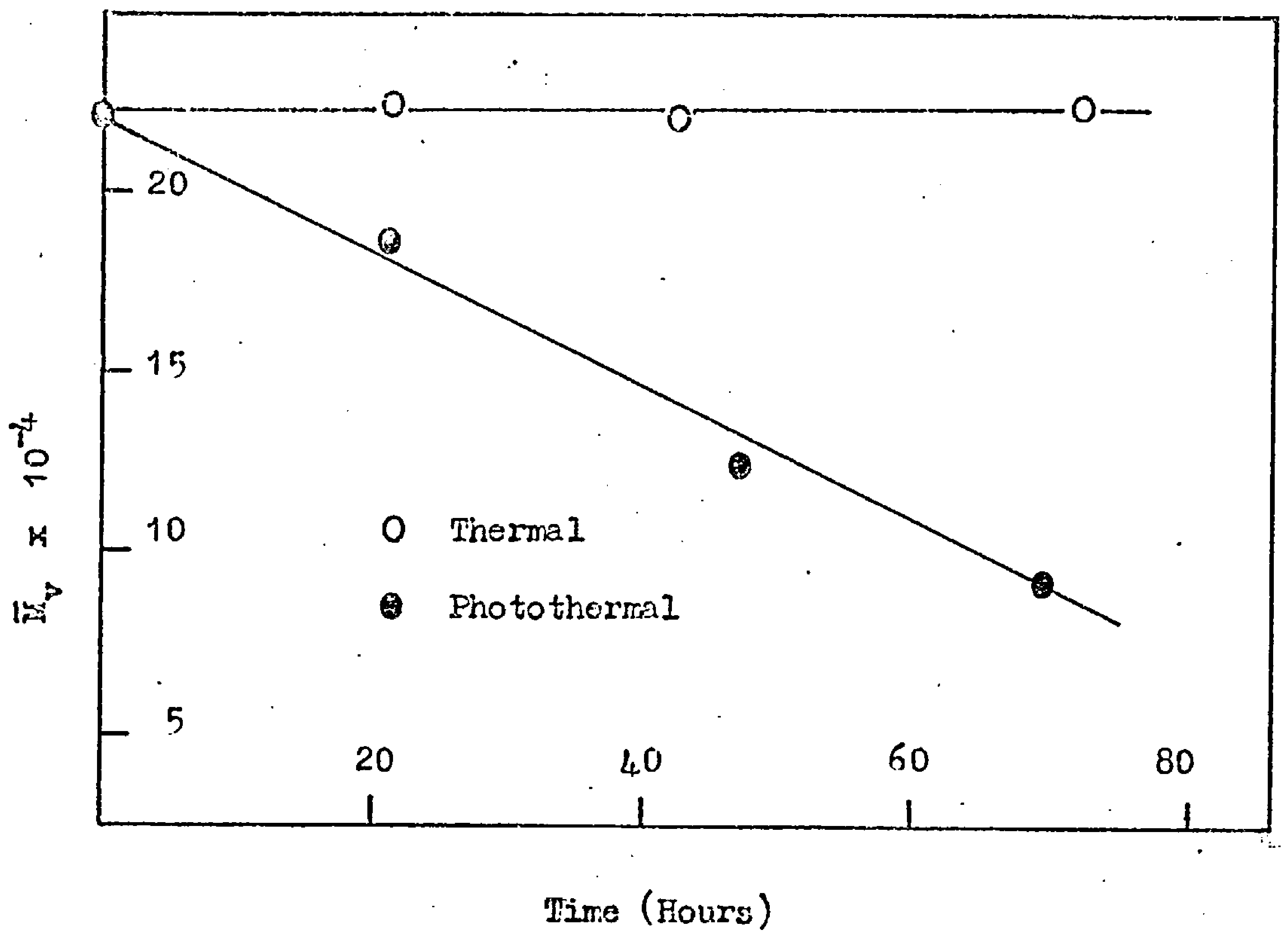


FIGURE 4.5 Molecular Weight as a function of time of degradation at 200°C.

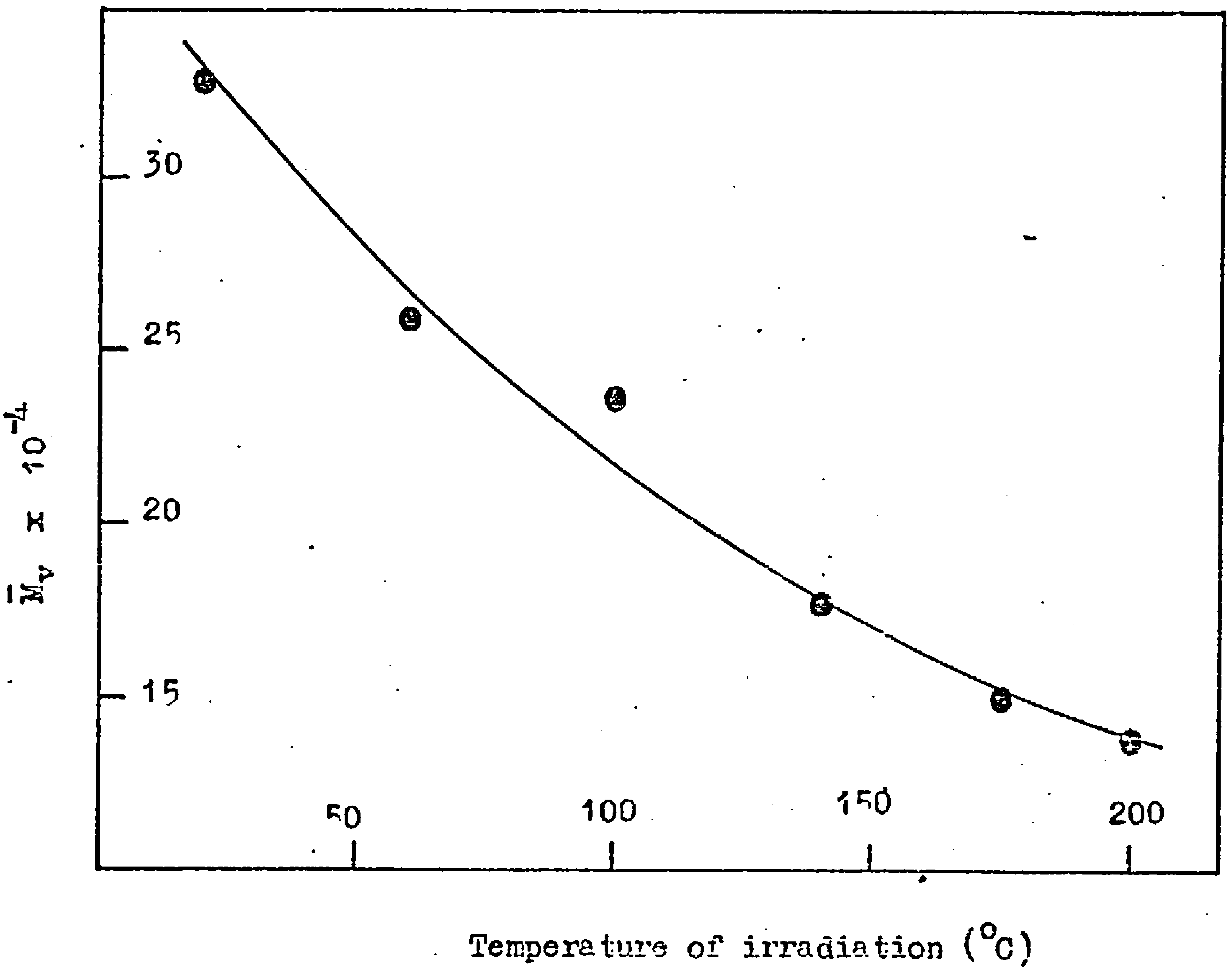


FIGURE 4.6 Molecular Weight as a function of temperature of irradiation. Samples photodegraded for 41 hours.

Time of Irradiation (Hours)	Intrinsic Viscosity $[\eta]$	Molecular Weight ($\bar{M}_v$)
0	2.03	222.300
17	2.35	267,900
27	2.53	293,800
44	2.84	338,800
65	3.03	377,600

TABLE4.1 Molecular weight data at 20°C (FIGURE 4.4)

	Time of Degradation (Hours)	Intrinsic Viscosity $[\eta]$	Molecular Weight ($\bar{M}_v$)
A	0	2.03	222,300
	22	2.06	227,000
	43	2.03	222,300
	66	2.06	227,000
B	0	2.03	222,300
	21.5	1.77	187,100
	47	1.27	123,900
	70	1.00	92,040

TABLE 4.2 Molecular weight data at 200°C (FIGURE 4.5).

A Thermal ; B Photothermal.

Temperature of Irradiation(^{o}C)	Intrinsic Viscosity $[\eta]$	Molecular Weight (M_v)
20	2.83	330,000
60	2.34	262,100
100	2.14	237,700
140	1.69	177,000
175	1.48	150,300
200	1.40	140,000

TABLE 4.3 Molecular Weight data at several temperatures (FIGURE 4.6).

a) Thermal Volatilisation Analysis (TVA)

This technique continuously measures the rate of evolution of volatile material during a linearly programmed temperature increase of the sample. Experimental details are recorded in Chapter 2.

FIGURE 4.7 (a) illustrates the behaviour of unirradiated polypropylene. Concurrent production of all the volatiles is indicated by the fact that the rate maximum on each trace occurs at the same temperature. The lack of coincidence of the traces indicates a mixture of condensable and non - condensable products, a different amount of material being condensed out at each of the initial cold traps below - 45°C. The non - condensables in the - 196°C trap were found to be hydrogen and methane.

The thermogram obtained from a sample pre - irradiated for 65 hours at 20°C is represented in FIGURE 4.7(b). The only significant difference from the thermogram of unirradiated polypropylene is the fact that the production of volatiles commences at a lower temperature (T_o°C). Concurrent production of all degradation products is again indicated and the rate maximum in both thermograms occurs at the same temperature (T_{max}°C).

Data from the thermograms of polypropylene pre - irradiated at 20°C for different times are presented in TABLE 4.4

Thermograms were also obtained for samples pre - irradiated for a fixed time (41 hours) over a range of temperatures. Data are given in TABLE 4.5. T_o is observed to decrease with increasing temperature of pre - irradiation.

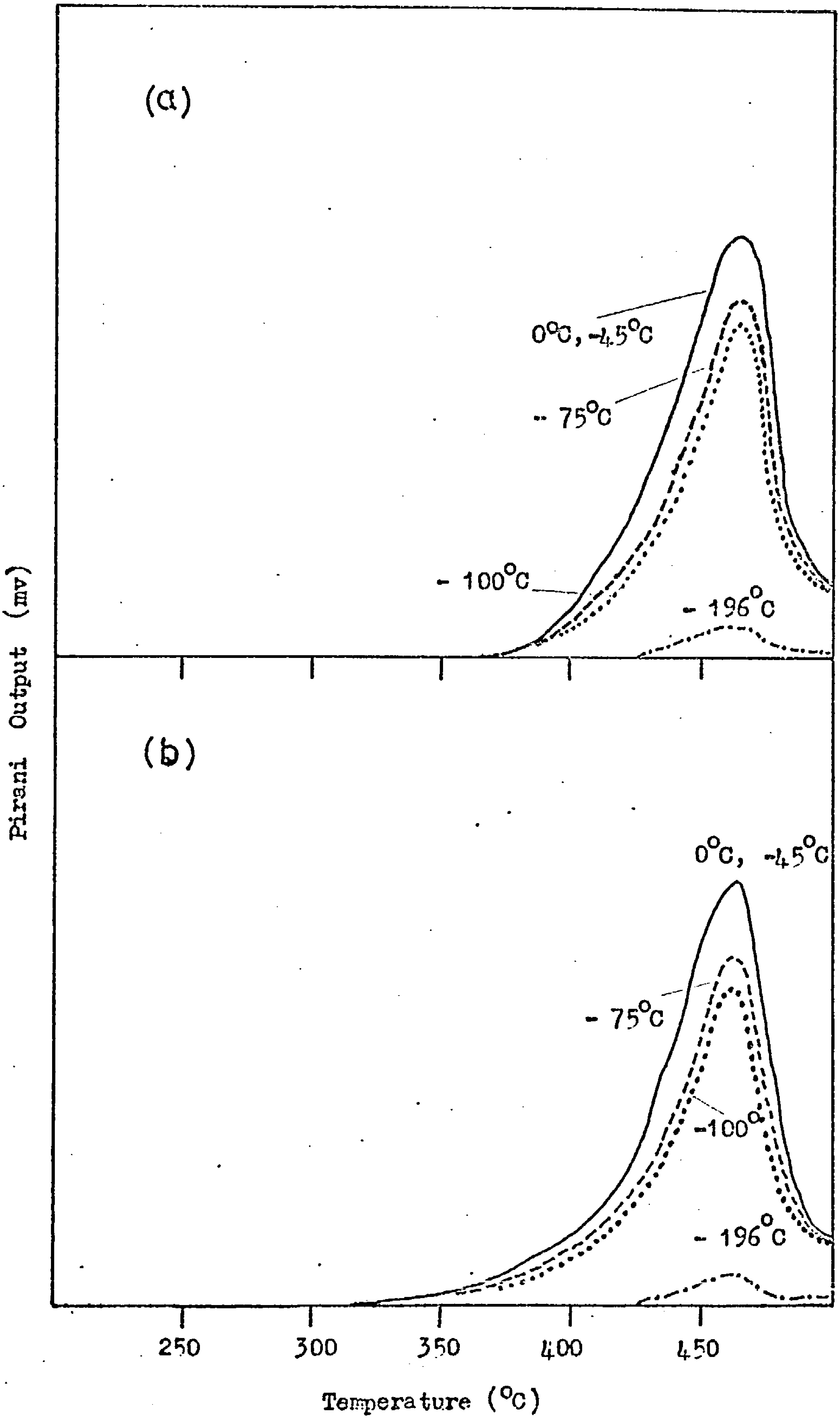


FIGURE 4.7 Differential Condensation TVA curves for

(a) unirradiated PP, and

(b) PP pre - irradiated for 65 hours at 20°C.

Time of Irradiation (Hours)	T_o(°C)	T_{max}(°C)
0	385	464
17	379	464
27	367	468
44	367	464
65	352	467

TABLE 4.4 TVA data for samples pre - irradiated at 20°C.

Temperature of Irradiation (°C)	T_o(°C)	T_{max}(°C)
20	366	464
100	376	465
140	363	466
175	361	464
200	358	464

TABLE 4.5 TVA data for samples pre - irradiated for 41 hours over a range of temperatures.

b) Isothermal Degradation

Isothermal degradations were carried out using the apparatus illustrated in FIGURE 2.8. Details of weight loss, cold ring and volatile production were obtained as described in Chapter 2.

FIGURE 4.8 (TABLE 4.6) shows the straight line resulting from the plot of weight loss, due to thermal degradation for 17 hours at 335°C, as a function of time of pre - irradiation at 20°C. It is apparent that pre - irradiation destabilises polypropylene. For example, 70 hours pre - irradiation increases thermal weight loss by 21 % of the original sample.

In the same FIGURE, a similar plot was constructed for polypropylene discs which had not been pre - melted. These samples were opaque and hence unable to transmit ultra - violet light. In this case, there is observed an initial sharp increase in weight loss which levels out after a pre - irradiation time of about 20 hours. The flat portion of the curve is seen to intersect the straight line, obtained for pre - melted samples, at a point corresponding to ca. 70 hours pre - irradiation. This observation was verified in the following manner. A pre - irradiation time of 40 hours was taken as being representative of the flat portion of the curve, and opaque samples, pre - irradiated for this period, were thermally degraded at 335°C for times up to 26.5 hours. Similar degradations were carried out on pre - melted samples, pre - irradiated for 70 hours. The result of plotting, for both sets of data, percentage weight loss as a function of time of thermal degradation is a coincident straight line (FIGURE 4.9).

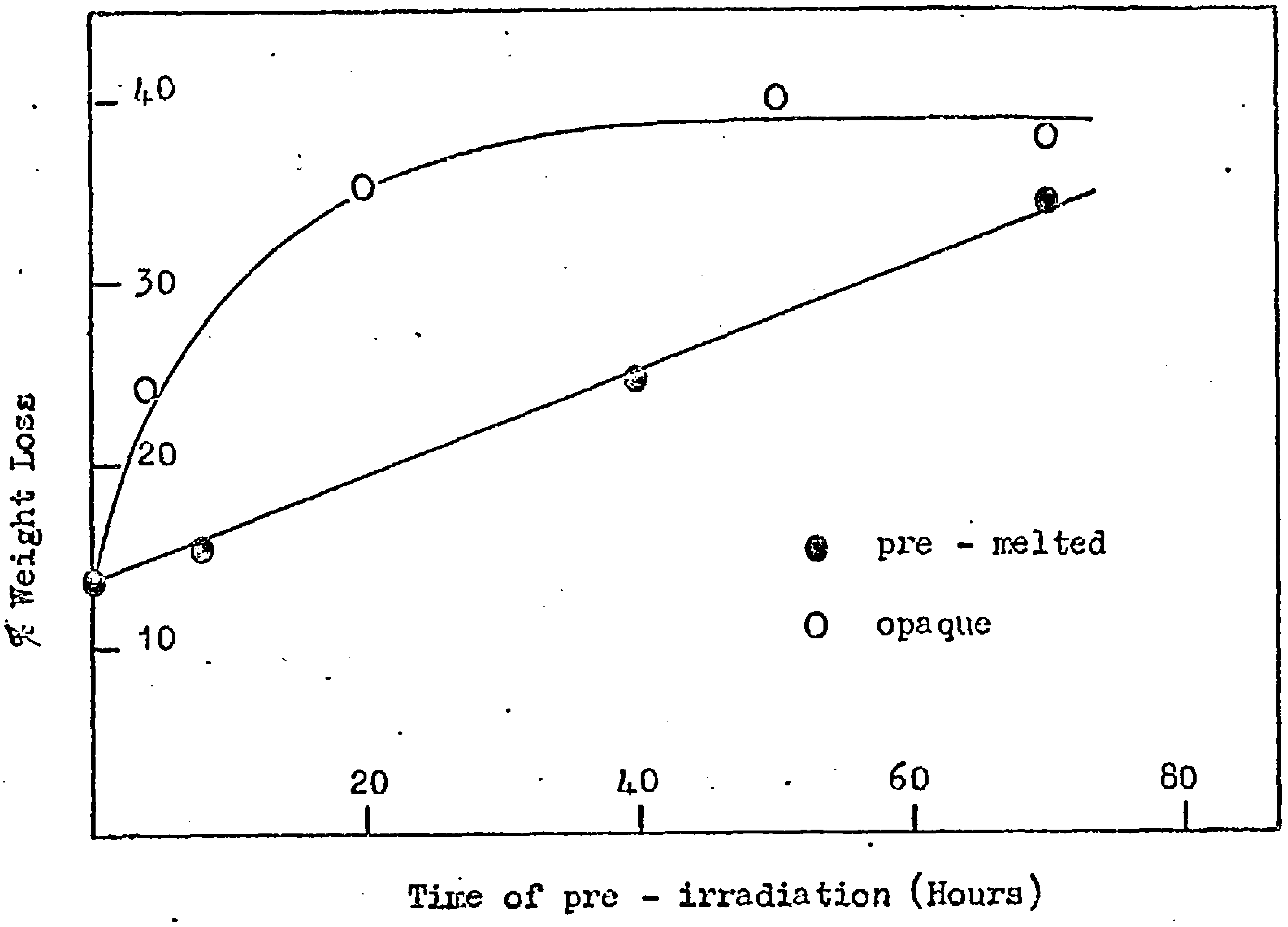


FIGURE 4.8 Weight loss, due to thermal degradation for 17 hours at 335°C, as a function of time of pre - irradiation at 20°C.

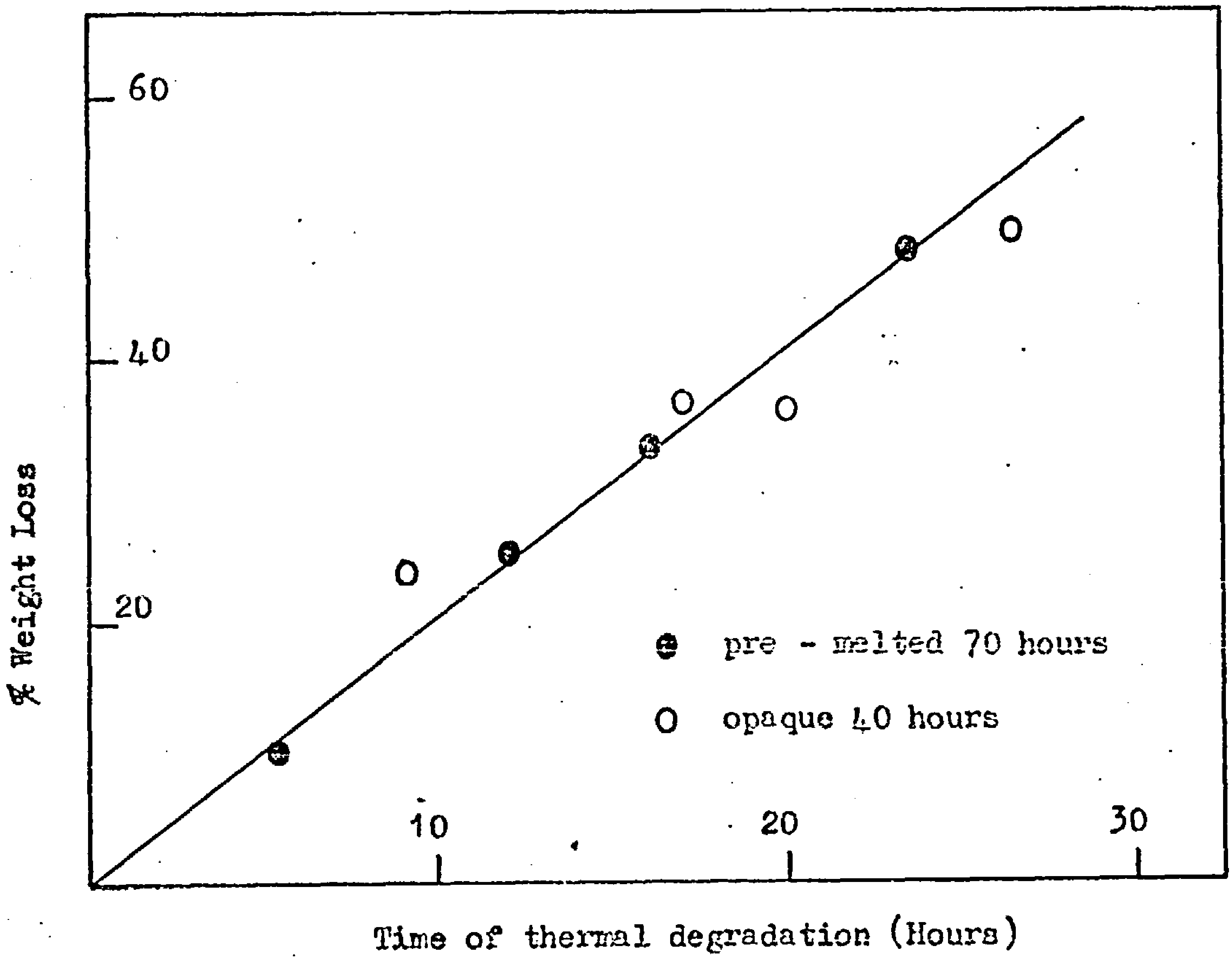


FIGURE 4.9 Weight loss as a function of time of thermal degradation at 335°C for samples pre - irradiated at 20 C for fixed times.

	Time of Pre - Irradiation (Hours)	% Original Polymer Sample		
		Weight Loss	C.R.F.	Gases
A	0	14.0	7.7	6.3
	8	15.5	9.0	6.5
	40	25.0	13.5	11.5
	70	35.0	19.9	15.1
B	0	14.0	7.7	6.3
	4	24.6	13.2	11.4
	20	36.3	20.8	15.5
	50	40.5	23.6	16.9
	70	37.8	21.6	16.2

<u>TABLE 4.6</u> Thermal Weight loss data for pre - irradiation at 20°C(FIGURE 4.8). A pre - melted ; B opaque.

	Time of Thermal Degradation (Hours)	% Original Polymer Sample		
		Weight Loss	C.R.F.	Gases
A	5.5	9.7	5.2	4.5
	12	25.1	14.3	10.8
	16	33.6	19.0	14.6
	23.5	47.8	29.0	18.8
B	9	23.8	13.0	10.8
	17	37.0	21.5	15.5
	20	36.0	20.7	15.3
	26.5	49.6	30.0	19.6

<u>TABLE 4.7</u> Thermal degradation data for FIGURE 4.9.

A pre - melted samples irradiated for 70 hours

B opaque samples irradiated for 40 hours

This curious effect of pre - irradiation on the volatilisation of opaque samples may possibly be explained in the following way. Since the samples are opaque, incident radiation tends to be reflected from the surface and only a small percentage is expected to penetrate a very thin surface layer of polymer. Owing to internal scattering, this light which enters the polymer has a long path length resulting in a rapid increase in subsequent volatilisation. Virtually complete damage is done to the thin surface layer at a very early stage in the photolysis and underlying layers are protected by this surface layer from further irradiation. Thus the volatilisation curve is seen to flatten out.

Evidence suporting this explanation was obtained in the following manner. Two opaque discs were pressed in the usual way. One was irradiated for 70 hours and the other for 35 hours on each of its two surfaces. On subsequent thermal degradation the latter sample showed a markedly greater extent of volatilisation.

It was considered of interest to determine whether a similar phenomenon could be observed in the volatilisation curve obtained from opaque polypropylene samples pre - irradiated in air. The photolysis of polypropylene in air has been well documented (53,54,56,57) and involves the introduction of hydroperoxide and carbonyl structures which can be readily detected by infra - red analysis. The concentration of these oxygen - containing groups is found to increase with time of irradiation.

FIGURE 4.10 shows the result of plotting, for both pre - melted and opaque samples, percentage weight loss, due to thermal degradation for 6 hours at 335°C, as a function of time of pre - irradiation at

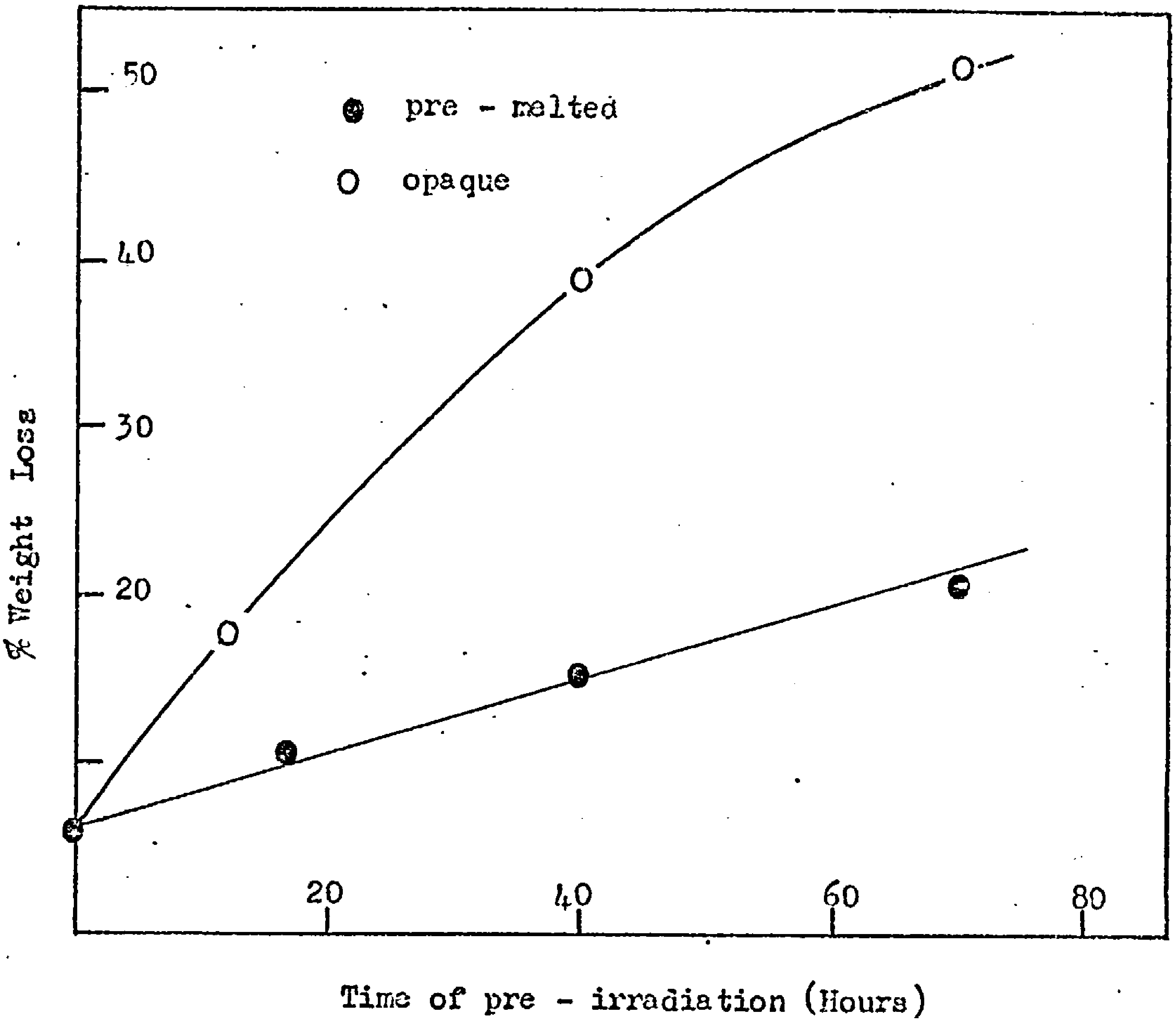


FIGURE 4.10 Weight loss, due to thermal degradation for 6 hours at 335°C, as a function of time of pre - irradiation in air at 20°C.

	Time of Pre - irradiation (hours)	% Original Polymer Sample		
		Weight Loss	CRF	Gases
A	0	6.0	3.6	2.4
	17	10.7	5.1	5.6
	40	15.5	7.3	8.2
	60	20.8	9.6	11.2
B	0	6.0	3.6	2.4
	11.5	17.8	10.6	7.2
	40.5	39.0	23.4	15.6
	70	52.0	30.8	21.1

TABLE 4.8 Thermal degradation data for pre - irradiations in air at 20°C.
A pre - melted ; B opaque. (FIGURE 4.10).

