

The Photolysis of Poly-Acyl  
Styrene Polymers

by

© Kenneth G. Whiting ©

A M.Sc. Thesis submitted to the Department of Chemistry  
in partial fulfillment of the requirements for admittance  
to the Degree of Master of Science.

Lakehead University

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## Abstract

The following is a study of the long wave (wavelength  $\geq 300$  nm) photolysis of a series of poly acyl styrenes, in particular, poly-*p*-acetyl-styrene (PPAS), poly-*p*-propionyl-styrene (PPPS), poly-*o*-acetyl-styrene (POAS), poly-*o*-propionyl-styrene (POPS).

All photoreactions are initiated from the carbonyl triplet. It is seen that in the solid state, below  $T_g$  the main photoprocesses that take place in all systems are Norrish I cleavage and photoreduction. In addition, the *ortho* polymers have the proper structure to allow for photoenolization. Gas product analysis of these *ortho* polymers, in the solid state below  $T_g$ , suggest evidence for ground state control. Transient spectroscopy does indicate the presence of enol formation in these *ortho* polymers. Viscosity studies on solutions showed that secondary reactions with these polymers include competitive cross linking and chain scission. There is a definite solvent effect observed for all of these systems and the solvent quality has an effect on the balance of these secondary reactions. A detailed explanation of this solvent effect is discussed.

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## Introduction

### 1.1 Basic Photochemistry

Photochemistry deals with those processes in which light interacts with matter and brings about chemical reactions.<sup>1</sup> Upon absorption of a photon, the electronically excited molecule can undergo a number of photophysical processes which compete with the photochemical processes and return it to the ground state.<sup>1,2</sup>

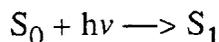
One of the basic laws of photochemistry, that of Grotthus and Draper, states that only photons that are actually absorbed by a molecule are capable of producing a photochemical change. This however, does not mean that absorption of a photon will necessarily bring about a photochemical change in the system as there may well be other more favourable processes by which the system can dissipate energy to return to its ground state (for example, fluorescence, phosphorescence, etc).<sup>1</sup>

The absorption of a photon is a resonance process which only occurs if the energy of the photon is equal to the energy difference between the the ground state and an excited state (usually the first excited state) of the absorbing species. The energy of the photon, E is expressed as follows, for example:

$$E = h\nu = E_2 - E_1$$

Where  $E_2$  and  $E_1$  are the energies of the excited and the ground states, respectively,  $\nu$  is the frequency, and  $h$  is Planck's constant.

Transition occurs between ground state singlet and excited state singlets as there can be no change in multiplicity:



According to the Frank Condon Principle this electronic transition takes place faster than the time required for atomic displacement (typically  $10^{-16}$  s, compared

to a vibration period of  $10^{-13}$  s ) [Fig. 1.1 and 1.2].<sup>4</sup>

The excited state of a system can dissipate energy via a number of photophysical processes or by undergoing a photochemical change. These processes are summarised in Fig. 1.1 and are described below. Photophysical processes allow excited electronic excitation to be dissipated, either by emission of a photon (luminescence) or by transferring the energy to other forms (usually to the vibrational modes of the system) [Fig. 1.1].<sup>1</sup>

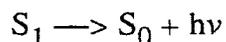
Vibrational relaxation is one of the forms of radiationless decay which occurs by a transition from a high vibrational level of a given electronic state to the lowest vibrational level of that electronic state. In this instance the energy is dissipated as heat. This process is very fast ( $k \leq 10^{12} \text{ s}^{-1}$ ) [Fig. 1.1].<sup>2</sup> Internal conversion also occurs with the electronic energy being dissipated in the vibrational modes, and the system returns to a ground electronic state [Figures 1.1 and 1.2].<sup>1,2</sup> It should be noted that, with vibrational relaxation and internal conversion, no change in multiplicity occurs.

Intersystem crossing involves a change in the electronic multiplicity. This radiationless decay occurs between two vibrational levels of two different electronic states that have equal, or almost equal, energy [Fig. 1.1 and 1.2]. This flip in spin converts the system from a singlet state to a triplet state, or *vice versa*:



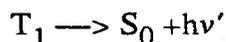
where  $T_1$  is the first triplet state. The time for intersystem crossing from a singlet to a triplet state ranges from  $10^{-8}$  to  $10^{-11}$  s [Fig. 1.1].<sup>2</sup> Luminescence involves the emission of a photon as the electron returns to its ground state, as follows:

1) Fluorescence: This is a radiative transition between electronic states of the same multiplicity. Usually fluorescence occurs between the lowest vibrational level of the first excited singlet state and the the lowest vibrational level of the electronic ground state as follows:



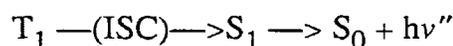
This is also known as prompt fluorescence. The process is very fast ( $10^{-6}$  to  $10^{-11}$  s) due to the lack of change in multiplicity.<sup>1,2</sup>

2) Phosphorescence: This is a radiative transition between states of differing multiplicities and usually takes place between the lowest vibrational level of the first triplet state and the lowest vibrational level of the ground singlet state as follows:



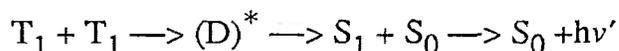
Because there is a change of electron spin, the process is slower ( $10^{-5}$  to 10 s).<sup>1,2</sup>

Delayed fluorescence occurs as follows. From reverse intersystem crossing in which the triplet is converted into the singlet, which fluoresces in the following manner:



This is sometimes referred to as e-type emission.<sup>1,2</sup>

Delayed fluorescence can also be brought about by triplet-triplet annihilation to yield the first excited singlet state, from which fluorescence can occur. One singlet ground state system is also formed as follows:



where  $(D)^*$  is an excited intermediate complex. This process is also referred to as p-type emission. Triplet-triplet annihilation is a bimolecular process that requires that the two excited species get close enough together to form a complex. This is basically an energy transfer process:



Where  $D^*$  and  $A^*$  are the excited donor and acceptor molecules, respectively, and  $(D-A)^*$  is the excited transition complex.<sup>1,2</sup>

The transition states are known as excimer or exciplex complexes, depending on the nature of the donor and acceptor molecule. Excimer complexes arise from an energy transfer between chromophores of the same species, the excited chromophores in the same molecule for example.<sup>1,2</sup> Exciplex complexes arise from an energy transfer between chromophores that belong to two different molecules. Triplet-triplet annihilation can arise from either excimer or exciplex formation.<sup>1,2</sup>

Fig.1.1  
POTENTIAL ENERGY DIAGRAM REPRESENTING  
PHOTOPHYSICAL PROCESSES INVOLVING ELECTRONICALLY  
EXCITED STATES  $S_1$  AND  $T_1$

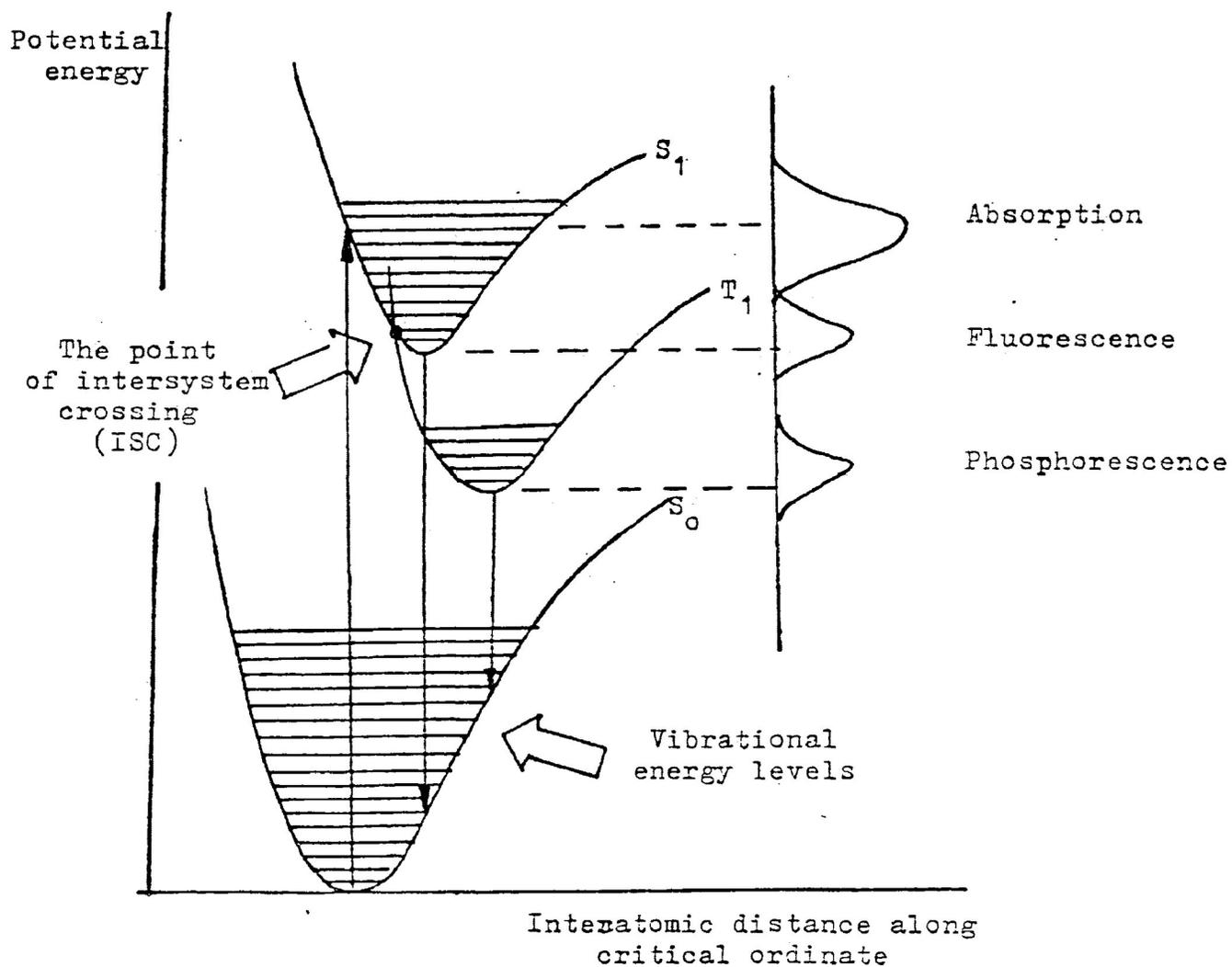
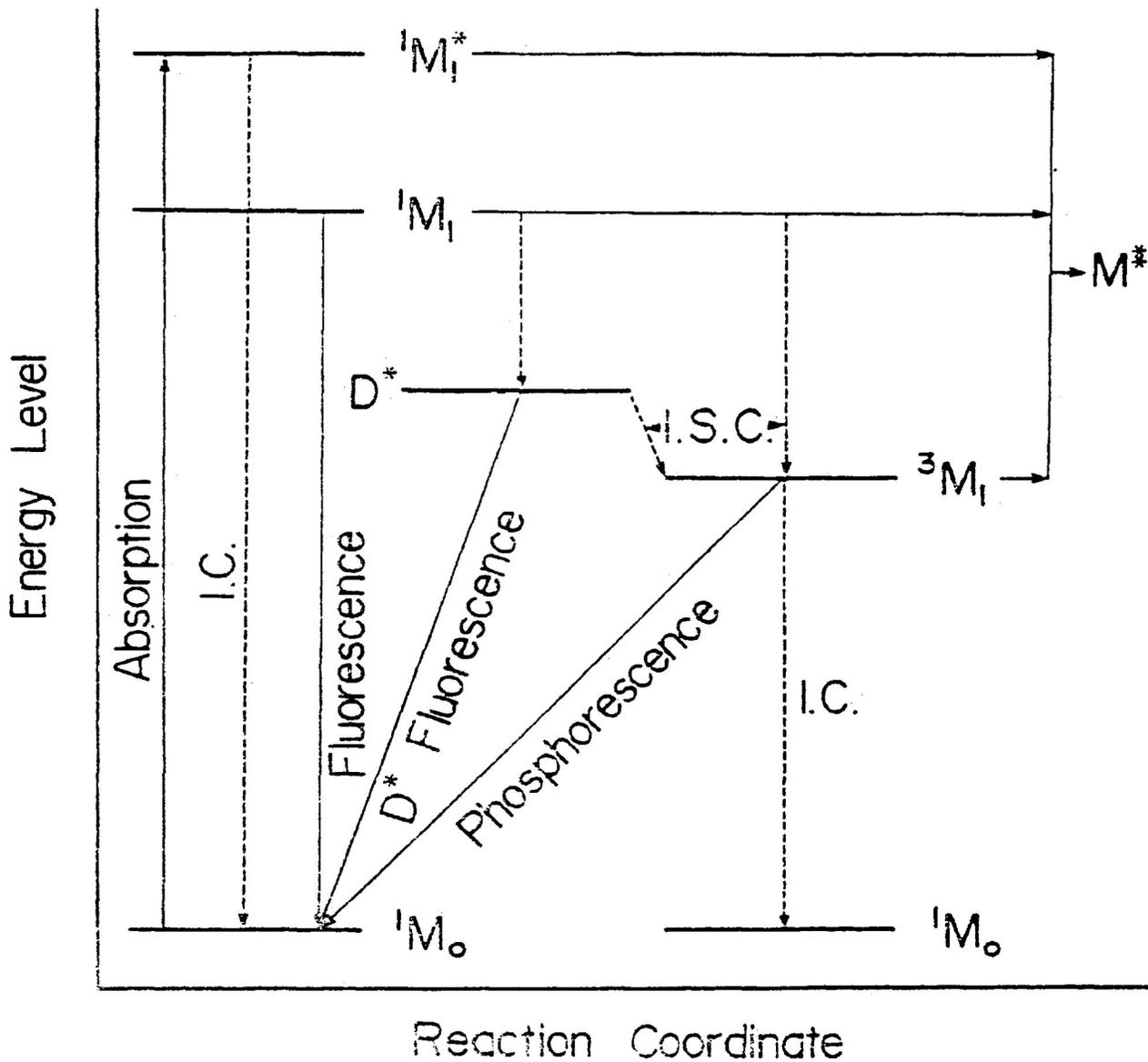


Figure 1.2 - Excited States and Photophysical Transitions in a 'Typical' Polymer System



Radiative transitions are given by bold lines, radiationless processes by dashed lines.  $D^*$  represents the eximer.  $M^*$  represents energy directly available for photochemical reactions.

## 1.2 Photoreactions of Ketones

The photoreactions of small ketone molecules have been widely studied over the past 50 years and these studies have shed a lot of light on the mechanisms of these reactions. This understanding of reactions of small keto molecules has led to a better understanding of the mechanisms of reactions that take place in large keto molecules. The carbonyl function is very interesting from a photochemical point of view. This chromophore is capable of absorbing light in the near ultraviolet region, sometimes within the range of terrestrial sunlight radiation (wavelengths  $>290$  nm).

Many studies have been carried out on the photochemistry of ketones, the classical work being done by Bamford and Norrish around the mid 1930's.<sup>2</sup> For most simple aliphatic ketones there is a single absorption in the near ultraviolet region (at 280 nm) and this is associated with the  $n \rightarrow \pi^*$  transition of the carbonyl group. In the case of aromatic ketones, there are two absorptions with the first absorption occurring around 310 nm, and it is associated with the  $n \rightarrow \pi^*$  transition of the carbonyl function. The second transition occurs around 280 nm and is associated with the  $\pi \rightarrow \pi^*$  transition of the aromatic ring. (see Fig. 1.3 for a typical ultraviolet spectrum of an aromatic ketone molecule). The shift to the longer wavelengths shown by  $n \rightarrow \pi^*$  transitions in the aromatic ketones is due to the inductive effect of the aromatic ring, which lowers the energy between the ground and excited states of the carbonyl group.<sup>2</sup>

It is the  $n \rightarrow \pi^*$  transition of the carbonyl function that gives rise (via excited states) to the numerous photoreactions of ketones. The absorption associated with having the  $n \rightarrow \pi^*$  transition is very weak, (an extinction coefficient of  $\leq 150 \text{ cm}^{-1} \text{ mol}^{-1}$ )<sup>2</sup>. The reason for this being that the  $\pi^*$  carbon orbitals and the non-bonding orbitals of the oxygen are orthogonal to each other, and the  $n \rightarrow \pi^*$  transition is symmetry forbidden. The transition is spin allowed however, so the transition probability is low.<sup>2</sup>

Photoreactions of aliphatic ketones can arise from either the excited singlet or triplet state of the carbonyl. However, photoreactions of aromatic ketones tend to arise only from the triplet state of the carbonyl because of the high efficiency of intersystem crossing (quantum yields for ISC are around unity for the aromatic ketones).<sup>2</sup>

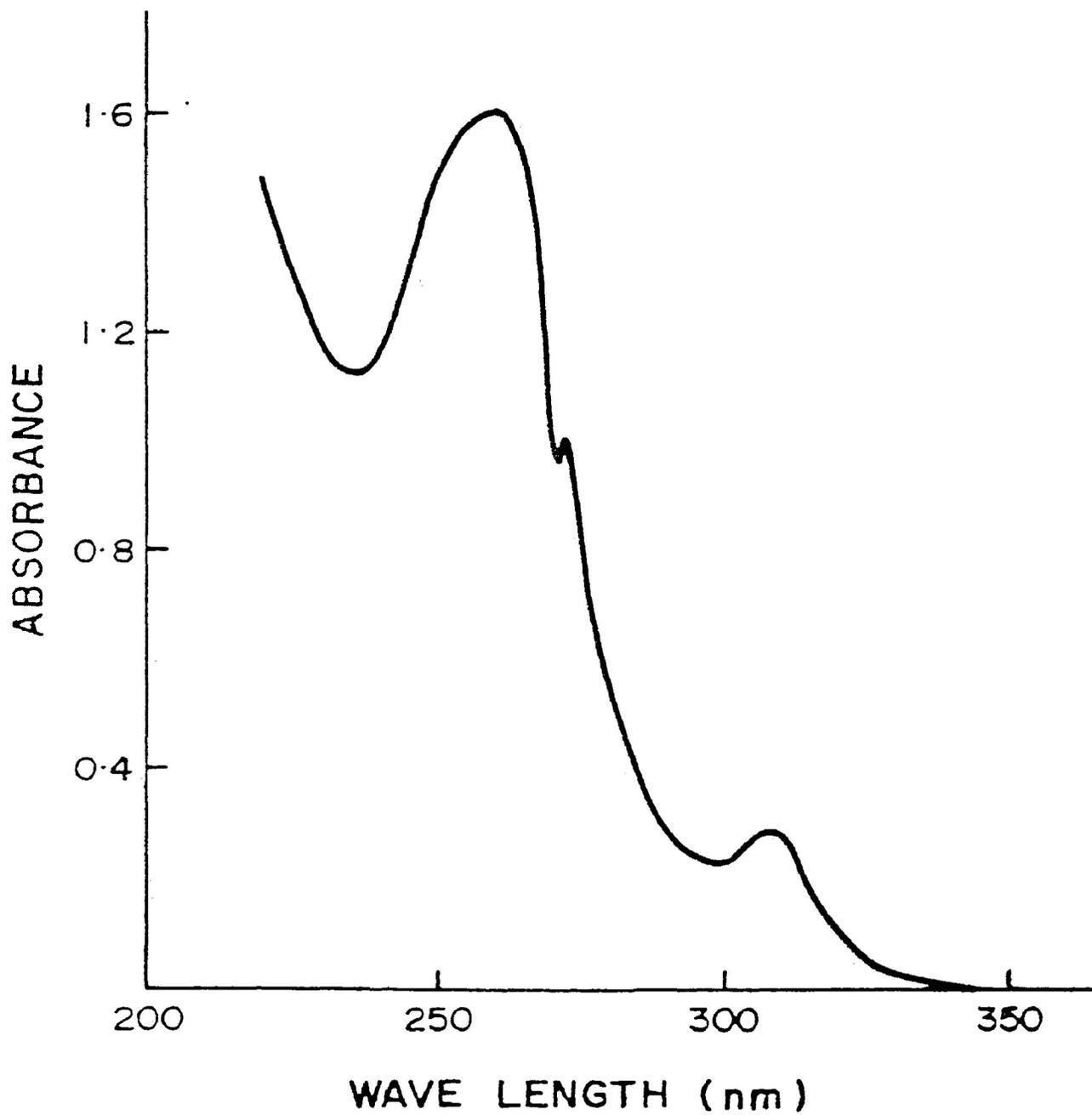


Fig.1.3 'Typical' UV Spectrum of an Aromatic Ketone

Photoreactions of ketones can be classified as follows: 1) Alpha Cleavage (Norrish Type I reaction), and 2) Hydrogen Abstraction Reactions which include a large number of reactions, including the Norrish Type II reaction, photoreduction, and a number of other inter and intramolecular hydrogen abstraction reactions. Details of these reactions will be discussed below.

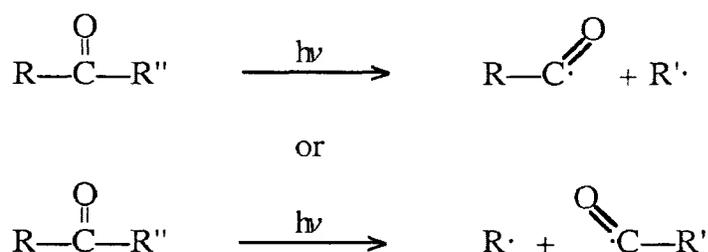
Two factors that greatly influence the photochemistry of aliphatic ketones are the carbonyl concentration and the effect of the solvent.<sup>5</sup> Forgeteg and Berces<sup>5</sup> have shown that the rates of non-radiative transitions of singlet acetone, acetone d<sub>6</sub>, and hexafluoro-acetone are greater in solution than in the gas phase. At the same time, singlet lifetimes of acetone seem to be independent of the solvent polarity. It has been found by Encinas<sup>6</sup> that the solvent effect for aliphatic ketones having gamma hydrogens is pronounced, and is reflected in a decrease in the fluorescence lifetime with increasing solvent polarity. This effect was attributed to an increase in the rate of the Norrish Type II reaction. (which will be discussed in detail below). The main reaction pathway of excited singlet aliphatic ketones that do not contain gamma hydrogens, is believed to be through intersystem crossing (ISC) and the rate is dependent on substitution in the position alpha to the carbonyl function. ISC tends to decrease with increasing methyl substitution.

Forgeteg and Berces<sup>5</sup> showed that the quantum yields of triplet formation in a series of alpha substituted aliphatic ketones depended on: 1) the extent of alpha substitution, 2) the concentration of the ketone, and 3) the nature of the solvent.

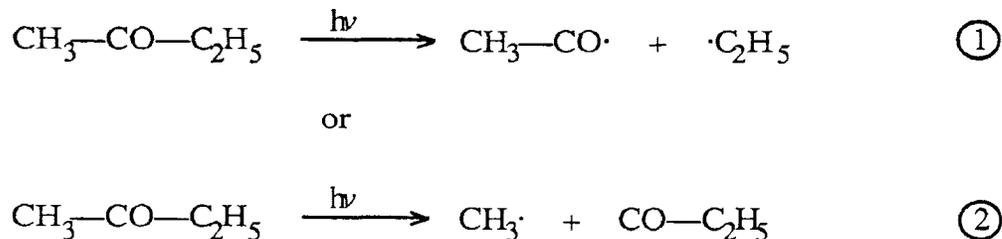
Triplet yields decrease with increasing alpha methyl substitution which was attributed to the lower rates of ISC for multiple alpha substituted ketones compared to that of straight chained ketones. Also, the rate of Norrish Type I cleavage, arising from the singlet ketone, varies with alpha substitution; increased substitution decreases the strength of the carbon-carbon bond alpha to the carbonyl function leading to an increase in the rate of alpha bond scission. This competing factor decreases the rate of ISC and, hence, quantum yields of triplet state formation become considerably less than unity for these ketones.<sup>5</sup> The decrease in triplet state yield with increasing solvent polarity, increasing alpha methyl substitution, and increasing ketone concentration suggests that singlet excimers are formed. All these factors are known to increase the rate of excimer formation.<sup>5</sup>

### 1.2.1 Alpha Cleavage (Norrish Type I Reaction)

This reaction is simply the homolytic cleavage of bonds adjacent to the carbonyl chromophore resulting in the formation of two free radicals.<sup>2</sup>



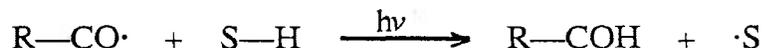
Where R and R' are two alkyl or aryl groups. If the two groups are different, then both reactions may occur. There is, however, a preference for cleavage of the weaker bond when the wavelength of the light is longer. For example, methyl-ethyl-ketone can undergo the following reactions:



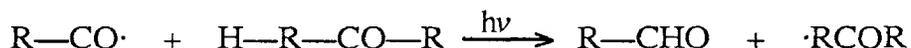
It has been shown that the quantum yield ratios of the two reactions ( $\phi_1/\phi_2$ ) vary with the energy of the incident light.<sup>2</sup> For example, at 310 nm the ( $\phi_1/\phi_2$ ) ratio is approximately 40, meaning that reaction (1) is favoured. However, if the wavelength of incident light is decreased to 254 nm, the ( $\phi_1/\phi_2$ ) ratio drops to 2.4. The increase in the energy of the light leads to the formation of the less stable methyl radicals.<sup>2</sup> In effect the reaction pathway depends critically on the stability of the radicals formed. As alkyl groups become more substituted the stability of the radicals formed is greater and, hence, the probability of their formation increases.<sup>2,3</sup>

The fate of the radicals formed depends on the environment in which the reaction takes place. If the reaction takes place in a solvent which has an easily abstractable hydrogen atom, for example, the radicals react with the solvent molecule

(S-H).



If the reaction is carried out with liquid or the solid phase ketones, the radical can abstract an hydrogen from another ketone molecule:



Again, the the point of abstraction depends on the strength of the carbon-hydrogen bond and, with it, the stability of the new radical formed. Tertiary hydrogens are abstracted more readily than secondary hydrogens, which are in turn preferred to primary hydrogens.

It is also possible for the (R—C—O·) radical to undergo decarbonylation.<sup>7</sup> Gould<sup>7</sup> has investigated the photocleavage of dibenzyl ketones and it was observed that these systems undergo alpha cleavage (the rate of cleavage was measured to be  $10^{10} \text{ s}^{-1}$ ).<sup>7</sup> Again the cleavage pattern depends on the relative stability of the radicals.



The rate of decarbonylation is also dependent on the structure of the new radical (R'·) formed. The more substituted the position alpha to the carbonyl is, the greater the stability of the new radical produced and, hence, the faster the rate of decarbonylation.

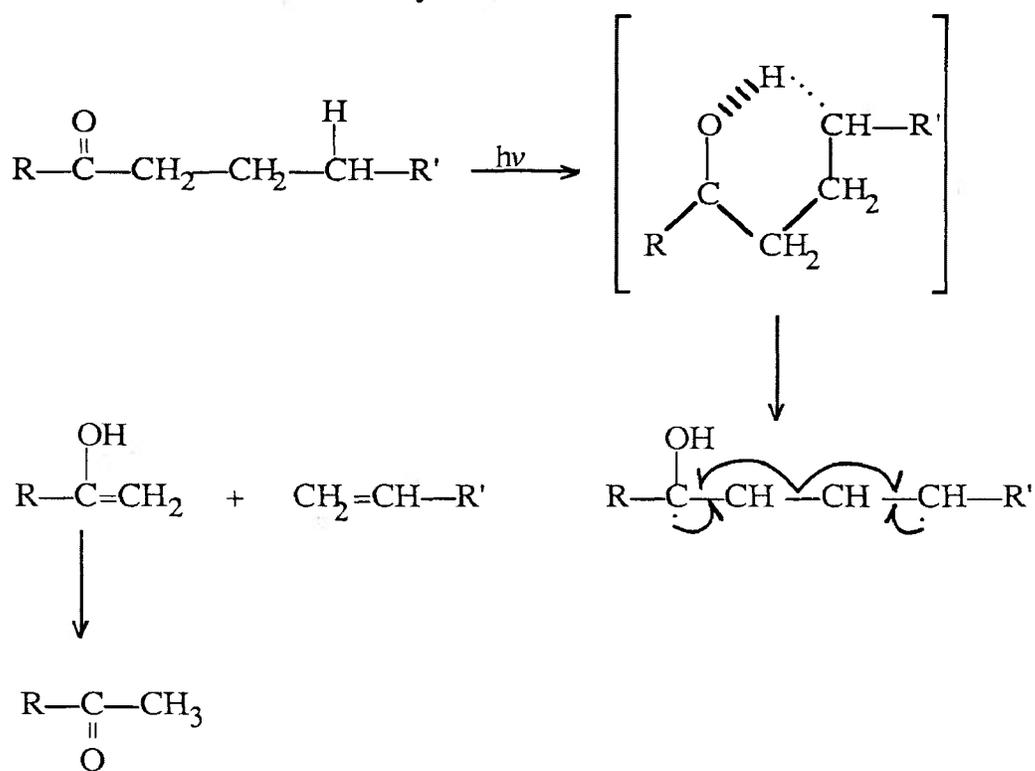
Gould<sup>7</sup> has shown that for the reaction:



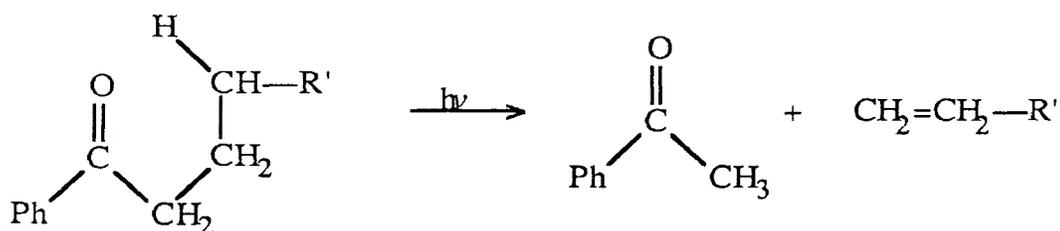
the rate of decarbonylation is 7.5 times greater if R is a methyl group as opposed to an hydrogen atom.

### 1.2.2 Hydrogen Atom Abstraction

The classical hydrogen atom abstraction reaction is known as the Norrish Type II reaction, which is an intramolecular type hydrogen abstraction. For the Norrish Type II reaction, the atom that is abstracted is in the gamma position, to the carbonyl group and this imposes some structural limitations on the reaction. The reaction leads to cleavage of the alpha-beta carbon-carbon bond (relative to the carbonyl function), yielding an unsaturated species and an enol. The enol rapidly tautomerizes back to another carbonyl function.<sup>1,2,3</sup>



It was observed by Yang<sup>8</sup> that cyclobutanol is also formed in such an elimination and it was proposed that the reaction proceeds through a 1,4-biradical intermediate.<sup>8</sup> Wagner<sup>9</sup> confirmed the presence of a 1,4-biradical intermediate through biradical trapping experiments. Phenyl-vinyl-ketone also undergoes a Type II elimination reaction from its lowest excited triplet state:



Quantum yields for the Type II reaction tend to be quite low in hydrocarbon solvents, since the 1,4-biradical disproportionates back to the starting ketone. At the same time polar solvents tend to stabilize the the biradical, and hence, increase the quantum yields to about unity. The biradical trapping experiments on phenyl alkyl ketones allow for determination of biradical lifetimes, which were of the order of  $10^{-6}$  -  $10^{-7}$  s and the triplet lifetimes of these systems were found to be of the order of  $10^{-8}$ s. These short triplet lifetimes are typical for systems that undergo the Norrish II reaction.

In order for the gamma hydrogen to be abstracted it has to be in the proximity of the excited carbonyl (as Winnik<sup>10</sup> terms it "within the reactive volume about the carbonyl function") and this is what imposes conformational control over the biradical formation. The gamma hydrogen atom has to be in the syn conformation (relative to the carbonyl function); which leads to a strain free 6-membered intermediate in the chair configuration.<sup>11</sup> This means that if the gamma hydrogen is in the anti conformation the system must rotate (about a carbon-carbon) to bring the system into a syn conformation prior to undergoing to Type II reaction. If the triplet lifetime is much shorter than the time it takes for the bond rotation into the syn conformation, then the only ketones that will react to form the 1,4-biradical are those that are already in the syn conformation. This imposes, what Wagner<sup>11,12</sup> refers to as, ground state control on the system.

The first example of ground state control was observed by F.D. Lewis<sup>13</sup> in 1-benzoyl-1-methyl-cyclohexane. It was observed that this system undergoes both alpha cleavage as well as gamma hydrogen abstraction. it was also found that both competing reactions occur from two kinetically different triplets. Quenching experiments indicated that the products of the two different reactions are quenched with different efficiencies. The measured rate constant for alpha cleavage was found to be  $2 \times 10^7 \text{ s}^{-1}$ , whereas the rate constant for gamma hydrogen abstraction was found to be  $6 \times 10^8 \text{ s}^{-1}$ .<sup>13</sup>

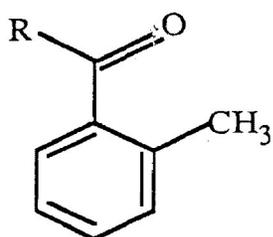
This system is capable of existing in two different conformations:



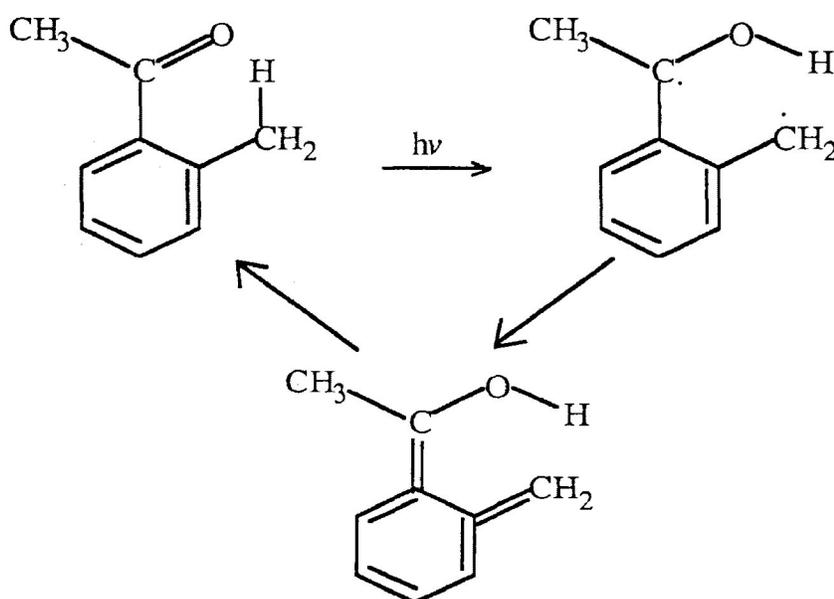
Alpha cleavage arises from the triplet state in the anti conformation, whereas the gamma hydrogen abstraction arises from the triplet in the syn conformation. The fact that both of these reactions are observed indicates that the triplet reacts faster than the system can undergo a conformational change (ring inversion). The rate constant of ring inversion is of the order of  $10^5 \text{ s}^{-1}$ . This means that the conformation of the system at the time of excitation determines which reaction will occur.

Ground state control was also observed by Wagner<sup>11,12</sup> with 4-benzoyl-4-methyl-piperidines. Again it was observed that these systems underwent both alpha cleavage as well as gamma hydrogen abstraction (these two reactions arise from two conformationally different triplets). The product from alpha cleavage (benzaldehyde) was found to represent 75% of the products. Indicating that the reactants are mostly in the anti conformation at the time of excitation. One interesting aspect of these reactions was that of the quencher selectivity. In the presence of sufficient quencher the alpha cleavage reaction was completely quenched. However, the only reaction arising from the gamma hydrogen abstraction, was cyclization. It is known that cyclobutanol formation from the 1,4-biradicals is not quenched. The rate constant for gamma hydrogen abstraction was  $2 \times 10^8 \text{ s}^{-1}$ , which is much larger than that for the cyclohexane derivative. This rate enhancement reflects a stereoelectronic effect; the lone pair of electrons on the nitrogen lie trans periplanar to the axial gamma hydrogen-carbon bond.

If the triplet lifetime is longer than the time it takes for the system to undergo a conformational change then one gets what Wagner<sup>11,12</sup> refers to as rotationally controlled hydrogen abstraction, which is seen clearly in the photoenolization of *ortho*-alkyl-phenyl-ketones.<sup>11,12,14</sup>



The triplet abstracts the gamma hydrogen to yield the 1,4-biradical, which decays to form the enol, which in turn tautomerizes back to the ketone. A simplified mechanism of the reaction is :



Wagner's<sup>11,12</sup> studies of 2-methyl-acetophenone and 2-methyl-benzo-phenone show that enolization arises from two conformationally different triplets, one with a lifetime of the order of 1 nanosecond and the other of the order of 30 nanoseconds.

The triplet that arises from the ketone in the syn conformation was assigned the 1 nanosecond lifetime. This is because it compares to the triplet lifetime of 8-methyl-tetralone (has a triplet lifetime of the order of 1 nanosecond), which is locked in the syn conformation. The triplet with the 30 nanosecond lifetime has been assigned to the ketone in the anti conformation. In the anti conformation there is no gamma hydrogen within the reactive volume around the carbonyl. Therefore, the carbonyl group must rotate into the syn conformation in order to allow hydrogen

atom abstraction, and this rotation has to occur over a substantial potential barrier.

Studies by Wagner<sup>11,12</sup> on a number of these *o*-alkyl-phenyl-ketones indicate that this rotation is the rate determining step for the hydrogen abstraction reaction.<sup>15</sup> Therefore, enolization of the syn triplet involves gamma hydrogen abstraction whereas, the longer lived triplet is due to the anti conformer and rotation must precede gamma hydrogen abstraction.

Valerophenones<sup>11</sup> with *ortho*, methyl, deuterated methyl, and ethyl groups all undergo a competitive Type II photoelimination (Norrish Type II reaction) and photoenolization, the rate of photoenolization being roughly constant for these systems. This would indicate that gamma hydrogen abstraction is not the rate determining step for enolization, compared to the Type II reaction in which rate constant is dependent on the dissociation energy of the carbon-hydrogen bond. In addition, it was observed that additional ring substituents, which decrease rates of gamma hydrogen abstraction (by stabilizing the ketone pi, pi\* triplet) have no effect on the longer lived triplet.

Scaiano<sup>14</sup> proposed that in addition to there being two distinct triplets (arising from two distinct ground states) there are two conformationally different enols formed. However, both systems proceed through a common 1,4-biradical intermediate and triplet lifetimes for *o*-methylbenzaldehyde (in wet acetonitrile) were reported<sup>14</sup> to be 1.1 and 95 nanoseconds for the syn and anti conformers, respectively. It was found that the syn triplet represents 58% of the reaction mixture; and 42% is made up of the anti conformer. The biradicals are produced with a quantum yield of 0.83 and have a relatively long lifetime (1.5 microseconds)<sup>14</sup>, which means that once the biradical is formed it has time to undergo rotation about a carbon-carbon bond and form the anti conformer, and hence, decay of the biradical one can expect two conformationally different enols.

