THE PHOTOLYSIS OF PARA-SUBSTITUTED STYRENE POLYMERS

by

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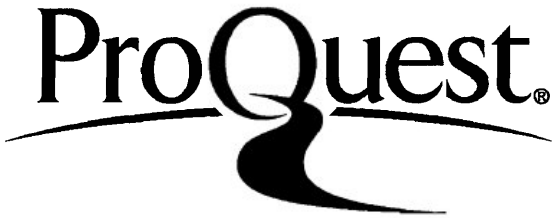

ABSTRACT

This thesis describes the photolysis of para-substituted styrene polymers. Poly(vinylacetophenone), poly(p-bromostyrene), poly(p-chlorostyrene), poly(p-fluorostyrene), poly(p-isopropylstyrene), poly(p-methoxystyrene), and poly(p-*tert*-butylstyrene) films have been irradiated with short-wave ultraviolet radiation (wavelengths less than 300nm) under high vacuum at 25°C. Poly(vinylacetophenone) has also been irradiated with long-wave ultraviolet radiation (wavelengths greater than 300nm) under high vacuum at 25°C.

During short-wave irradiation, the primary photochemical reactions are the result of absorption and transfer of energy by the phenyl segments to bonds in the main polymer chain and the para-substituent. The long-wave irradiation of poly(vinylacetophenone) involves the absorption and transfer of energy by the carbonyl function in the para-acetyl group to bonds in the para-substituent, a Norrish Type I reaction being observed.

The nature and extent of the secondary photochemical reactions (i.e., crosslinking, chain scission, coloration and volatile product formation) are discussed in terms of electronic (inductive and conjugative) effects, bond dissociation energies and steric factors

associated with the para-substituent.

Changes in the macromolecular structure of the polymers have been investigated by infrared, ultraviolet-visible, fluorescence, and mass spectroscopy as well as changes in molecular weight and solubility measurements.

In all polymers, except for poly(p-chlorostyrene) and poly(vinylacetophenone) irradiated with long-wave radiation, hydrogen was the major reaction product. Its formation may be attributed to α-C-H bond fission in the main chain followed by recombination or abstraction. In addition, volatile products characteristic of partial or total para-substituent cleavage were also detected.

The pronounced yellowing of the polymers during irradiation was observed to be concomitant with the release of hydrogen and has been attributed to the build-up of main chain conjugations.

The possibility of diffusion controlled reactions was also investigated and found to be unimportant for the polymer films used in this study.

ACKNOWLEDGEMENTS

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1

INTRODUCTION

1.1 Energy Absorption and Transfer - General Considerations

The absorption of light by a molecule with the production of an excited electronic state is a necessary, but not sufficient, condition leading to a photochemical reaction.(1) Light absorbed by the system will generally lead to a transition from the electronic ground state, $^1M_0$, (usually singlet) to a higher energy state, $^1M_1^*$, as shown in figure 1.1.(1) Once in an excited state the molecule has additional energy that can be dissipated either through photophysical processes or by undergoing a photochemical reaction (frequently dissociation to produce a pair of free radicals). Usually, the excited molecule will first undergo a rapid (approximately 10^{-12} sec. (2)) decay to the lowest vibrational level of the excited state followed by a radiationless process (internal conversion) to a vibrational level of $^1M_0$ and further decay to a lower vibrational level of the ground state. Many of the photophysical processes that can occur to relieve the excited molecule of excess energy depend on the lifetime of the excited singlet, $^1M_1$, (typically 10^{-6} to 10^{-9} sec. (2)). Energy may be lost through the radiative process of fluorescence as well as the radiationless process of intersystem crossing to yield the triplet

state, $^3M_1$. Molecules in the triplet state are longer lived than excited singlet state molecules and, as a result, more time is available for transitions and chemical reactions to take place. Radiative transitions from the triplet to the ground singlet state are termed phosphorescence and may have lifetimes ranging from 10^{-5} to 10 seconds.(2)

The processes discussed so far are essentially unimolecular processes but in addition, bimolecular photophysical processes are very important in systems where electronically excited states can exist.(1) One such process is the energy transfer between chromophores of the same species resulting in the formation of an excimer (i.e., interactions involving a transfer of energy between a chromophore in the $^1M_1$ state and a chromophore in the $^1M_0$ state of the same polymer molecule). An excimer is a distinct excited species having an energy level lower than the excited singlet state and can undergo a variety of photophysical processes including fluorescence, energy transfer and triplet formation.(1) An energy transfer between chromophores of different molecules may result in the formation of an excited complex called an exciplex (i.e., interactions involving a transfer of energy between a chromophore in the $^1M_1$ state and a chromophore in the $^1M_0$ state of a different molecule). Both excimers and exciplexes may also be formed through the mutual annihilation of two $^3M_1$ molecules(1):

$$^3M_1 \qquad ^3M_1 \longrightarrow D^* \longrightarrow {}^1M_1 \qquad {}^1M_o \qquad (1)$$

where: D^* represents the excimer or exciplex complex.

It is important to note that in polymer systems the chromophores must be co-planar and, in a system such as polystyrene, they must be in a two-unit sequence (i.e., adjacent units) for intrachain excimer formation.(3)

In addition to the photophysical processes discussed above, photochemical processes may arise from a molecule in an excited electronic state. Energy can be made available for a photochemical reaction by a molecule in an upper excited electronic state, $^1M_1^*$, an excited singlet state, $^1M_1$, or an excited triplet state, $^3M_1$, as shown in figure 1.2.

In general, photochemical processes can be divided into two categories depending upon the wavelength of incident radiation. Wavelengths in the 200nm to 300nm region are used in short-wave photolysis and wavelengths greater than 300nm (i.e., solar radiation received by the earth) are used in long-wave photolysis. The latter of the two studies are of significance to the actual outdoor weathering of many polymer systems.

1.2 The Ultraviolet Absorbance of Polystyrene

The ultraviolet absorption spectrum of polystyrene, illustrated in figure 1.3, has a maximum absorption at 255nm and an absorption co-efficient, ε', of $4000cm^{-1}$(4) due to the $\pi \rightarrow \pi^*$ transition of the benzene ring. The absorption co-efficient is derived from the Beer-Lambert relationship(5) and combines the values of the extinction co-efficient and the concentration associated with solution spectra:

$$A = \log I_0/I_t = \varepsilon \cdot c \cdot \ell \quad (2)$$

$$= \varepsilon' \cdot t \quad (3)$$

where: A is the absorbance

ε is the extinction co-efficient

c is the concentration

ℓ is the pathlength

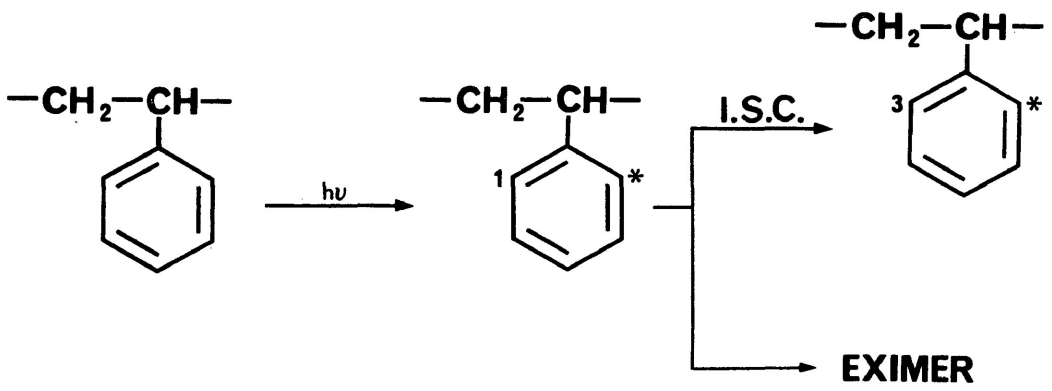
t is the film thickness.

1.3 Short-wave Photolysis of Polystyrene

1.3.1 Primary Reactions

1.3.1.1 Photophysical Processes

Absorption of light by the phenyl segments first produces the excited singlet state which is transformed via intersystem crossing to yield both the triplet state and the excimer complex:



(4)

The fluorescence spectra of pure polystyrene consists of a single broad and structureless band due to the formation of excimers(6) (see figure 1.4). As previously noted, excimer formation results from an intramolecular transfer of energy between two adjacent phenyl segments on the same polymer chain.

1.3.1.2 Photochemical Processes

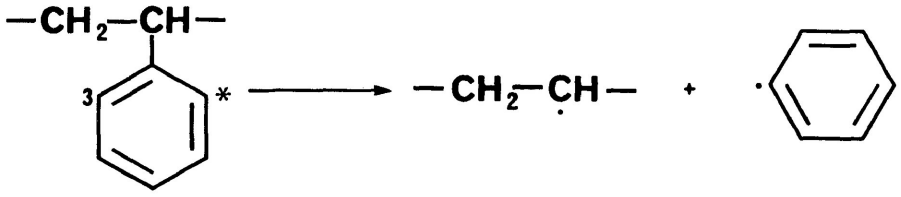
The principal manifestations of short-wave photolysis of polystyrene, in the absence of oxygen, are volatile product formation, chain scission and crosslinking.

The vibrationally excited singlet may undergo reactions by fission of bonds adjacent to the phenyl group. In particular, four bonds can be involved; α-C-H, main chain C-C, C-phenyl and phenyl-H. It is energetically possible that all of these bonds can be broken (see

figure 1.5) provided that energy transfer to the particular bond occurs efficiently during the lifetime of the excited singlet.

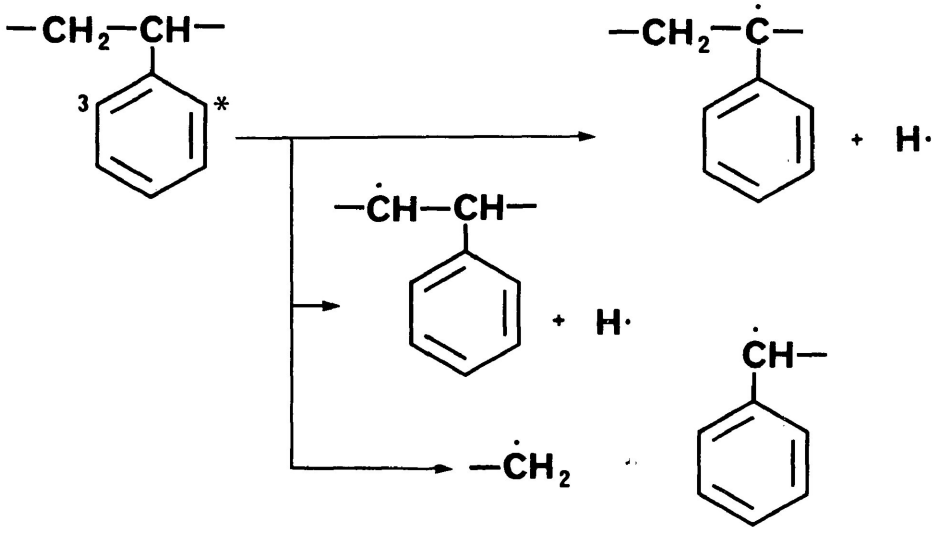
It is likely however, and has been suggested by Reinisch et al.(7), that the majority of photochemical reactions of polystyrene originate from the triplet state. The energy of the triplet excited ring may be:

i) used for dissociation of the phenyl-C bond:



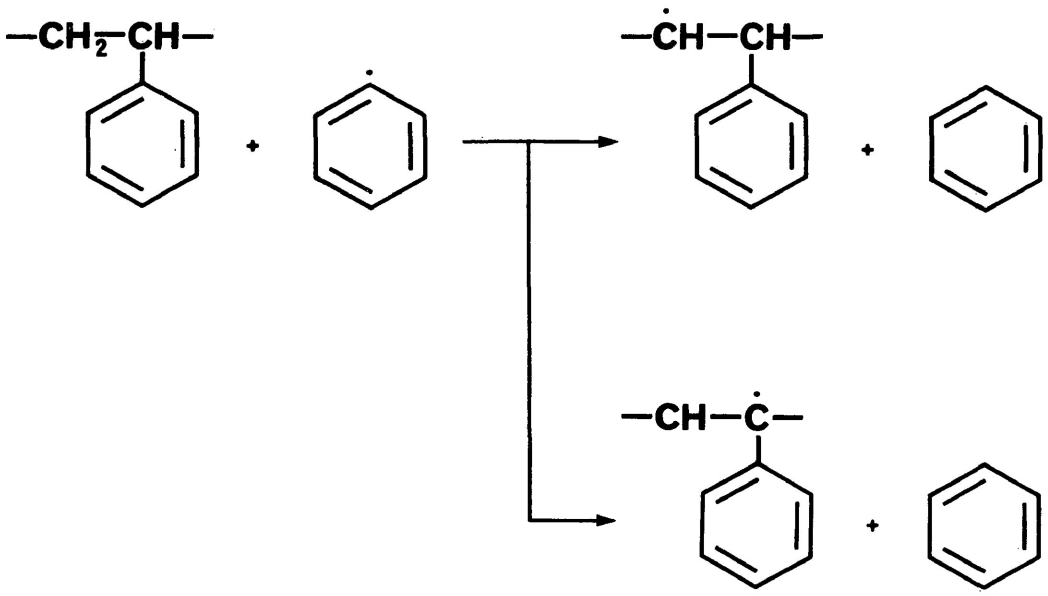
(5)

ii) transformed by intramolecular energy transfer processes to the C-H or C-C bonds on the main polymer chain, resulting in the fission of bonds:



(6)

Phenyl radicals are very reactive and have limited mobility in the polymer matrix (i.e., a very high macroscopic viscosity would impose a large cage effect). They could be expected, on escape from the cage, to abstract hydrogen from the α and β atoms in the backbone of the main polymer chain:



(7)

Fission of the C-C bond in the main chain will be subject to similar very large cage effects (i.e., chain scission will depend on diffusional separation of two large radicals in a high viscosity medium). The probability of escape from a cage can be related to D, the diffusion co-efficient which is given by:

$$D = \frac{k \cdot T}{\beta \cdot v \cdot h} \qquad (8)$$

where: k is the Boltzman constant

η is the bulk viscosity

β is a constant

V is the effective volume of the separating species.

For low temperatures and high viscosity, the value of the diffusion co-efficient will be low and the separation of two large radicals (i.e., two main chain segments) will be highly unlikely. This is reflected in the value of the quantum yield for chain scission in polystyrene which has a value of 9×10^{-5} at 25°C.(8) In other words, the separation and subsequent recombination of smaller radicals is more probable in a high viscosity medium. Radicals that do not escape the cage may undergo recombination within the cage . Energy will be evolved as a result of the recombination and will depend on the nature of the chemical bond formed:

$$(R_1 + R_2)_{CAGE} \longrightarrow R_1 - R_2 + \Delta H \qquad (9)$$

$$\Delta H = E_D(R_1 - R_2) \qquad (10)$$

where: E_D refers to the dissociation energy of the chemical bond.

If some of the energy, ΔH, can be removed, a bond will be formed that will survive vibrations. If energy is not removed, the excited chemical bond will break on vibration. For carbon-carbon bonds,

it is possible that energy can be removed more easily since there are more vibrational degrees of freedom.

On the basis of bond dissociation energies (shown in figure 1.5) it can be predicted that in polystyrene the elimination of α-hydrogen and main chain scission are energetically preferred. This can be rationalized by considering the three types of C-H bonds and the C-C bond found in the molecule. The aromatic hydrogen, the secondary, the tertiary hydrogens and the main chain carbon-carbon bond have approximate dissociation energies of 104, 76, 71, and 70 kcal/mole respectively (see figure 1.5).(9) Values for bond dissociation energies are not available for polymers, but are calculated using Benson's method.(10) It is important to note that when cage effects are considered, separation of small hydrogen atoms become favoured at the expense of phenyl-C and C-C bond fission. There is however, the possibility that vibrationally excited species are involved, in which case the probability of bond scission cannot be assessed using this Arrhenius type of approach which pre-supposes purely thermal activation.

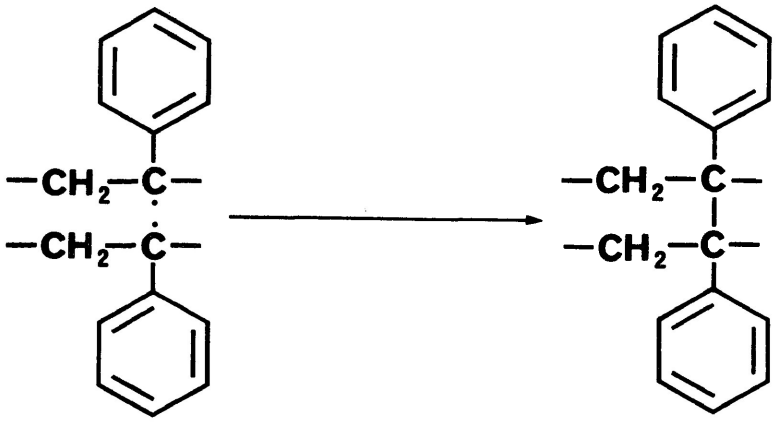
1.3.2 Secondary Reactions

Secondary reactions are the result of interactions of primary radicals with respect to additions to the phenyl ring, formation of

crosslinks, chain scission and the elimination of small molecules.

1.3.2.1. Crosslinking

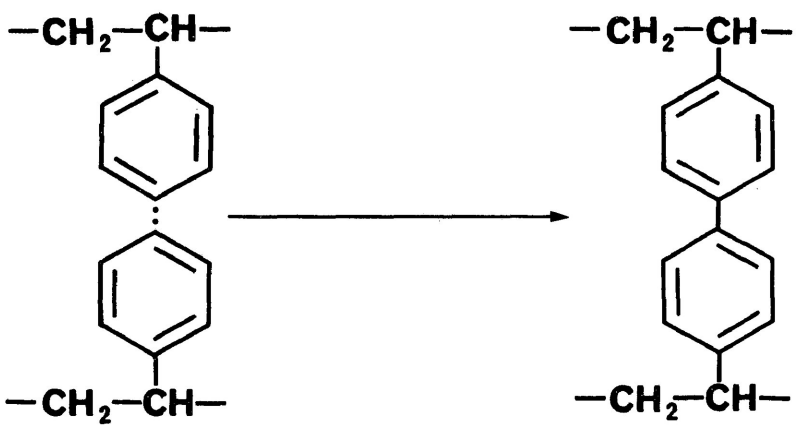
Grassie and Weir(9) have reported that polystyrene becomes insoluble when irradiated under high vacuum with ultraviolet radiation. Insolubility can be directly related to the degree of crosslinking between different chain segments. This can be visualized by considering the recombination of two benzylic radicals;



(11)

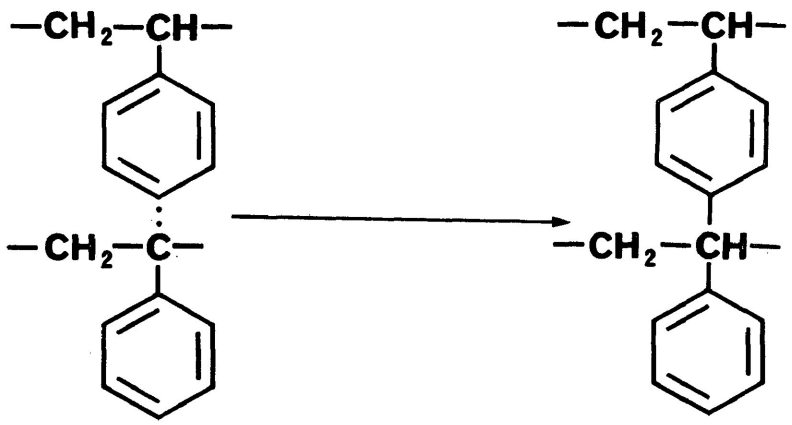
The nature of the crosslinked polymer depends upon the type of radical formed as well as the orientation (i.e., mobility) of the radical centre. For example, crosslinking can occur through phenyl segments if proper orientation between adjacent chains has been attained:

i)



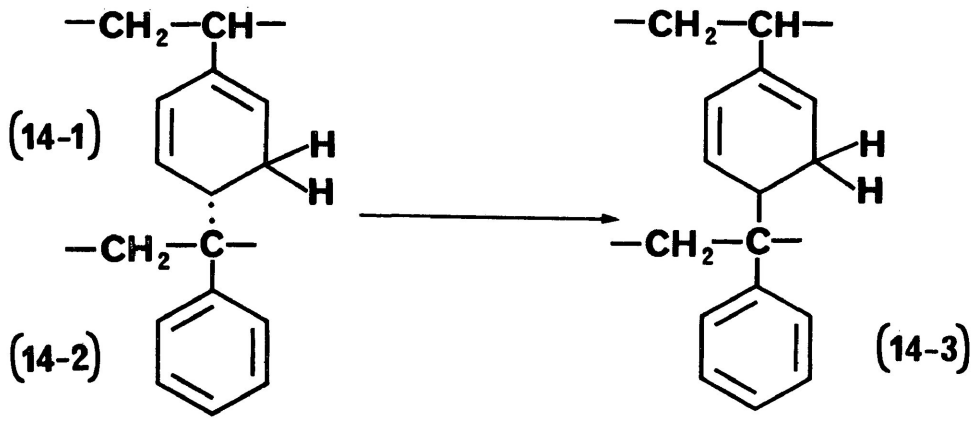
(12)

ii)



(13)

Furthermore, E.S.R. investigations of polystyrene following gamma radiolysis have confirmed the presence of cyclohexadienyl-type radicals, (14-1), and benzylic radicals, (14-2).(11-18) On the basis of these observations, Wall and Brown(19) have suggested another mechanism for crosslinking in which recombination between cyclohexadienyl and benzylic radicals yields a substituted cyclohexadienyl structure, (14-3):

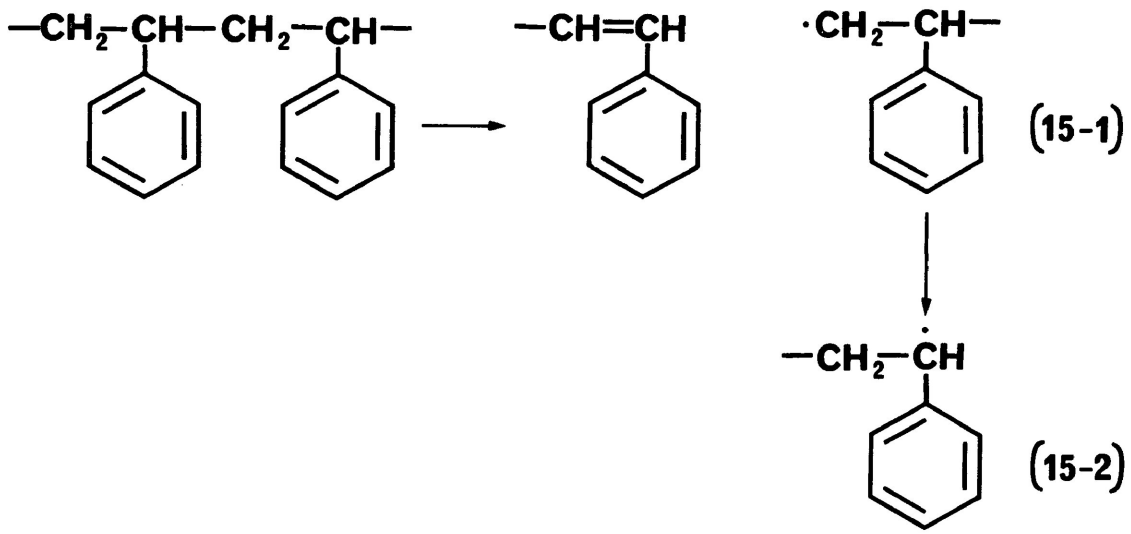


(14)

This mechanism has also been suggested by Slovokhotova et al.(20) following the irradiation of polystyrene with high speed elections.

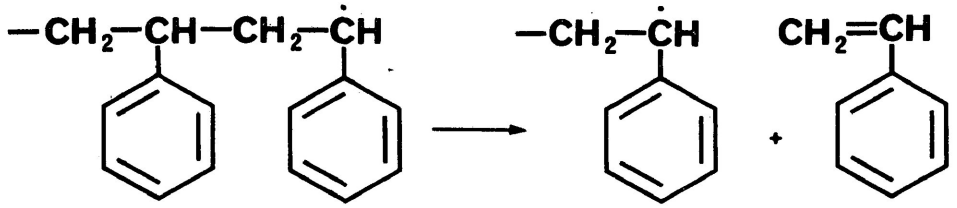
1.3.2.2 Chain Scission

Ranby and Rabek(21) have suggested that macroradicals may disproportionate giving rise to a scission process:



(15)

The radical formed by the scission, (15-1), is unstable and isomerizes to yield an end of chain radical, (15-2). Such a radical, resulting from an isomerization or hydrogen abstraction at a chain end, may lead to chain unzipping with the formation of monomer, (16-1);



(16)

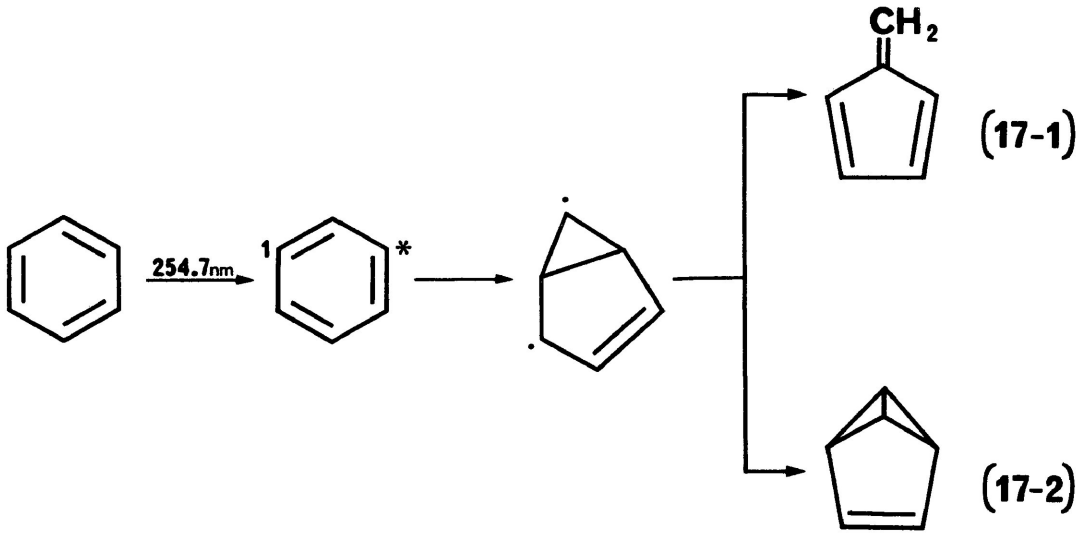
(16-1)

It is important to note that for this type of reaction the activation energy is fairly high and is therefore, not important at low temperatures.

1.3.2.3 Coloration

During the vacuum photolysis of polystyrene with ultraviolet radiation, a yellow discoloration was observed. The apparent yellowing appears to be a surface phenomenon characteristic of changes that occur in the macromolecular structure during irradiation. The successive build-up of discolored layers has the net effect of reducing the intensity of incident radiation to the bulk of the polymer. In the opinion of Ranby and Rabek(21) the yellow coloration is due to the photoisomerization of benzene molecules present in the photodegraded

polymer or benzene rings in polystyrene to fulvene, (17-1) and benzvalene, (17-2):



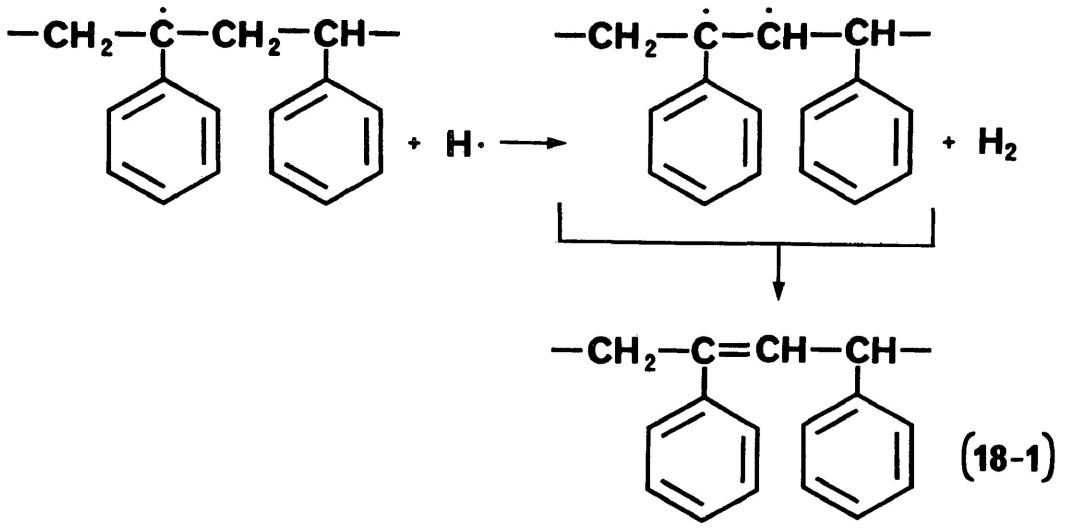
(17-1)

(17)

(17-2)

Fulvene is relatively unstable and cannot be isolated unless a trapping procedure is used. Substituted fulvenes however, are relatively stable (as evinced by their commercial availability). It is possible that photoisomers (17-1) and (17-2) could be present in the degraded polymer if they remained attached to the main polymer chain (i.e., involved in crosslinks).