20°C in air. As before, pre - irradiation of an opaque sample gives rise to a greater extent of thermal volatilisation than its pre - melted counterpart. However, unlike the reaction in vacuum, there is no evidence of a flattening out of the volatilisation curve. This may be expained by the fact that an extra variable, the diffusability of oxygen, has been introduced. Oxygen is able to diffuse into an unmelted (opaque) disc more readily than into one which has been pre - melted. Thus a combination of the effects of oxygen and UV radiation will cause volatilisation to increase with time of irradiation.

FIGURE 4.11 compares the straight lines obtained by plotting weight loss, due to thermal degradation for 17 hours at 335°C, versus time of pre - irradiation at 20°C and 200°C. Pre - irradiation at 200°C clearly destabilises polypropylene to a greater extent than at 20°C. In FIGURE 4.12 the thermal stability of polypropylene is shown as a function of temperature of pre - irradiation. Samples were pre - irradiated for 41 hours at several temperatures in the range 20° - 200°C and thermally degraded for 17 hours at 335°C.

c) Product Analysis

The products of thermal degradation of pre - irradiated polypropylene were separated and collected as outlined in Chapter 2. The residue, cold ring and gaseous volatiles were shown, by infra - red analysis, to be identical to those produced in the thermal degradation of the irradiated polymer.

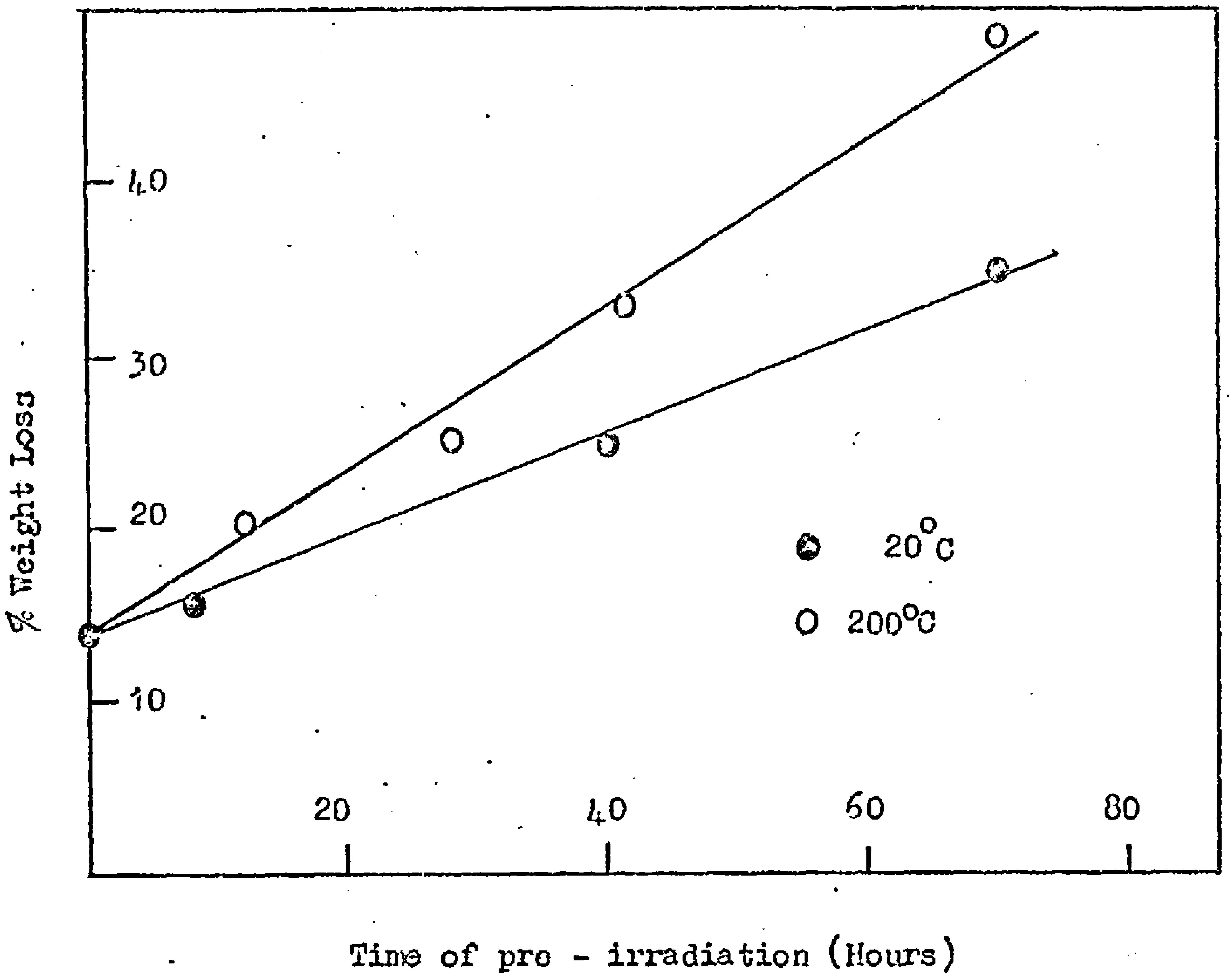


FIGURE 4.11 Weight loss, due to thermal degradation for 17 hours at 335°C, as a function of time of pre - irradiation at 20°C and 200°C.

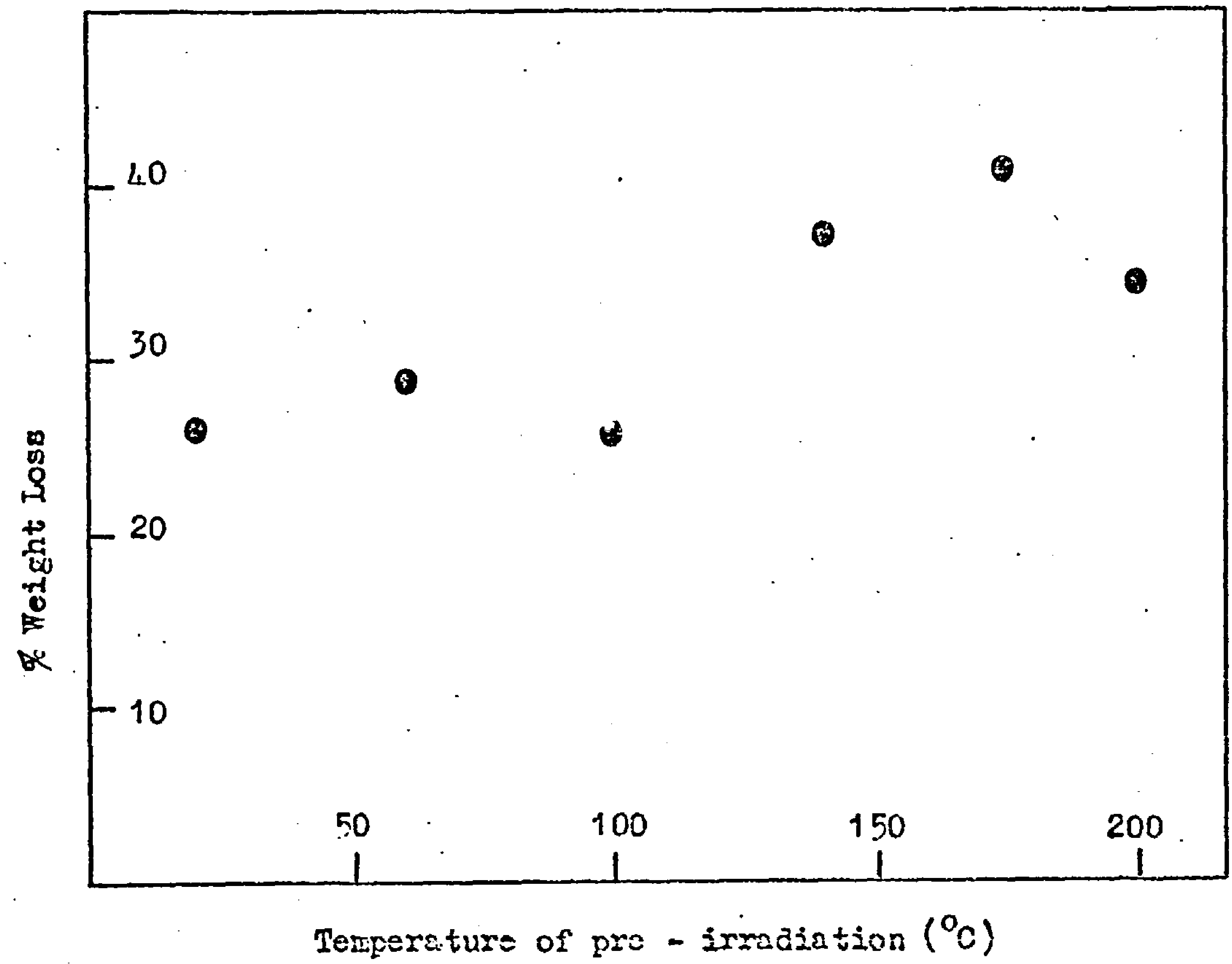


FIGURE 4.12 Weight loss, due to thermal degradation for 17 hours at 335°C, as a function of temperature of pre - irradiation. Samples were irradiated for 41 hours.

Time of Pre - Irradiation (Hours)		% Original Polymer Sample Weight Loss	C.R.F.	Gases
A	See TABLE 4.6 (A)			
B	12	20.4	10.9	9.5
	27	24.8	13.5	11.3
	41	32.8	13.5	14.1
	70	48.6	29.4	19.2

TABLE 4.9 Thermal degradation data for pre - irradiations at 20°C (A) and 200°C (B). (FIGURE 4.11).

Temperature of Pre - Irradiation (°C)	% Original Polymer Sample Weight Loss	C.R.F.	Gases
20	26.0	14.0	12.0
60	29.2	15.6	13.6
100	25.8	13.8	12.0
140	37.8	20.4	17.4
175	41.5	22.3	19.2
200	33.5	18.0	15.5

TABLE 4.10 Thermal degradation data for samples pre - irradiated for 41 hours over a range of temperatures (FIGURE 4.12).

4.5 Conclusions

From the foregoing investigation the following features emerge ;

(1) In irradiations at 20°C, 27.6 % of incident radiation is scattered and reflected.

(2) At low temperatures crosslinking predominates over scission reactions in the photolysis of polypropylene. At higher temperatures (above ca. 100°C) the reverse is true.

(3) Pre - irradiation destabilises polypropylene.

(4) The higher the pre - irradiation temperature, the greater the destabilisation.

(5) The products of thermal degradation of pre - irradiated polypropylene appear to be identical to those of the unirradiated polymer.

CHAPTER FIVE

INFLUENCE OF CHROMOPHORIC IMPURITIES AND SAMPLE MORPHOLOGY

This chapter is primarily concerned with an investigation into some of the factors which may affect the vacuum photolysis of polypropylene. Various possible impurities and the morphology of the sample are considered in particular.

5.1 Chromophoric Impurities

As discussed in Chapter 1, pure polypropylene is not expected to absorb at longer wavelengths than 2000 Å and any such absorption must result from chromophoric impurities. These impurities, which may be polymeric or small molecule, can be excited to higher energy levels, undergo reactions to form free radicals and may eventually interact with the polymer, initiating degradation. Among the chromophoric impurities to be anticipated in polypropylene are hydroperoxide and carbonyl containing structures and transition metal residues (50).

(a) Initiation due to oxidation products of PP

Hydroperoxide and carbonyl groups may be introduced into the polymer by air oxidation during polymerisation or processing, or by very slow metal - catalysed oxidation at room temperature (83).

The maximum of the first absorption band of alkyl hydroperoxides lies in the region of 2000 Å, with the tail of the band extending to about 3200 Å. Thus the radiation employed in this study (2537 Å), will be absorbed as well as a part of the spectrum of natural sunlight (3200 - 2900 Å). Hydroperoxides contain an oxygen - oxygen bond with overlapping lone pair orbitals giving rise to low energy bonding and high energy anti - bonding orbitals, both of which are filled with electrons. Thus light absorption is probably due to transitions between the two closer lying levels, $\pi^* p_{x,y} \rightarrow \sigma p_z$. The net result is cleavage of the O - O bond and the creation of two free radicals.

$$ROOH \xrightarrow{h\nu} R\dot{O} + \dot{O}H$$

The ultra - violet absorption spectra of aliphatic ketones show an absorption, $\lambda_{max} \sim 2800$ Å, which extends to almost 3400 Å (84), the relatively small extinction coefficient being an indication of the 'forbidden' nature of this singlet - singlet, $n - \pi^*$ transition. The two main photochemical reactions of such ketones are the Norrish type I and type II processes which have been described in detail in Chapter 1.

b) Initiation due to Metal Impurities.

The effective catalyst systems in stereospecific polymerisations are formed by the combination of a reducible compound of transition elements of group IV to VII with a reducing organo - metallic compound of metals of group I to III. The most commonly used system for the polymerisation of propylene to isotactic PP (and the one used to prepare the present polymer) consists of crystalline $TiCl_3$ with an aluminium alkyl.

Polyolefins obtained using these Ziegler - Natta catalysts always contain transition metal residues which cannot easily be removed. The concentration of such metal impurities (normally < 50ppm) and their chemical nature, generally depend on the purification process (50). The main components of these residues are probably TiO_2 and Al_2O_3 and examination of the absorption spectra of these compounds shows that TiO_2 absorbs at wavelengths shorter than 4000 Å and Al_2O_3 at wavelengths shorter than 3000 Å (85).

It has been proposed (50) that catalyst residues act as sensitisers in the photooxidation of polyolefins according to a mechanism that should involve light absorption and the production of free radicals through a photo - excited electron transfer from the anion to the cation. Photosensitisation by trace amounts of Fe^{3+}, from production machinery, has also been proposed in the oxidation of certain polymers (86). The ultra - violet absorption spectrum of Fe^{3+} reveals an absorption, $\lambda_{max} = 2300$ Å.

5.2 Degree of Crystallinity (sample morphology)

The physical properties of a polymer are determined by the structure, particularly in the case of crystalline polymers which may occur in two different morphological forms, spherulitic and single crystal.

By cooling extremely dilute solutions of crystallisable polypropylene, the polymer solute material will precipitate in the form of single crystals, composed of lamellae with a thickness of the order of 100 Å and with lateral dimension of at least one micron (87). The simplest crystals are monolayers, with more complicated ones containing 10 to several hundred lamellae, all originating from the same nucleus. It has been estimated (88) that a single crystal contains of the order of 10^8 molecules.

The normal form of polymers which are crystallised from the melt develops through the growth of sperulites. These are birefringent aggregates of crystals, starting usually from a heterogeneous nucleus and spreading out in a spherical fashion until they fill practically the entire volume of the bulk crystallised polymer (87,89). Spherulites consist of radial fibrils composed of lamellae of the same order of thickness as those of single crystals. The polymer chains, oriented perpendicular to the sperulite radius and hence to the fibrils, are folded in a regular fashion with a fold period corresponding to the thickness of the lamellae.

Although the sperulites themselves are crystalline, the spaces between them are not. Even under the most favourable conditions, polypropylene (and polymers in general) will never achieve full crystallinity because of chain entanglements, structural imperfections and insufficient rate of crystallisation. An increase in the rate of cooling (i.e. the rate of crystallisation) from the melt, of a polypropylene sample will result in a lower degree of crystallinity by virtue of an increase in the number of spherulites and a decrease in their size.

5.3 Aim of this Investigation

With the factors discussed in the previous sections in mind, the aims of the work described in the remainder of the present chapter are as follows : -

a) Analysis of the polypropylene sample for oxygen and metal impurity content.

b) Investigation of the effect of adding TiO_2, Al_2O_3 and Fe_2O_3 on the vacuum photolysis of the polymer.

c) Determination of the role of sample morphology (degree of crystallinity) on the photolysis of polypropylene, both in vacuum and in air.

5.4 Experimental

a) Sample Preparation

(i) Samples containing metal oxide additives.

Titanium dioxide, aluminium oxide and ferric oxide were all obtained as finely divided powders. A mixture of each metal oxide (0.5 % w/w) with polypropylene was prepared by mixing in a mortar for a period of 30 minutes. These mixtures were pressed into discs, melted in vacuum and quenched at - 196°C, as described in chapter 2.

(ii) Samples of varying degree of crystallinity.

Owing to the polymorphism of polypropylene, the preparation of samples of reproducible morphology requires the strict control of film thickness, nature of the substrate and quenching conditions (90). Pressed polymer discs were prepared as before. By cooling from the melt at different rates, samples of varying degrees of crystallinity were obtained. Details of cooling procedures are given in TABLE 5.4.

b) Procedure

Photodegradations were carried out at room temperature for times up to 20 hours, using the apparatus depicted in FIGURE 2.7 (a). The intensity of the light beam incident on the polymer samples was 2.68×10^{16} quanta/sec.

The effect of photolysis was determined by the weight loss characteristics of subsequent isothermal degradation experiments. Thermal degradations were carried out using the apparatus illustrated in FIGURE 2.8 and details of weight loss, cold ring and production of volatiles were obtained as described in Chapter 2.

5.5 . Results

a) Analysis of the polypropylene sample.

The hydroperoxide contents of three separate 5 mg samples of the polymer were obtained as described in Chapter 2. The average level was 1.10 x 10^{-7} moles per 5 mg sample, a value very near the lower limit of detection of the technique (1 x 10^{-7} moles per 5 mg sample). Thus the hydroperoxide content of the polymer is shown to be very low indeed. The concentration of carbonyl groups in the polymer is sufficiently small as to be undetected by IR analysis.

Trace impurities of titanium and aluminium were detected by means of colorimetry. The exact concentrations could not be accurately determined but they are estimated to be $<$ 100 ppm. No traces of ferric impurities were observed.

b) Effect of addition of metal oxides on photolysis

FIGURE 5.1 (TABLE 5.1) shows the curve resulting from the plot of weight loss, due to thermal degradation for 3 hours at 354°C, as a function of time of pre - irradiation at 20°C for a 0.5 % by weight mixture of TiO_2 with polypropylene. The corresponding curve for the original polypropylene sample is included for comparison. Similar comparisons are made for 0.5 % by weight mixtures of Al_2O_3 and Fe_2O_3 with polypropylene in FIGURES 5.2 and 5.3 (TABLES 5.2 and 5.3) respectively.

In all cases destabilisation is observed to increase with time of irradiation. This has been attributed (Chapter 4) to crosslinking of the polymer. Addition of TiO_2 is shown to slightly

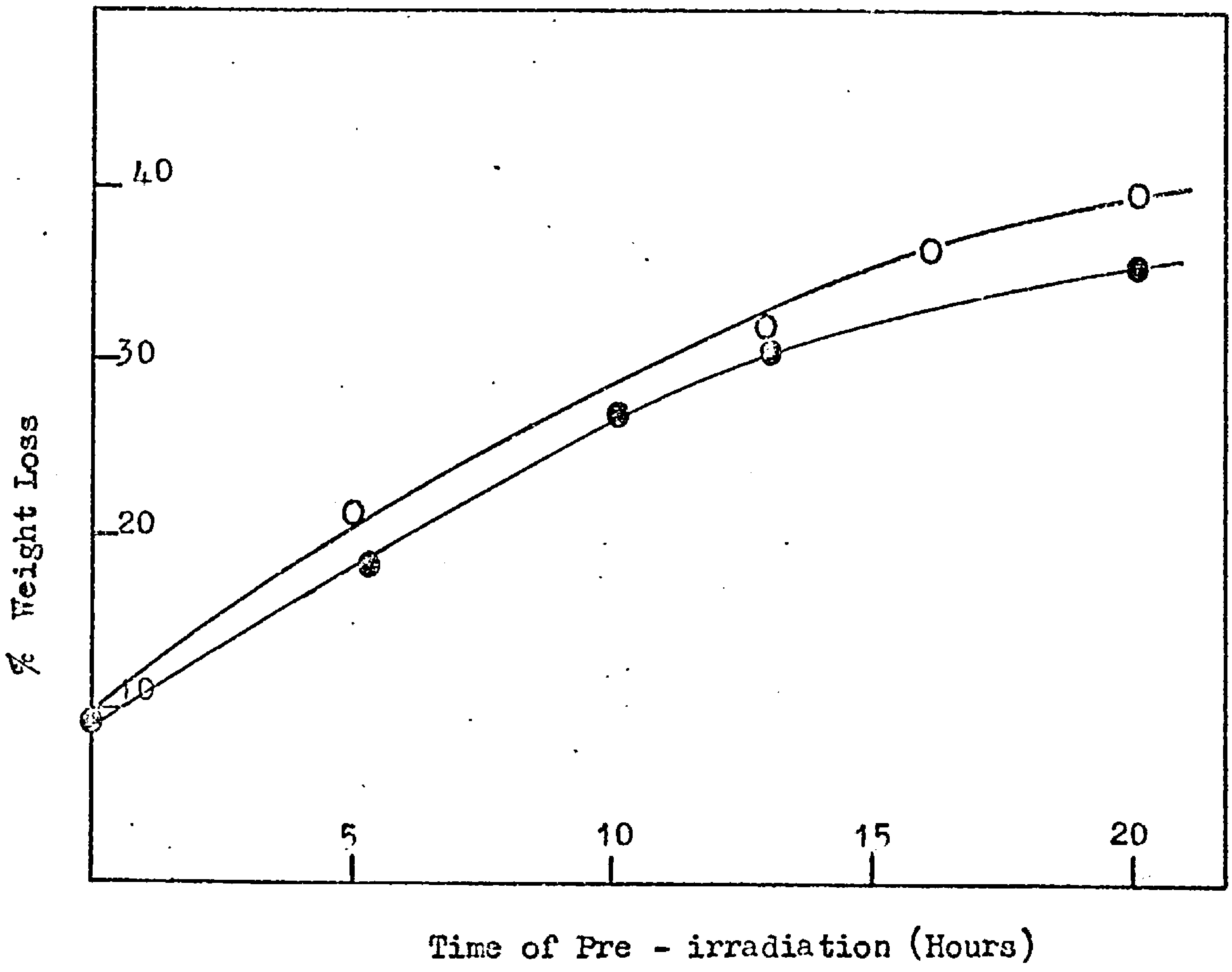


FIGURE 5.1 Effect of addition of TiO_2 on the photolysis of polypropylene.

● PP ; ○ PP + 0.5 % TiO_2

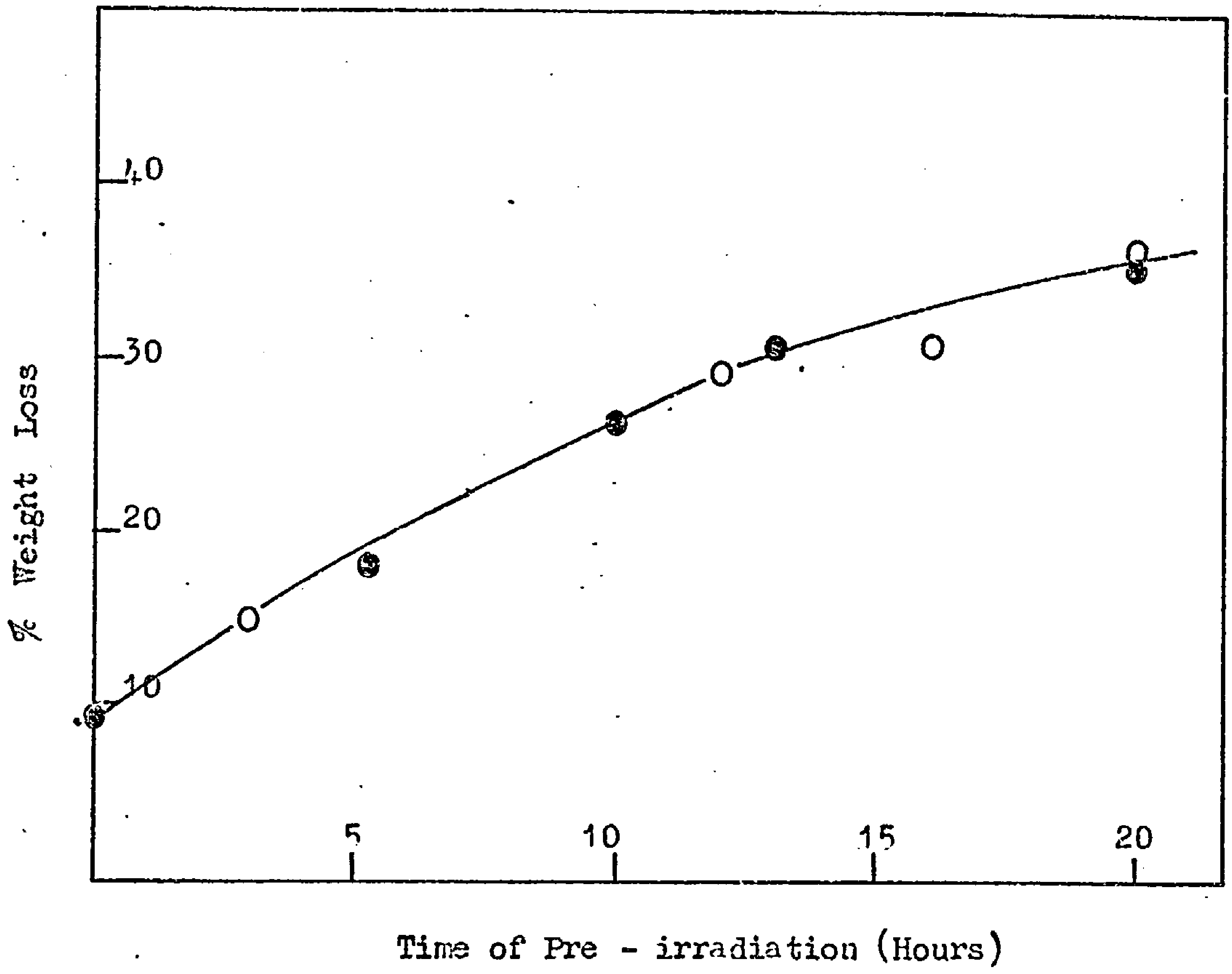


FIGURE 5.2 Effect of addition of Al_2O_3 on the photolysis of polypropylene.

● PP ; ○ PP + 0.5 % Al_2O_3

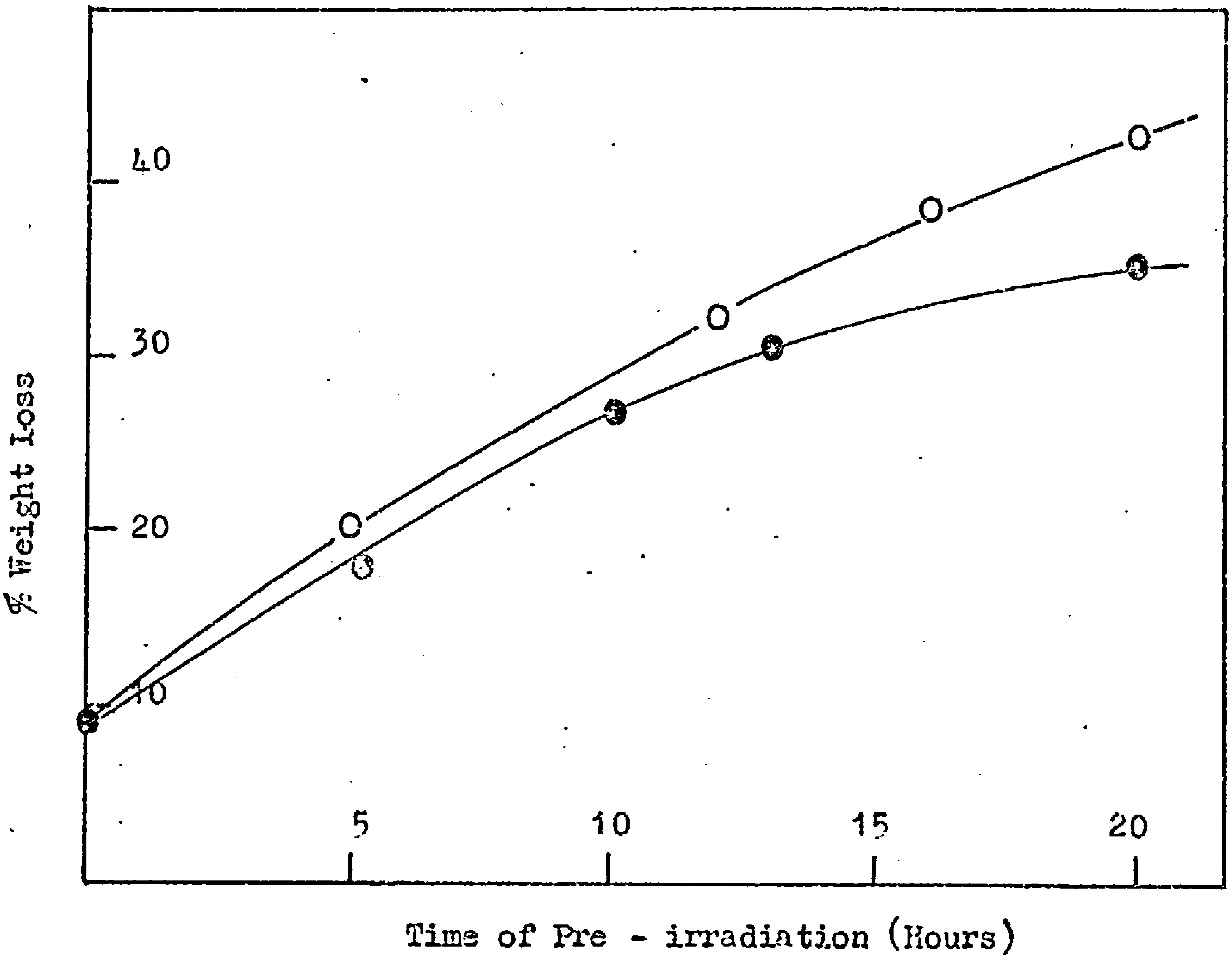


FIGURE 5.3 Effect of addition of Fe_2O_3 on the photolysis of polypropylene.