The reactions are summarized in Fig 1.4 :

For ketones that contain delta hydrogens it is possible that the carbonyl triplet could approach sufficiently close to abstract that hydrogen resulting in the production of a 1,5-biradical. Early work done by Wagner<sup>16</sup> examined the rate of delta hydrogen abstraction compared to that of gamma hydrogen abstraction. Delta-methoxy valerophenone contains both delta and gamma hydrogen atoms, and the presence of a methoxy group adjacent to a methylene group is known to enhance the reactivity of the carbon-hydrogen bonds thus the reactivity of the delta and

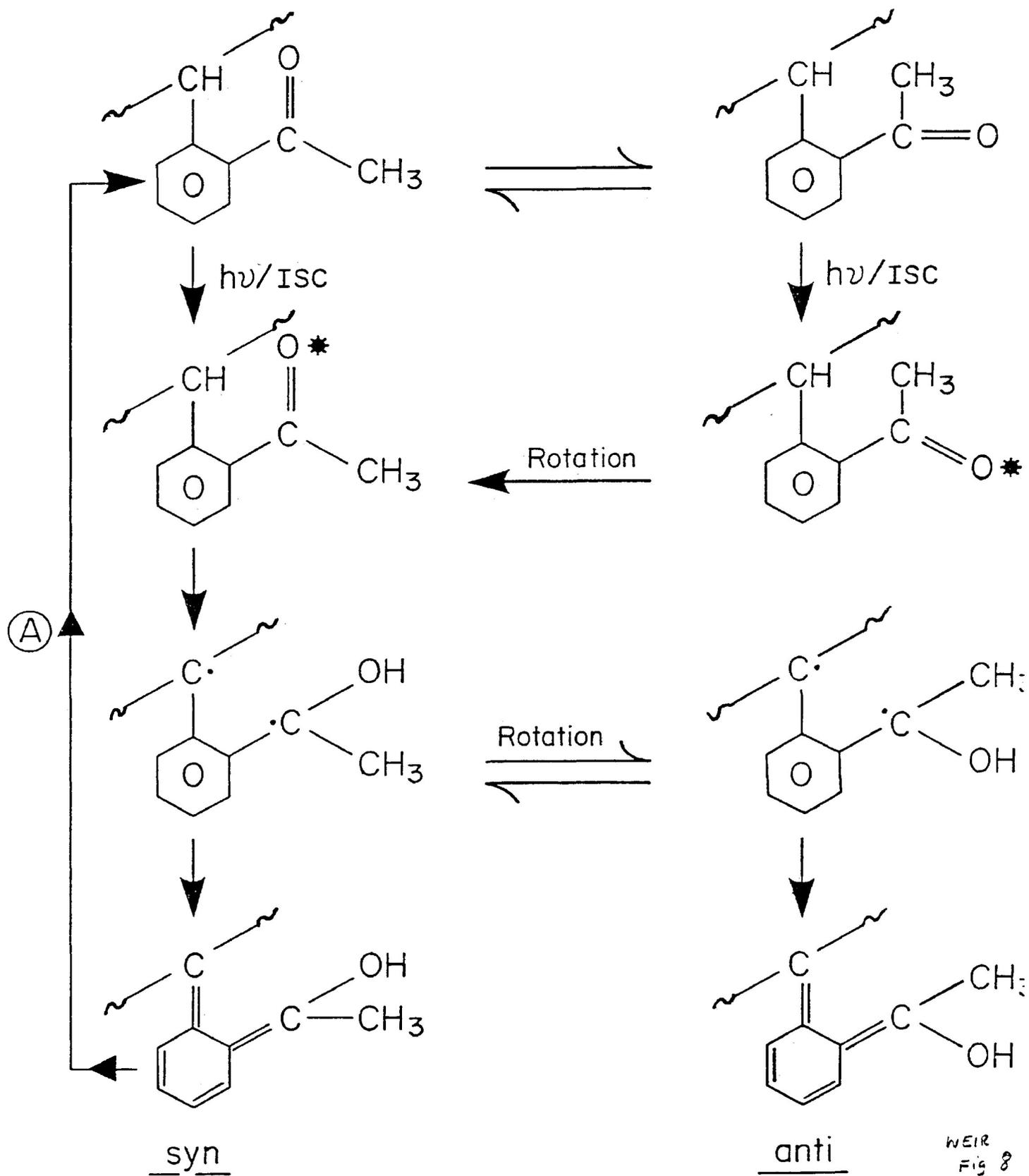
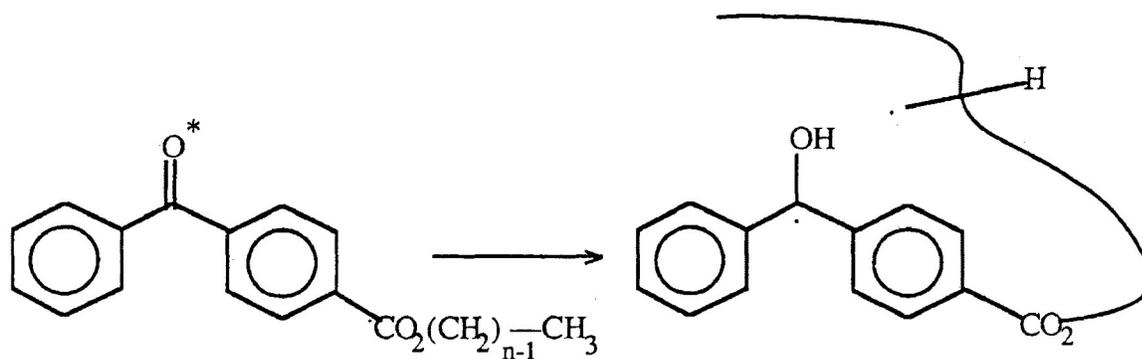


Fig.1.4 Photoenolization of 2-Methylacetophenone

gamma hydrogens should be similar. It was shown that both delta and gamma hydrogen abstraction were taking place with a gamma/delta reactivity ratio calculated to be 20, indicating that the gamma hydrogen is 20 times more reactive than the delta hydrogen, despite the enhanced reactivity of the delta hydrogen. In addition, where deuterium replaces the gamma hydrogen the gamma/delta reactivity ratio is reduced to 5.

The 1,5-biradical can undergo reactions similar to the 1,4-biradical counterpart. For example, it can undergo disproportionation back to the original ketone, cyclization to form cyclopentanol, or farther reaction (abstraction) with solvent or other ketone molecules. However the most common reaction observed is cyclization. The geometry of the carbon atoms to which delta and gamma hydrogens are bonded has no effect on the reactivity of hydrogen abstractions and alkyl substitutions in the beta and delta position have little effect on gamma hydrogen abstraction, but such substitutions to have a large effect on delta hydrogen abstraction.<sup>16</sup> The transition states for both gamma and delta hydrogen abstractions involve a 6 and 7-membered cyclic intermediate system, respectively, the 7-membered species being less favored from both statistical and an energetic point of view. However, the 6-membered cyclic transition state has the ability to form a relatively strain free chair configuration, which this is not possible for the 7-membered intermediate.<sup>12,16</sup> When there are no accessible gamma hydrogens, delta hydrogen abstraction will readily take place. Wagner<sup>11,12</sup> has observed that with several *o*-alkoxy phenyl-ketones, the main products of irradiation are benzohydroxyfurans which arise from the cyclization of the 1,5-biradicals, produced by delta hydrogen abstraction.

Winnik<sup>10</sup> has examined remote hydrogen abstractions in a series of *n*-alkyl-esters of 4-benzoyl-benzoic acid in order to assess chain coiling probabilities.



The rate of remote hydrogen abstraction is proportional to the probability that a given methylene group will occupy the reactive volume around the excited carbonyl triplet during its lifetime. Hydrogen abstraction occurred to a negligible extent when  $n < 9$ , however, it increases by about  $0.5 \times 10^4 \text{ s}^{-1}$  for each additional methylene group. The rate constants reflect an increase in the probability of forming cyclic configurations as chain lengths increase. At  $n=20$  the observed rate constant is  $4.6 \times 10^4 \text{ s}^{-1}$ , with an approximately equal probability that any one of the hydrogens from C-10 and C-19 will undergo abstraction.

### 1.3 The Photochemistry of Keto Polymers

In polymeric systems the carbonyl group is important, not only in its own right, but also because it is known to initiate and propagate the photooxidation processes as a result of exposure of these polymers to terrestrial sunlight radiation.<sup>1</sup> The mechanisms of the photochemical reactions of small molecule carbonyl compounds, in both the gas phase and solution have been extensively studied and it has been found that the behaviour of the carbonyl chromophore does not change significantly from small molecules to long chain polymers. However, there are a few significant differences, and these often reflect the long chain nature of the polymer and the restricted environment the system imposes on the dynamics of the polymer chain.<sup>1,17</sup>

The major photochemical reactions that originate from the excited  $n \rightarrow \pi^*$  triplet state of the carbonyl are:

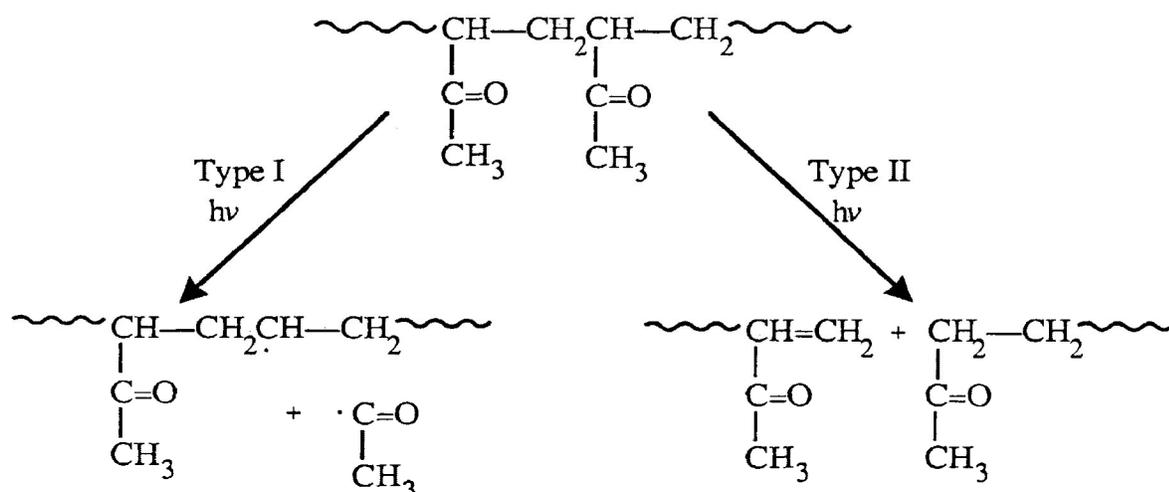
1) Norrish Type I Reaction: Alpha cleavage which results in the production of free radicals.

2) Norrish Type II reaction: A photoelimination reaction which results in the formation of an olefin and another ketone.

3) Photoreduction: This reaction results from the remote hydrogen abstraction by a carbonyl to form an enol. This can be either inter, or intramolecular in nature depending on the location of the hydrogen atom to be abstracted.

The Norrish Type I reaction is usually important only when a tertiary radical (relatively stable) is produced and the environment allows for diffusion of the two radicals away from each other.

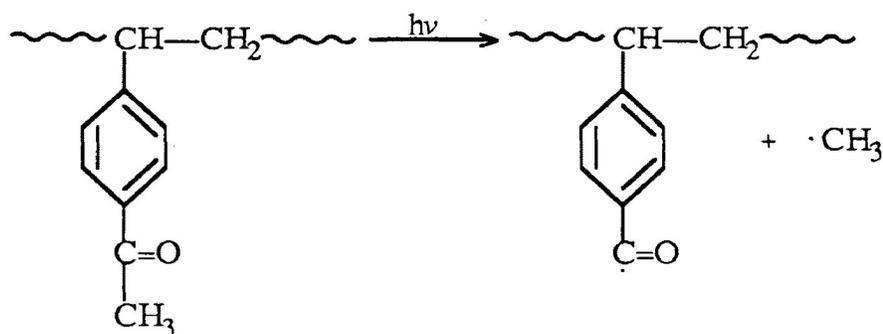
The photochemistry of keto-polymers was studied by Guillet and Norrish and it was seen that poly methyl vinyl ketone (PMVK) underwent both Norrish Type I and Type II reactions.<sup>18,19</sup>



The Type II reaction leads to main chain scission and hence to a reduction in the molecular weight of the polymer. The Type I reaction produces an acetyl radical from (alpha scission) which can stabilise itself by abstracting a hydrogen atom either from the polymer chain or from a solvent molecule. Also acetyl radicals, particularly those that are vibrationally excited can further decompose (to  $\text{CH}_3\cdot$  and  $\text{CO}$ ).

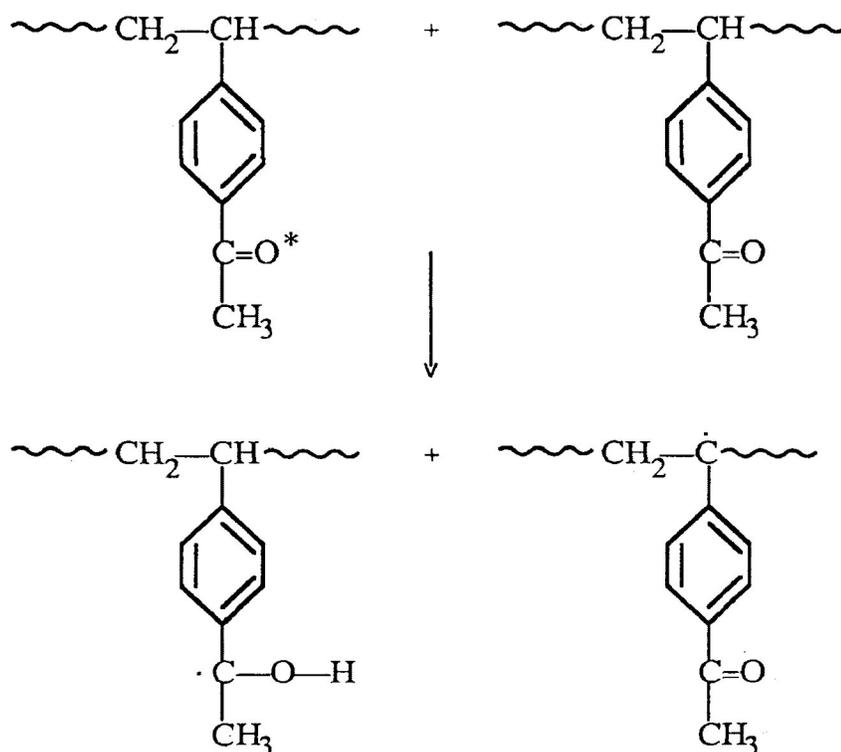
Guillet<sup>1</sup> has shown that in cases where both Norrish Types I and II reactions are possible, the probability of the Type II process occurring is usually greater. Also the efficiency of the Type I process is strongly dependent on the stability of the radical formed, and the ability of the radicals to diffuse away from each other before they recombine within the initial cages.

When a Norrish Type II reaction cannot occur, the only pathways by which photodegradation can occur are by the Norrish Type I reaction or by photoreduction as was shown by Weir and Milkie<sup>20</sup> (photolysis of poly-vinyl-acetophenone), (PVAP). Here a Norrish Type II reaction is impossible due to the lack of any gamma hydrogens; but, photodegradation can only occur via a Norrish Type I or by photoreduction. A mechanism for the Norrish type I reaction of PVAP is given as:



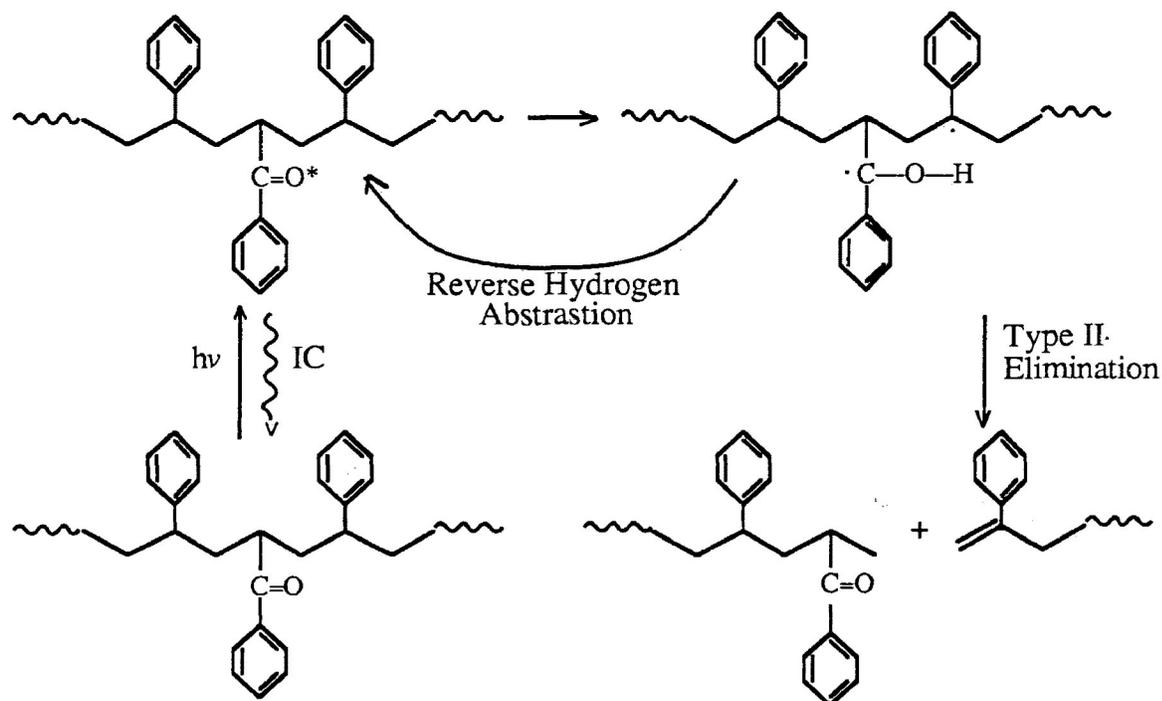
The main product from photolysis of PVAP is methane, indicating that alpha scission is taking place (methyl radicals abstract a hydrogen atom from the polymer backbone). The lack of carbon monoxide and acetaldehyde in the gas products indicate that alpha cleavage does not produce acetyl radical. The loss of a methyl radical leaves a benzoyl radical which can be stabilised by electron delocalisation.<sup>20</sup>

For photoreduction, the remote hydrogen abstraction reaction can be either inter, or intramolecular in nature. If the polymer chain is fairly tightly coiled and the hydrogen on another part of the same polymer chain is within the "reactive volume" about the excited carbonyl function, intramolecular hydrogen abstraction will take place more readily. If the hydrogen atom on another polymer chain is within the reactive volume of the triplet then intermolecular hydrogen abstraction occurs.



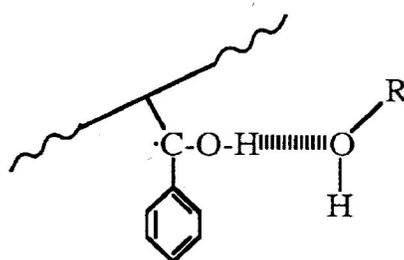
In either case the hydrogen abstraction reaction results in the production of a radical on the polymer backbone and this can initiate secondary reactions (ie. cross linking, chain scission reactions).

Guillet and Ng<sup>17</sup> have studied the photochemistry of a series of styrene-co-vinyl aromatic ketones e.g. styrene and phenyl-vinyl-ketone, (and derivatives of phenyl-vinyl-ketone). Scaiano showed that phenyl-vinyl-ketone is capable of undergoing a Norrish Type II photoelimination and the polymer also undergoes the same reaction, which results in chain scission. Copolymers of styrene and phenyl-vinyl-ketone undergo similar photodegradation via a Norrish Type II elimination, which leads to main chain scission. Guillet and Ng<sup>17</sup> examined the effect of solvent, ketone content, and ketone structure on the Type II process. The excited carbonyl function of the phenyl-vinyl-ketone unit is known to react through the triplet manifold where it abstracts a gamma hydrogen to form the 1,4-biradical intermediate in the first step of the Type II elimination process. The 1,4-biradical can then further react to continue the Norrish Type II reaction and give main chain scission, or the system can undergo reverse hydrogen abstraction followed by radiationless decay to regenerate the original ketone system.



Guillet observed that an increase in ketone content in the copolymers increased quantum yields for the Norrish Type II reaction. Phenyl-vinyl-ketone,  $M_1$ , has a higher reactivity ratio than styrene,  $M_2$ ,  $r_1=1.1$ , and  $r_2=0.107$  (styrene). If the ketone feed is low ( $< 5\%$ ), and the percent conversion high, the phenyl-vinyl-ketone monomer is consumed in the early stages of the reaction and this results in the formation of a few polymer chains with a large number of ketone units, and an even larger number of polystyrene molecules, which are unreactive.<sup>17</sup> As the ketone feed is increased there is a greater chance that more phenyl-vinyl-ketone units will be incorporated into more of the polystyrene chains, and this would result in an apparent increase in the quantum yield for the Type II elimination reaction.

The Type II elimination reaction proceeds through a 1,4-biradical intermediate (a 1-hydroxy-1,4-biradical), and it has been shown by Wagner<sup>6</sup> that the alcohol can hydrogen bond to it.



This stabilises the biradical and consequently suppressing the reverse hydrogen abstraction and this would result in an increase in the quantum yield of the Type II process. Wagner<sup>21</sup> has indeed shown that this is the case; as alcohol content is increased in the solution, there is an increase in the quantum yield for the Type II reaction.

In the case of polymers, the solvent also has an indirect effect on the chain. In a good solvent the polymer chain "swells" or expands because of favourable solvation (polymer-solvent interaction), or because of a weak solvent-polymer interaction being overcome by the stronger interchain repulsion. On the other hand, as the solvent becomes worse, the polymer chains coil up and contract.<sup>17,22</sup>

Schnabel<sup>22</sup> has also investigated the effect of solvent quality on the photochemistry of poly-phenyl-vinyl-ketone (PPVK), which undergoes main chain scission (Type II reaction). In order for the polymer fragments to diffuse apart they have to disentangle themselves from one another, and the tightness of the coiling of the chain will affect the rate of this disentanglement. Solvent quality has a direct effect on how tightly the polymer chain is coiled, and it will have an effect on the rate of disentanglement (Schnabel refers to chain coiling as coil density).

It was observed that the rate constant for the combination of macroradicals decreases with increasing coil density and it was assumed that the rate constant for the diffusion controlled polymer-polymer interactions would decrease on improvement of the solvent quality, as a result of the thermodynamic excluded volume effect. As the solvent quality improves the interpenetration of coils should be more difficult due to the increasing repulsive potential.

Schnabel<sup>22,23</sup> has shown that there is a critical chain length above which intermolecular interactions determine the rate of disentanglement, and below which these interactions become negligible. If the polymer undergoes chain scission the fragments are relatively free when it is highly expanded, unless the molecular weight is very high. When the molecular weight is very high the segmental motion is

hindered and this results in a slower rate of fragment separation. As solvent quality becomes worse, the coil density is increased, the segment density is increased and this leads to a hindrance of segmental motion and with it a reduction in the rate of fragment separation. This effect is very dependent on the chain length.

Schnabel<sup>22</sup> has shown that for PPVK the solvent quality does indeed affect the rate of mutual separation of the fragments of a polymer chain. The reduction in solvent quality results in a higher coil density (more coil-coil contacts) and this in turn leads to an increase in the rate of entanglement, and a reduction in the rate of diffusion of the polymer fragments. In the same way, as solvent quality increases the coil density decreases (the number of coil-coil contacts decreases) and the rate of disentanglement increases. Hence, the rate of separation of polymer fragments increases and this is reflected by an increase in the rate of main chain scission.

Guillet, *et al*<sup>24</sup> have studied the transient spectra and rates of reaction of PPVK and a number of its derivatives, co-polymers and a number of model compounds.

Hrdlovic<sup>25</sup> has shown from photochemical studies of poly ketones (the type II elimination reaction in particular) that the quantum yields for photo-fragmentation tend to be comparable to those of the lower molecular weight analogues, and it was concluded that the alkylketone groups act as independent isolated chromophores. On the other hand, studies of quenching (inter and intramolecular) of these macromolecules show that triplet energy can be transferred along the polymer chain,<sup>26,27</sup> with triplet energy transfer playing an important role in the photochemistry of these molecules.

Photochemical and photophysical studies have shown that the addition of electron donating groups to the ring in phenyl-vinyl ketone lead to an increase in the lifetime of the triplets. For unsubstituted PPVK the triplet lifetimes of 74 ns.<sup>24</sup> Guillet observed that substituents in the 4 position (of the phenyl) increased in the triplet lifetime, the only exception being fluorine. It was also shown that methoxy substitution gave a fairly long lived triplet, and this was attributed to the  $\pi \rightarrow \pi^*$  nature of the low lying triplet.

The effect of a non-solvent on the triplet lifetime was investigated and it was shown that the presence of hexane reduced the triplet lifetime of copolymers slightly, while it significantly reduced the triplet lifetimes for the homopolymers. This is explained in terms of the tightening up of the polymer coil due to the non-solvent

and then self quenching starts to play a role. It was also seen that the quantum yields for chain scission tended to be lower for polymers in solid films than for those in solution.<sup>28</sup> This is probably associated with a large cage effect and with the imposition of restrictions upon the diffusion of the fragments. Thus, one could expect an increase in the reverse hydrogen abstraction reaction from the 1,4-biradical to regenerate the starting ketone. Also it has been proposed that there is some self quenching by the polymer, the quencher for the Type II reaction being the unsaturated species that is produced as a result of this reaction.<sup>27</sup> In another series of studies on the photochemistry of keto polymers in the solid phase<sup>29,30,31</sup> it has been shown that the physical state of the polymer controls the rate determining step for these reactions, the free volume in the polymer matrix being critical.<sup>29</sup> At extremely low temperatures no molecular motion is possible in the polymer,<sup>31</sup> the only photoprocess that is possible being phosphorescence emission, an electronic process and requires no molecular motion. As the temperature is gradually increased, the free volume of the polymer also increases and molecular motion in the polymer can take place, ie. rotation of phenyl rings, methoxy groups, *etc.* At the glass transition temperature  $T_g$  the segmental motion of the polymer backbone is also possible and further increases in temperature beyond  $T_g$  results in larger increases in the free volume.<sup>31</sup> Thus, the rigidity of the polymer matrix and the mobility of the polymer molecules will determine the probability of the achievement of the conformation requirement for a photochemical reaction.

It is known that photochemical reactions can bring about conformational changes in the polymer, and under certain conditions can bring about changes in the bulk properties of the polymer.<sup>29</sup> This is referred to as the photomechanical effect, a unimolecular reaction in which the polymer undergoes structural rearrangement.<sup>29</sup> In order for this to occur, the system has to be flexible with sufficient free volume so that rotations necessary for a change in conformation can take place. This process is impossible at low temperatures.<sup>29</sup>

The effect of temperature on the quantum yields for the Norrish Type II reactions in co-polymers of polystyrene and phenyl-vinyl-ketone has also been studied<sup>31</sup> and it has been observed that at low temperatures the quantum yields for this reaction are low, but it increases with increasing temperature; this gradual increase in quantum yield with increasing temperature continuing up to the glass transition temperature, at which point the quantum yield increases significantly.

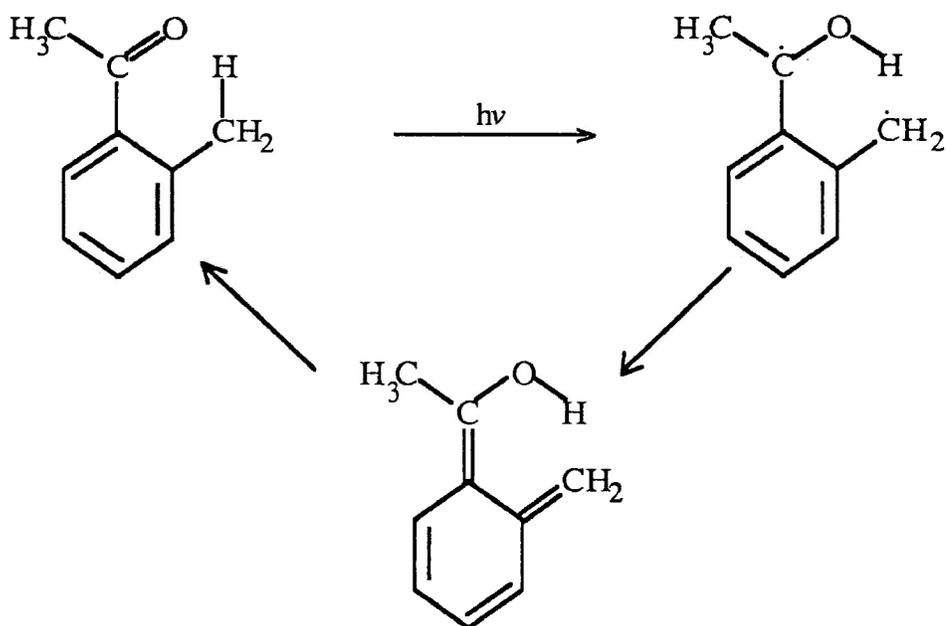
This effect, that of restricted free volume below  $T_g$ , in turn, prevents the system from achieving the six membered intermediate state required for the Type II reaction. At  $T_g$ , however, there is sufficient free volume and molecular motion to allow the desired conformation to allow for a Type II reaction to be achieved.

Murai<sup>30,32</sup> has investigated the hydrogen abstraction reaction of benzophenone in alcoholic solvents and it was observed that the hydrogen abstraction does occur over a wide temperature range. However, when the temperature is below  $T_g$  of the solvent, then the radical formed, as a result of the hydrogen abstraction reaction, can react within the solvent cage. When the temperature is above  $T_g$  then the ketyl radical produced can diffuse out of the solvent cage to react. Brauchkle<sup>29</sup> has shown that in the case of hydrogen abstraction, by benzophenone in the solid state, the matrix rigidity and viscosity play an important role in the hydrogen abstraction and also control the tightness of the cages, and the probability of escape from them.

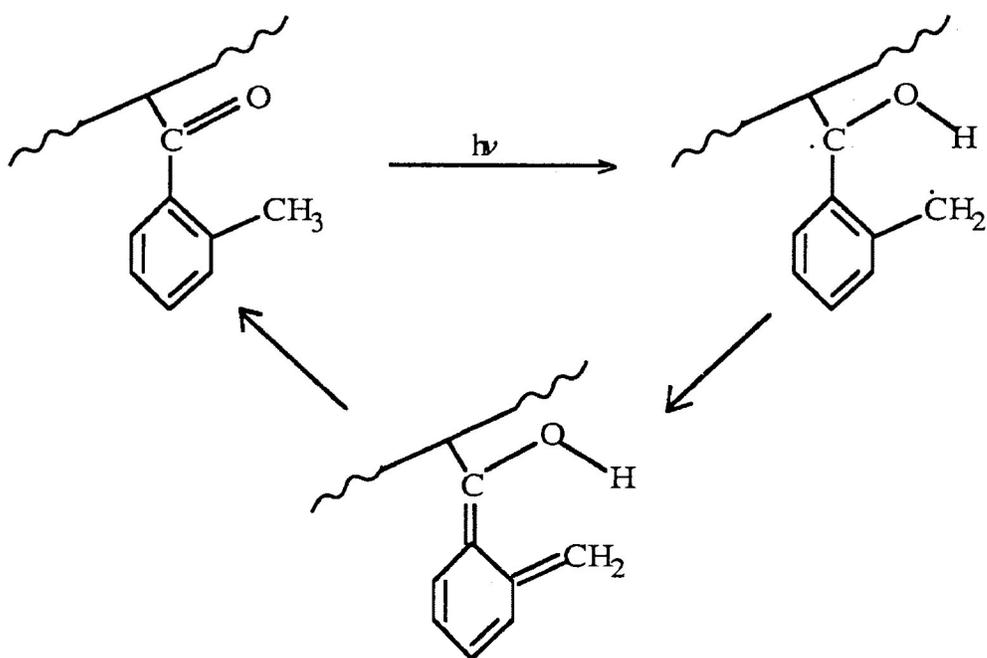
An extensive amount of work has been carried out over recent years to develop methods of stabilising polymers to photodegradation; the classical method being the addition of photostabilisers. These small molecules are incorporated into the polymer, where they absorb the harmful ultraviolet light or dissipate the absorbed energy in a way which protects the chain itself.<sup>3</sup> An alternate is to incorporate the stabilising material directly into the polymer chain itself. This stabilising species, which is co-polymerised to the polymer chain, has to be able to channel the degradative energy into non-degradative processes.

One such type of system was investigated by Wagner<sup>11</sup> i.e. the photoenolisation of *ortho* alkyl ketones which undergo a reversible, photo-induced keto-enol tautomerisation in the presence of ultraviolet light. These molecules undergo a gamma hydrogen abstraction involving the triplet manifold, to yield the 1,4-biradical which decays to yield the enol form which, in turn tautomerises back to the keto form, thereby dissipating the energy in a non-degradative way.

This process can be summarised by the following scheme:

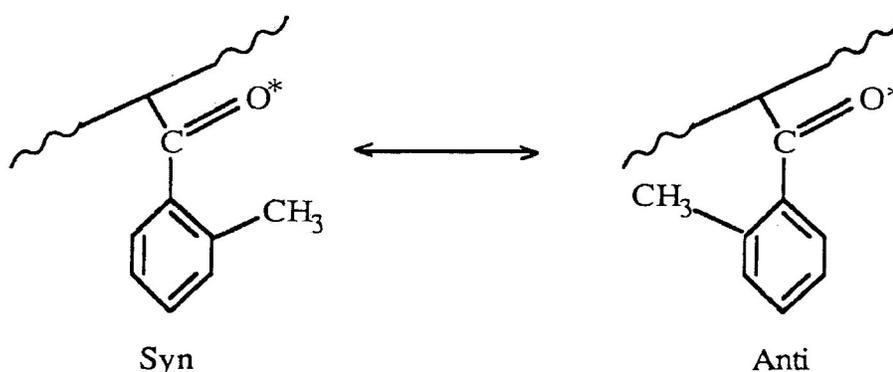


It can be seen that the occurrence of this process is very dependent on the structure of the ketone. Scaiano<sup>33,34</sup> has investigated polymers which have similar structures, i.e. copolymers of phenyl-vinyl-ketone and *o*-tolyl-vinyl-ketone. It is well known that poly-*o*-tolyl-vinyl-ketone is very stable to ultraviolet light, and this has been attributed to a similar photoenolisation process:



Relative rates of the photoprocesses which could place in the two components of the co-polymer (ie. the Norrish Type II reaction and the photoenolization reaction) were investigated. It was initially expected that if there was no energy transfer the quantum yields of photodegradation would be directly related to the abundance of each component in the copolymer. It was shown that the presence of *o*-tolyl-vinyl-ketone in the copolymer reduced the photodegradation rate of the phenyl-vinyl-ketone component. However, the reduction was higher than that expected from the concentration of the *o*-tolyl-vinyl-ketone; this provided evidence for triplet energy migration in the phenyl-vinyl-ketone segments with the otherwise degradative triplet energy being transferred to the *o*-tolyl-vinyl-ketone units which act as energy sinks.

*O*-tolyl-vinyl-ketone unit has two conformationally different triplets:



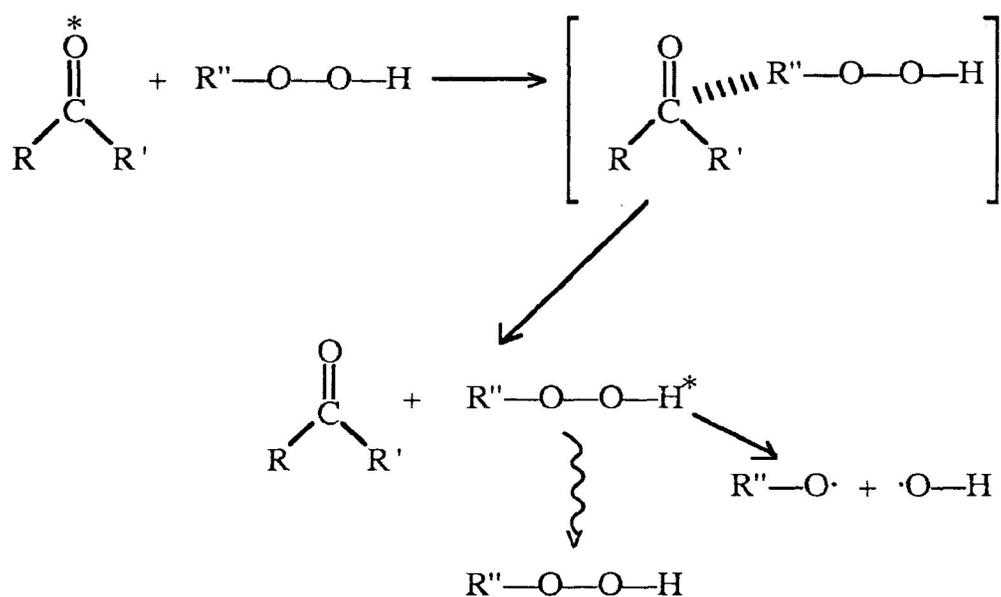
The enolization reaction is a conformationally dependent reaction, ie. there has to be a gamma hydrogen within the reactive volume around the carbonyl triplet, and in order for this to occur the system has to be in the syn conformation. Quenching plots of with 1-methyl-naphthalene as a quencher with these copolymers tended to be linear, indicating that this technique used was not able to distinguish between the two triplets. In addition, conformational equilibrium is a relatively slow process (compared with the lifetime of the triplet) and this imposes some ground state control on the system, only the *o*-tolyl- vinyl-ketone molecules that are in the proper syn conformation at the time of excitation undergoing enolization. The energy transfer process is also a very fast process as seen by the detection of only one triplet in the *o*-tolyl-vinyl-ketone, and this indicates that the triplet energy rapidly "hops" through the anti conformers until a syn conformer energy sink is reached.

One study Guillet and Ng<sup>35</sup> on the energy transfer from an excited ketone

polymer to smaller molecules (hydroperoxides), showed that both singlet and triplet  $n \rightarrow \pi^*$  states of the carbonyl in a co-polymer of styrene and phenyl-vinyl-ketone could be quenched by a small molecule (tert-butyl hydroperoxide). It is known that in the near ultraviolet region that both aromatic and aliphatic ketones are more strongly absorbing than hydroperoxides; thus, it was proposed that the decomposition of the hydroperoxide was brought about by an energy transfer from the carbonyl unit and this was indeed verified by Guillet<sup>35</sup> with the energy transfer process being very efficient. It was shown that the rate constant for quenching of the triplet, by the hydroperoxide, ( $\sim 10^8 \text{ s}^{-1}$ ) was greater than the rate constant for the Type II elimination reaction from the phenyl-vinyl-ketone group and no products which would have come from the reaction between the 1,4-biradical and the peroxide quencher were detected. Therefore, it was proposed that the triplet is quenched before it can abstract the gamma hydrogen to form the biradical.

A possible mechanism for the transfer of energy from the excited carbonyl to the hydroperoxide has been proposed; a complex (of a finite lifetime) being formed between the excited carbonyl and the ground state of the quencher. The coupling of the electronic energy of the carbonyl  $n \rightarrow \pi^*$  with the vibrational energy of the peroxide occurs in an exciplex intermediate and this leads to depopulation of the excited  $\pi^*$  state of the carbonyl and the transfer of energy to the vibrational modes of the peroxide which undergoes dissociation.<sup>35</sup>

A simplified mechanism is shown below:



Where R''-O-O-H is the ground state hydroperoxide.

Quenching of the carbonyl  $\pi^*$  state by olefins, dienes, amines, and disulphides has also been postulated to involve an exciplex, and the quenching constant for co-(styrene-phenyl-vinyl-ketone) by hydroperoxide is of the same order of magnitude as the quenching constant for amines which have been shown to go through a charge transfer exciplex.<sup>35</sup> The Arrhenius parameters for the triplet quenching of this system are typical of those associated with a bimolecular collision process involving an encounter intermediate.<sup>35</sup> Guillet also observed a solvent effect in the quenching of these systems. In aromatic solvents there appeared to be an enhancement of the quenching with solvents of high dielectric constant, and this would indicate that there is a stabilization of any polar intermediate (involved in the quenching process).<sup>35</sup>

The process of triplet energy transfer has previously been mentioned, and has been the object of many studies on account of its role in the primary step in polymer degradation process. Evidence for triplet energy migration can be obtained from both photophysical and photochemical studies, but both approaches involve quenching of the triplet state by a triplet acceptor. In chain molecules triplet migration is generally assumed to occur when the value of the Stern Volmer constant is increased relative to that of small molecules.

Two underlying assumptions are made when carrying out quenching studies:

1) The triplet lifetime of the chromophore does not change when the quencher is co-polymerized into the polymer.