Grassie and Weir(22) have attributed the discoloration in polystyrene to the build-up of conjugated bond sequences in the polymer backbone:



(18)

(18-1)

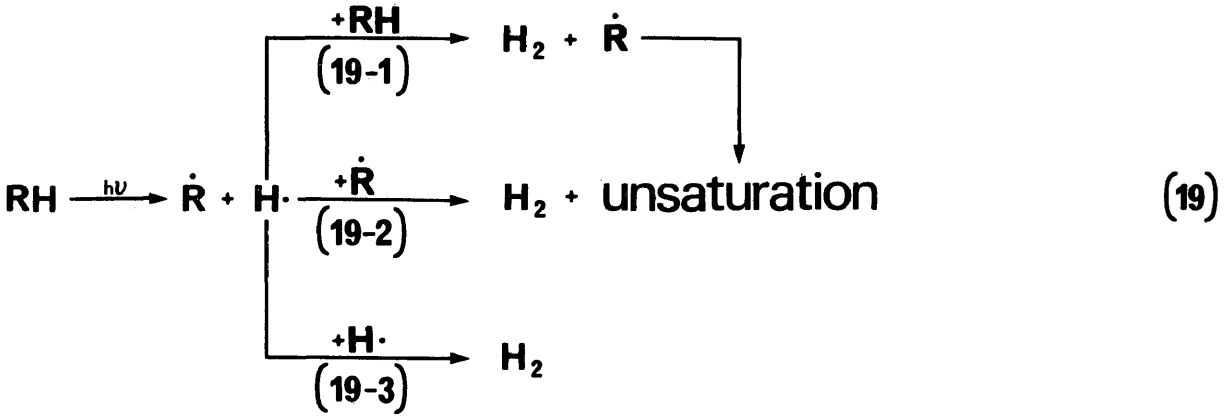
Infrared spectra of polystyrene films during photolysis have been observed to exhibit an increase in a shoulder at $825cm^{-1}$ on the band at $840cm^{-1}$. This increase in absorption has been attributed to the out-of-plane C-H vibrations characteristic of a trisubstituted ethylene system, (18-1).(22) In addition to the increase in intensity of the $825cm^{-1}$ shoulder, Slovokhotova et al.(20) have observed a decrease in intensity of the band at $1376cm^{-1}$ attributed to a decrease in the number of C-H bonds in the main polymer chain.

Ultraviolet spectra coupled with volatile product analysis have shown that the absorption in the 240nm region (attributed to the absorption by conjugated segments in the main polymer chain) increases concomitantly with the appearance of hydrogen.(22)

Collectively, experimental results strongly indicate the yellow discoloration to be associated with the build-up of main chain unsaturations.

1.3.3.4 Volatile Products

During the vacuum photolysis of polystyrene the only gaseous product observed was hydrogen.(22) The following reaction scheme has been suggested by Grassie and Weir(22) to explain the origin of hydrogen:



(19)

Hydrogen radicals are very mobile and can either diffuse out of the high viscosity medium and recombine with other hydrogen radicals (reaction (19-3)) or abstract hydrogen from the main polymer chain (reactions (19-1) and (19-2)), and hence provide a mechanism for coloration. The absence of benzene from volatile products reflects the limited mobility of phenyl radicals and their inability to diffuse out of a high viscosity medium, as suggested earlier.

1.4 Long-wave Photolysis

Many polymers contain only C-C, C-H, C-O, C-N, and C-Cl bonds and are not therefore expected to absorb light of wavelengths greater than 190nm.(21) The fact that free radicals are formed after irradiation with wavelengths greater than 300nm indicates that some types of chromophores must be present in these polymers.(21) The chromophores are usually incorporated into the polymer during the polymerization process (i.e., impurities) and are largely responsible for the initiation of photooxidation (see figure 1.6).

The ultraviolet absorbance spectra of polystyrene shows no absorbance at wavelengths greater than 300nm (i.e., no chromophores in the pure polymer). However, Lawrence(23) has observed a decrease in the number average molecular weight during the long-wave vacuum photolysis of polystyrene.

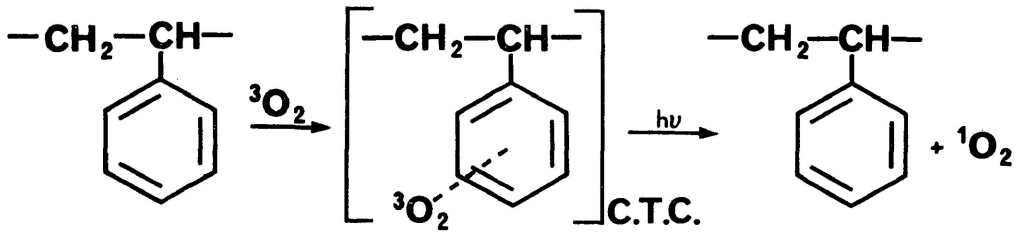
Lawrence and Weir(24) have suggested that residual peroxide groups (resulting from the incorporation of oxygen during the polymerization process) are the 'weak links' in the main polymer chain and contribute to the initiation of photooxidation by photolysis to alkoxy radicals which may abstract hydrogen atoms resulting in alkyl radicals, and ultimately, in the presence of oxygen, hydroperoxides(25) (see figure 1.6). The peroxide bond has a dissociation energy of

36 kcal/mole(26) and a broad absorbance with a maximum around 313nm(2) due to an $n \rightarrow \pi^*$ transition. Iodine scavenger experiments performed on polystyrene in an oxygen-free benzene solution have indicated that the active wavelength of absorption was 313nm and that no iodine incorporation (i.e., peroxide cleavage) occurred even after long periods of exposure to radiation of wavelengths greater than 300nm from which the 308nm to 320nm band had been removed with a potassuim biphthalate filter.(24)

It has been suggested that end-of-chain phenyl alkyl ketones, resulting from in-chain peroxide cleavage, are the initiating centres for photooxidation.(25,27) George(28) has observed that polystyrene, prepared either thermally or by free radical initiation, exhibits a phosphorescence spectrum that has, in part, been attributed to phenyl alkyl ketones on the ends of polymer chains. It has been observed that prolonged exposure (i.e., greater than 150 hrs.) of polystyrene under high vacuum to a mercury tungsten phosphor lamp significantly lowers the carbonyl emission intensity.(27) Subsequent irradiation in the presence of oxygen of this previously photolyzed sample results in a lower rate of photooxidation than the original polymer indicating that phenyl alkyl ketones are important in the initiation of photooxidation.(27)

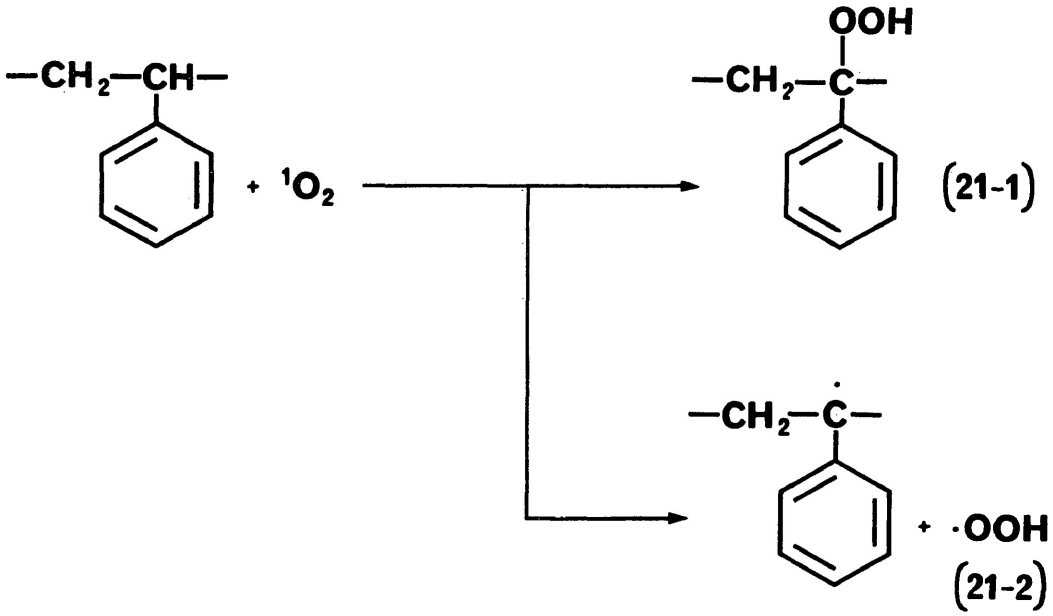
Ranby and Rabek(29) have suggested that polystyrene may

form a charge transfer complex (C.T.C.) with molecular oxygen. This complex, after excitation, would produce singlet oxygen by an intramolecular energy transfer process:



(20)

Singlet oxygen may then react with polystyrene to form a hydroperoxide, (21-1), or hydroperoxy radical, (21-2), to commence the initiation cycle:



(21)

However, there is no direct evidence that singlet oxygen is formed from a charge transfer complex of the type suggested above.(30) It would appear more likely that the charge transfer complex is involved

in the initiation step (i.e., formation of hydroperoxides directly from the break-down of the charge transfer complex) and that any singlet oxygen formed from such a complex will be relatively unimportant in the initiation of photooxidation.

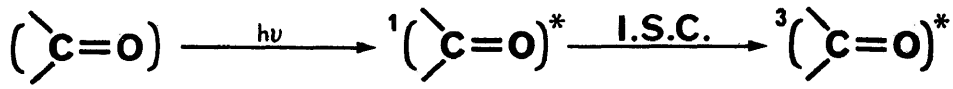
There are however, situations in other polymer systems which could lead to the formation of singlet oxygen. In particular, polycyclic aromatic hydrocarbons in polluted air are readily absorbed by polymer systems(31,32) and can be easily excited to singlet and triplet states to produce singlet oxygen by collision(33,34):

$$RH_o \longrightarrow {}^{1\text{ or }3}RH_1 \xrightarrow{{}^3O_2^*} {}^1O_2^* \qquad RH_o \qquad (22)$$

Some of these compounds when added to polyethylene affect the photodegradation of the polymer by sensitizing the abstraction of allylic hydrogen in unsaturated groups incorporated as an 'improper' bond.(35,36) Polycyclic hydrocarbons are also important in the sensitized photooxidation of poly(methyl methacrylate), presumably involving singlet oxygen.(37,38)

Polymers containing carbonyl groups, either as part of their structure or formed by various uncontrolled reactions during processing or synthesis, undergo degradation when exposed to light of wavelengths greater than 300nm. Ranby and Rabek(21) have observed

that carbonyl groups, when exposed in the region of 270nm to 330nm are easily excited to singlet and triplet states which could initiate a number of photochemical reactions:

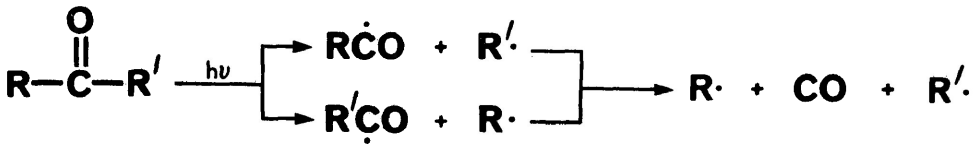


(23)

Of particular importance is the formation of singlet oxygen by collision with the excited triplet. Singlet oxygen may then react with atoms allylic to any unsaturations present in the main polymer chain to produce hydroperoxides and initiate photooxidation.

Photochemical reactions characteristic of carbonyl groups have been classified as Norrish reactions of Types I, II, and III(21):

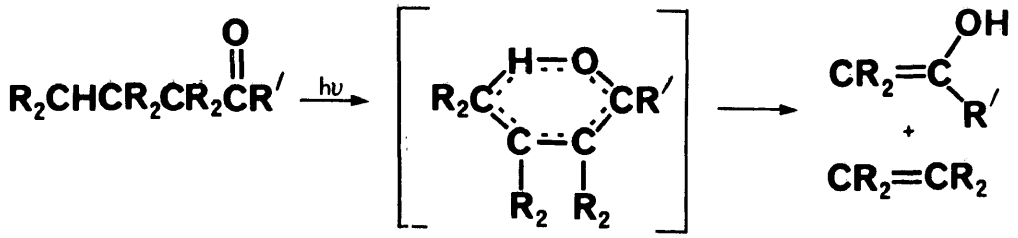
i) A Norrish Type I reaction involves cleavage (homolytic) of the chemical bond between the carbonyl group and an adjacent carbon atom:



(24)

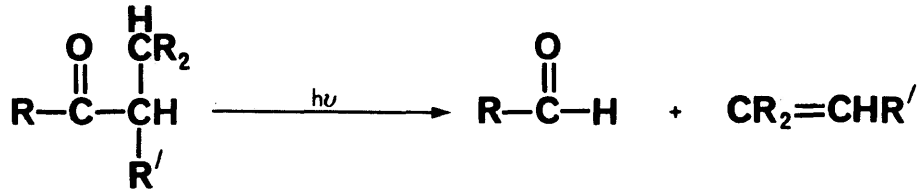
ii) A Norrish Type II reaction is a non-radical intramolecular process involving the formation of a six membered cyclic intermediate and abstraction of a hydrogen from the γ-carbon to yield an olefin,

alcohol or aldehyde:



(25)

iii) A Norrish Type III reaction is a non-radical intramolecular process involving the transfer of a hydrogen atom from the β-carbon followed by cleavage of the carbon-carbon bond adjacent to the carbonyl to yield an aldehyde and an olefin:



(26)

1.5 Substituted Styrene Polymers

1.5.1 Primary Processes

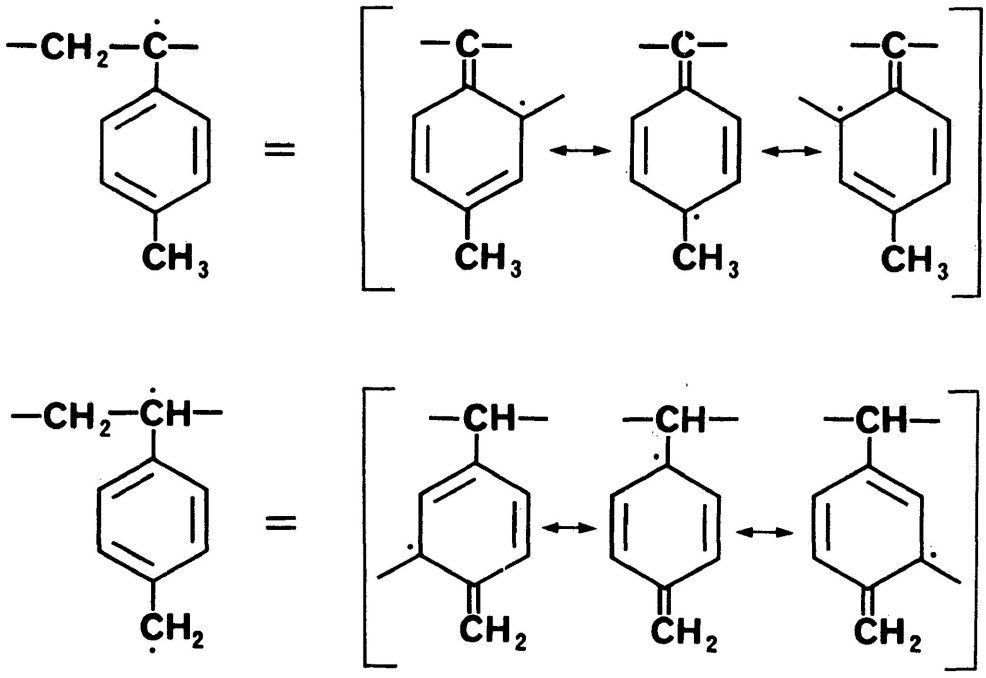
Introducing substituents into the phenyl ring of polystyrene may have drastic effects on the ease of radical formation as well as the stability of radicals thus formed.

The vacuum photolysis of poly(p-methylstyrene), PPMS, and poly(p-*tert*-butylstyrene), PPTB, have been studied by Weir(39) and Nicholas(40) respectively. Both systems undergo photochemical

reactions characteristic of polystyrene (i.e., crosslinking, yellow discoloration, and the formation of volatile products).

The energy requirements for carbon-hydrogen and carbon-carbon bond fission in PPMS are not known, but calculated values using Benson's method indicate; α-C-H, 80 kcal/mole; C-H of the p-methyl group, 84 kcal/mole and C-CH_3, 88 kcal/mole.(39) Benzylic radical formation in PPMS, as in polystyrene, requires the least amount of energy. The formation of a benzylic radical has been reported(40) to be energetically preferred in PPTB requiring an approximate 85 kcal/mole compared to 91 kcal/mole needed for the formation of tertiary butyl radicals.

A low temperature study on the nature of radical centres formed in PPMS during ultraviolet irradiation has been reported by Chernova et al.(41). Specifically, alkylbenzyl radicals formed by removal of a proton from the methyl group on the ring were identified during the photolysis. Paramagnetic centres characteristic of radicals localized on the main chain by elimination of hydrogen were not observed however, and it was suggested that the free electrons of the radicals formed on the main chain of PPMS may be delocalized in the phenyl ring:

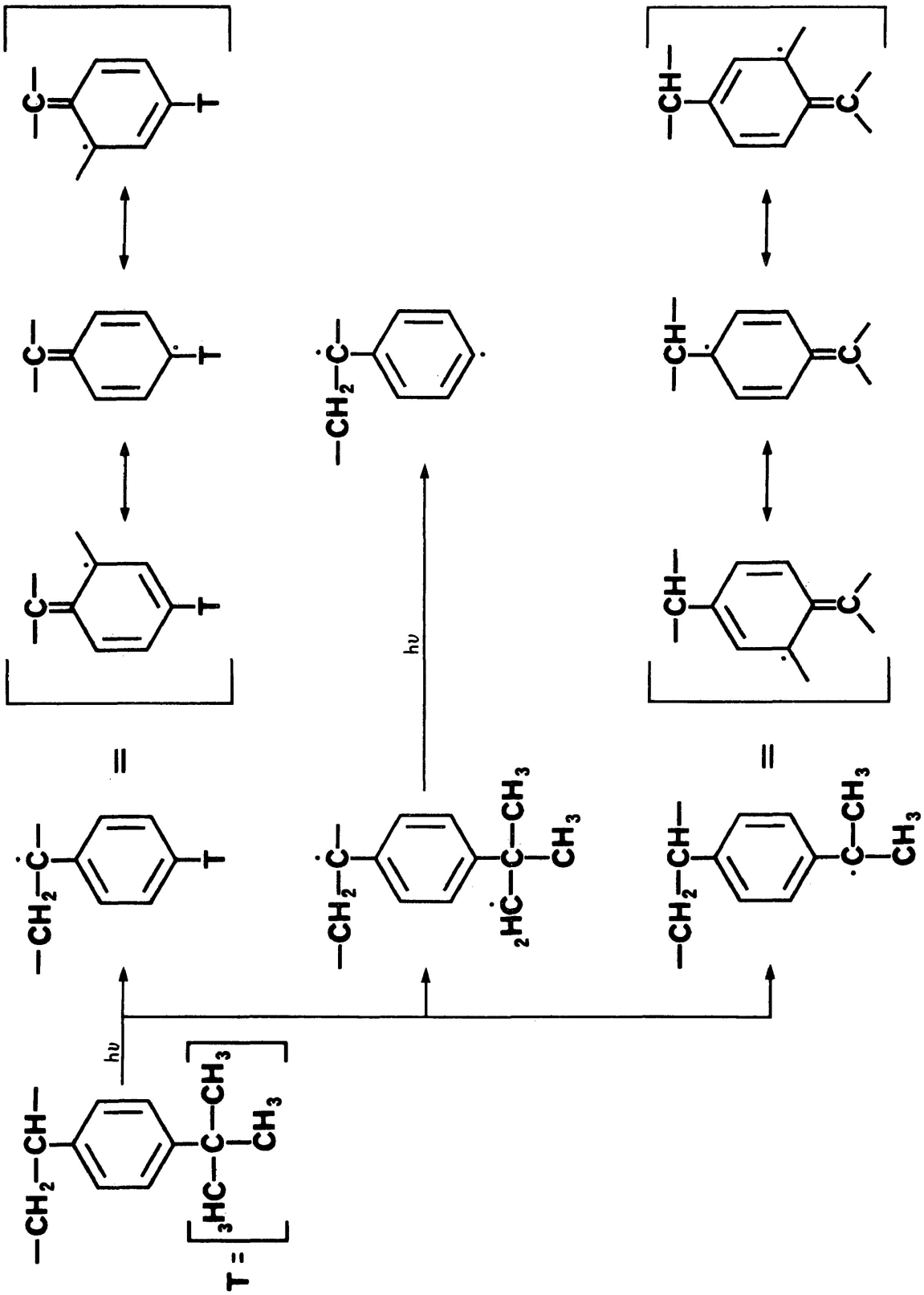


(27)

Similar delocalizations may be rationalized for PPTB (see 28).

It is important to note that the investigation of the paramagnetic centres in PPMS was performed at 77 K and it is doubtful that the results of such studies can be directly applied to room temperature irradiation.

(28)



1.5.2 Secondary Processes

Charlesby(42) has developed a relationship which is applicable to simultaneous chain scission and crosslinking of a polymer having an initial random molecular weight distribution:

$$S + S^{\frac{1}{2}} = \alpha/\beta + 1/b \cdot P_o \cdot \mathcal{D} \qquad (29)$$

where: S is the weight fraction of the soluble portion of the polymer after receiving a radiation dose $\mathcal{D}$

P_o is the initial number average degree of polymerization

α refers to the probability of chain scission

β refers to the probability of crosslinking.

Using the modified Charlesby relationship (in which $\mathcal{D}$ has been replaced by $I_0 \cdot t$; the intensity of radiation for a time t), a plot of $S + S^{\frac{1}{2}}$ versus t^{-1} yields an intercept of value α/β. Values of α/β for polystyrene(24), PPMS(39), and PPTB(40) have been reported and are listed in table 1.1:

TABLE 1.1

Polymer	α/β
Polystyrene	0.42
PPMS	0.26
PPTB	0.09

For polystyrene, the value obtained indicates that crosslinking is approximately twice as likely as chain scission. However, values obtained for PPMS and PPTB indicate that the degree of crosslinking is very dependent on the nature and configuration of the para-substituent, presumably being able to participate in the crosslinking.

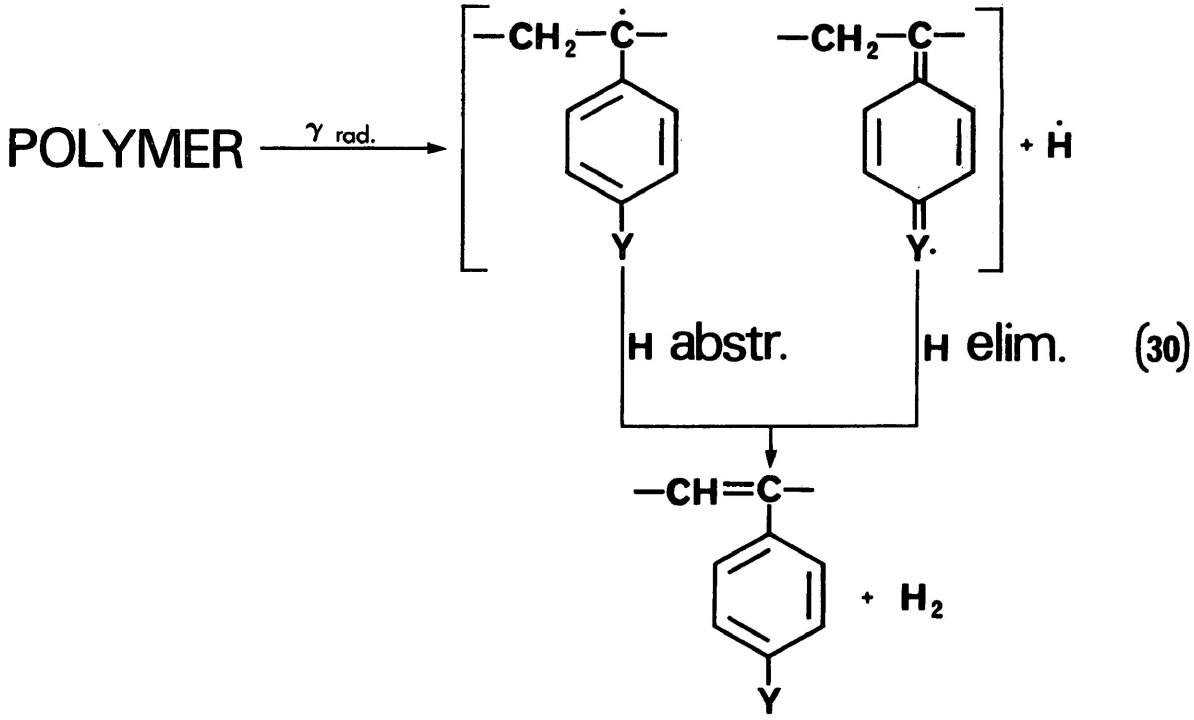
The vacuum photolysis of PPMS results in the production of significant amounts of hydrogen as well as small amounts of methane, ethane and traces of styrene, p-methylstyrene and toluene (i.e., residual solvent).(39) Nicholas(40) has observed traces of methane and ethane during the vacuum photolysis of PPTB. The nature of the volatile products indicates that radicals form on the main polymer chain as well as on the phenyl ring and the para-substituent.

Both PPMS and PPTB discolor during vacuum irradiation (attributed to the build-up of main chain conjugated sequences).(39,40)

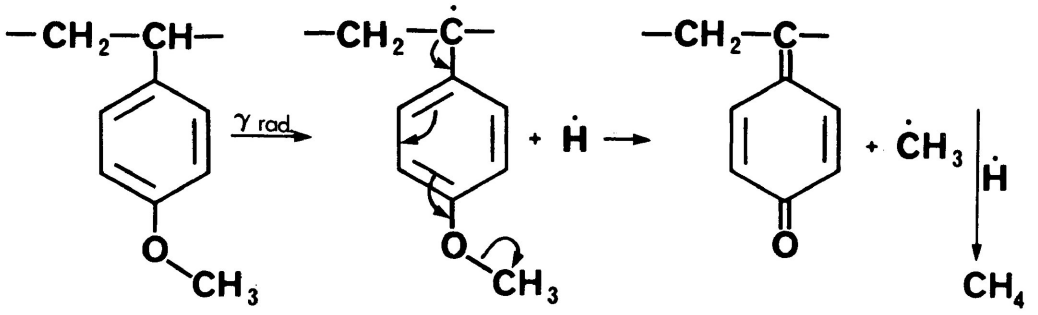
1.5.3 Gamma Irradiation of Para-subsituted Styrene Polymers

The degradation of a number of para-substituted polystyrenes on exposure to gamma radiation has been studied. In particular, Burlant *et al.*(43) have reported radiation-induced degradation for polystyrene, PPMS, poly(p-bromostyrene), poly(p-chlorostyrene), poly(p-methoxystyrene), poly(p-cyanostyrene), and poly(p-nitrostyrene).

The variation in electronegativity of the para-substituent has the effect to; i) alter the electronic environment about the main chain atoms and, ii) influence the effective delocalization of charge on the macroradical (i.e., resonance stability). For these para-substituted polymers, in every case except for poly(p-methoxystyrene), hydrogen was the only gaseous product evolved during the radiolysis. The nature of the volatile products from the radiolysis of α-deuterated para-substituted polystyrenes have indicated that the majority of hydrogen is liberated from the atoms on the backbone of the main polymer chain.(43) This result is consistent with the observations made during the gamma irradiation of deuterated polystyrene which established that the backbone atoms are the predominant source of hydrogen.(19) A reaction scheme has been proposed by Burlant et al.(43) to account for the hydrogen produced during radiolysis:

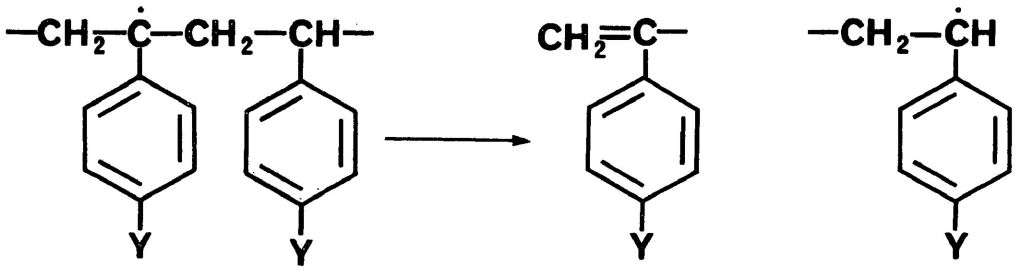


In addition to hydrogen, poly(methoxystyrene) liberated methane which has been accounted for by the following reaction scheme(43):



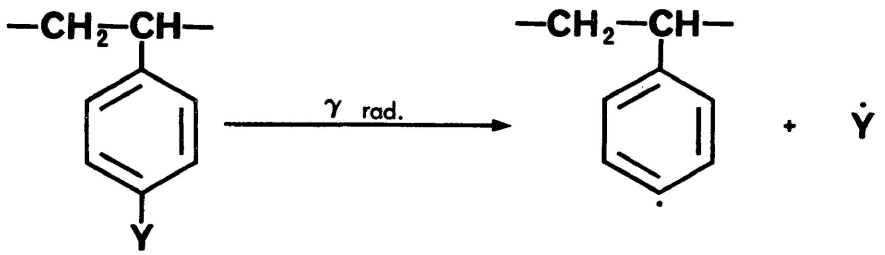
(31)

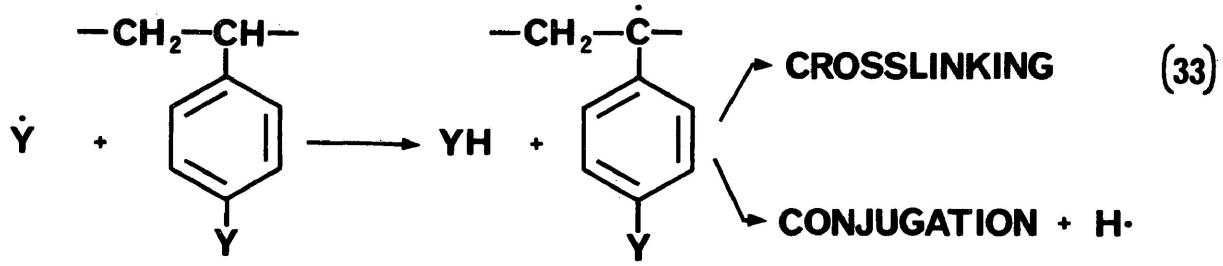
Halogens, halides, nitrogen oxides, and nitriles were absent from the volatile products following irradiation of the corresponding substituted polymers, indicating that the bond between the para-substituent and the phenyl ring is not cleaved and that the aromatic ring is not involved in crosslinking.(43) With the exception of the halopolymers, all of the para-substituted polystyrenes studied by Burlant et al.(43) crosslinked to a lesser extent than polystyrene. This effect has been explained in terms of stability of the intermediate polymer radical formed during irradiation (i.e., delocalization of the unpaired electron on the α-carbon atom of the main chain by resonance interaction with the para-substituent would render it less available for coupling with a radical site on an adjacent chain).(43) The main chain radical may also initiate chain scission by diproportionation of the tertiary radical(43):



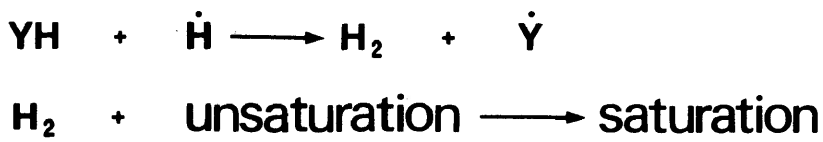
(32)

Both p-halostyrenes exhibited an unusually high sensitivity to cross-linking. A radical chain reaction initiated by gamma-induced cleavage of the aromatic C-halogen bond has been suggested to account for the observed behaviour(43):





(33)



Pravednikov and Mendelev(44) have reported that the gamma irradiation of poly(p-isopropylstyrene) also results in a high degree of cross-linking. They have suggested that radicals formed on the para-substituent by hydrogen abstraction, recombine with radicals on adjacent chains to form crosslinks through the para-substituent.