● PP ; ○ PP + 0.5 % Fe_2O_3

	Time of Pre - irradiation (Hours)	% Original Polymer Sample		
		Weight Loss	Cold Ring	Gases
A	0	9.5	5.8	3.7
	5.25	18.2	10.8	7.4
	10	27.0	16.4	10.6
	13	31.0	18.7	12.3
	20	35.6	21.2	14.4
B	0	9.3	5.5	3.8
	5	21.8	13.2	8.6
	13	31.9	19.1	12.8
	16	36.5	21.0	15.5
	20	39.6	24.4	15.2

TABLE 5.1 Data for Figure 5.1

A = PP ; B = PP + 0.5 % TiO_2

	Time of Pre - irradiation (Hours)	% Original Polymer Sample		
		Weight Loss	Cold Ring	Gases
A		see TABLE 5.1 (A)		
B	0	9.4	5.7	3.7
	3	14.9	8.9	6.0
	12	29.5	17.9	11.6
	16	30.9	18.6	12.3
	20	36.4	21.8	14.6

TABLE 5.2 Data for FIGURE 5.2

A = PP; B = PP + 0.5 % Al_2O_3

Time of Pre - irradiation (Hours)		% Original Polymer Sample Weight Loss	Cold Ring	Gases
A		see TABLE 5.1 (A)		
B	0	9.0	5.4	3.6
	5	20.6	12.5	8.1
	12	32.6	19.8	12.8
	16	38.4	23.4	15.0
	20	45.5	28.3	17.2

TABLE 5.3 Data for FIGURE 5.3

A = PP ; B = PP + 0.5 % Fe_2O_3

accelerate the photolysis of polypropylene whereas the addition of Al_2O_3 is seemingly without influence. Perhaps the most surprising result is the fact that Fe_2O_3 proves to have a greater accelerating effect on the photolysis of polypropylene than does TiO_2.

It was not considered worthwhile to vary the concentration of the additives since the quantity added (0.5%) is far in excess of the amount likely to be found in any polypropylene sample and addition of smaller amounts would lead to inaccuracies in weighing and mixing.

It is possible that the mixtures of metal oxide and polymer are not sufficiently intimate, considering that in the original polymer the metal oxide will be 'molecularly' dispersed. Even so, it is reasonable to expect the high concentration added to have some effect if it is catalytically active.

c) Effect of crystallinity on photolysis.

TABLE 5.4 illustrates the effect of quenching temperature on degree of crystallinity of a polypropylene sample. Values obtained by density and X - ray methods show good agreement.

FIGURE 5.4 (TABLE 5.5) shows the co - incident curves resulting from the plot of weight loss, due to thermal degradation for 3 hours at 354°C, as a function of time of pre - irradiation at 20°C for samples of varying morphology. This co - incidence was reproducible. The values in TABLE 5.5 must, however, be affected to some extent by variations in transparency associated with samples of differing crystallinity. The variation of percentage transmission at 2537 Å with rate of cooling was found to be 61 % (sampleA), 63 % (sample B) and 70 % (sample C). Correction for this variation in transmission will not, however, appreciably

Sample	Degree of Crystallinity (%) Density	 X - ray
A	70.0	72.7
B	63.0	61.5
C	47.0	52.2

TABLE 5.4 Crystallinity data for samples of polypropylene cooled from the melt at different rates.

A cooled with furnace switched off, but still in position (see FIGURE 2.7)

B cooled with furnace lowered i.e. at 20°C

C quenched with liquid nitrogen i.e. at - 196°C.

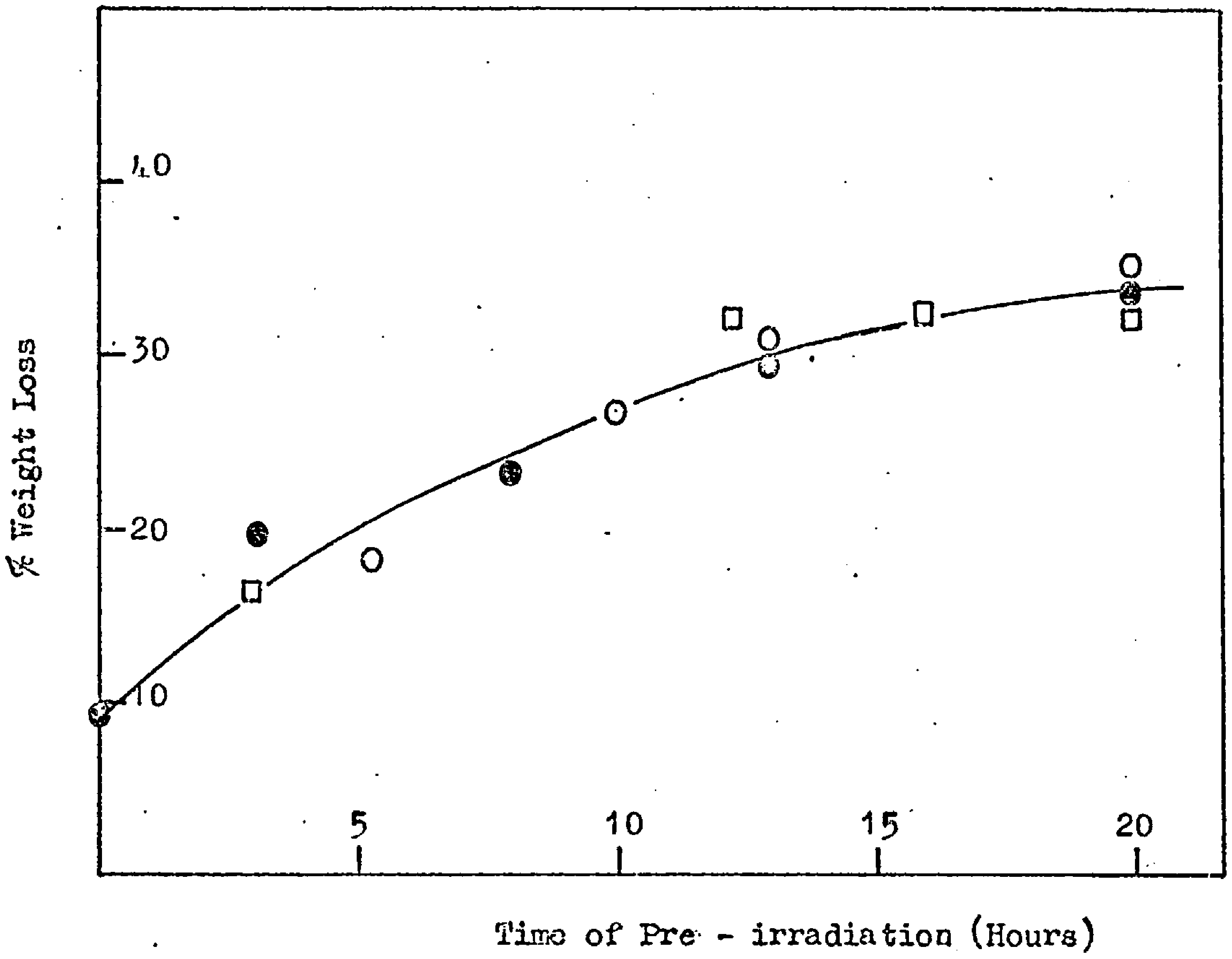


FIGURE 5.4 Effect of degree of crystallinity on the photolysis of polypropylene in vacuo.

□ sample A ;

● sample B ;

○ sample C .

A,B and C as defined in TABLE 5.4.

	Time of Pre - irradiation (Hours)	% Original Polymer Sample		
		Weight Loss	Cold Ring	Gases
A	0	9.5	5.8	3.7
	3	16.6	9.4	7.2
	12.25	32.5	19.4	13.1
	16	32.5	19.6	12.9
	20	32.6	19.6	13.0
B	0	9.5	5.8	3.7
	3	20.0	11.8	8.2
	8	23.5	13.5	10.0
	13	29.8	19.0	10.8
	20	33.5	20.0	13.5
C	0	9.5	5.8	3.7
	5.25	18.2	10.8	7.4
	10	27.0	16.4	10.6
	13	31.0	18.7	12.3
	20	35.6	21.2	14.4

<u>TABLE 5.5</u> Data for FIGURE 5.4

A,B and C as defined in TABLE 5.4.

alter the curve in FIGURE 5.4.

FIGURE 5.5 (TABLE 5.6) shows similar plots for samples of differing crystallinity pre - irradiated in air. Once again a co - incident curve is obtained. Pre - irradiation in air introduces hydroperoxide and carbonyl structures which accelerate the thermal breakdown of polypropylene. Evidence of these oxygen containing groups, the concentration of which increases with time of irradiation, can be readily obtained by IR analysis.

Thus from FIGURES 5.4 and 5.5 it seems reasonable to conclude that morphological variations have relatively little effect on the photolysis of polypropylene, either in vacuo or in air.

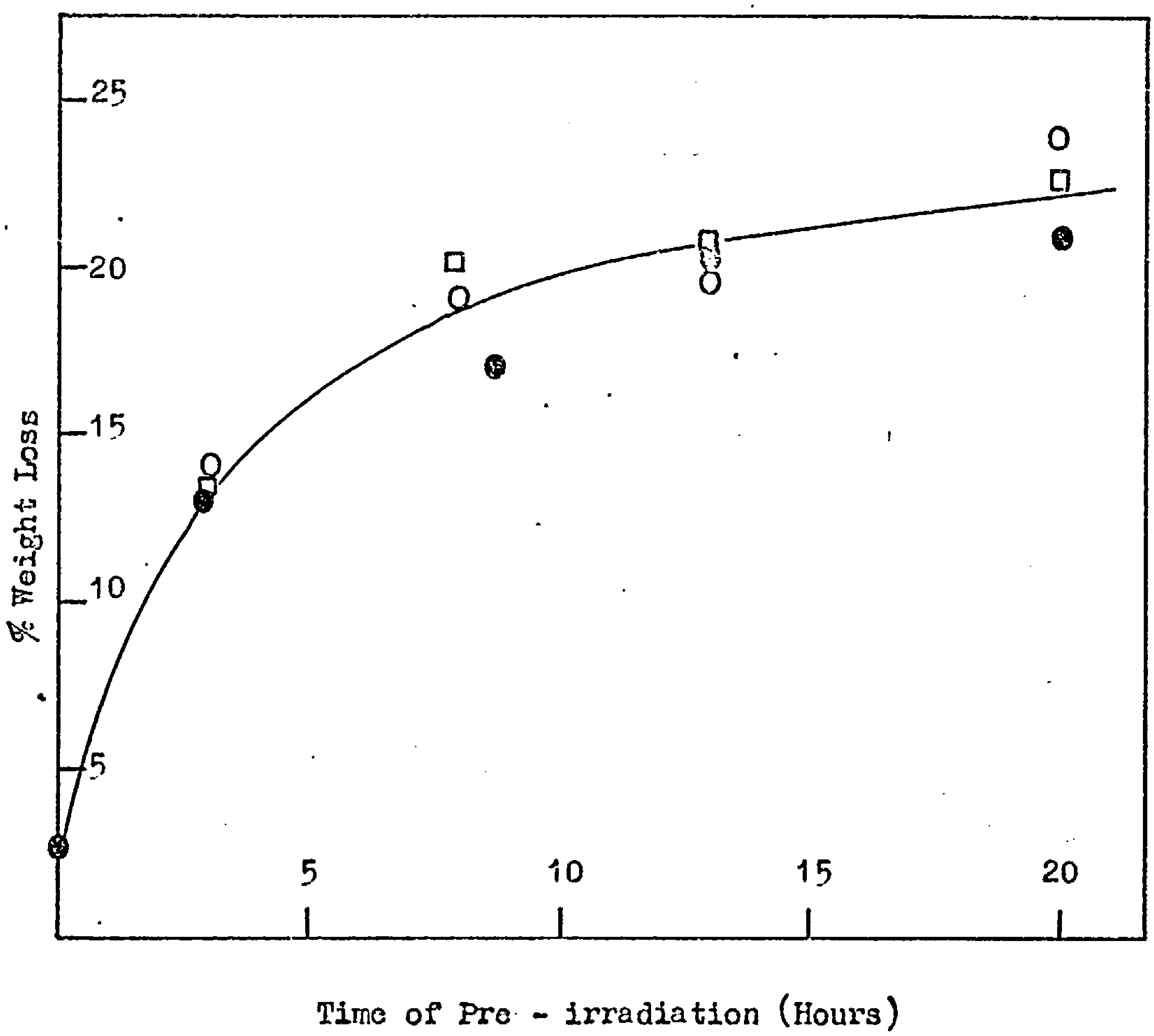


FIGURE 5.5 Effect of degree of crystallinity on the photolysis of polypropylene in air.

Symbols as in FIGURE 5.4.

	Time of Pre - irradiation (Hours)	% Original Polymer Sample Weight Loss	Cold Ring	Gases
A	0	2.5	1.5	1.0
	3	13.2	7.1	5.1
	8	20.3	11.4	8.9
	13	21.0	11.7	9.3
	20	22.9	12.7	10.2
B	0	2.5	1.5	1.0
	3	13.5	7.6	5.9
	8.7	17.0	9.5	7.5
	13	20.6	11.5	9.1
	20	20.9	11.6	9.3
C	0	2.5	1.5	1.0
	3	14.1	7.8	6.3
	8	19.2	10.8	8.4
	13	19.5	11.0	8.5
	20	24.2	13.5	10.7

<u>TABLE 5.6</u> Data for FIGURE 5.5

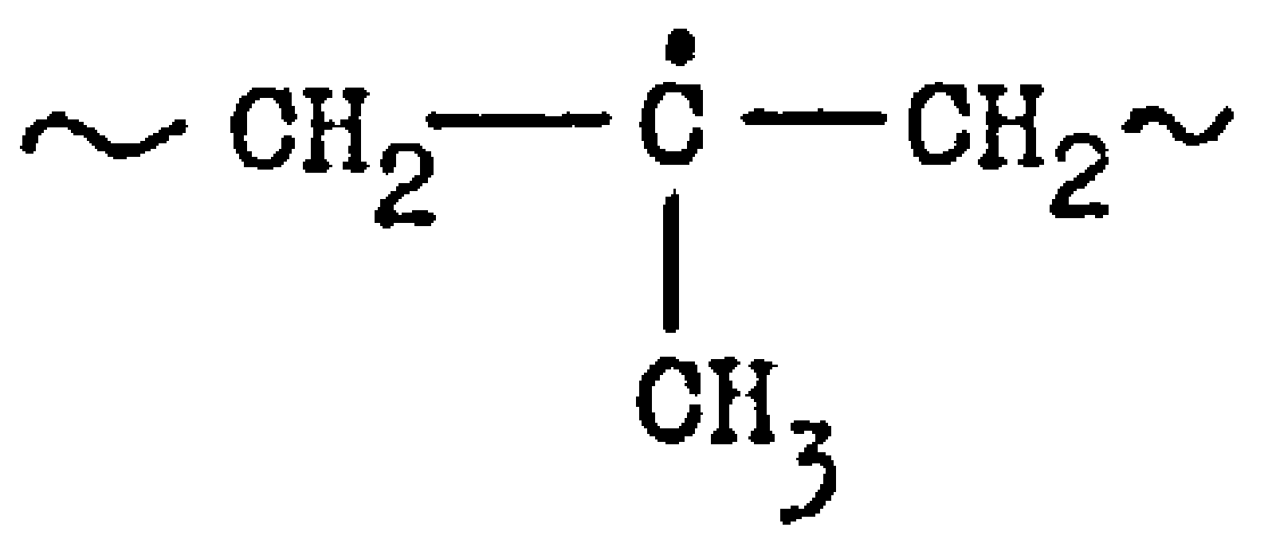
A, B and C as defined in TABLE 5.4

CHAPTER SIX

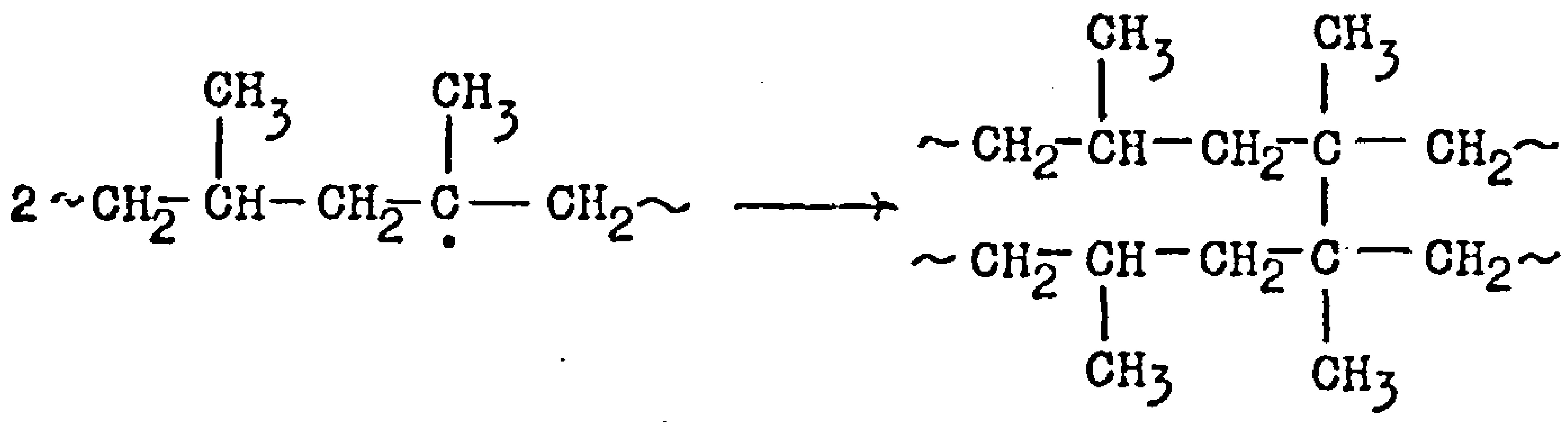
REVIEW OF THE PHOTOLYSIS OF POLYPROPYLENE

6.1 Low Temperature Investigation (20° - 200°C)

(a) Effect of UV Light

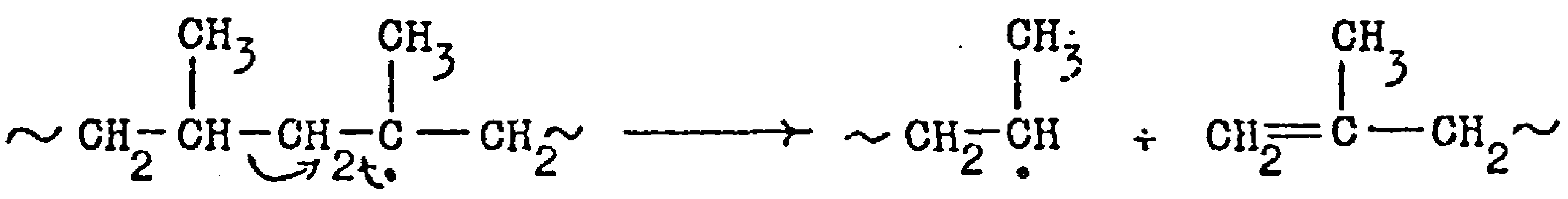
Ranby and Yoshida (64) have demonstrated by means of ESR that irradiation of isotactic polypropylene with 2537 Å light at 77°K produces methyl radicals in addition to alkyl radicals of the type,  $\sim CH_2-\dot{C}(CH_3)-CH_2\sim$. In this investigation, the major volatile products of photolysis at temperatures in the range 20° - 200°C were found to be hydrogen and methane, necessary products of the radical formation proposed by Ranby and Yoshida. Such alkyl radicals are to be expected to undergo competing crosslinking and scission reactions at higher temperatures.

Crosslinking



$$2\sim CH_2-CH(CH_3)-CH_2-\dot{C}(CH_3)-CH_2\sim \longrightarrow \begin{matrix}\sim CH_2-CH(CH_3)-CH_2-C(CH_3)-CH_2\sim \\ | \\ \sim CH_2-CH(CH_3)-CH_2-C(CH_3)-CH_2\sim\end{matrix}$$

Scission



$$\sim CH_2-CH(CH_3)-CH_2-\dot{C}(CH_3)-CH_2\sim \longrightarrow \sim CH_2-\dot{C}H(CH_3) + CH_2=C(CH_3)-CH_2\sim$$

In the present work, photolysis of polypropylene at 20°C is observed to result in crosslinking of the polymer. This is contrary to the opinion of Hatton and Jackson (66) who claim that unmodified polypropylene may be crosslinked by UV radiation only in the presence of a sensitiser and with a suitable bridging molecule. However, confirmation of the occurrence of direct crosslinking of polypropylene may be found in a paper by Kujirai (67) who detected crosslinking by means of swelling and gel fraction measurements.

Competition between crosslinking and scission is, however, found to be markedly dependent upon temperature of irradiation. Crosslinking predominates over scission at temperatures up to about 100°C ; above this temperature, scission reactions become more important. No special significance can be attributed to this temperature. A probable explanation is the following ; since the primary steps in the interaction of radiation, the reactions forming free radicals, are virtually independent of temperature, only the influence of the mobility of the polymer chains will show a dependence on temperature. At lower temperatures, the low mobility of polymeric radicals favours crosslinking by radical combination or by addition to an unsaturated site in another chain. As the temperature of photolysis is raised, the increased mobility of the macroradicals encourages chain scission at the expense of crosslinking. A similar observation has been made in the degradation of polystyrene by high energy radiation. This polymer has a high crosslinking to scission ratio at room temperature (91) but no longer undergoes predominant crosslinking at temperatures slightly above its glass - transition temperature(92).

b) Thermal Stability of Pre - irradiated Polypropylene.

Pre - irradiation of polypropylene reduces its thermal stability. Indeed, the higher the temperature of pre - irradiation the greater is the rate of thermal breakdown. Since the products of thermal degradation of pre - irradiated polymer are virtually identical to those of the unmodified polymer, it is reasonable to assume that degradation occurs by the same mechanism of scission of carbon - carbon bonds to produce polymer radicals which then undergo mutual disproportionation or hydrogen abstraction reactions.

This destabilisation may be explained by considering the chemical structure of the irradiated polymer. The effect of radiation on any given sample will be to introduce carbon - carbon bonds joined to tertiary or quaternary carbon atoms in addition to carbon - carbon double bonds. The relative amounts of these bonds, resulting from crosslinking and chain scission respectively, will depend upon the temperature of pre - irradiation. Both types of bond are suspected to be more susceptible to thermal cleavage than the normal carbon - carbon single bonds of the polymer backbone. Indeed the greater rate of thermal breakdown for polymer pre - irradiated at higher temperatures indicates that the double bonds resulting from scission are more labile than the single bonds formed in crosslinks. This enhanced rate of thermal degradation of polypropylene crosslinked by UV light shows good agreement with the findings of Veselovskii (93) who pyrolysed a sample of isotactic polypropylene crosslinked by high energy radiation.

c) Influence of Metal Additives

The addition of different metal oxides to polypropylene has been found to have a varied effect on its vacuum photolysis. TiO_2 slightly accelerates the photodegradation reaction whereas Al_2O_3 is seemingly without influence. Fe_2O_3 proves to have a greater catalytic effect than TiO_2.

There is a long history of the action of transition metal oxides as photosensitisers. In 1938, Goodeve and Kitchener (85) recorded the photosensitised bleaching of adsorbed dyes by TiO_2 and Al_2O_3. The much weaker sensitising effect observed for Al_2O_3 was attributed to its considerably weaker UV absorption. This explanation may also account for the apparent ineffectiveness of Al_2O_3 as a catalyst in the photolysis of polypropylene. The notable photosensitisation action of Fe_2O_3 is probably a direct consequence of its greater absorption. The species Fe^{3+} (λ_{max} = 2300 Å) has been shown (94) to absorb very strongly, having an extinction coefficient of ca. 10^4 at its peak maximum. This high extinction coefficient may account for the ability of trace amounts of Fe^{3+} (2-3ppm) to photosensitise the autoxidation of polyamides(86).

The mechanism which is generally accepted for the photosensitising action of transition metal compounds involves a photoexcited electron transfer. The anion is the electron donor and the primary act of adsorption involves the formation of an intermediate followed by several reactions including dissociation ;

$$M^{n+}X^{-} + h\nu \xrightarrow{a} \left[M^{(n-1)+}X^{\cdot}\right]$$

$$\left[M^{(n-1)+}X^{\cdot}\right] \xrightarrow{b} M^{(n-1)+} + X^{\cdot}$$

where M is the transition metal and X^- is the anion. The free radicals so produced may initiate degradation of polypropylene by abstraction of tertiary hydrogen atoms to form alkyl radicals.

The results of the present investigation into the influence of metal oxide additives upon the vacuum photolysis of polypropylene complement the findings of other workers (95,96) who photodegraded the polymer in an atmosphere of oxygen. The overall conclusion is that metal oxide impurities, whether from catalyst residues (TiO_2,Al_2O_3) or from production machinery (Fe_2O_3), are, at least in part, responsible for the initiation of degradation of isotactic polypropylene by ultra - violet light.

d) Effect of Sample Crystallinity

Morphological variations have relatively little effect on the photolysis of isotactic polypropylene, either in vacuo or in air. This lack of dependence of degree of crystallinity on the photostability of the polymer is perhaps more surprising under the latter conditions.

It is obvious that the oxidation of polymer samples requires access of molecular oxygen to the polymer chains. It has been shown (97) for polyethylene that crystalline regions are impermeable and amorphous regions permeable to most gases, although the amorphous permeability has been observed to be dependent on the size, shape and size distribution of crystallites. Although the morphological state of polypropylene is more complicated than that of polyethylene because of the coexistence of three phases (amorphous, smectic and crystalline), the oxygen diffusion characteristics of both polymers may be assumed to be similar since the smectic and crystalline states can be expected to have similar permeabilities. However, the experimentally observed independence of rate of photooxidation (which is oxygen - pressure dependent and hence diffusion controlled) and sample morphology may indicate that there is little variation in overall permeability with degree of crystallinity.

Kato, Carlsson and Wiles (98), who employed light of wavelength greater than 3000Å, arrived at a similar conclusion. On the other hand, a complex dependence of photooxidation of polypropylene on sample crystallinity has been proposed by McTigue and Blumberg (99). These authors, employing a Fade - Ometer, observed the rate of photoxidation to increase with degree of crystallinity. Direct correlation of the three sets of data is, however, not possible owing to wide differences in the irradiation conditions and in the nature of the sample form.

However, the fact remains that elimination of complicating variables such as oxygen permeability and oxygen solubility (as in the vacuum experiments of this study), which enables the morphological dependence of the incidence of ultra - violet light to be examined more precisely, still reveals no inter - connection.

6.2 High Temperature Investigation (200 - 354°C)

Thermal degradation experiments carried out in the temperature range 300 - 354°C yielded a broad spectrum of hydrocarbon fragments in keeping with the well established mechanism of random scission of carbon - carbon bonds, producing polymer radicals, which then undergo mutual disproportionation, or hydrogen abstraction reactions.

Photolysis in this range resulted in a similar spectrum of hydrocarbon products, the only notable difference being the enhanced production of ethylene. Since the nature and distribution of the products of photothermal degradation closely resemble those of thermal degradation, it is reasonable to conclude that the mechanisms of breakdown are very similar. The major effect of photolysis of the polymer at any particular temperature within this range is to accelerate the thermal reaction occurring at that temperature. Thus, in such a photothermal degradation, energy is supplied to the polymer sample in two distinct forms. However, once absorbed by the polymer, the origin of the energy loses its significance.

Photolyses at temperatures above the melting point but below the threshold temperature for thermal volatilisation of the polymer, result in a similar range of products which, however, include proportionally more methane. Very little volatilisation is observed, even for extremely long exposures, indicating that the energy content of the system is insufficient to allow extensive scission, transfer and volatilisation of chain fragments. The photo - production of methyl radicals is temperature independent and hence formation of methane in such amounts is easily rationalised.

It is rather curious to note that the deteriorative effect on the polymer of ultra - violet radiation alone, (calculated in Chapter 3) increases with temperature. One possible explanation may be that as the temperature of photothermal degradation is raised, a more rapid build up of unsaturation (produced by thermal breakdown) results, providing an increased concentration of chromophoric structures.

6.3 Conclusions

The vacuum photolysis of polypropylene involves bond cleavage to produce polymer radicals. The subsequent reactions of these macroradicals is markedly temperature dependent. At ambient temperatures, there exists a competition between crosslinking and chain scission reactions, whereas at temperatures approaching the crystalline melting point of the polymer, the latter process predominates. At higher temperatures, the polymer radicals undergo extensive transfer reactions, producing molecules of sufficiently low molecular weight to be volatile. This high temperature photodegradation is analogous to the thermal breakdown of the polymer.

Photolysis at ambient temperatures appears to be sensitised by certain metal containing impurities such as Titanium Dioxide and Ferric Oxide. The rate of photolysis has been shown to have relatively little morphological dependence.

CHAPTER SEVEN

THE PHOTO - INDUCED INTERACTION OF POLYPROPYLENE AND POLY(METHYL METHACRYLATE).

A few of the facts behind the rapidly increasing commercial importance of polymer blends have already been discussed in Chapter 1. With regard to isotactic polypropylene, it is suspected that blending with other, more polar polymers may improve its poor dyeability, resulting from its non - polarity and high crystallinity. One such proposed for this purpose is poly(methyl methacrylate) (100).

It was therefore considered worthwhile to investigate the UV light stability of mixtures of polypropylene and poly (methyl methacrylate). A further feature of interest was the possible occurrence of photo - induced grafting of poly (methyl methacrylate) to polypropylene which, indeed, might improve dyeability, above that achieved by simply blending the two polymers.

7.1 Structure of Polymer Blends

Any explanation of observed interactions in polymer blends must take into account the physical state of the system. In general, unlike macromolecules are incompatible in the solid state (101).

a) Nature of Incompatibility

Incompatibility is observed in solution when unlike polymers, present in a common solvent above a limiting total concentration, slowly separate into two layers with a clearly defined phase boundary between them. Analysis of the two layers shows that one polymer is concentrated in the upper layer, while the other is predominantly in the lower layer. This behaviour has been shown to be typical of systems containing two polymers and so compatibility of macromolecules tends to be the exception rather than the rule (102,103).

The phenomenon of incompatibility is also apparent in the solid phase. When polymer blends are prepared by melt mixing, solution blending or latex mixing the resulting composite is usually opaque or hazy in appearance, owing to the heterogeneity of the mixed system. Although achievement of a clear mixed polymer film is often taken as a sign that the polymer pair is compatible (104), this is not always the case. An incompatible blend can be transparent if the refractive indices of the two polymers are similar or if the partical size of the discrete phase is appreciably smaller than the wavelength of visible light (105).

The internal structures of polymer mixtures have been studied by a variety of techniques including viscosity measurements (106), variation of activation energies (107), and phase separation in solution(102). Microscopic studies on incompatible polymer pairs indicate that two separate phases exist, corresponding to the two polymers. While one component tends to form a continuous phase, the other separates into micelles of dimensions 1 - 15 microns which form a disperse phase in the continuous matrix of the first polymer (104).

b) Factors Affecting Incompatibility

I Nature of Polymers

There is no obvious relationship between the phase separation of two macromolecules and the chemical nature of their monomeric units. Predictions of polymer compatibility based on structural similarities, whether main chain or substituent, have proved to be of little value. For example, polystyrene and poly (ortho methyl styrene) are compatible in solution whereas mixtures of ortho and para methyl styrene are not compatible (108).