2) The triplet acceptor does not preferentially absorb over the polymer chromophore.<sup>36</sup>

It is possible to avoid these problems and compare the quenching efficiency of a small molecule with that of the acceptor molecule bound to the polymer chain by co-polymerization (or by chemical modification). However, evaluating the local concentrations of the quencher in the polymer coils is difficult. Most photochemical studies are based on the photodegradation of the polymers because of the relatively large effect that results from few chain scissions.<sup>36</sup>

Lukac<sup>37</sup> and coworkers investigated the influence of diffusion control of triplet quenching on the photolysis of poly-phenyl-vinyl-ketone (PPVK), and

compared the quenching efficiency of low molecular weight quenchers (naphthalene, biphenyl, and 2,5-dimethyl-2,4-hexadiene) to those of co-polymers of PPVK and 1-vinylnaphthalene, and 2-vinylnaphthalene. It was found that the quenching efficiency of the co-polymerized naphthalenes in the polymer chain was 21 times greater than that of the small molecule quenchers and from this they concluded that triplet energy migration was occurring in the PPVK chain.<sup>37</sup>

Weill<sup>36</sup> reexamined these results, taking the local concentration of the quencher in the polymer coil into account. It was confirmed that the rate of external intermolecular quenching, by naphthalene, is much lower ( $k = 320.1 \text{ mol}^{-1}$ ) than that of the internal quenching by PPVK co-1-vinylnaphthalene ( $k = 950.1 \text{ mol}^{-1}$ ) and PPVK co-2-vinyl-naphthalene ( $k = 701.1 \text{ mol}^{-1}$ ) and that triplet energy does migrate along the polymer chain. The difference in the quenching rates for 1 and 2 vinylnaphthalenes has been attributed to steric factors, the case of triplet energy transfer from acetophenone groups adjacent to the naphthalene groups being dependent on the close approach of the homopolymer.

Scaiano<sup>38</sup> also investigated triplet energy transfer in PPVK. For triplet-triplet energy transfer to take place, the exchange mechanism which operates requires that the donor and acceptor groups be close enough to allow for sufficient overlap of their electron clouds. Transfers between similar chromophores is difficult to study because the transfer process does not lead to any observable phenomena. Most studies tend to make use of small differences between the donor and acceptor groups, (for a polymer the difference could be that one chromophore is closer to the end of the polymer chain). This energy migration can bring about chemical or physical changes in the polymer, far away from the site of initial excitation. The process of migration has practical applications in the field of photostabilization where it is desired to channel the energy into a suitable energy sinks to reduce photodegradation in the polymer.<sup>38</sup>

Scaiano's study of the photolysis of PPVK showed that the degree of degradation as a function of irradiation time shows a sharp initial increase but levels off with time. This effect cannot be explained in terms of depletion of reactive centers, or ultraviolet screening by degradation products or impurities in the polymer. According to Scaiano intermolecular triplet quenching by the unsaturated chromophores produced from the Norrish Type II photofragmentation process is responsible. These groups are very good quenchers, their high efficiency being due

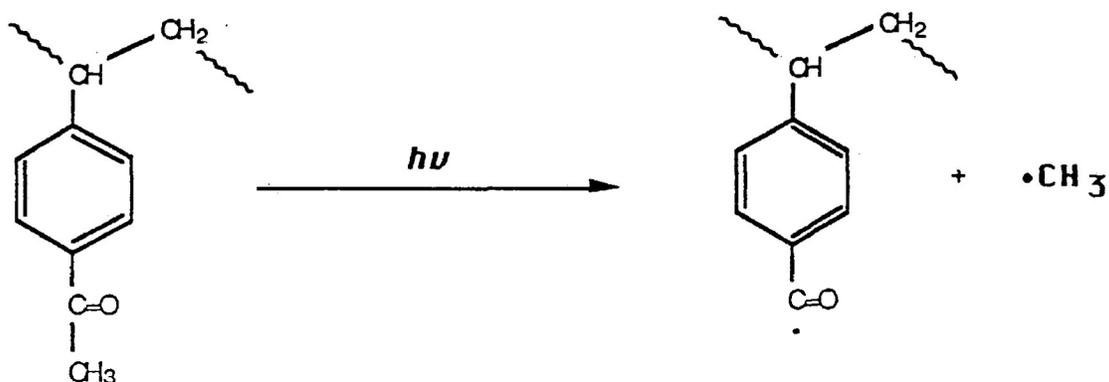
to fast energy transfer between them and the triplets.

Energy migration models usually postulate a "critical radius" which is a measure of how far the triplet energy travels during its lifetime. Scaiano<sup>38</sup> uses an analogous parameter, the "critical chain length", which for a QQ type polymer is interpreted as the average number of chromophores visited during the lifetime of the triplet. Scaiano managed to determine a critical chain length for PPVK is (750).<sup>38</sup>

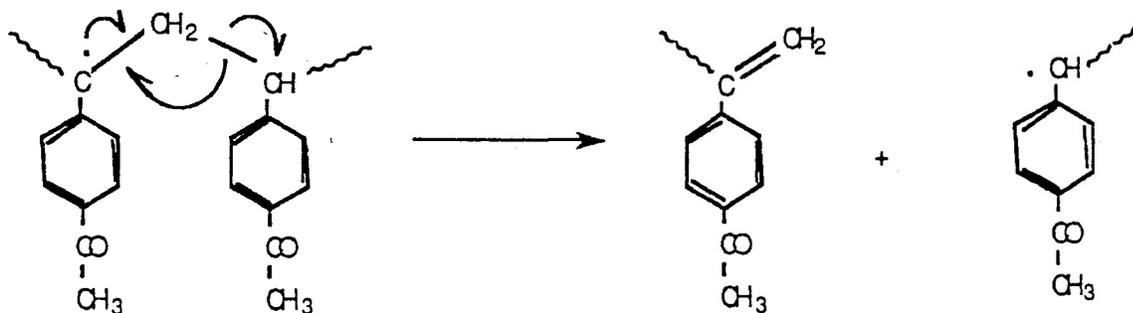
Most previous studies of the energy migration in polymers have been carried out on systems where the donor and acceptor molecules are not part of the same polymer, but are additives which act as impurity traps. The problem with this approach is the formation of aggregates by the impurity. Scaiano studied the case where the donor and acceptor are both the same group, excitation, migration, and quenching being intramolecular and the location of the quencher group is known. Thus there is no chance of having sequential quencher groups, and any polymer chain will have a maximum of two quencher groups. He estimated a rate constant for the energy migration based on the value of the critical chain length, and a rate constant for the Type II photo-fragmentation process, the rate constant for the latter being  $1.7 \times 10^{-7} \text{ M}^{-1} \text{ s}^{-1}$  (as measured by laser flash photolysis). Using this value the rate constant for energy migration was estimated to be  $1.6 \times 10^{12} \text{ s}^{-1}$ , which implies that the energy visits each chromophore for around 1 ps. The high value suggests that the geometries of both ground state and the lowest triplet state are identical. Scaiano states that this efficient energy transfer is not the result of remote transfers between parts of the polymer. Studies on methyl-methacrylate co-phenyl-vinyl-ketone 2-vinylnaphthalene show that this type of energy transfer is possible, but the time scale for this process is in the order of hundreds of nanoseconds. It was also shown that the shorter the polymer chains are the more efficient is the quenching of the triplet energy, the triplet being more likely to encounter an end group during its lifetime.

### 1.4 Aims of Present Work

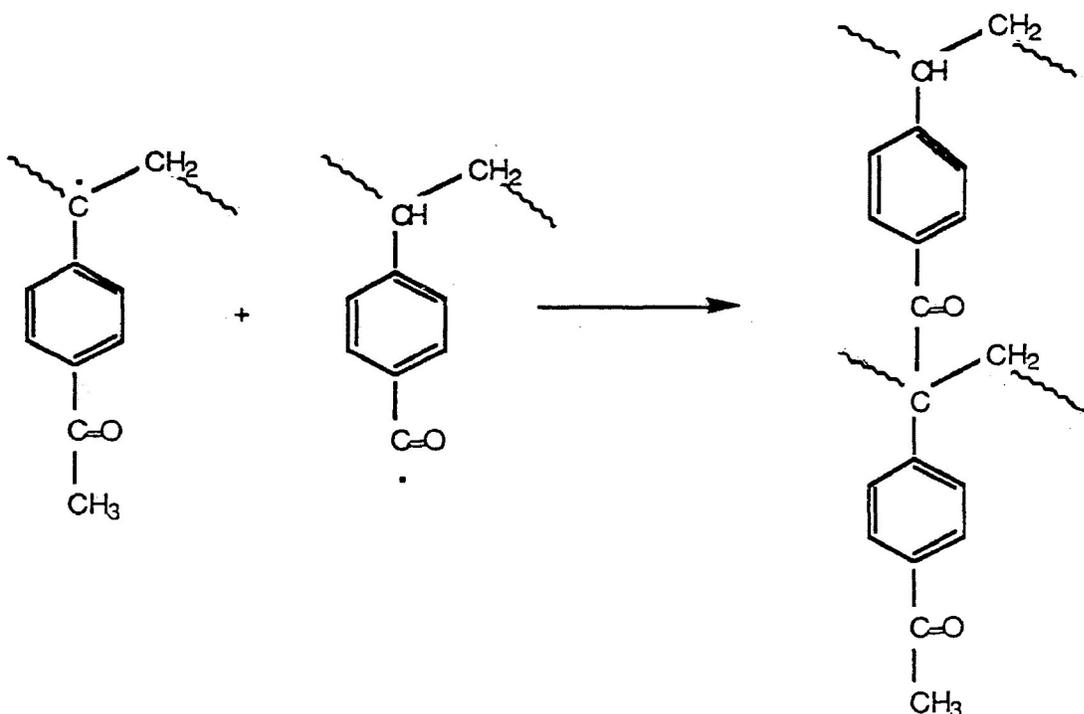
Weir *et al.* <sup>20,44,45</sup> have carried out some studies on *para* substituted poly acyl styrenes e.g. poly-*para*-acetylstyrene (PPAS) and it has been shown that this system undergoes a Norrish type I reaction to produce methyl radicals. For example, PPAS:



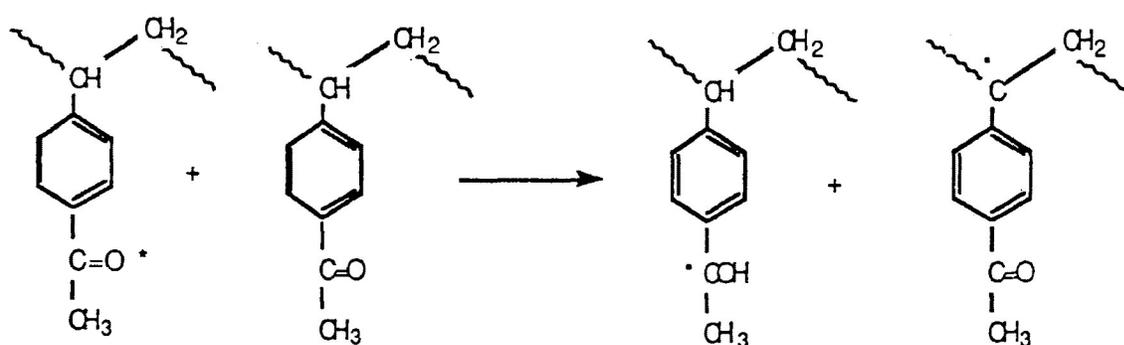
The methyl radicals then are able to abstract a hydrogen atom from the polymer backbone (a tertiary hydrogen) to yield methane and a tertiary radical in the polymer. It is these tertiary radicals which lead to secondary reactions in the polymer (cross linking and chain scission reactions). Chain scission reactions are beta scission reactions which arise from the tertiary radical. For example, PPAS:



In addition, cross linking reactions arise from the combination of two polymer radicals. For example, PPAS:



It is also possible for these polymers to undergo a photoreduction reaction which also produces a tertiary radical in the polymer backbone. For example, PPAS:

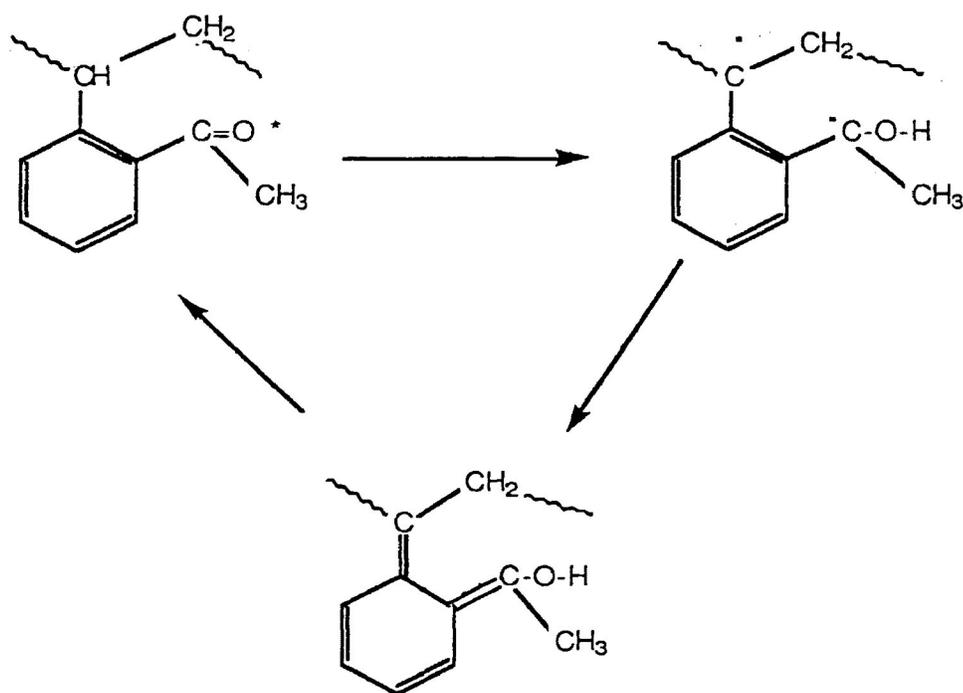


It is the aim of this present work to carry out further studies on PPAS and another *para* substituted poly acyl styrene e.g. poly *para* propionyl styrene (PPPS) and to compare the reactivity of these two similar polymer systems to ultraviolet light. In addition a study of the *ortho* substituted counterparts of these polymers

will be studied and a comparison of the reactivity of these systems will be carried out. It is also hoped to be able to propose plausible reaction mechanism for the photolysis of these systems.

It is expected that the photochemistry of PPPS will be very similar to that of PPAS (PPPS should undergo a Norrish type I reaction to yield ethyl radicals and a polymer radical). Also, the secondary reactions should be similar (starting with tertiary hydrogen abstraction by the ethyl radical followed by cross linking or chain scission reactions). It is also possible for PPPS to undergo a photoreduction reaction in much the same way as PPAS.

For the case of the *ortho* substituted polymers it is possible for these systems to also undergo both the Norrish type I reaction and a photoreduction reaction, followed by secondary reactions. In addition, these polymers have the proper structure to allow for a photoenolization reaction to occur. For example, POAS:



This enolization reaction should increase the stability of these polymer to photodegradation.

## Materials and Methods

### 2.1 Materials

The polystyrene ( $M_w = 118,000$ ) was obtained from Scientific Polymer Products Inc. Acetyl chloride, propionyl chloride, phosphorus pentoxide, phosphorus oxychloride, phenylethylchloride, dimethyl sulphate, benzene, aluminium trichloride, and 2-methyl-acetophenone were all obtained from Aldrich Chemical, Co. Magnesium sulphate and sodium carbonate came from Fisher Scientific Co. Xylene, carbon disulphide, methanol, propanol, sodium hydroxide, were supplied by BDH. Chlorobenzene was also supplied by BDH and was further purified by distillation. Methylene chloride was supplied by Caladon Laboratories Ltd.

#### 2.1.1 Procedure

Poly-*p*-acetyl-styrene was synthesised by the procedure described by Braun, Cherdron, and Kern<sup>39</sup> with a few modifications as follows:

A 500 ml 3-necked flask was equipped with a condenser and dropping funnel. 100 ml of carbon disulphide and 13 g of aluminium trichloride was placed in the flask along with 6 g of acetyl chloride. 5 g of polystyrene in 100 ml of carbon disulphide was added drop- wise to the mixture and the mixture was then boiled under reflux for one hour. The condenser was then removed from the flask and replaced with a three way connecting tube and a distillation condenser. After distilling off the carbon disulphide the reaction was quenched by the addition of 300 ml of cold HCl. In order to ensure complete destruction of the aluminium trichloride and to remove any impurities, the product was washed with two 300 ml portions of 5% HCl, followed by five 100 ml portions of distilled water and then two 100 ml portions of methanol. The crude product was then dissolved in methylene chloride

and precipitated from methanol three times. The resulting polymer was then dried *in vacuo* at 50°C.

Poly-*p*-propionyl-styrene was also synthesised by this method by replacing the acetyl chloride with the molar equivalent of propionyl chloride.

Poly-*o*-acetyl-styrene was synthesised by first preparing the monomer unit (*o*-acetyl-styrene) followed by polymerisation. The monomer was synthesised in a three step process. The first step involved the synthesis of *n*-acetyl-phenylethylamide. This was followed by the synthesis of 1-acetyl-3,4-dihydroisoquinoline from the amide. This isoquinoline was then converted to the monomer.

The *n*-acetyl-phenylethylamide was synthesised by the procedure outlined by Whaley and Hartung<sup>40</sup> with a few modifications as follows:

50 ml of phenylethylamine in 80 ml of 20% NaOH in ethanol was placed in a 500 ml round bottom flask. 34.8 ml of acetyl chloride was then added dropwise to the mixture. The mixture was kept cold in an ice bath during the addition of the chloride. The mixture was then filtered and the liquid portion kept. The crude product was then dissolved in ether. The ether was then removed by distillation under low pressure and the final product was collected by distillation under vacuum.

1-acetyl-3,4-dihydroisoquinoline was synthesised by the procedure outlined by Whaley and Hartung<sup>40</sup> as follows:

15g of *n*-acetyl-phenylethylamide, 30g of phosphorus pentoxide, 30g of phosphorus oxychloride, and 275ml of dry xylene was placed in a 1000ml 3-necked round bottom flask, equipped with a reflux condenser and a mechanical stirrer. The mixture was boiled under reflux for 1 hour under anhydrous conditions. The mixture was then cooled in an ice bath and ice water was added to the mixture to hydrolyse any excess phosphorus pentoxide. The aqueous layer was then separated and washed with benzene. The solution was then made strongly alkaline with 20% NaOH solution (a large excess of water was required to keep the inorganic salts in solution). The desired base was extracted with benzene and dried with magnesium sulphate. The isoquinoline was then precipitated by bubbling HCl gas through the solution.

The *o*-acetyl-styrene was synthesised by the procedure outlined by Gensler, Healy, Onskuus, and Bluhm<sup>41</sup> as follows:

A 1000ml 3-necked round bottom flask was equipped with a mechanical

stirrer and a reflux condenser. 12g of 1-acetyl-3,4-dihydroisoquinoline, 48 ml of dimethyl sulphate, 300 ml of 40% NaOH solution (in water), and 300ml of water were placed in the flask. The mixture was then boiled under reflux for three hours. After cooling, the product was extracted with ether. The ether solution was then washed, first with a 5% HCl solution, then by a 5% sodium carbonate solution. The ether was then removed by distillation under low pressure and the final product was collected by distillation under vacuum.

The substituted styrene monomer was then polymerized thermally at 80°C under a nitrogen environment. The polymerization time was 20 hours and the conversion was kept low (<20%). The crude polymer was then dissolved in methylene chloride and precipitated with methanol three times. The polymer was then dried *in vacuo* at 50°C.

## 2.2 Polymer Characterisation

### 2.2.1 Infrared Spectroscopy

The IR spectra were recorded on a Perkin-Elmer 1320 Infrared Red Spectrophotometer.

Fig 2.1 - 2.4 show IR spectra of these polymers.

POPS and POAS: Both IR spectra of these polymers show a strong absorption at  $1690\text{ cm}^{-1}$ , which is characteristic of C=O stretching. The absorption at  $750\text{ cm}^{-1}$  is characteristic of an *ortho* substituted aromatic ring.

PPPS and PPAS: The spectra of these polymers show a strong absorption at  $1680\text{ cm}^{-1}$  which is characteristic of C=O stretching. The absorptions at  $850$  and  $800\text{ cm}^{-1}$  are characteristic of a *para* substituted aromatic ring.

### 2.2.2 Ultraviolet spectroscopy

The Ultraviolet spectra were recorded on a Bausch and Lomb Spectronic 2000 Ultraviolet/visible spectrophotometer.

Fig 2.5 shows the UV spectrum of POAS; all other polymer systems showed a similar spectrum. All polymers show a strong absorbance around 250 nm

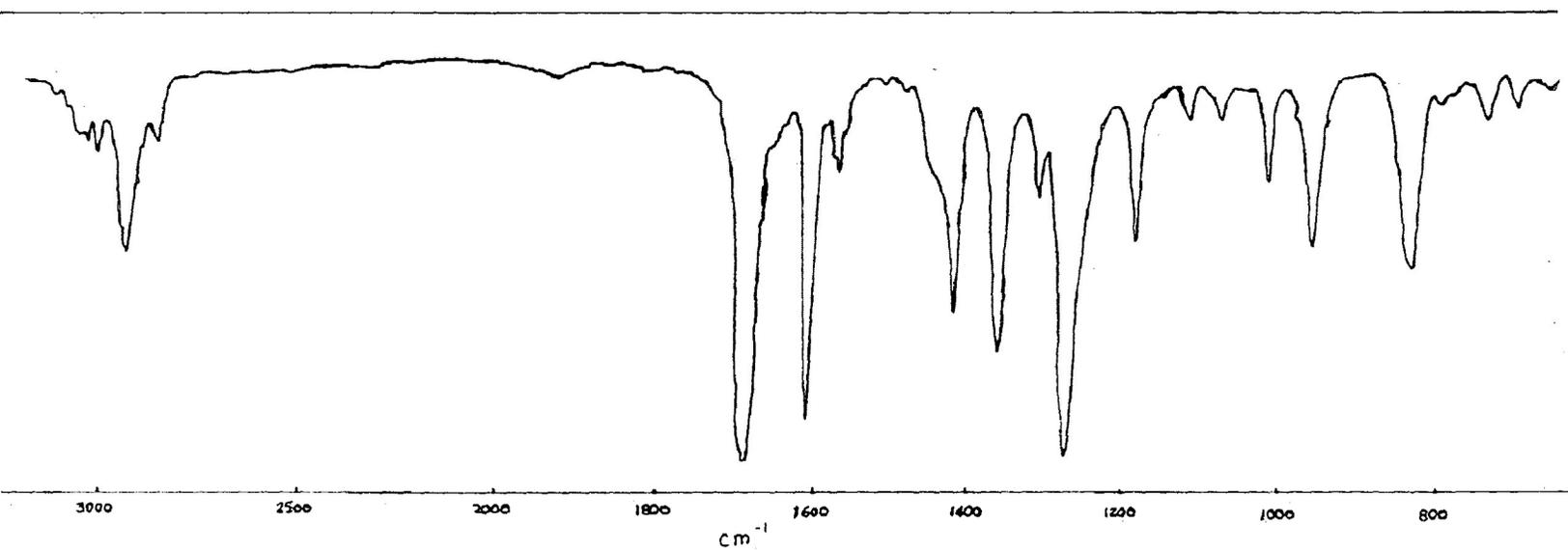


Fig.2.1  
IR Spectrum of PPAS

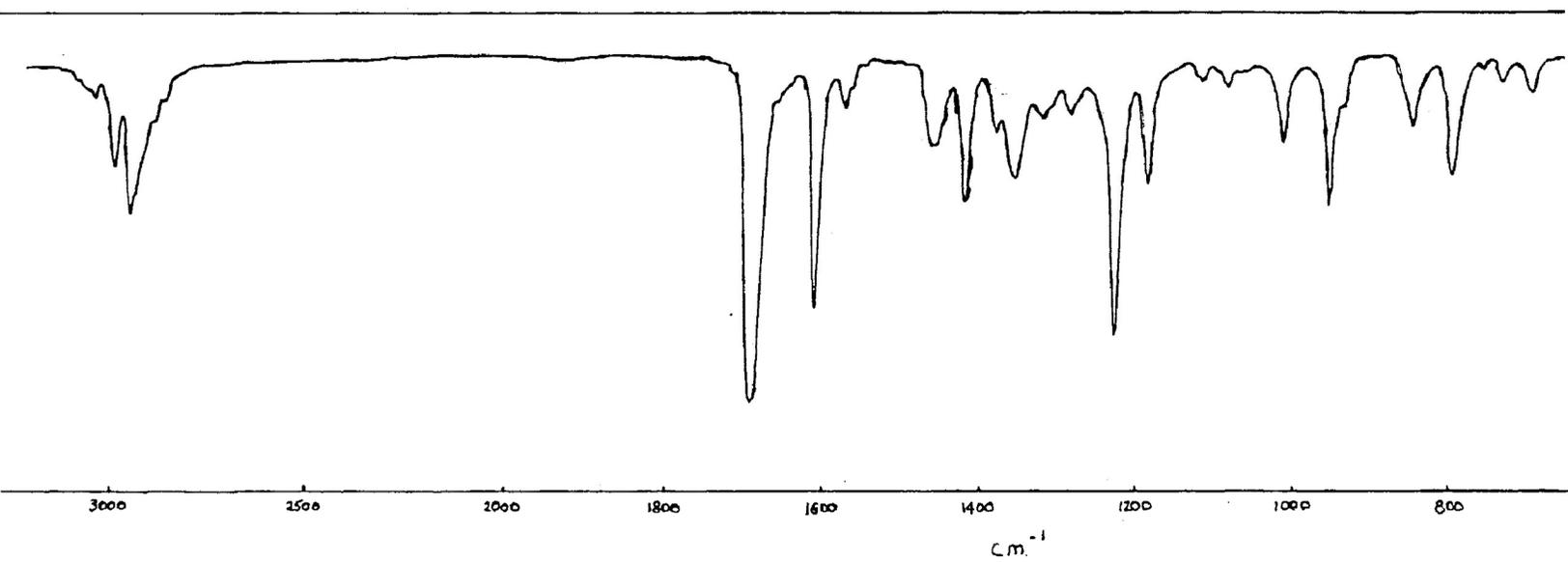


Fig.2.2  
IR Spectrum of PPS

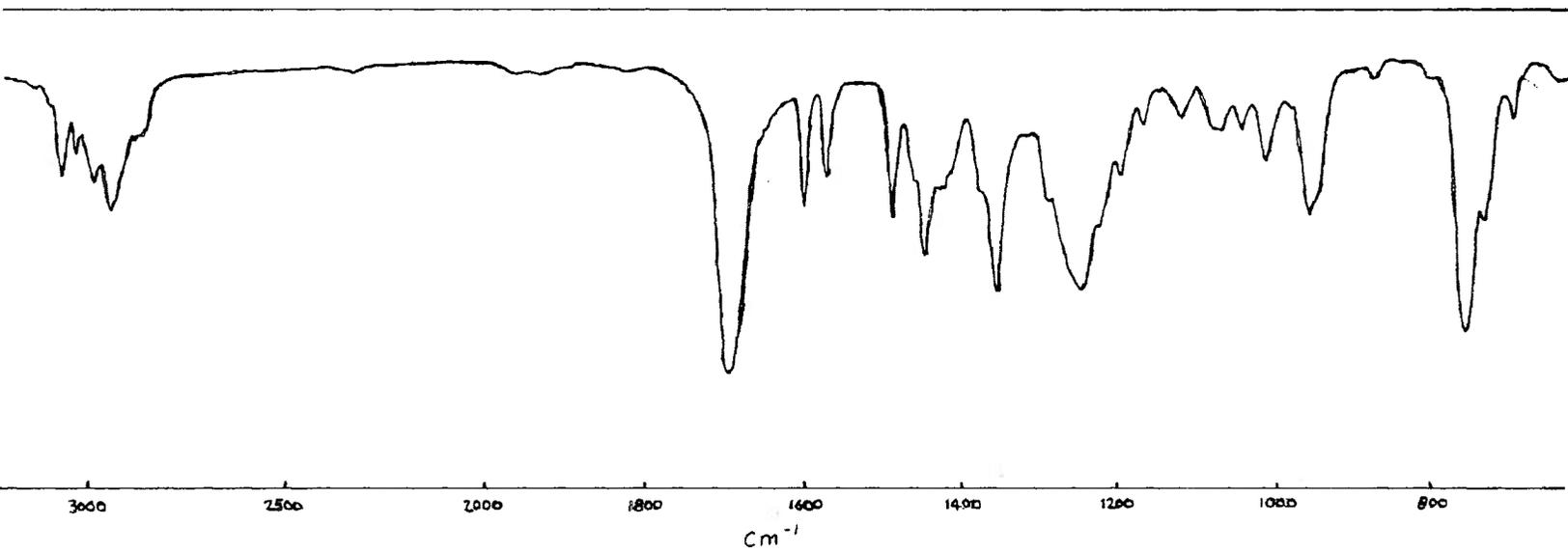


Fig.2.3  
IR Spectrum of POAS

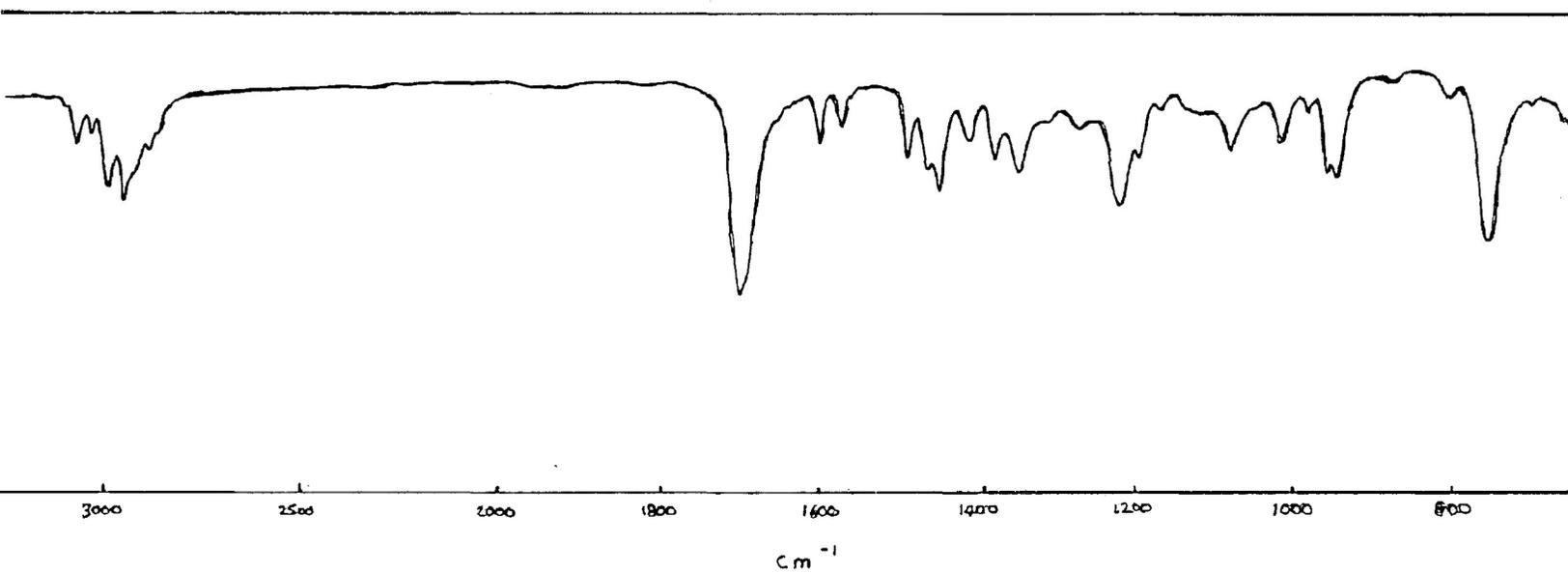


Fig.2.4  
IR Spectrum of POPS

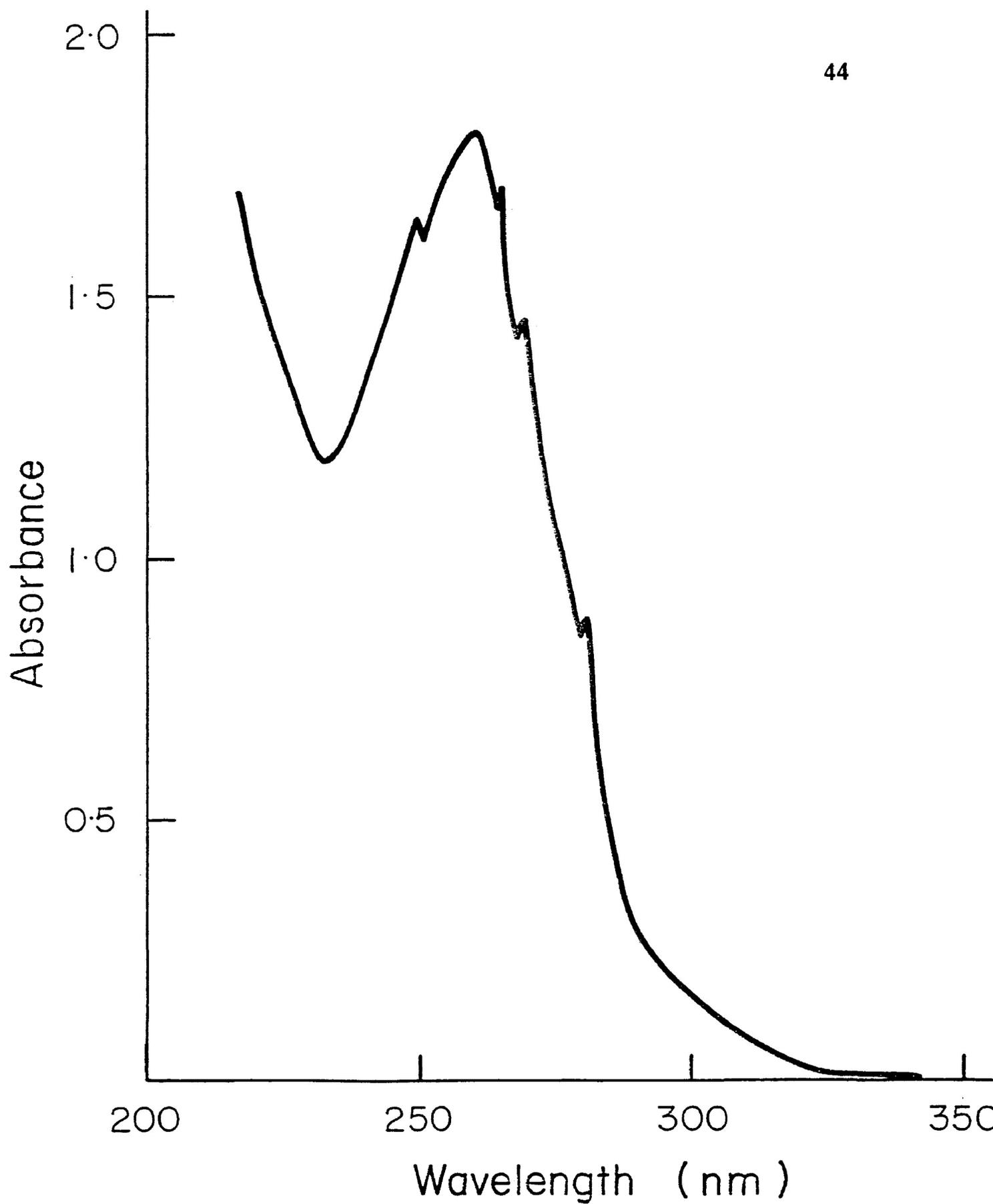


Fig. 2.5 UV Spectrum of POAS

which is attributed to the  $\pi \rightarrow \pi^*$  transition of the aromatic ring. There is a weak absorbance that appears at 310 nm and this is attributed to the weak  $n \rightarrow \pi^*$  transition of the carbonyl function.

The extinction coefficients for the  $n \rightarrow \pi^*$  transition of the carbonyl group are 85 and 94 l/mol·cm for POPS and PPPS, respectively; and 91 and 90 l/mol·cm for POAS and PPAS, respectively.

### 2.2.3 Nuclear Magnetic Resonance

Fig 2.6 - 2.9 show C-13 nmr spectra of these polymers and Table 2.1 gives the interpretation of these spectra

### 2.2.4 Molecular Weight Determination

For PPPS and PPAS, the molecular weight of the polymer was calculated on the assumption that the chains of the starting material (polystyrene) remain intact during the acylation reaction. The molecular weight for the styrene monomer unit is 104. For the PPPS monomer unit, the molecular unit is 160, and for PPAS, the molecular weight of the monomer unit is 148.

The weight average molecular weight for the starting polystyrene was 118,000 and after acylation the weight average molecular weight will increase by the mass of the acyl group. Therefore, for PPPS, the weight average molecular weight will be 181,538 and for PPAS, the weight average molecular weight will be 167,923.