1.6 Aims of Present Work

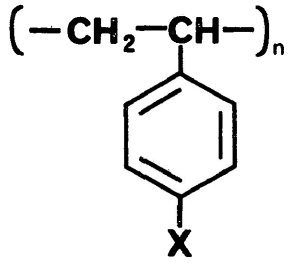
The results of gamma radiolysis of para-substituted styrene polymers shows clearly the importance of the group in the para-position.

Nicholas(40) and Weir(39) have both suggested that the secondary reactions (with respect to chain scission, crosslinking and volatile product formation) are dependent on the electronic and steric factors associated with the para-substituent.

However, to date no comprehensive study has been made on the influence of para-substituents on the ultraviolet degradation of para-substituted styrene polymers.

The aim of the present work is to investigate the primary and secondary processes occurring during the ultraviolet irradiation of the para-substituted styrene polymers in (34) and attempt to make a

correlation between structure and reactivity.



X = $-COCH_3$, $-Br$, $-Cl$, $-F$, $-CH(CH_3)_2$, $-OCH_3$, $-C(CH_3)_3$ (34)

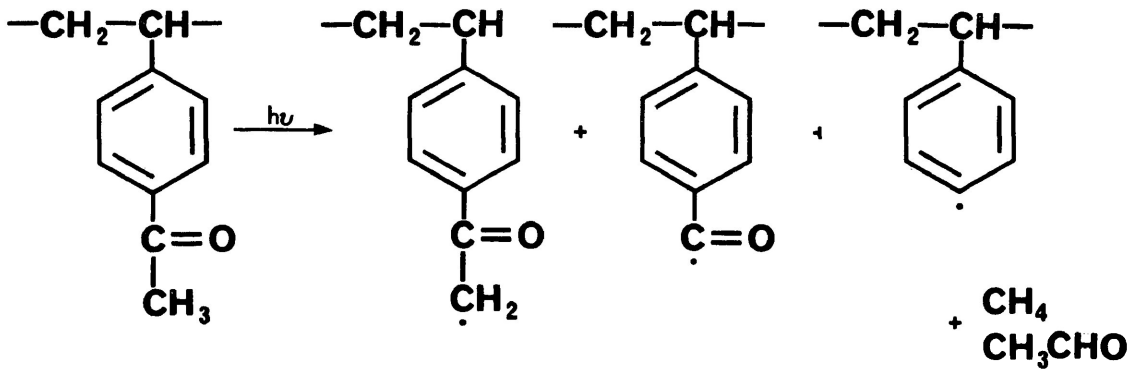
In order of the values of X given, the following abbreviations have been assigned: poly(vinylacetophenone), PVAP; poly(p-bromostyrene), PPBr; poly(p-chlorostyrene), PPCl; poly(p-fluorostyrene), PPF; poly(p-isopropylstyrene), PPIP; poly(p-methoxystyrene), PPMO, and poly(p-*tert*-butylstyrene), PPTB.

With the exception of PVAP, the only chromophore present in the pure polymer is the phenyl ring. On irradiation with ultraviolet light a number of photochemical reactions are possible, the course of which may depend on the nature of the para-substituent.

Elimination of hydrogen from the α-carbon atom of the main polymer chain is the most likely reaction to occur as a result of intramolecular energy transfer processes. The energy required for α-C-H bond fission may vary from that in polystyrene depending upon the electronic characteristics of the para-substituent. Partial or total

cleavage of the para-substituent is also likely and is dependent on the efficiency of intramolecular energy transfer as well as the energy required for bond dissociation.

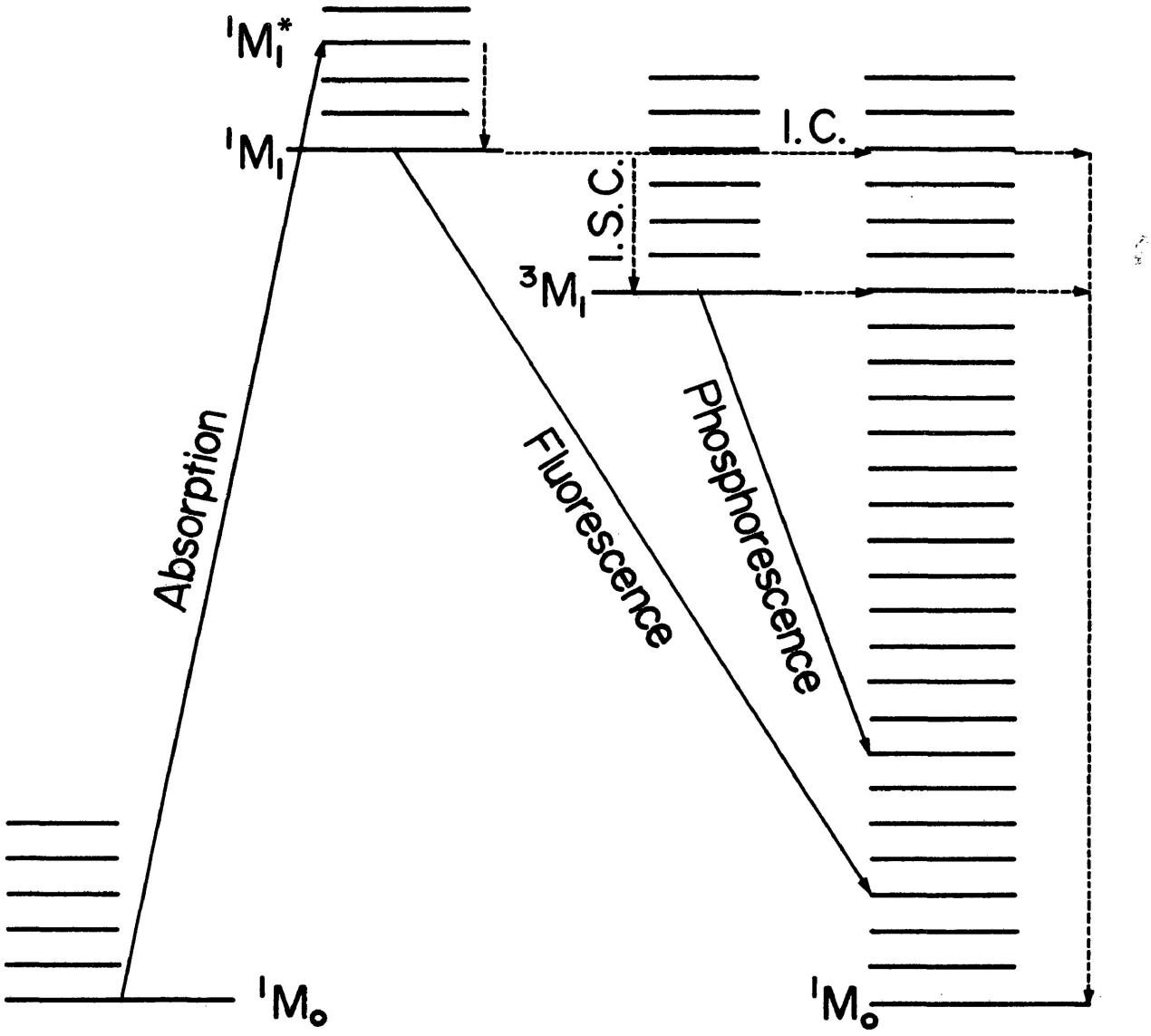
Poly(vinylacetophenone) has an additional chromophore in the para-substituent and can be expected to undergo photochemical reactions characteristic of carbonyl containing compounds. In addition to loss of hydrogen from the acetyl group, PVAP may undergo a Norrish Type I reaction resulting in partial or total cleavage of the para-substituent:



(35)

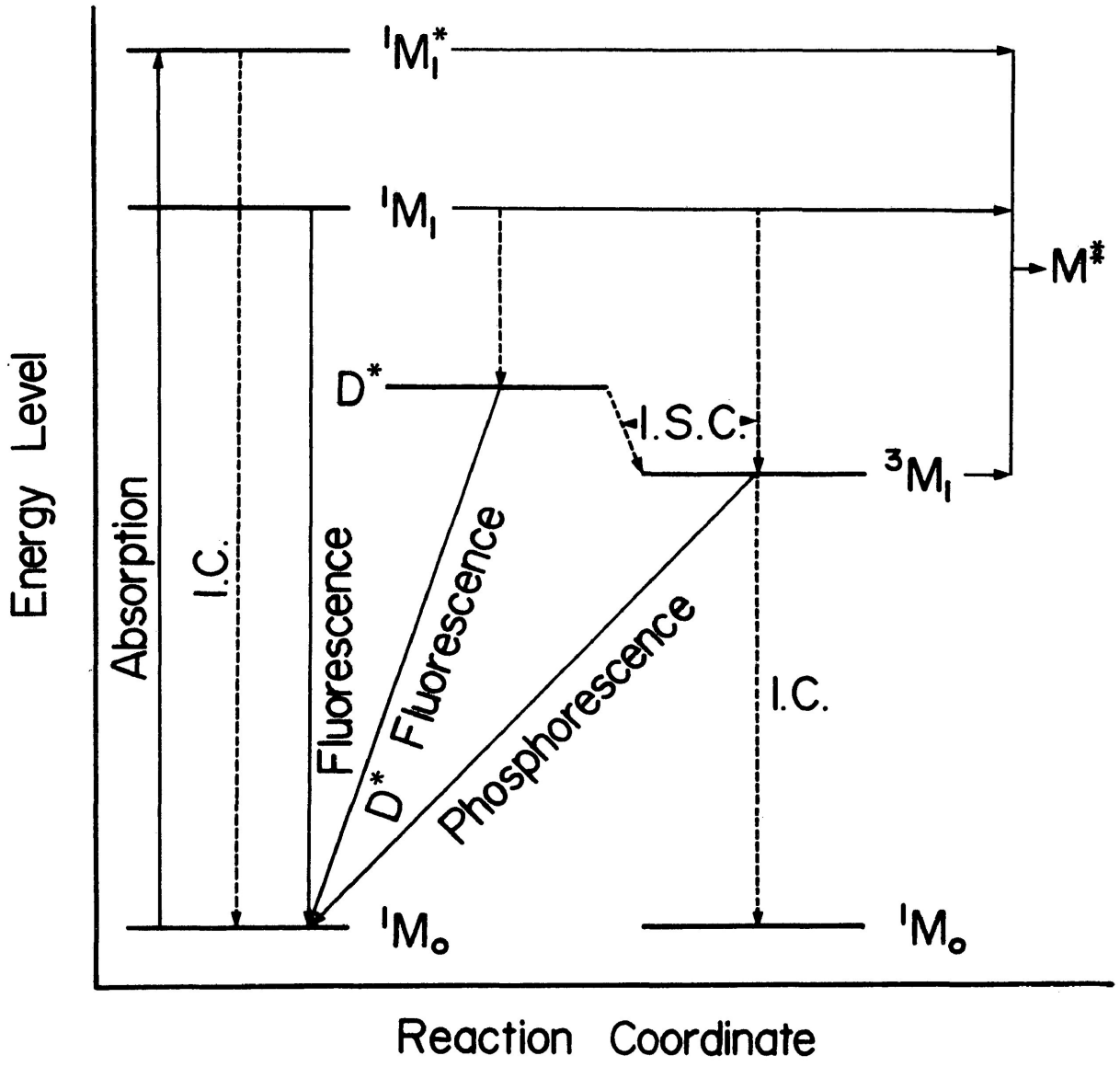
Radicals formed either on the main chain, on the para-substituent, or on the phenyl ring, can be expected to undergo reactions of chain scission and crosslinking. The nature and extent of the secondary reactions may be directly related to electronic and steric factors associated with the substituent in the para-position of the phenyl ring.

Figure 1.1 - Excited States and Photophysical Transitions in a 'Typical' Organic Molecule (45):



Radiative transitions are given by bold lines, radiationless processes by dashed lines :
I.C. – internal conversion
I.S.C. – intersystem crossing
Vertical dashed lines are vibrational relaxation processes.

Figure 1.2 - Excited States and Photophysical Transitions in a 'Typical' Polymer System (7):



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

Figure 1.3 - The U. V. Absorption Spectrum of Polystyrene Film (21):

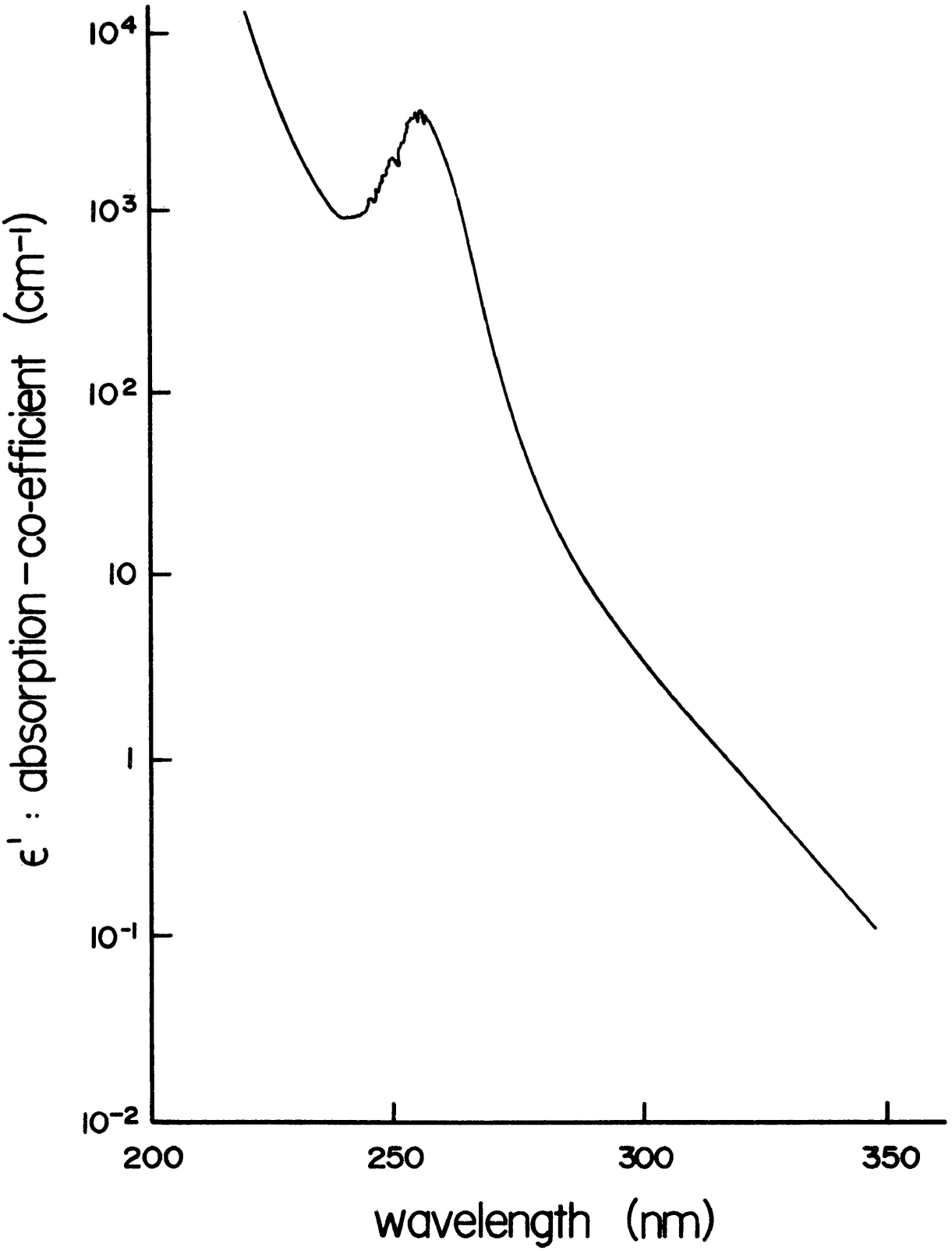


Figure 1.4 - The Fluorescence Spectrum of Polystyrene Film (6):

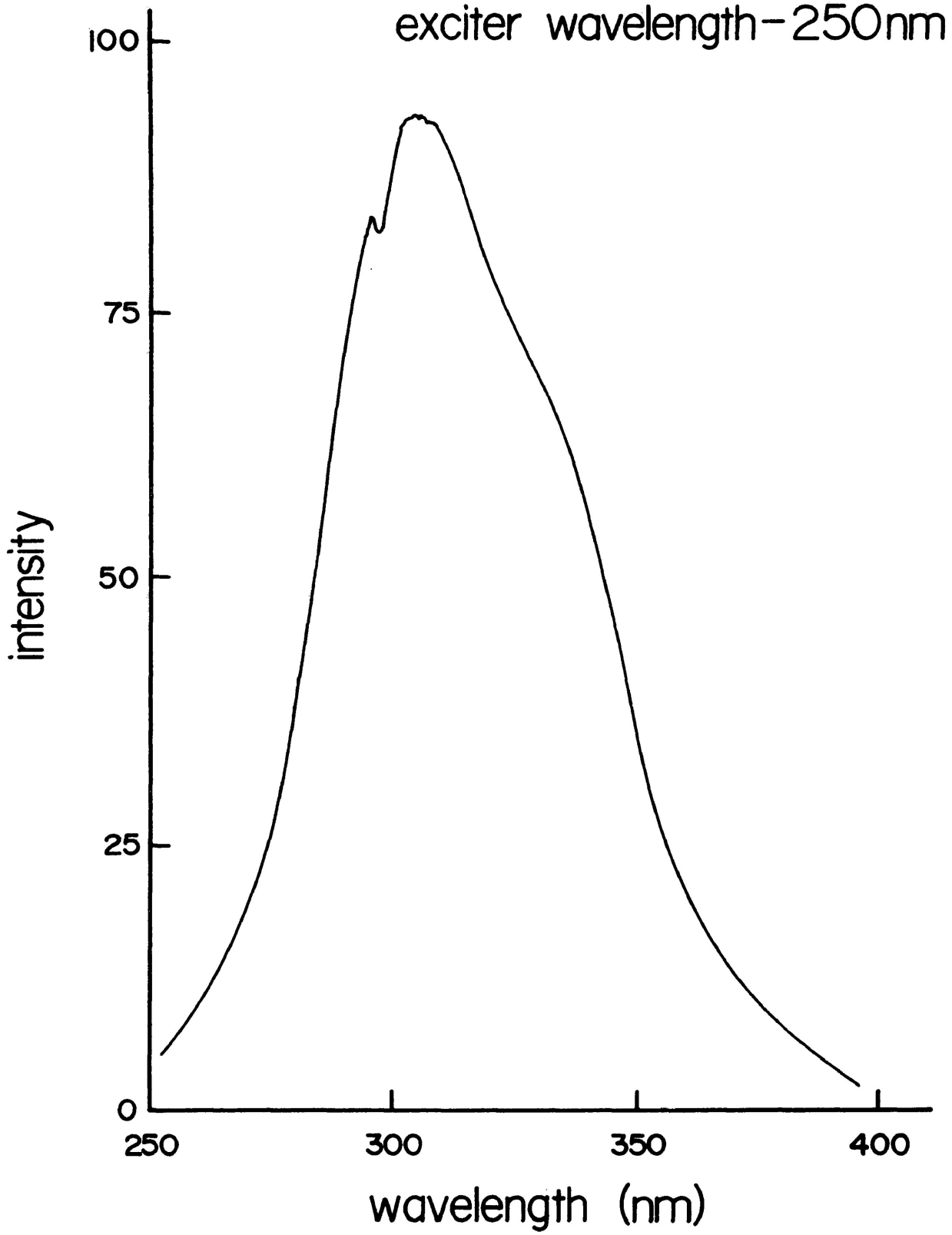
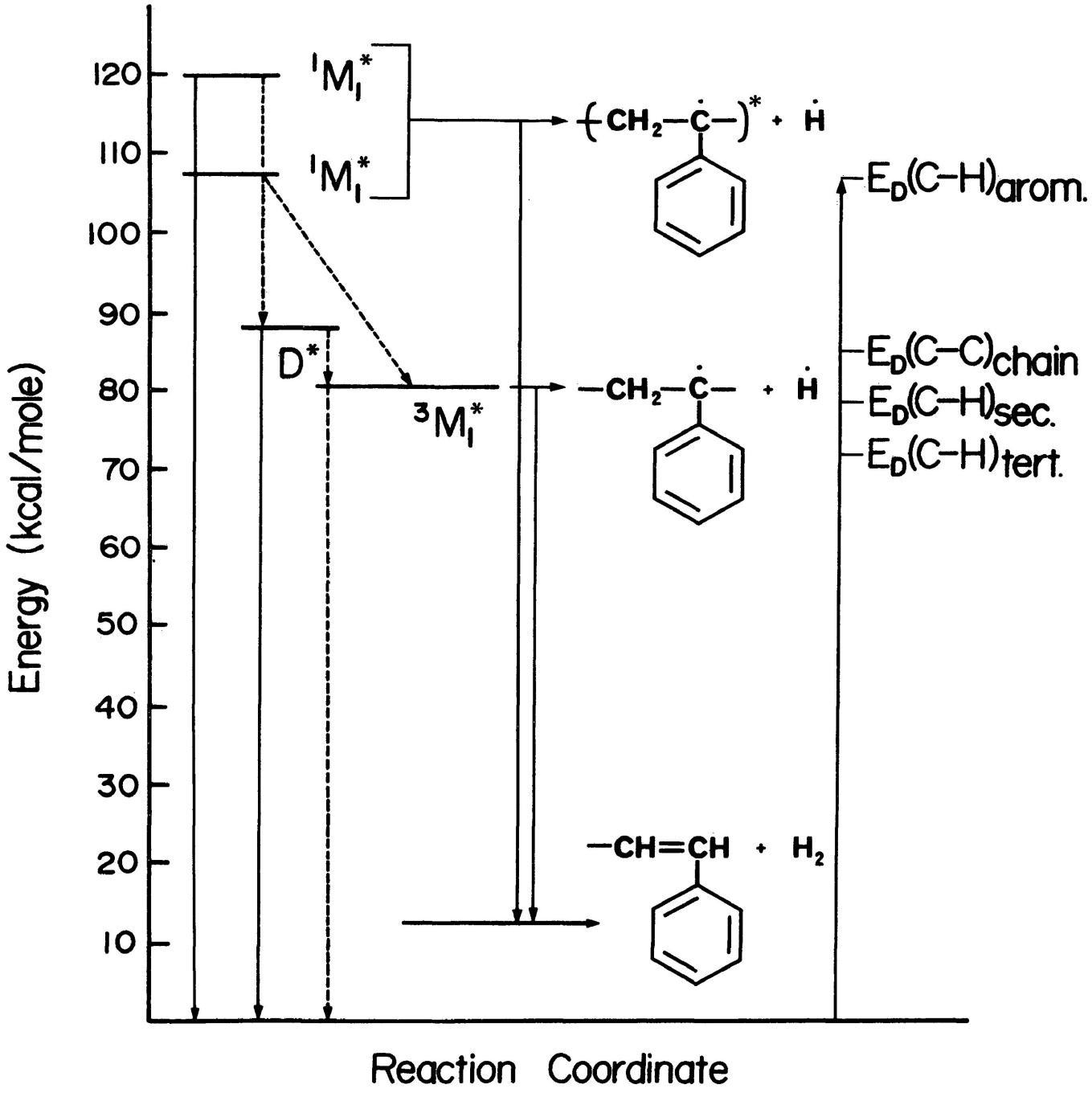
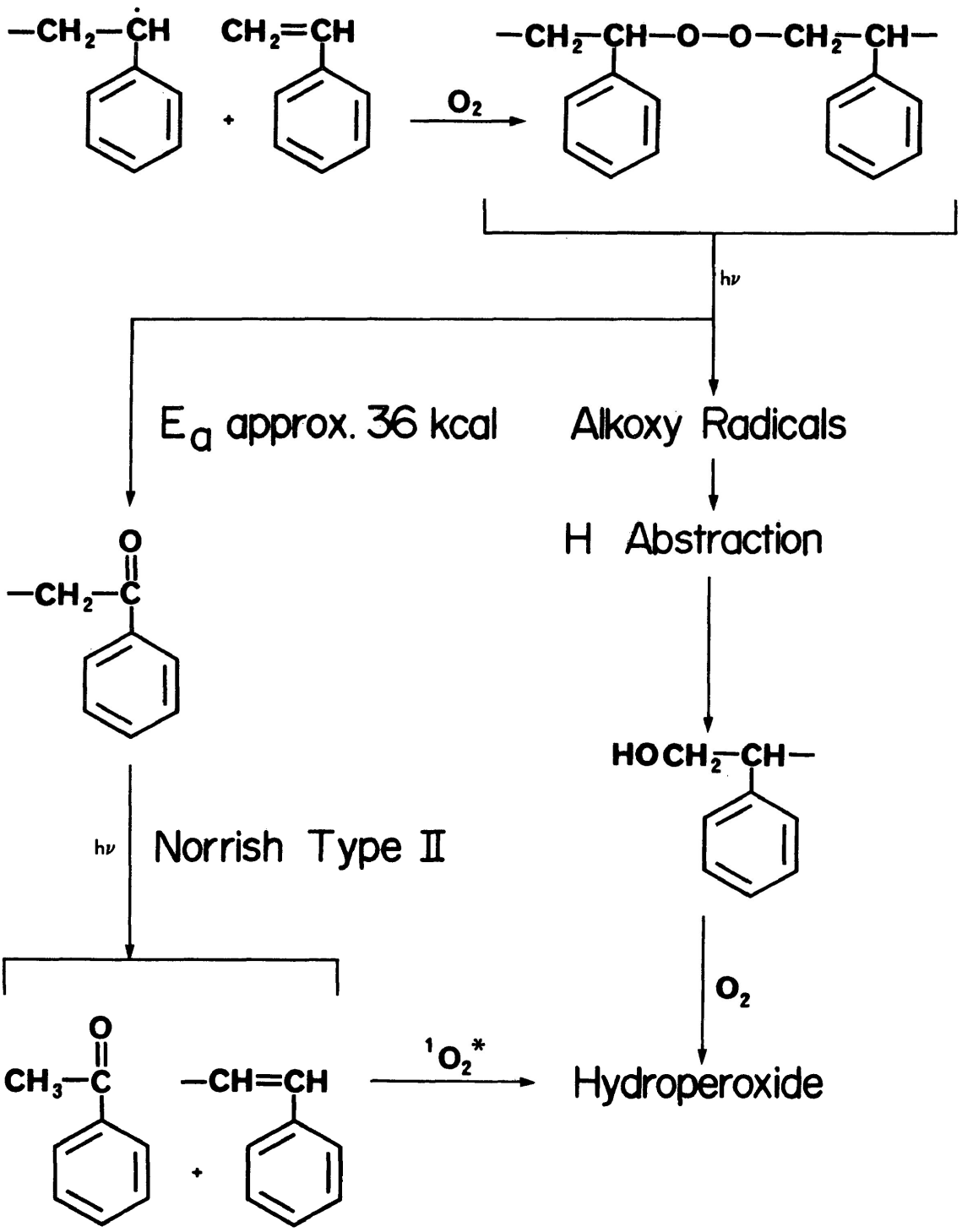


Figure 1.5 - Energy Levels and Bond Dissociation Energies in Polystyrene (7):



E_D values were calculated using Benson's method.

Figure 1.6 - Initiation of Photooxidation: O_2 Incorporated During Polymerization (27):



CHAPTER 2

MATERIALS, APPARATUS AND EXPERIMENTAL TECHNIQUES

2.1 Polymers Supplied

The following polymers were used as received from the Aldrich Chemical Company; poly(p-bromostyrene), poly(p-chlorostyrene), poly(p-isopropylstyrene), poly(p-methoxystyrene), and poly(p-*tert*-butylstyrene).

2.2 Polymer Preparation
2.2.1 Poly(vinylacetophenone)
2.2.1.1 Materials

Polystyrene (Lot 4b, M.Wt. 110,000, Mw/Mn less than 1.06 and Lot 1c, M.Wt. 200,000, Mw/Mn less than 1.06) was obtained from the Pressure Chemical Company. Acetyl chloride (reagent grade) was obtained from the Baker Chemical Company, aluminum chloride (anhydrous) and carbon disulphide (reagent grade) from the Fisher Scientific Company. Chloroform (reagent grade) was supplied by Caledon Laboratories, hydrochloric acid from McArthur Industries and absolute ethanol from Consolidated Alcohols Limited.

2.2.1.2 Procedure

The procedure as described by Braun, Cherdron and Kerr(47) was used with a few modifications.

A 500ml three-necked flask equipped with a mechanical stirrer, reflux condenser and dropping funnel was charged with 100ml of carbon disulphide and 30gm of anhydrous aluminum chloride. After adding 15gm of freshly distilled acetyl chloride, a solution of 11.5gm of polystyrene in 150ml of carbon disulphide was added dropwise with stirring. The reaction mixture was then refluxed for 1½ hours. The reflux condenser was 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 300ml of cold 5% HCl. In order to insure complete destruction of aluminum chloride and removal of gross impurities, the product was washed with two 300ml portions of 5% HCl followed by five 100ml portions of distilled water and finally, two 100ml portions of ethanol.

The crude product was dissolved in chloroform and precipitated three times by dropwise addition of solution to a beaker containing ethanol, equipped with a magnetic stirrer. Finally, the polymer was concentrated by filtering and dried in vacuo at 50°C.

2.2.1.3 Polymer Characterization

Infrared Spectra: The spectrum of the product (see figure 3.1) showed the appearance of a strong peak at 1689cm^{-1} due to the C=O stretching vibration of the acetyl group. A peak at 830cm^{-1} confirmed the presence of a para-disubstituted benzene ring.