Thus the phenomenon of polymer incompatibility, arising when the inter-molecular forces between like macromolecules are greater than those between unlike polymer chains, is extremely sensitive to the structure of the polymer chains involved.

II Concentration of Polymers (for solutions)

In mixed solutions of unlike polymers, the phenomenon of phase separation is strongly dependent on the concentration of the solutes. However, even where incompatibility exists, phase separation does not occur until the concentration of each polymer is in the region of 15 - 70 mg/ml, depending on the solvent (109).

III Molecular Weight of Polymers

Since the incompatibility of unlike polymers is a consequence of molecular size, it is not surprising that molecular weight has been shown to play an important role in phase separation. The higher the molecular weight of the species involved, the more complete is the separation of phases (108).

IV Temperature

No detailed investigation into the effect of temperature on phase separation has yet been carried out. However, lowering the temperature, lowers the limiting concentration at which phase separation occurs (108) and appears to increase the rate of separation into the two phases (102).

c) Consequence of Incompatibility

Up to the present time, no way has been found to overcome the mutual incompatibility of unlike macromolecules. Therefore any polymer blend will not form a true mixture, and certainly not a solid solution. In the solid state, any chemical interaction which takes place between the components of such a system must either take place at phase boundaries, or involve the diffusion of a species formed in one phase into the second phase.

d) Reproducibility of Sample Form.

The most serious consequence of the heterogeneity of polymer blends is the difficulty of achieving reproducible sample form in a series of experiments. The ultimate test of any method for preparing a blend will be the reproducibility of the subsequent degradation experiments.

Richards and Salter (69) obtained their blends of polystyrene and poly (alpha methyl styrene) by freeze - drying a solution of the two polymers in benzene. Pavlinec's method (110) involved intensive stirring of atactic polypropylene and poly (vinyl acetate) in air at 105^{o}C for up to 25 minutes. A technique widely used is that devised by Grassie, McNeill and Cooke (111), and developed by McNeill and Neil (112), in which films are cast by evaporation of a solution of the polymers in a common solvent. Owing to the insolubility of polypropylene at ambient temperatures, the method used in this study was that originated by Mizutani (100). Mixtures were obtained by evaporating to dryness, with continuous stirring, a slurry of polypropylene in an acetone solution of poly (methyl methacrylate).

7.2 Experimental

a) Source of Polymers

The polypropylene sample used in this work was that described previously in Chapter 2. Poly (methyl methacrylate) was prepared in the following manner. Methyl methacrylate (B.D.H. Limited) was washed with alkali to remove inhibitor, then several times with distilled water and dried over calcium chloride. The purified monomer was degassed twice and distilled three times in vacuo, the first and last 10 % being discarded on each occasion. Bulk polymerisation was carried out at 60°C in a sealed dilatometer, using azodiisobutyronitrile as initiator. The polymer was isolated by precipitation in Analar methanol and purified by several reprecipitations from Analar toluene solution. Complete removal of solvent was ensured by vacuum drying the polymer at 60°C for several days.

The number average molecular weight of the poly (methyl methacrylate) sample prepared in this way was measured osmotically and found to be 516,000(0.1 % initiator).

b) Sample Form

Blend preparation was the same as that of Mizutani (100). Polymer mixtures were compressed to form opaque discs in the manner described in Chapter 2. Each disc was melted in vacuo (ca. 170°C) and quenched in liquid nitrogen, thus ensuring a low degree of crystallinity and a favourable sample for UV irradiation.

A similar procedure was carried out for the study of unmixed polymers.

Degradation results for mixed samples were found to be reproducible and hence the experimental conditions were considered to be satisfactory for this study.

c) Photolysis Apparatus

Polymer samples, prepared as above, were irradiated in the cell illustrated in FIGURE 2.7 (a). The intensity of the light beam incident on the samples was 2.68×10^{16} quanta/sec.

d) Thermal Methods of Analysis

Thermal volatilisation analysis (TVA), thermogravimetry (TG) and isothermal degradations at 354°C (using the apparatus illustrated in FIGURE 2.8) were carried out on pre - irradiated blend of poly (methyl methacrylate) and polypropylene, with a view to revealing any possible photo - induced interaction taking place between the polymers.

However, before this could be attempted, the influence of poly (methyl methacrylate) on the thermal degradation of polypropylene, and vice versa, had to be evaluated. This was done by comparing mixed and unmixed systems of the polymer pair, under similar thermal degradation conditions. The main technique employed was one, using TVA, developed by McNeill and Neil (112) for this purpose. The experimental procedure involved the use of a twin - limbed degradation tube, with a flat base to each limb (FIGURE 7.1). Known weights of each polymer were placed in the separate limbs of the tube and a normal TVA experiment carried out. The experiment was then repeated with equal weights of the polymer blend in each limb of the tube, such that the total

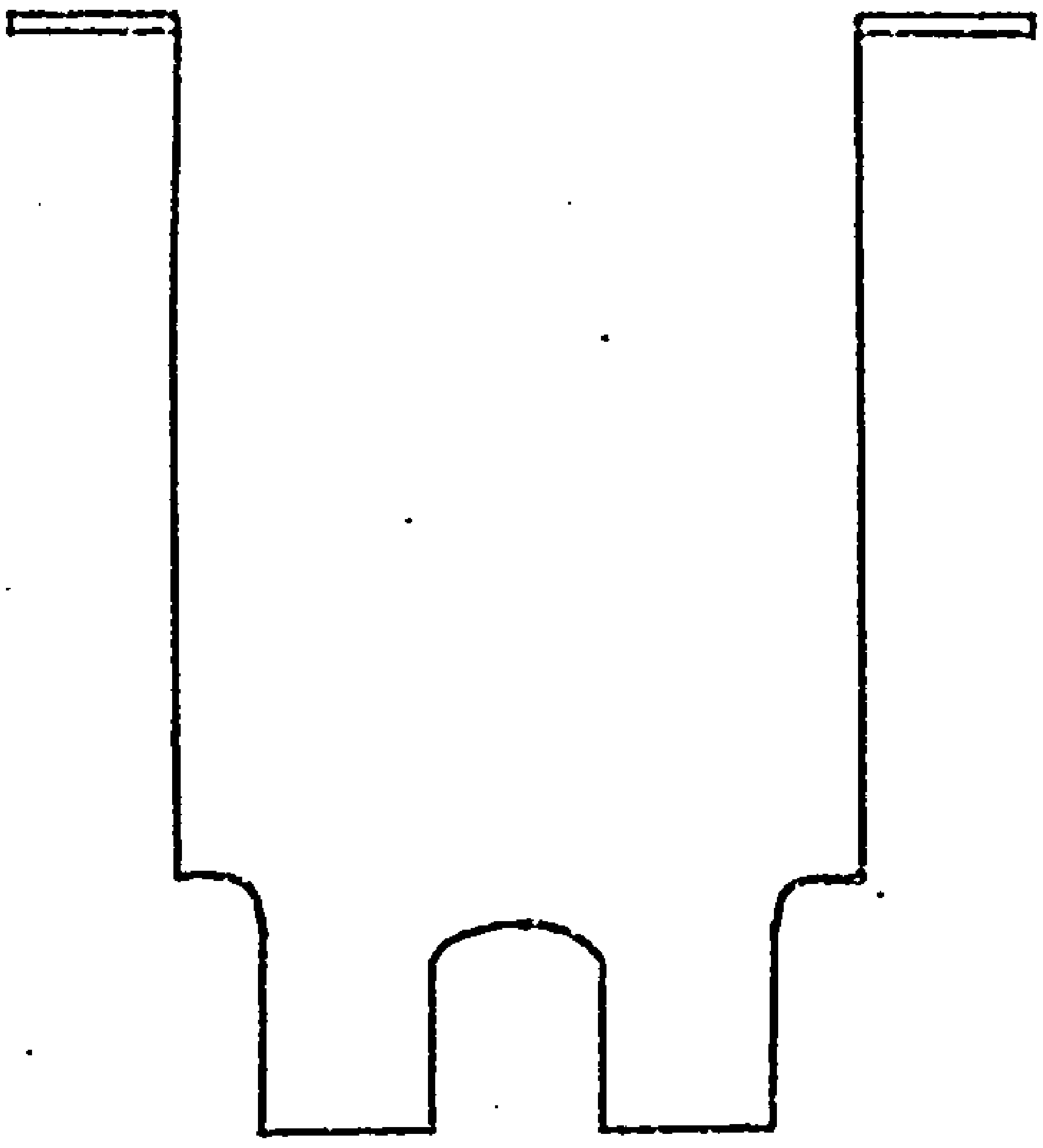


FIGURE 7.1 Twin - limbed degradation tube for TVA studies.

weight of each polymer was the same in each case. Thus a comparison could be made, under the same conditions, of the behaviour of the two polymers degraded separately, and as a blend. Care was taken that the degradation tubes were inserted in the oven in such a way that the samples were always in the same position in the oven.

c) Acetone - Extraction of Degraded Samples

Each sample was dissolved in para - xylene under a nitrogen atmosphere and the hot solution allowed to cool slowly over a period of several hours. The resulting suspension was decanted into Analar methanol and the precipitate was filtered, washed with methanol and dried overnight in a vacuum oven. The material obtained was extracted by acetone in a soxhlet extractor for 20 hours under a nitrogen atmosphere. The residue was dried for 24 hours in a vacuum oven prior to analysis.

7.3 Thermal Degradation of Poly (methyl methacrylate) - Polypropylene Blends.

Mizutani (100) has reported that if a mixture of PP and a vinyl polymer (e.g. PMMA) is heated at an elevated temperature, the active radicals, generated by scission of the vinyl polymer chain, are effective in accelerating the breakdown of PP. This thermal interaction of PMMA and PP was investigated further, using the techniques of TVA and thermogravimetry, prior to examination of the effects of pre - irradiation on the thermal stability of these two polymers.

a) TVA Experiments

I Poly (methyl methacrylate) (PMMA)

It has long been established that the thermal degradation of PMMA gives rise to almost quantitative yields of monomer (113). The decomposition of this polymer is a radical chain depolymerisation process, occurring in two stages. The first, the lower temperature reaction, consists of unzipping to monomer of radicals produced exclusively at unsaturated end structures. At higher temperatures (above 300°C), the main backbone of the polymer becomes unstable, and random scission of carbon - carbon bonds occurs producing radicals which again unzip to monomer as the exclusive product. In both processes the zip length of depolymerisation is very large, and transfer reactions are believed to be unimportant.

TVA curves for PMMA, shown in FIGURE 7.2 (a), exhibit the typical behaviour of a single substance giving a limiting rate in the - 75°C line. The two peaks correspond to monomer production by the two different methods of initiation, the first being due to depolymerisation initiated at chain ends and the second to initiation of unzipping by random chain scission. The respective heights of the two peaks have been shown (114) to be markedly dependent on the molecular weight of the polymer. For low molecular weight samples, the first peak becomes greater and the second peak correspondingly reduced. With very high molecular weight samples, the first peak merely appears as a shoulder on the second peak.

II Polypropylene (PP)

The thermal degradation of PP has been described in detail in Chapter 1. Breakdown of this polymer involves random scission of carbon - carbon bonds, producing polymer radicals, which then undergo mutual disproportionation, or hydrogen abstraction reactions.

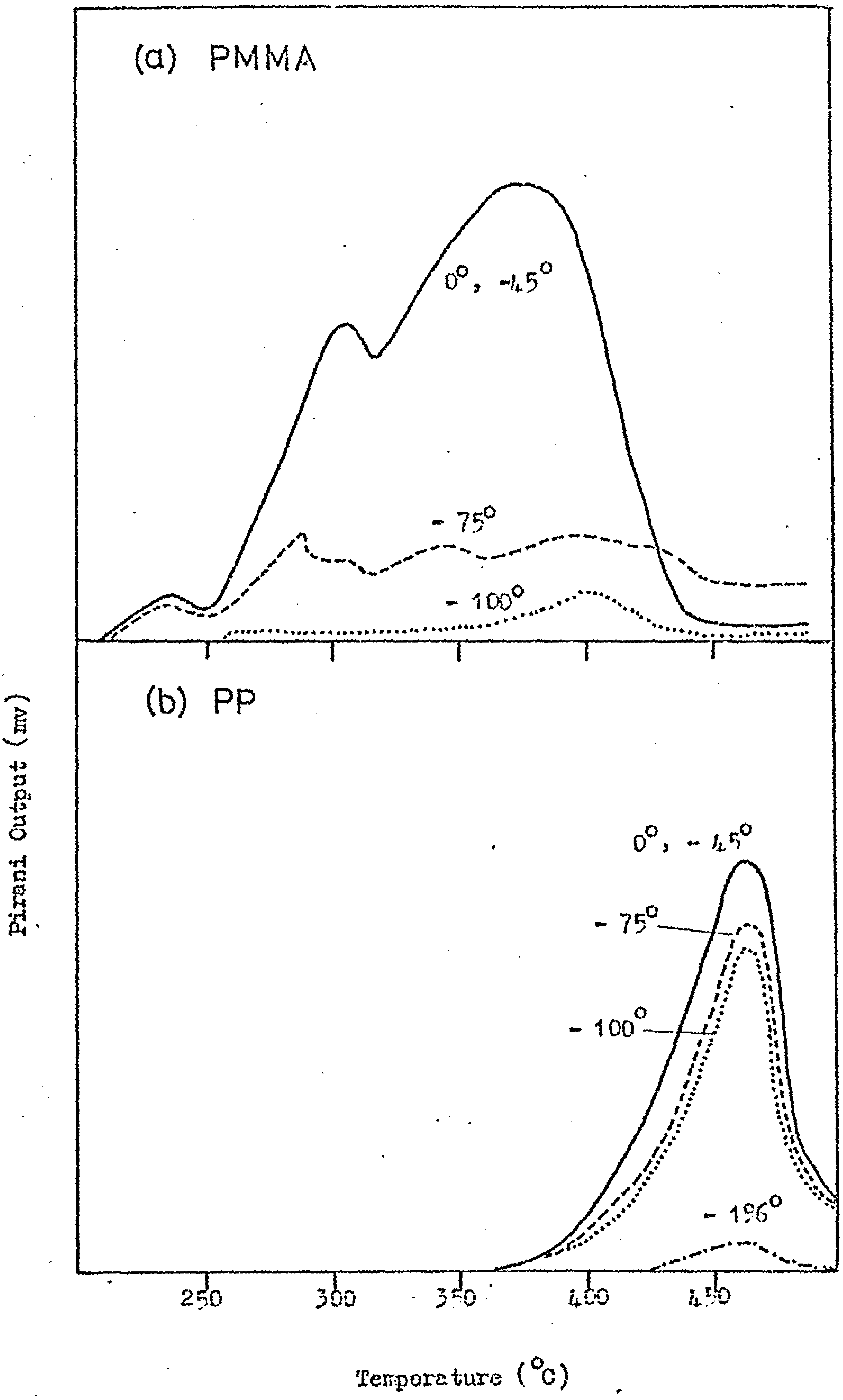


FIGURE 7.2 TVA curve for 50 mg samples of (a) PMMA and (b) PP Heating rate ; 10°/min.

The TVA curves obtained from PP have already been illustrated in FIGURE 4.7 and interpreted in Chapter 4. The thermogram is reproduced in FIGURE 7.2 (b) to facilitate comparison with curves from mixed polymer systems.

III PMMA - PP mixtures

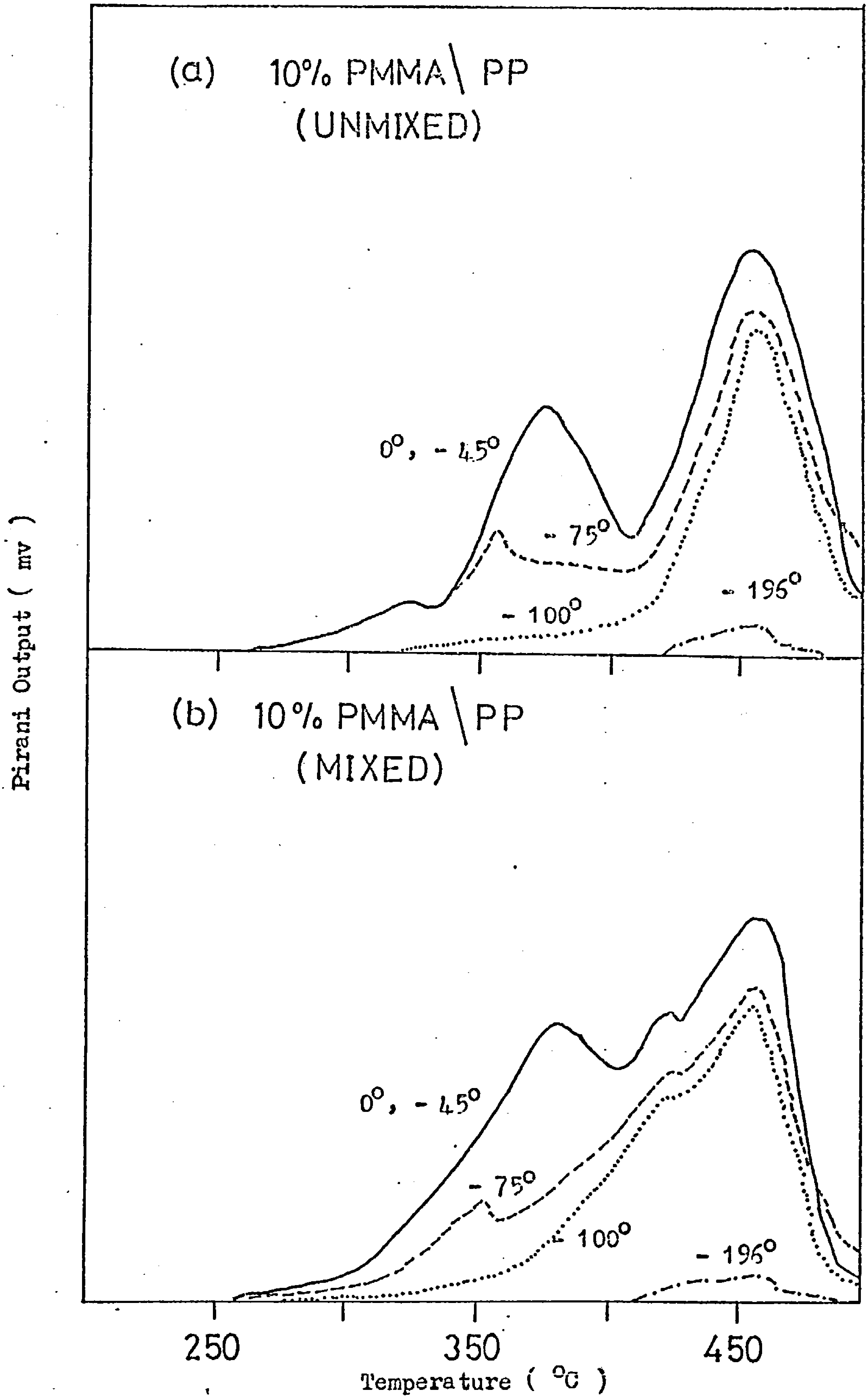
Thermograms obtained from a 10 % blend of PMMA in PP, examined as mixed and unmixed systems are shown in FIGURE 7.3. The TVA trace for the unmixed system illustrates the overlapping of the volatilisation peaks of both polymers. The PP peak, with concurrent production of volatiles, occurs at higher temperatures than the peaks due to PMMA. The limiting rate at - 75°C, due to methyl methacrylate monomer, is clearly apparent however.

There are a few differences between the mixed and unmixed traces, the most obvious being the appearance of an extra peak (T_{max} ~ 426°C) as a shoulder on the PP peak, for mixed systems. The peak corresponding to monomer production from chain scission of PMMA occurs at slightly higher temperatures, than in the unmixed system, indicating stabilisation of PMMA in the blend. The T_{max} of the PP peak, however, remains unaltered.

Similar results were obtained from the thermograms of blends of different compositions (1%, 3% and 5% by weight PMMA in PP).

b) Thermogravimetry

TG curves were obtained for PMMA and PP as shown in FIGURE 7.4 (a). As can be seen, both polymers decompose in single stages, leaving approximately zero residual weight at 450° C. From these curves, the curve which would be expected for a 1 : 1 mixture by weight, in the absence of interaction, was constructed. This is compared with the actual experimental TG curve for the



<u>FIGURE 7.3</u> TVA curve for simultaneous degradation of PMMA (5mg) and PP (45mg), (a) unmixed and (b) mixed. Heating rate ; 10°/min.

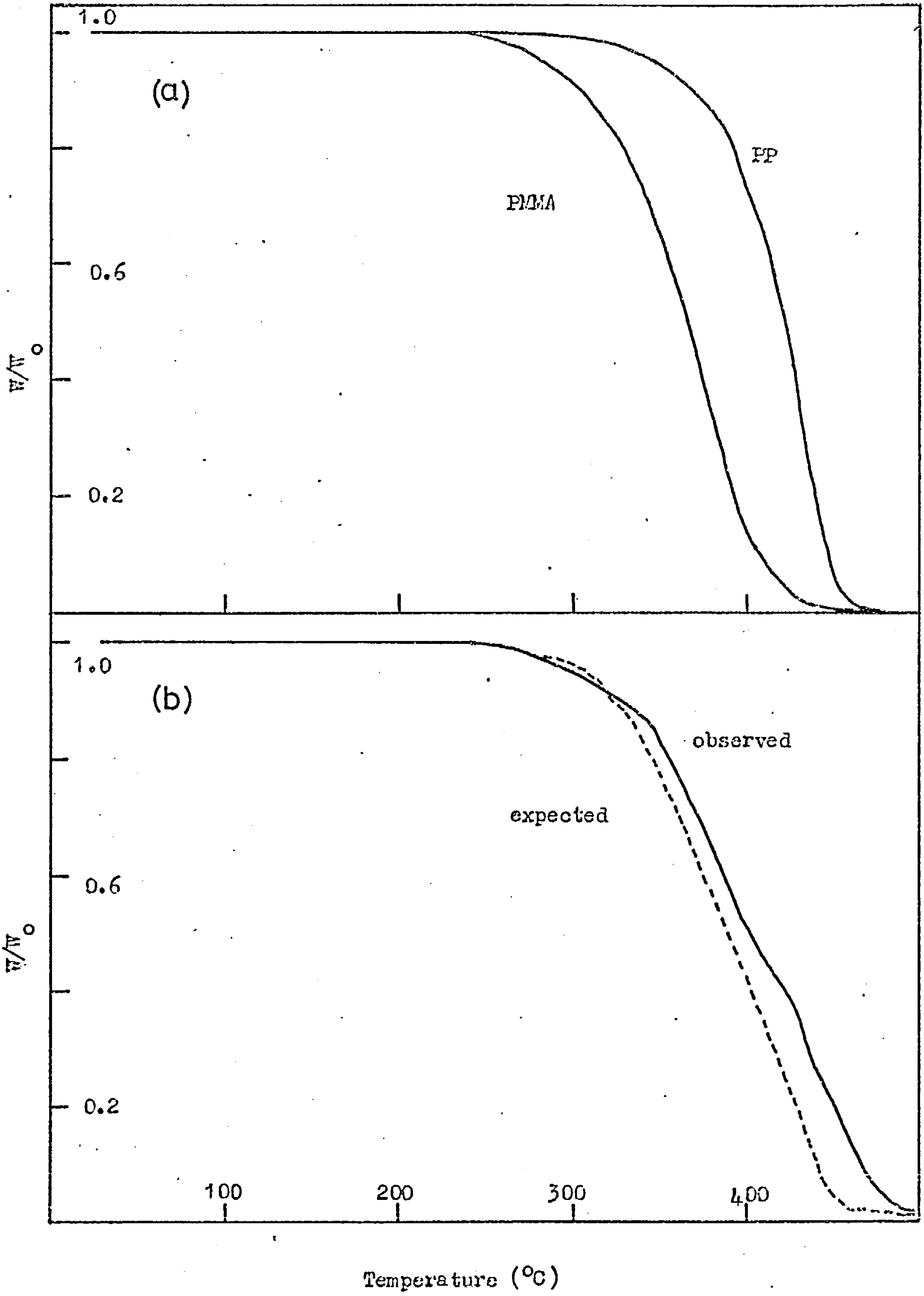


FIGURE 7.4 TG curves for degradation of (a) PMMA and PP and (b) a 1 : 1 by weight mixture of the two polymers. Continuous line : observed behaviour ; dotted line ; behaviour expected in absence of interaction between the polymers.
Dynamic nitrogen atmosphere, heating rate 10°/min.

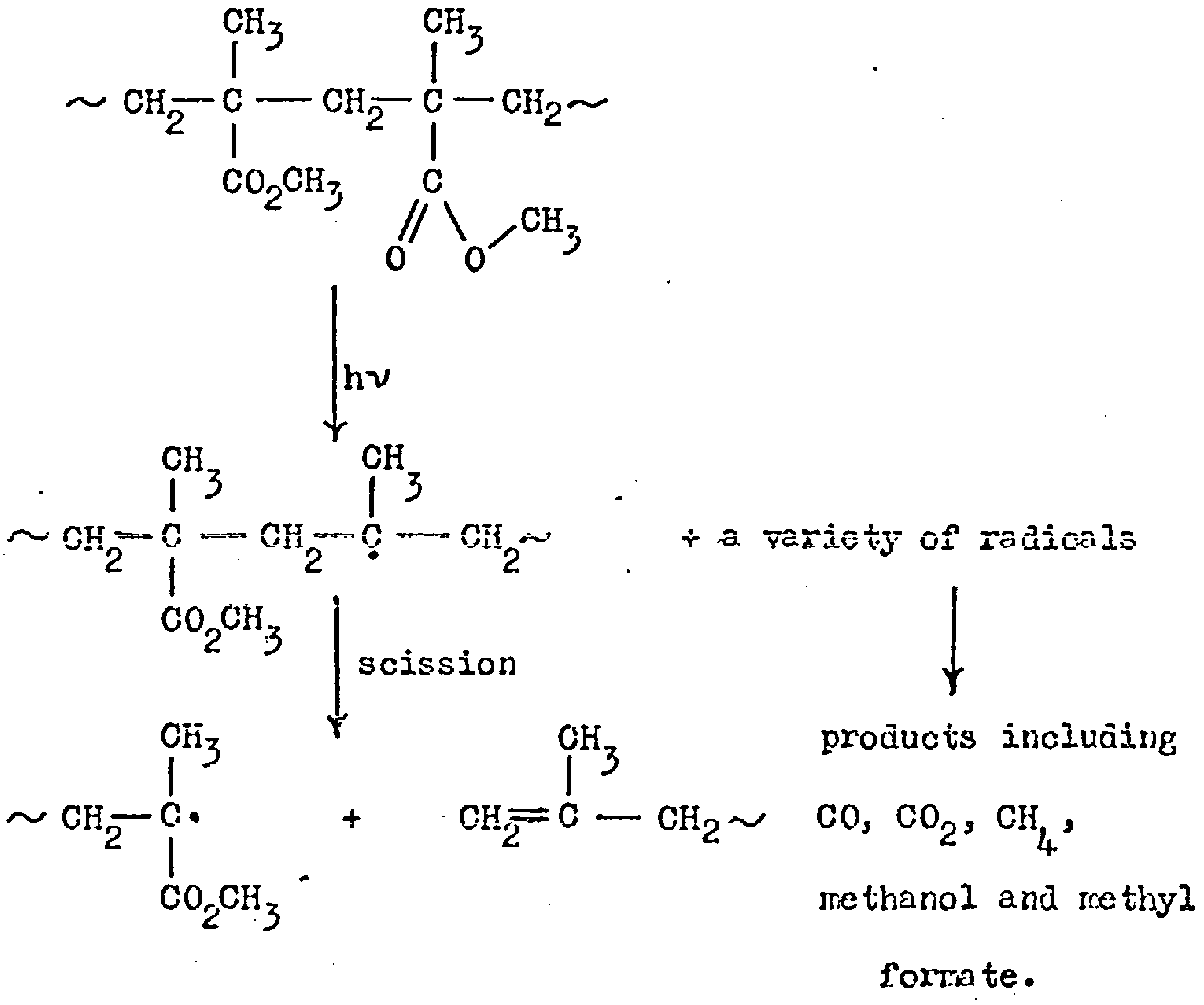
mixture, in FIGURE 7.4 (b). The weight loss of the blend is different from that expected in the absence of interaction, the main effect being increased stability in the higher temperature range, under programmed heating conditions.

7.4 Photolysis of blends of PMMA and PP

Before reporting the effect of ultra - violet radiation on any polymer blend, it is appropriate to briefly outline the photolysis of the component polymers. However, since the photo - degradation of PP has been described in earlier chapters of this thesis, attention is focussed on PMMA.

a) Photolysis of PMMA

Near room temperature, photodegradation of this polymer, in solution or as a solid, results in random cleavage of the main chain without depolymerisation. The accepted mechanism is as follows ;



However, at temperatures above its glass transition temperature, PMMA depolymerises to monomer on exposure to uv light. A temperature of ca. 160°C is necessary to allow free diffusion and escape of monomer (3). There is disagreement over the mode of initiation. Cowley and Melville (3) conclude that the reaction is end - initiated while Jellinek and Wang (115), who irradiated the polymer in solution, claim that the mechanism is one of random initiation followed by unzipping.

b) Photolysis of PMMA -PP blends at 20°C.

Bond samples of various compositions were photodegraded at 20°C for times up to 20 hours and, as expected, were found to have suffered no detectable weight loss. A comparison of the IR spectra of irradiated samples with the spectrum of the corresponding un - irradiated blend revealed no extra absorptions. In addition, acetone extraction was successful in removing all traces of PMMA from photolysed blends. This may suggest that graft or block copolymers are not formed when mixtures of PMMA and PP are irradiated.

c) Photolysis of PMMA - PP blends at 150°C.