For POPS and POAS, which was prepared by polymerization of the monomer, the molecular weights of these polymers were determined by viscometric techniques to yield a viscosity average molecular weight. The limiting viscosity of a polymer solution is related to the molecular weight of the polymer by the Mark-Houwink equation. <sup>3</sup>

$$[\eta] = KM^a \quad (2.1)$$

Where  $[\eta]$  is the limiting viscosity,  $M$  the viscosity average molecular weight, and  $K$  and  $a$  are constants. The limiting viscosity is related to the specific viscosity  $\eta_{sp}$  by :

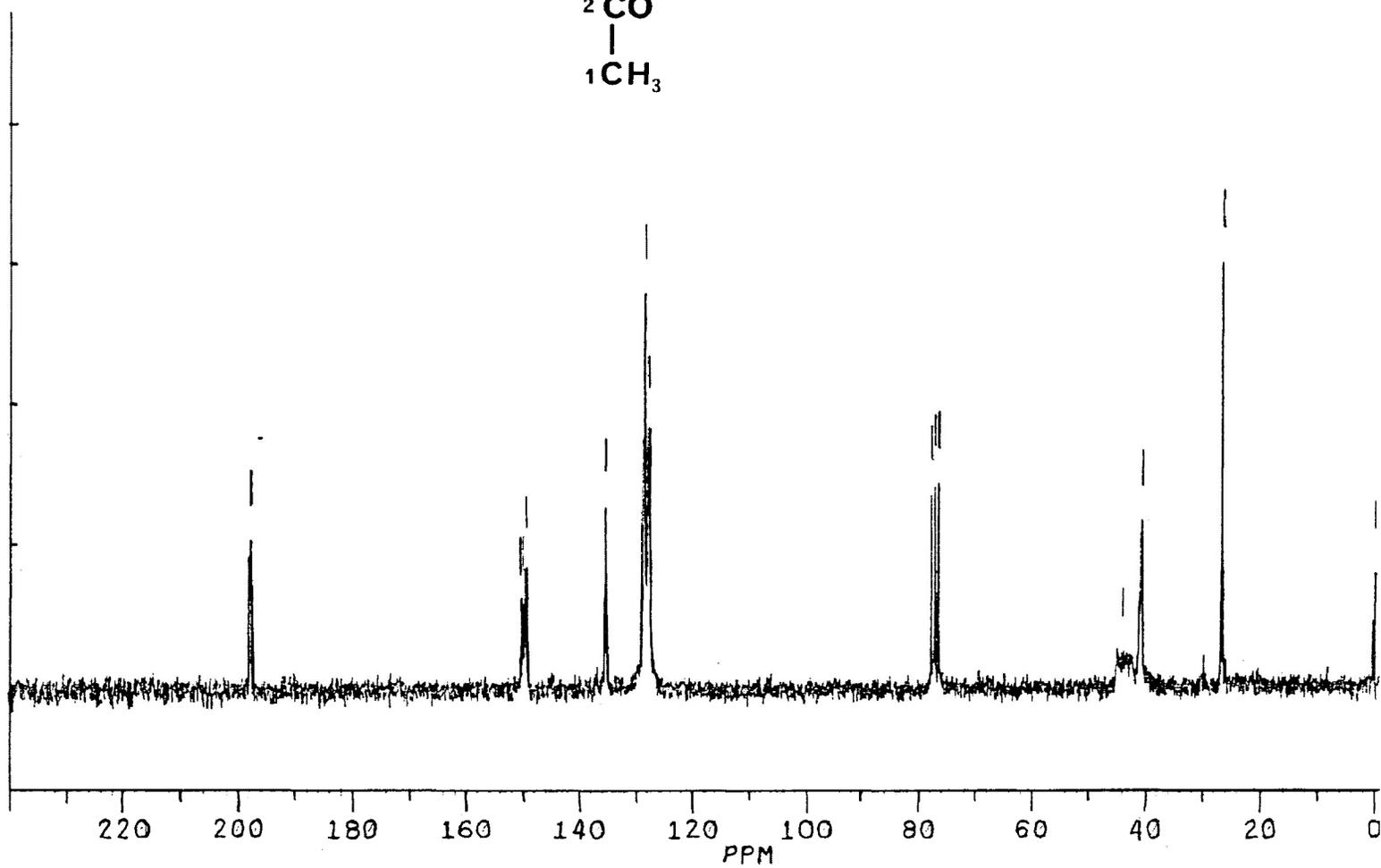
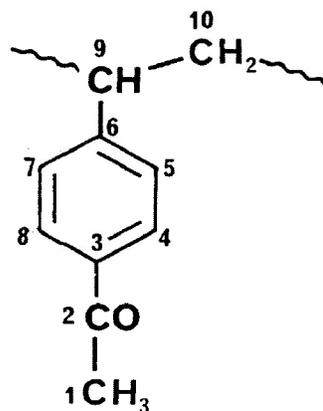


Fig. 2.6

<sup>13</sup>C Spectrum of PPAS (refer to Table 2.1 for interpretation of spectrum)

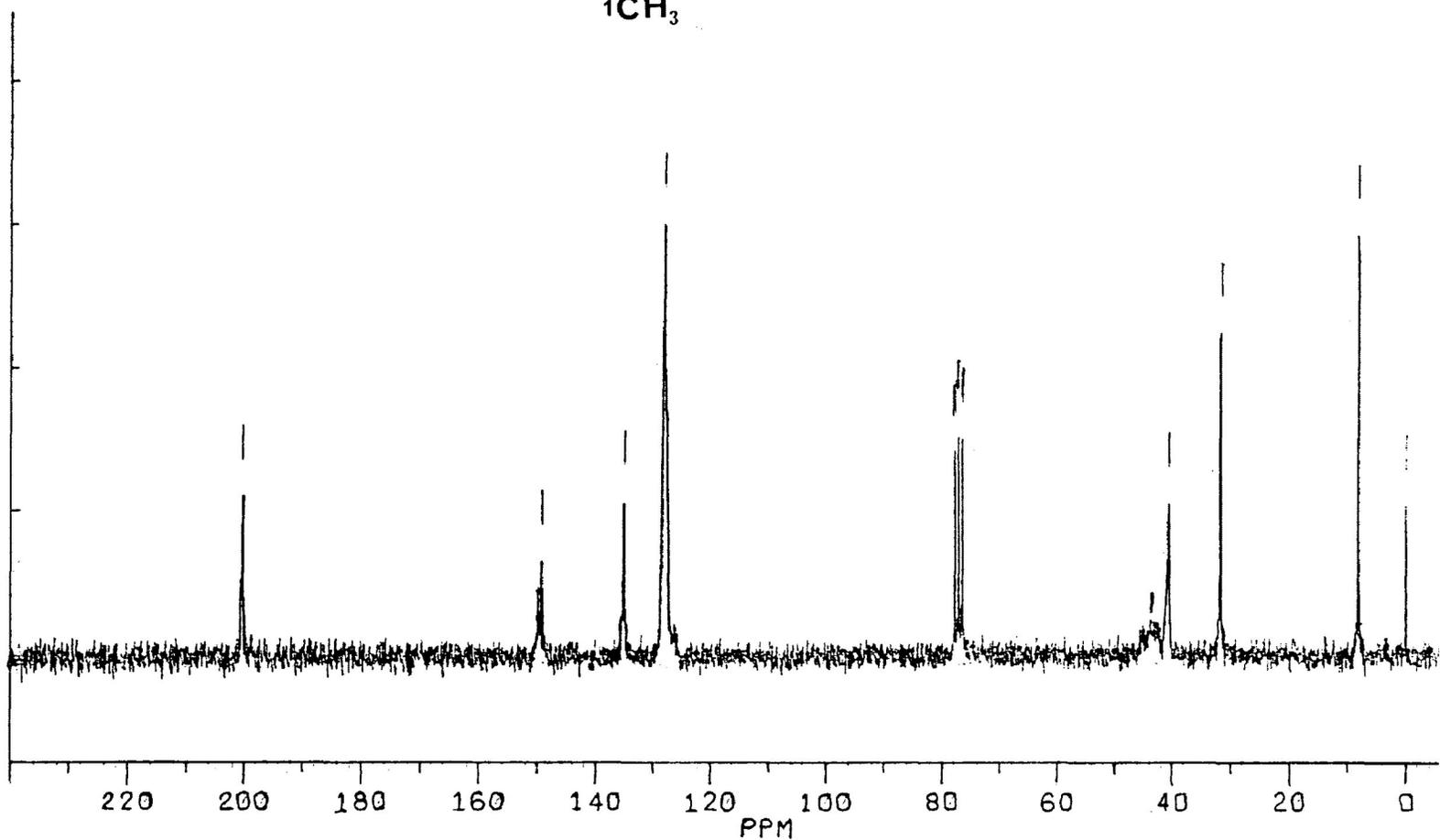
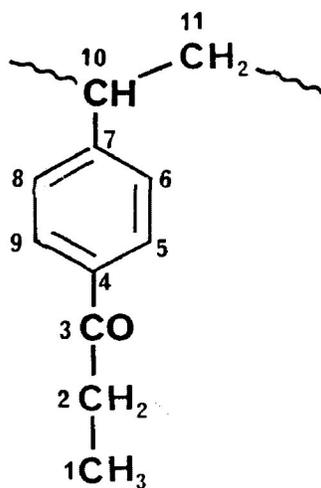


Fig. 2.7

<sup>13</sup>C Spectrum of PPPS (refer to Table 2.1 for interpretation of spectrum)

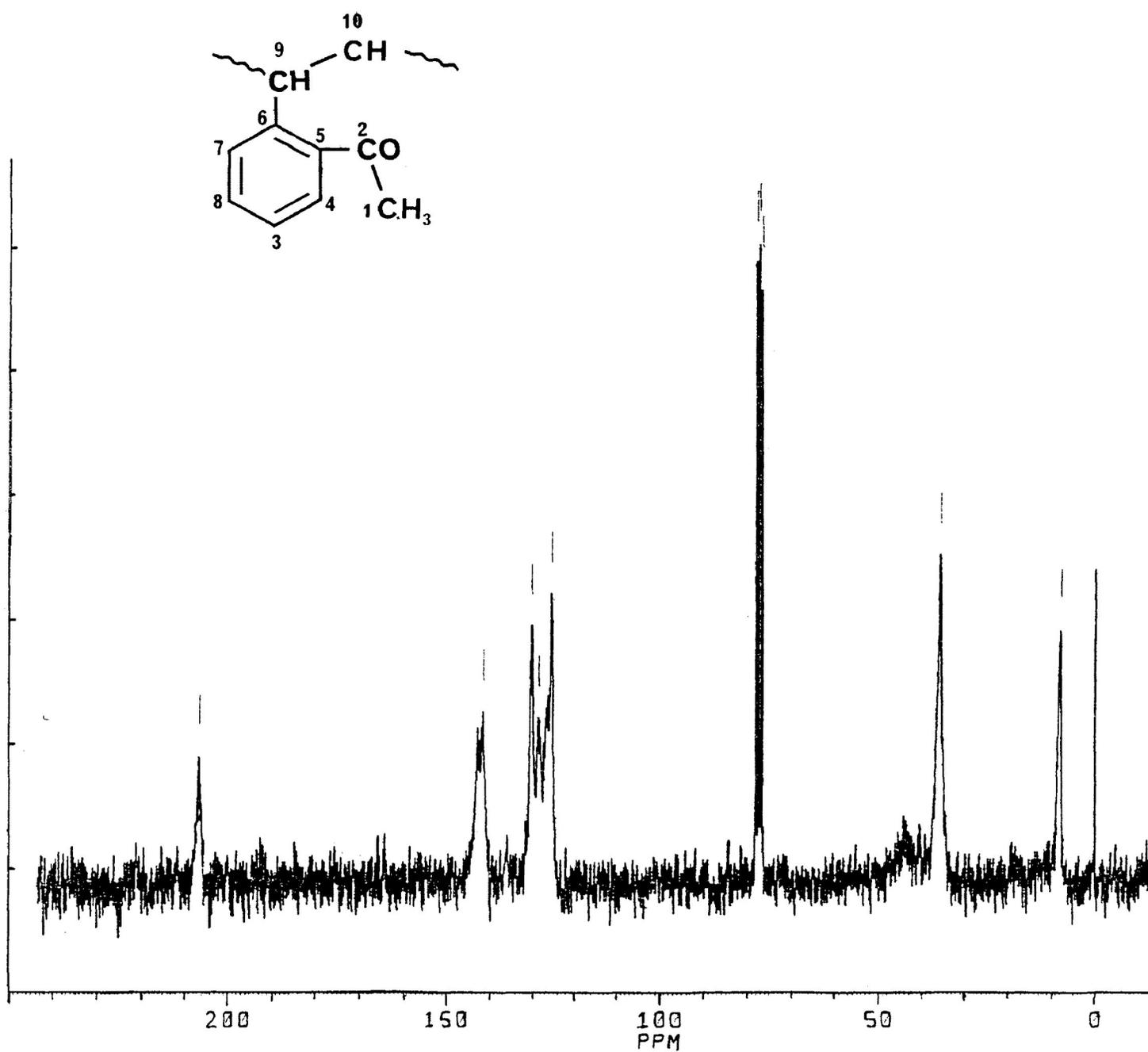


Fig. 2.8

<sup>13</sup>C-NMR Spectrum of POAS (refer to Table 2.1 for interpretation of spectrum)

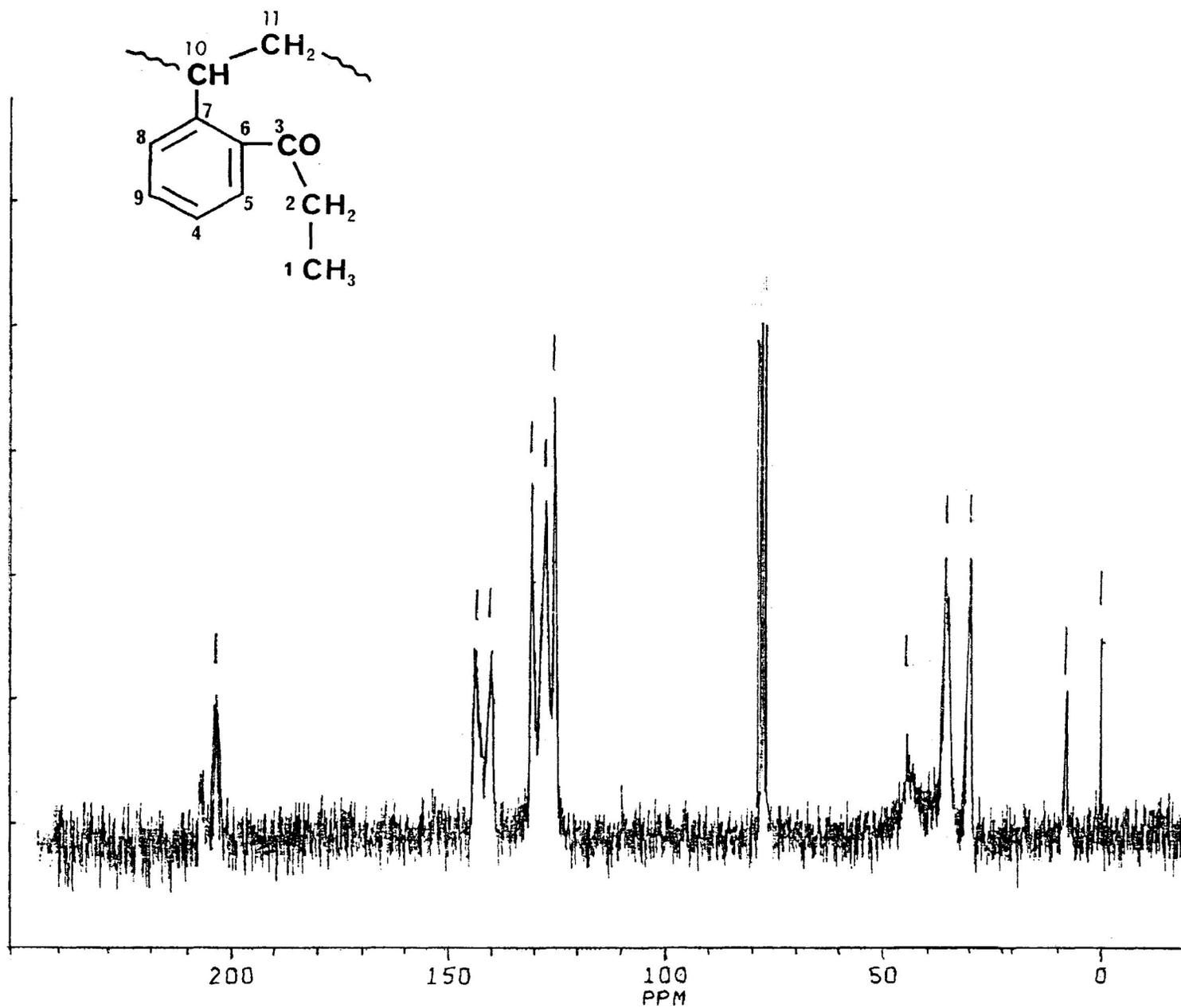


Fig. 2.9

<sup>13</sup>C Spectrum of POPS (refer to Table 2.1 for interpretation of spectrum)

Table 2.1

## C-13 nmr Analysis of Polymers

## Chemical Shift (PPM)

Carbon Atom	PPAS	POAS	PPPS	POPS
1	26	8	8	8
2	197	206	32	35
3	135	125	200	203
4	128	128	135	125
5	127	141	128	140
6	149	143	128	127
7	127	125	149	130
8	128	129	128	125
9	40	44	128	143
10	42	35	41	45
11	—	—	44	29

$$n_{sp}/c = [\eta] + Kc[\eta]^2 \quad (2.2)$$

Where K is a constant (0.47) and c is the concentration of the polymer solution (g/100ml). The specific viscosity of the polymer solution can then be related to the time of flow of the solution through the viscometer by:

$$n_{sp} = (t - t_0) / t_0 \quad (2.3)$$

Where  $t_0$  and  $t$  are the times of flow for the solvent and the solution, respectively.

Viscosity measurements were initially made using a Cannon-Ubbelohde dilution viscometer. The temperature was kept constant at 20°C in a Cannon constant temperature bath (Cannon Instrument Corp.).

As the molecular weights of the *para* substituted polymers are known it was possible to determine the Mark-Houwink constants from solutions of the *para* substituted polymers using two polymers of differing molecular weight. The weight average of the PPPS and PPAS polymers that were used were 181,538 and 126,307 for PPPS and 167,423 and 113,846 for PPAS. Times of flow for the solvent and solutions were made and the values of the Mark-Houwink constants were calculated to be as follows:

$$\begin{aligned} \text{PPPS} \quad K &= 4.4 \times 10^{-4} \pm 2.09 \times 10^{-4} \\ a &= 0.6793 \pm 0.130 \end{aligned}$$

$$\begin{aligned} \text{PPAS} \quad K &= 5.6 \times 10^{-4} \pm 1.5 \times 10^{-4} \\ a &= 0.6812 \pm 0.090 \end{aligned}$$

It was assumed that these values would not change significantly for the *ortho* substituted polymers so the molecular weights of the *ortho* substituted polymers were calculated using these values.

A 1% solution of the *ortho* polymer was made up in 10 ml of chlorobenzene and the time of flow of the solvent and solutions were made in a Cannon

Ubbelohode dilution viscometer. The molecular weights of the POPS polymer was then calculated to be 22,866; while the molecular weight was calculated to be 44,824.

### 2.3 Photochemical Techniques

For IR analysis a thin film of polymer was prepared on a sodium chloride plate by evaporation of a solution of polymer. The polymer was irradiated by placing the film in a quartz tube fitted with a ground glass joint to ensure an air tight seal. The system was degassed with nitrogen prior to sealing.

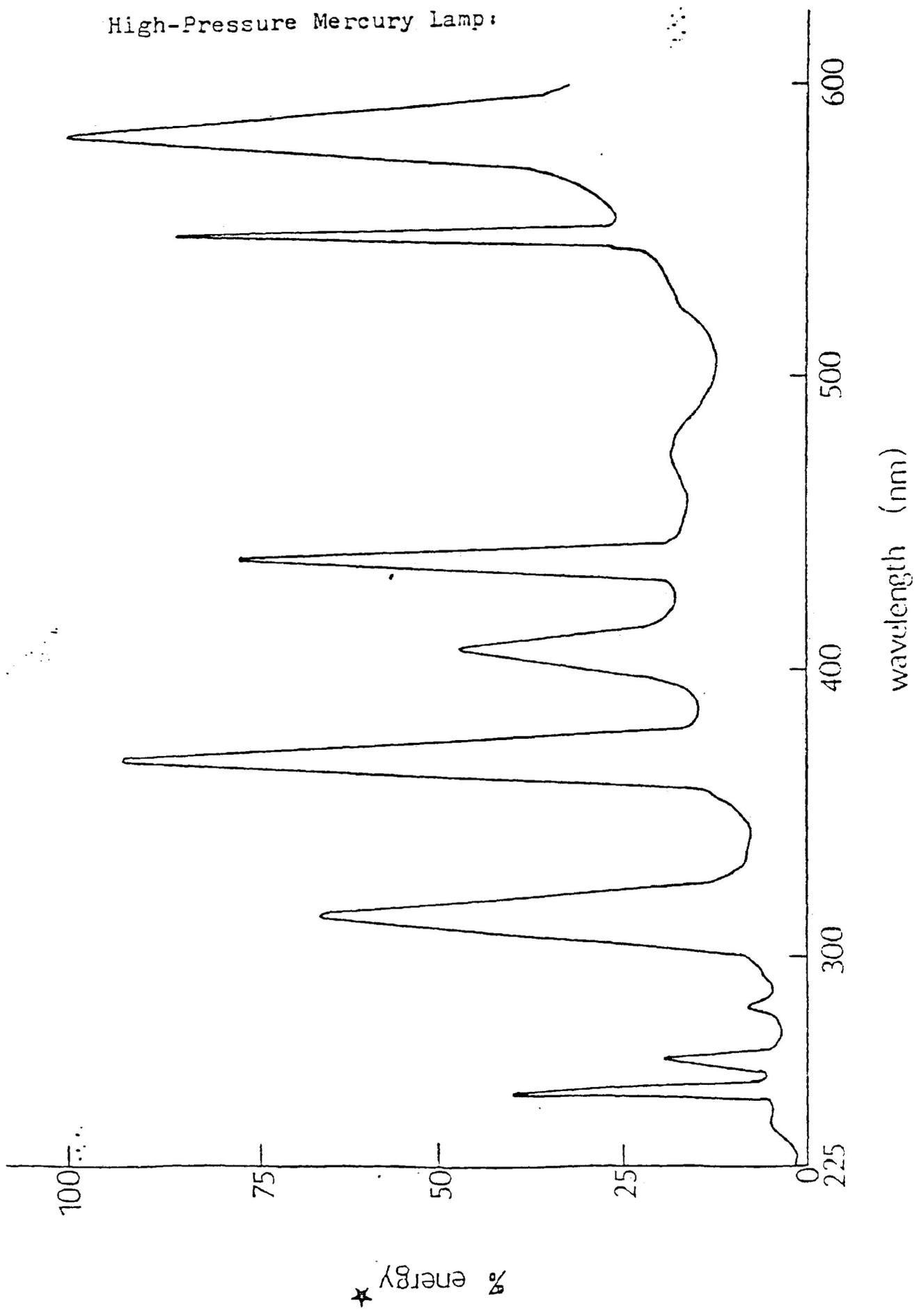
For UV analysis, a thin film of polymer was evaporated on the inside wall of an anaerobic UV quartz cell. The cell was equipped with a ground glass joint to ensure an air tight seal and the system was degassed with nitrogen prior to sealing.

For gas product analysis, 0.01g of polymer was prepared on a quartz slide by pressing the polymer onto the slide while carefully heating the slide. The slide was then placed in a vycor tube equipped with a ground glass joint. The vycor tube was then attached to a high vacuum system (Fig.2.10) and degassed until  $10^{-5}$  mm Hg was obtained. The pressures were monitored with an Edwards G6B Pirini gauge and an Edwards IG5G ion gauge. The vycor tube was surrounded by a water jacket to ensure a constant temperature of 25°C during the irradiation of the film.

For molecular weight measurements a 1% solution of polymer was made up in methylene chloride. The solution was then placed in a specially designed viscometer (Fig. 2.11) equipped with a ground glass joint. To ensure the removal of oxygen, the system was degassed with nitrogen for 20 minutes prior to sealing the viscometer. Only long wave ultraviolet light was required, therefore, a pyrex filter was employed to ensure that radiation  $\geq 300\text{nm}$  was transmitted.

For IR, UV, and molecular weight measurements the distance of the sample from the light source was kept constant at 10 cm. The lamp used for the investigation was an Ace Hanovia Quartz Mercury vapour lamp (200w). The spectral distribution of the lamp is given in Fig. 2.12.

Fig. 2.12 Spectral Distribution of the Hanovia (654A10)  
High-Pressure Mercury Lamp:



\* - based on 100% at 578nm

## 2.4 Analytical Techniques

### 2.4.1 Infrared Spectrophotometry

Films of polymer were prepared on sodium chloride plates which were, in turn, sealed in an oxygen free environment and exposed to long wave ultraviolet radiation. The IR spectra were then recorded after 5 and 10 hours of irradiation using a Perkin-Elmer 1320 Infrared Spectrophotometer.

### 2.4.2 Ultraviolet Spectrophotometry

The ultraviolet measurements were made using a Bausch and Lomb Spectronic 2000 UV/Visible spectrophotometer.

Films of polymer were evaporated on the inside of anaerobic quartz cells. The cells were degassed with nitrogen for 20 minutes and sealed. UV spectra were initially recorded and then the films were exposed to long wave ultraviolet radiation. The spectra were then recorded after 2.5, 5, and 10 hours of irradiation.

### 2.2.3 Gas product Analysis

Apparatus: A system was constructed around a Micromass Q7 Quadrupole Mass Spectrometer (VG-Micromass Limited) fitted with a photomultiplier, to monitor volatile products produced during vacuum photolysis (Fig. 2.10). In particular, two independent systems were employed, each isolated by a high vacuum stopcock.

The gas inlet system consisted of an oil-vapour diffusion pump (D1) (Edwards model E01) backed by an Edwards ES1 rotary pump. Adjoining glassware contained liquid nitrogen traps (L1 and L2), isolation stopcocks and a ground glass joint (J1), to accept a modified quartz reaction vessel. To maintain polymer films at 25°C during irradiation a quartz tube was fitted with a water jacket through which thermostatically controlled distilled water was circulated. Pressures in the inlet system were monitored with an Edwards G6B Pirani Gauge (G1) and a IG6G ion gauge (G2). The enclosure, containing the ultraviolet lamp and fan was



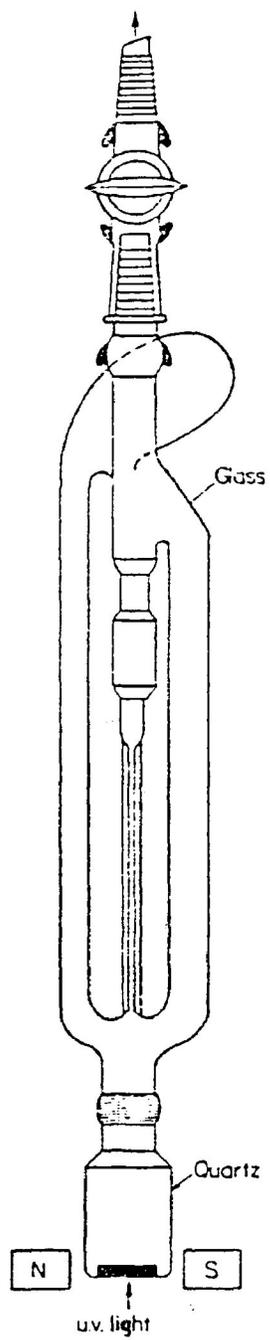


Fig. 2.11

Viscometer for photochemical studies

designed for irradiation of the polymer system for controlled periods of time (Fig. 2.13). The high pressure mercury lamp, reflector, and quartz reaction tube were separated by a removable divider and enclosed in a light tight stainless steel container. This allowed for the lamp to stabilize for 20 minutes prior to irradiation of the sample (warm-up procedure). The distance of the sample from the lamp was constant at 8 cm.

The mass spectrometer head (H) was rigidly mounted in an insulated enclosure fitted with an heating element. An Edwards mercury-vapour diffusion pump (model EM2) (D2) was fitted with a flap-valve (V) and a liquid nitrogen trap (L4) and was backed with an Alcatel rotary pump (model 2004). Pressures, typically  $1 \times 10^{-7}$  torr, were monitored with an Edwards IG5G ion guage (G3). An electronic safety device was constructed to protect the mass spectrometer while in operation against possible vacuum failure.

Procedure: The mass spectrometer was operated with a photomultiplier voltage of 2.5 Kv and a filament voltage of 2.4 mA (tungsten filament). A scan of the entire mass range (1-120 amu) was then made. All spectra were recorded on a Fisher Recordall Series 5000 strip chart recorder, with the sensitivity set at 100 mV, or 1 V.

Polymer films on quartz plates were placed inside a modified vycor tube which was coupled directly to the inlet system at port J1. All connections were made and sealed with Apiezon T high vacuum grease.

The diffusion pump (D1) was isolated by closing stopcocks S1 and S2 and the reaction tube was 'rough' pumped by opening stopcocks S3, S4, and S5. When the pressures were within diffusion pump limits, stopcock S3 was closed and stopcocks S1 and S2 were opened to lower the pressure inside the reaction vessel to  $1 \times 10^{-6}$  Torr. When the pressure inside the reaction vessel had stabilized at the lower limit, the reaction vessel was the isolated by closing stopcock S5. The mass spectrometer was evacuated by isolating the diffusion pump, D2, by closing stopcock S9 and the flapvalve. Stopcocks S9 and S10 were opened and the pressure inside the spectrometer head and adjoining glassware was reduced to within the diffusion pump limits. Stopcock S10 was closed and stopcock S9 and the flapvalve were opened to reduce the pressure inside the system to  $1 \times 10^{-7}$  Torr.

After the mass spectrometer had been pumped down for several hours, a

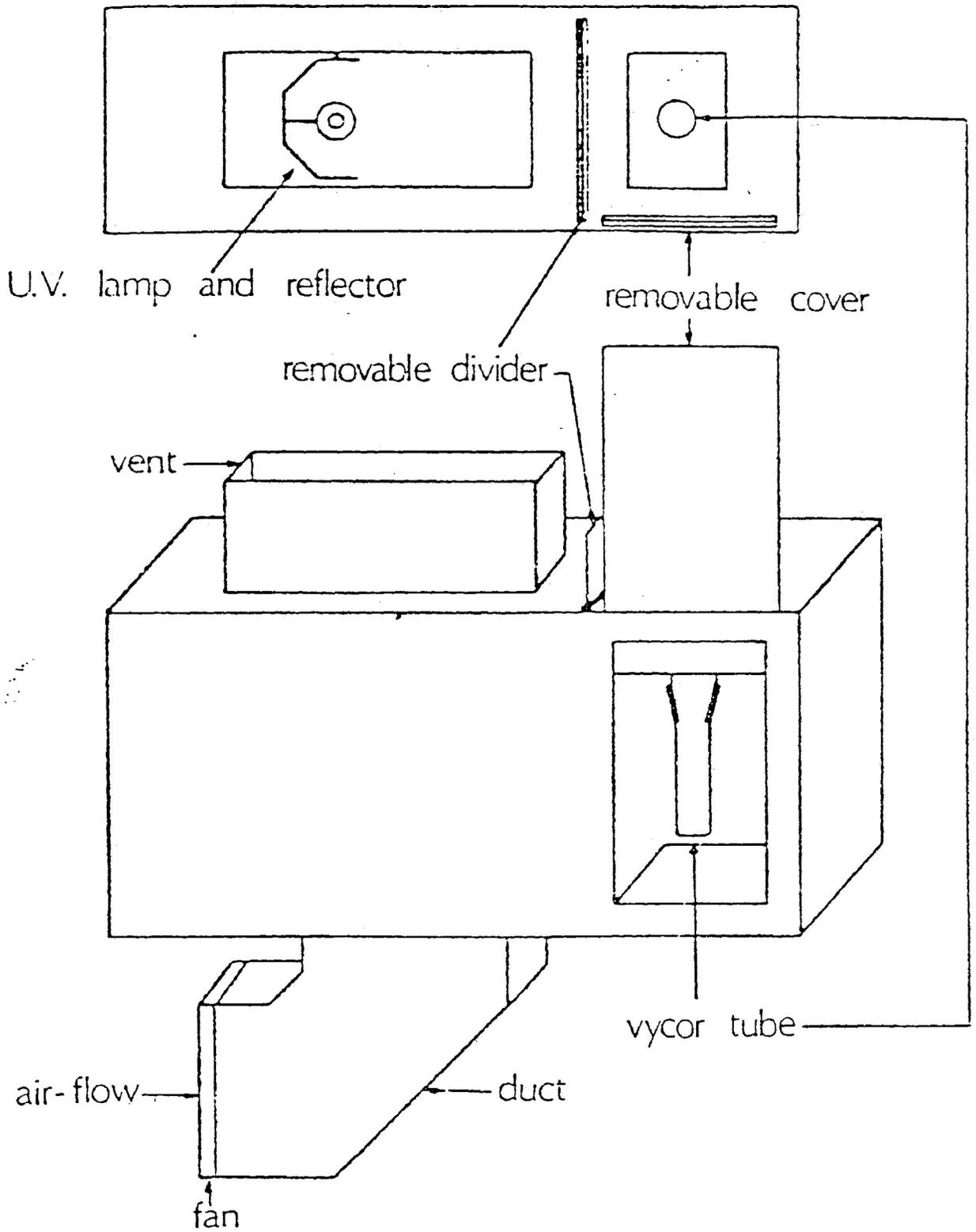


Fig. 2.13  
Exposure Enclosure

background spectrum was recorded. Stopcock S8 was closed and after 2 and 3 hours, gaseous products inside the reaction vessel were sampled by briefly opening and closing stopcock S7. Products contained in the adjoining glassware were admitted to the mass spectrometer by opening stopcock S8. At the end of each scan, stopcock S8 was closed and the mass spectrometer was pumped down. A background was recorded prior to each analysis during irradiation.

Between product analyses, the mass spectrometer was 'baked' at 275°C for 24 hours under reduced pressure to remove all traces of products left over from the previous films.

Volatile product analysis provided a qualitative analysis of the gaseous products produced during photolysis of these polymer films.

#### 2.2.4 Molecular Weights

First a 1% solution of the polymer was prepared in a suitable solvent (chlorobenzene). Viscosity measurements were then made in a modified Cannon Ubbelohde dilution viscometer (Fig 2.11) that contained a quartz reaction chamber to allow for irradiation of the polymer solution. Viscosity measurements were carried out in a sealed environment. The viscometer contained a ground glass joint to ensure an air tight seal and all measurements were carried out in a nitrogen environment to eliminate any photooxidation of the polymer system.

Initially, time of flow readings were taken on the solvent and the solution. The polymer was then irradiated under long wave UV and viscosity measurements were made after 30, 60, 90, 120, 180, 240, and 300 minutes of irradiation.

#### 2.2.5 Transient Spectroscopy

Sample preparation: Polymer samples were prepared in methylene chloride to a concentration that gave an optical density in the range of 0.3-0.7. Then 1ml of sample was placed in a Supersil cell with a 3mm path length. Room temperature was used for all transient spectroscopy studies.

Apparatus: The apparatus used for transient spectroscopy is explained by Scaiano.<sup>42,43</sup> The excitation source is a Molecron UV-24 nitrogen laser which

produces 8-10 ns pulses of up to 10 mJ at 337.1 nm. The excitation dose was adjusted to between 0.5 and 10 mJ by the use of suitable neutral density filters. The pulses were concentrated on the samples by a combination of spherical and cylindrical lenses.

The monitoring system consists of a Pulses 200-W xenon lamp as a light source, a high intensity B & L or PRA-B204 monochromator, and an RCA-4840 photomultiplier tube at the detection end; only six dynodes were used. The angle between the excitation beam and the monitoring beam was approximately 15°. The system is fully interphased with a PDP11/03 computer which controls the experiment, gathers data, processes information, produces suitable files on storage devices, and provides copies of graphics and other useful information to reproduce the experiment.

The laser is pulsed at a frequency of 1 Hz and has been synchronized with a line frequency. Pulsing the laser regularly leads to very reproducible pulse energies. When a pulse is needed for the experiment, an Uniblitz shutter is triggered following an "enable" command from the computer; at the same time, a second shutter opens to allow the monitoring beam to reach the analysing monochromator. Another command activates the lamp pulser. All these commands are controlled via different bits from the low-byte output from a 16-bit parallel interface (DEC-DRV11). The synchronizer-sequence unit generates pulses to activate all the units (shutters, pulser, detector, etc.) once every second (with suitable delays); the computer's role is to enable the desired units to gather information. This type of approach makes it easy to correct for background luminescence by enabling only some of the units. The high byte output and 16-bit input in the DRV11 interface are used to control the driver unit (PRA Model 1611) of the PRA-B204 monochromator. The computer provides the pulse to drive the stepping motor, and the wavelength is checked by feeding the BCD output of the PRA-1611 unit in the 16-bit input of the DRV11 parallel; DEC-Fortran-IV extension routines are used to process the data. Typical slits are 0.5 mm for input and 1 mm for output.

A DEC-ADV11-A, A/D interface is used in order to measure the intensity of the monitoring beam and is also available to monitor other parameters during the experiment. The photomultiplier signals are terminated into 93 ohm and into a

7A16A plug in used in a R7912-Tektronix transient digitiser. The latter contains 4 K local memory in which each trace, plus all associated "knob" settings are stored. A Tektronix 607 storage monitor displays every trace by the transient digitiser; the memory from the latter is read by the computer via a CP-4100/CP bus Tektronix interface. The trace information from the R7912 digitiser consists of 512 "x" or timebase values; each one of the "x" coordinates can have one, several, or no "y" (vertical, or voltage) values associated with it. In order to process the data it is important to generate a trace such that each "x" value is associated with only one "y" value. In order to achieve this, software was generated by Scaiano and colleagues rather than using software from the manufacturer. For every "x" value, the "y" values are averaged, if more than one "y" value is generated, or interpolated if that "x" value contains no "y" value. In processing the data in this manner one must use very strict criteria in evaluating the quality of a given trace, since it would be very easy to generate excellent looking traces from very little information.

A programmable photomultiplier power supply has been built around a Model LR-2N, Venus PMT power supply (Subtech Ltd.). The computer has been programmed to set the high voltage so that a suitable current will be drawn from the photomultiplier, based on wavelength signal during photolysis shots, etc. The computer commands are fed into the power supply via one channel (17442) from a DEC-AA11-A 12-bit D/A converter. This unit was extremely useful for the automatic recording of transient spectra.

In general, the time resolution (in terms of the interval between points) that can be achieved with the R7912 digitiser amply exceeds that required for nanosecond experiments. It is generally preferred to handle 100 points rather than the 512 and to accomplish this the center 400 points are "nested" into groups of 4, giving 100 points which are generally displayed on the traces. In general 5 to 30 traces are averaged to carry out a kinetic measurement and 3 to 8 traces at each wavelength for the spectrum

After the data has been processed, all graphic outputs were displayed on a Tektronix 4010-1 terminal, and a 4631 Tektronix unit provides hardcopies. The results are also stored on double density flexible disks.

The risetime of the system was approximately 1ns, but the actual 'window' in which measurements could be carried out was 10 ns to 500 microseconds. The rate at which data

could be collected was approximately 1 trace every 3 s, though it should be noted that this rate is controlled by the rate at which the capacitors used for the lamp pulser are recharged.

## Results

### Introduction

The following are the results of investigations of the long wave photolysis of PPAS, PPPS, POAS, and POPS (wavelength  $\geq 300$  nm)

### 3.1 Transient Spectroscopy

Transient spectra were recorded for solutions of these polymers in order to gain an insight into the transient species produced upon irradiation. In addition, the transient spectrum of a model compound (2-methyl-acetophenone) was recorded in an attempt to identify some of the transient species.

Fig.3.1 shows a typical transient spectrum of 2-methyl-acetophenone in methylene chloride. There are two distinct species produced; one with a very short lifetime and one with a long lifetime. The broken line on the spectrum shows the fit of the long lived species to first order decay kinetics. The two plots to the right of the actual spectrum show how good a fit the experimental data is to the first order decay kinetics.

Fig 3.2 - 3.8 have all been reproduced to allow for clearer presentation of the results.

In Fig 3.2, the transient spectrum of PPAS in methylene chloride is shown, the single transient species with having a lifetime of 184 ns. The addition of a known triplet quencher (1,3-octadiene, or oxygen) results in a reduction of the signal strength due to the transient.

Fig. 3.3 shows a transient spectrum of PPPS in methylene chloride. The decay that is of a single transient species with a lifetime of 147 ns. The addition of known triplet quencher (1,3-octadiene, or oxygen) results in a reduction in the signal strength due to the transient species.

Fig. 3.4 shows the transient spectrum of POAS in methylene chloride. The decay of an extremely long lived transient species, with a lifetime of 4.5  $\mu$ s can be

seen.

Fig. 3.5 shows the transient spectrum of POAS in methylene chloride, but looking at a shorter time scale than Fig 3.4. Here it is possible to see a short lived transient species with a lifetime of 161 ns. Both spectra (Fig. 3.4 and Fig. 3.5) are unaffected by the addition of known triplet quenchers (1,3-octadiene, or oxygen) .

Fig. 3.6 shows the transient spectrum of POPS in methylene chloride and the presence of a short lived transient species with a lifetime of 125 ns. No long lived transient species was detected. The strength of the signal due to the decay of this transient is unaffected by the addition of known triplet quenchers (1,3-octadiene, or oxygen).

Fig 3.7 shows the transient spectrum of a model compound (2-methyl-acetophenone) in methylene chloride. The spectrum shows the decay of a long lived transient species with a lifetime of 4.5  $\mu$ s. It was also observed that there is another transient present with a much shorter lifetime which is more clearly resolved in Fig. 3.8. This transient has a short lifetime (176 ns). Both long and short lived transients are unaffected by the addition of known triplet quenchers (1,3-octadiene, or oxygen).

### 3.2 Infrared Spectra

Infrared spectra were recorded for all polymers prior to and after 5 and 10 hours of long wave ultraviolet irradiation. All spectra showed no significant change in the signal at  $\sim 1680 \text{ cm}^{-1}$  (carbonyl absorption). See Fig 3.9 for the spectrum of a PPS film (all other spectra were similar).

### 3.3 Ultraviolet Spectra

Ultraviolet spectra were recorded for all polymers prior to and after 2.5, 5, and 10 hours of long wave ultraviolet irradiation. The absorption at 310 nm , which is due to the  $n \rightarrow \pi^*$  transition, showed no significant change after irradiation. See Fig. 3.10 for a typical spectrum (PPS film), all other polymers showed similar results.