Ultraviolet Spectra: One major peak was observed at 257nm with an absorption co-efficient of 6900cm^{-1} attributed to the $\pi \rightarrow \pi^*$ transition of the benzene ring. (see figure 3.17)

Estimated Molecular Weights: Of the two samples of poly(vinylacetophenone) prepared, molecular weights were calculated on the assumption that the chains of the starting material remained intact during acetylation. In particular, with an initial molecular weight of 110,000 and a repeat unit, C_8H_8, of 104.08 a.m.u., 1056.88 units will be contained in the starting material. The repeat unit for poly(vinylacetophenone), $C_{10}H_{10}O$, is 146.10 a.m.u. and assuming complete acetylation, the final molecular weight would be 154,410. Similarly, with an initial molecular weight of 200,000 and assuming complete acetylation, the resulting molecular weight would be 280,745.

2.2.2 Poly(p-fluorostyrene)

2.2.2.1 Procedure

P-vinylfluorostyrene (Aldrich Chemical Company) was purified by washing several times with dilute potassium hydroxide followed by washing with water and drying over anhydrous $MgSO_4$ (BDH Chemicals). The monomer was then distilled under reduced pressure (27mm Hg), the fraction between 26 and 29°C being retained. The purified monomer was immediately isolated and stored at 8°C.

2,2'-azobisisobutyronitrile, AIBN, (Aldrich Chemical Company) was recrystallized twice from a saturated solution of ethanol at 0°C. The crystals were filtered, vacuum dried and stored at 8°C. A solution containing 0.041 grams of purified AIBN in 10mls of ethanol was placed in a 125ml dilatometer which contained a ground glass joint for evacuation. Purified monomer was introduced into the dilatometer containing AIBN, the ethanol being removed by a flow of dry nitrogen. The reaction vessel was connected to a high vacuum apparatus (see figure 2.1) and the contents degassed three times by the alternate freezing and thawing technique.

Polymerization was carried out under high vacuum (typically 10^{-5}mm Hg) in the presence of 0.05% AIBN at 78 ± 0.1°C for 15 hours.

The crude product was dissolved in chloroform and purified three times by dropwise addition to a beaker containing ethanol, equipped with a magnetic stirrer. The polymer was collected by filtering and dried under high vacuum.

2.3 Molecular Weight Determination

Dilute solution techniques were used to characterize the polymers with toluene at 25 and 30°C. Solutions were prepared in volumetric flasks and filtered through Hirsch funnels (porosity 10-15 microns) before use. A Cannon constant temperature bath (Cannon Instrument Corp.) and Cannon Ubbelohde dilution viscometers were employed.

Molecular weights were calculated using a modified computer program (see appendix A) based on Huggins and Kraemer equations(48):

$$\frac{\eta sp}{C} = \{\eta\} + k' \cdot \{\eta\}^2 \cdot C \qquad (36)$$

$$\frac{\ell n\ \eta r}{C} = \{\eta\} - k'' \cdot \{\eta\}^2 \cdot C \qquad (37)$$

where: ηsp is the specific viscosity
ηr is the relative viscosity
$\{\eta\}$ is the intrinsic viscosity
k' and k'' are viscometer constants
C is the concentration of the solution.

It is important to note that since efflux times were sufficiently long, kinetic energy corrections were neglected in the calculations.

The polymers studied had the characteristics shown in table 2.1.

2.4 Film Preparation

Polymers were irradiated in the form of thin films prepared by evaporating methylene chloride solutions of the polymer on quartz and potassium bromide plates. Films were subsequently stored under high vacuum for a minimum of 24 hours before irradiation.

Films prepared in this manner were too thin to be measured by mechanical means (i.e., micrometer). As an alternative, the technique of interferometry was adopted to determine film thickness. In particular, aluminum was vacuum deposited onto the quartz plate containing the polymer film, a small portion of which was removed to provide a step between the surface of the film and the plate. Measurements (fringe line offset method) from an interferrogram observed with a Varian Interferometer (model 980-4000) were used to calculate film thickness. Generally, film thickness ranged from 2 to 15 $\pm$ 0.30 microns depending on the type of investigation sought during irradiation.

2.5 Photochemical Techniques

Films prepared on quartz and potassium bromide plates were placed into vycor tubes (2.5cm in diameter and 10.5cm in length) sealed at one end, the other fitted with a ground joint. The transmission characteristics of the tubes are shown in figure 2.2. To ensure reproducability of all spectral investigations during the course of irradiation, the plates were mounted in stainless steel holders (for infrared studies) or anchored into quartz cuvettes (for ultraviolet and fluorescence observations).

The vycor tubes containing the samples were attached to a high vacuum system (see figure 2.1) and degassed until a constant pressure of 10^{-5}mm Hg was obtained. Pressures were monitored with an Edwards B6 Pirani guage and an Edwards IG6B ion guage.

Films were irradiated under high vacuum with the output of a high-pressure mercury lamp (Hanovia 654A10), the spectral distribution of which is shown in figure 2.3. The mercury lamp was fitted with a polished aluminum reflector (Hanovia 6531-02) and lamp to film distance was maintained at 8.5cm. The incident radiation intensity on the films was 1.8mW/cm^2 (measured with an Ultraviolet Intensity Meter, Ultra-Violet Products Inc., model J-225).

An extremely simple but efficient enclosure was designed to irradiate thin polymer films with short and long-wave ultraviolet radiation for controlled time intervals. Shown in figure 2.4, the high-pressure mercury lamp, reflector and the quartz reaction tube were separated by a removable divider and enclosed in a light-tight stainless steel container. This allowed the output from the mercury lamp to stabilize for approximately 20 minutes (i.e., warm-up procedure) before exposure was made.

Lamp temperature was continually monitored by means of a chromel-alumel thermocouple and microvoltmeter (Kiethley model 155). A fan, located at the rear of the enclosure was adjusted to maximize lamp output (measured with an Ultraviolet Intensity Meter, Ultraviolet Products Inc., model J-255) and maintain the temperature of the lamp envelope within manufacturers specifications.

Prior to exposure for short-wave studies, a quartz beaker filled with double distilled water was fitted around the vycor sample tube. A stainless steel coil was placed in the beaker behind the quartz tube, through which thermostatically controlled water was continually pumped to maintain a constant sample termperature of 26^{o}C during irradiation. The same method of sample temperature control was used in the long-wave photolysis of poly(vinylacetophenone) except a pyrex beaker was used to filter out radiation of wavelengths less than 295nm.

It has been reported that the absorption characteristics of polymer films can be represented by the Beer-Lambert relationship (see equations (2) and (3)). The absorption co-efficients for the polymers studied have been determined from the slopes of absorption versus thickness plots (see figures 2.5 to 2.11) and are reported in table 2.2.

2.6 Analytical Techniques

2.6.1 Infrared Spectra

Films of thickness 10 to 15 microns were prepared on potassium bromide plates and mounted in stainless steel holders. Infrared spectra were recorded immediately before and after irradiation using a Beckman IR12 spectrometer. Infrared spectra of the insoluble fraction, isolated afer prolonged exposure, were also recorded in the form of KBr discs (6-8% product by weight). For direct comparison, KBr discs were prepared and recorded from unexposed polymers (6-8% polymer by weight).

2.6.2 Ultraviolet-Visible Spectra

Films of thickness 3 to 6 microns were prepared on minature (0.7cm by 2.5cm) optically pure quartz plates. The plates were mounted inside conventional quartz cuvettes and secured by two stainless steel springs. Ultraviolet (200-300nm) and visible (300-700nm) spectra were

obtained immediately before and during irradiation using a Cary 14 Spectrophotometer.

2.6.3 Fluorescence Spectra

Films of thickness 3 to 8 microns were prepared on minature (0.7cm by 2.5cm) optically pure quartz plates and mounted diagonally inside quartz fluorescence cells. Fluorescence spectra were recorded immediately before and after irradiation with a Perkin Elmer 204 Fluorescence Spectrophotometer.

2.6.4 Mass Spectra
2.6.4.1 Apparatus

A special 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 (see figure 2.12). 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 joint, J1, to accept a modified quartz reaction

vessel. To maintain polymer films at 26°C during irradiation a quartz tube was fitted with a water jacket through which thermostatically controlled distilled water was circulated. Pressures in the gas inlet system were monitored with an Edwards B6 Pirani guage, G1, and a IG6B ion guage, G2. The enclosure containing the ultraviolet lamp and fan was the same as that described earlier, lamp to film distance being 8.0cm.

The mass spectrometer head, H, was rigidly mounted in an insulated enclosure fitted with heating elements. An Edwards mercury-vapour diffusion pump (model EM2), D2, fitted with a flap-valve, V, and a liquid nitrogen trap, L4, was backed with an Alcatel rotary pump (model 2004). Pressures, typically 2×10^{-7}mm Hg were monitored with an Edwards IG6G ion guage, G3. An electronic safety device was constructed to protect the mass spectrometer while in operation against a possible vacuum failure (i.e., power interruption and/or lack of cooling water for the diffusion pump).

2.6.4.2 Procedure

The mass spectrometer was operated with a photomultiplier voltage of 2.5 Kv. and filament current of 2 milliamperes (tungsten filament). A scan of the entire mass range (i.e., 1 to 120 a.m.u.) was

made in 100 seconds. Selected regions of the mass range were also scanned (i.e., 1 to 3 a.m.u. for H_2 and 12 to 17 a.m.u. for CH_4) in reduced time intervals of 10 seconds. All spectra were recorded on a Hewlett-Packard strip chart recroder (model 7128A) fitted with a variable span input module (model 17500A).

Polymer films on quartz plates were placed inside the modified vycor tube which was then coupled directly to the inlet system at port J1. All connexions were made with Dow Corning high vacuum silicone grease. Aluminum foil was placed around the connexion at J1 to prevent the joint from freezing as a result of exposure to ultraviolet radiation.

Isolating the diffusion pump, D1, by closing stopcocks S1 and S2, the reaction tube was 'rough' pumped by opening stopcocks S3, S4, and S5. When pressures were within diffusion pump limits, stopcock S3 was closed and stopcocks S1 and S2 were opened to lower the pressure inside the manifold to 2×10^{-6} mm Hg. When the pressure inside the manifold had stabilized at the lower limit, the reaction vessel was isolated by closing stopcock S5.

The mass spectrometer was evacuated by first isolating the diffusion pump, D2, by closing stopcock S9 and the flap-valve, V. Stopcocks S9 and S10 were opened and the pressure inside the spectro-

meter head and adjoining glassware was reduced within diffusion pump limits. Stopcock S10 was closed, stopcock S9 and the flap valve were opened reducing the pressure inside the system to 2×10^{-7} mm Hg.

After the mass spectrometer had been pumped for several hours, a background spectra was recorded. Stopcock S8 was closed and, prior to irradiation and at selected times during irradiation, gaseous products inside the reaction vessel were sampled by briefly opening and closing stopcock S7. Product contained in the adjoining glassware was admitted to the mass spectrometer by opening stopcock S8. At the end of each scan, stopcock S8 was closed and the mass spectrometer pumped. A background was recorded prior to each analysis during irradiation.

Between product analyses of different polymer films, the mass spectrometer was 'baked' at 275°C for 12 hours under high vacuum to remove traces of products left from previous films.

Volatile product analysis provided a qualitative and semi-quantitative examination of gaseous products liberated during photolysis by monitoring products as a function of exposure time. The unusually high sensitivity of the instrument also permitted an investigation into the possibility of diffusion controlled reactions by observing product formation as a function of temperature. In particular,

the polymer film contained in the modified quartz vessel was cooled to 12°C and maintained within ±1°C during irradiation. Following an exposure of 2.5 hours to ultraviolet radiation, background and sample spectra were recorded as previously outlined, beginning at 12°C and at 5°C steps to a limit of 52°C.

2.6.4.3 Calibration

Quantitative mass spectral measurements were recorded as relative peak height values. To provide a correlation between relative peak heights and number of moles, the mass spectrometer was calibrated with hydrogen, methane, ethane, carbon monoxide and carbon dioxide.

A sample bottle of internal volume equal to 55.57ml fitted with two high vacuum stopcocks and a ground joint was flushed with each of the gases and partially evacuated following connexion to the high vacuum apparatus (see figure 2.1). The pressure inside the sample bottle was measured with a McLeod guage (Edwards, model H.S.I.A.).

Assuming ideal behaviour at pressures of 10^{-5} to 10^{-2}mm Hg for each of the gases used, the number of moles contained in the gas bottle was obtained by calculations involving the ideal gas law.

Mass spectra were recorded of each gas at various pressures.

The data obtained was combined with calculated values of the number of moles, the results of which are graphically represented in figure 2.13.

2.6.5 Molecular Weight and Soluble Fraction Determination

Following exposure under high vacuum at 26°C, films were dissolved in methylene chloride and filtered through Hirsch funnels (porosity 10-15 microns). The insoluble fraction was repeatedly washed with methylene chloride, dried and weighed. Solvent was removed from the soluble fraction by evaporation followed by pumping under high vacuum for several hours before weighing.

The soluble fraction was redissolved in toluene and characterized by dilute solution viscometry using a Cannon constant temperature bath and a Cannon Ubbelohde dibution viscometer. Molecular weights were calculated using a modified computer program (see appendix A), kinetic energy corrections being neglected throughout.

Figure 2.1 - High Vacuum Apparatus:

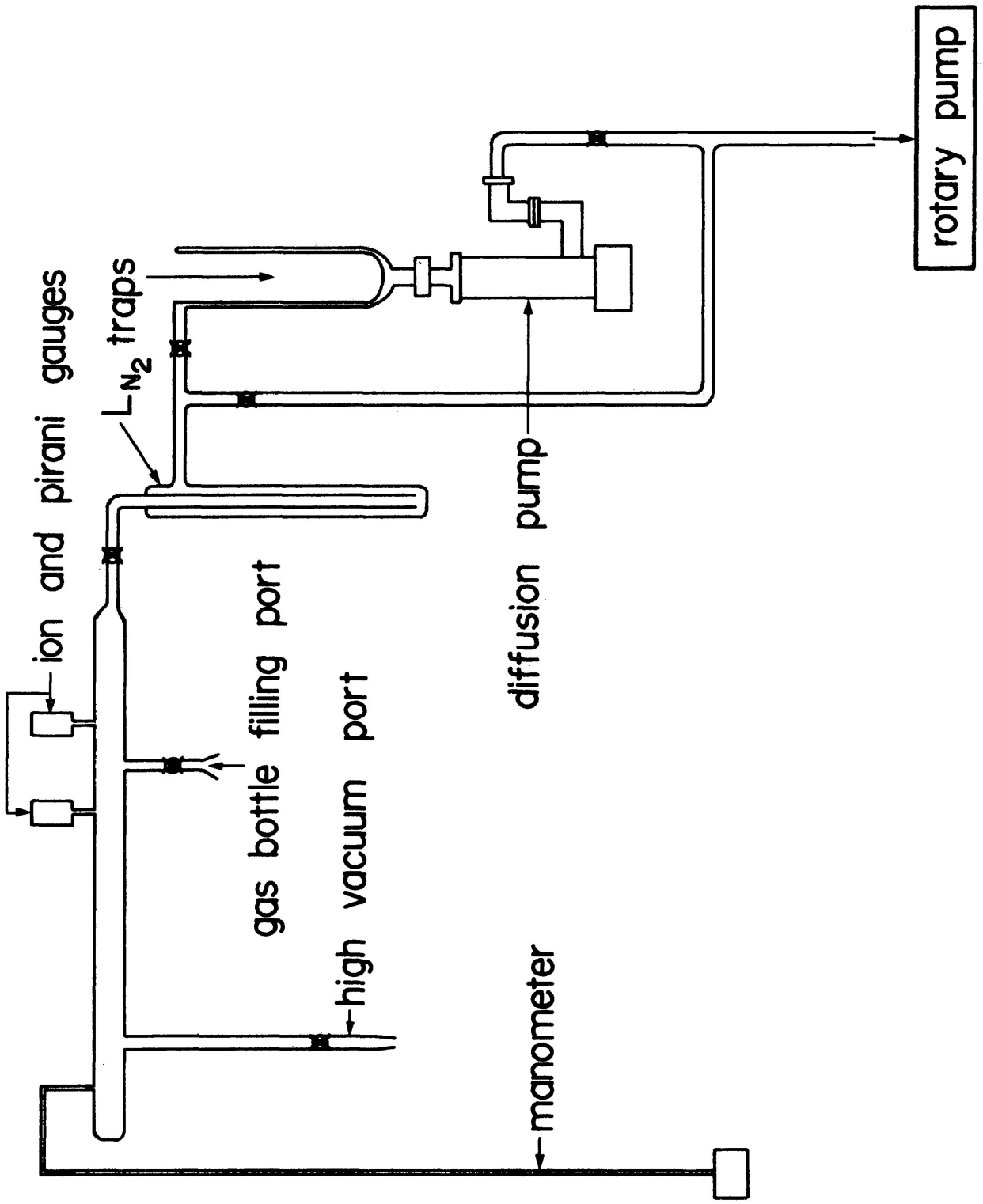


Figure 2.2 - Transmission Characteristics of the Irradiation Vessel:

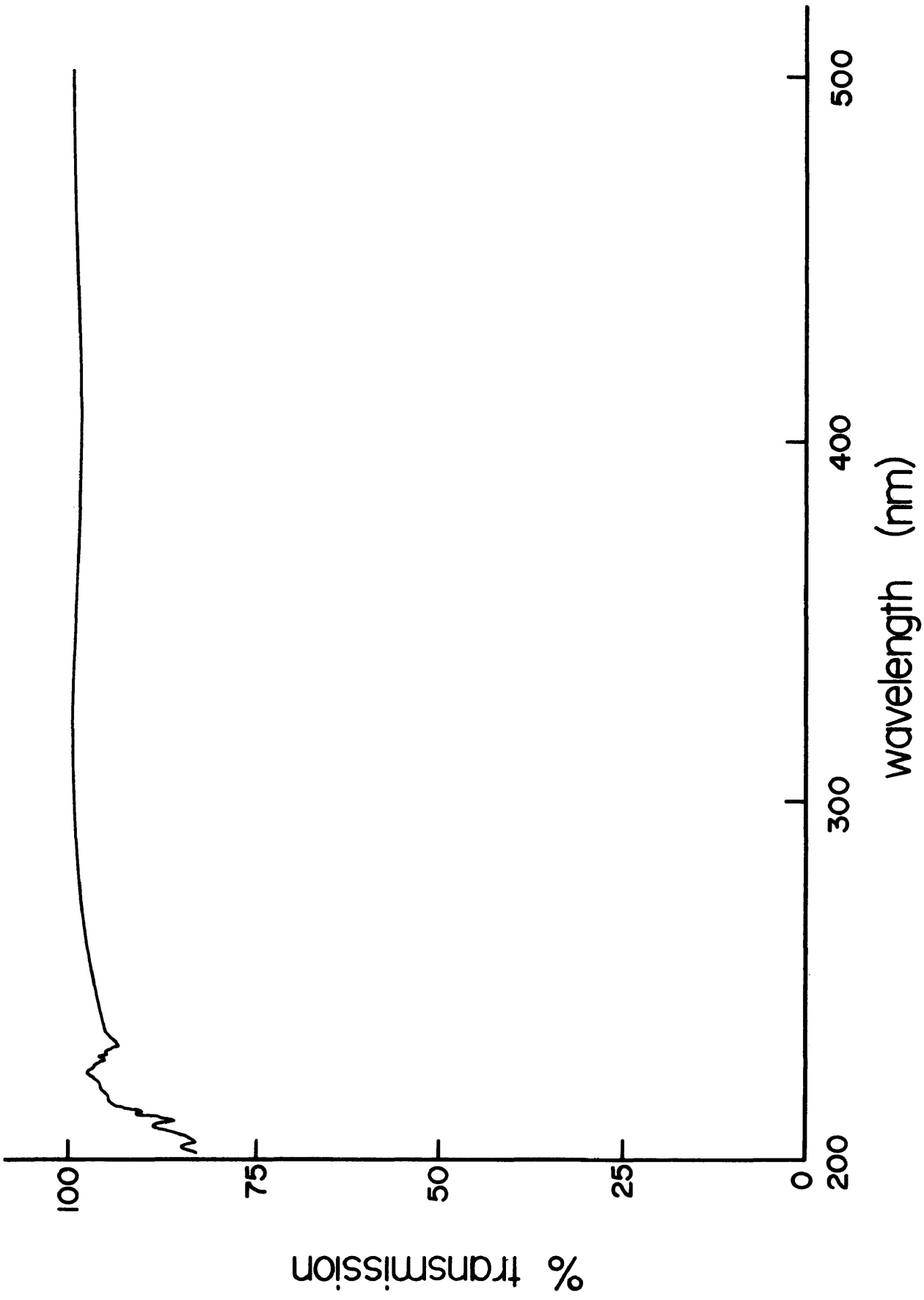


Figure 2.3 - Spectral Distribution of the Hanovia (654A10) High-Pressure Mercury Lamp:

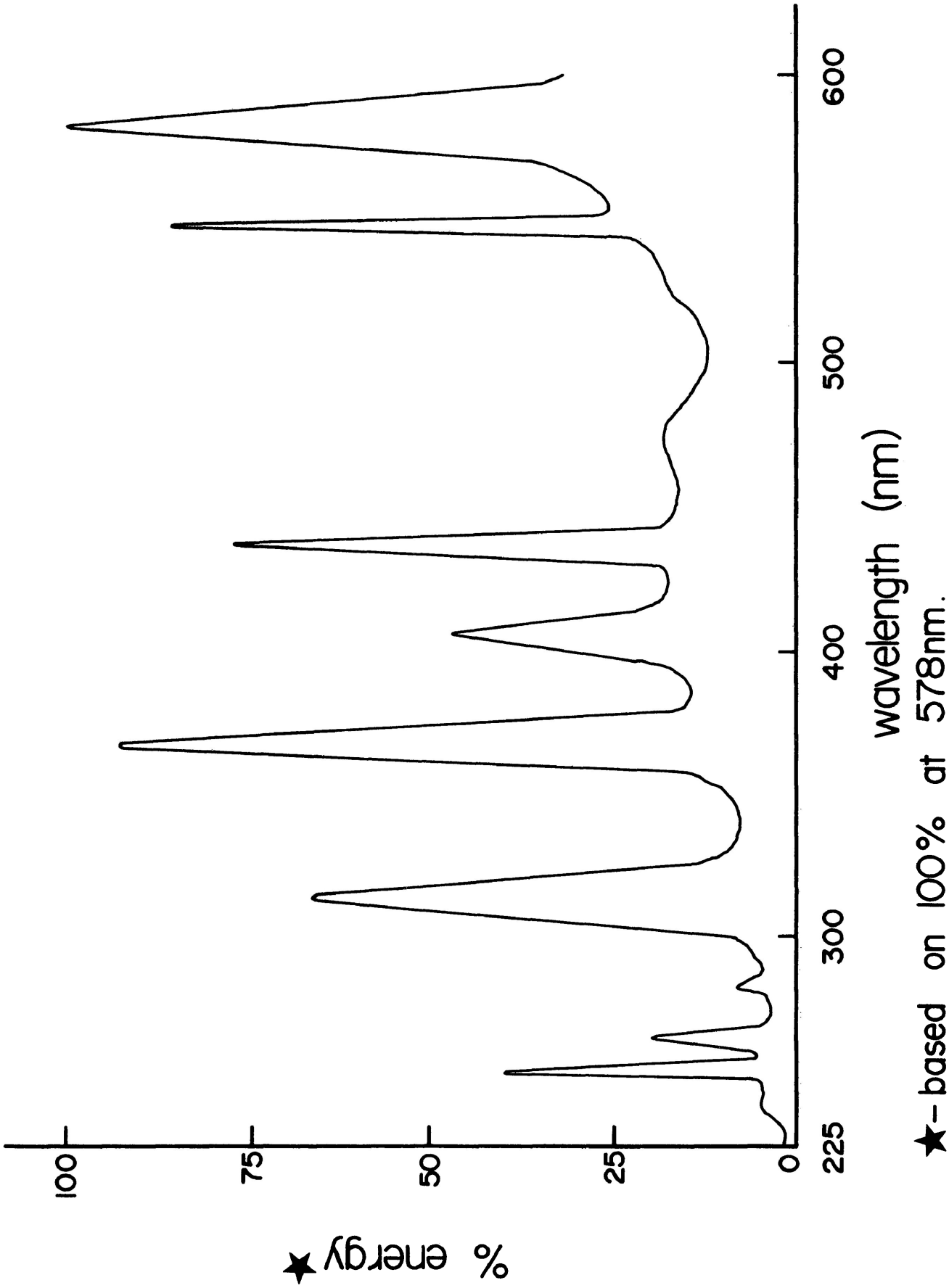


Figure 2.4 - Exposure Enclosure:

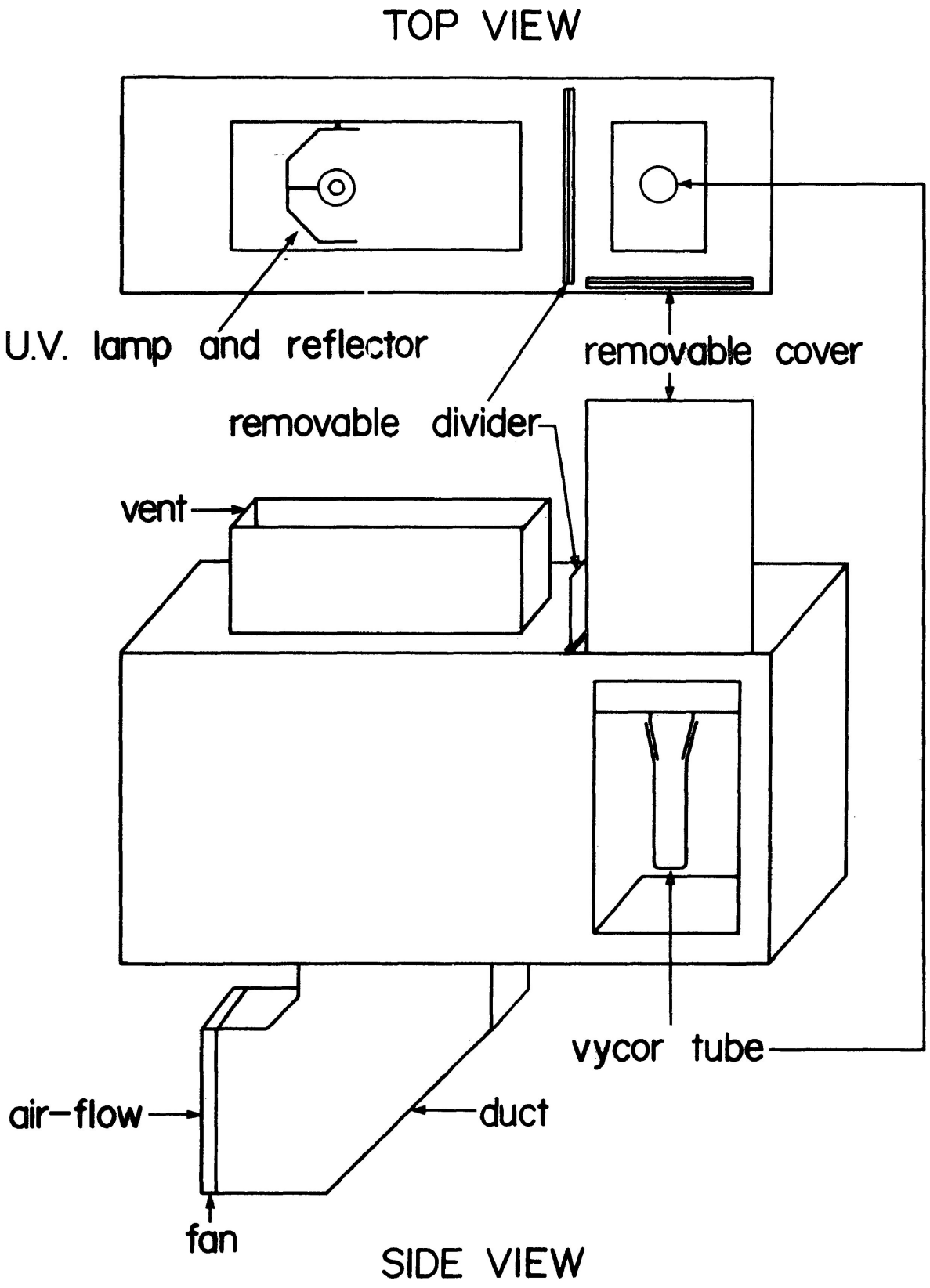


Figure 2.5 - U. V. Absorbance as a Function of Film Thickness for Poly(vinylacetophenone):

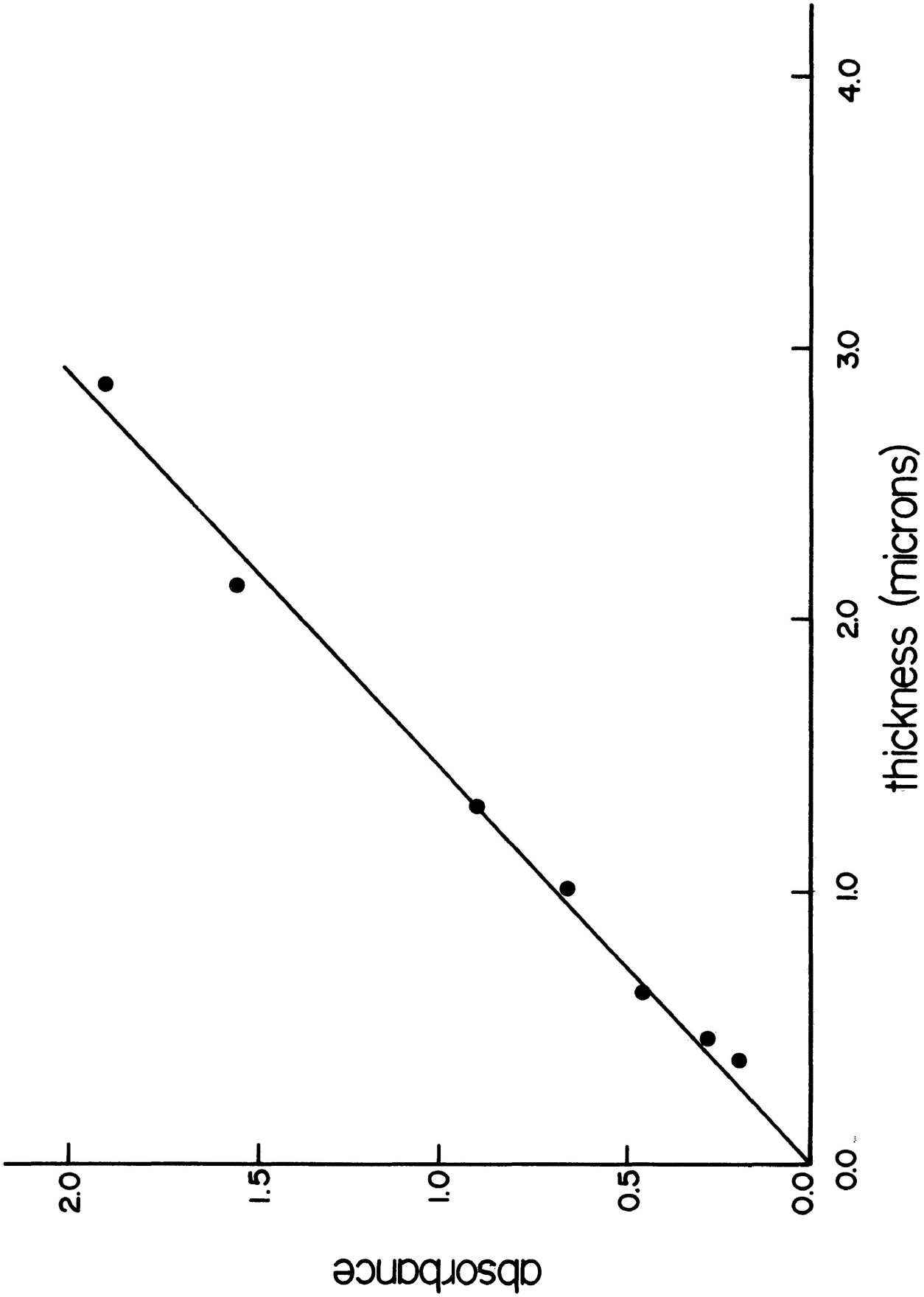


Figure 2.6 - U. V. Absorbance as a Function of Film Thickness for Poly(p-bromostyrene):