Samples of a 10 % blend were irradiated at 150°C for times up to 20 hours. The only significant product was identified as methyl methacrylate monomer. In FIGURE 7.5, percentage weight loss is plotted as a function of time of irradiation. After approximately 5 hours, 10 % of the original sample weight is lost, presumably corresponding to the amount of PMMA blended. The only two samples which possessed carbonyl bands in the IR spectra of their residues were those irradiated for $\frac{1}{2}$ hour and 1 hour. (Both samples had incurred weight losses of less than 10 %). This carbonyl content, however, was removable by

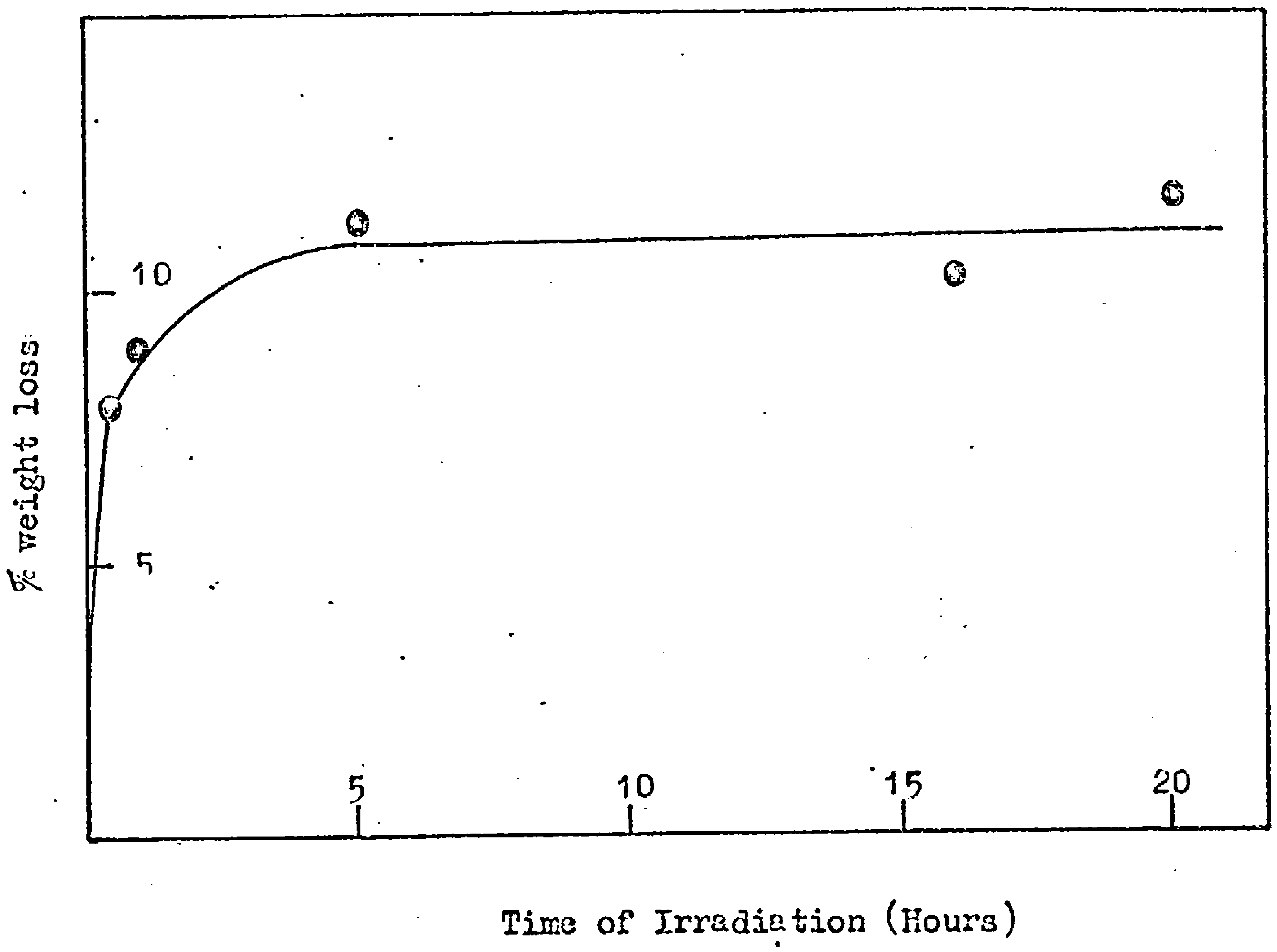


FIGURE 7.5 Weight loss versus time of irradiation at 150°C of a 10 % blend.

Time of Irradiation (Hours)	% Weight Loss
0.5	8.1
1	9.1
5	11.4
16	10.2
20	11.8

TABLE 7.1 Data for FIGURE 7.5.

acetone extraction again suggesting that no grafting had taken place.

7.5 Thermal Degradation of Pre - irradiated Blends.

a) Comparison of the thermal degradation of irradiated and un - irradiated blends of varying composition.

Three PMMA - PP mixtures (1%, 3% and 5% by weight PMMA) were prepared as described in the experimental section of this chapter. One sample from each blend was irradiated in vacuo at 20°C for 20 hours before being thermally degraded for 3 hours at 354°C. An un - irradiated sample from each blend was subjected to the same thermal treatment.

FIGURE 7.6 shows the result of plotting percentage weight loss versus PMMA content of the blend, for these degradations. It is evident that the thermal stability of any one blend is decreased only slightly by pre - irradiation. This is not the case with unblended PP. It can be seen from the same figure that pre - irradiation markedly reduces the thermal stability of PP.

IR spectra were run of the total gaseous volatiles produced during each of the above thermal degradations. Each spectrum resembled a superimposition of the spectrum of methyl methacrylate monomer on that of the normal gaseous volatiles produced by PP. This may be clearly seen from FIGURE 7.7 which contains IR spectra of a) gases from the thermal degradation of PP for 10 hours at 354°C ; b) gases from a 3 % blend thermally degraded for 3 hours at 354°C ; c) methyl methacrylate vapour. The optical density (OD) of the peak at 1740 cm^{-1}, attributed to methyl methacrylate, in each of the spectra resulting from blend degradations, was measured by

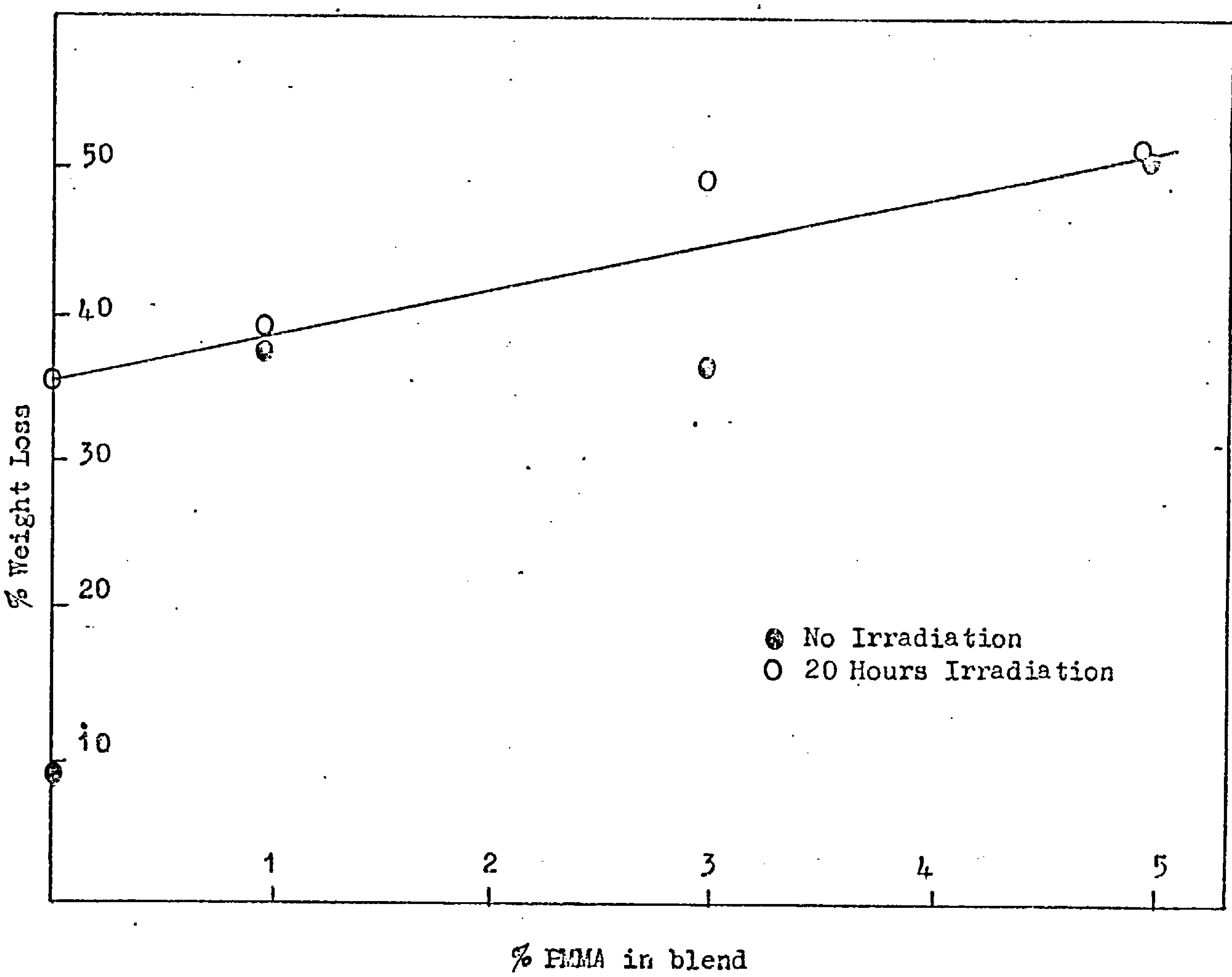


FIGURE 7.6 Weight loss versus PMMA content of a series of blends. Irradiated and unirradiated samples thermally degraded for 3 hours at 354°C.

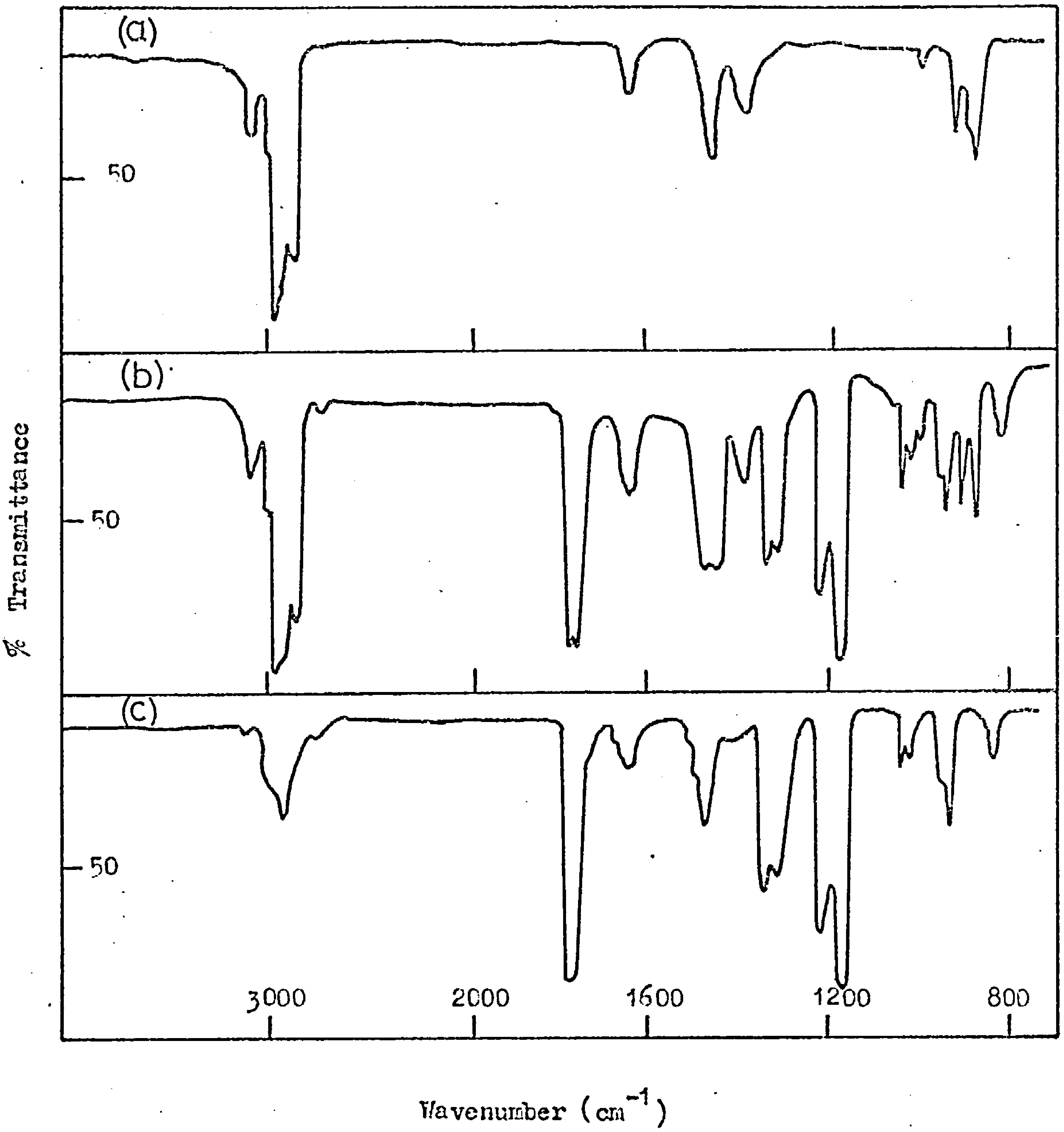


FIGURE 7.7 IR spectra of ;

a) Volatiles from PP thermally degraded for 10 hours at 354°C.

b) Volatiles from a 3 % PMMA - PP blend thermally degraded for 3 hours at 354°C.

c) Methyl methacrylate vapour.

the usual baseline method. This provided a measure of the methyl methacrylate content of the total gases from each degradation. The result of plotting $OD_{1740\,cm^{-1}}$ as a function of PMMA content of the blend, for both irradiated and un - irradiated samples, is shown in FIGURE 7.8. It is obvious that pre - irradiation decreases the amount of methyl methacrylate in the gaseous volatiles.

IR spectra of all the residues were examined but were found to have neglible carbonyl content. This was surprising considering Mizutani's claim (100) to have produced block and graft copolymers of PMMA and PP by thermal degradation of mixtures of the two polymers. This worker's evidence constituted the detection of carbonyl bands in the IR spectra of the residues of blends thermally degraded under conditions similar to those employed in this study.

The short chain fragments of each degradation were also subjected to IR analysis. The only notable difference from the spectrum of the cold ring produced by unblended PP (FIGURE 3.8) is the appearance of a broad band at 1735 - 1740 cm^{-1} and another, sharper absorption at 1185 cm^{-1}. These are respectively assigned to carbon - oxygen double and single bond stretching. The optical densities of the peaks at 1740 cm^{-1} and 890 cm^{-1} were measured from each spectrum. The latter absorption, present in the spectrum of the cold ring from the degradation of unblended PP, was used as an internal standard. The plots of the ratios of the optical densities of these two peaks as a function of blend composition for both irradiated and un - irradiated samples, is shown in FIGURE 7.9. It is clear that, in each blend studied, the effect of pre - irradiation is to increase the carbonyl content of the cold ring fraction.

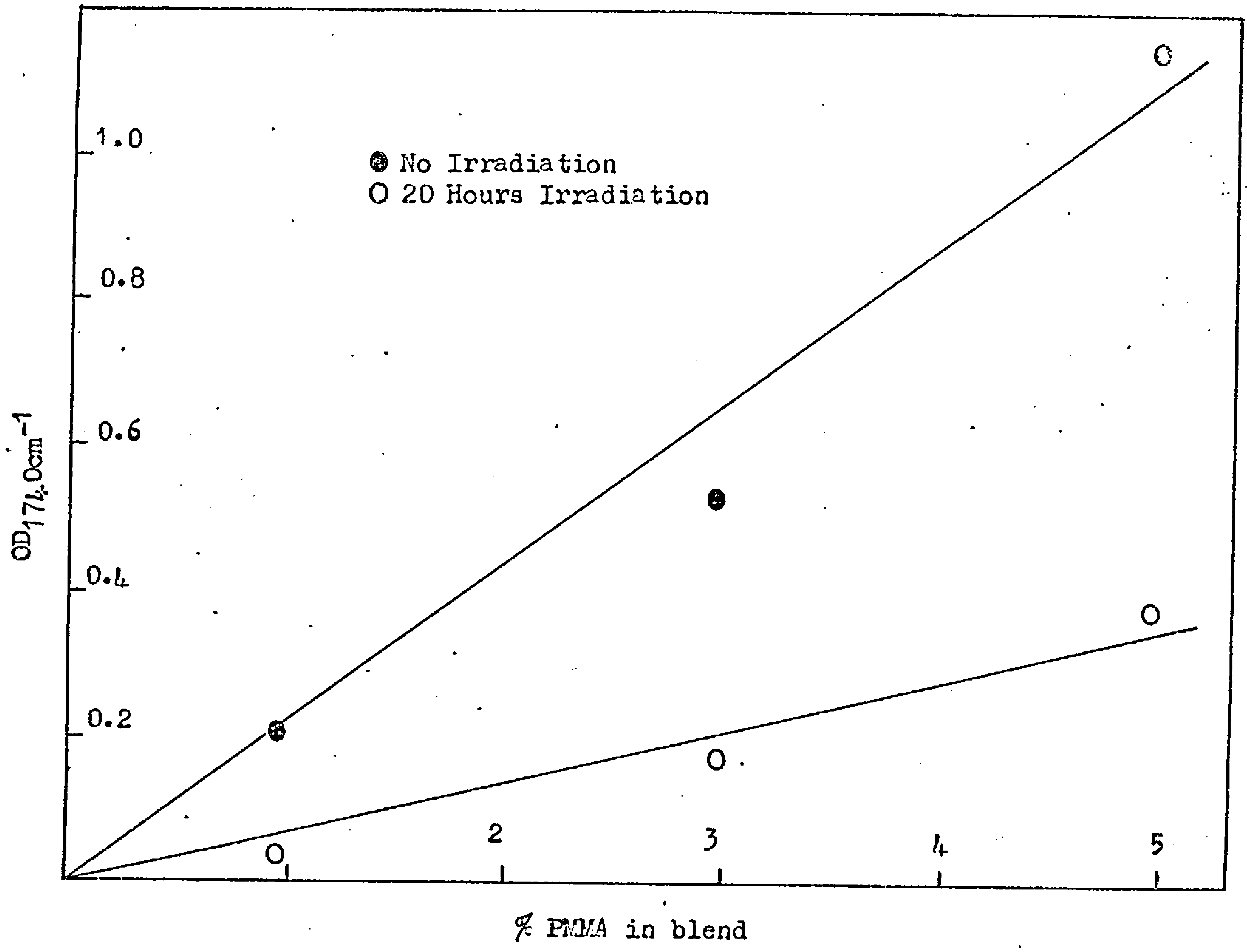


FIGURE 7.8 $OD_{1740cm^{-1}}$ as a function of PMMA content of a series of irradiated and un - irradiated blends.

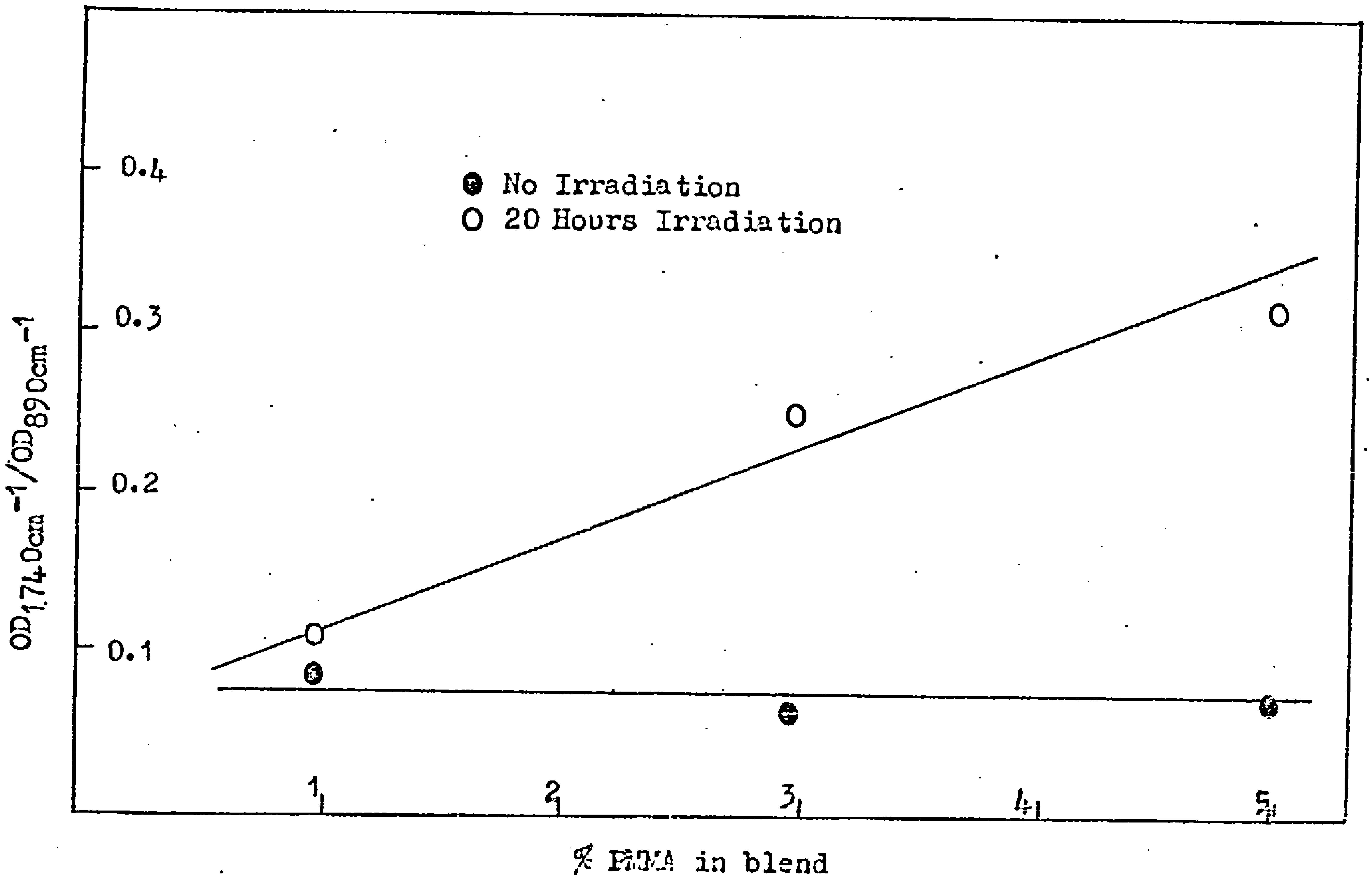


FIGURE 7.9 $OD_{1740cm^{-1}}/OD_{890cm^{-1}}$ versus PMMA content of a series of irradiated and unirradiated blends.

	% PMMA in blend	% Original Blend Sample		
		Weight Loss	Cold Ring	Gases
A	0	9.5	5.8	3.7
	1	37.7	23.1	14.6
	3	36.8	19.3	17.5
	5	51.0	27.5	23.5
B	0	35.6	21.1	4.4
	1	39.6	23.8	15.8
	3	49.5	30.8	18.7
	5	50.3	29.6	20.7

TABLE 7.2 Data for FIGURE 7.6

A No irradiation B 20 hours irradiation

% PMMA in blend	$OD_{1740cm^{-1}}$	
	No irradiation	20 hours irradiation
1	0.203	0.032
3	0.592	0.180
5	1.160	0.393

TABLE 7.3 Data for FIGURE 7.8

% PMMA in blend	$OD_{1740cm^{-1}}/OD_{890cm^{-1}}$	
	No irradiation	20 hours irradiation
1	0.087	0.111
3	0.060	0.256
5	0.069	0.318

TABLE 7.4 Data for FIGURE 7.9

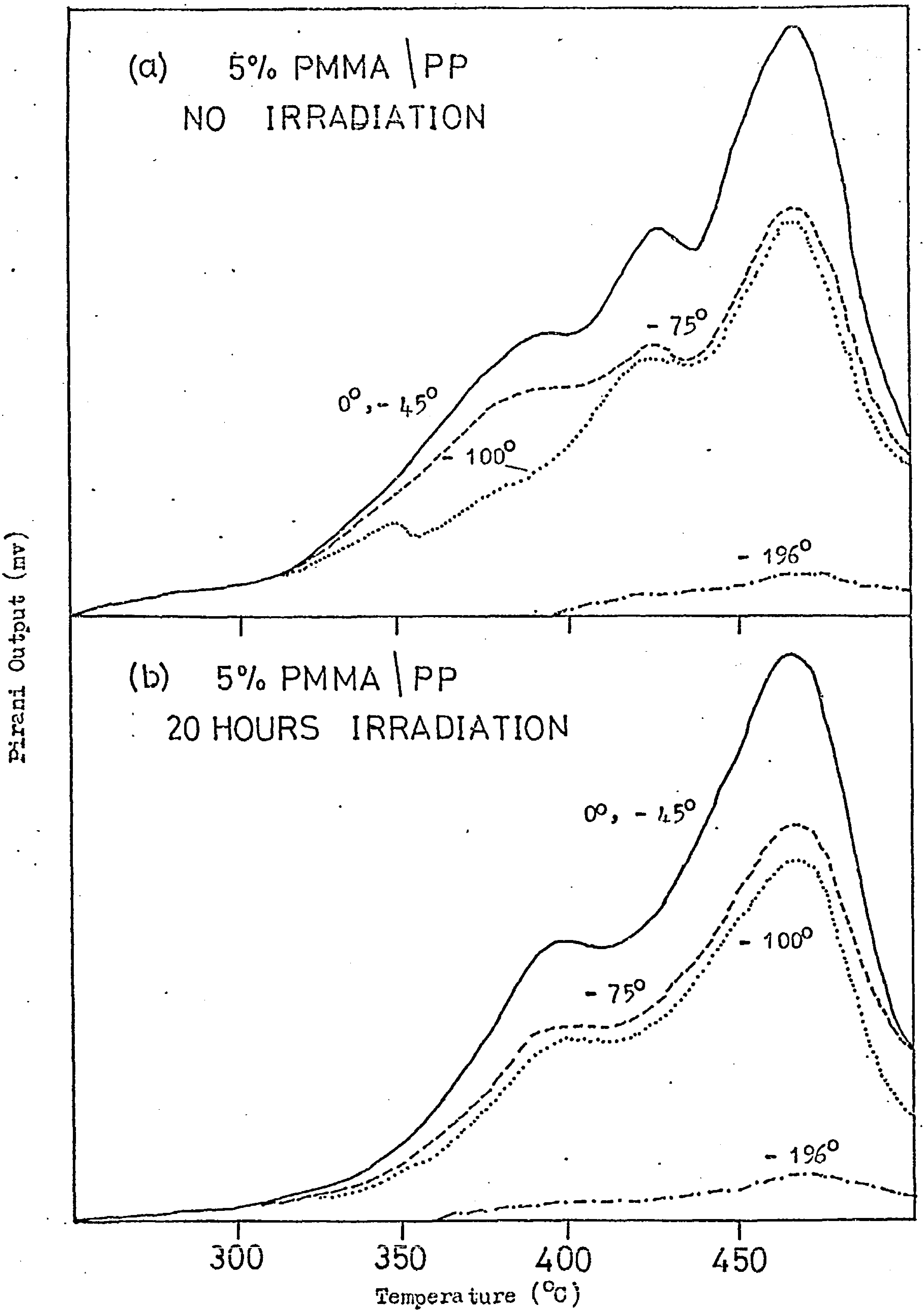
Thus these results indicate that irradiation of PMMA - PP blends brings about some kind of interaction such that, on subsequent thermal degradation, there is less methyl methacrylate produced in the gaseous volatiles and more carbonyl containing material in the short chain fragments than in the corresponding thermal degradation of un - irradiated blends.

A significant feature emerges from examination of the TVA curves of irradiated and un-irradiated blend samples. As can be seen for a 5 % blend in FIGURE 7.10, pre - irradiation causes the previously discussed 'interaction' peak to disappear. The volatiles producing this peak were isolated and were discovered to be predominantly methyl methacrylate. This finding is consistent with the decreased amount of methyl methacrylate found in the gaseous volatiles of pre - irradiated blend samples which were isothermally degraded. Although this peak is no longer present in the thermogram of an irradiated sample, there is still evidence of polymer interaction, as comparison with the TVA curve of an unmixed 10 % PMMA - PP system (FIGURE 7.3 (a)) reveals.

b) Dependence of time of pre - irradiation on the thermal degradation of blends.

The effect of time of photolysis of a blend on the subsequent thermal degradation was investigated by irradiating samples for several times up to 20 hours at 20°C and studying the thermal volatilisation characteristics as before. The 3 % PMMA - PP blend was chosen for this purpose.

FIGURE 7.11 shows the result of plotting percentage weight loss, owing to thermal degradation for 3 hours at 354°C, versus time of pre - irradiation. A similar plot for polypropylene has



<u>FIGURE 7.10</u> TVA curves for a 5% PMMA - PP blend.

a) un - irradiated

b) irradiated for 20 hours at 20°C

20 mg samples ; heating rate 10°/min.