### 3.4 Gas Product Analysis

The results of these measurements serve as both a quantitative and qualitative analysis of the amount of gas products produced as a result of long wave ultraviolet irradiation of these polymer systems.

For both PPAS and PPPS the main gas product produced was methane, with small amounts of ethane being detected. See Fig 3.11 for a plot of the amount of gas products produced for PPAS vs. the time of irradiation. Plots for the other polymer systems were similar and the initial rates of gas product formation are tabulated in Table 3.1. For POPS and PPPS the main gas products detected was ethane with significant amounts of methane being detected. Also for PPPS trace amounts of butane was detected. The initial rates of gas product formation for these polymers is also tabulated in Table 3.1.

### 3.5 Molecular Weights

From the initial viscosity measurements a number of quantities were calculated. Firstly, the limiting viscosity  $[\eta]$  was calculated from equations 2.2 and 2.3 and from this quantity the number of chain scissions per polymer molecule ( $S$ ) was obtained by use of from the following equation:

$$S = \left[ \frac{[\eta]_0}{[\eta]_t} \right]^{1/a} - 1$$

Where  $[\eta]_0$  is the limiting viscosity prior to irradiation,  $[\eta]_t$  is the limiting viscosity after time  $t$  of irradiation, and  $a$  is the Mark Houwink constant. The use of this equation is justified since the polydispersity index did not change to any measurable extent over the irradiation times used.

Fig 3.12 - 3.33 show plots of  $S$  vs time of irradiation for solutions of these

polymers, in chlorobenzene under varying conditions.

Fig 3.12 shows a plot of  $S$  vs irradiation time for PPAS and POAS in an attempt to investigate the different rates of chain scission for these two isomeric polymers. It is noted that POAS undergoes chain scission at a slower rate than PPAS.

Fig 3.13 shows a plot of  $S$  vs irradiation time for PPS and POPS. It is again noted that the *para* substituted polymer undergoes chain scission at a faster rate than its *ortho* substituted counterpart.

Fig 3.14 - 3.17 examines the affect of known triplet quencher (naphthalene) on the rates of chain scission. It is observed that the presence of naphthalene does decrease the rate of chain scission for PPS and PPAS, with the rate of decrease being proportional to the concentration of naphthalene. However, for the case of POPS and POAS the presence of naphthalene seems to give rise to an increase in the rate of chain scission for these systems.

Fig 3.18 - 3.19 examines the affect of another known triplet quencher (1,3-cyclooctadiene). For the case of POPS and POAS it was observed that the presence of quencher gave rise to a decrease in the rate of chain scission. However, for the case of the *para* substituted polymer the presence of 1,3-cyclooctadiene resulted in precipitation of the polymer out of solution upon irradiation, thereby making measurements impossible.

Fig 3.20 - 3.21 examines the affect of a hydrogen donor system (cumene) on the rate of chain scission. It was observed that for both POPS and POAS that the addition of cumene increases the rate of chain scission. Again for the case of PPS and PPAS the addition of cumene resulted in precipitation of the polymer out of solution upon irradiation.

Fig 3.22 - 3.25 examines the affect of an energy transfer agent bromotrichloromethane (BrTCM). It was observed that the presence of BrTCM does give rise to an increase in the rate of chain scission for all polymers studied.

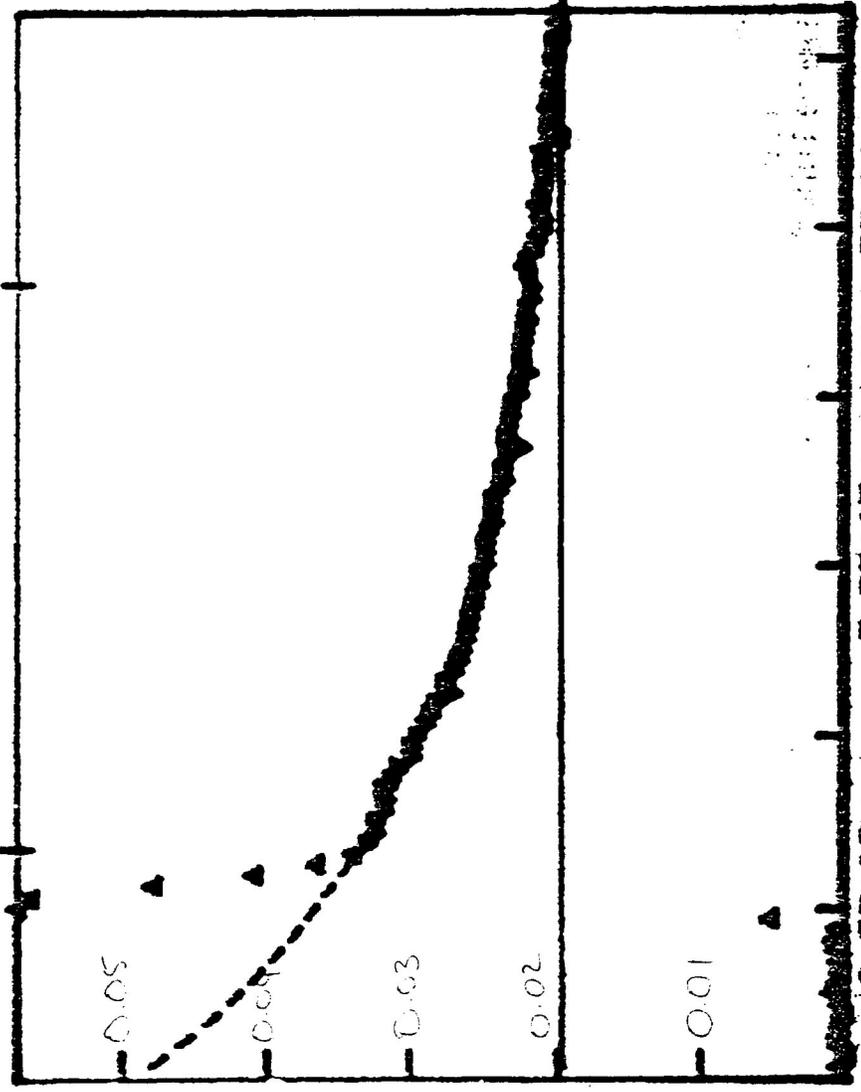
Fig 3.26 - 3.27 examines the affect of another transfer agent (isopropanol). It was observed that the presence of isopropanol to solutions of POAS and POPS gives rise to an increase in the rate of chain scission. For the case of PPS and PPAS the addition of isopropanol results in the precipitation of the polymer out of solution upon irradiation, thereby making measurements impossible.

Fig 3.28 - 3.29 examines the affect of solvent quality on the rate of chain scission. Methanol was used to decrease the quality of the solvent. It was observed that the addition of methanol to the solution resulted in an increase in the rate of chain scission for POPS and POAS. For the case of the *para* substituted polymers the addition of methanol resulted in precipitation of polymer out of solution upon irradiation.

Fig 3.30 - 3.32 also examines the affect of solvent quality on the rate of chain scission. Here cyclohexane was used to decrease the quality of the solvent. It was observed that the addition of cyclohexane to the solvent resulted in an increase in the rate of chain scission for POPS and POAS. For the case of PPPS the addition of cyclohexane results in a negative rate of chain scission. For the case of PPAS the addition of cyclohexane results in rapid precipitation of polymer out of solution upon irradiation.

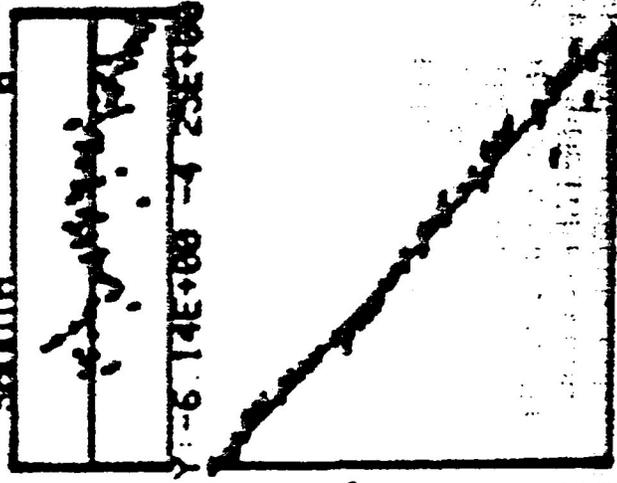
Fig.3.1 --- Transient Spectrum of 2-Methyl-Acetophenone in Chlorobenzene 68

X-ORIG 0 00E-01 YICI 2 50E+03 YIC 000 00E+00  
 Y-ORIG -4 41E-04 YICI 1 00E-02 YIC 000 00E+00  
 2-ME ACETOPHENONE IN CHLOROBENZENE  
 FILENAME KMAP1 A1 WINDOW 21 2 74 1  
 ORDER AND TYPE 1 0 TOP 00 0 05490  
 K(ALOC10 K) -2.22E+05(5 347)SOU K= 3621  
 LIFETIME(NS) -4496.2 END 00: 0.0197  
 1000/T= 3.401  
 20MV 2US



X: 3.30E+03 Y: 0.0197  
 X: 7.5E+03 Y: 0.0197  
 X: 1.0E+04 Y: 0.0197  
 X: 1.5E+04 Y: 0.0197  
 X: 2.0E+04 Y: 0.0197  
 X: 2.5E+04 Y: 0.0197  
 X: 3.0E+04 Y: 0.0197  
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 X: 8.0E+04 Y: 0.0197  
 X: 8.5E+04 Y: 0.0197  
 X: 9.0E+04 Y: 0.0197  
 X: 9.5E+04 Y: 0.0197  
 X: 1.0E+05 Y: 0.0197

14 ON 17 JAN 1980  
 0 TIME 15.170  
 0000 221 5  
 SNOTS 10  
 HDZF 100 0  
 LASER(B) 2  
 PULSER(F) 1  
 10 1  
 ERR 235 0  
 WL(NM) 390.04  
 CORREL -0.99318  
 POINTS 54  
 %CHAN 97.71  
 EXPOS 20  
 TEMP(K) 294.0  
 SMOOTH 8



X: 3.30E+03 Y: 0.0197  
 X: 6.14E+03 Y: 0.0197  
 X: 1.0E+04 Y: 0.0197  
 X: 1.5E+04 Y: 0.0197  
 X: 2.0E+04 Y: 0.0197  
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 X: 9.0E+04 Y: 0.0197  
 X: 9.5E+04 Y: 0.0197  
 X: 1.0E+05 Y: 0.0197

Optical Density

Time (NS)

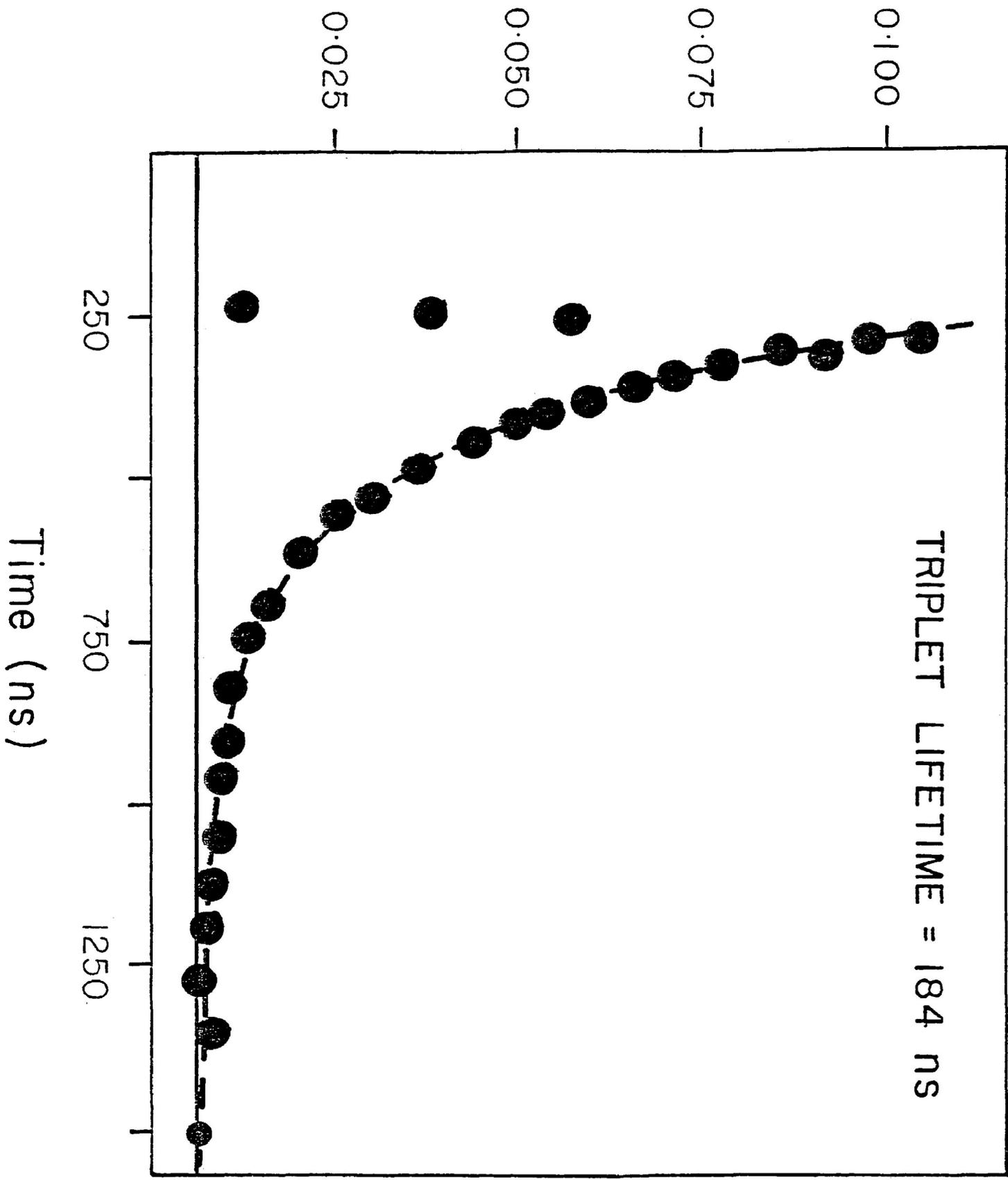


Fig. 3.2 --- Transient Spectrum of PPAS in Chlorobenzene

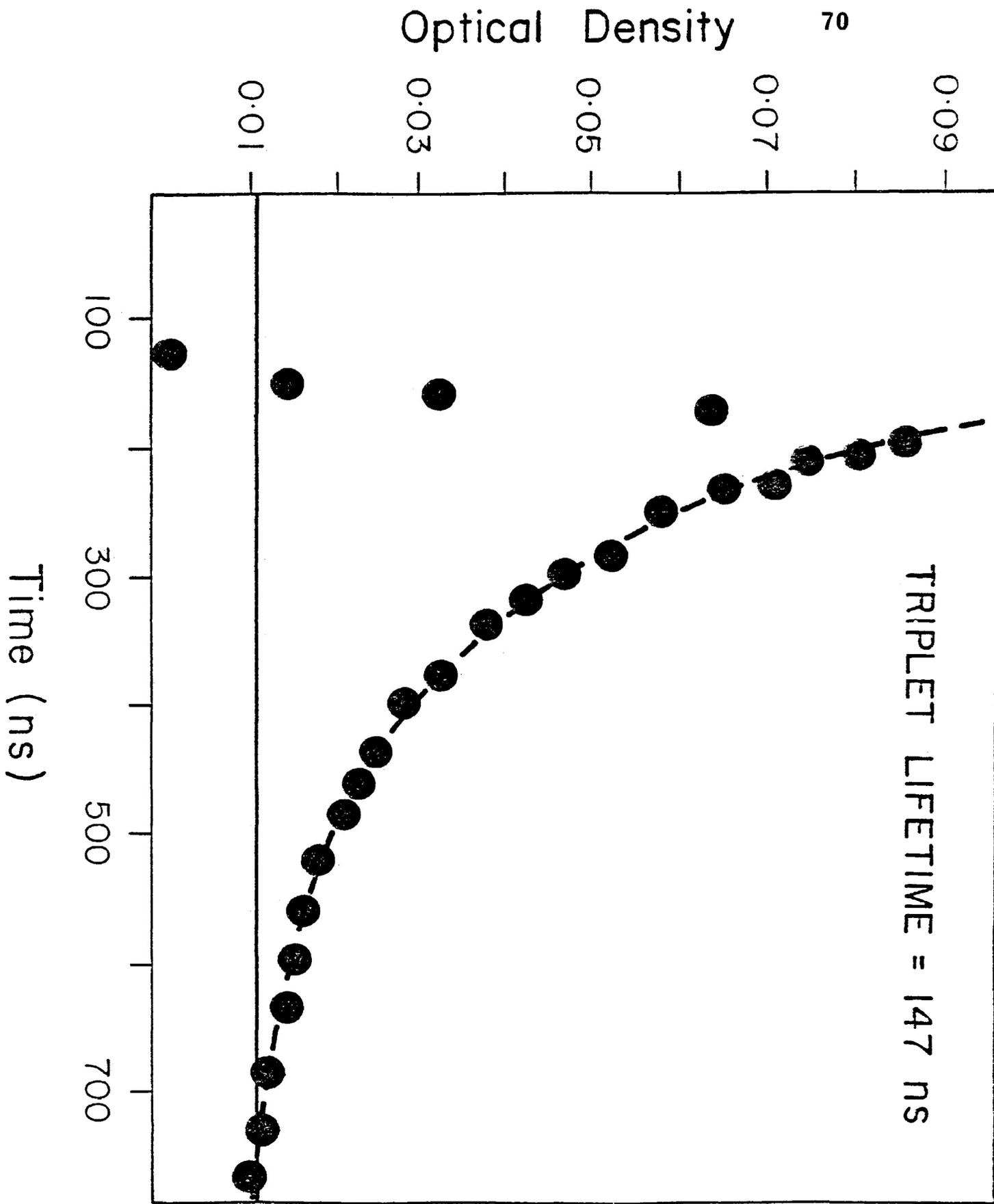


Fig.3.3 --- Transient Spectrum of PPPS in Chlorobenzene

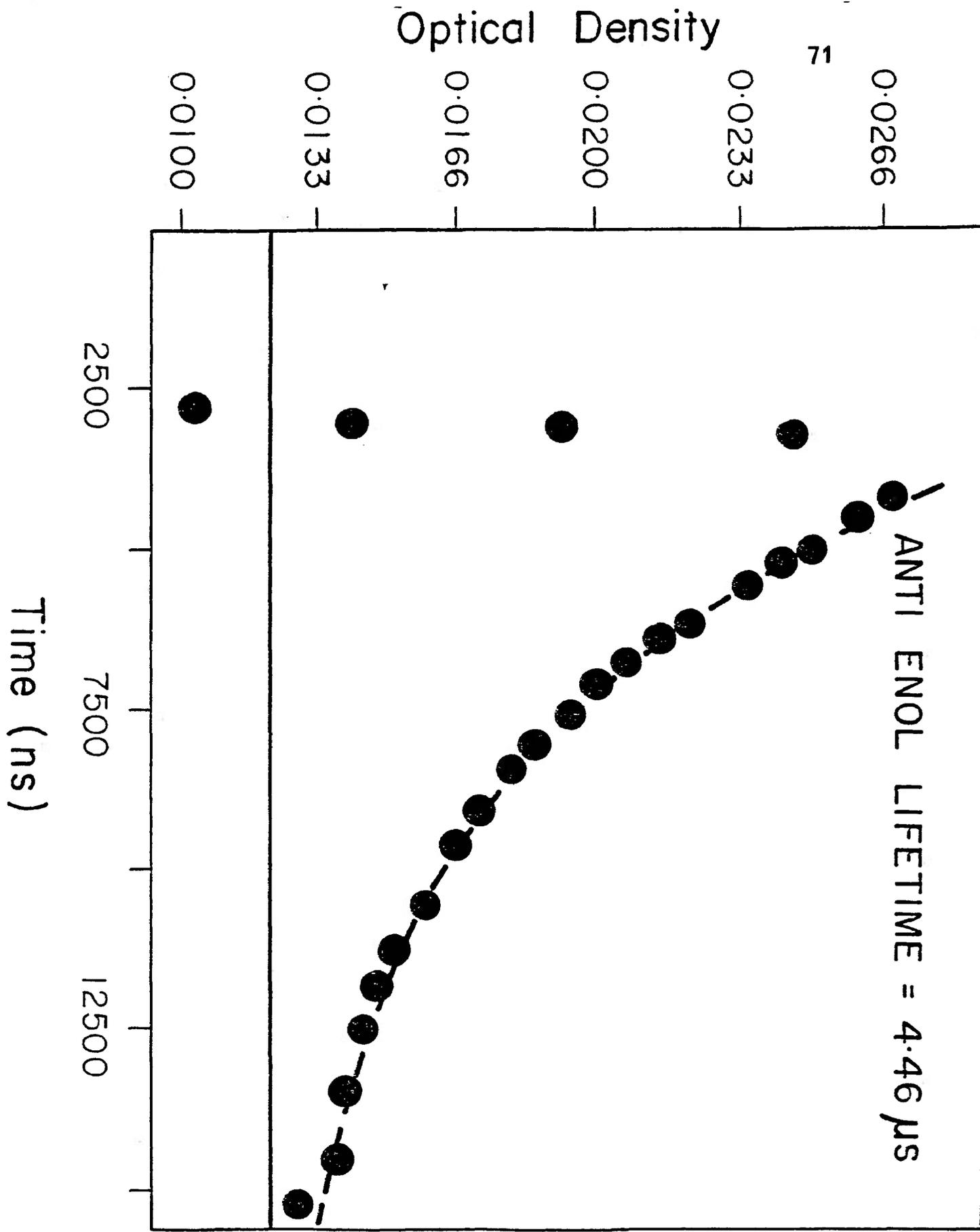


Fig. 3.4 --- Transient Spectrum of POAS in Chlorobenzene

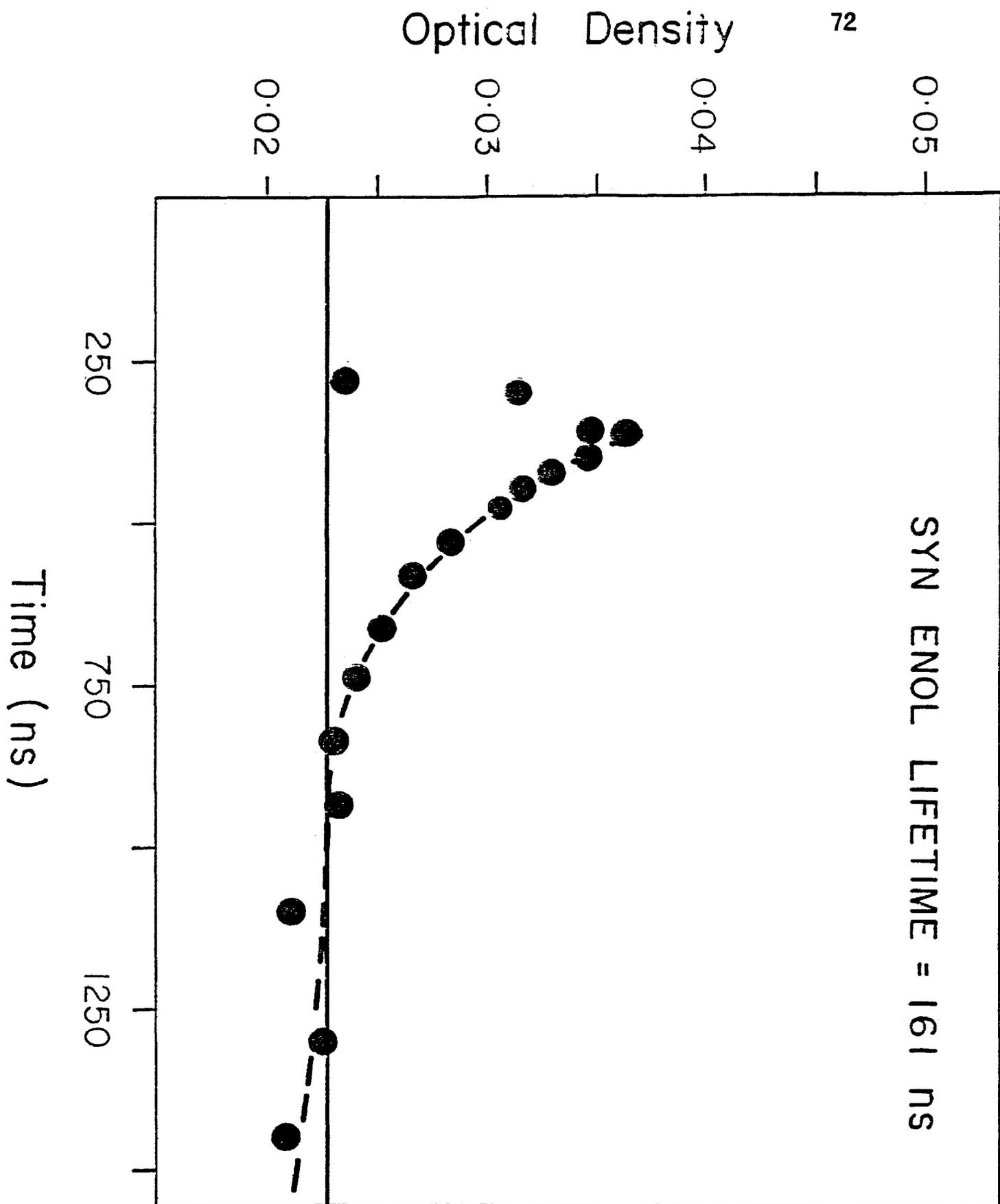


Fig.3.5 --- Transient Spectrum of POAS in Chlorobenzene

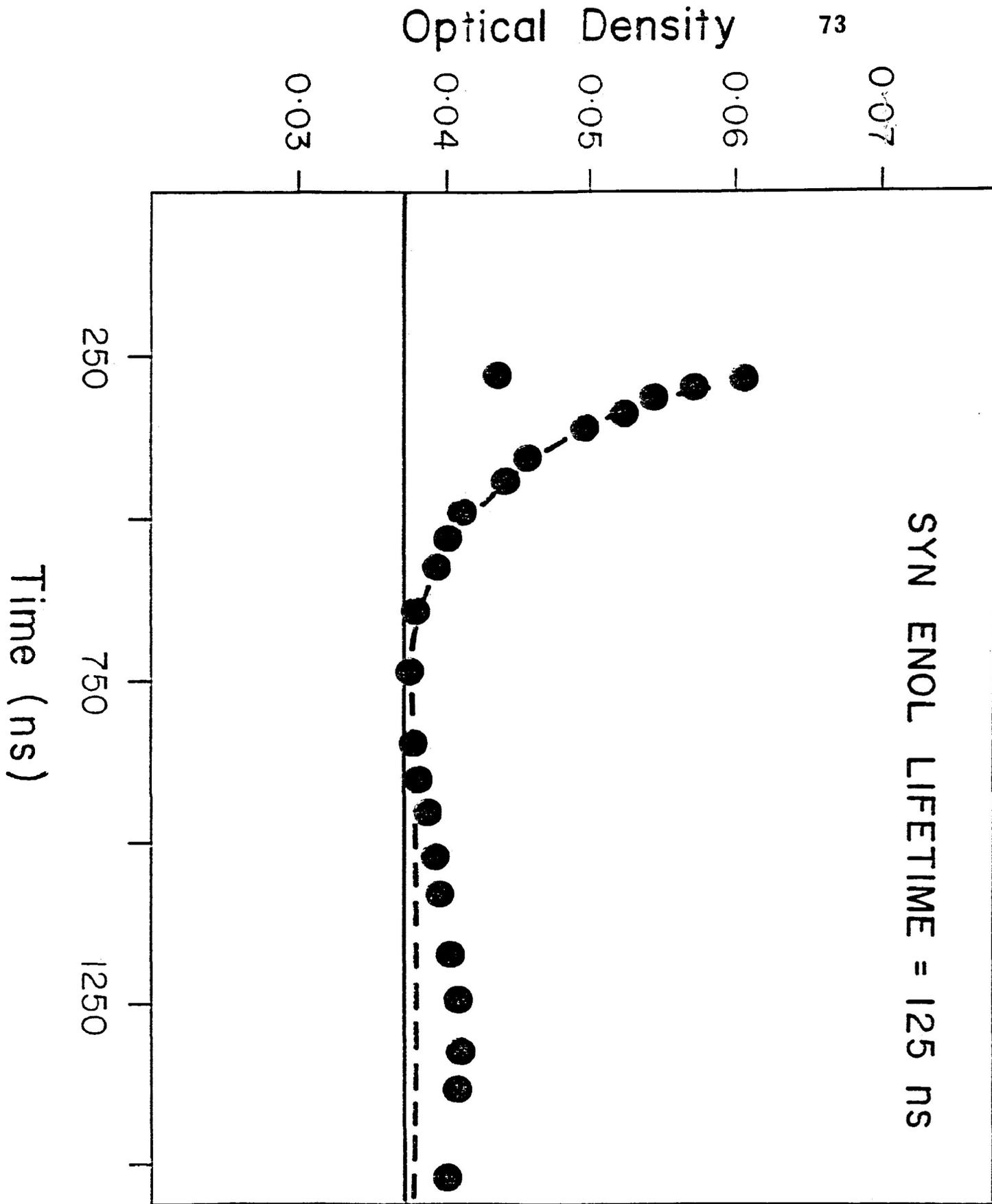


Fig.3.6 --- Transient Spectrum of POPS in Chlorobenzene

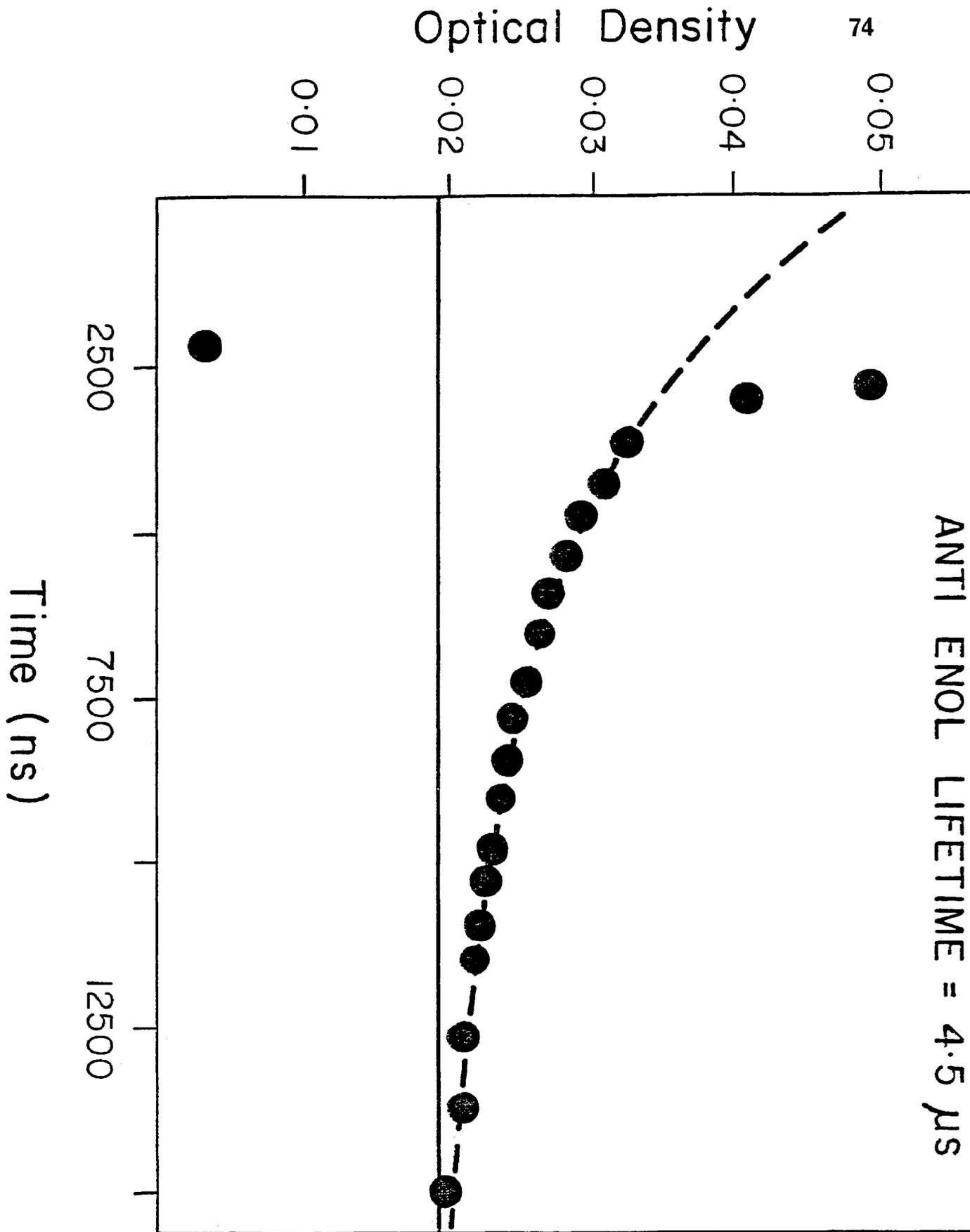


Fig.3.7 Transient Spectrum of 2-Methyl-Acetophenone in Chlorobenzene

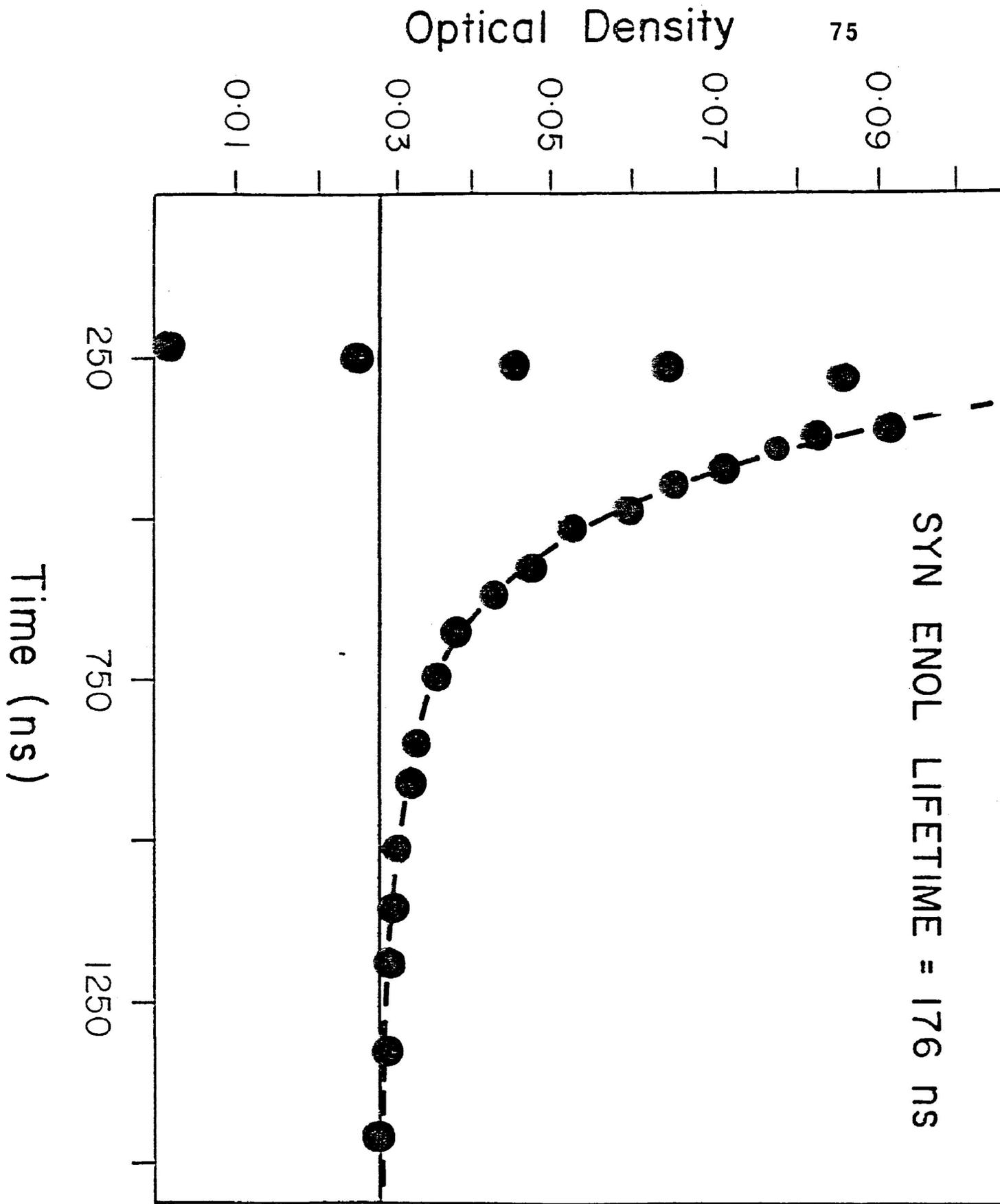


Fig.3.8 --- Transient Spectrum of 2-Methyl-Acetophenone in Chlorobenzene

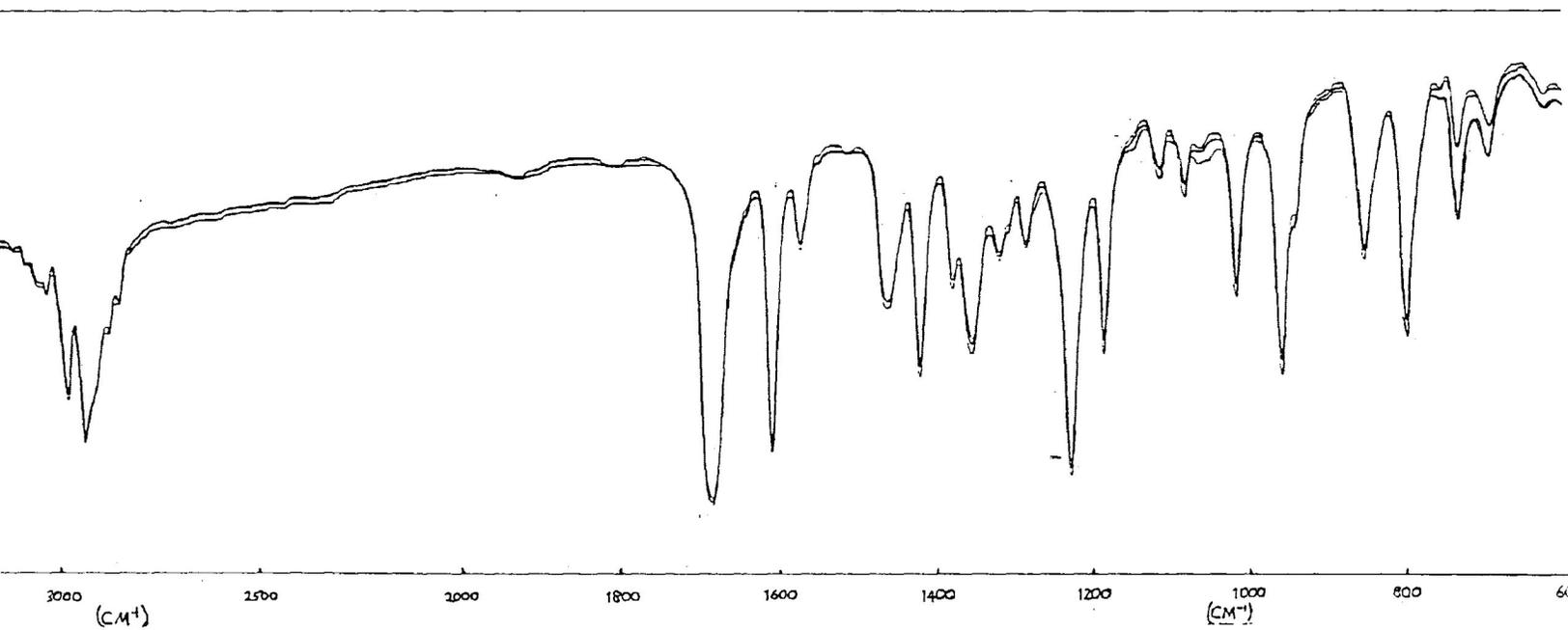


Fig. 3.9

Changes in IR Spectrum for PPS Films Upon Irradiation

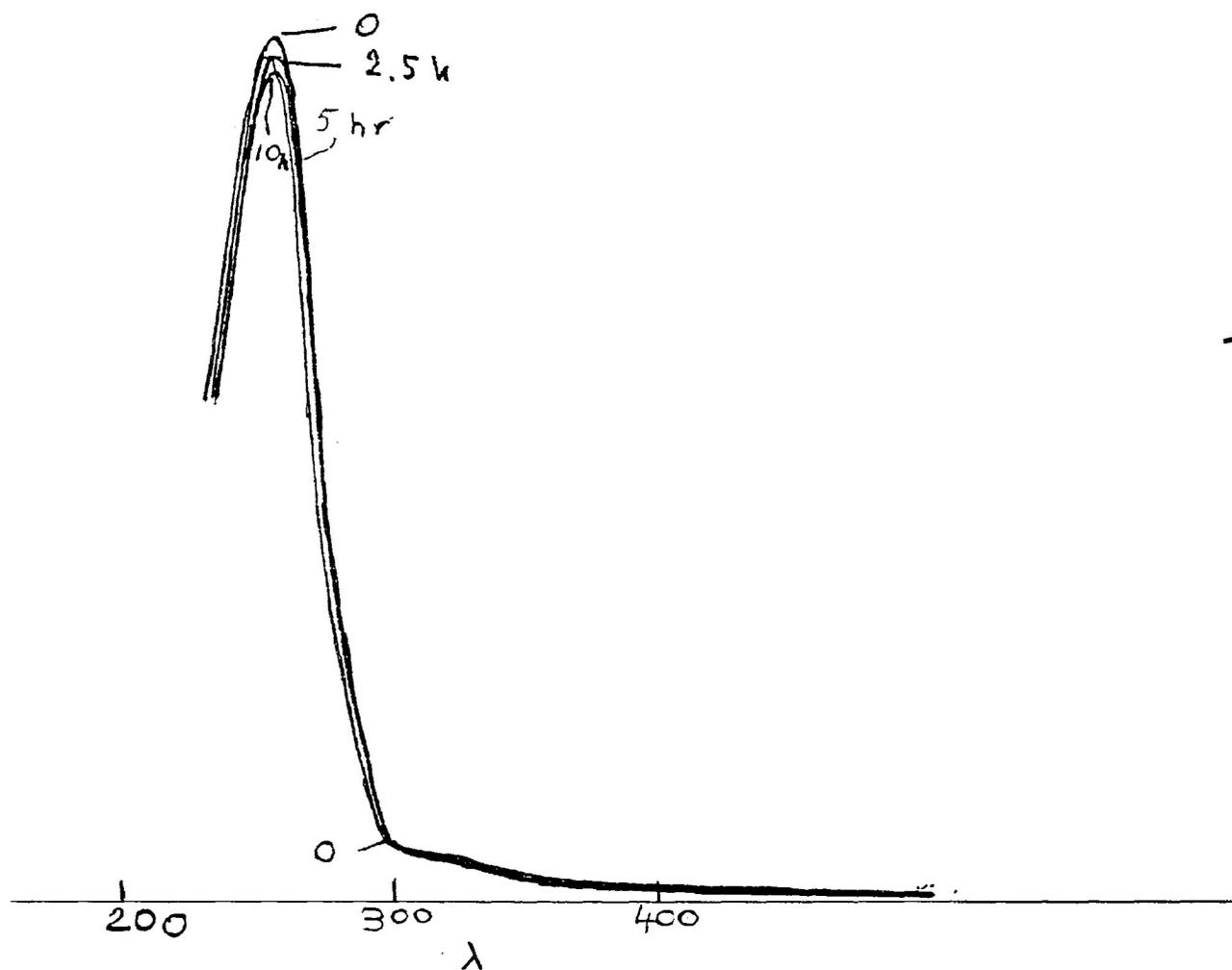


Fig. 3.10 ---

Changes in UV Spectrum for PPS Films Upon Irradiation

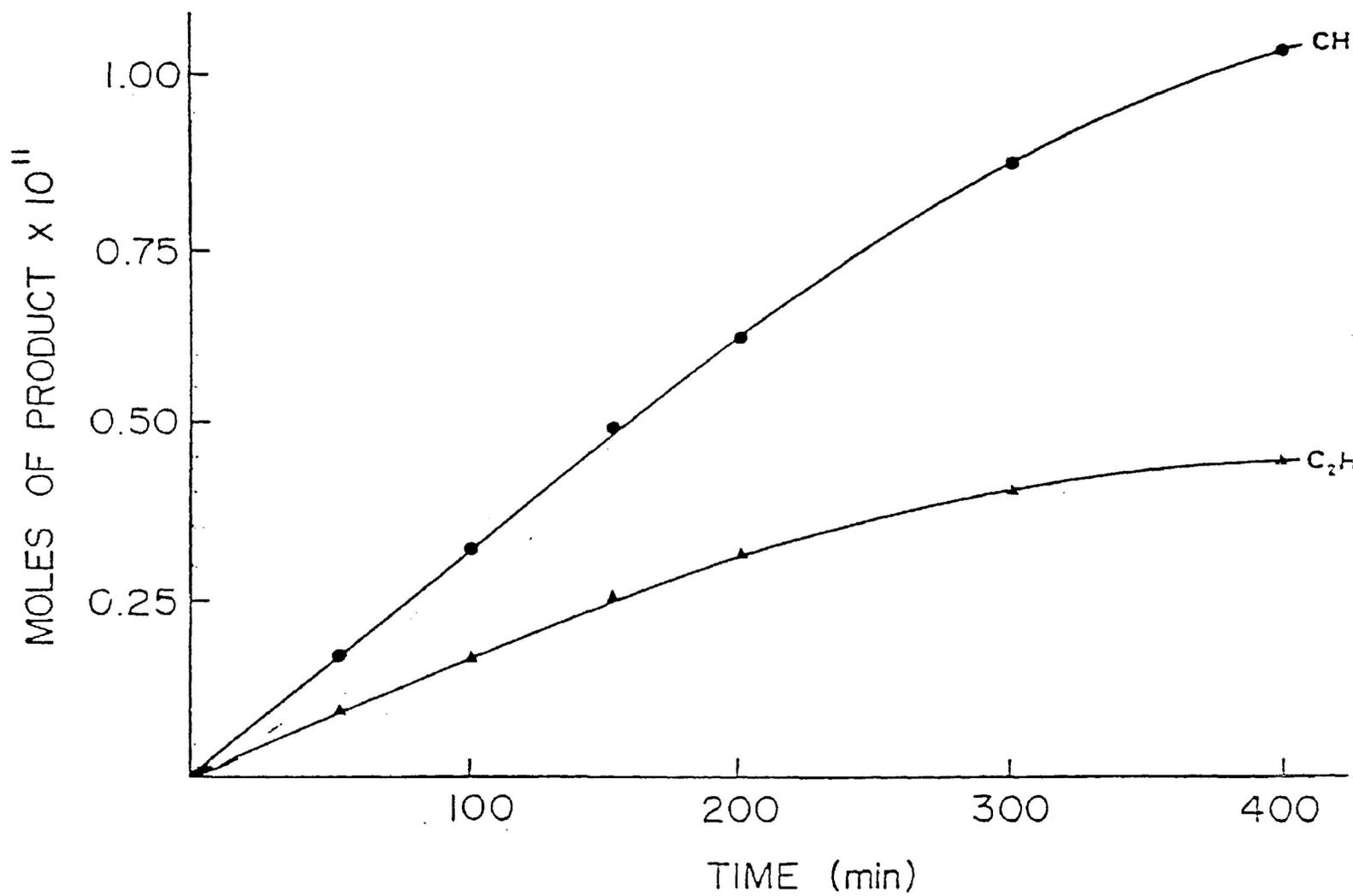


Fig. 3.11 --- Plot of Volatile Gas Formation for PPAS with Irradiation Time

Table 3.1

## Rates of Formation of Volatile Gas Products

		PPAS	POAS	PPPS	POPS
Rate of Formation (moles/min)	CH <sub>4</sub>	$3.2 \times 10^{-14}$	$1.78 \times 10^{-15}$	$1.35 \times 10^{-14}$	$9.0 \times 10^{-16}$
	C <sub>2</sub> H <sub>6</sub>	$1.0 \times 10^{-14}$	$3.2 \times 10^{-16}$	$2.8 \times 10^{-14}$	$1.6 \times 10^{-15}$

Fig. 3.12 --- Plot of S vs Irradiation time for PPAS and POAS in Chlorobenzene

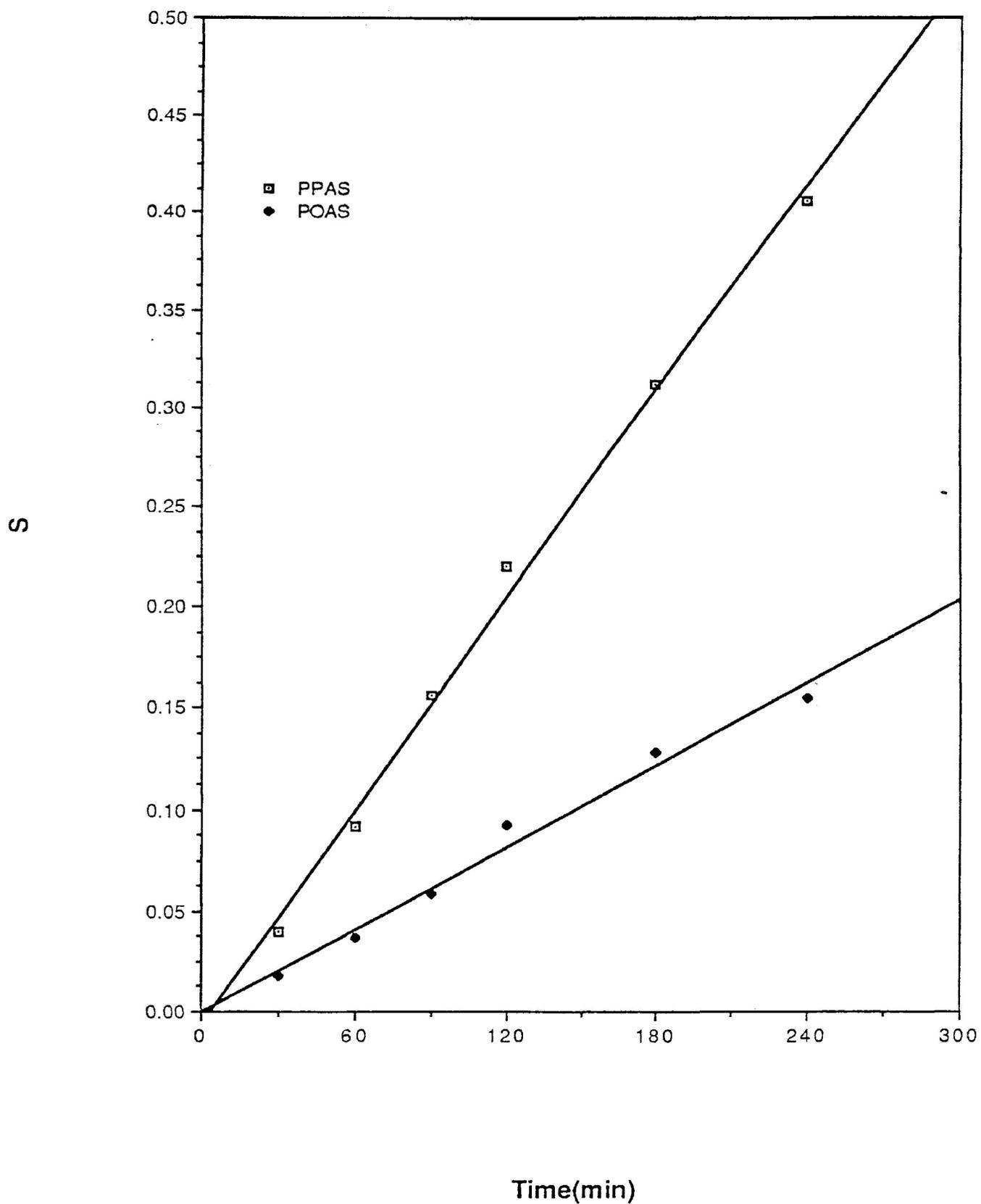


Fig. 3.13 --- Plot of S vs Irradiation time for PPPS and POPS in Chlorobenzene

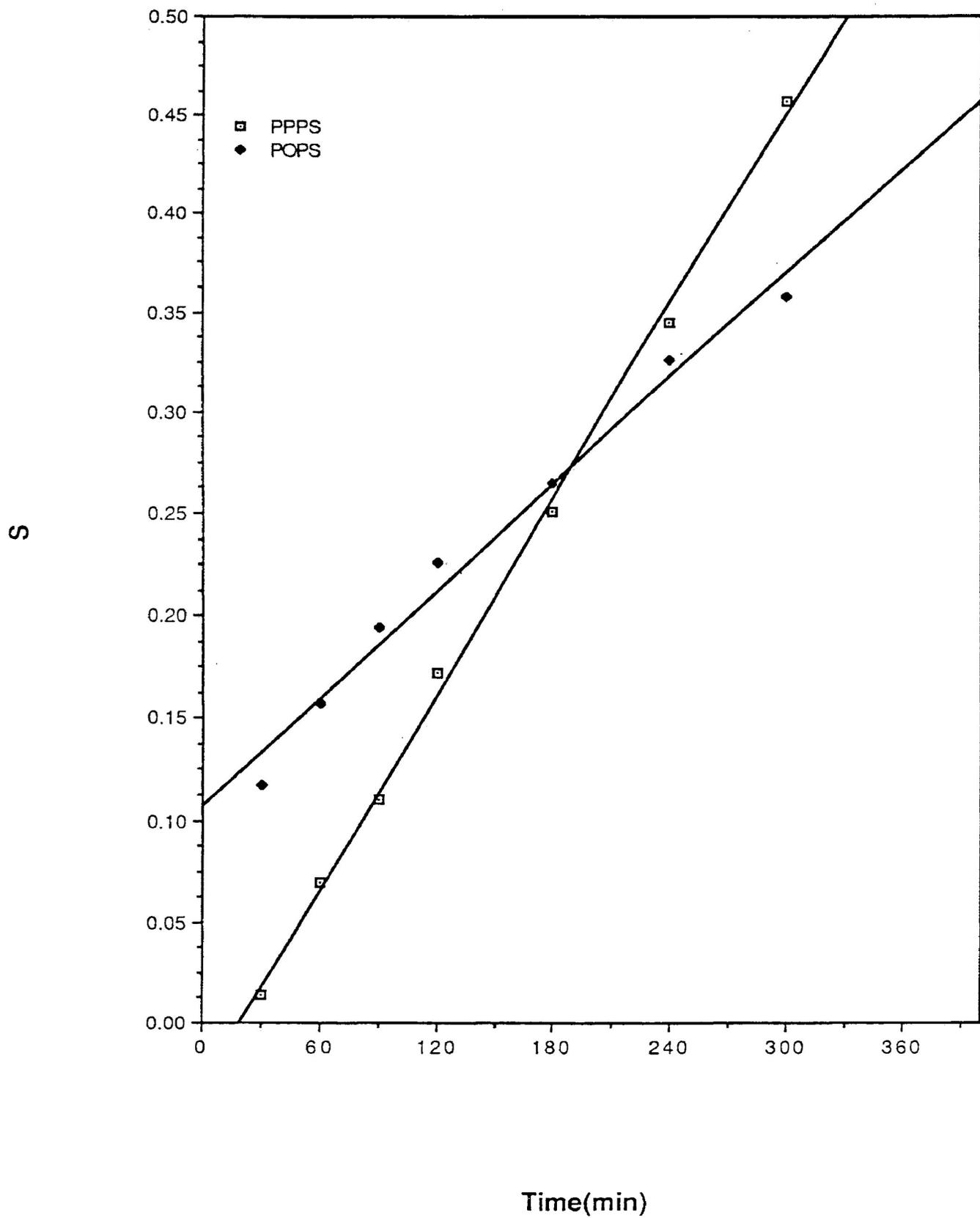


Fig. 3.14 --- Plot of S vs Irradiation time of PPPS in the presence of naphthalene

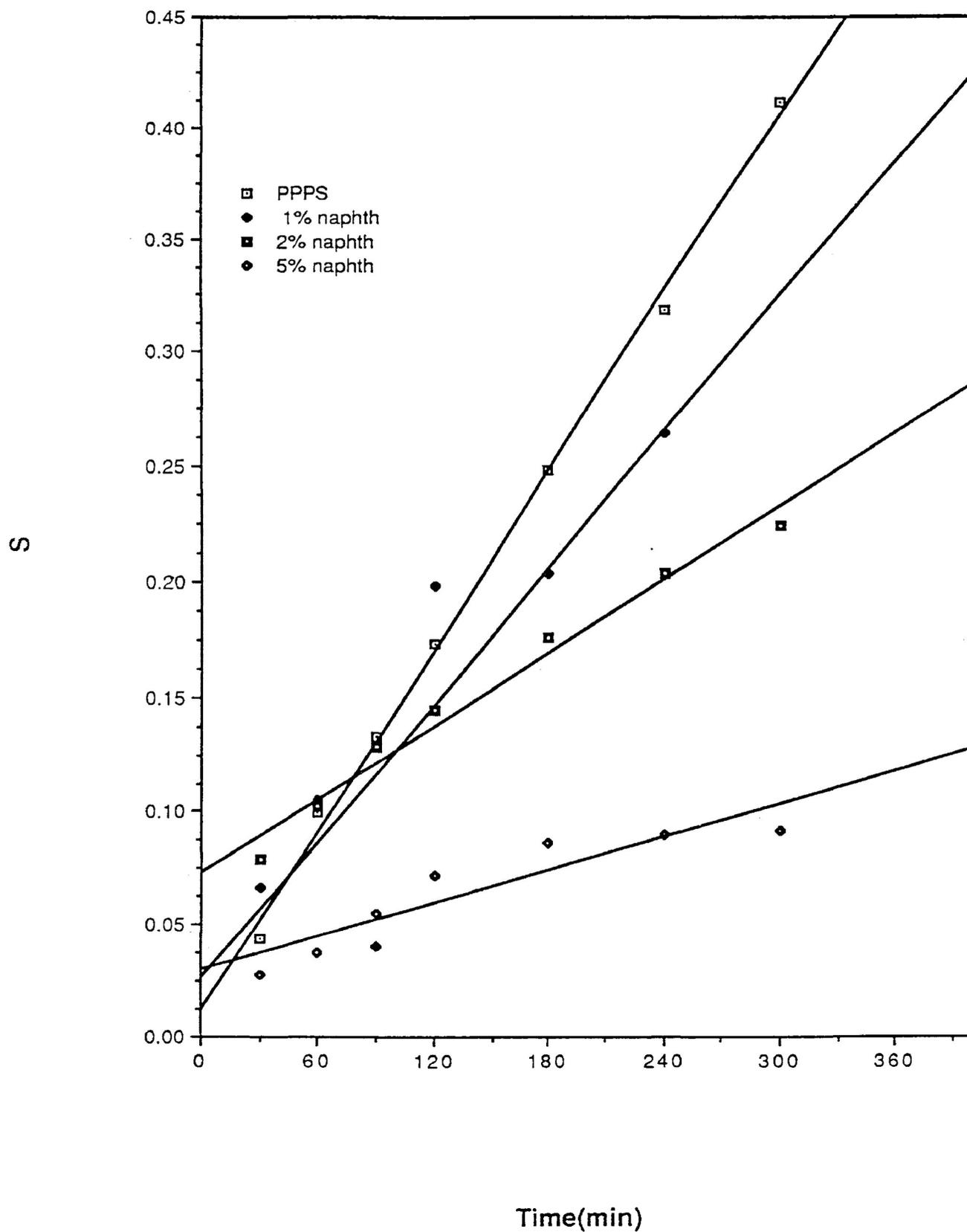


Fig. 3.15 --- Plot of S vs Irradiation time of PPAS in the presence of naphthalene

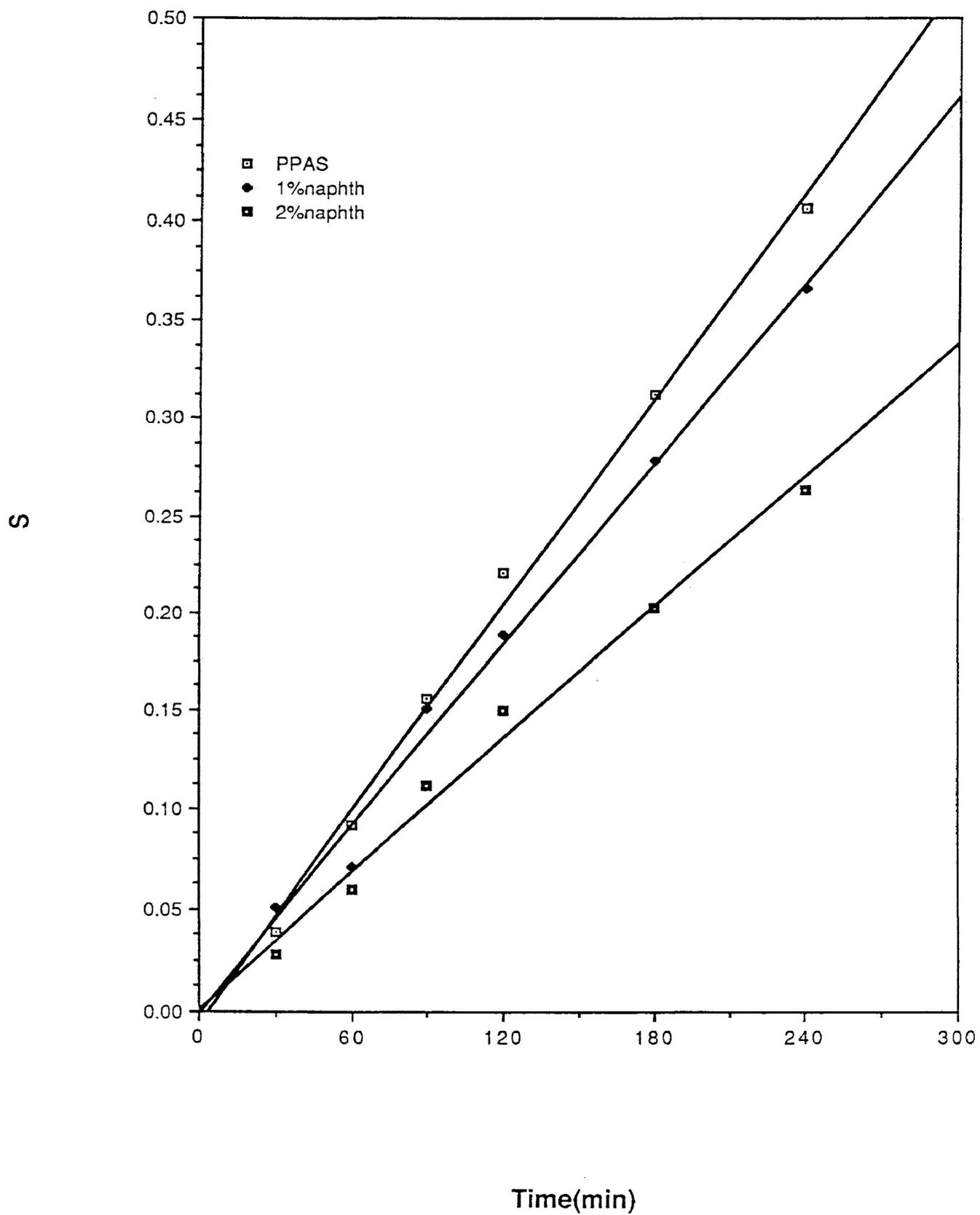


Fig. 3.16 --- Plot of S vs Irradiation time of POAS in the presence of naphthalene

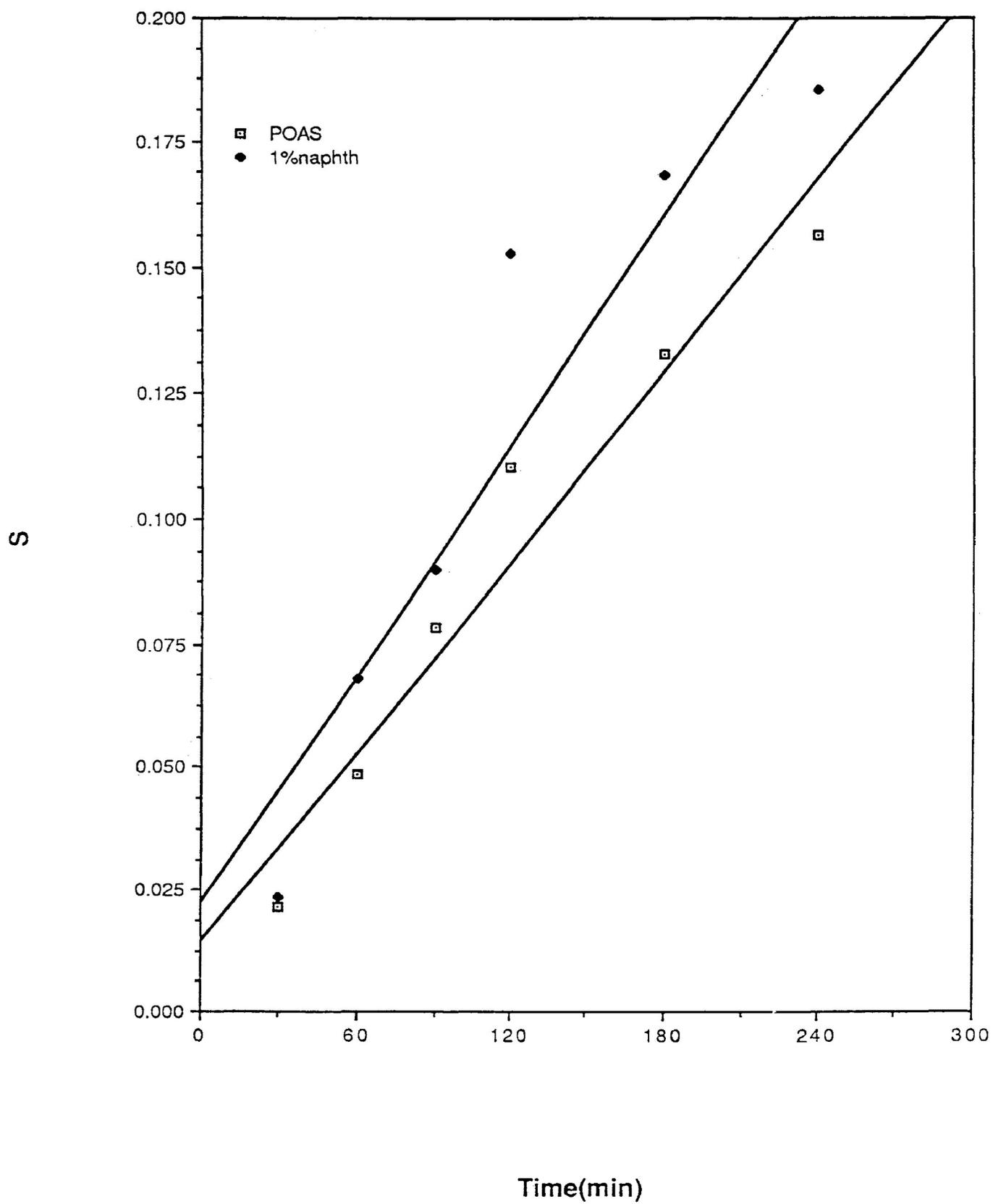


Fig. 3.17 --- Plot of S vs Irradiation time of POPS in the presence of naphthalene

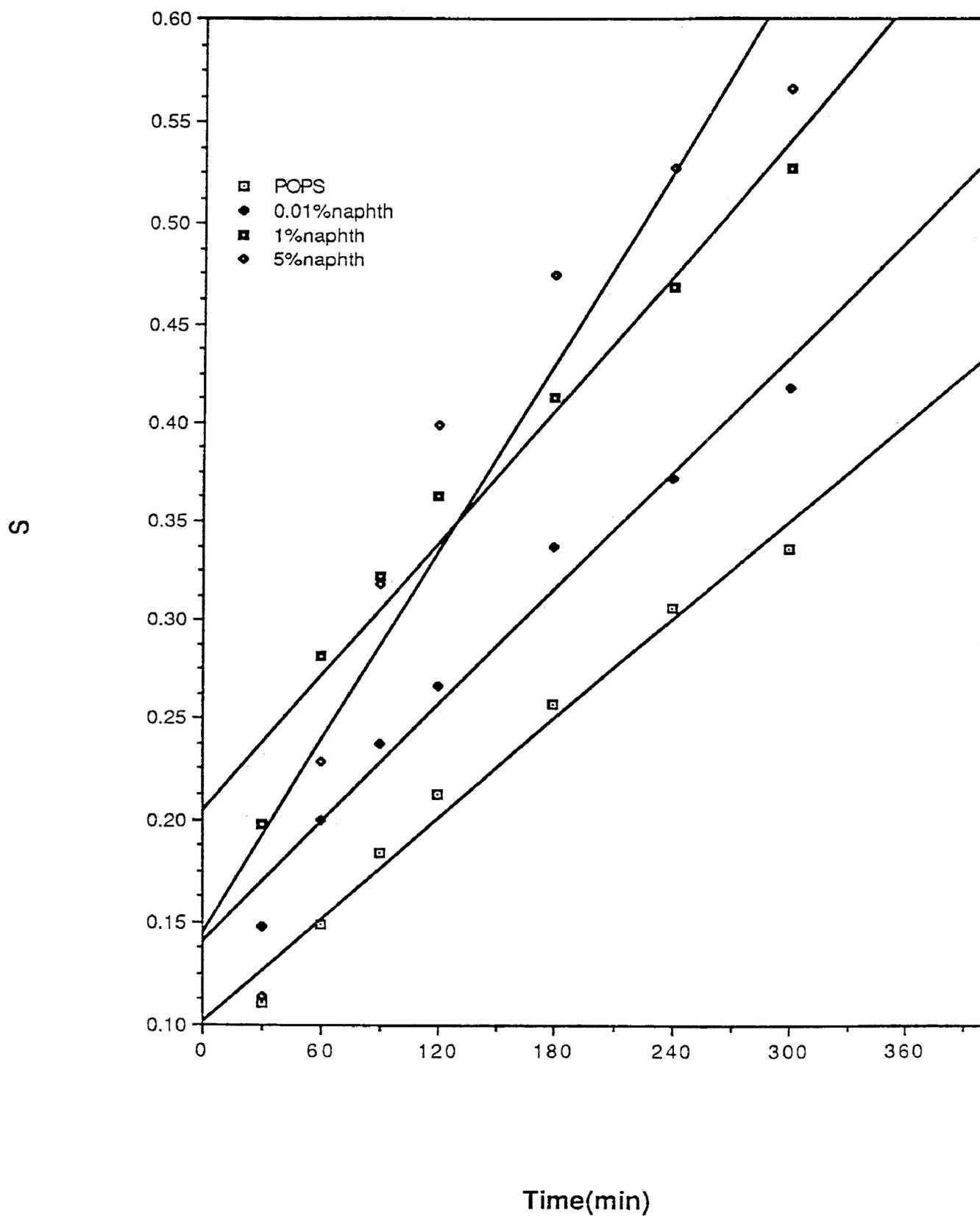


Fig. 3.18 --- Plot of S vs Irradiation time of PCPS in the presence of 1,3 cyclooctadiene

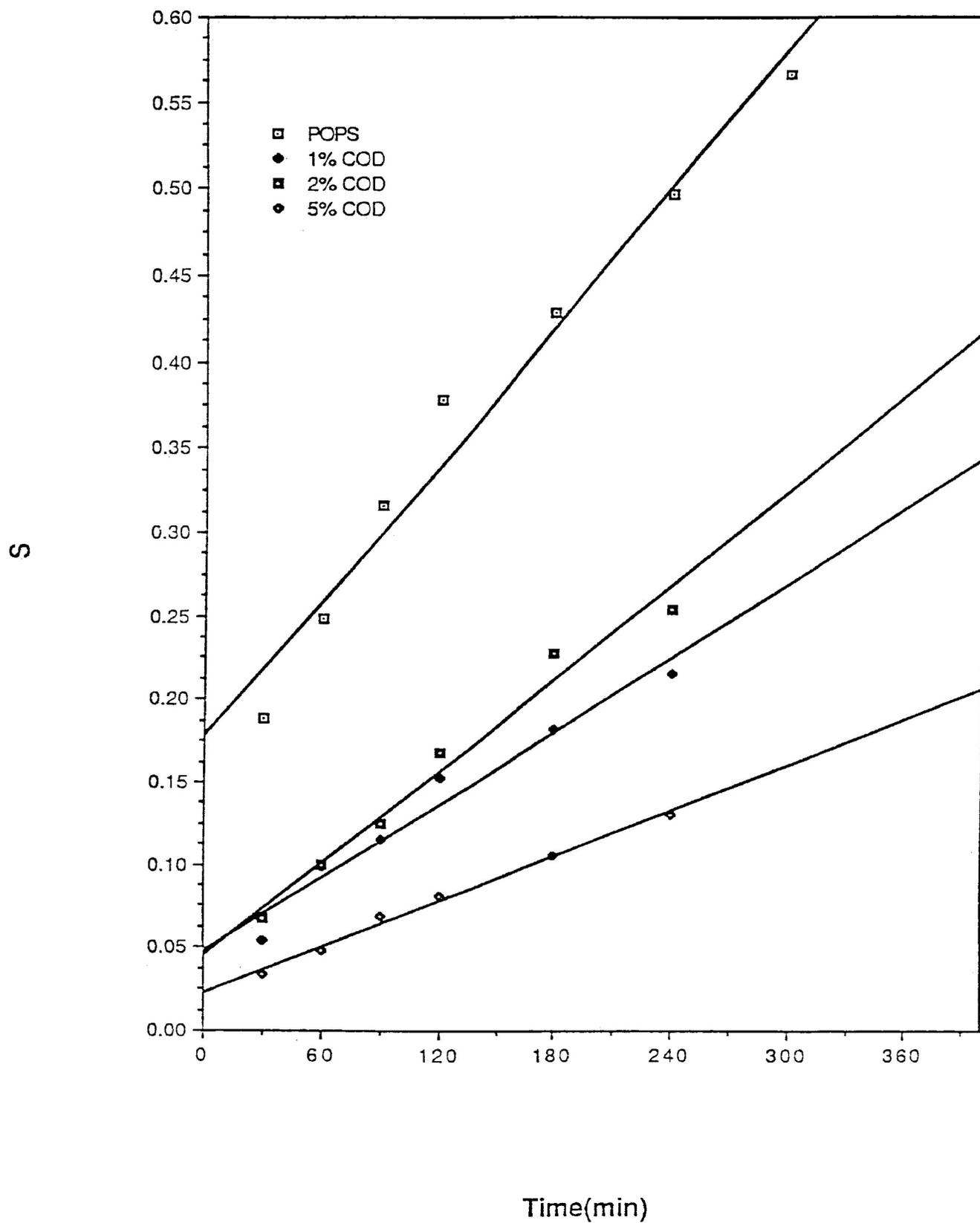


Fig. 3.19 --- Plot of S vs Irradiation time of PCAS in the presence of 1,3 cyclooctadiene