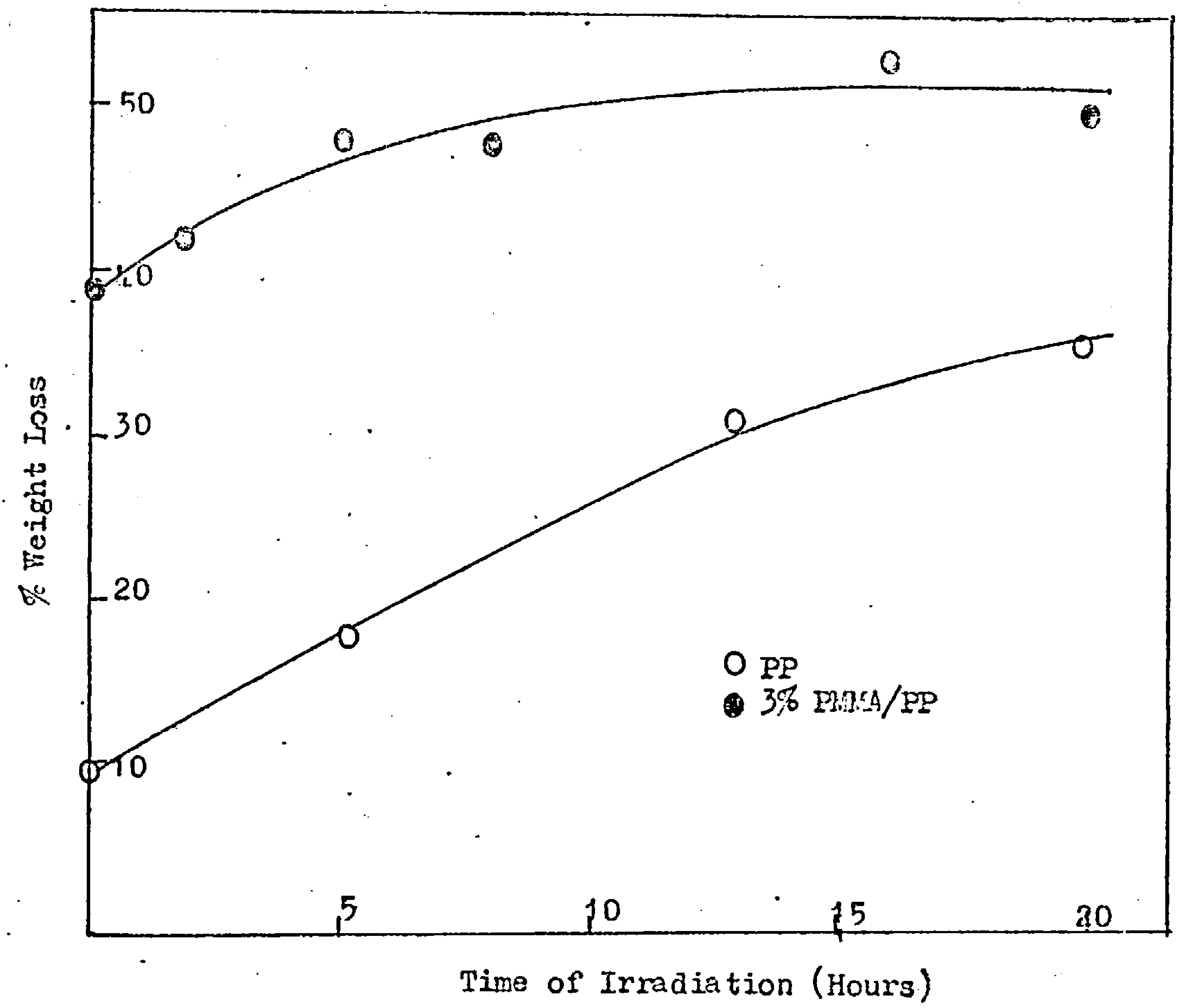


FIGURE 7.11 Weight loss versus time of pre - irradiation at 20°C for samples thermally degraded for 3 hours at 354°C.

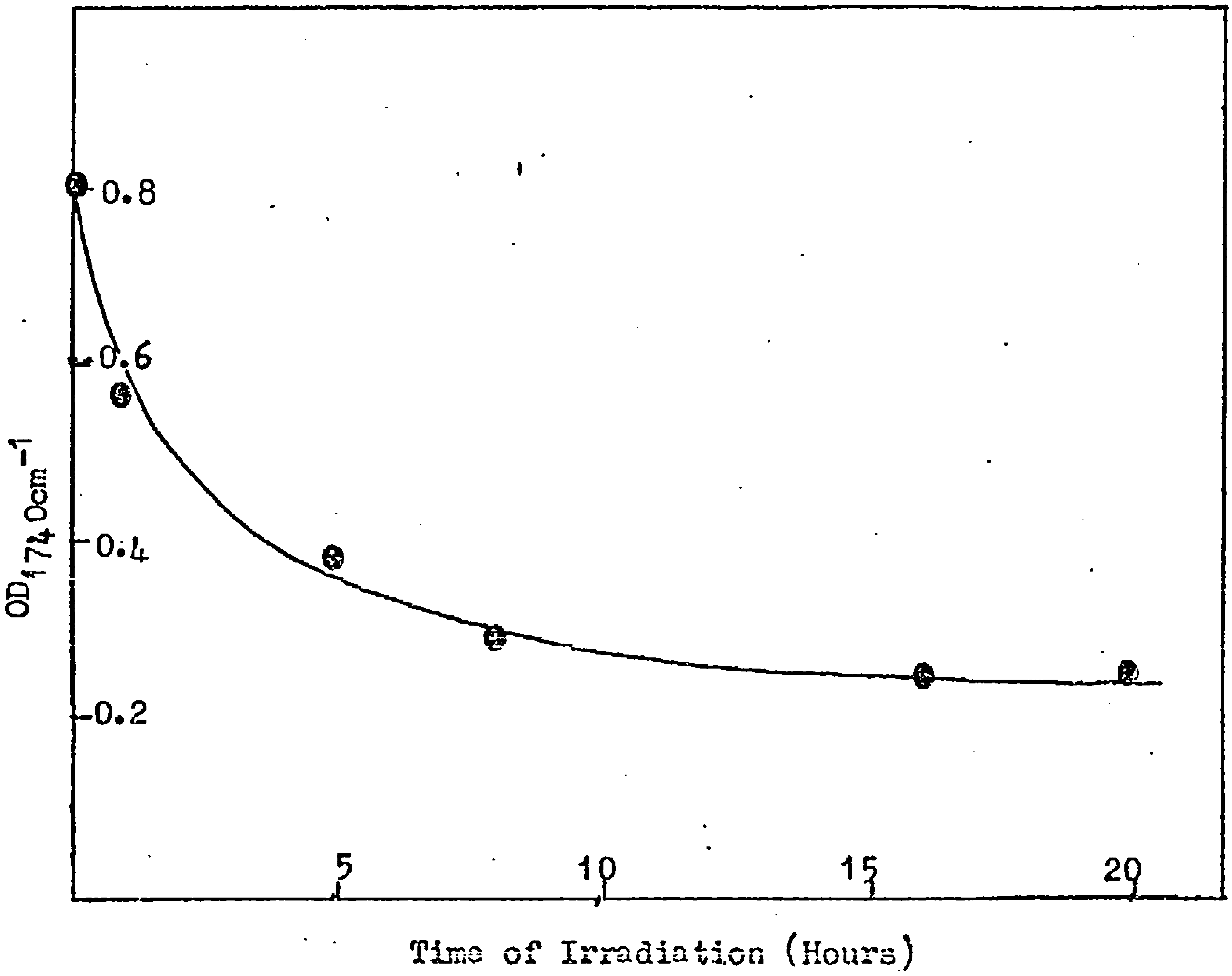


FIGURE 7.12 Measure of the carbonyl content of the gaseous volatiles from the thermal degradation(3 hours at 354°C) of a 3 % PMMA - PP blend versus time of pre - irradiation.

	Time of Pre - irradiation (Hours)	% Original Sample		
		Weight Loss	Cold Ring	Gases
A	0	39.1	22.7	16.4
	1	42.0	25.0	17.0
	5	48.2	31.5	16.7
	8	47.2	28.5	18.7
	16	52.8	33.9	18.9
	20	49.5	30.8	18.7
B	0	9.5	5.8	3.7
	5.25	18.2	10.8	7.4
	13	31.0	18.7	12.3
	20	35.6	21.2	14.4

TABLE 7.5 Data for FIGURE 7.11

A 3 % PMMA -PP blend ; B PP

Time of Pre - irradiation (Hours)	OD $1740cm^{-1}$
0	0.805
1	0.578
5	0.387
8	0.291
16	0.2481
20	0.252

TABLE 7.6 Data for FIGURE 7.12

been included for comparison. Once more it can be seen that pre - irradiation does not greatly influence the thermal stability of a blend. The effect is small compared to the instability resulting from pre - irradiation of unblended PP and also from the blending of a small amount of PMMA with PP.

Again, the optical densities of the peaks at 1740 cm^{-1} were obtained from the IR spectra of the gases evolved during each thermal degradation. A plot of these values as a function of time of pre - irradiation is shown in FIGURE 7.12. The methyl methacrylate content of the gaseous volatiles is observed to decrease with time of pre - irradiation for times up to ca. 5 hours, after which there is a levelling off of monomer evolution.

From examination of a series of TVA degradations of blend samples, pre - irradiated for different times up to 20 hours (FIGURE 7.13), it can be seen that photolysis for 5 hours is sufficient to ensure the disappearance of the 'interaction' peak. Since formation of this peak has been attributed to methyl methacrylate production, this finding is consistent with the interpretation of the curve in FIGURE 7.12.

c) Thermal Degradation of Blends Pre - irradiated at 150°C.

Samples of a 10 % PMMA - PP blend were irradiated at 150°C for times up to 20 hours prior to thermal degradation for 3 hours at 354°C. The weight loss - time curve for the photolysis is shown in FIGURE 7.5, virtually the only product being methyl methacrylate. The curve resulting from the plot of weight loss, incurred by thermal degradation, versus time of pre - irradiation (FIGURE 7.14), is practically a mirror - image of the one in FIGURE 7.5. There is an initial, sharp decrease in weight loss

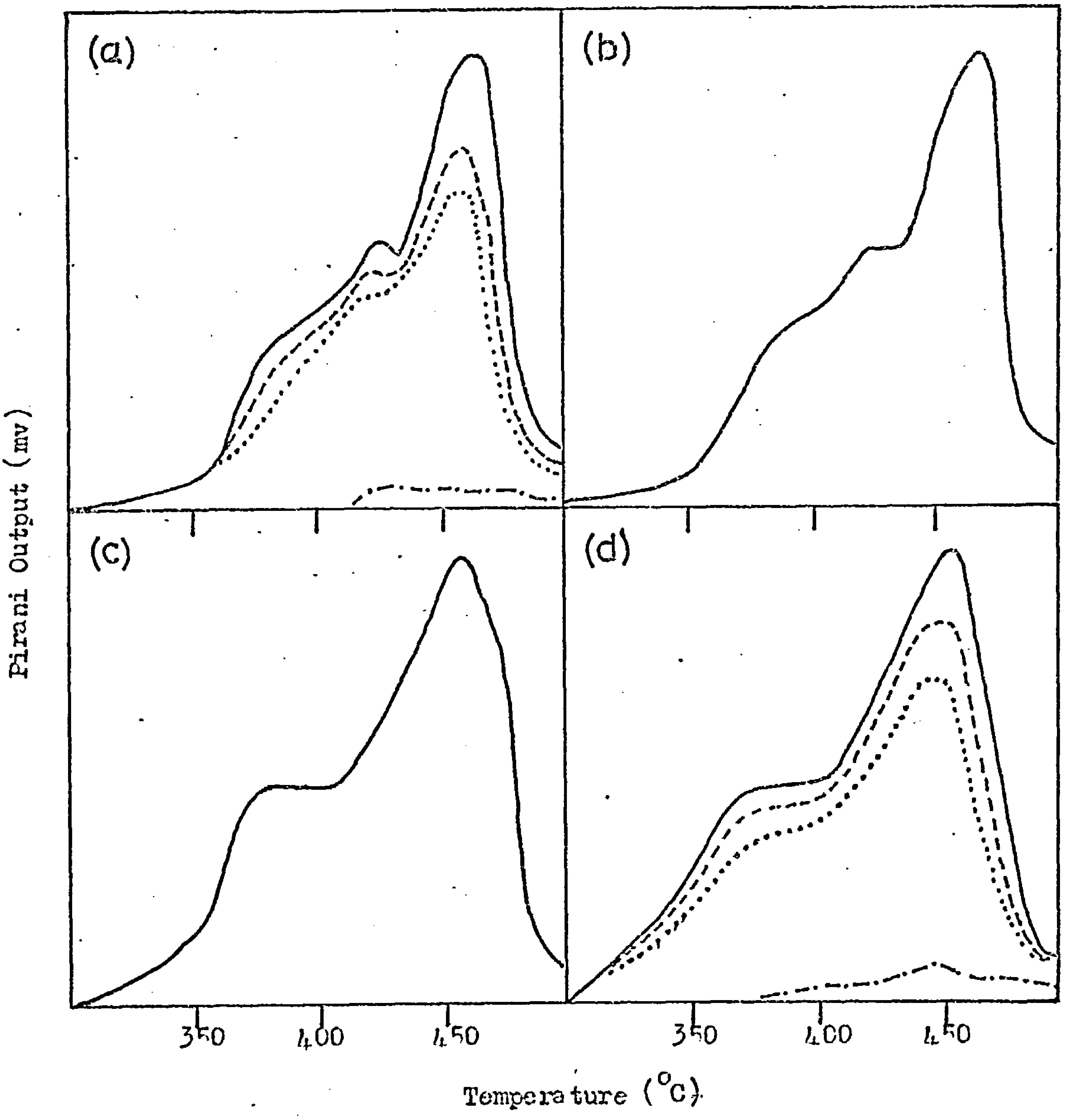


FIGURE 7.13 Series of TVA curves for samples of a 3 % PMMA - PP blend pre - irradiated at 20°C for different times,

a) t = 0 hours b) t = 1 hour
c) t = 5 hours d) t = 8 - 20 hours

Heating rate 10°/min.

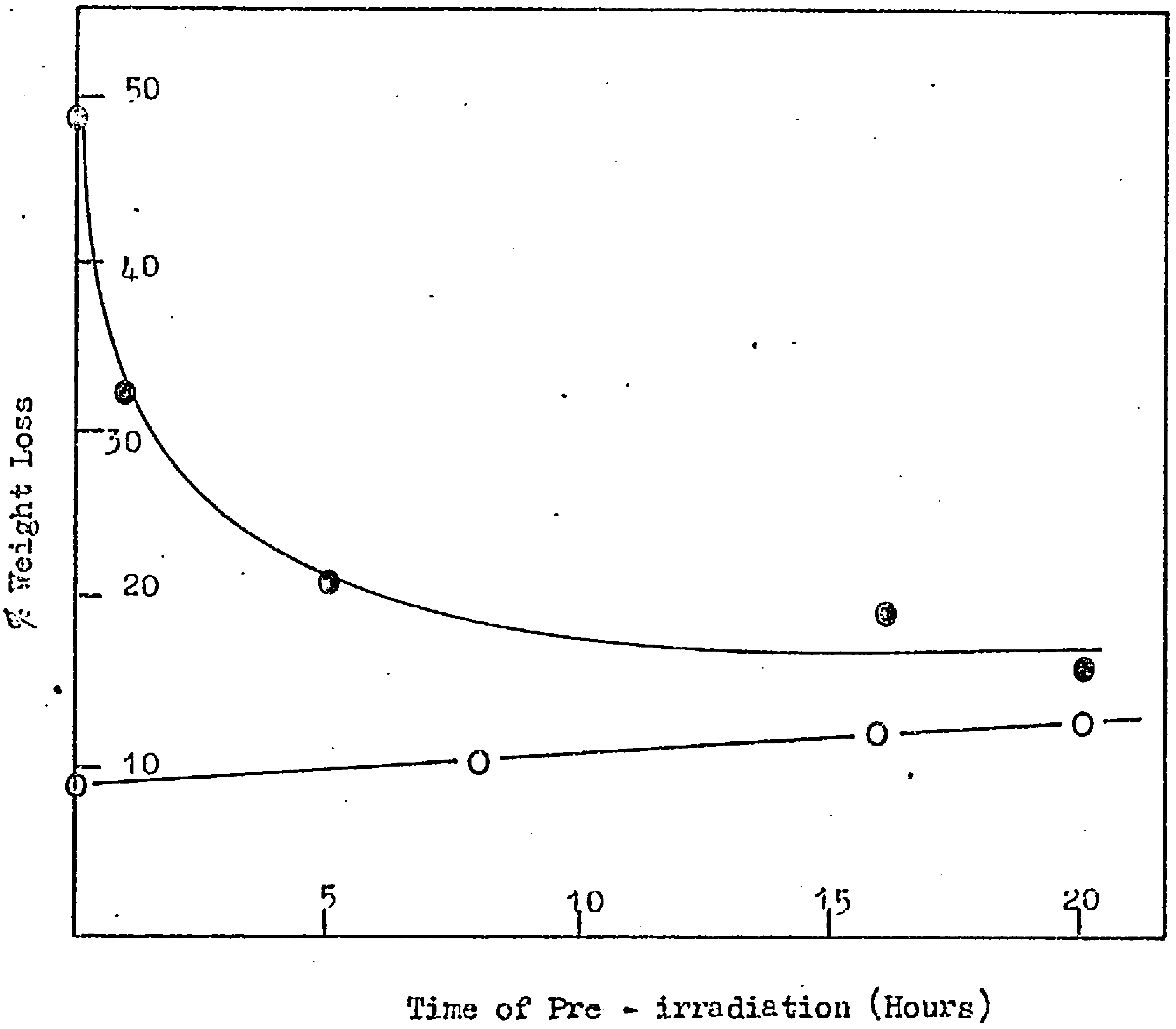


FIGURE 7.14 Weight loss versus time of pre - irradiation at 150°C for samples thermally degraded for 3 hours at 354°C.

● 10 % PMMA - PP

○ PP

Time of Pre - irradiation (Hours)		% Original Sample		
		Weight loss	Cold Ring	Gases
A	0	48.4	24.0	24.4
	1	32.1	17.6	14.5
	5	20.6	10.6	10.0
	16	19.6	10.0	9.6
	20	16.1	8.2	7.9
B	0	9.5	5.8	3.7
	8	10.5	6.4	4.1
	16	11.9	7.2	4.7
	20	12.8	7.8	5.0

<u>TABLE 7.7</u> Data for FIGURE 7.14

A 10 % PMMA - PP ; B PP

which levels out after about 5 hours pre - irradiation. Indeed, after 20 hours pre - irradiation the subsequent thermal weight loss is approximately equal to that for unblended PP, pre - irradiated for the same period. Thus it is apparent that the thermal stability of PP, pre - irradiated as a blend at 150°C, depends much more upon the amount of residual PMMA in the blend than upon the interaction of PMMA radicals or methyl methacrylate monomer with PP radicals or molecules.

d) Thermal degradation of blends of PP and pre - irradiated PMMA

PMMA films, cast from methyl acetate, were photolysed for 20 hours at 20°C, causing the number average molecular weight (measured by osmometry) to fall from 516,000 to 25,000. Degraded films were dissolved in acetone and blends with PP were prepared as previously outlined.

FIGURE 7.15 is a representation of the TVA trace of a PMMA film irradiated for 20 hours at room temperature. Two features are immediately obvious when comparison is made with the thermogram of an unirradiated sample (FIGURE 7.2(a)). Volatilisation commences at lower temperatures for the photolysed sample and there is no peak corresponding to depolymerisation initiated at chain ends.

The TVA curve resulting from a 3 % blend of photodegraded PMMA and PP is shown in FIGURE 7.16. It is evident that there is little difference from the thermogram of a blend of similar composition containing undegraded PMMA (FIGURE 7.13). In addition

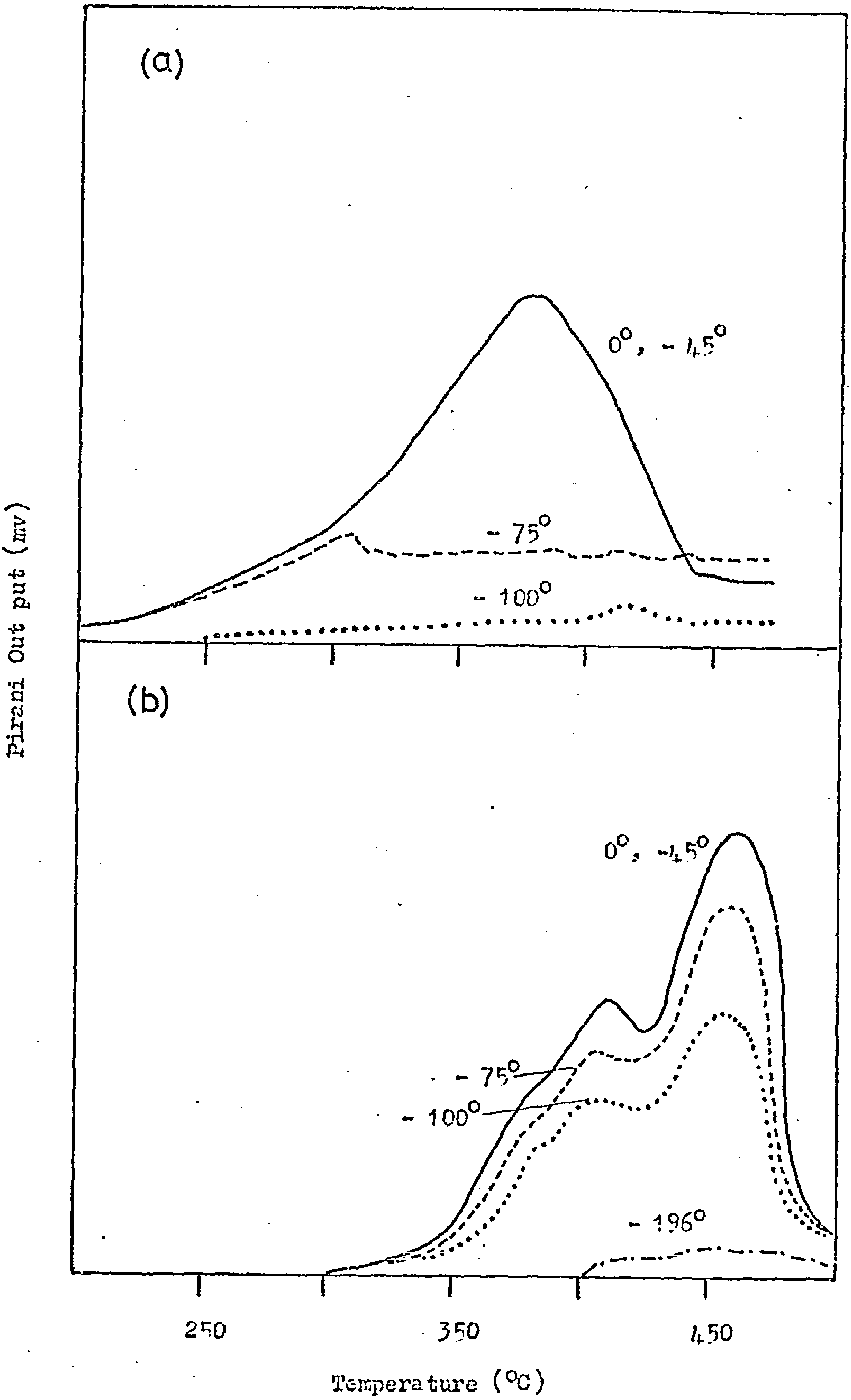


FIGURE 7.15 TVA curves of :

a) PMMA pre - irradiated at 20°C for 20 hours
b) a 3 % PMMA - PP blend containing this degraded PMMA. 20 mg samples;
Heating rate 10°/min.

pre - irradiated blends containing degraded PMMA produce thermograms similar to those resulting from blends containing undegraded PMMA, pre - irradiated for the same time.

Isothermal degradations at 354°C give rise to weight loss, cold ring and volatile characteristics, similar to those obtained for a blend of similar composition containing undegraded PMMA.

Thus it is apparent that photolysis of PMMA followed by blending with PP, cannot be equated to photolysis of a PMMA - PP blend.

7.6 Discussion

a) Nature of the Thermal Interaction

Any explanation of the thermal behaviour of PMMA - PP blends must account for the following facts : -

(i) The presence of thermally degrading PMMA greatly accelerates the decomposition of PP.(Section 7.5(a))

(ii) PMMA is stabilised in the presence of PP, under programmed heating conditions.(Section 7.3(a) and (b)).

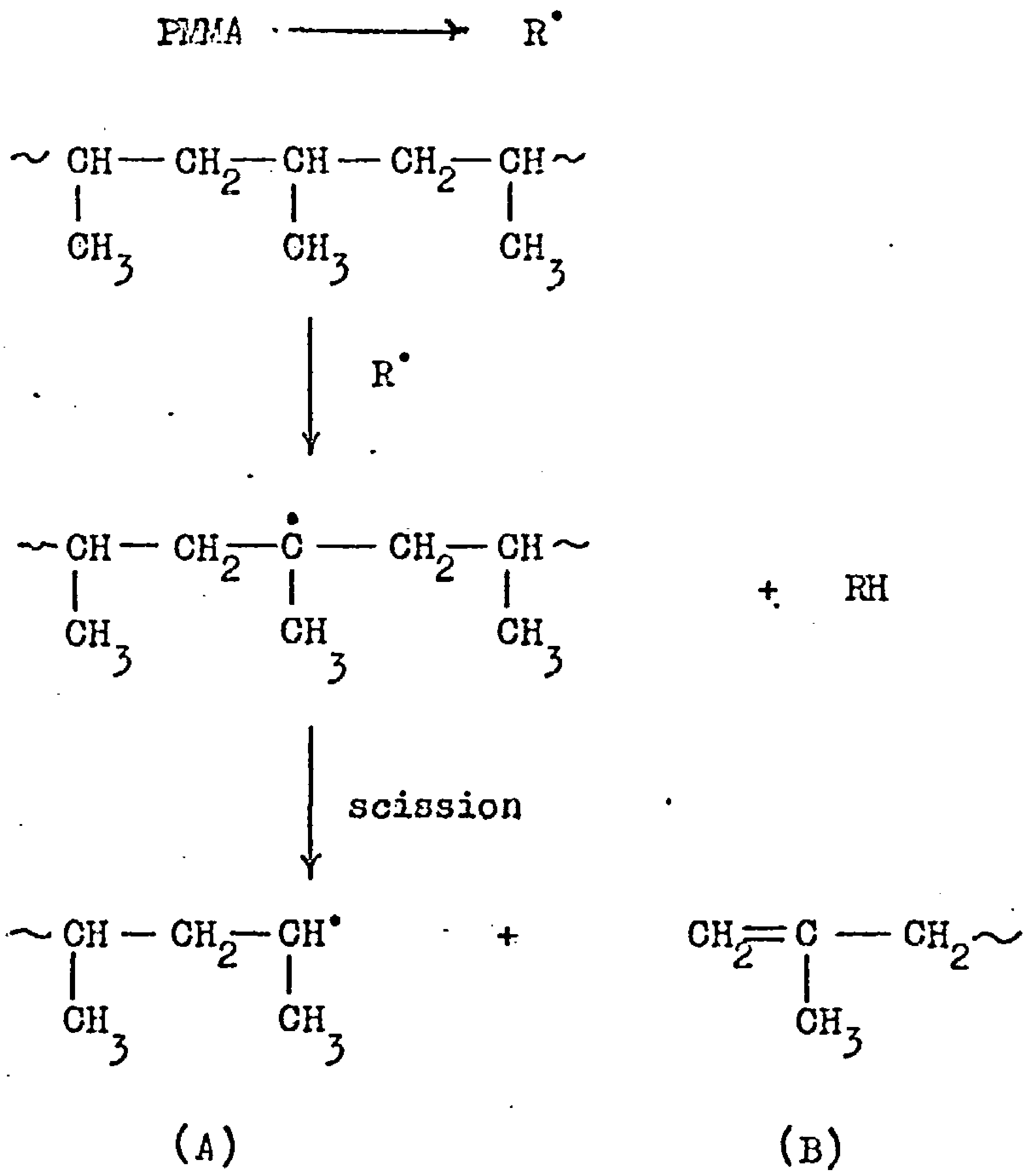
(iii) There is a marked delay in the production of a quantity of methyl methacrylate in PMMA -PP blends degraded by TVA ('interaction peak' in thermograms of mixed blends)(Section 7.3(a)).

(iv) A small amount of carbonyl containing material is present in the short chain fragments of degraded blends(Section 7.5(a)and(b)).

(v) There are no traces of PMMA in the residues of degraded blends (Section 7.5).

The accelerated breakdown of PP may be explained in terms of the interaction of a radical species from degrading PMMA with the

PP macromolecules, causing chain scission of PP and ultimately volatilisation.



The most probable interaction involves hydrogen abstraction to form tertiary polypropylene radicals as outlined above. It is likely that thermal decomposition of PP will proceed by a mechanism similar to that proposed by Tsuchiya and Sumi (31). This mechanism, of which A and B are intermediates, is outlined in chapter 1.

Since samples prepared from PMMA - PP mixtures were heterogeneous indicating an incompatible system, any species formed during the decomposition of PMMA must, in order to react with a PP molecule, be capable of migrating across a phase boundary. Because of the severe restrictions on the motion of a PMMA macroradical, it appears more likely that the attacking species is a small radical, or a small molecule which can diffuse from one phase to the other, before undergoing some kind of radical reaction. How ever, by proposing macroradical participation in the interaction of the two polymers, many of the above features may be explained. Since the proportion of PMMA is small in any of the blends studied, it is possible that interaction with PP can occur at phase boundaries, without the need for extensive diffusion of radicals.

Before considering the results of this investigation, it is appropriate to review some of the evidence for and against macroradical involvement in the thermal degradation of polymer blends. In the thermal degradation of mixtures of atactic PP and poly (vinyl acetate) (PVA), Pavlinec (110) detected very small amounts of grafting of the two polymers, but only at the beginning of the degradation. As an explanation, he proposed the interaction of PVA radicals,formed by partial deacylation, with fragments of PP macromolecules which had decomposed simultaneously. Mizutani (100) has reported the formation of graft and block copolymers during the thermal degradation of PP - Vinyl polymer blends, and has also postulated an interaction involving a vinyl polymer radical and a PP radical or molecule. On the other hand, McNeill and Neil (112) have shown that the radical species from degrading poly (vinyl chloride) responsible for accelerated breakdown of PMMA is a chlorine radical and not a macroradical $(\sim CH{=}CH{-}\dot{C}H{-}CH_2\sim)$. These workers discovered that thermal degradation of a mixture of PMMA and dehydrochlorinated PVC, a material shown by ESR to contain macroradicals, did not lead to increased volatilisation from PMMA. Dodson (116) has recently attempted to detect polymer radical interaction in the thermal degradation of mixtures of polystyrene (PS) and PVC labelled with Cl^{36}. Films were partially degraded below the temperature for initiation of PS breakdown. The PVC content of each blend was then extracted and the PS residue monitored for radioactivity. None was detected suggesting that grafting of PVC to PS does not occur. These are a few of the conflicting opinions in the literature on this topic.

In this investigation, however, no indications were found of the formation of block or graft copolymers. Indeed, thermal degradations of PMMA - PP blends of similar composition and under similar experimental conditions (280° - 340°C for times up to 4 hours) to those of Mizutani (100), did not succeed in producing grafting. These findings appear reasonable, considering the stability of PMMA at such temperatures.