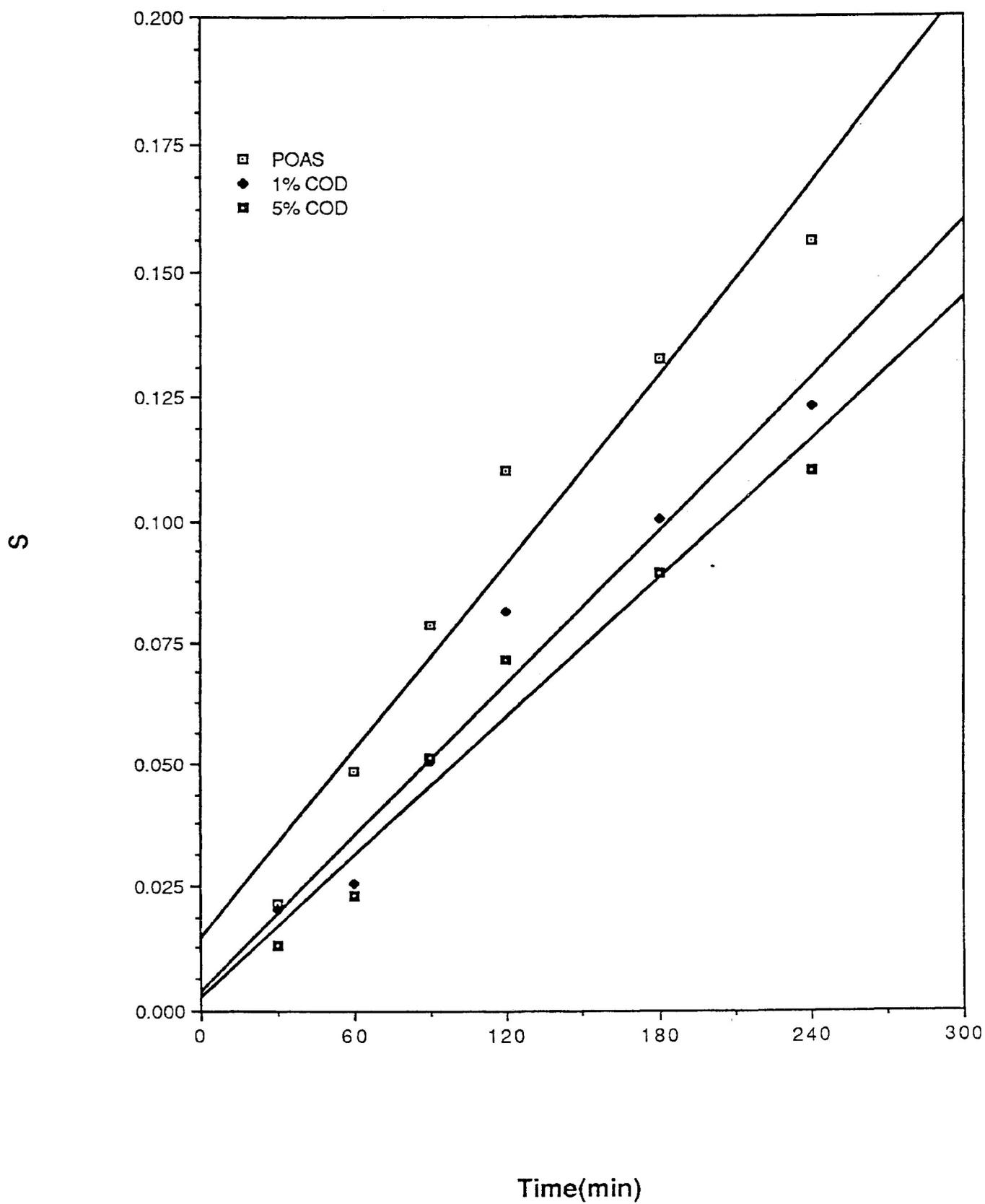


Fig. 3.20 --- Plot of S vs Irradiation time of POAS in the presence of cumene

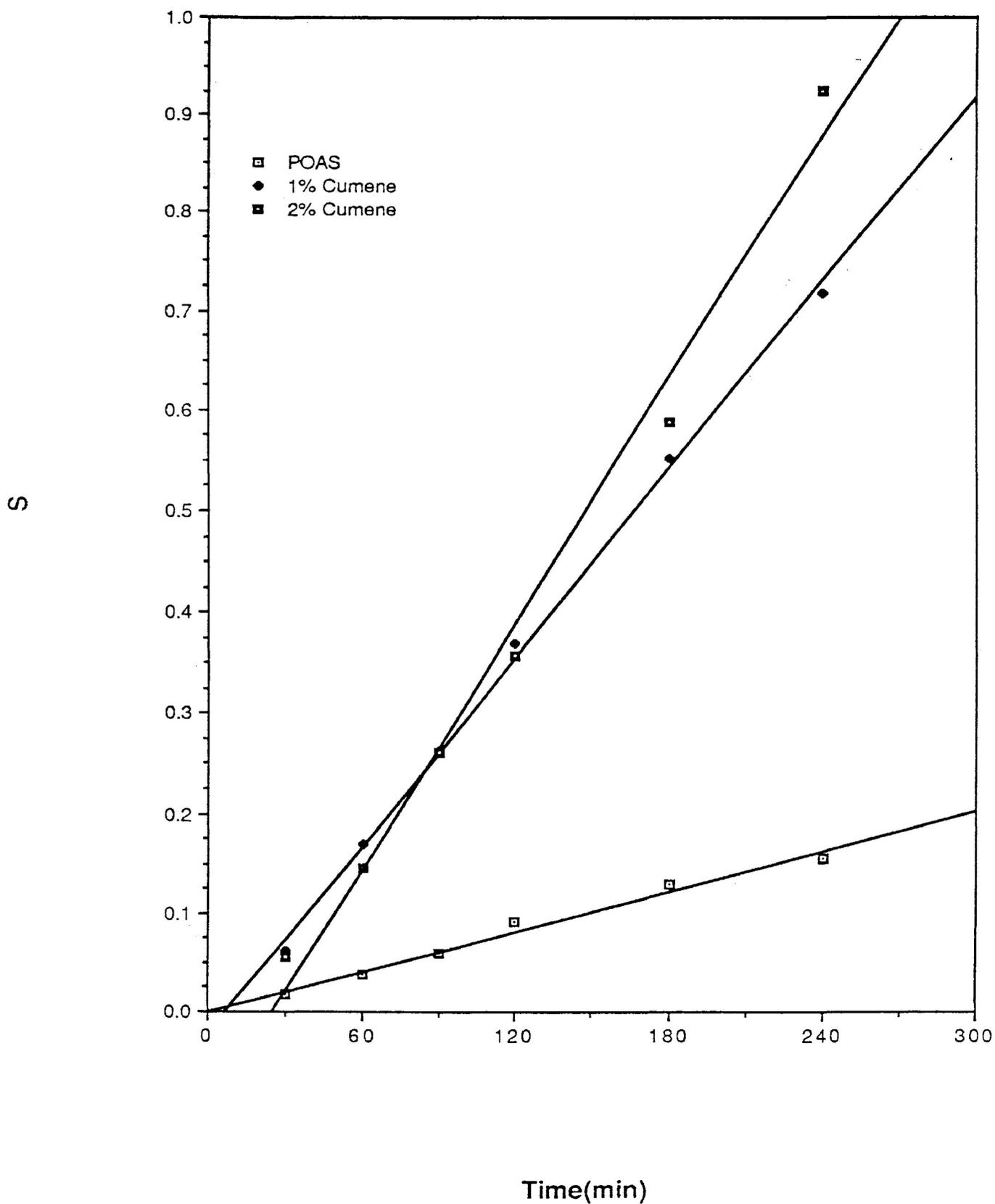


Fig. 3.21 --- Plot of S vs Irradiation time of POPS in the presence of cumene

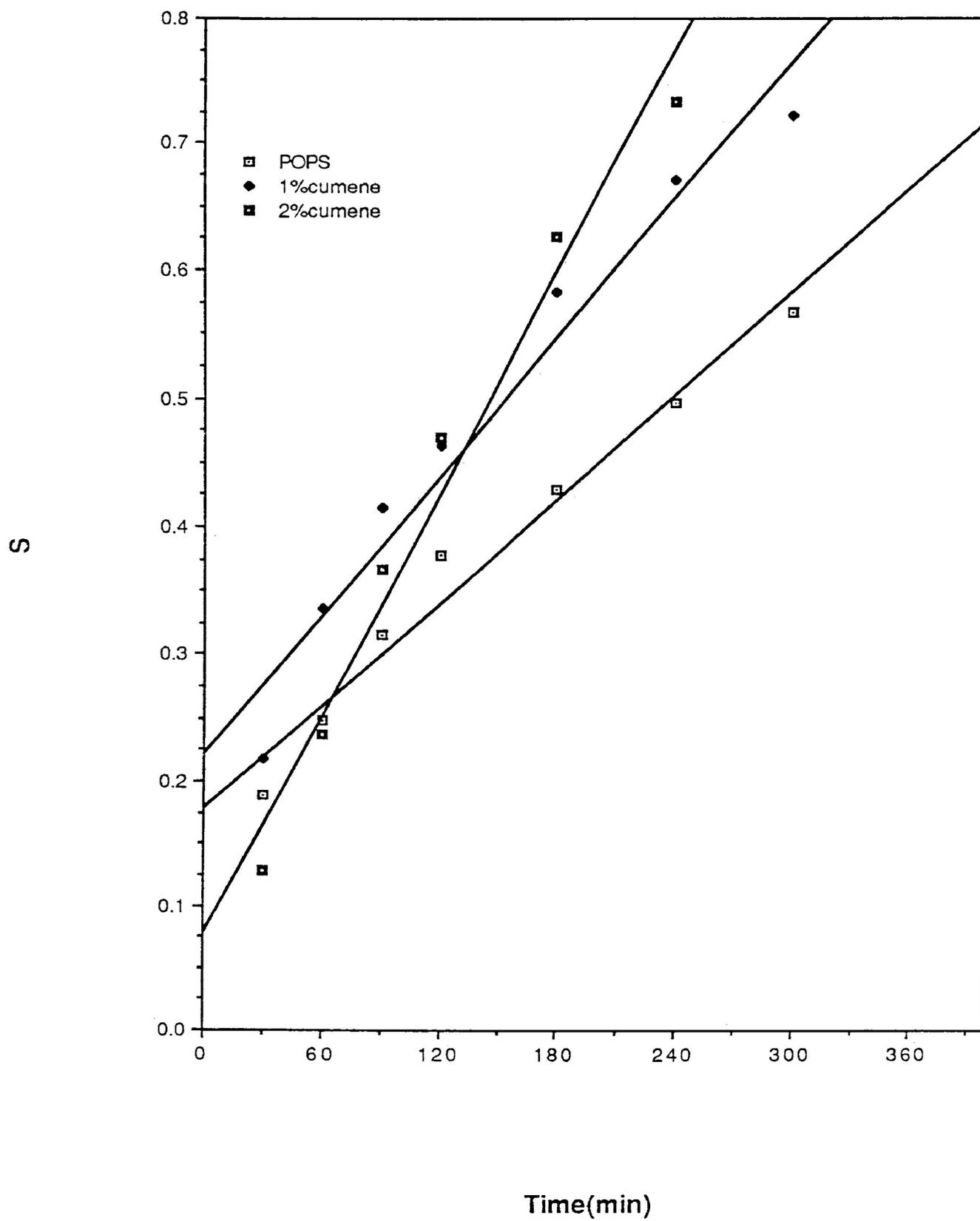


Fig. 3.22 --- Plot of S vs Irradiation time of PPPS in the presence of Bromotrichloromethane

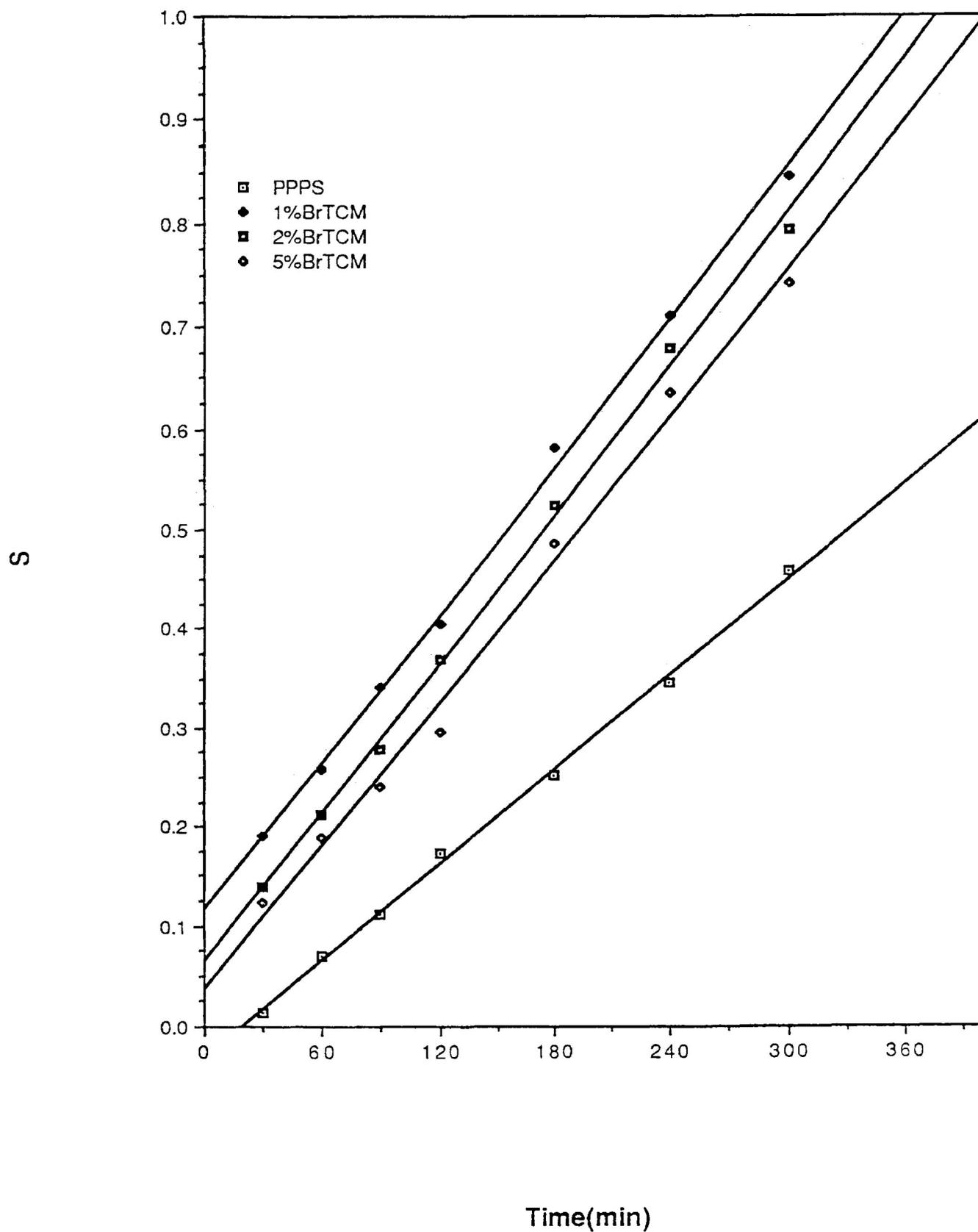


Fig. 3.23 --- Plot of S vs Irradiation time of PPAS in the presence of Bromotrichloromethane

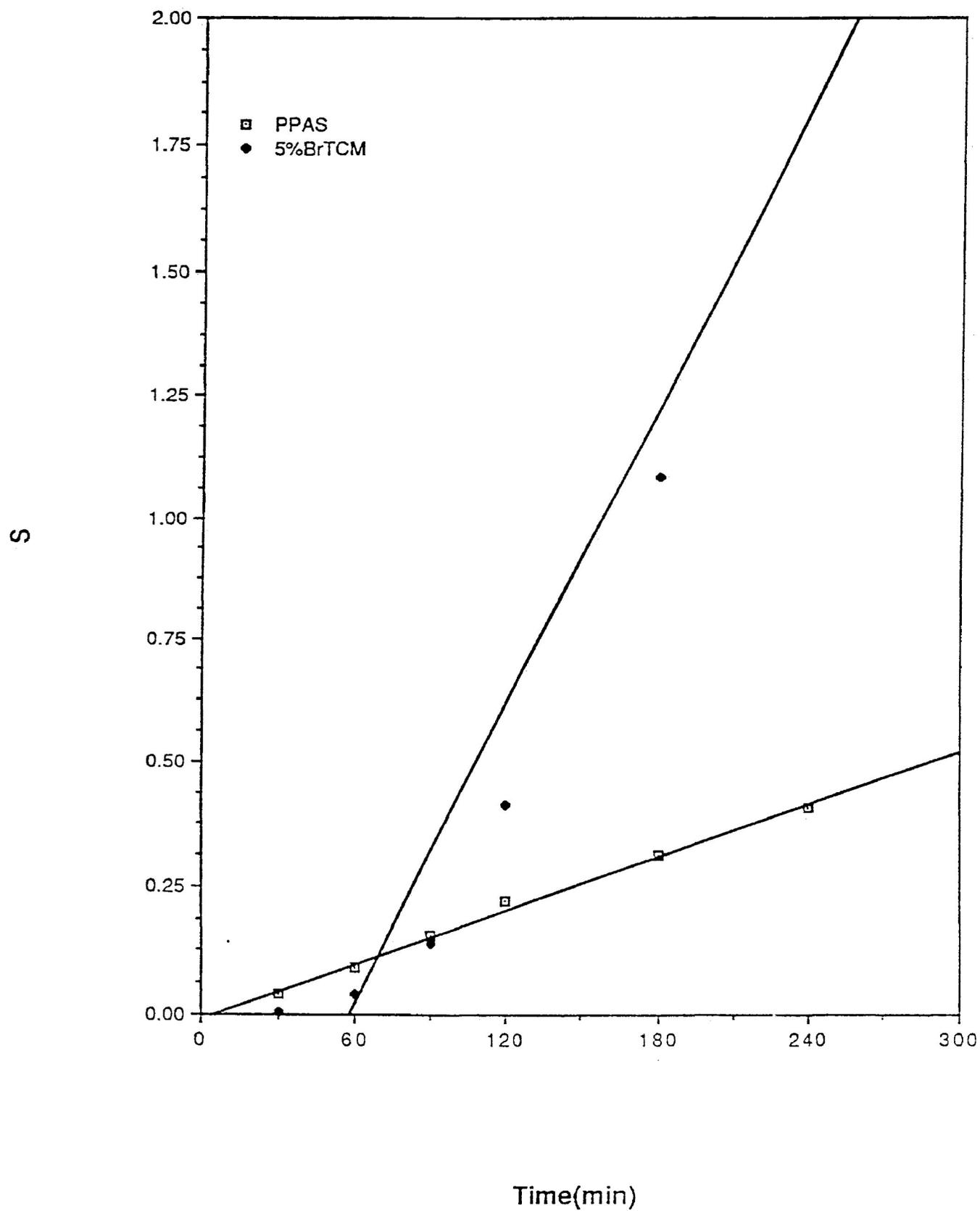


Fig. 3.24 --- Plot of S vs Irradiation time of POPS in the presence of Bromotrichloromethane

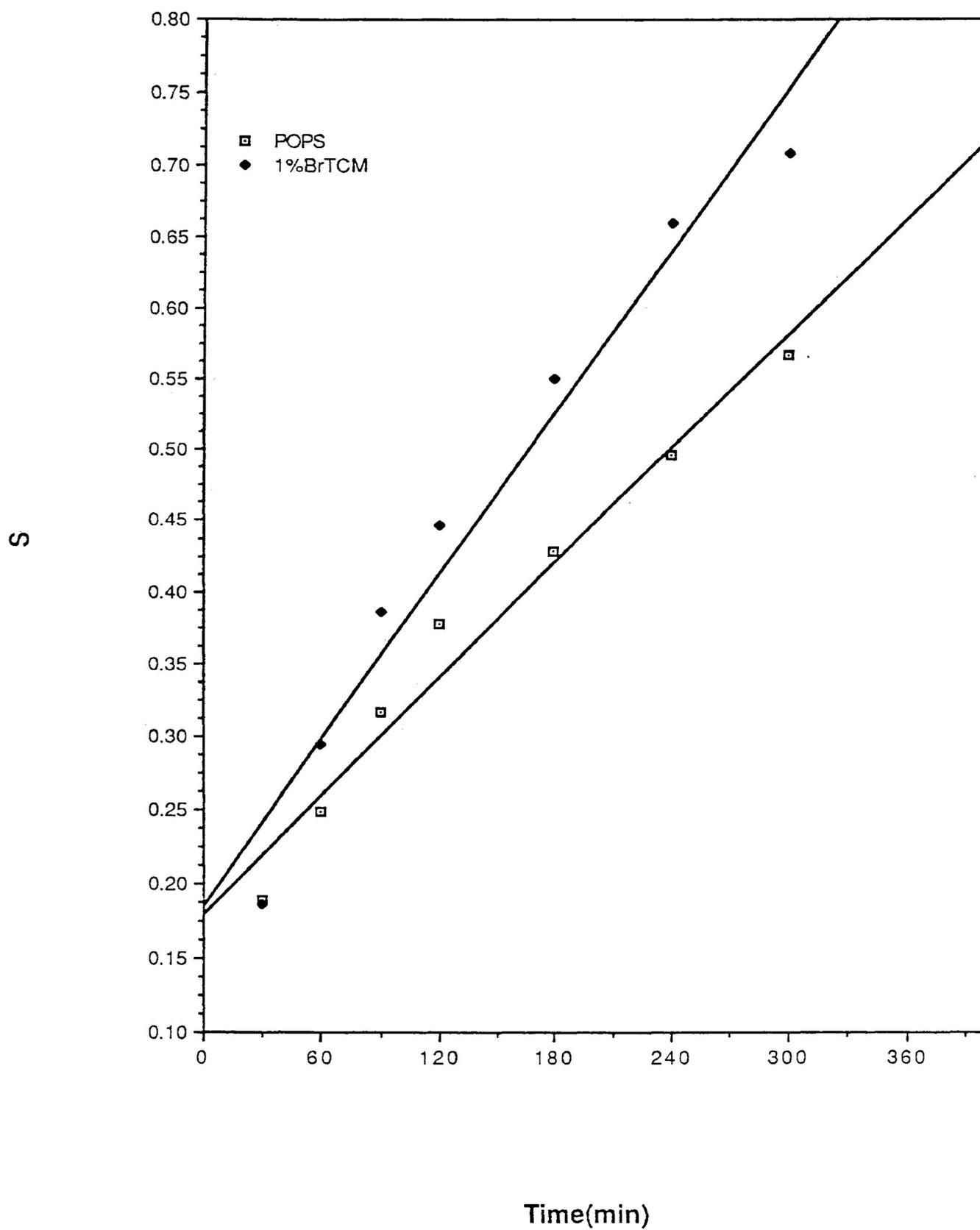


Fig. 3.25 --- Plot of S vs Irradiation time of POAS in the presence of Bromotrichloromethane

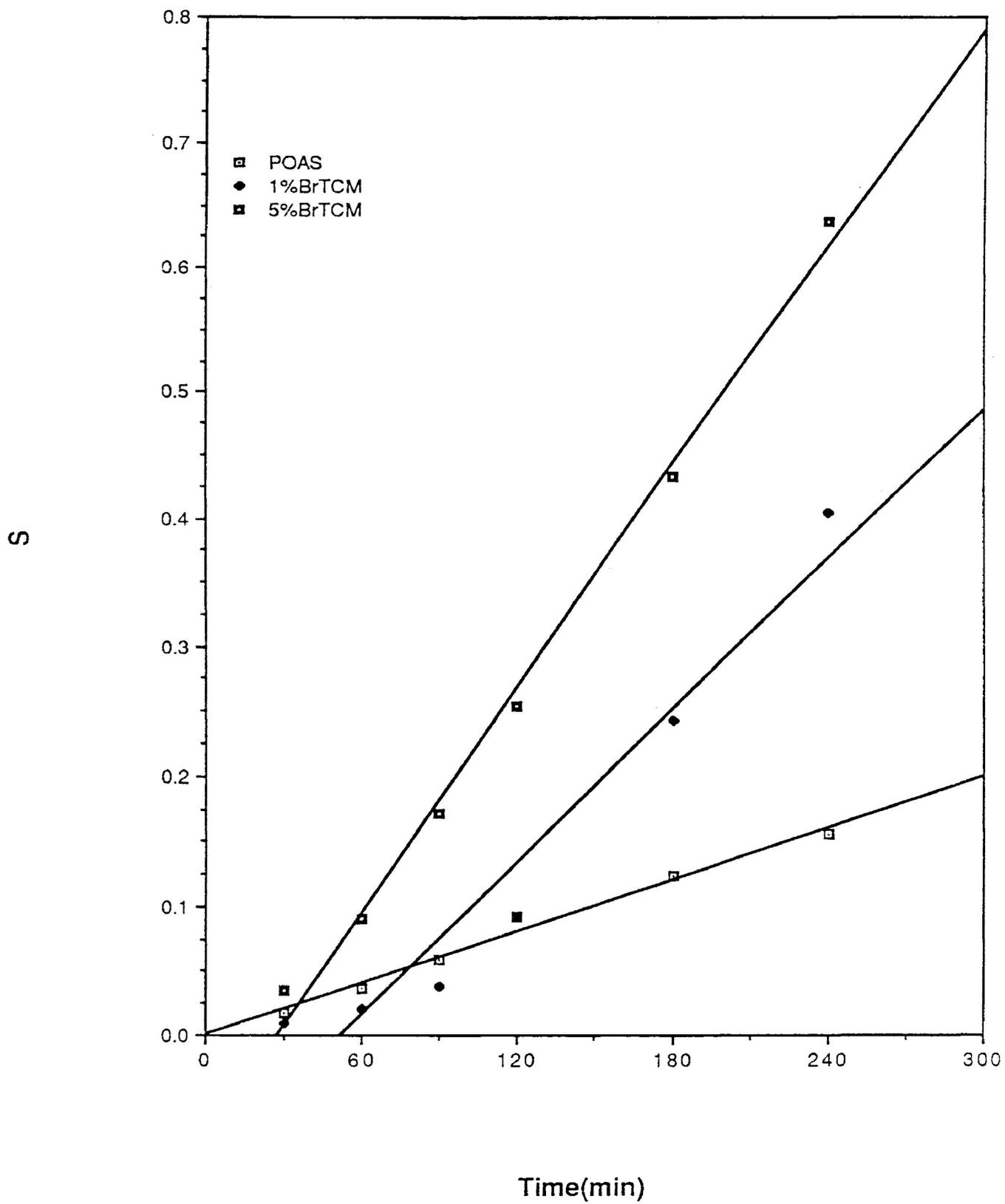


Fig. 3.26 --- Plot of S vs Irradiation time of POAS in the presence of isopropanol

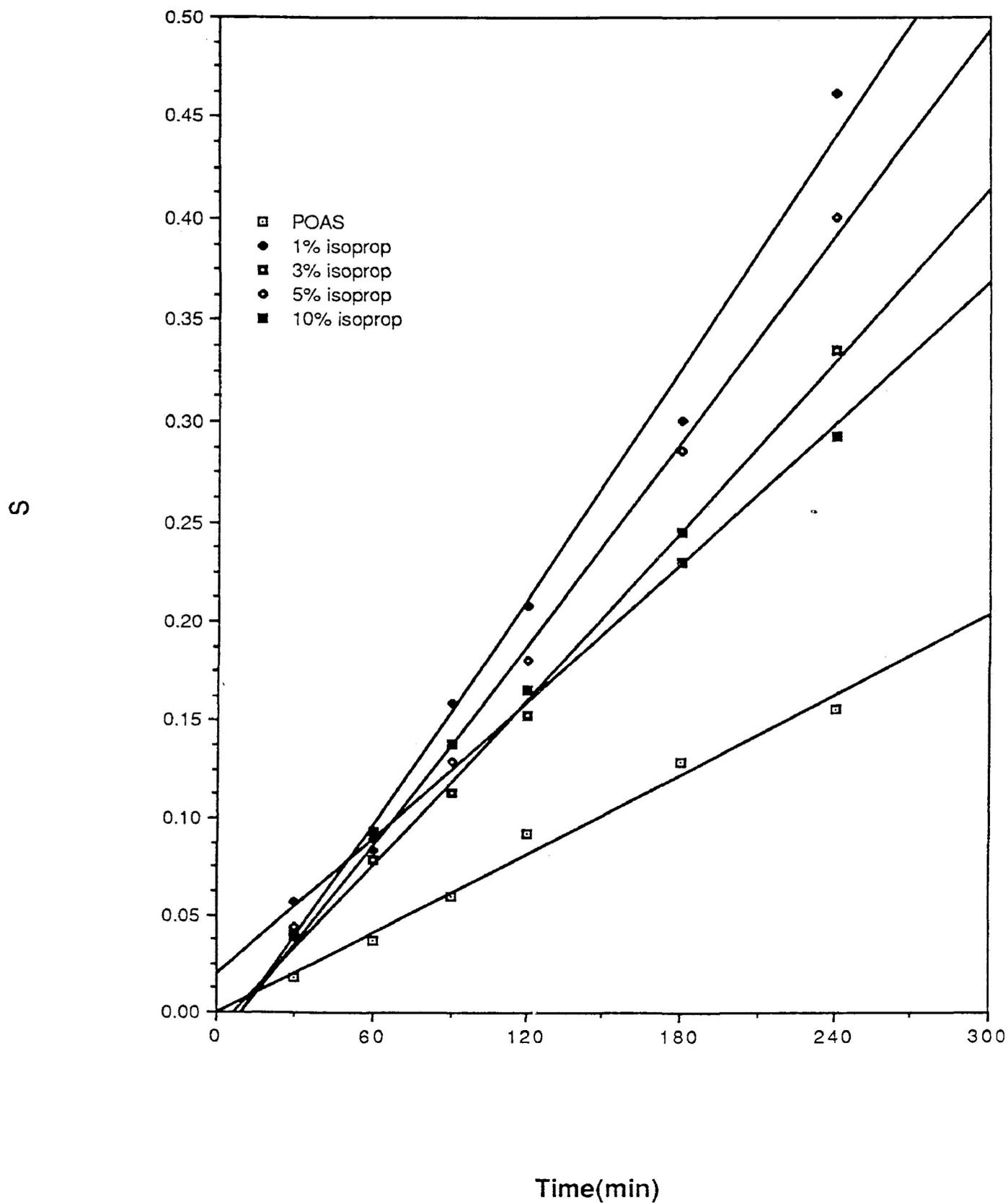


Fig. 3.27 --- Plot of S vs Irradiation time of POPS in the presence of isopropanol

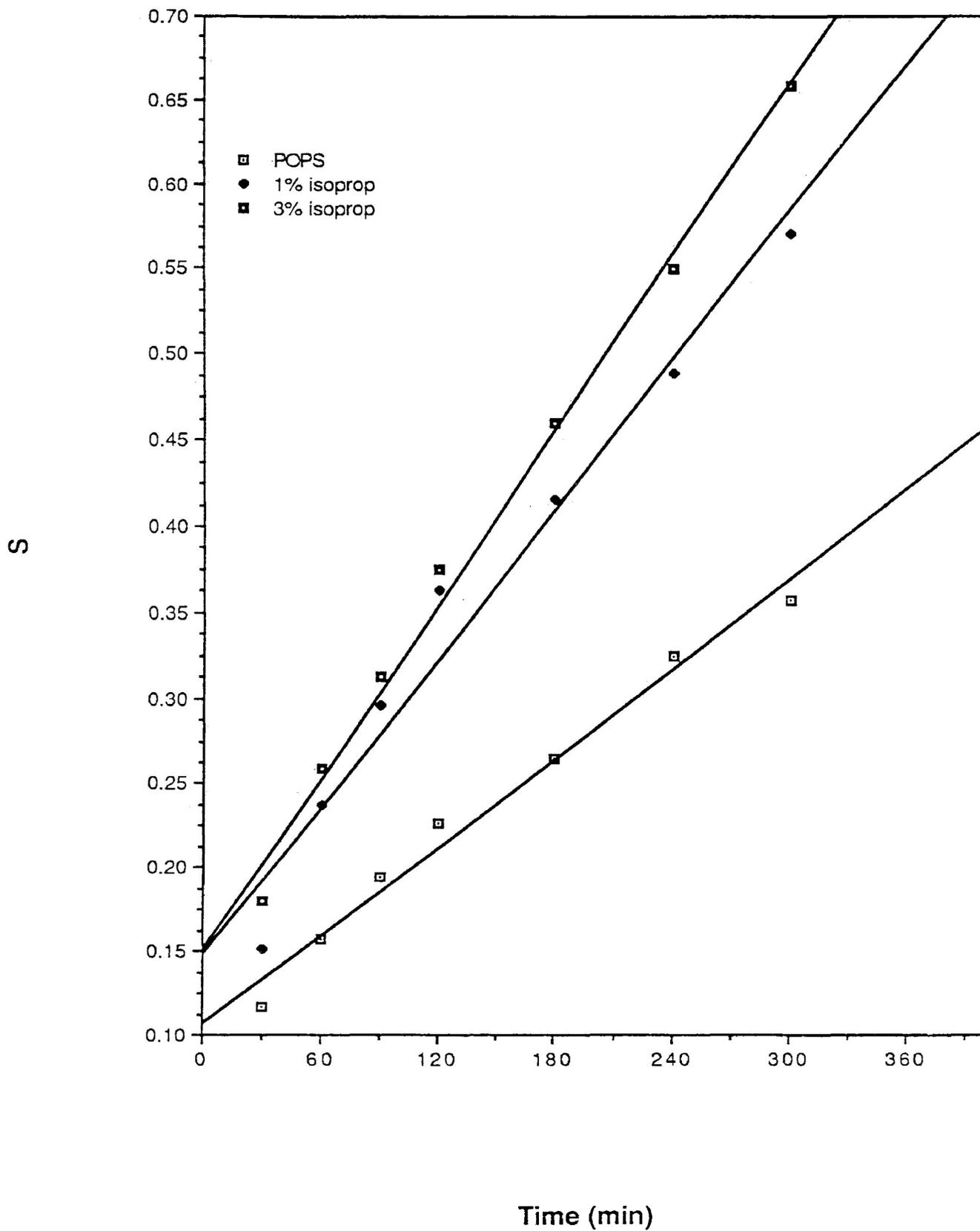


Fig. 3.28 --- Plot of S vs Irradiation time of POAS in the presence of methanol

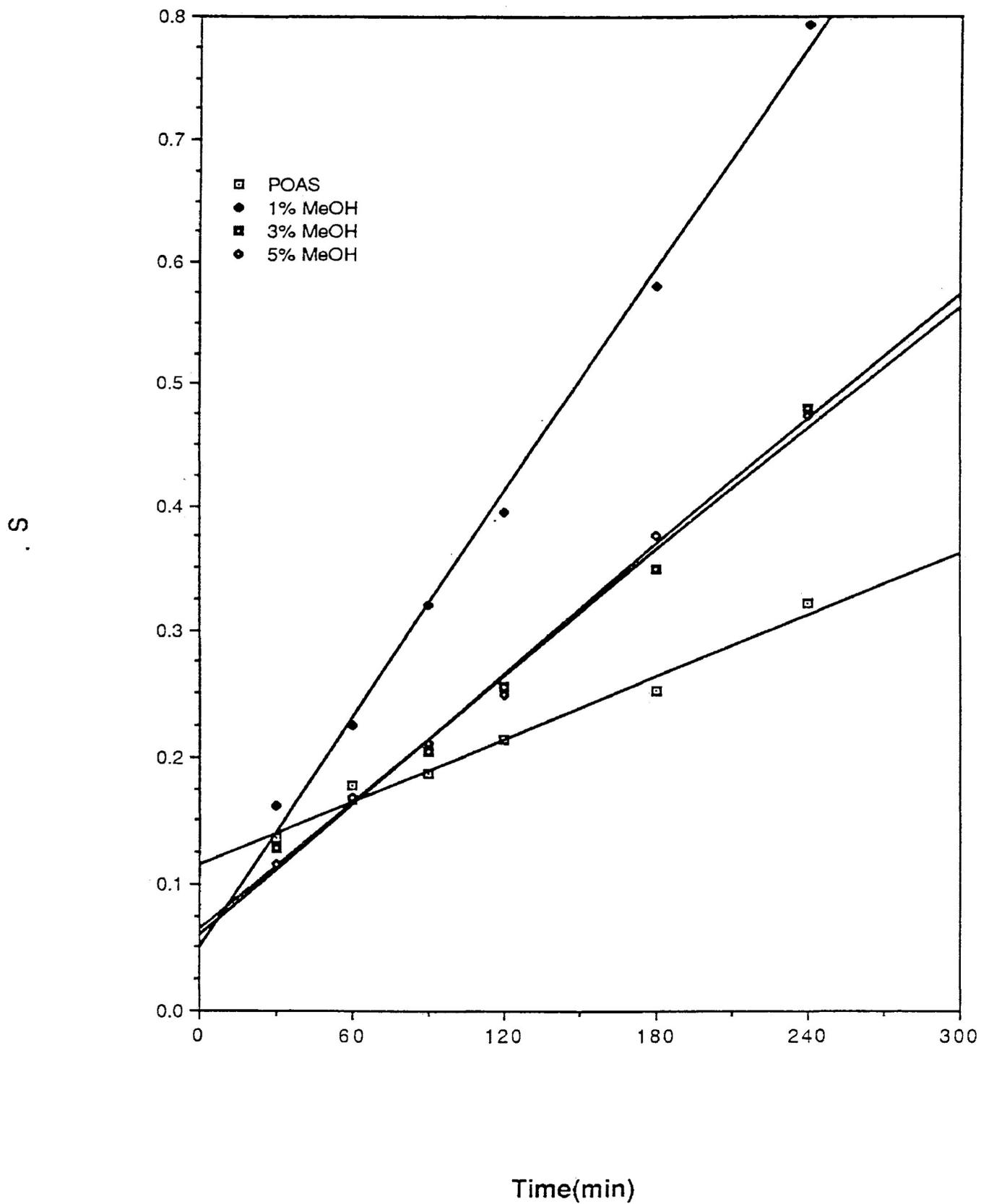


Fig. 3.29 --- Plot of S vs Irradiation time of POPS in the presence of methanol

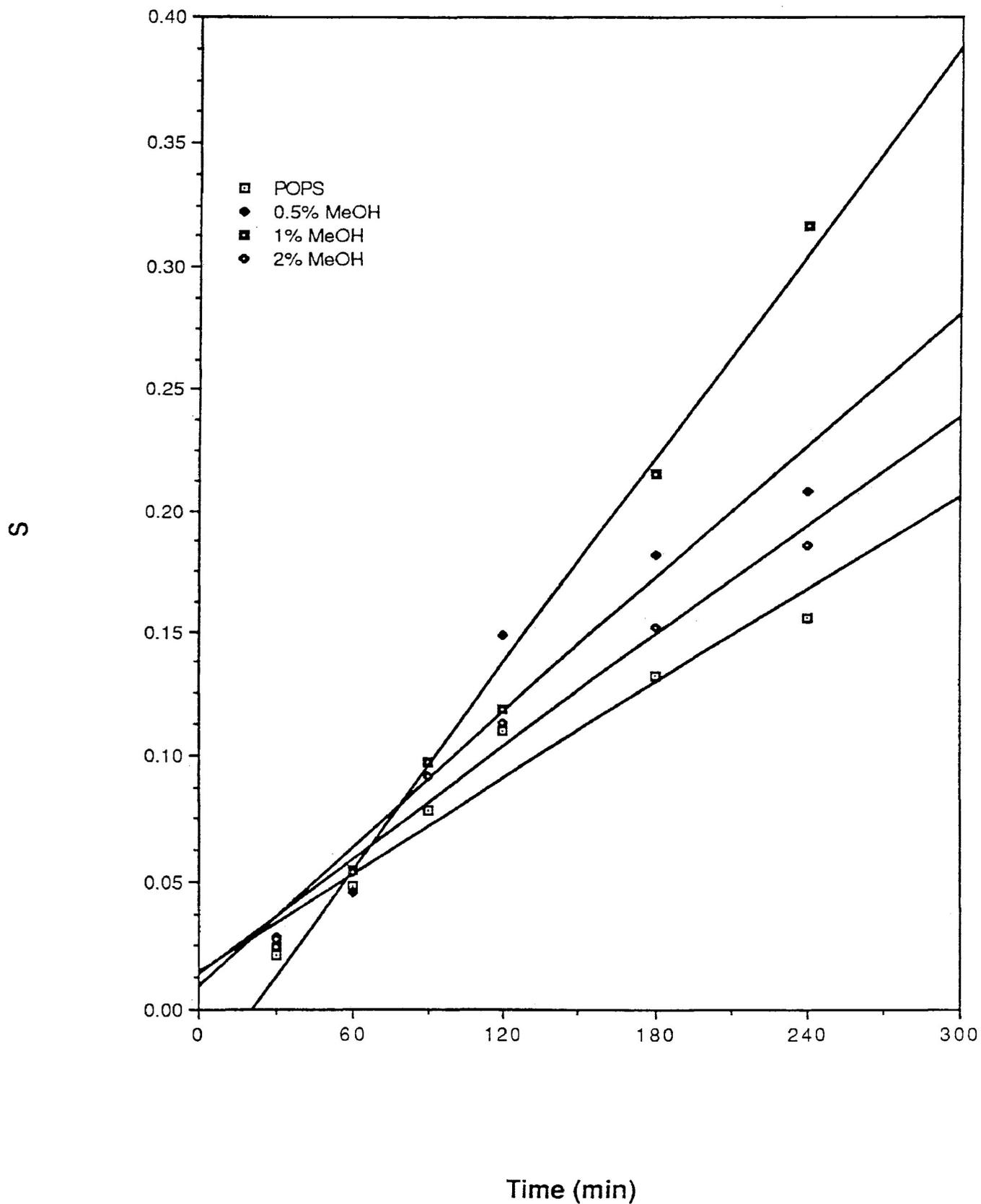


Fig. 3.30 --- Plot of S vs Irradiation time of POAS in the presence of cyclohexane

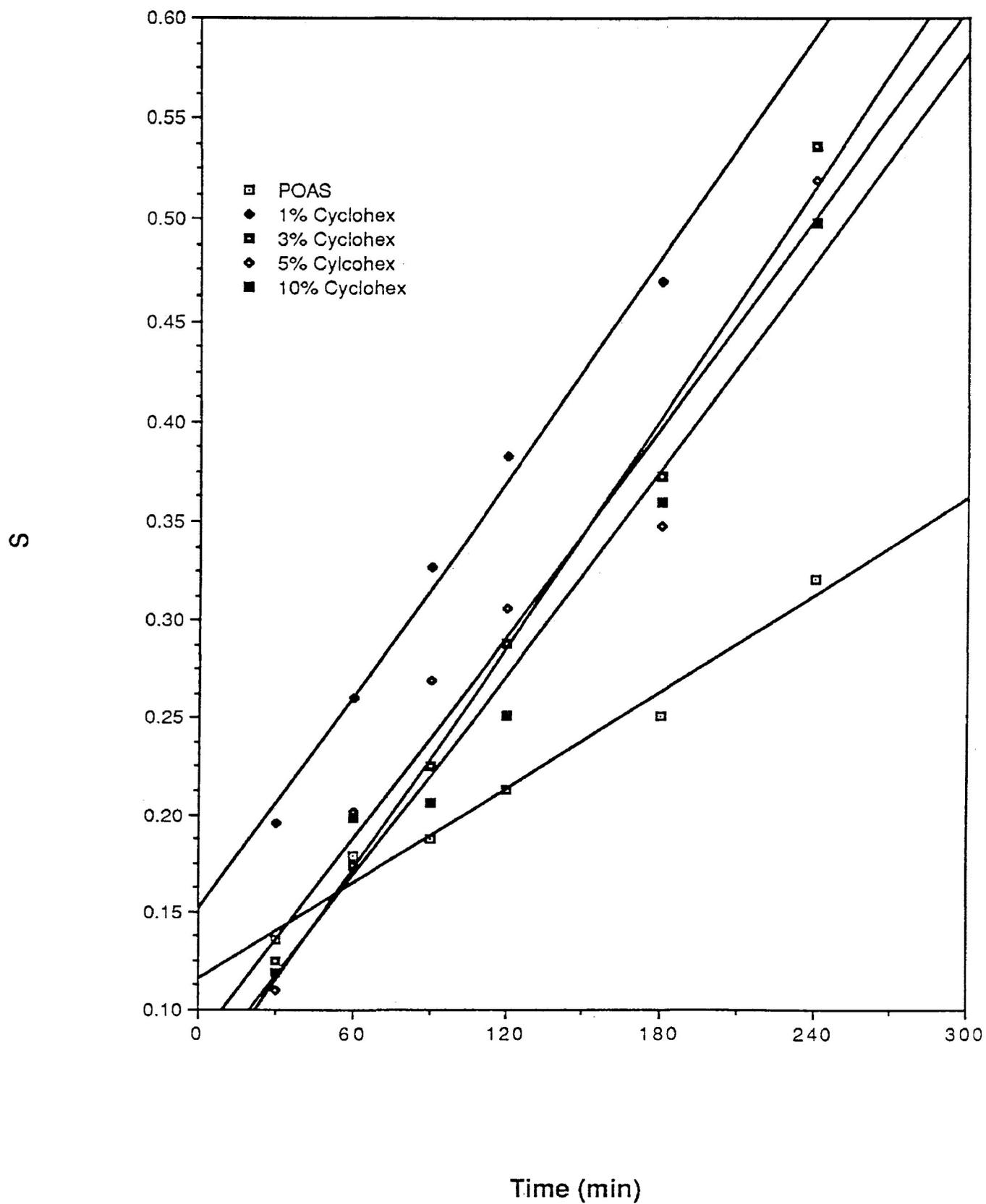


Fig. 3.31 --- Plot of S vs Irradiation time of POPS in the presence of cyclohexane