However, there appears to be evidence for macroradical participation in that, under conditions of programmed heating, the decomposition of PMMA is slightly delayed when blended with PP. After initial scission of the PMMA chain, the macroradicals may stabilise by means of hydrogen abstraction from PP, thus postponing depolymerisation to higher temperatures. It is possible that the 'interaction' peak in the TVA thermogram of a mixed blend may be an indication that temporary grafting of PMMA radicals to PP chains occurs at some stage during the decomposition. A PMMA chain, grafted in this manner, could then scission and depolymerise at higher temperatures, releasing the monomer detected in the 'interaction' peak. However, this theory could not be substantiated since no evidence of grafting was found in the residues of blends partially degraded by TVA to a temperature just below that corresponding to the formation of the 'interaction' peak.

The above postulate, and indeed it can only be a postulate, could explain the presence of carbonyl containing material in the short chain fragments of thermally degraded blends. Depolymerisation of temporarily grafted PMMA side chains is expected to be extensive under the prevailing thermal conditions. Unzipping may be complete in some branches, but in others the possibility exists that one or two methyl methacrylate units per chain may remain grafted to the PP backbone. If this is the case, the question arises - why is the carbonyl containing material detected in the cold ring and not in the residue ? It may be that a small amount of this material is present in the residue but, owing to its small concentration in relation to the bulk of the residue, detection is not possible. More likely, attachment of a unit (or units) of methyl methacrylate to a particular section of a PP chain will destabilise that region of the chain thus encouraging chain scission and volatilisation to the cold ring.

An alternative postulate for the presence of carbonyl containing material in the short chain fragments is the following : During thermal degradation of a PMMA - PP blend, the situation may arise in which a PP radical, formed either by chain scission of the PP itself or by hydrogen abstraction by a radical species from degrading PMMA, finds itself surrounded by an atmosphere of methyl methacrylate monomer produced by depolymerisation of PMMA chains. An equilibrium would then be set up in which methyl methylacrylate could polymerise and depolymerise at the site of the PMMA radical.

$$P^{\bullet} + nM \rightleftharpoons P - (M)_n$$

Under the prevailing thermal conditions the degree of polymerisation would be very small. Again chain scission and volatilisation to cold ring could occur at such branch points.

Although a similar equilibrium has been proposed by Chapiro (117) who grafted acrylonitrile on to PP by means of high energy radiation, the interaction of methyl methacrylate monomer with PP radicals is considered to be unlikely since, under the high vacuum conditions employed, the methyl methacrylate will quickly diffuse out of the polymer blend. This is reflected in results obtained from the photolysis of PMMA - PP mixtures at 150°C. The methyl methacrylate produced by photo - depolymerisation of PMMA prefers to escape as monomer rather than interact with the PP radicals which are simultaneously produced.

Thus, results indicate that the radical species from degrading PMMA, which accelerates the thermal decomposition of PP, may be polymeric in nature although no definite proof in the form of graft or block copolymers has been found.

b) Nature of the Photo - Interaction.

The following features emerge in the photolysis of PMMA - PP blends and their subsequent thermal degradation : -

i) There is no evidence for the formation of graft or block copolymers on photolysis of blends at room temperature or at 150°C.

ii) Pre - irradiation only slightly decreases the thermal stability of any one blend.

iii) Pre - irradiation decreases the amount of methyl methacrylate in the gaseous volatiles of subsequent thermal degradation.

iv) Pre - irradiation increases the quantity of carbonyl containing material in the cold ring produced during subsequent thermal degradation.'

v) Pre - irradiation causes the disappearance of the 'interaction' peak in the TVA thermograms of mixed blends.

vi) Blends of photolysed PMMA with PP possess similar thermal degradation characteristics to those of blends containing un - irradiated PMMA.

The most obvious explanation for the reduction in the quantity of methyl methacrylate in the gaseous volatiles and the increase in the amount of carbonyl containing material in the short chain fragments, is that pre - irradiation at 20°C produces grafting of PMMA to PP. As the time of irradiation increases, the extent of chain scission of the PMMA component of the blend increases and hence the length of the grafts becomes shorter and the greater the number of PMMA chains grafted on to the PP backbone. Subsequent thermal degradation unzips these already short side chains producing a little methyl methacrylate and leaving one or more methyl methacrylate units at frequent intervals along a chain. Again this branching will produce weak points in the PP chain, encouraging chain scission and volatilisation to the cold ring. Thus by virtue of a larger number of shorter grafts, less methyl methacrylate is produced in the gaseous volatiles and more carbonyl material is found in the short chain fragments. This also accounts for the absence of an 'interaction' peak, attributed to methyl methacrylate production, in the TVA thermogram of a mixed blend.

However, there is no evidence of the formation of graft or block copolymers to support this theory. This might be expected considering the difficulty a macroradical would experience in migrating across a phase boundary at ambient temperatures. Nevertheless, the possibility does exist that grafting occurs at phase boundaries and that the grafted molecules are sufficiently polar to dissolve in hot acetone, thus escaping detection in extracted residues.

Another possible explanation for the observed phenomena is that photolysis of PMMA in the blend produces trapped polymer radicals or unstable points in relatively short PMMA chains, which can then interact with PP. as previously outlined, on subsequent thermal degradation. A similar scheme has been put forward by David and coworkers (118) to explain their discovery that if PMMA is irradiated with gamma or 2537 Å UV radiation and then warmed to 160°C, thermal depolymerisation occurs. These authors believe that depolymerisation is initiated at unstable points, of an unknown nature, formed in the PMMA during irradiation.

However, in the present investigation, it seems unlikely that interaction occurs in such a manner. Photolysis of PMMA followed by blending with PP does not degrade thermally similarly to a pre - irradiated blend of similar composition. Indeed, results are similar to those obtained from the thermal degradation of the corresponding un - irradiated blend.

In conclusion, taking all available evidence into consideration, irradiation of PMMA - PP blends appears to effect an interaction of the two polymers probably involving grafting of short chain PMMA radicals to a PP backbone.

7.7 Other Polymer Blends containing Polypropylene

It is of interest to compare the behaviour of PP - PMMA blends with that of other polymer blends containing PP. The following systems were examined using the technique of TVA ;

PP - PVC Poly(vinyl chloride)
PP - PS Polystyrene
PP - PAMS Poly(alpha methyl styrene)
PP - PE Polyethylene

The origin of the polymer samples is detailed in TABLE 7.8. In each system, equal weights of powdered polymer were ground together and degradation samples were prepared by pressing and pre - melting as before.

(a) PP - PVC

The TVA thermogram of PVC is represented in FIGURE 7.16. The main peak is attributed to evolution of hydrogen chloride and the tail above ca. 375°C, to production of volatile material arising from decomposition of the polymer backbone.

Thermograms for mixed and unmixed systems of PP and PVC (FIGURE 7.17) clearly indicate the presence of some form of interaction between the two degrading polymers. The evolution of hydrogen chloride (first peak) is slightly delayed in mixed systems although the T_{max} for the second peak (corresponding to volatilisation of products from degradation of PP) is unchanged.

This delay in the formation of hydrogen chloride from PVC blends is not a phenomenon unique to mixtures with PP. McNeill

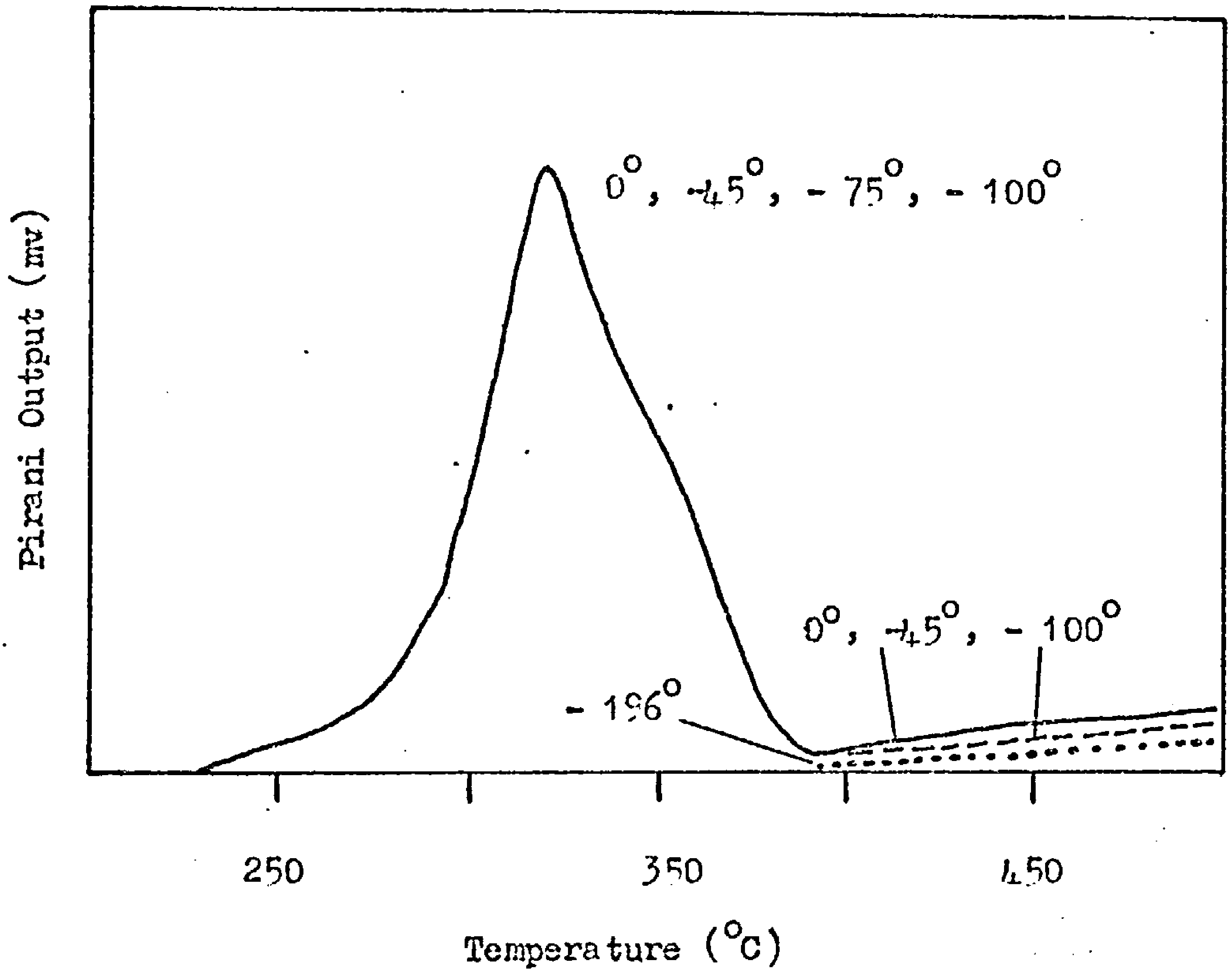


FIGURE 7.16 TVA curves for PVC; 25 mg sample. Heating rate 10°/min.

Polymer	Mn	History
PVC	16,000	British Geon 101 polymer, additive free.
PS	116,000	Thermal polymerisation in bulk at 140°C.
PAMS	-	Anionic polymerisation at - 82°C.
PE	-	Shell low density polymer, additive free.

TABLE 7.8 Polymer Samples

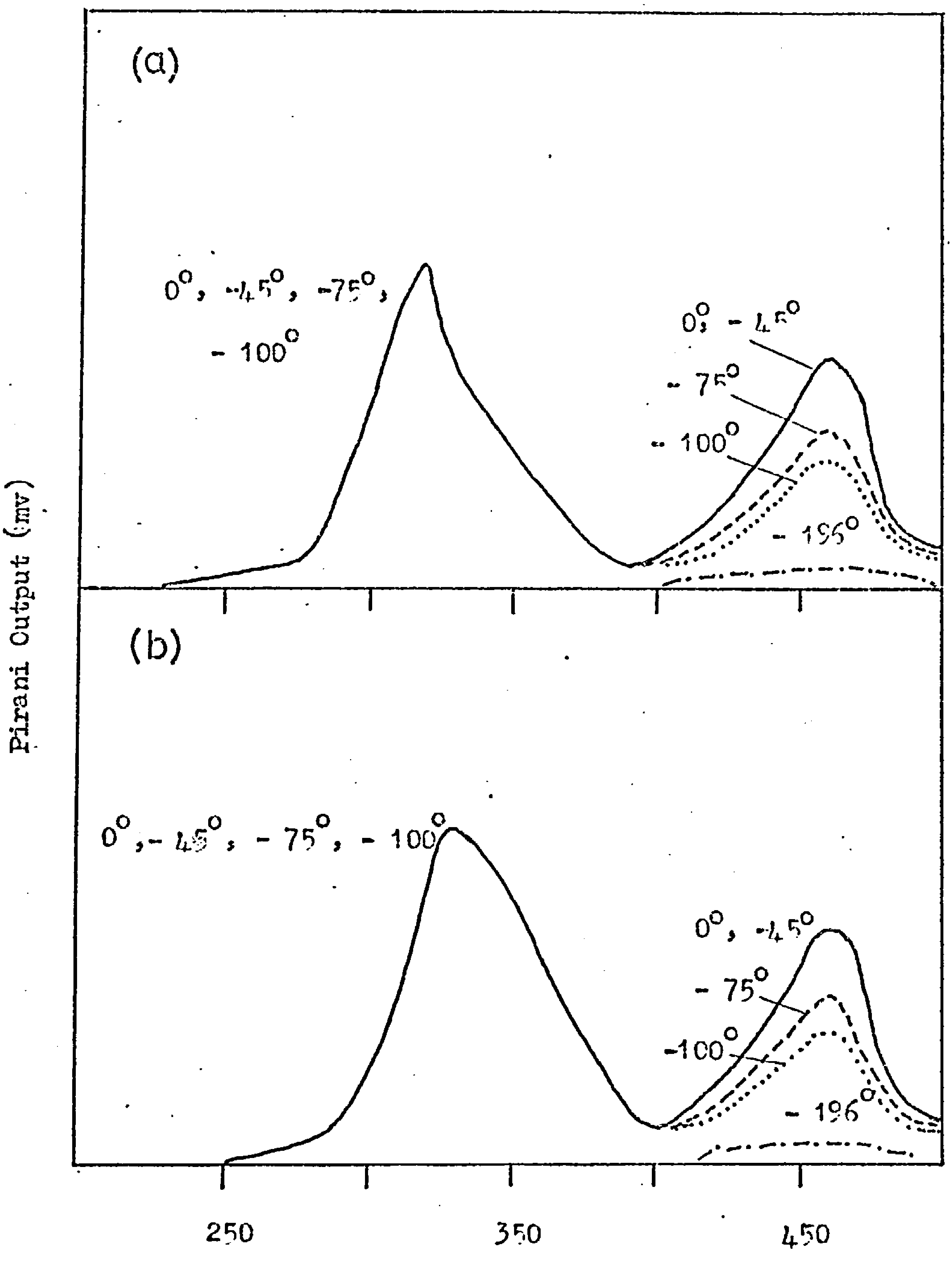


FIGURE 7.17 TVA curves for simultaneous degradation of PVC (12.5 mg) and PP (12.5 mg) (a) unmixed and (b) mixed

Heating rate : 10°/min.

and Neil (112) have made similar observations in several other polymer blends with PVC as the common polymer. These authors, assuming that chlorine radicals act as chain carriers in a free - radical dehydrochlorination of PVC, propose that some of these small, mobile radicals may migrate from the PVC phase into the second polymer phase, abstract a hydrogen atom and produce a macroradical in that phase. Thus the chain carriers which behave in this way are not available to attack PVC molecules causing the average kinetic chain length in the PVC decomposition to fall accounting for the observed delay in hydrogen chloride production.

If chlorine radicals are capable of attacking polypropylene, then the PP radicals so produced would be expected to undergo chain scission reactions, causing the molecular weight to fall. The fact that the PP degradation peak is not displaced to lower temperatures is consistant with this view since it has been shown in Chapter 4 that the T_{max} value for PP samples is independent of molecular weight.

FIGURE 7.18 shows the TVA thermogram of 1 : 1 by weight mixture of PP and PVC, pre - irradiated at 20°C for 20 hours. Comparison with an equivalent un - irradiated sample (FIGURE 7.17 (b)) reveals no obvious photo - induced interaction of the two polymers. This is not unexpected since photolysis of PVC at room temperature has been shown (119) to result in crosslinking through combination reactions of radicals on adjacent polymer chains. These macroradicals, resulting from hydrogen chloride elimination, are unlikely to migrate between phases at ambient temperatures. In addition, any possible interaction of chlorine

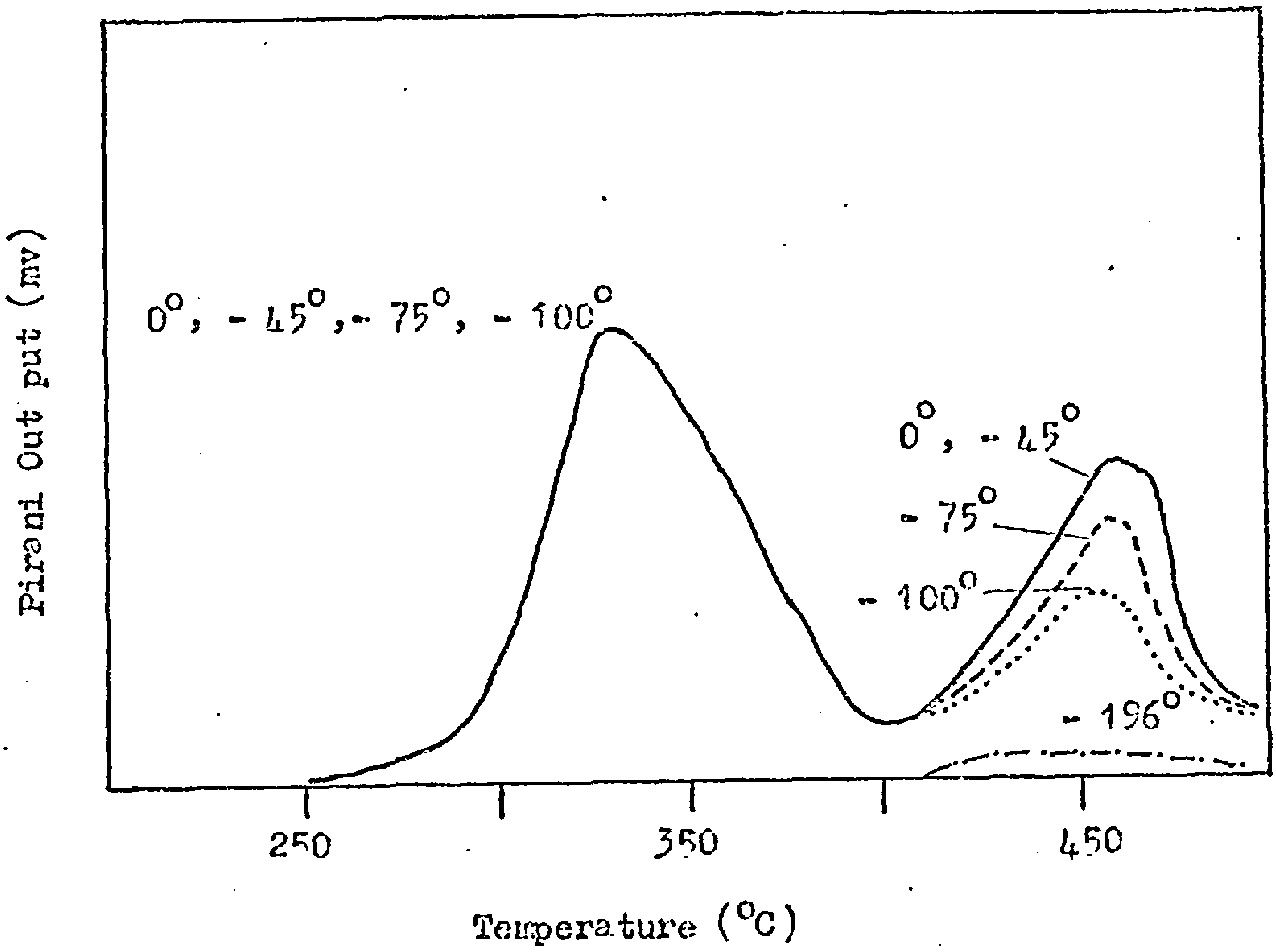


FIGURE 7.18 TVA curves for a 1 : 1 by weight mixture of PVCand PP pre - irradiated for a 20 hours at 20°C. 25 mg sample ; Heating rate 10°/min.

radicals will introduce competition between scission and crosslinking reactions in PP which would not be manifested in the TVA thermogram.

b) PP - PS

The TVA thermogram of PS is illustrated in FIGURE 7.19. The degradation peak has been shown (76) to result from evolution of styrene monomer. With the possible exception of dimer, all products other than monomer (i.e. trimer, tetramer and higher products) are expected to collect as cold ring fraction.

TVA thermograms for mixed and unmixed systems (FIGURE 7.20) again provide clear evidence of an interaction between PP and PS. The second peak in the unmixed system (due to PP degradation) is removed to lower temperatures in mixed systems, and is, indeed, incorporated by the PS peak, the T_{max} of which remains unaltered. Dodson (116) has obtained similar results while investigating blends of PS and PE.

Since in both mixed and unmixed systems, the PS degradation peaks (arising from evolution of monomer) remain virtually identical, it is to be suspected that monomer or radical species leading to monomer will have relatively little interaction with PP. It is more likely that small radical species leading to production of dimer, trimer etc. are involved. Such radicals are expected to be sufficiently small to migrate from the PS phase to the PP phase and, by means of hydrogen abstraction, to initiate PP degradation at lower temperatures. The displacement to lower temperatures of the PP peak is readily explained by considering the temperatures at which the hydrogen abstraction reactions are taking place (> 400°C). At these temperatures, the energy content of the system is such that chain scission and

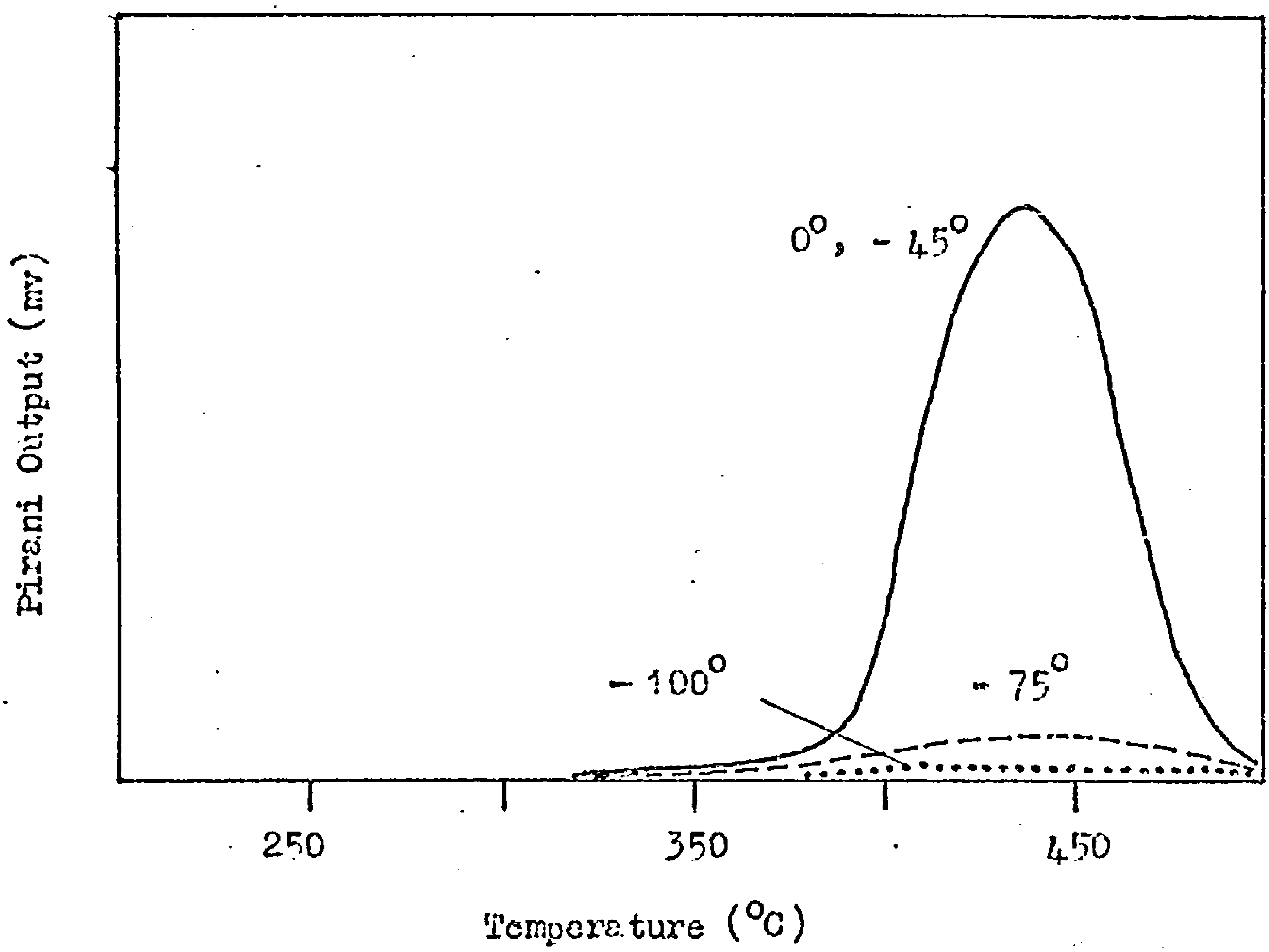


FIGURE 7.19 TVA curve for polystyrene ; 25 mg sample Heating rate 10°/min.

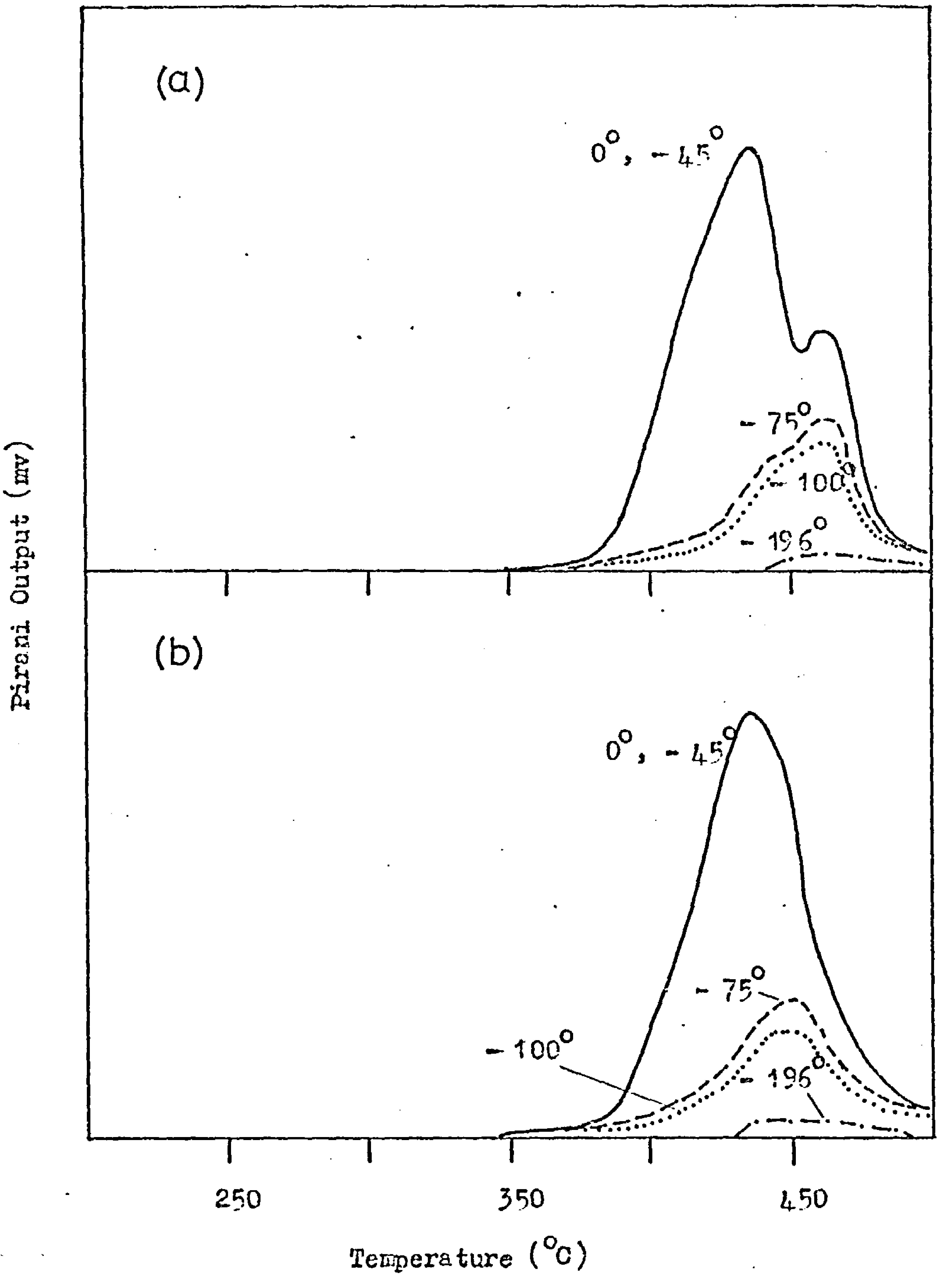


FIGURE 7.20 TVA curves for simultaneous degradation of PS (12.5mg) and PP (12.5 mg)
(a) unmixed and (b) mixed
Heating rate : 10°/min.

transfer reactions will continue until the molecules produced are of sufficiently low molecular weight to be volatile.(cf. PP - PVC blends where hydrogen abstraction is suspected to occur at ca. 300°C).

FIGURE 7.21 represents the TVA thermogram of a 1 : 1 by weight blend of PP and PS, pre - irradiated at 20°C for 20 hours. Once again there is apparently no photo -induced polymer interaction. As is the case for PVC, ambient temperature photolysis of PS results in crosslinking (120). Thus interaction with PP is unlikely for the reasons previously mentioned.

c) <u>PP - PAMS</u>

The thermal degradation of PAMS resembles that of PMMA in that it exhibits no transfer in undergoing almost quantitative depolymerisation to monomer. The TVA thermogram of PAMS, represented if FIGURE 7.22, is consistent with evolution of a single product.

FIGURE 7.23 contains thermograms for mixed and unmixed systems of PP and PAMS ; once again there is clear evidence of polymer interaction in mixed systems. Although there is no displacement of the peaks corresponding to degradation of PP and PAMS, an additional peak ($T_{max} \sim 385^\circ C$) appears as a shoulder on the PAMS peak. This situation is analagous to the degradation of mixtures of PP and PMMA where it was suggested that the 'interaction' peak resulted from delayed unzipping to monomer of short PMMA chains temporarily grafted to PP . It is possible that such events are taking place in the PP - PAMS system.