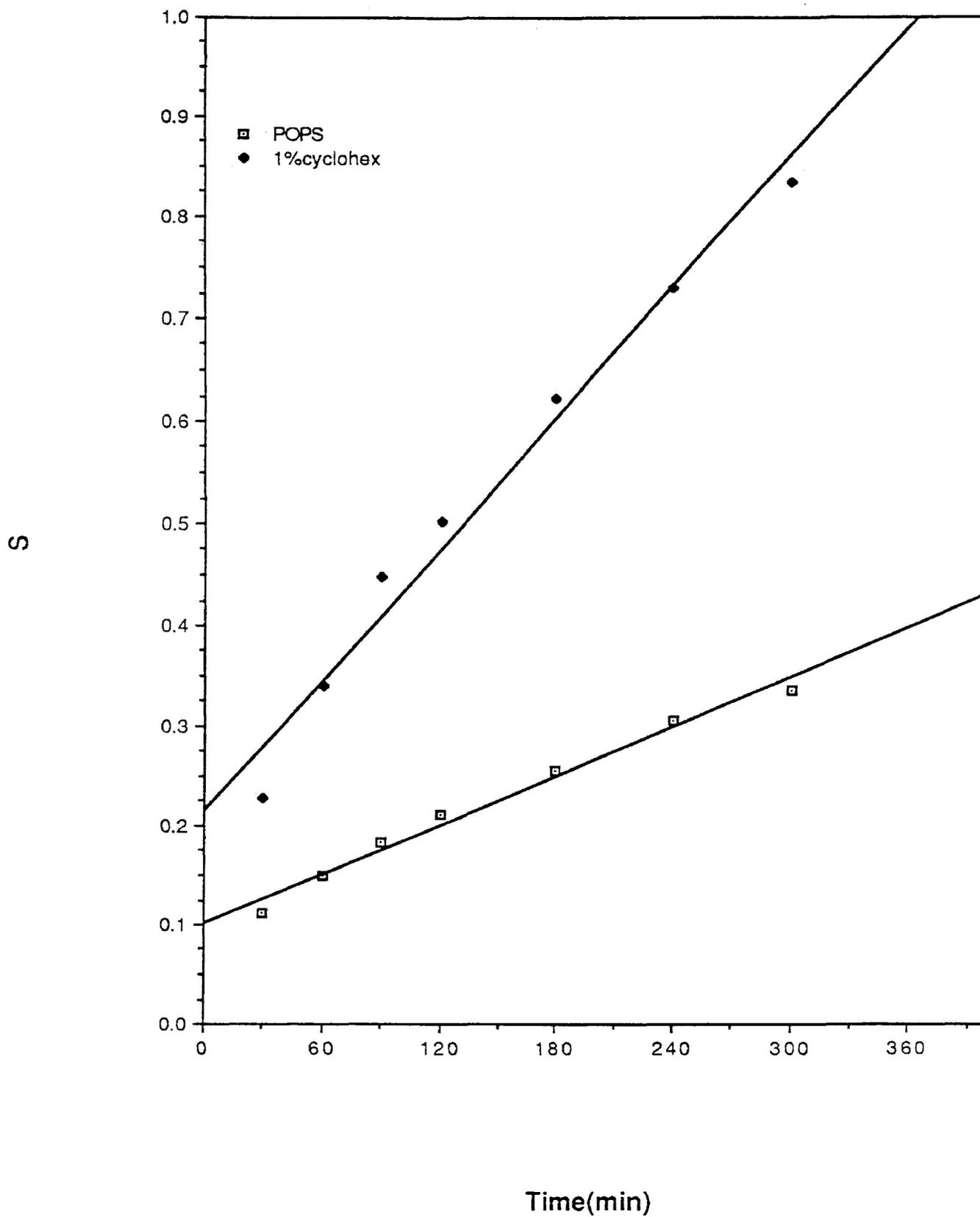
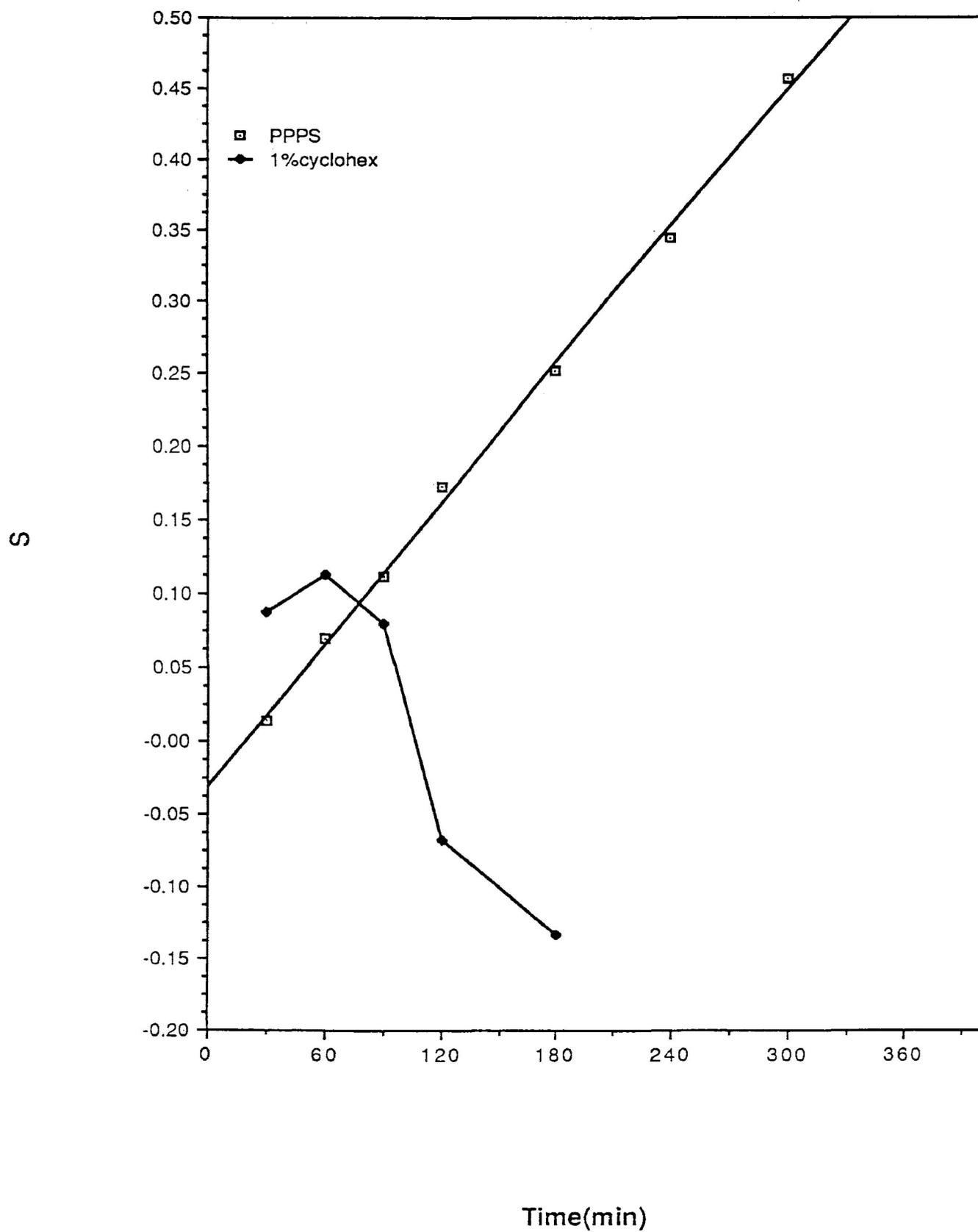


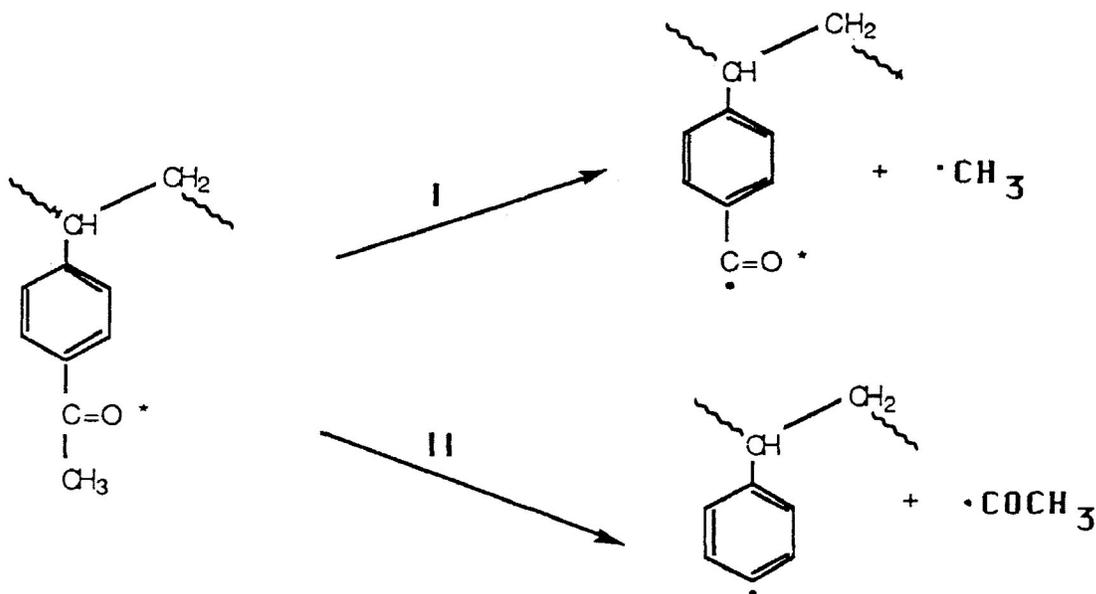
Fig. 3.32 --- Plot of S vs Irradiation time of PPPS in the presence of cyclohexane



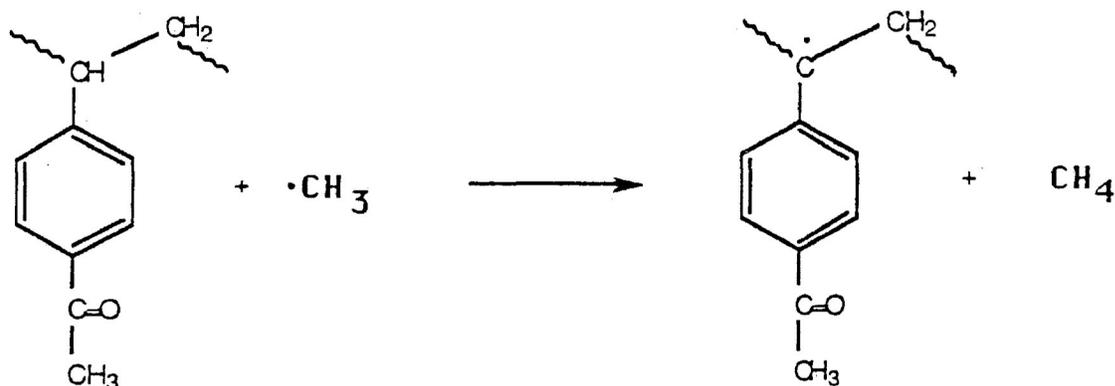
### Discussion

The results of IR and UV investigations indicate no significant loss of the carbonyl function, but it is possible that these techniques are insufficiently accurate to see any changes that take place during the irradiation time used. Also, it is possible, that because we are dealing with a polymer film most of the photochemical reactions are taking place on the surface. This would leave most of the carbonyl functions in the bulk of the polymer unaffected and the IR absorption from these would not indicate small loss of carbonyls from the surface. In addition, we are looking at changes in the  $n \rightarrow \pi^*$  transition, (UV spectrum) which has a low extinction coefficient, thus this technique is less reliable.

Results from gas product analysis show that for POAS and PPAS the main product was methane with smaller amounts of ethane being produced. Both POAS and PPAS can be expected to undergo alpha cleavage of the carbonyl triplet to yield a methyl radical, or an acetyl radical (methyl radicals giving rise to methane and ethane). For example, PPAS:



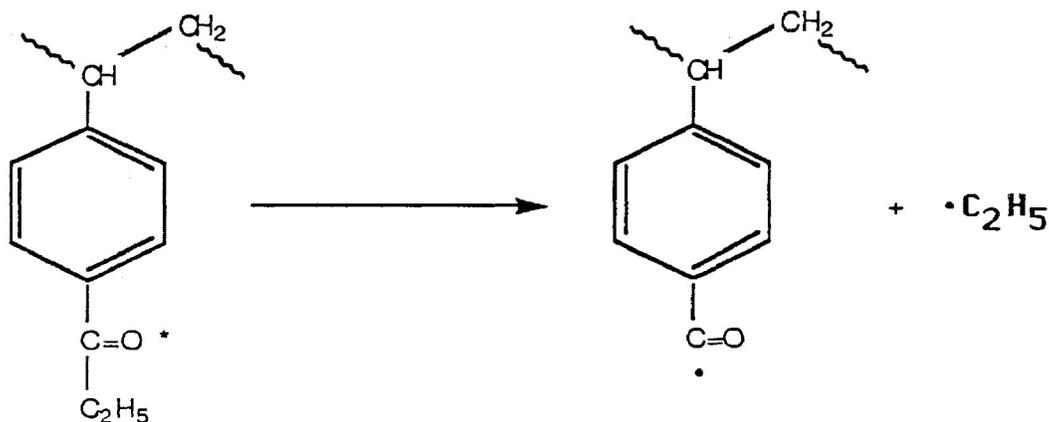
The fact that there was no evidence of acetyl radical formation indicates that reaction II does not occur. It could also be predicted that reaction I would be preferred over reaction II since, the ketyl radical produced from reaction I can partially stabilize itself by delocalization of the free electron in the aromatic ring. This stabilization is not possible for the benzyl radical produced from reaction II. The methyl radical is very reactive and will readily abstract a hydrogen atom from the polymer backbone, with abstraction of the tertiary hydrogen being energetically more favourable.



In addition the combination of two methyl radicals gives rise to ethane.



In the case of PPS and POPS the main gas product was ethane. This again arises from alpha cleavage of the propionyl group.



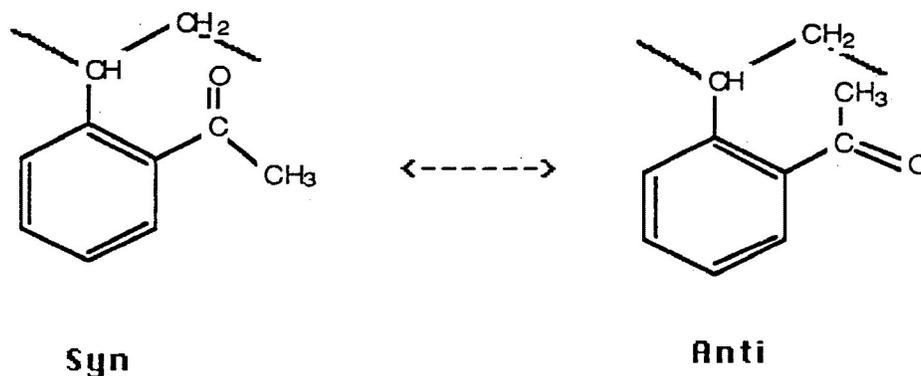
The ethyl radical then abstracts a tertiary hydrogen from the polymer backbone to form ethane. It was also observed that methane was produced, and this is attributed to  $\beta$  cleavage to produce a methyl radical. The resulting polymer radical can also stabilize itself by delocalization of the free electron with the aromatic ring through the carbonyl function.

It has been reported by Weir<sup>49</sup> that short wave photolysis (wavelengths  $\leq 254$  nm) of poly-*p*-ethylstyrene (PPES) yields a significant amount of methane. This is the result of  $\beta$  scission (of the ethyl group) to yield a methyl radical and a polymer radical. The polymer radical is capable of stabilizing itself by delocalization.

It was also noted that the rate of gas product formation is significantly lower for the *ortho*substituted polymers (compared to *para* substituted counterparts), indicating that there is another process which competes with alpha cleavage. As previously mentioned, the *ortho* polymers have a structure which allows a photoenolization process to occur. This process would compete with alpha cleavage and would result in a reduction of yields of the gas products.

Weir *et al.*,<sup>46</sup> has reported  $T_g$  for POAS and POPS to be  $110^\circ\text{C}$  and  $115^\circ\text{C}$ , respectively. Therefore, films of these two polymers, at the experimental temperatures of  $25^\circ\text{C}$  were well below  $T_g$ , and there would be limited movement of the polymer chain, and pendant acyl groups. Therefore, the syn  $\rightarrow$  anti conformational rotation is restricted, so chromophores that are in the anti conformation at the time of excitation would be more likely to undergo alpha scission before they can rotate into the syn conformation from which they can enolize. For

steric reasons it is predicted that these *ortho* polymers are mainly in the syn conformation.. The anti conformation requires that the methyl group (or even larger ethyl group) lie in close proximity of the polymer backbone. In the case of the syn conformation these groups are farther apart:



The presence of any gas products from the *ortho* polymers indicates that not all the excited chromophores lie in the syn conformation. This could be evidence for ground state control for these reactions. Chromophores in the anti conformation at the time of irradiation react via alpha cleavage whereas, chromophores in the syn conformation at the time of irradiation react by enolization.

### Transient Spectroscopy

For PPAS and PPS, the transient spectra show a single species. In addition, the presence of known triplet quenchers (1,3-octadiene, or oxygen) to the polymer solution do reduce the strength of the absorbance signal due to this transient species. For this reason it is believed that this transient is the carbonyl triplet and it is seen that they are very short lived (184 ns and 147 ns for PPAS and PPS, respectively).

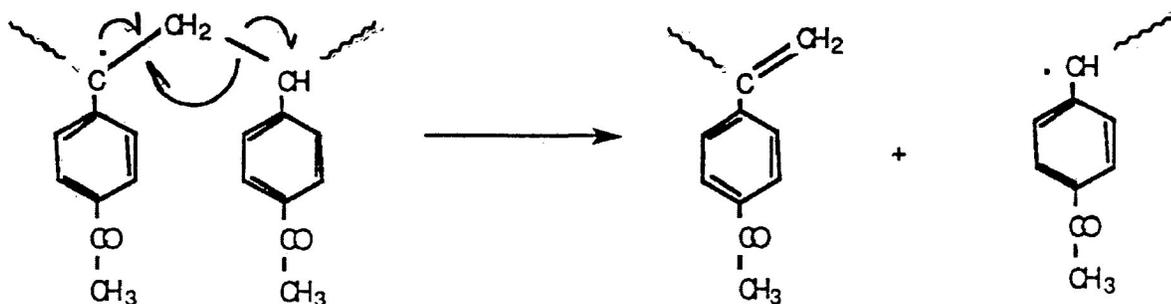
Transient spectra of POAS shows the decay of two distinct transient species, one with a very short lifetime (161 ns) and one with a lifetime in the microsecond range. Neither species is affected by triplet quenchers so it can be concluded that the transients are not triplets. The transient spectroscopy of 2-methyl-acetophenone has been extensively studied<sup>11,12,44,45,47,48</sup> and the behaviour of this system is similar

of POAS. The transient spectra of 2-methyl-acetophenone shows the decay of two distinct transient species; one with a very short lifetime (176 ns) and one with a lifetime in the microsecond range, and these transient species are not affected by triplet quenchers. It has been determined by Scaiano<sup>48</sup> that the transient species observed in 2-methyl-acetophenone are the syn and anti enols. The syn enol can decay by reverse intramolecular hydrogen abstraction to regenerate the starting ketone. Because the process is intramolecular in nature the lifetime of this enol is very short (in the nanosecond range). However, for the case of the anti enol, the system cannot undergo reverse intramolecular hydrogen abstraction. The decay of this enol is an intermolecular process which requires the close contact of two enols followed by hydrogen abstraction between the two, and because of this, the decay of the anti enol will be longer.

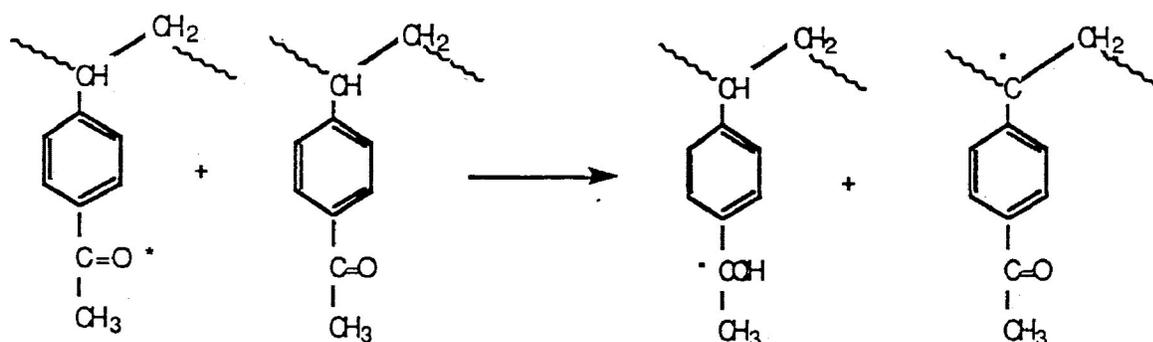
It is therefore concluded that the transient species observed in POAS are associated with the syn and anti enols. The short lived transient corresponds to the decay of the syn enol, which involves reverse hydrogen abstraction. The longer lived transient involves the decay of the anti enol, which requires close contact between two enols, either from two different polymer chains or from two different sites on the same polymer chain.

For the transient spectra of POPS it was observed that there was a short lived transient present (125 ns) and this species is also unaffected by triplet quenchers. This decay is associated with the decay of the syn enol. There was no anti enol observed however, the decay of the anti enol could be masked out by the growth of a new transient species. To date we have not been able to resolve the nature of this species.

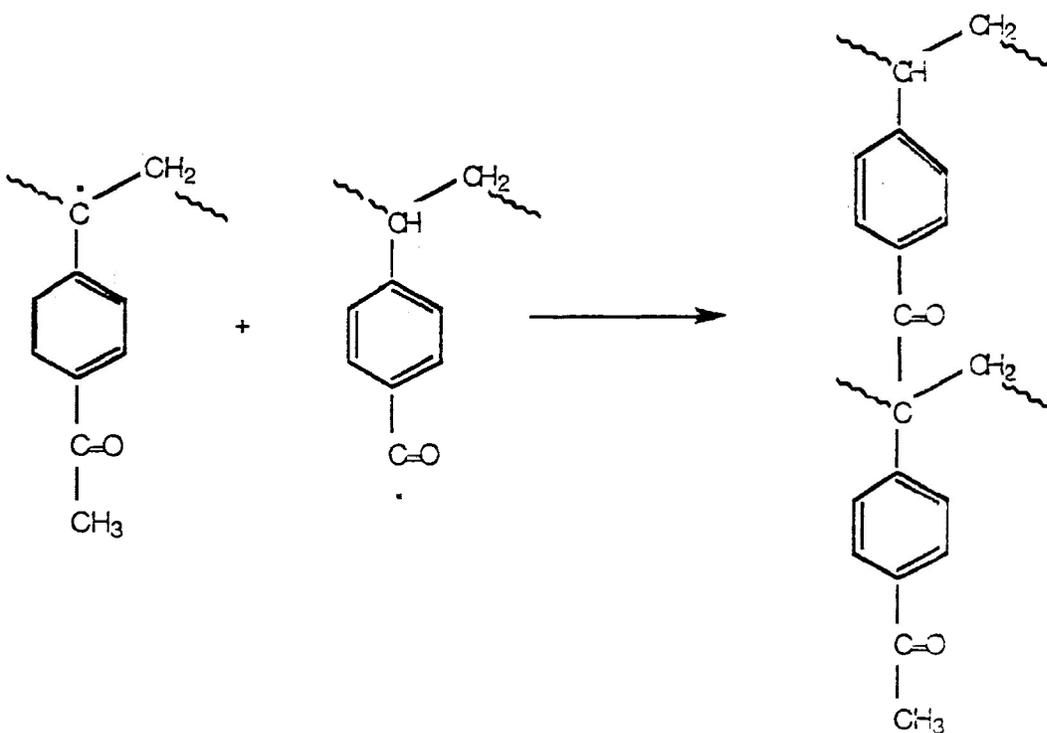
Molecular weight measurements examine the rates of chain scission for these polymers. As previously mentioned chain scission of these polymers is by  $\beta$  scission of the tertiary radical. For example, PPAS:



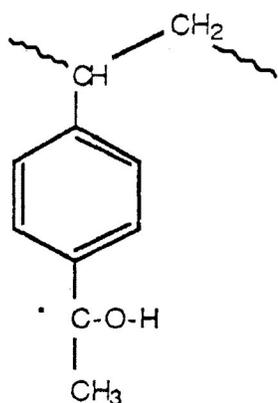
Therefore, the prerequisite to chain scission is the generation of this tertiary radical. This can be brought about by hydrogen abstraction by a methyl or ethyl radical (from alpha cleavage reactions). Also, a tertiary radical can be generated in a photoreduction reaction involving the triplet carbonyl. For example, PPAS:



However, it is also possible for two polymer radicals to combine to give rise to cross links, and this results in an increase in the molecular weight. For example, PPAS:



It is also possible for the radical from the photoreduction process to take part in cross linking reactions:



If cross linking takes place between two different polymer chains, the net result is an increase in the molecular weight. However, if the cross linking takes place between two radicals from different sites on the same polymer chain then there is no change in the molecular weight of the polymer.

For simplicity, intermolecular cross linking will be referred to as cross linking

reactions, whereas intramolecular cross linking will be referred to as cyclization reactions.

It was observed from molecular weight measurements for PPAS and PPPS, that by varying the conditions of the solution, it was possible to favour either cross linking or chain scission reactions. For example, PPAS and PPPS in chlorobenzene underwent mainly chain scission. However, the addition of methanol results in precipitation of these polymers upon irradiation. Since the solubility of a polymer is reduced when the molecular weight is increased, it can be concluded that cross linking reactions are taking place.

Thus, cross linking and chain scission reactions are competing with each other, and while both take place in the polymer solution upon irradiation varying the conditions of the solution can favour one reaction over the other.

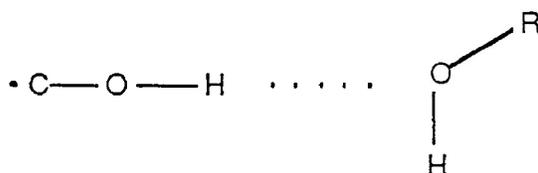
For POAS and POPS it can also be predicted that both chain scission and cross linking reactions are possible; however, the polymer radical from photo-reduction is in a sterically isolated position and this would make approach of another polymer radical difficult. In addition, alpha scission is less favoured for the *ortho* polymers than for the *para* systems. This is because the *ortho* polymers are capable of undergoing enolization which competes with alpha scission. As previously mentioned for the polymer in the solid state below  $T_g$  there is some ground state control; however, in solution the restriction on the syn  $\rightarrow$  anti rotation no longer exists so any excited chromophores in the anti conformation can easily rotate into the syn conformation where they can enolize. For this reason it is believed that alpha cleavage in the *ortho* polymers, in solution will be negligible, so we have few or no ketyl radicals produced. This factor would lead to a reduction in the chance of cross linking/cyclization reactions. Therefore, it would be expected that the balance would lie in favour of chain scission. This is reflected in all molecular weight measurements of the *ortho* polymers where it was not possible to favour cross linking over chain scission (there were no observed cases where POPS or POAS precipitated out of solution upon irradiation).

It is therefore obvious that any factor that affects the rate at which these polymer radicals form will affect the rate at which these secondary reactions take place. The presence of triplet quencher has the effect of quenching the carbonyl triplet and stopping the photoreactions at their source. This is indeed observed for

the *para* substituted polymers (using naphthalene as the quencher). For both PPAS and PPS the presence of naphthalene in the solution reduces the rate of chain scission, the rate decreasing as the concentration of naphthalene increases (see Fig 3.16 and 3.17). However, for the *ortho* polymers no such quenching is observed (Fig 3.14 and 3.15), but it is possible to observe quenching with 1,3-cyclooctadiene. It is possible that a large rigid molecule like naphthalene is unable to approach closely enough to the sterically isolated carbonyl triplet of the *ortho* polymers, but the more flexible 1,3-cyclooctadiene molecule is able to approach the carbonyl triplet and facilitate the energy transfer required for quenching.

A factor pointed out by Schnabel<sup>22</sup>, that affects the rate of chain scission of a polymer is the quality of the solvent. A polymer molecule dissolved in a good solvent will "swell" and by decreasing the quality of the solvent the polymer chain tends to "coil up" into a tighter ball and the tightness affects the rate at which polymer fragments can disentangle themselves and diffuse away from each other. The more compact the polymer chains are, the more polymer-polymer contact points, and the smaller the rate of fragment disentanglement. Therefore, from this argument it is expected that the rate of chain scission will decrease with decreasing solvent quality. Likewise, as the solvent quality increases the polymer tends to "swell" thereby decreasing the number of polymer-polymer contact points, the rate of disentanglement of polymer fragments increases and this is observed as an increase in the rate of chain scission.

Also, as previously mentioned by Guillet<sup>17</sup> and Wagner<sup>21</sup> the presence of an alcohol in the solvent (ie. methanol) has the effect of stabilizing a hydroxy radical (which is an intermediate in the photoenolization process as well as the photoreduction process):

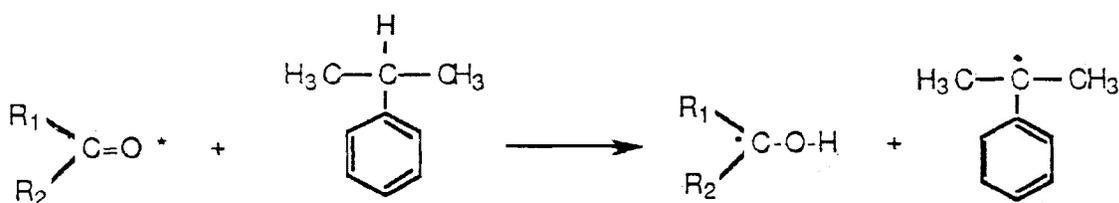


Applying this argument to the *ortho* polymers it is possible that the presence of an alcohol would tend to stabilize the hydroxy radical produced by photoreduction.

This would have the effect of favouring photoreduction., which would in turn favour tertiary radical formation, thereby increasing the rate of chain scission. However, the presence of an alcohol would also tend to stabilize the hydroxy-1,4-biradical intermediate in the photoenolization process. In addition, the alcohol could stabilize the enol itself. This would then favour enolization and have the effect of decreasing the rate of tertiary radical formation (decrease the rate of chain scission).

In addition, the presence of an alcohol in solutions of these polymers has the effect of decreasing the quality of the solvent and one of the effects of this has been previously mentioned.

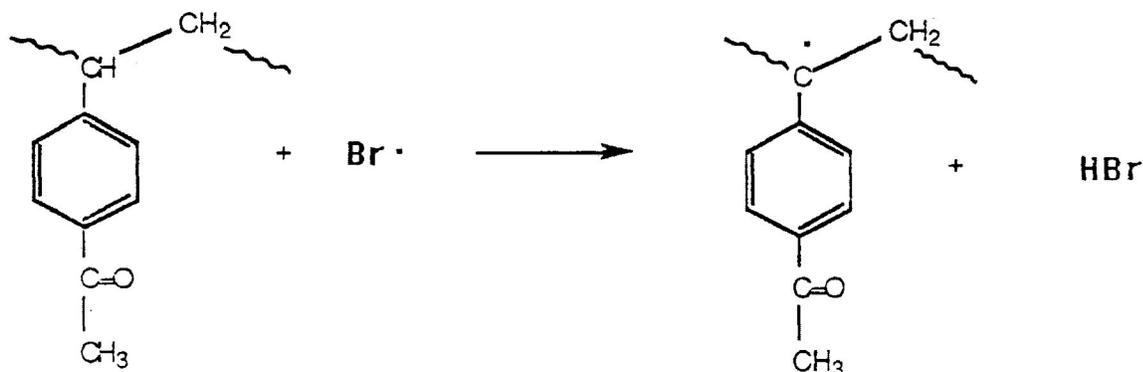
The addition of certain transfer agents, for example cumene, isopropanol, and bromotrichloromethane are predicted to react with the carbonyl triplet via an abstraction. For example, cumene:



The same reaction is possible for isopropanol and for bromotrichloromethane (except a bromine atom is transferred). This competes directly with photoreduction involving the polymers, and this reduces the rate of formation of tertiary radicals. However, cumene and isopropanol have the effect of reducing the quality of the solvent. In addition isopropanol, being an alcohol, can stabilize the intermediates of enolization and photoreduction. Bromotrichloromethane would actually improve the solvent quality.

Irradiation of polymer solutions that contained bromotrichloromethane tended to become red in colour. A similar discolouration of a polymer solution was observed when polymer solutions containing bromine were irradiated (wavelengths used here were beyond 320 nm). Here chain scission was also observed even though there could be no excitation of the carbonyl. Chain scission here is attributed to photodissociation of bromine molecules, followed by tertiary hydrogen abstraction

by bromine atoms:



It is possible for bromotrichloromethane that irradiation is able to bring about dissociation of the bromine carbon bond and the bromine atom can then abstract the tertiary hydrogen from the polymer. If this is the case, the addition of bromotrichloromethane would result in a large rise in the rate of chain scission. Thus the true effect of photoreduction can not be assessed by this technique.

Another solvent effect deals with the case where the tighter the polymer coil, the more likely there will be a tertiary hydrogen within the reactive volume about the carbonyl triplet, and this would promote photoreduction, and would give rise to an overall rise in the rate of tertiary radical formation as solvent quality decreases. In addition the tighter the polymer coil the more likely that two polymer radicals from the same polymer chain will approach closely enough to each other to allow cyclization. This would have the effect of shifting the balance of cross linking/cyclization reactions in favour of cyclization. At the same time, there are still tertiary radicals present which can undergo  $\beta$  scission. Therefore, observations would show an apparent increase in the rate of chain scission; not because more chain scissions are actually taking place, but because fewer competing cross linking reactions are taking place (as cyclization reactions are more favoured).

Actual results where solvent quality is decreased by the addition of cyclohexane (which has no secondary effect on the photochemistry) show that the decrease in solvent quality gave rise to an increase rate of chain scission. This would appear to support this argument. However, for the *para* polymers in the presence of

cyclohexane, cross linking reactions masked any chain scission. Here it would appear that Schnabel's explanation of the effect of solvent quality holds true. With the rate of polymer fragment disentanglement being hindered, the rate of chain scission, is decreased so the balance of cross linking to chain scission reactions lies in favour of cross linking.

The effect of solvent quality can also be used to explain the apparent increase in the rate of chain scission for the *ortho* polymers in the presence of naphthalene and cumene. Both systems are hydrocarbons which would act similarly to cyclohexane and decrease the quality of the solvent. From the observed results (Fig 3.14, 3.15, 3.20, 3.21) it would appear that a solvent effect is more pronounced than any quenching or hydrogen transfer. It is also possible that the steric isolation of the *ortho* carbonyl is not permitting the close approach of these molecules.

It was also observed that methanol and isopropanol have the effect of increasing the rate of chain scission for the *ortho* polymers (Fig 3.26 - 3.29). Again it would appear that solvent effect overshadows any hydrogen donation or intermediate stabilization. Also, the *para* polymers show a great deal of cross linking in the presence of methanol and isopropanol and the explanation for this is similar to that for the *para* polymers in the presence of cyclohexane.

For the case of the addition of bromotrichloromethane (Fig 3.22 - 3.25) it is observed that there is an increase in the rate of chain scission for all polymers. This appears to support the previous argument that bromotrichloromethane is actually undergoing dissociation, with the bromine atom then abstracting a tertiary hydrogen atom. This results in an increase in the rate of production of tertiary radicals.

### Conclusion

Triplet quenching indicate that the photolysis of these polymer systems originate from the carbonyl triplet. It is seen from gas product analysis studies on solid films, below  $T_g$ , that one the primary photoreaction is Norrish I cleavage and photoreduction, however the rate of this cleavage is significantly lower for the *ortho* substituted polymers compared to their *para* counterparts. This improved stability is attributed to photoenolization of the *ortho* polymers. Transient spectroscopy provides evidence of enol formation in these *ortho* polymers. The fact that there is any gas products detected in the *ortho* polymers suggests that there is some ground state control. The conformational *syn*  $\rightarrow$  *anti* rotation is restricted in solid films below  $T_g$ .

Viscosity measurements show that secondary reactions include competitive cross linking/cyclization and chain scission. These secondary reactions arise from polymer radicals produced from either Norrish I cleavage, photoreduction, or hydrogen abstraction by methyl or ethyl radicals (from Norrish I cleavage). However, for the *ortho* polymers in solution the only primary photoreaction that are possible are photoreduction and photoenolization. Norrish I cleavage will not occur in these *ortho* systems due to the ease of *syn*  $\rightarrow$  *anti* conformational rotation in solution.

The balance of these secondary reactions for all polymers in solution is very dependent on the quality of the solvent. For the *para* substituted polymers it is possible to favour one secondary reaction over the other by changing the quality of the solvent. For the case of the *ortho* substituted polymers changes in the quality of the solvent appears to enhance chain scission as solvent quality decreases. This arises from an enhancement of the photoreduction process. As the polymer coil becomes tighter (as solvent quality decrease) there is a greater chance that there will be a tertiary hydrogen within the reactive volume about the excited carbonyl. This would give rise to an increase the rate of tertiary radical production. Also because the hydroxy radicals from photoreduction (in the *ortho* polymers) are fairly sterically isolated the approach of two polymer radicals to give rise to cross linking will be restricted to a degree. As solvent quality decreases the tighter the polymer coil so it

could be expected that cyclization reactions would be more likely over cross linking. Therefore, decreasing solvent quality for the *ortho* polymers gives rise to an increase in the rate of chain scission because of the increased rate of photoreduction and the decrease in cross linking, as cyclization is more favoured.

### Suggestions for Future Work

It may be of interest to examine the photochemistry of other similar *ortho* substituted styrene polymers where the acyl group contains a longer hydrocarbon chain. It can be predicted that when the carbon chain exceeds C<sub>3</sub> then it is possible for a Norrish II reaction to take place. This would also compete with the photoreactions that take place in the polymers examined in this thesis.

It may also be of interest to carry out a farther examination of this solvent effect observed in the *ortho* polymers. Perhaps light scattering techniques can examine the degree of polymer coiling and provide farther insite into the dynamics of the photoreactions that thake place in these systems.

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