The photolysis of PAMS is also similar to that of PMMA. Stokes and Fox (121) have demonstrated the occurrence of random chain scission followed by unzipping of the resultant polymer radicals, both at 27°C and 115°C, the latter being just above a

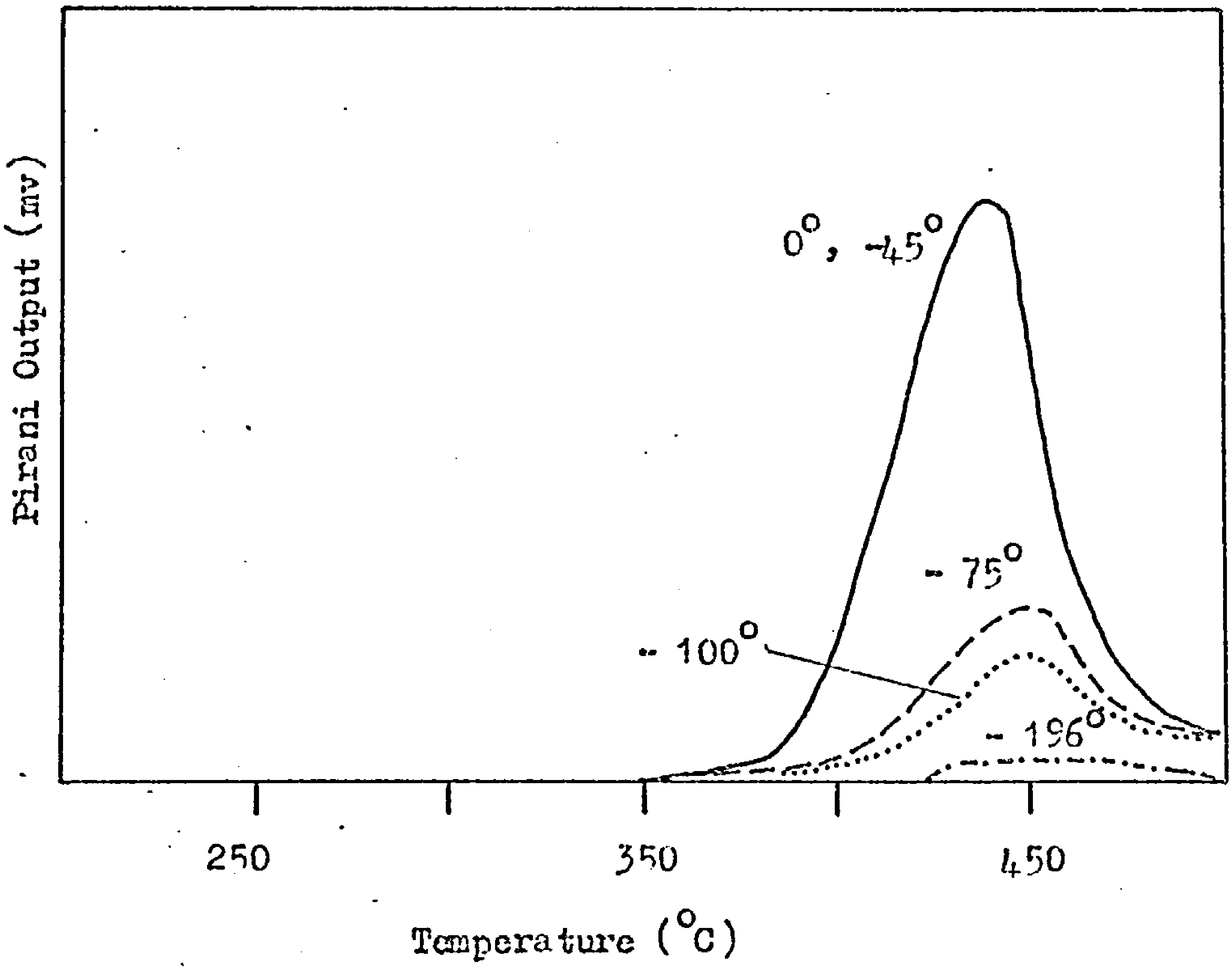


FIGURE 7.21 TVA curves for a 1 : 1 by weight mixture of PS and PP pre-irradiated for 20 hours at 20°C 25 mg sample ; Heating rate 10°/min.

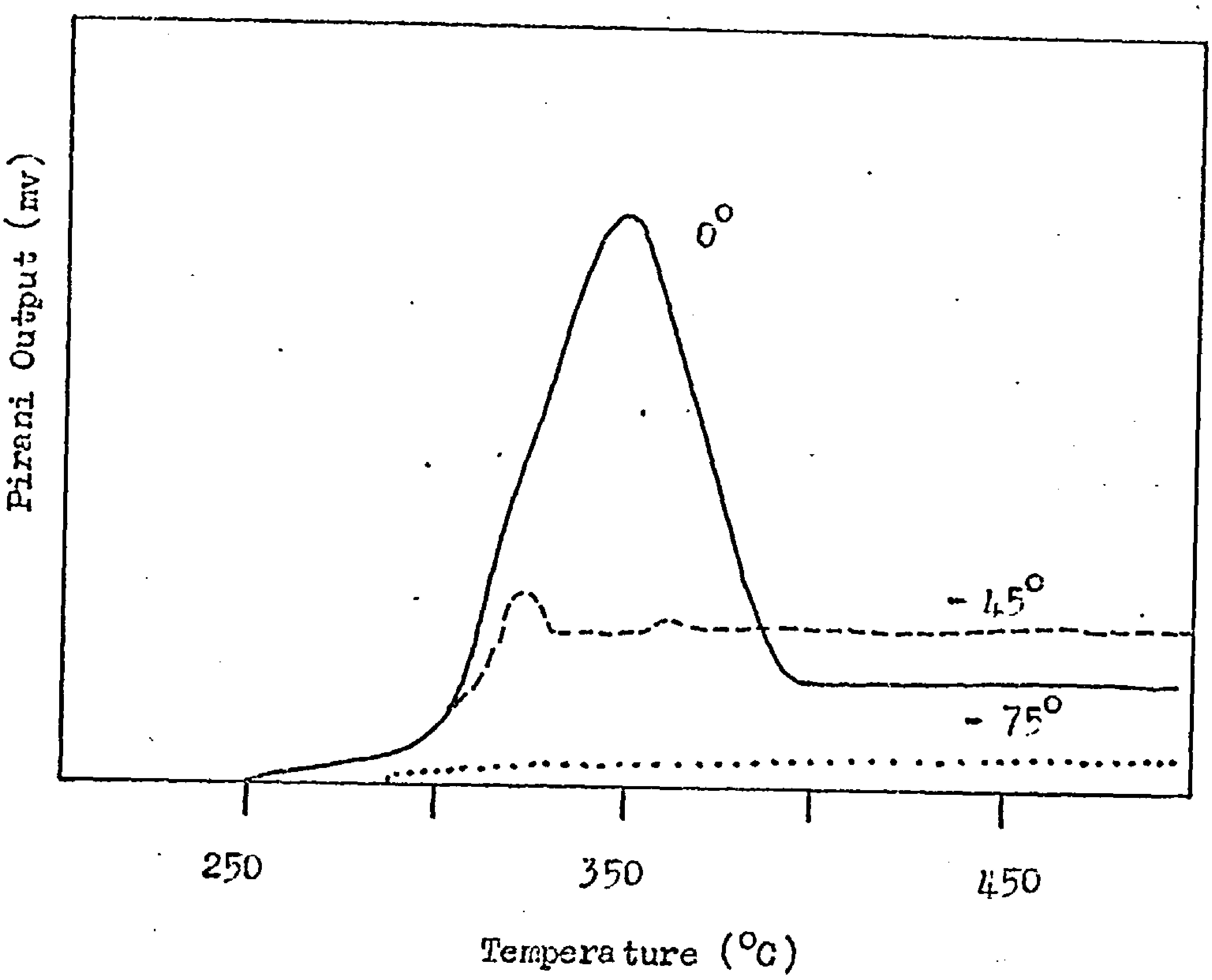


FIGURE 7.22 TVA curve for poly(alpha methyl styrene); 25 mg sample. Heating rate 10°/min.

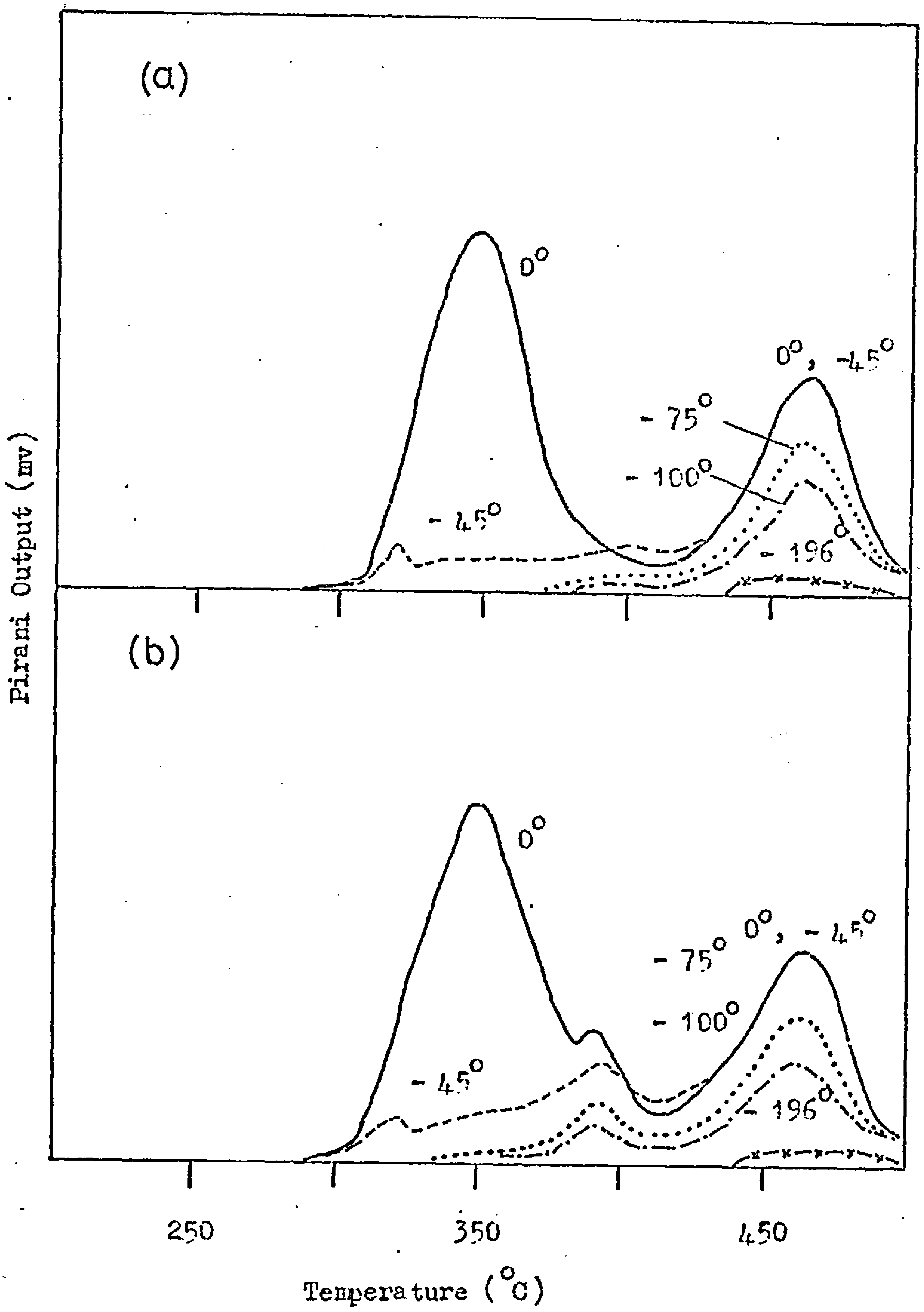


FIGURE 7.23 TVA curves for simultaneous degradation of PAMS (12.5 mg) and PP (12.5 mg)

(a) unmixed (b) mixed

Heating rate 10°/min.

second - order transition temperature. However, in this study, the ambient temperature photolysis of PP - PAMS blends evolved no monomer.

FIGURE 7.24 illustrates the TVA thermogram of a 1 : 1 by weight mixture of PP and PAMS, pre - irradiated at 20°C for 20 hours. In contrast to the situation in PP - PMMA blends, the 'interaction' peak doe not disappear. This is surprising considering the similar degradation characteristics of PAMS and PMMA. However it is possible that any photo - induced interaction may be masked by the high PAMS content (50 %) of the blends studied. Further experiments with mixtures containing lower proportions of PAMS may help to explain this apparent anomaly.

d) <u>PP - PE</u>

The thermal degradation of PE involves extensive inter - molecular transfer resulting in short chain fragments which condense on the cooled part of the degradation tube as cold ring fraction. Even with the 50 mg sample used, the amount of volatile material obtained is small. The lack of coincidence in the four TVA traces (FIGURE 7.25) indicates a mixture of condensable and non - condensable products. Concurrent production of all the products is indicated by the fact that the rate maximum on each trace occurs at the same temperature.

In FIGURE 7.26, the TVA thraces for a 1 : 1 by weight unmixed and mixed samples of PP and PE respectively are produced; but only in the former trace are the two peaks, corresponding to volatilisation of products from the degradation of each polymer, clearly distinguishable, There is no obvious interaction taking place in which degrading PP induces volatilisation of PE at lower temperatures than normal. Clearly a parallel can be drawn

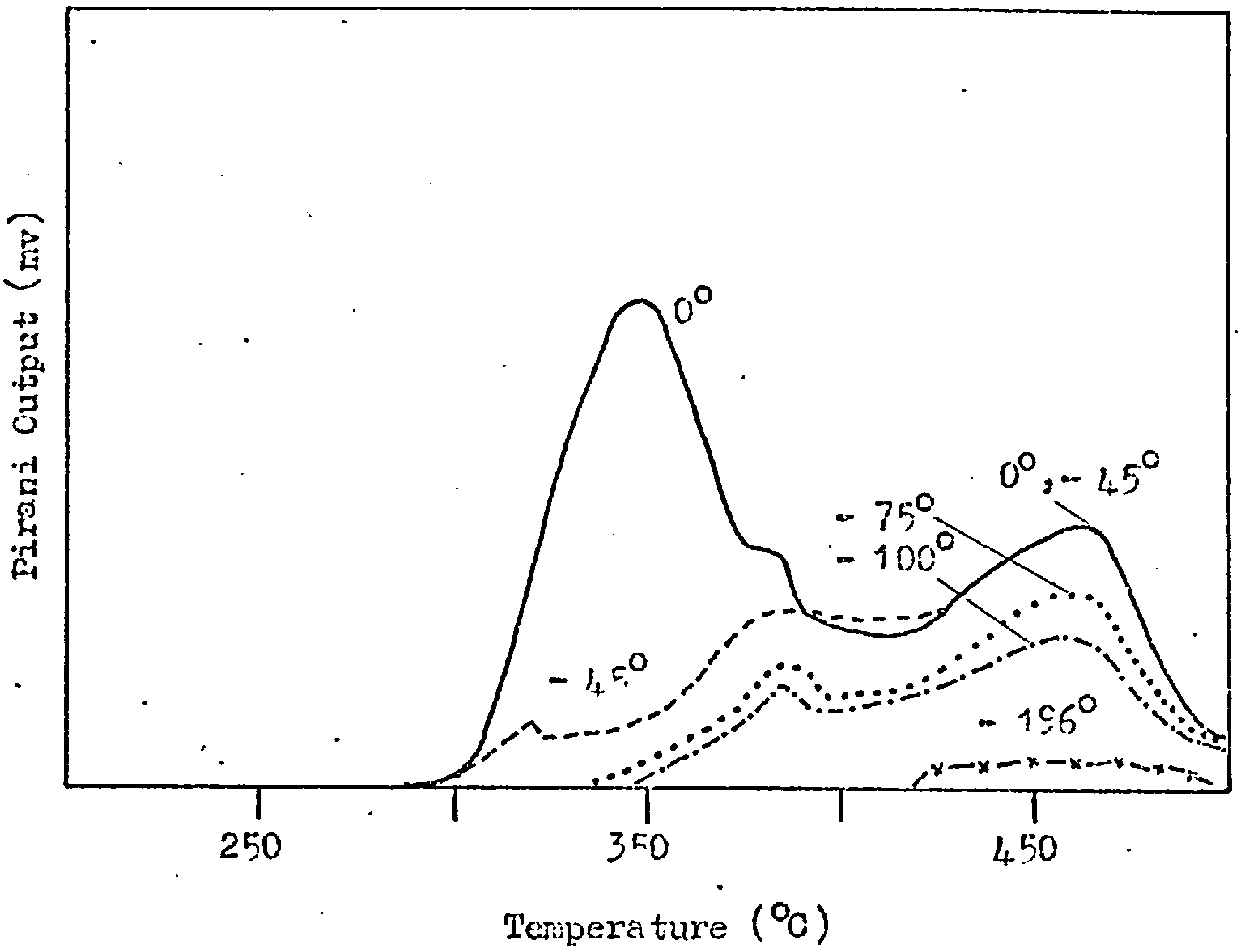


FIGURE 7.24 TVA curves for a 1 : 1 by weight mixture of PAMS and PP pre - irradiated for 20 hours at 20°C. 25 mg sample ; Heating rate 10°/min.

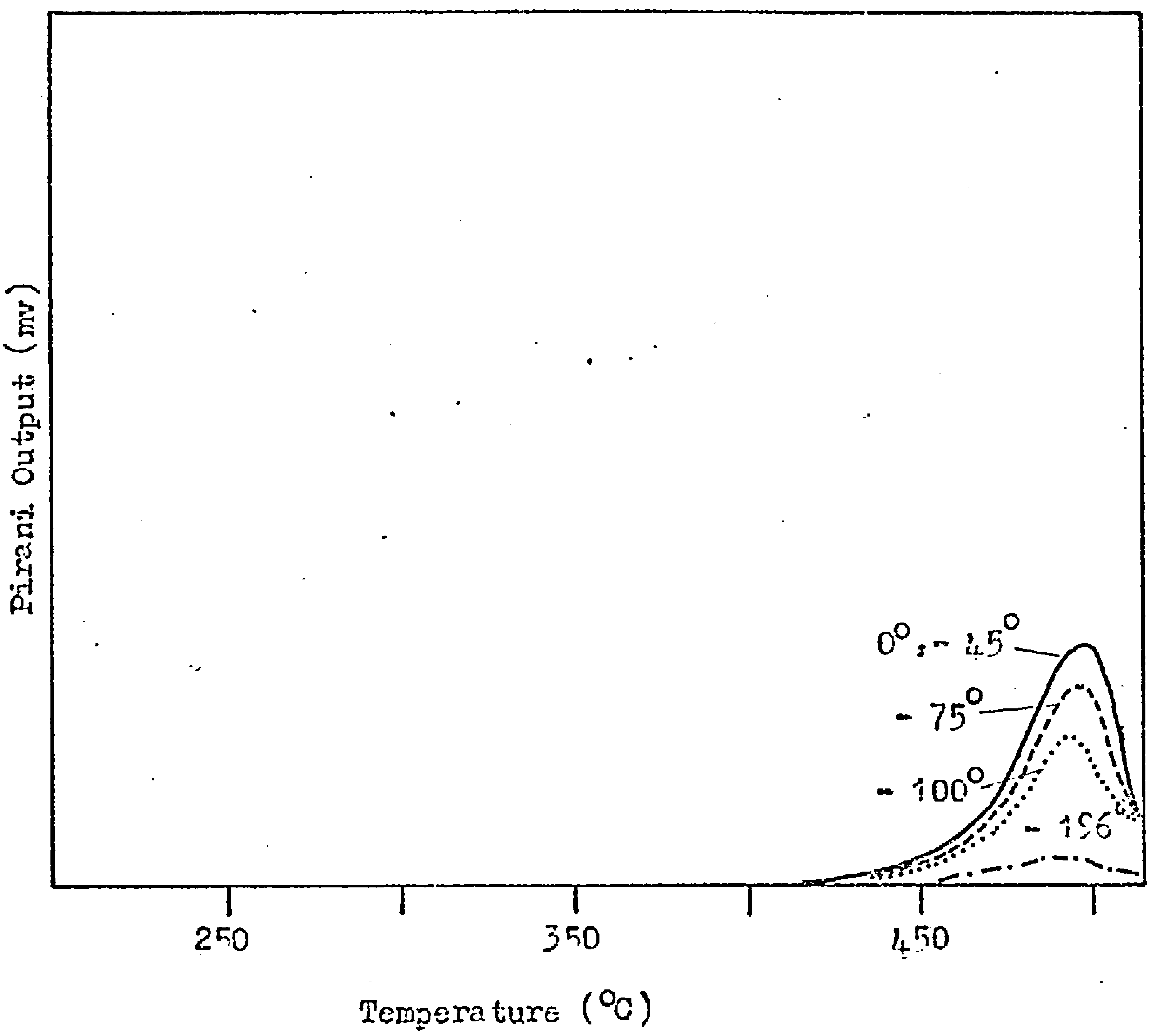


FIGURE 7.25 TVA curves for polyethylene ; 50 mg sample.
Heating rate 10°/min.

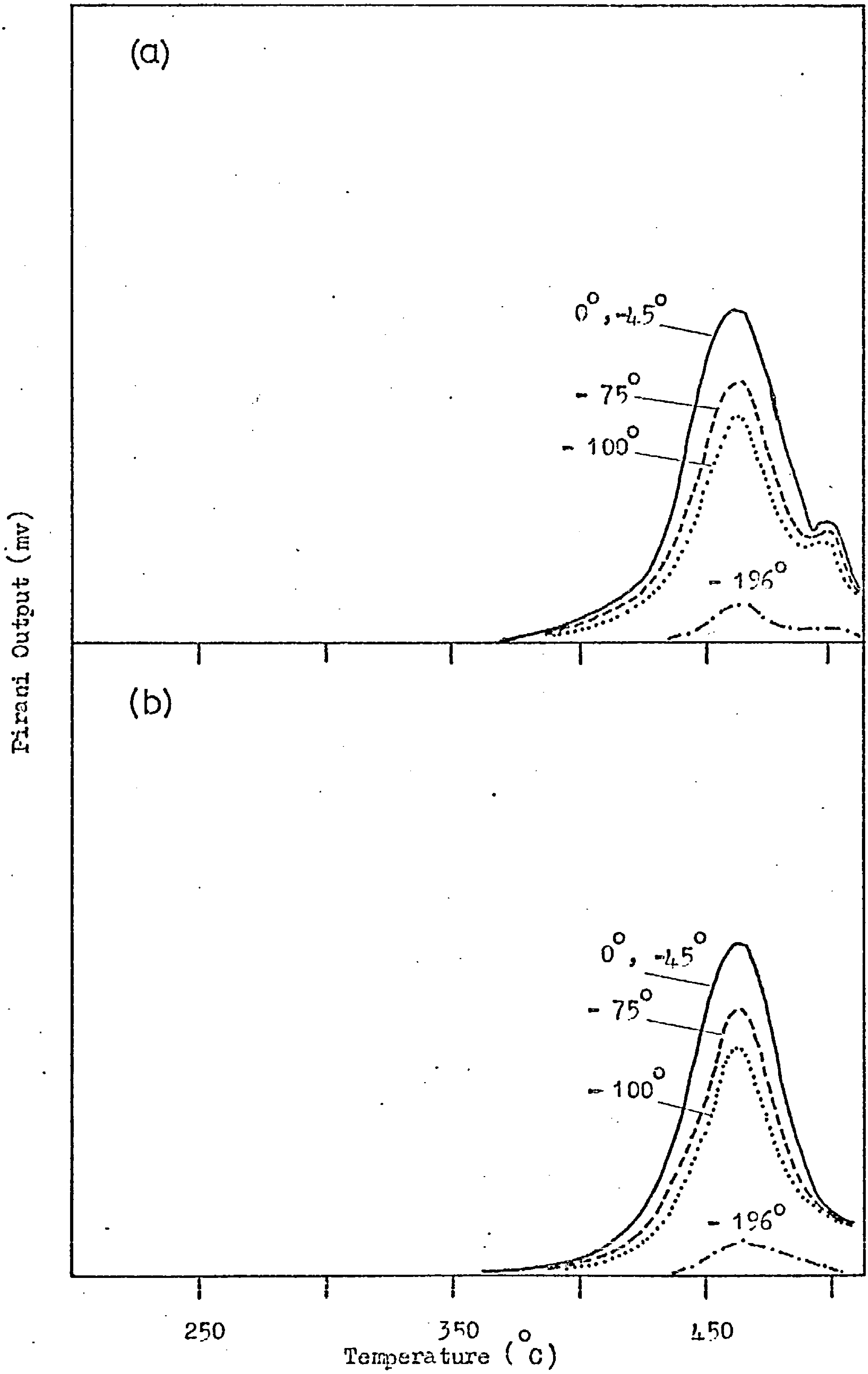
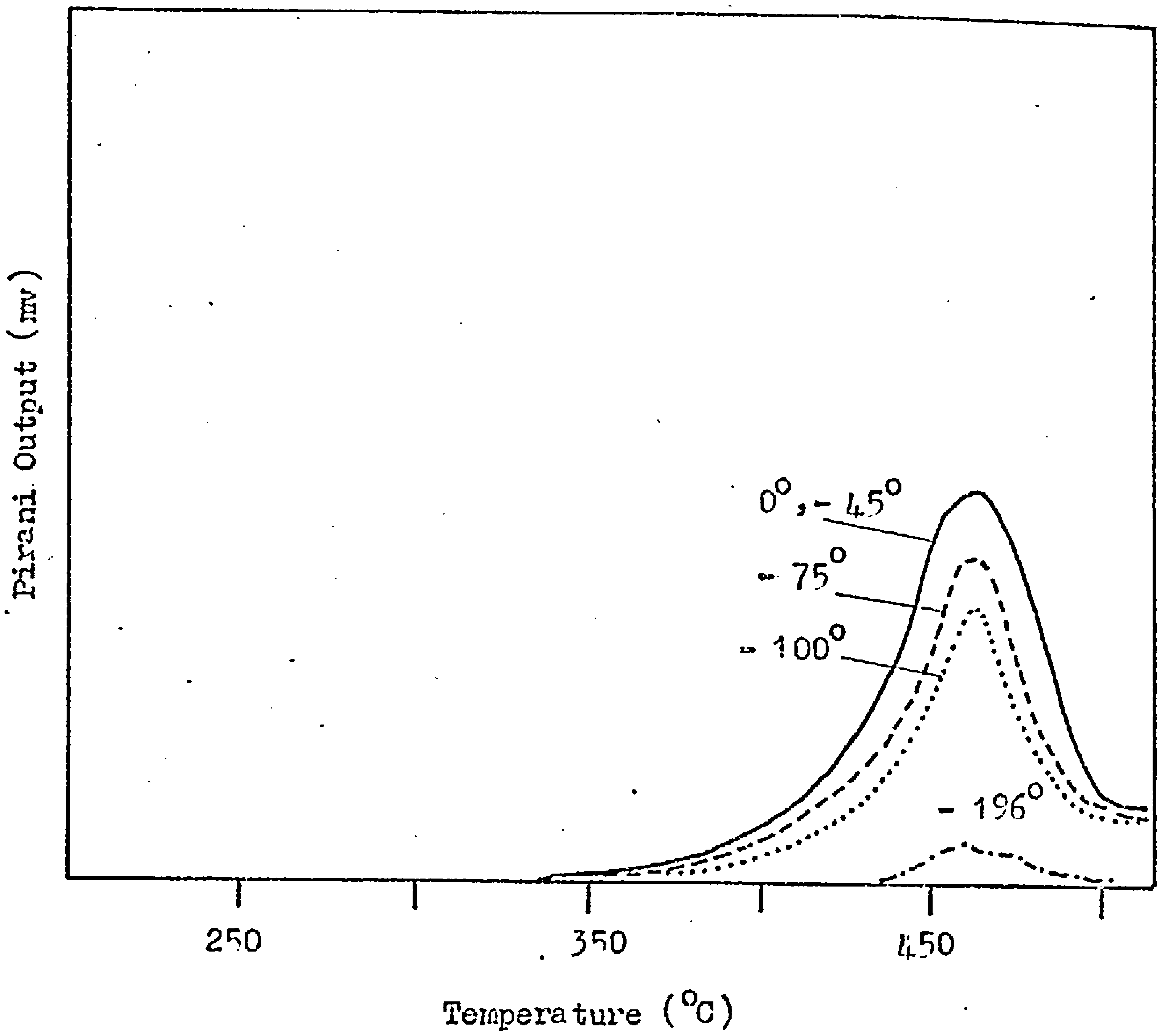


FIGURE 7.26 TVA curves for simultaneous degradation of PE and PP (25 mg) (a) unmixed and (b) mixed Heating rate 10°/min.



<u>FIGURE 7.27</u> TVA curves for a 1 : 1 by weight mixture of PE and PP pre - irradiated for 20 hours at 20°C. 50 mg sample. Heating rate 10°/min.

with the PS - PP system in which degrading PS destabilises PP.

FIGURE 7.27 illustrates the TVA thermogram of a 1 : 1 by weight mixture of PP and PE, pre - irradiated for 20 hours at room temperature. The only difference from the trace of its un - irradiated counterpart (FIGURE 7.26(b)) is the fact that the the PP degradation peak commences at lower temperatures. This finding is in keeping with the results of Chapter 4.

e) Conclusions

In addition to PP - PMMA mixtures, polymer interaction has been observed in the thermal degradation of four other polymer pairs containing PP as the common polymer. However, of the systems studied, only the interaction of PP and PAMS resembles that of the PP - PMMA system. The reason for this similarity almost certainly lies in the similar modes of thermal degradation of PMMA and PAMS. For this same reason, the destabilisations of PP by degrading PS and of PE by degrading PP also show similarities.

The thermal degradation of PVC is unique in this investigation in that it is primarily concerned with elimination reactions. Although the delay of hydrogen chloride evolution in PP - PVC blends has been attributed to interaction of chlorine radicals with PP, the possibility nevertheless exists that this may be caused by diffusion effects or reaction of hydrogen chloride with PP. However, considering the weight of evidence in other polymer blends containing PVC (112), polymer interaction appears more likely.

Further experimentation is required in the room temperature photolyses of the polymer blends before any firm conclusions may be drawn.

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