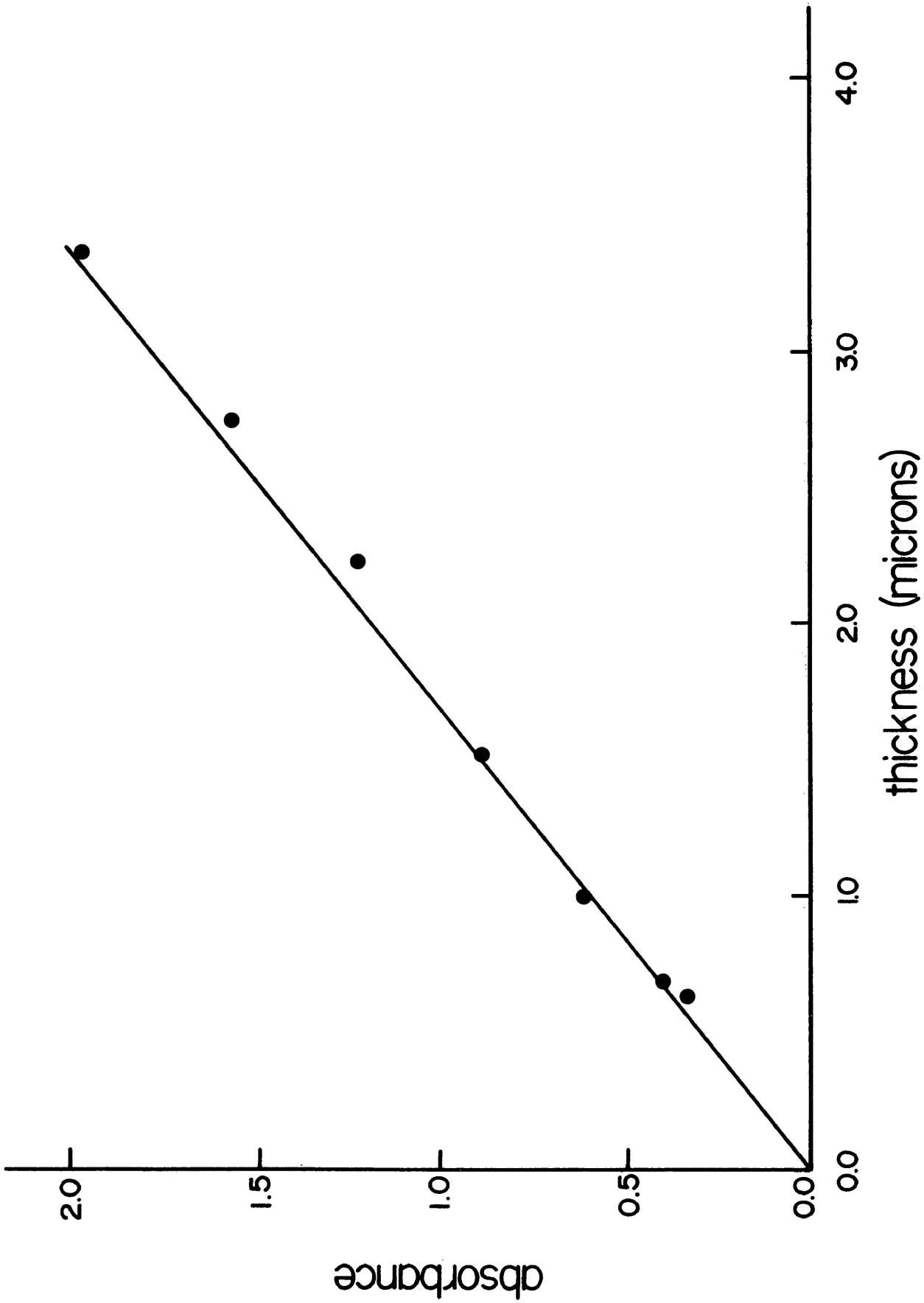


Figure 2.7 - U. V. Absorbance as a Function of Film Thickness for Poly(p-chlorostyrene):

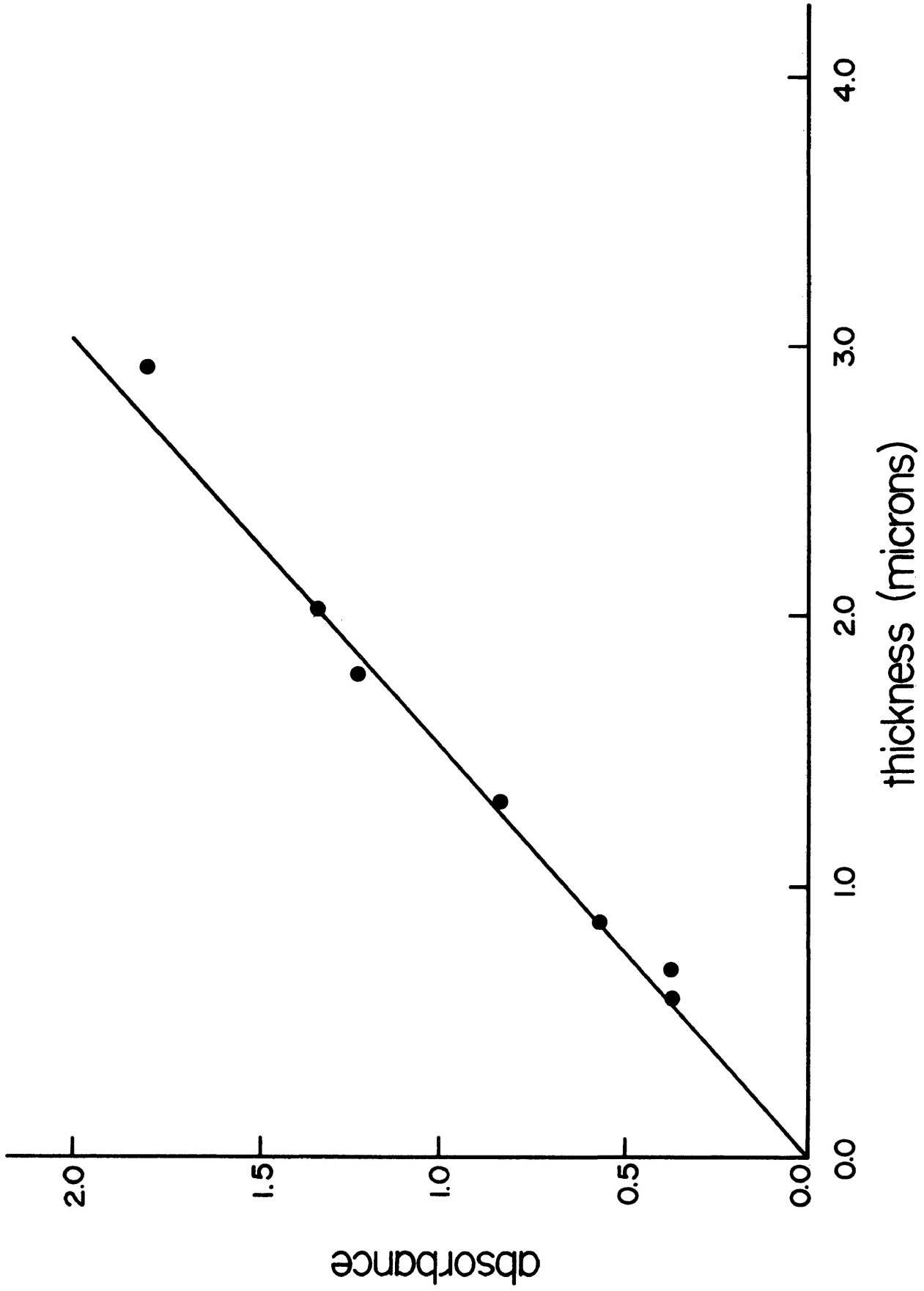


Figure 2.8 - U. V. Absorbance as a Function of Film Thickness for Poly(p-fluorostyrene):

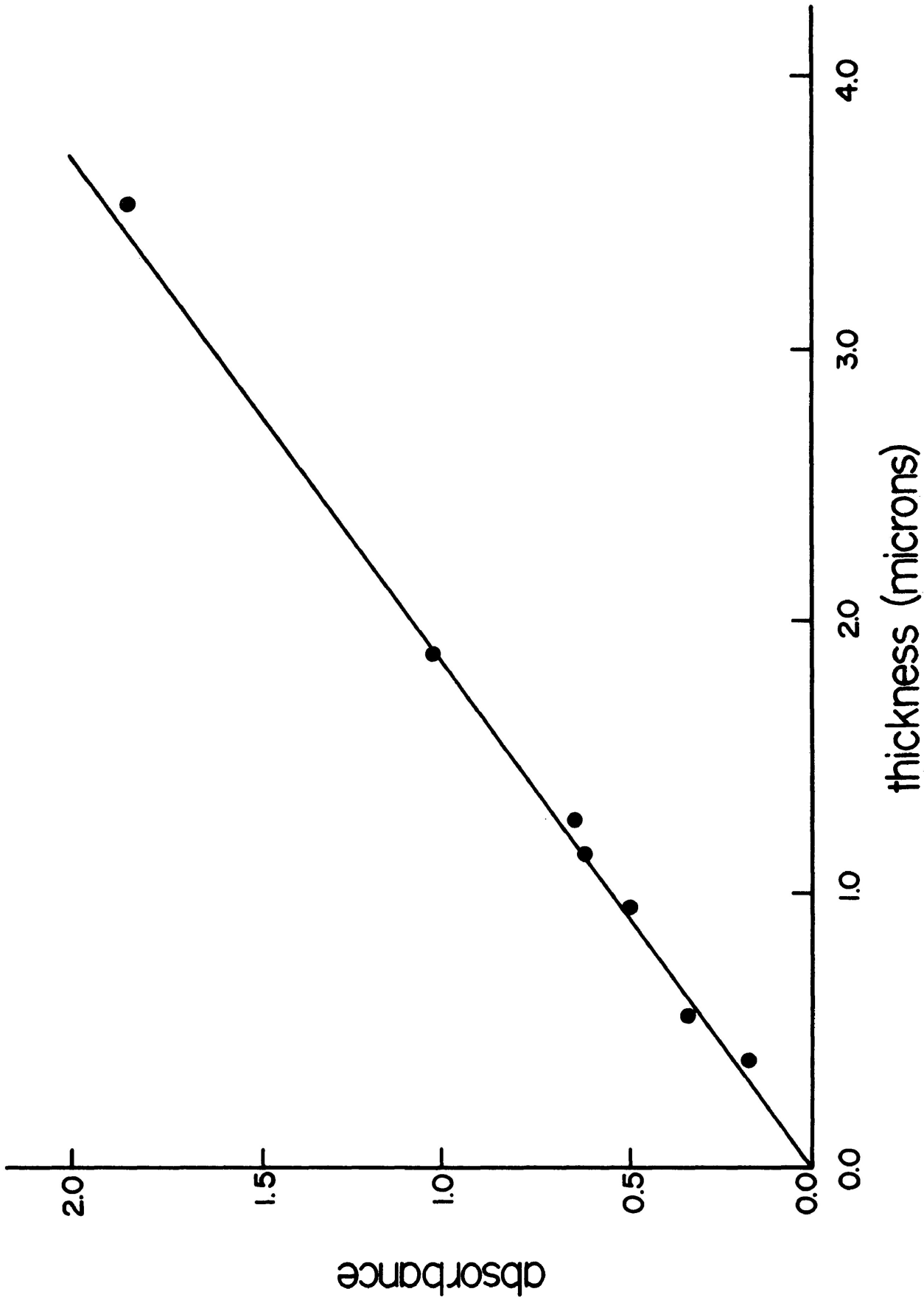


Figure 2.9 - U. V. Absorbance as a Function of Film Thickness for Poly(isopropylstyrene):

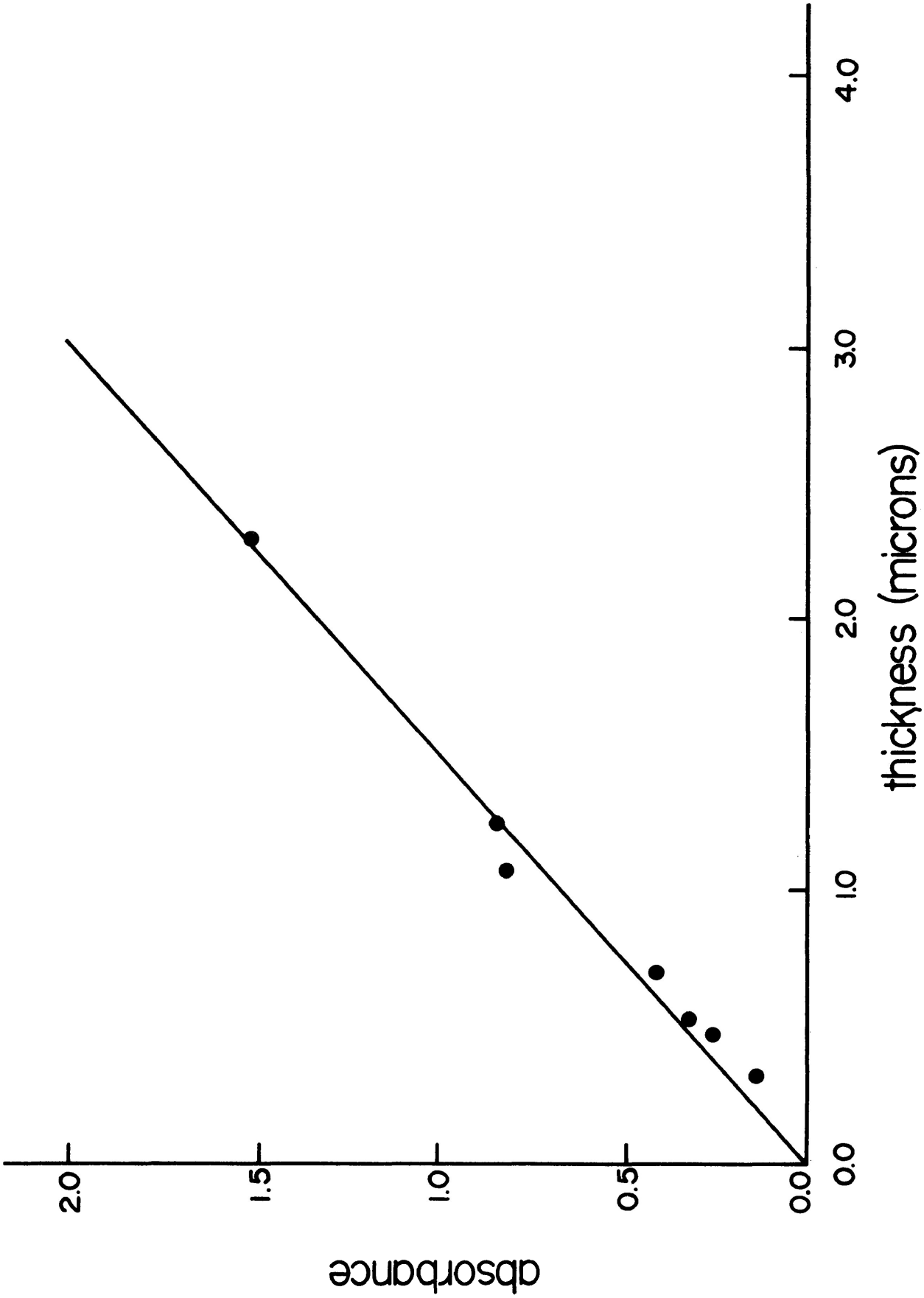


Figure 2.10 - U. V. Absorbance as a Function of Film Thickness for Poly(p-methoxystyrene):

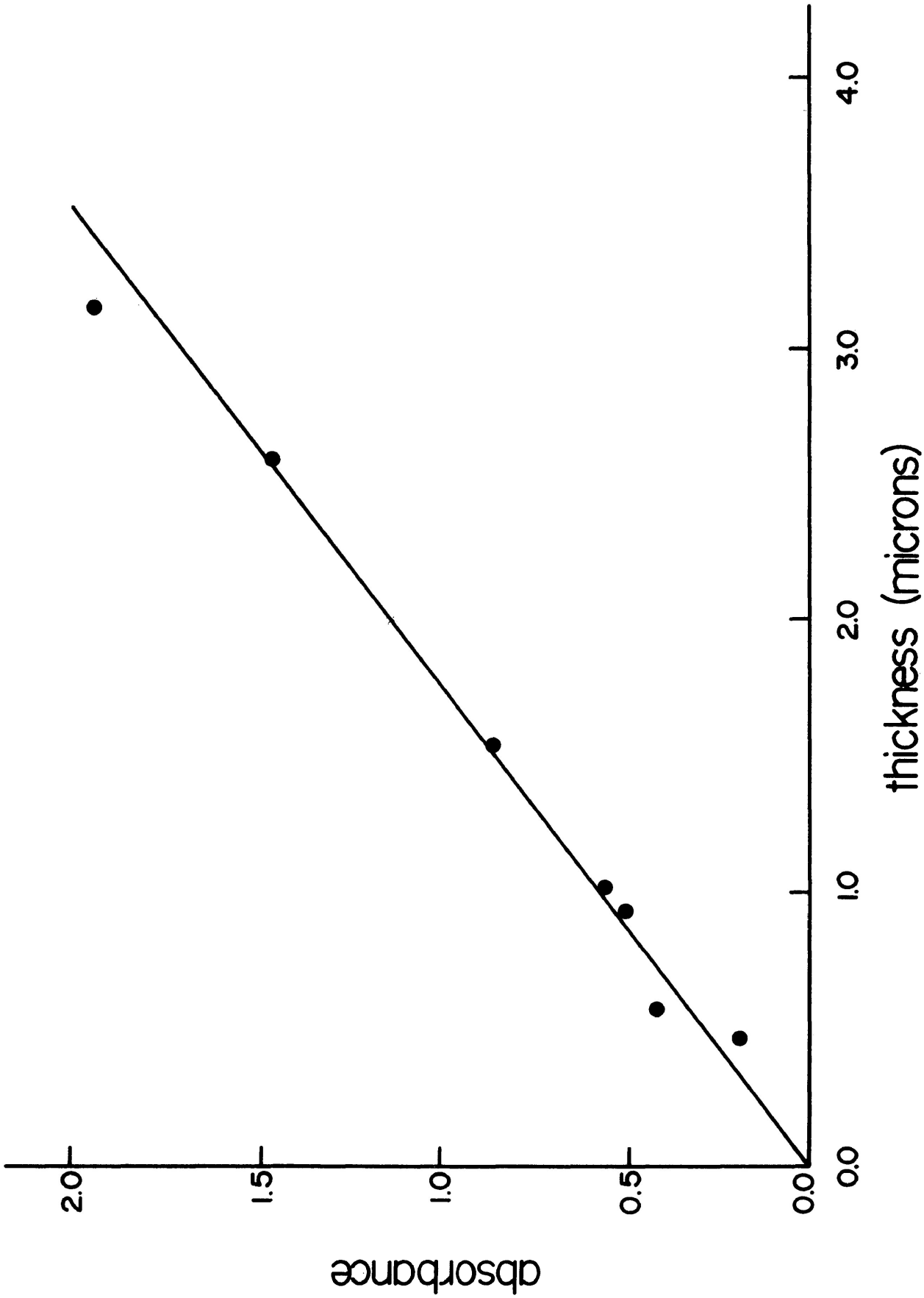


Figure 2.11 - U. V. Absorbance as a Function of Film Thickness for Poly(p-tertbutylstyrene):

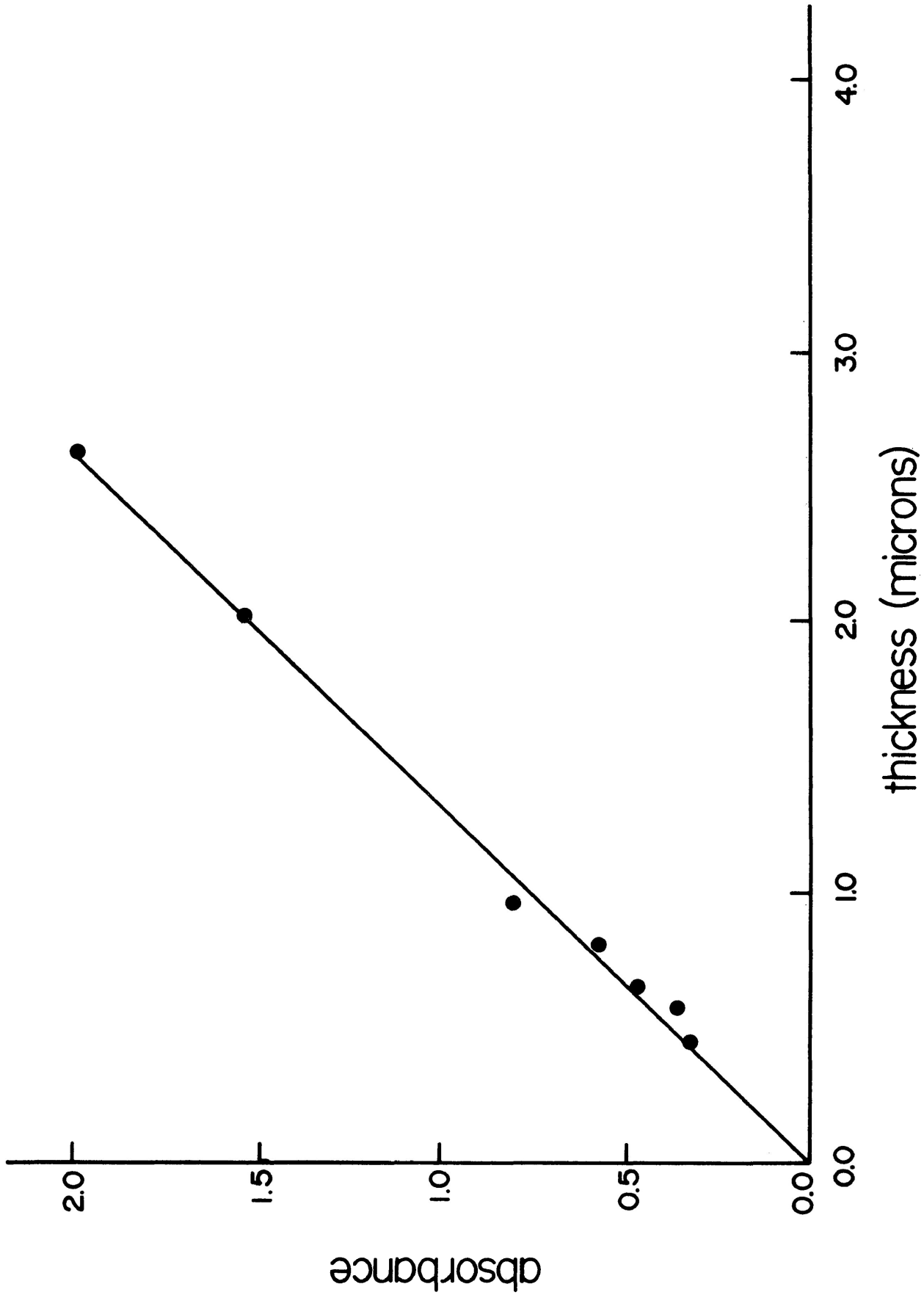


Figure 2.12 - Mass Spectrometer System:

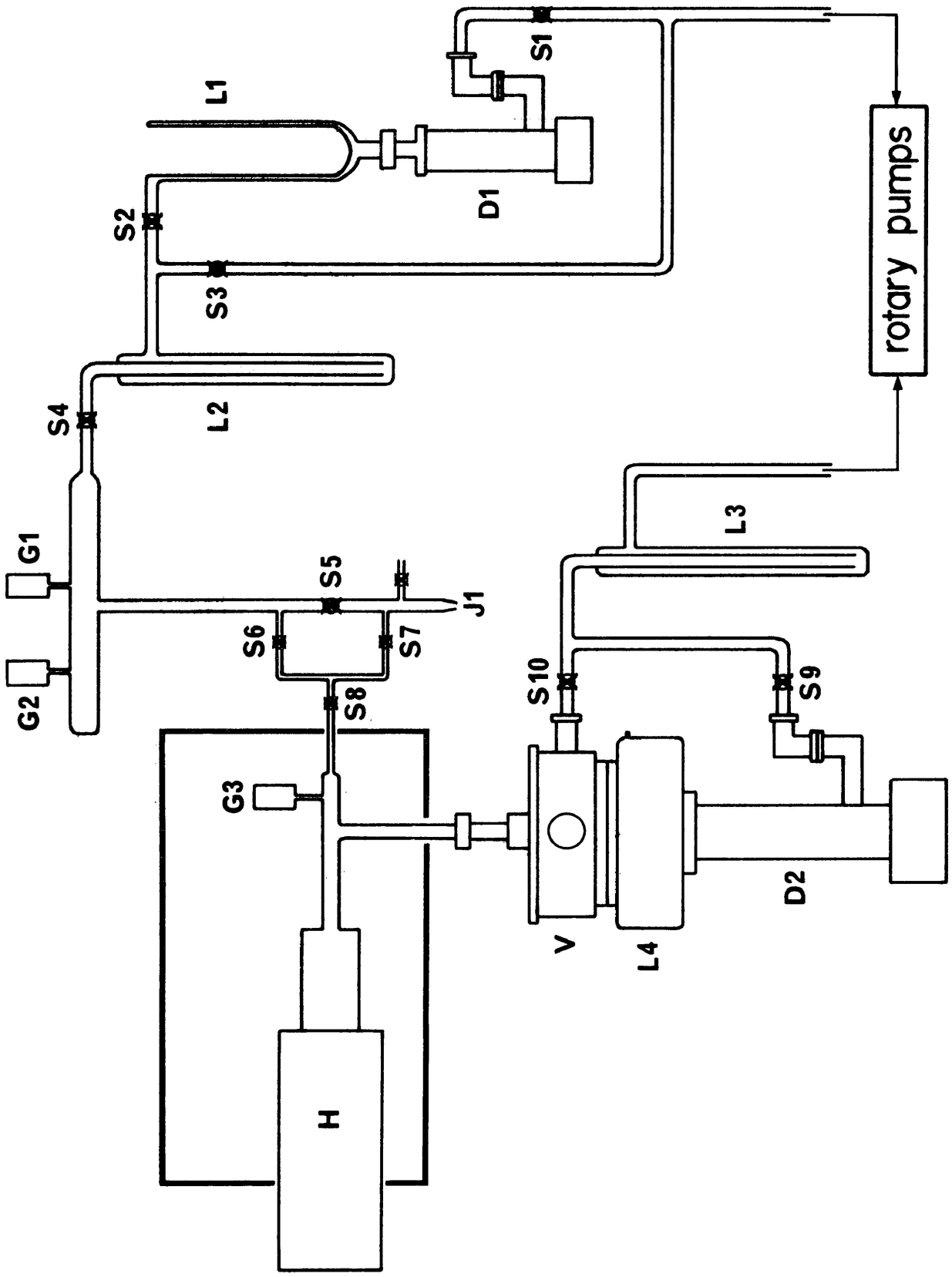


Figure 2.13 - Mass Spectrometer Calibration:
Relative Peak Height vs Number of Moles:

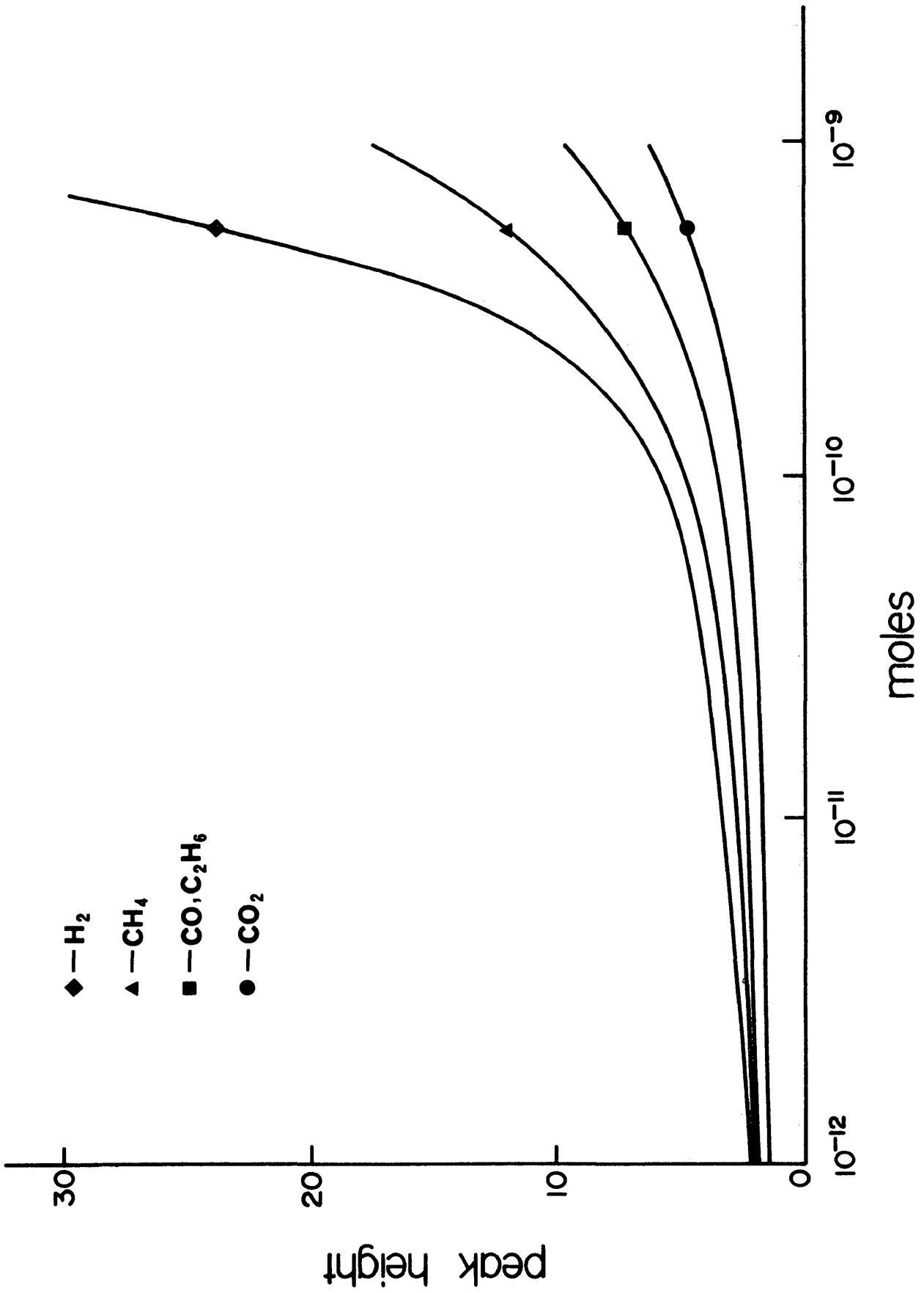


Figure 2.14 - Mass Spectrometer Calibration:
Relative Peak Height vs Pressure of Hydrogen,
Methane, Carbon Monoxide, Ethane and Carbon Dioxide:

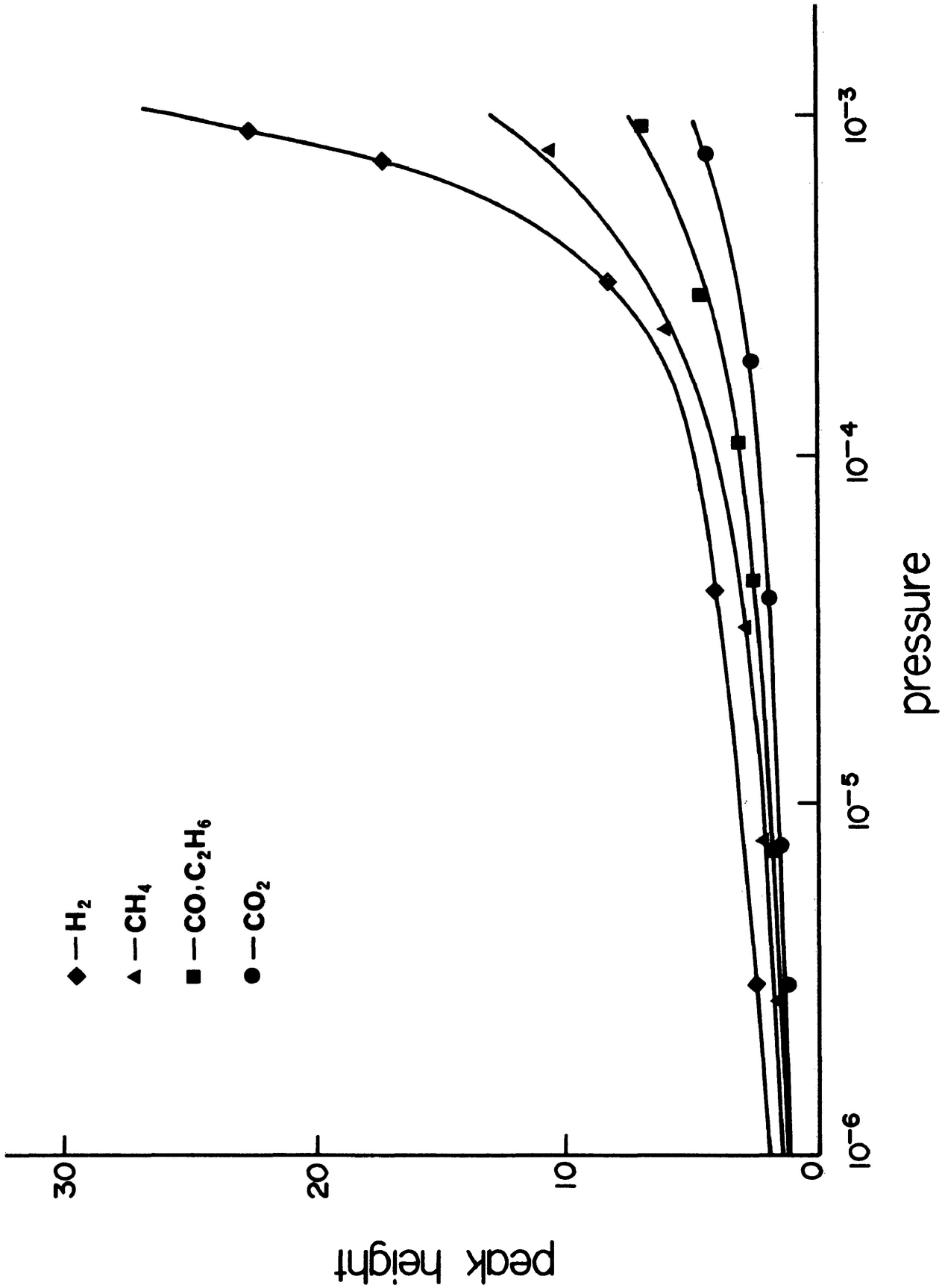


Table 2.1 - Dilute Solution Parameters for the Para-substituted Styrene Polymers:

Polymer	K	a	$\overline{Mn}$
PVAP	2.79×10^{-4} (★)	0.70 (★)	280,745
PPBr	1.82×10^{-4} (49)	0.57 (49)	54,700
PPCl	1.18×10^{-4} (49)	0.65 (49)	56,180
PPF	1.79×10^{-4} (☆)	0.63 (☆)	415,400
PPIP	1.23×10^{-4} (49)	0.69 (49)	38,060
PPMO	1.80×10^{-4} (49)	0.62 (49)	701,600
PPTB	1.50×10^{-4} (40)	0.65 (40)	101,500

★– calculated, see Appendix B
☆– calculated, see Appendix C

Table 2.2 - Absorption Characteristics of the Para-substituted Styrene Polymers:

Polymer	Absorption Co-efficient (cm^{-1})	λ_{max} (nm)
PVAP	6900	257.0
PPBr	6050	262.0
PPCl	6600	269.0
PPF	5420	266.5
PPIP	6305	259.0
PPMO	5610	279.0
PPTB	7700	255.0

CHAPTER 3

RESULTS

3.1 Introduction

The data presented in this chapter is the result of a systematic detailed investigation into the photodegradation of PVAP, PPBr, PPCl, PPF, PPIP, PPMO, and PPTB. With the exception of poly-(vinylacetophenone), all of the polymers contained a single chromophore (i.e., the phenyl ring). PVAP contained an additional chromophore (i.e., the carbonyl function in the para-acetyl group) and for this reason, the effects of both short and long-wave radiation were studied. PVAP-SW and PVAP-LW will be used to label the results obtained following exposure to short and long-wave radiation respectively.

Rather than interpret the results as they are presented, a thorough discussion will follow this chapter in an attempt to analyze all data collectively for each of the polymers studied.

3.2 Spectral Observations

Spectra were recorded in an attempt to provide an insight into changes that occur in the macromolecular structure during irradia-

tion (i.e., nature of the crosslinks and evidence for the formation of main chain unsaturations).

3.2.1 Infrared Spectra

The infrared spectra of PVAP-SW, PVAP-LW, PPBr, PPCl, PPF, PPIP, PPMO, and PPTB films prior to and after 100 hours irradiation are shown in figures 3.1 to 3.8 respectively. Since the majority of photochemical reactions are expected to occur within the surface layers, it is not surprising that the infrared spectra of these films following exposure show little modification (i.e., the bulk of the film would mask any changes occurring at the surface). Slight decreases in baseline transmission were observed throughout the entire series of spectra as well as the appearance of broad peaks in the 1650cm^{-1} to 1820cm^{-1} region.

The majority of changes were observed in the infrared spectra of insoluble fractions isolated from thin films exposed for 100 hours (see figures 3.9 to 3.16). Generally, new peaks were observed around 900cm^{-1} and 740cm^{-1} as well as weak broad absorption bands centered at 1700cm^{-1}. As with thin film spectra, a decrease in baseline intensity was observed throughout.

3.2.2 Ultraviolet-Visible Spectra

The ultraviolet-visible absorption spectra of PVAP-SW, PVAP-LW, PPCl, PPBr, PPF, PPIP, PPMO, and PPTB films, before and after 100 hours irradiation are shown in figures 3.17 to 3.24 respectively.

All polymers show absorptions in the ultraviolet region characteristic of electronic transitions associated with the phenyl ring. It is interesting to note that the carbonyl group on the para-substituent of PVAP does not give rise to an absorption band. This can be rationalized by taking into account a rather low extinction coefficient observed for the carbonyl group in acetophenone.(50) It is likely that geometrical factors associated with polymer systems would lower this value even further.

With the exception of PVAP-LW, PPMO, and PPF, the band of maximum absorption decreases in intensity and blends into a continous absorption extending from 500nm to 200nm during irradiation. The bands in both PVAP-LW and PPMO remain essentially the same while the absorption maxima in PPF increases during exposure. All fine structure associated with the absorption bands is retained in PVAP-LW, PPMO and PPF but is lost in the other polymers following prolonged irradiation.

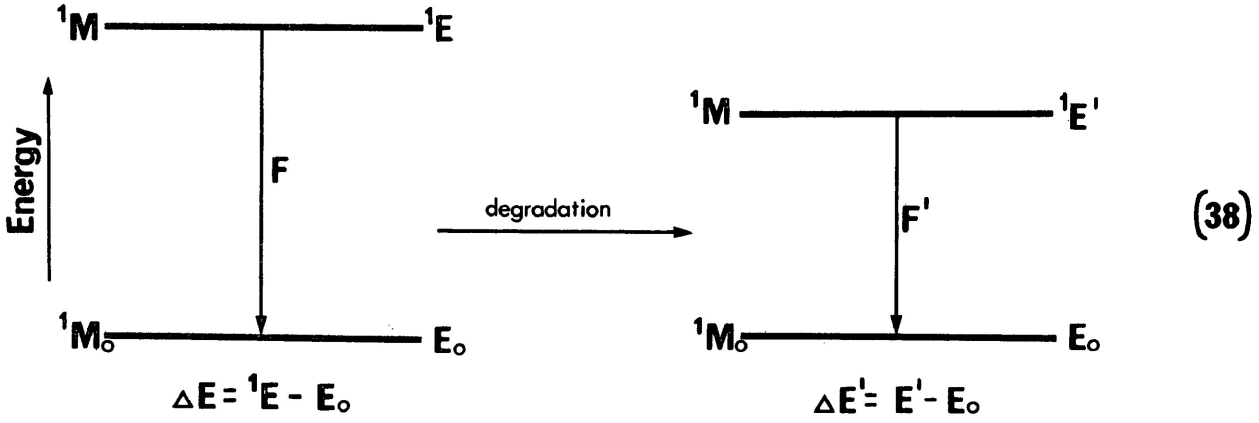
In the case of polystyrene (51) and poly(p-methylstyrene) (39) a yellow discoloration was reported during irradiation, a progressive increase in absorption around 400nm being observed. Similar observations are noted here for the polymer systems studied. Figure 3.25 shows the increase in absorbance at 400nm as a function of irradiation time for PVAP-SW, PPBr, PPCl, PPF, PPIP, PPMO, and PPTB respectively. It is interesting to note that PVAP-LW did not exhibit any increase in absorbance at 400nm. From figure 3.25 it can be seen that the extent of 'yellowing' varied considerably among the various polymers. The loss of linearity during the later stages of photolysis can be attributed to the discolored surface layers absorbing the ultraviolet light thereby reducing the intensity of incident radiation to the bulk of the film. Changes in the ultraviolet-visible spectra are indicative of changes in energy levels associated with $\pi \rightarrow \pi^*$ transitions of the phenyl ring arising from the formation of cross-links or main chain unsaturations.

3.2.3 Fluorescence Spectra

Fluorescence spectra of PVAP-SW, PVAP-LW, PPBr, PPCl, PPF, PPIP, PPMO, and PPTB films excited with 255nm radiation at 25°C are presented in figures 3.26 to 3.33 respectively, prior to and after 100 hours exposure.

The emission bands are the result of both singlet and eximer fluorescence. Following short-wave irradiation the bands are replaced by a broad dispersion centered at a longer wavelength than peaks observed for unexposed films. PVAP-LW shows little to no change in the emission spectra, a slight decrease in intensity of the peaks being observed.

It is suggested, that during irradiation, modifications in the structure of the polymer chain (i.e., crosslinking and main chain unsaturations) perturb the energy levels of the phenyl ring such that the singlet is at a lower energy level:



(38)

Lowering of the singlet energy level would result in a longer wavelength of fluorescence, F', since $\Delta E' < \Delta E$.

The decrease in emission intensity associated with singlet fluorescence can be explained by considering color and chemical quenching. During irradiation as the film discolors, it is likely that

fluorescent radiation is attenuated by the colored surface layers. Also, energy destined for pathways to the ground state via fluorescence, may be lost by an energy transfer process from the excited phenyl segments to adjacent conjugations on the main polymer chain or, in the case of PVAP, to the carbonyl group of the para-substituent. It is interesting to note however, that neither singlet fluorescence nor phosphorescence from the carbonyl group was observed prior to or following degradation even when the film was excited at longer wavelengths.

It is believed that eximer fluorecence is lost following irradiation and can be explained by considering geometrical factors. As previously noted in the introduction section of this thesis, adjacent phenyl segments on the same polymer chain must be co-planar for eximer formation. Hirayami(52), Chadros and Dempster(53) have reported that steric and geometric factors are extremely important in controlling eximer formation. It follows then that during the course of degradation, crosslinking, either through the parasubstituent or direct to the phenyl ring will upset the necessary configuration for intrachain eximer formation and consequently reduce the emission intensity.

3.3 Volatile Products

3.3.1 Introduction

The identification of volatile products produced during ir-

radiation provides information on the nature of the photochemical reactions taking place. The quantity of product detected is a direct measure of the efficiency of energy transfer from the chromophore (i.e., phenyl ring or in PVAP, the carbonyl group) to the particular bond undergoing fission.

The rates of formation of products may be governed by their rates of diffusion out of the high density polymer matrix. To examine the possibility for diffusion control, it is necessary to examine semi-quantitatively the amount of product formed either as a function of film thickness or temperature, following exposure for a predetermined period.

All mass spectral data is represented in terms of relative peak heights rather than number of moles, however, calibration curves have already been reported (see figure 2.12) to show the relationship between the number of moles and relative peak height.

3.3.2 Volatile Products as a Function of Irradiation Time

Figures 3.34 to 3.41 show the formation of products as a function of exposure time for films of PVAP-SW, PVAP-LW, PPBr, PPCl, PPF, PPIP, PPMO, and PPTB respectively. With the exception of PVAP-LW and PPCℓ, hydrogen was the major product. This can be accounted for

in most cases by the cleavage of C-H bonds in the tertiary position of the main chain and in some cases, the para-substituent. Other products characteristic of partial or total para-substituent cleavage were noted for all polymers studied. It is important to note the quantity (reflected by the relative peak height values) of volatile products liberated during photolysis; particular attention drawn to PVAP-SW, PVAP-LW, PPBr, and PPCl. Generally, the quantity of product formed depends upon the efficiency of intramolecular energy transfer as well as the dissociation energy of the particular bond in question. Bond dissociation energies for para-substituents are not known for polymers, however, approximate values can be assigned from dissociation energies reported for benzene analogues (see table 3.1).

3.3.3 Volatile Products as a Function of Temperature

Volatile products monitored as a function of temperature after films had been exposed for 2.5 hours are shown in figures 3.42 to 3.49 for PVAP-SW, PVAP-LW, PPBr, PPCl, PPF, PPIP, PPMO, and PPTB respectively. The majority of products showed a marked decrease with increasing temperature, consistent with a depletion in sample during analysis. A few of the larger products exhibited slight increases in formation with increasing temperature.

A complete discussion of the results presented in this sub-

section for the investigation of diffusion controlled reactions will appear in the discussion section of this thesis.

3.4 Molecular Weight Changes

3.4.1 Introduction

By monitoring changes in molecular weight it is possible to determine the extent of crosslinking and chain scission as a function of irradiation time. Generally, the para-substituent will alter the nature and extent of the secondary reactions. In particular, it may hinder or promote crosslinking either through itself by partial cleavage, or direct to the phenyl ring by complete cleavage. Depending upon the electronic configuration of the substituent, radicals formed on the main polymer chain may be sources for the formation of crosslinks or initiating centres for chain scission by disproportionation or unzipping.

3.4.2 Changes in Molecular Weight as a Function of Irradiation Time

Changes in molecular weight for PVAP-SW, PVAP-LW, PPBr, PPCl, PPF, PPIP, PPMO, and PPTB are numerically listed in table 3.2 and graphically represented in figure 3.50. Since the initial molecular weights varied considerably from polymer to polymer, a delta factor, (i.e., the number average molecular weight at exposure time x, $Mn_{t=x}$,

divided by the initial number average molecular weight, $Mn_{t=0}$, was used to represent changes occurring in the polymers studied so that all data could be collectively presented.

According to figure 3.50, during the initial stages of degradation crosslinking is the major reaction occurring in PPBr, PPCl, and PPIP and, to a much lesser extent, in PPMO and PPTB. PVAP-SW and PPF both exhibit characteristics of simultaneous chain scission and crosslinking, the latter becoming important in the later stages of degradation.

It is interesting to note the difference in behaviour between PVAP-SW and PVAP-LW, the latter showing virtually no change in molecular weight. This is not unexpected however, since two different chromophores are participating in the reactions. In considering PVAP-SW, the absorption of energy by the phenyl segments may be transferred intramolecularly to bonds in the main chain to initiate scission reactions or to bonds in the para-substituent to initiate the formation of crosslinks. It is highly unlikely that energy will be transferred to the main chain following absorption of energy by the carbonyl group in the para-substituent. It is more probable that reactions characteristic of carbonyl containing compounds (i.e., Norrish Type I reaction) will occur giving rise to a radical centre either on the para-substituent

or the phenyl ring to initiate crosslinking.

The ease with which a particular polymer crosslinks appears to be directly related to the electronic and steric factors, of the para-substituent. Briefly considering PPBr, PPCl, and PPF, bond dissociation energies of the para-substituent increases along the series (see table 3.1), consequently the degree of crosslinking decreases. These aspects will be discussed in more detail in the discussion section of this thesis.

3.5 Solubility Measurements

3.5.1 Introduction

The insolubility of a polymer following irradiation is directly related to the degree of crosslinking. Conversely, an increase in solubility denotes a decrease in molecular weight arising from scission reactions.

Both processes can be related by Charlesby's equation (see equation (29)). By plotting $S + S^{\frac{1}{2}}$ versus the inverse of irradiation time and extrapolating to zero exposure, an intercept of value α/β may be obtained. Recalling from Chapter 1, α and β are constants proportional to the probability of chain scission and crosslinking, respectively.

3.5.2. Data From Charlesby Plots

Data obtained from solubility measurements was analyzed according to Charlesby's equation, the results of which are reported in table 3.3.

For PVAP-SW, PPIP, and PPMO, crosslinking is approximately four times as likely as chain scission. For PPBr, PPCl, and PPF, crosslinking is approximately 20,8 and equally likely as chain scission, respectively.

As previously noted in molecular weight changes, the values of α/β reflect electronic and steric factors associated with the para-substituent.

It is important to note that extreme difficulty was encountered in obtaining data for Charlesby plots. The many variables inherent in such an analysis (i.e., film thickness and residual solvent in the soluble fraction) do not permit experimental values to be presented with a great deal of certainty. It must therefore be stated that the α/β values reported in table 3.3 be accepted with this in mind and should not be considered individually but collectively with other data.

3.6 Summary of the Results of Secondary Reactions

Table 3.4 represents a quantitative summary of the results of secondary reactions as implied by spectral observations, volatile product analysis, molecular weight changes and solubility measurements. Numerical values for chain scission, crosslinking and coloration have been assigned on the basis of an arbitrary scale from 1 to 10; the magnitude of the number indicating the extent of the particular reaction. Each column was assessed individually and may be used to provide comparisons between polymers, regarding the participation of the para-substituent in a particular secondary reaction. For a more detailed and accurate account, the reader is referred to the discussion section of this thesis.

Figure 3.1 - Thin Film I. R. Spectra of Poly(vinylacetophenone) Before and After 100 Hours Exposure to Short-wave Radiation:

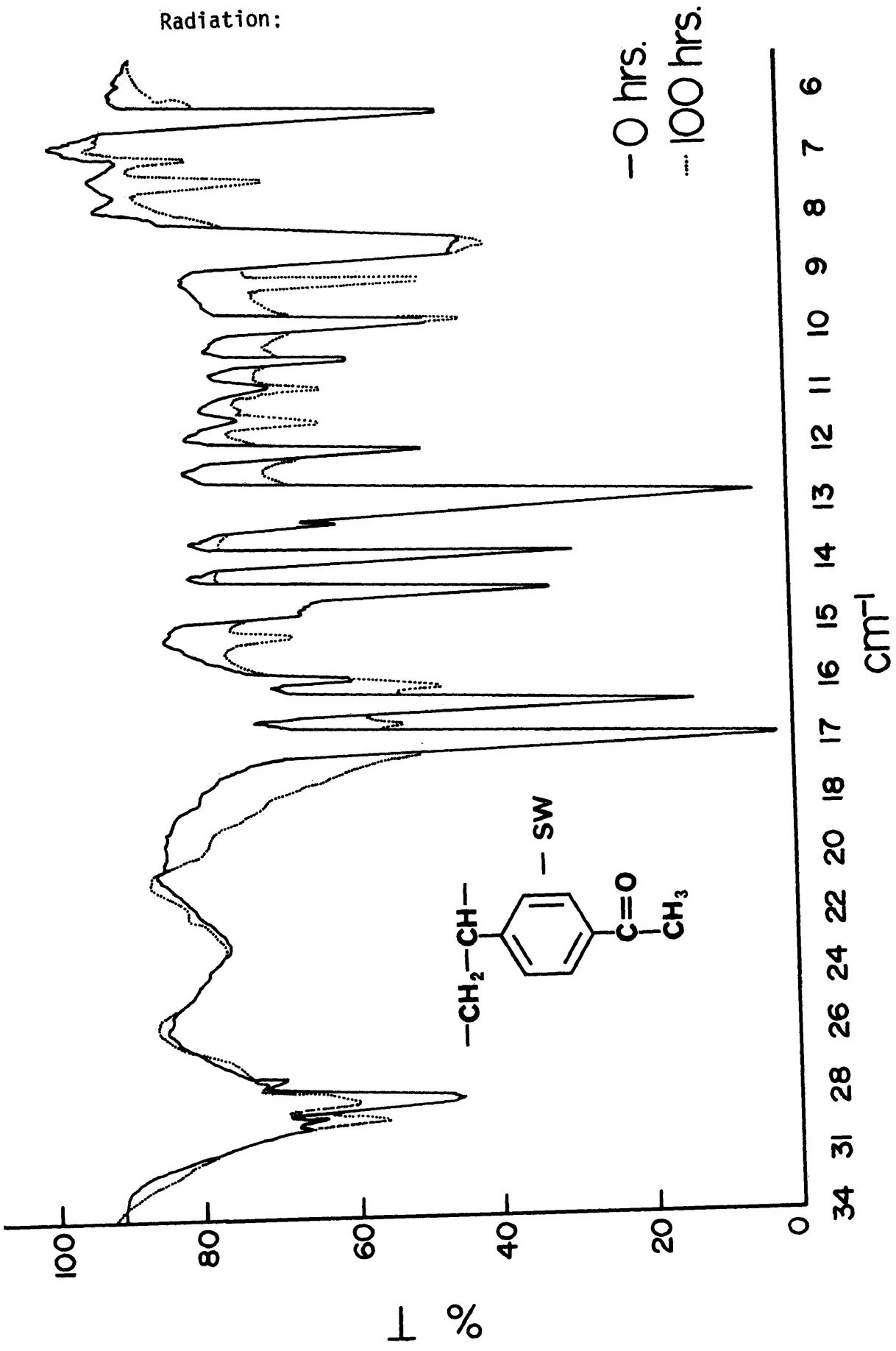


Figure 3.2 - Thin Film I. R. Spectra of Poly(vinylacetophenone) Before and After 100 Hours Exposure to Long-wave Radiation:

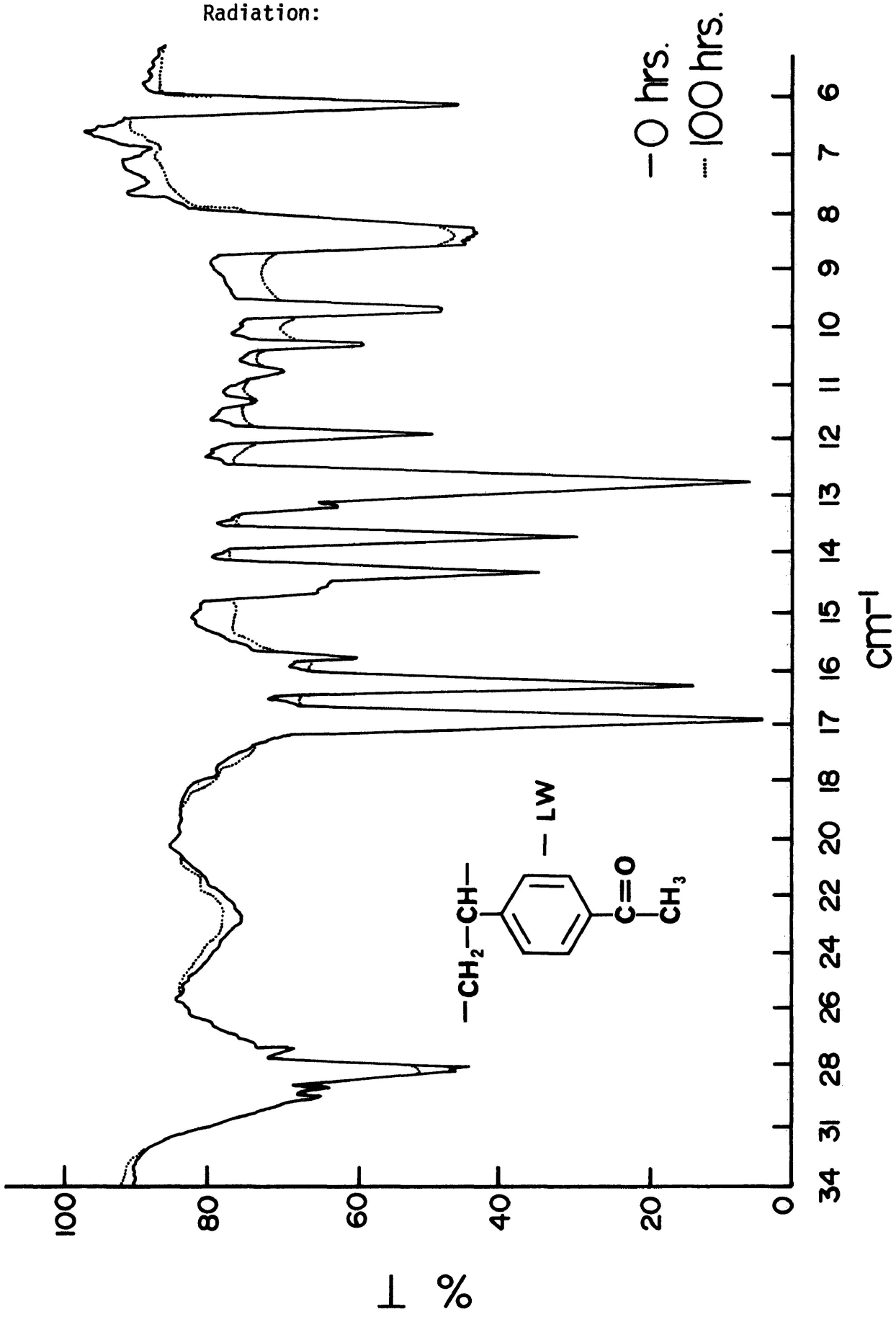


Figure 3.3 - Thin Film I. R. Spectra of Poly(p-bromostyrene) Before and After 100 Hours Irradiation:

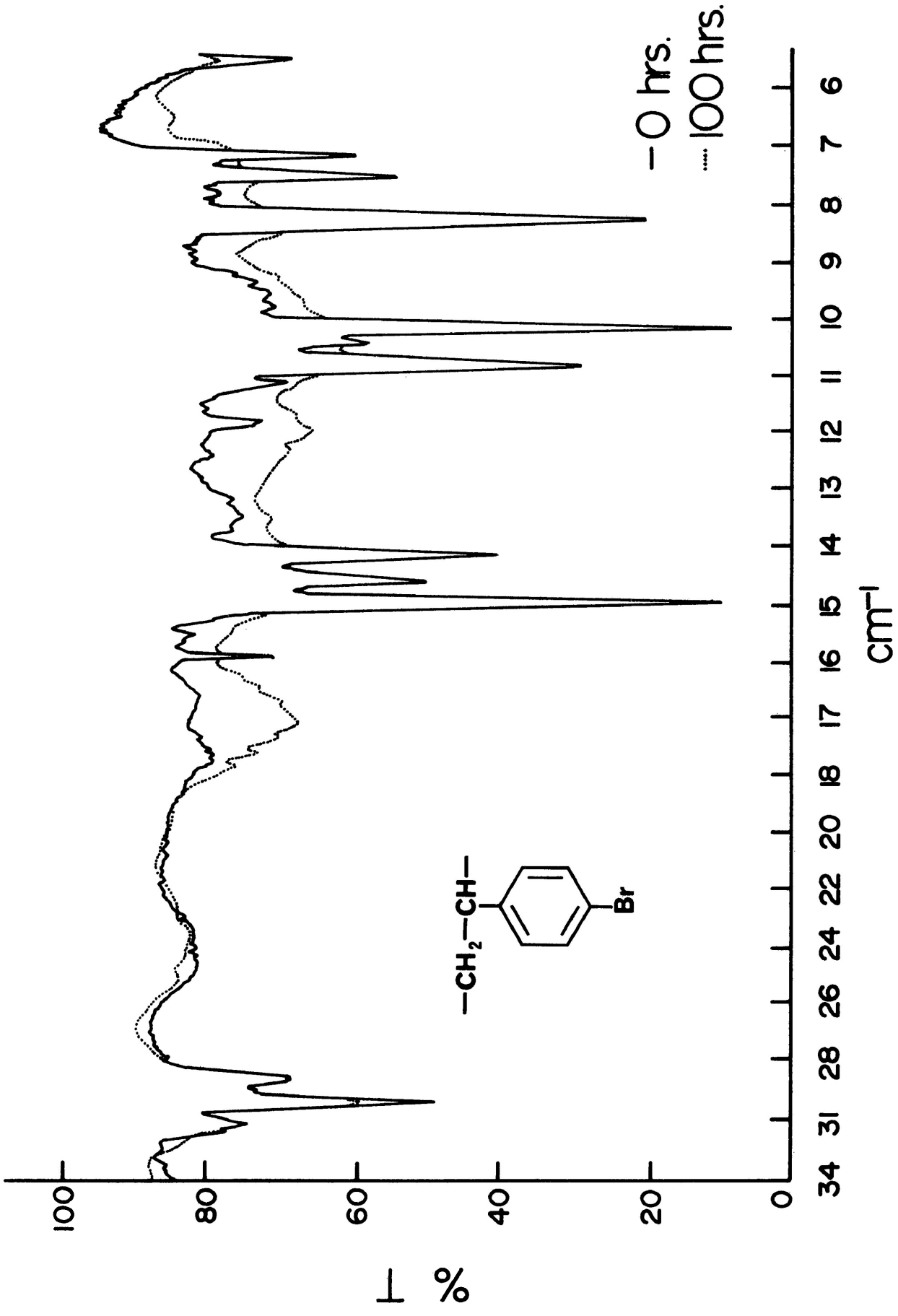


Figure 3.4 - Thin Film I. R. Spectra of Poly(p-chlorostyrene) Before and After 100 Hours Irradiation:

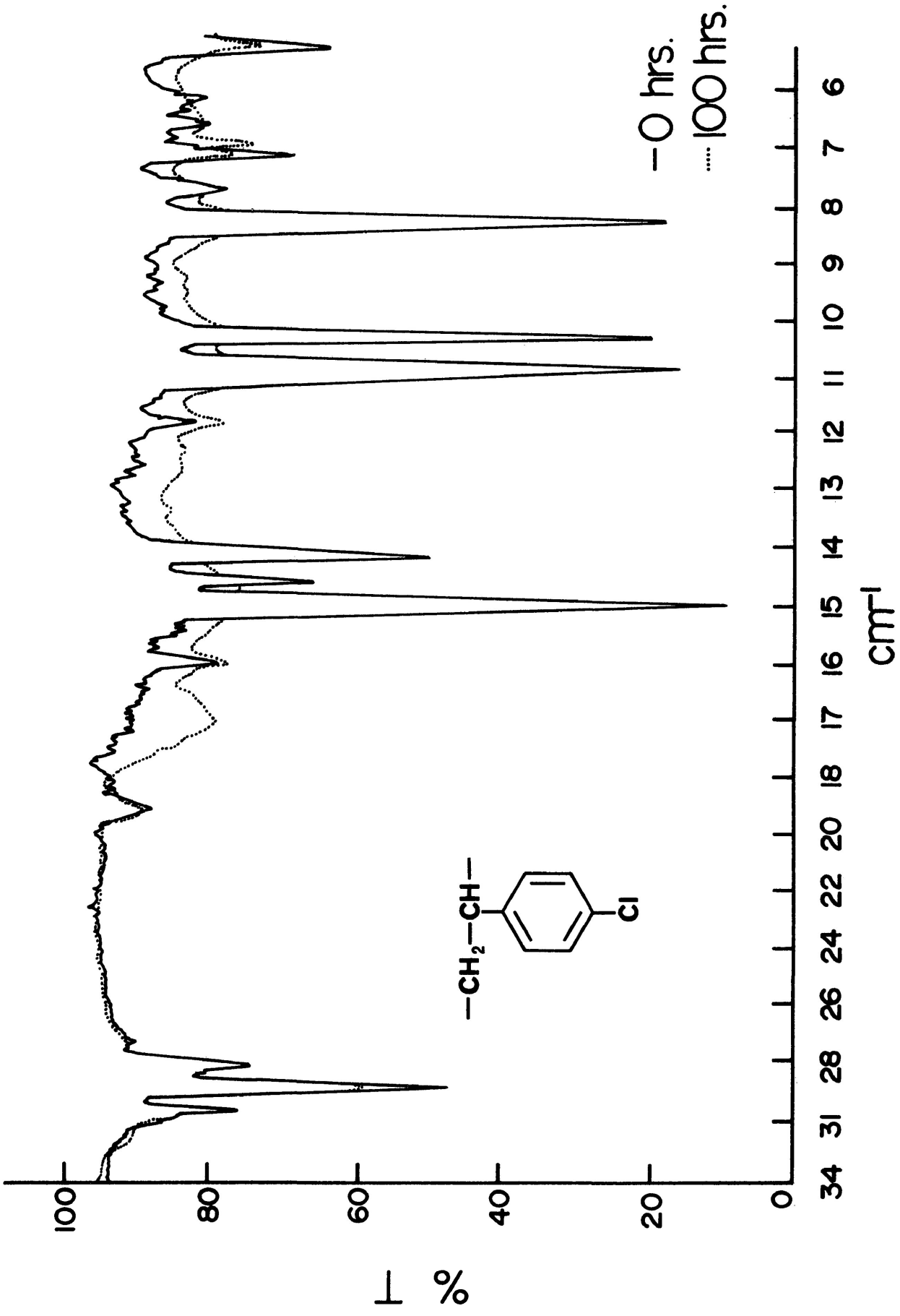


Figure 3.5 - Thin Film I. R. Spectra of Poly(p-fluorostyrene) Before and After 100 Hours Irradiation:

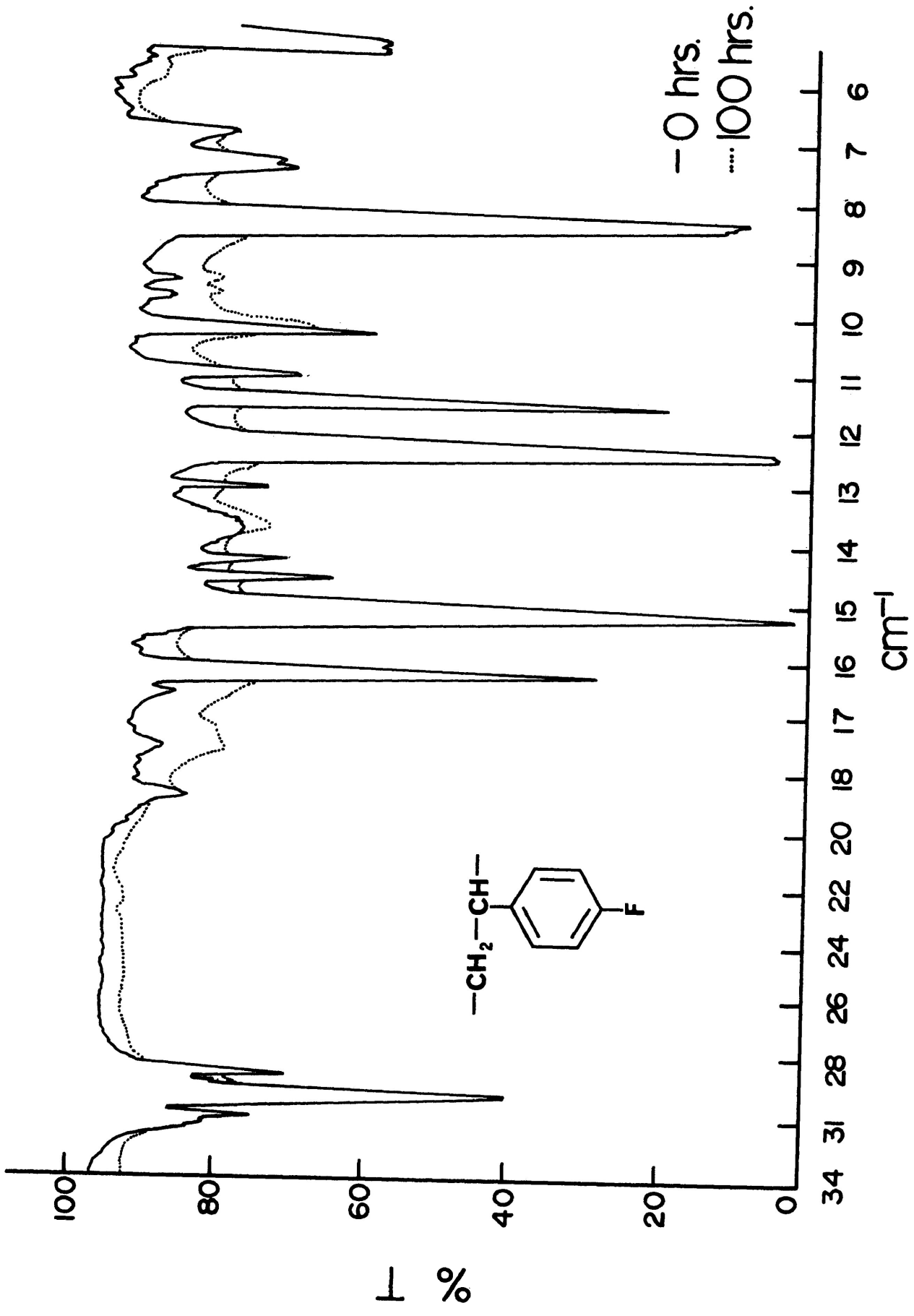


Figure 3.6 - Thin Film I. R. Spectra of Poly(p-isopropylstyrene) Before and After 100 Hours Irradiation:

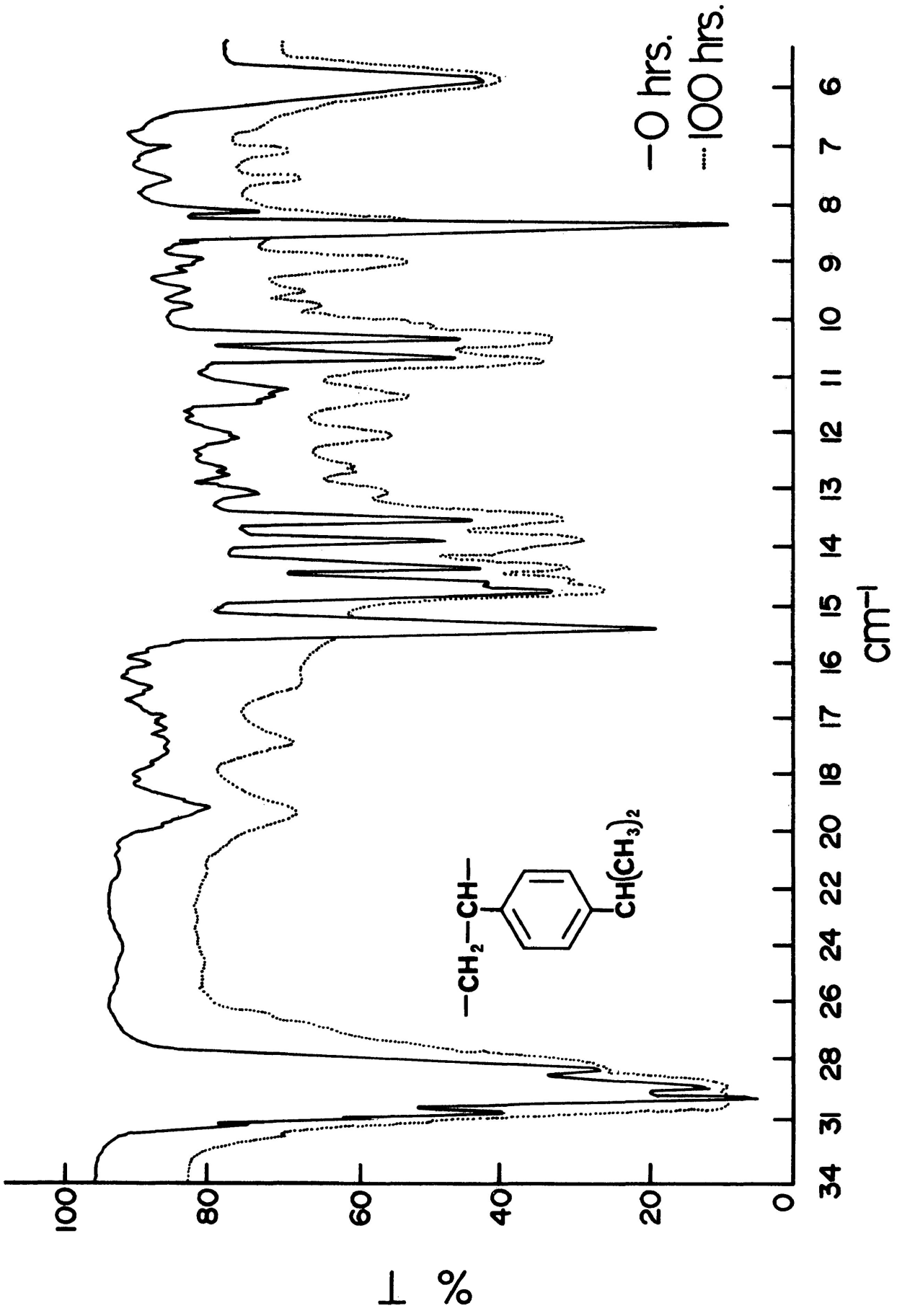


Figure 3.7 - Thin Film I. R. Spectra of Poly(p-methoxystyrene) Before and After 100 Hours Irradiation:

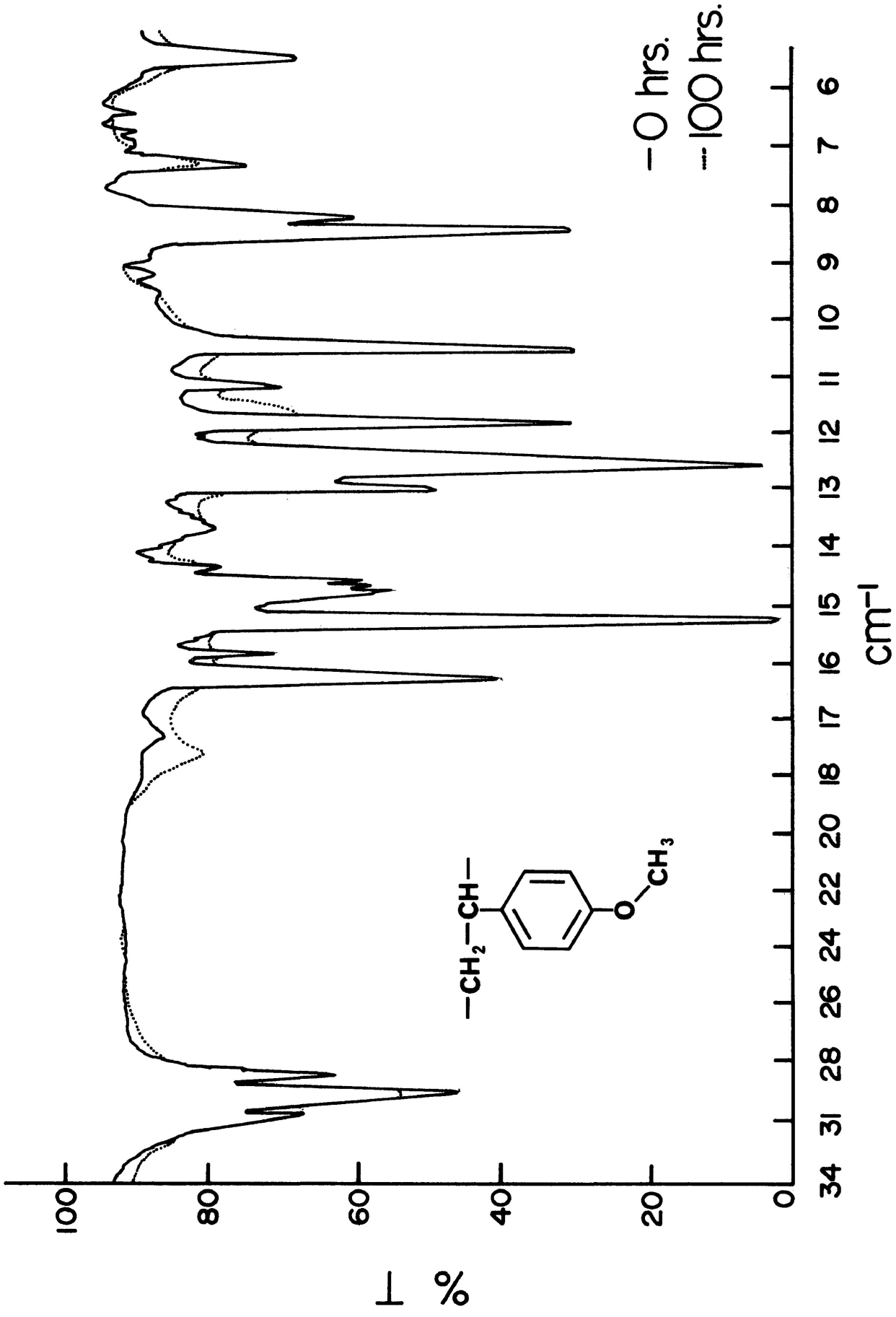


Figure 3.8 - Thin Film I. R. Spectra of Poly(p-*tert*-butylstyrene) Before and After 100 Hours Irradiation:

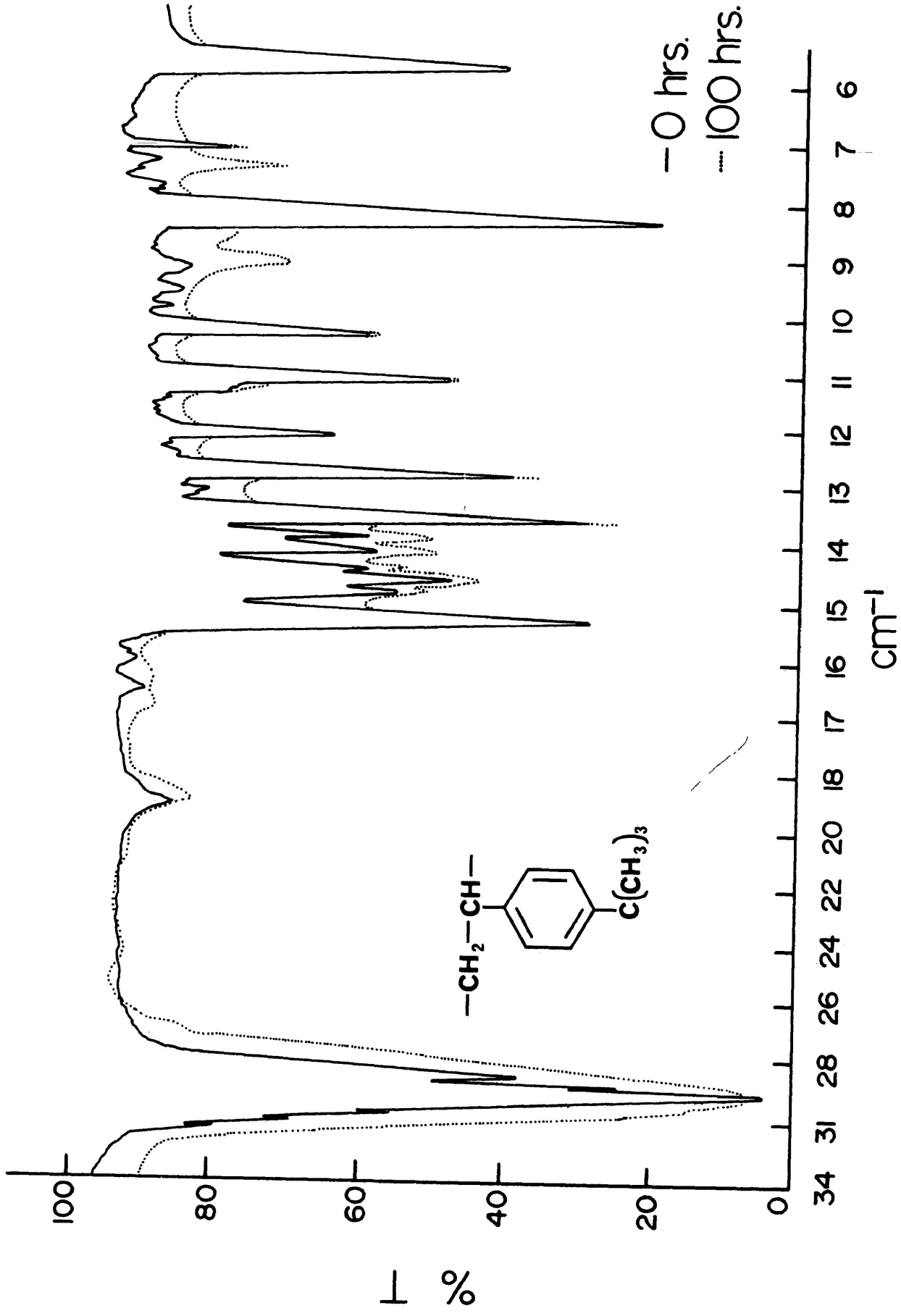


Figure 3.9 - I. R. Spectra of the Insoluble Product Isolated from Poly(vinylacetophenone) Following 100 Hours Exposure to Short-wave Radiation:

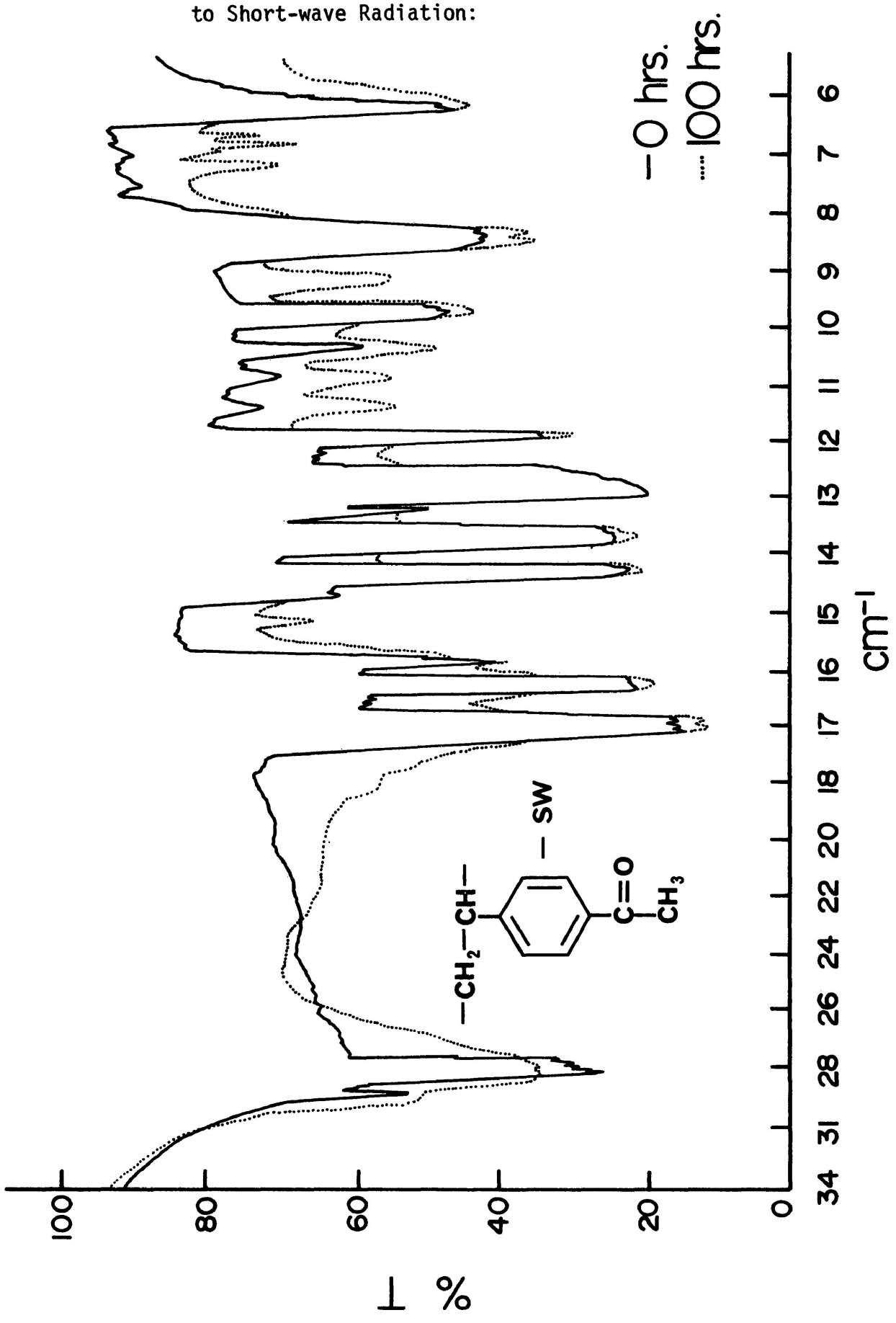


Figure 3.10 - I. R. Spectra of the Insoluble Product Isolated from Poly(vinylacetophenone) Following 100 Hours Exposure to Long-wave Radiation:

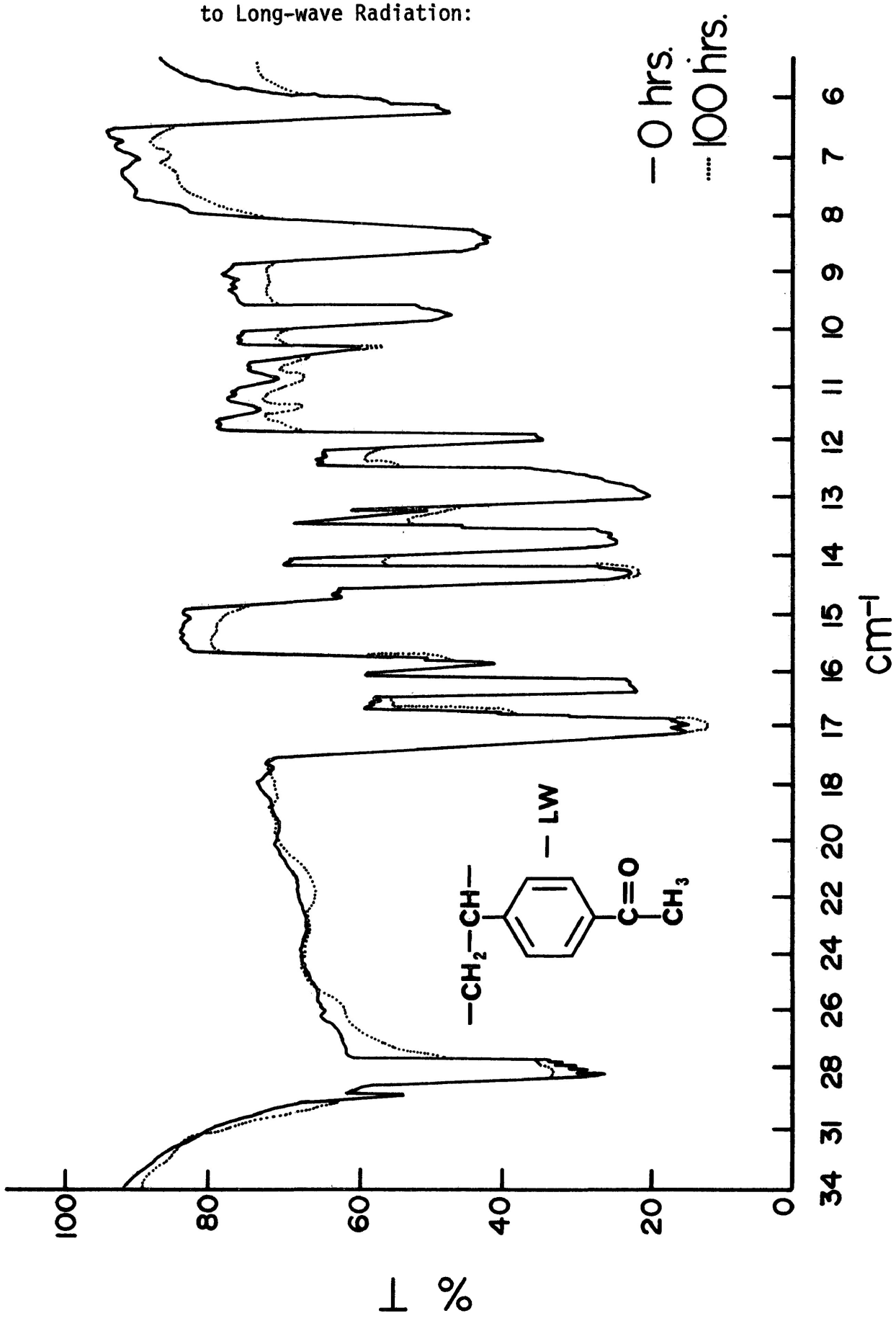


Figure 3.11 - I. R. Spectra of the Insoluble Product Isolated from Poly(p-bromostyrene) Following 100 Hours Irradiation:

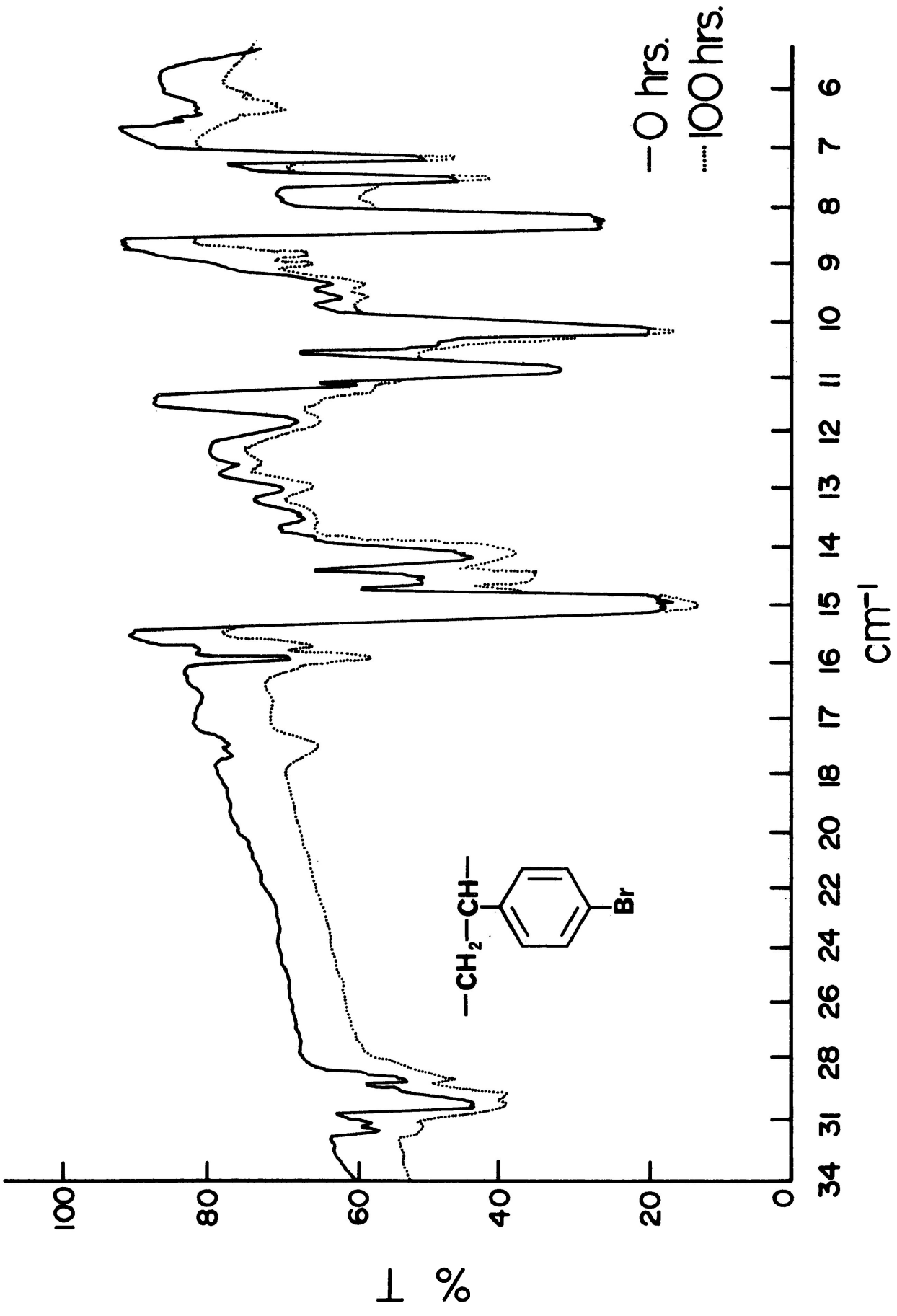


Figure 3.12 - I. R. Spectra of the Insoluble Product Isolated from Poly(p-chlorostyrene) Following 100 Hours Irradiation:

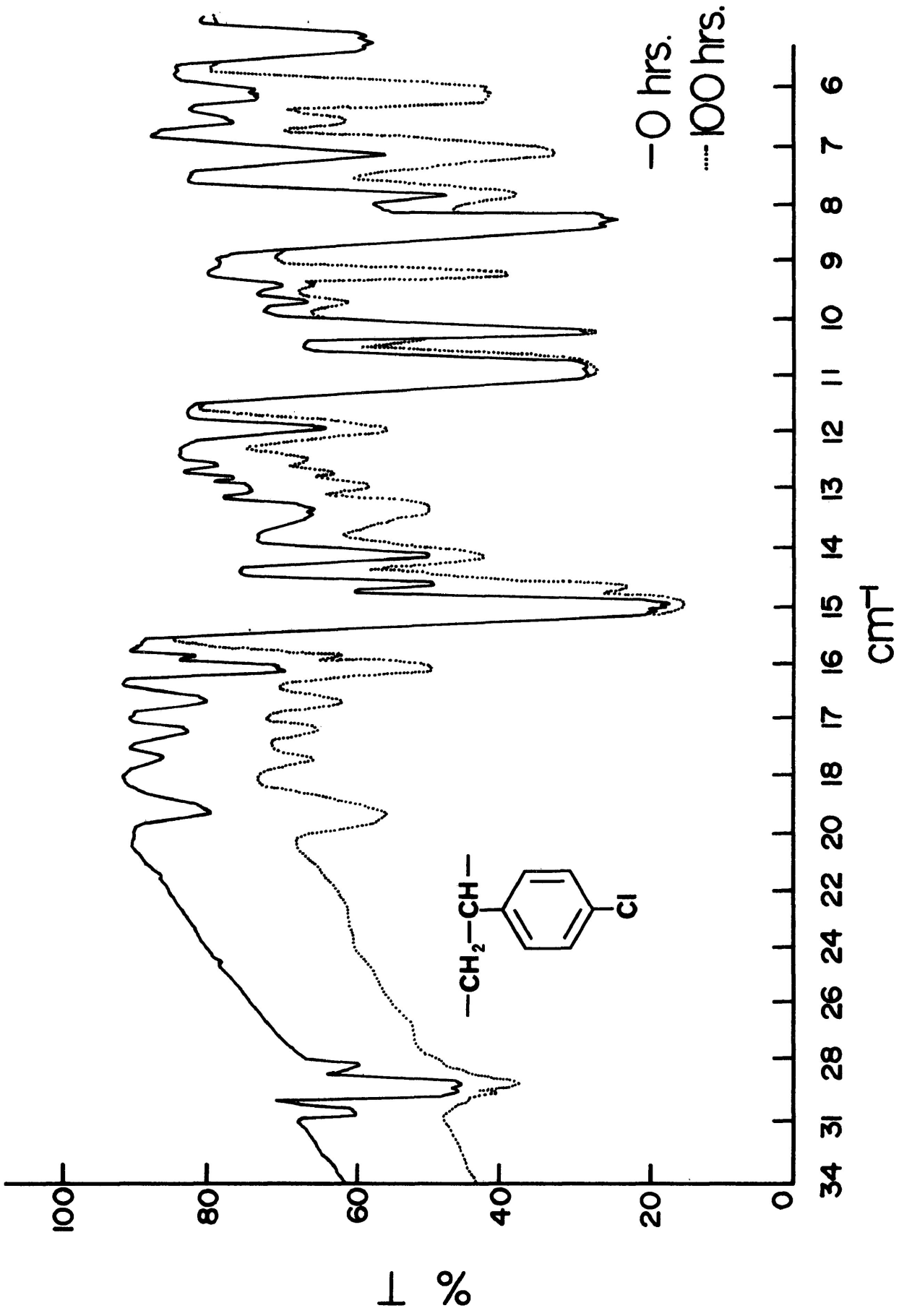


Figure 3.13 - I. R. Spectra of the Insoluble Product Isolated from Poly(p-fluorostyrene) Following 100 Hours Irradiation:

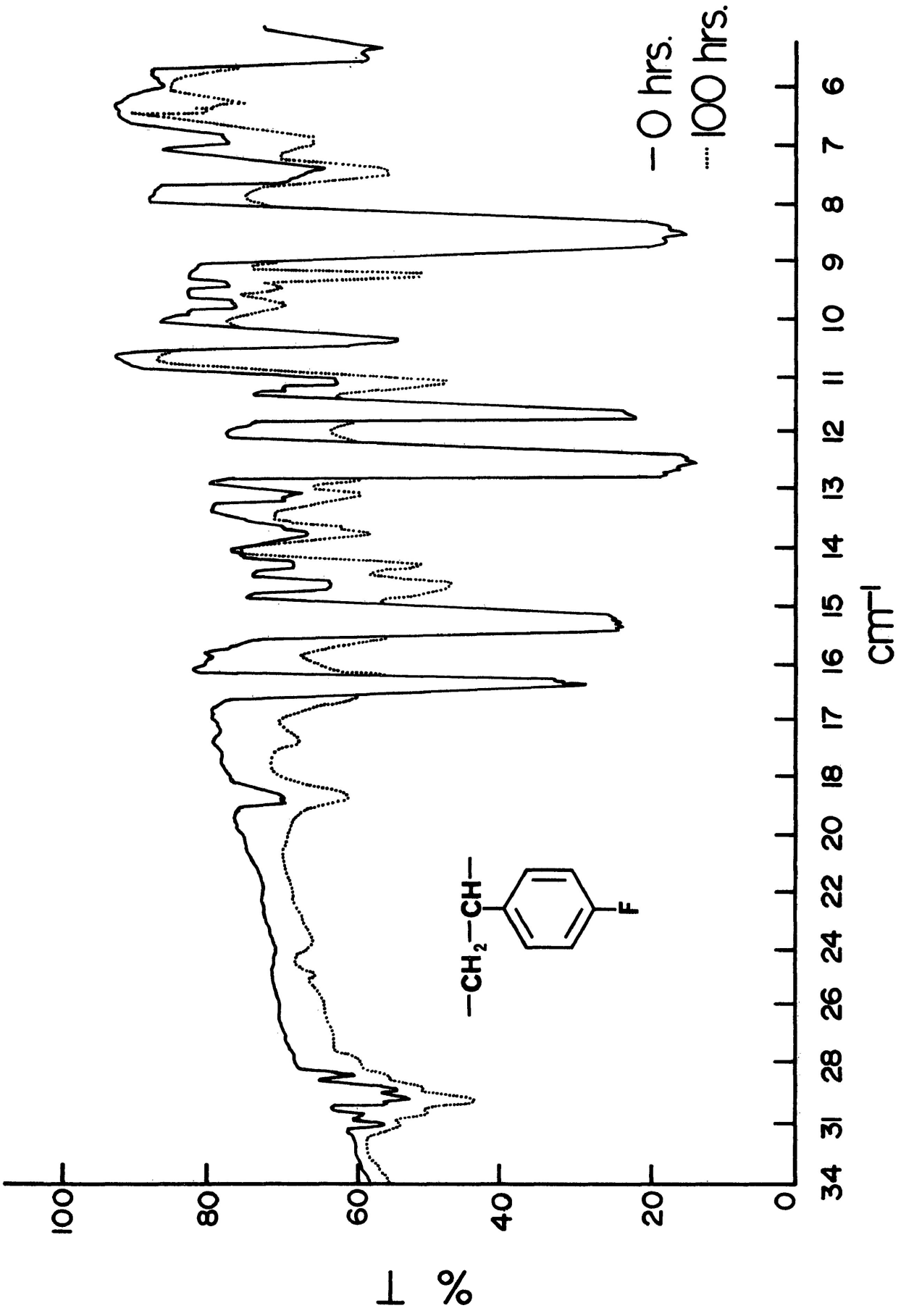


Figure 3.14 - I. R. Spectra of the Insoluble Product Isolated from Poly(p-isopropylstyrene) Following 100 Hours Irradiation:

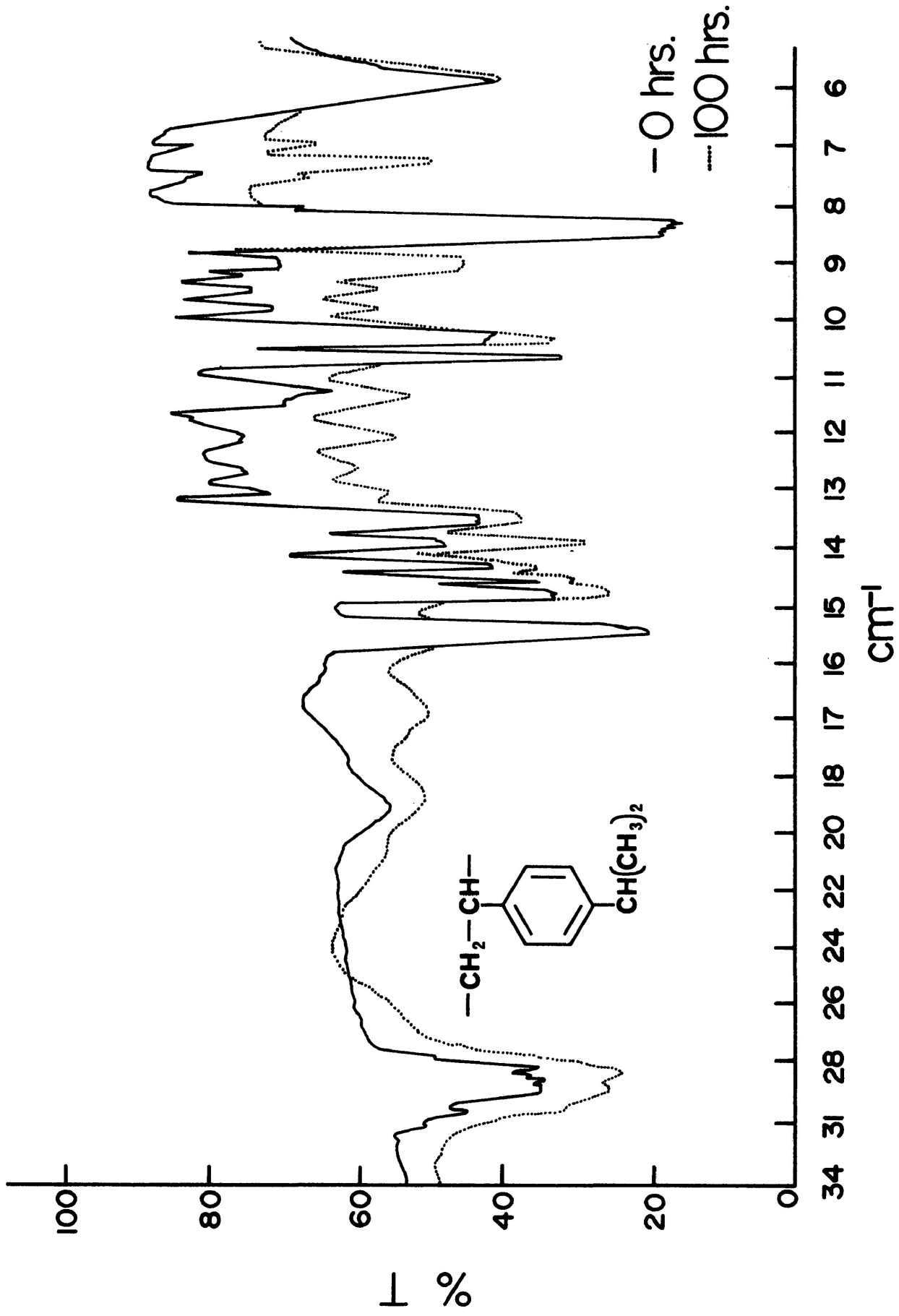


Figure 3.15 - I. R. Spectra of the Insoluble Product Isolated from Poly(p-methoxystyrene) Following 100 Hours Irradiation:

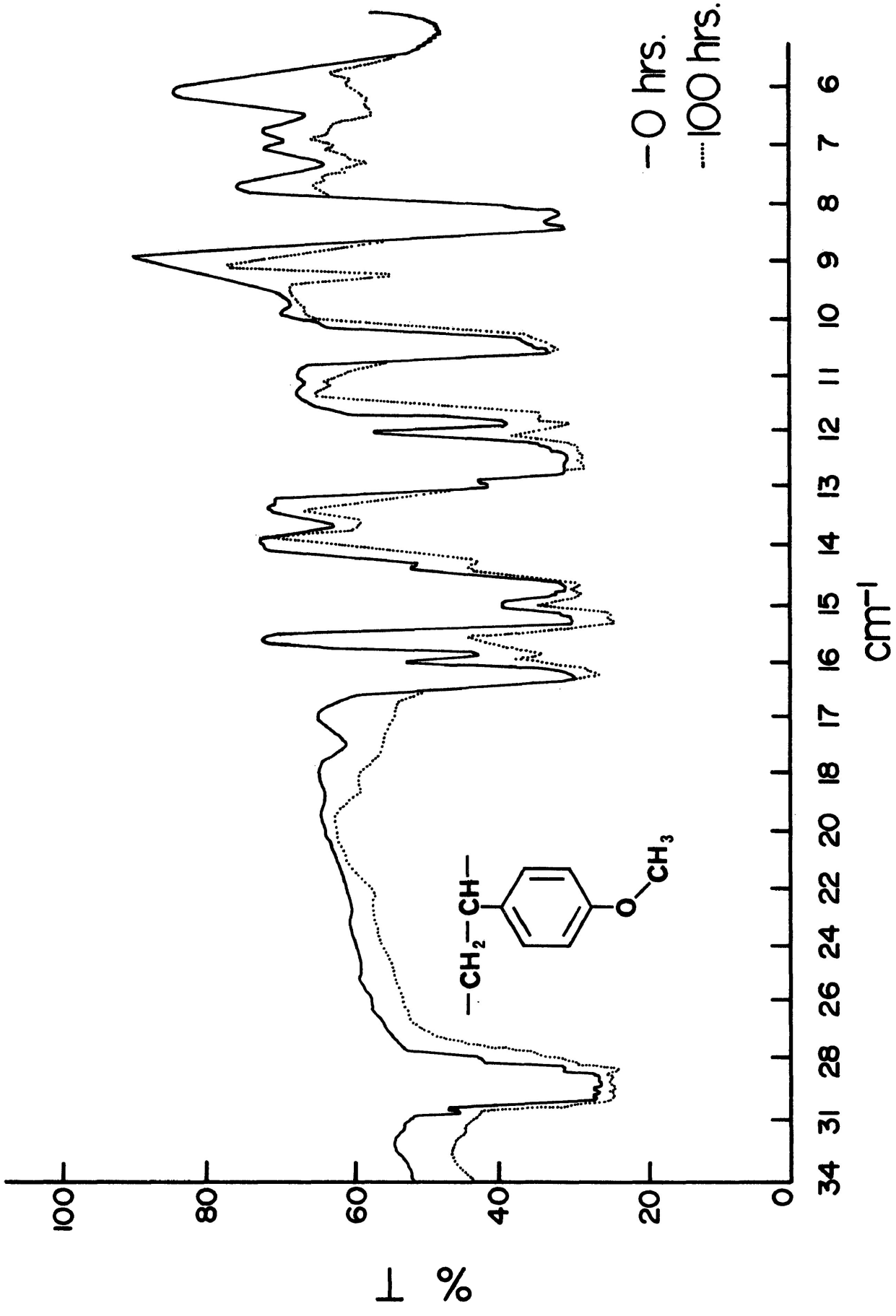


Figure 3.16 - I. R. Spectra of the Insoluble Product Isolated from Poly(p-*tert*-butylstyrene) Following 100 Hours Irradiation:

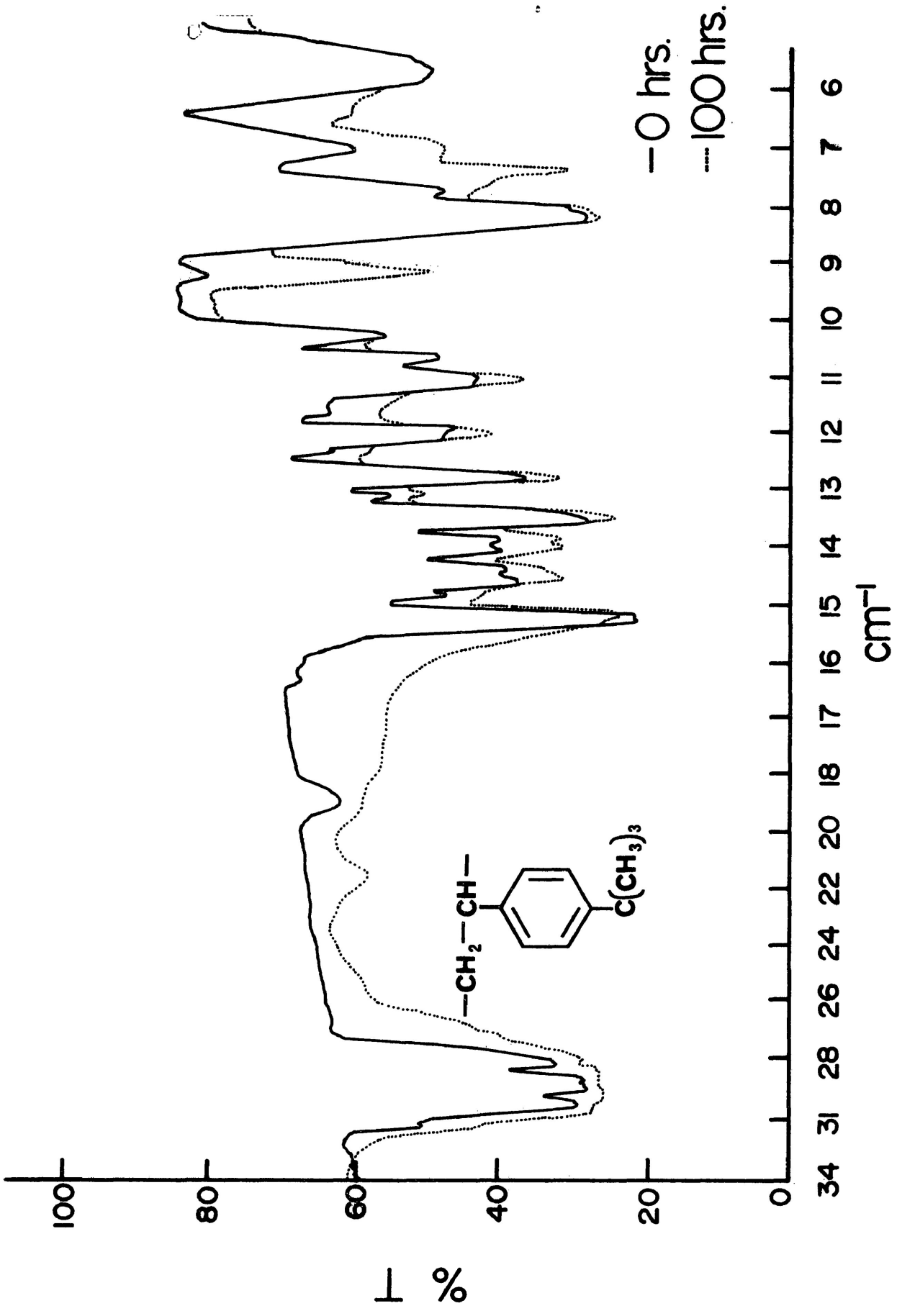


Figure 3.17 - U. V. Spectra of Poly(vinylacetophenone) Film Before and After 100 Hours Exposure to Short-wave Radiation:

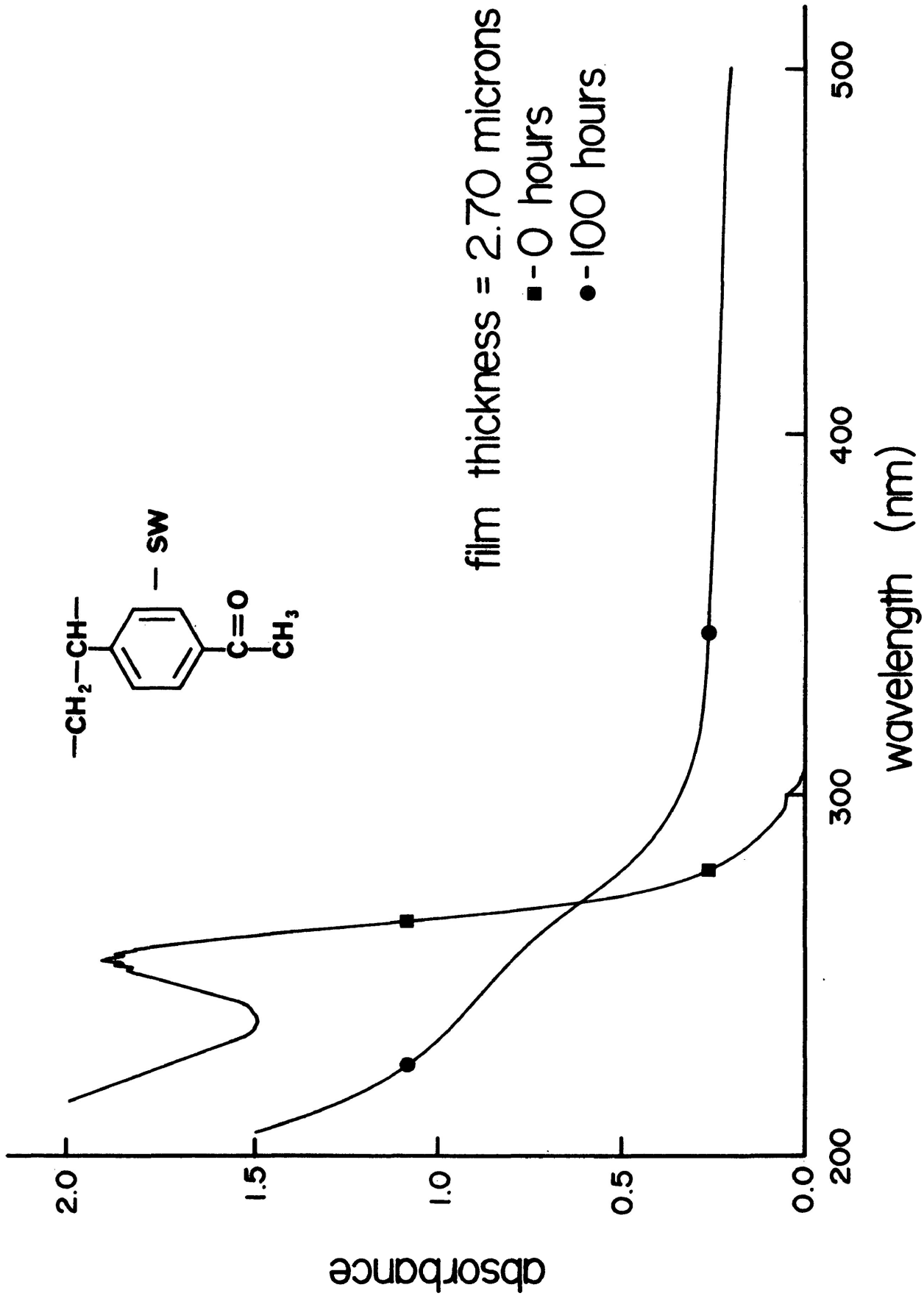


Figure 3.18 - U. V. Spectra of Poly(vinylacetophenone) Film Before and After 100 Hours Exposure to Long-wave Radiation:

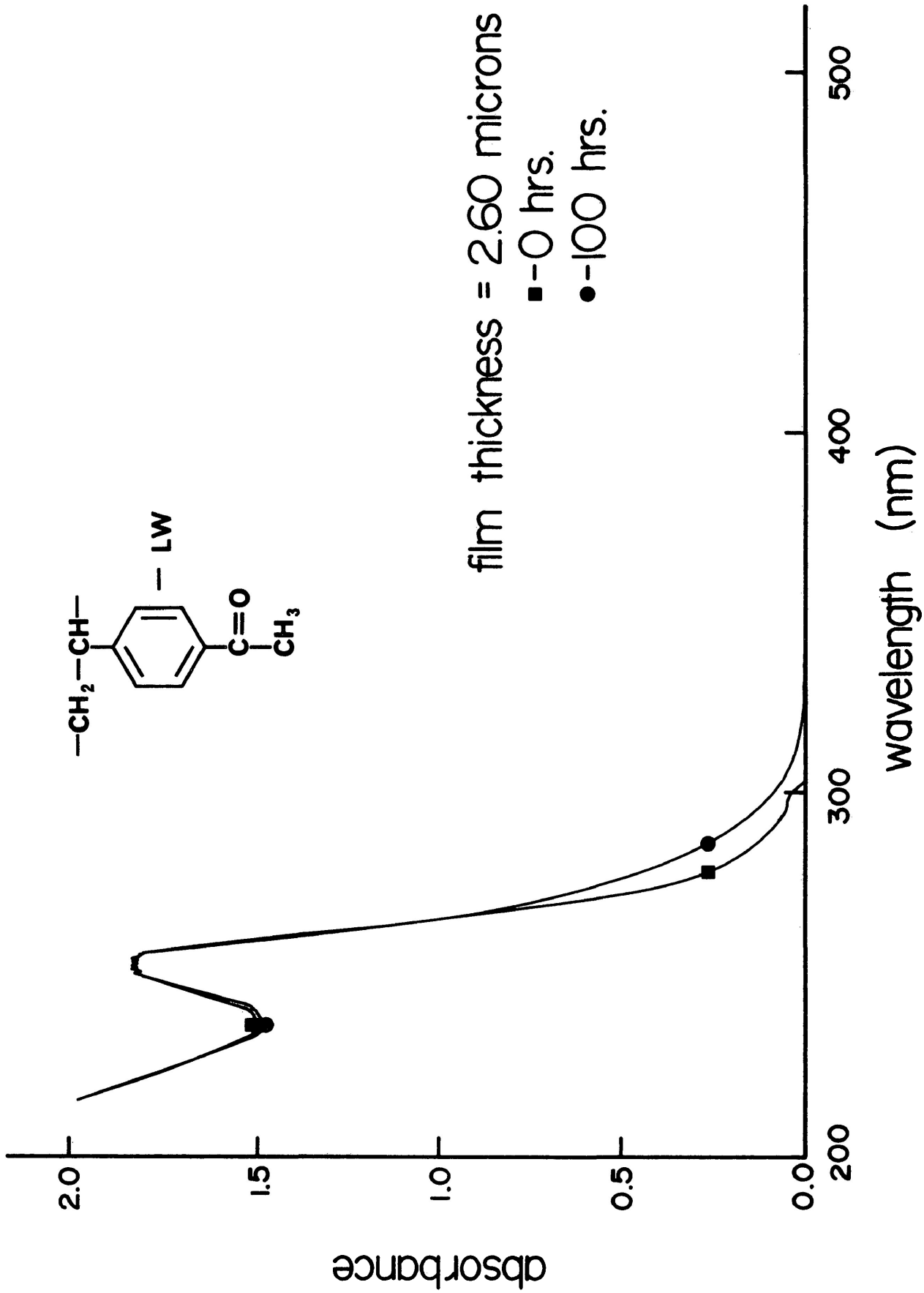


Figure 3.19 - U. V. Spectra of Poly(p-bromostyrene) Film Before and After 100 Hours Irradiation:

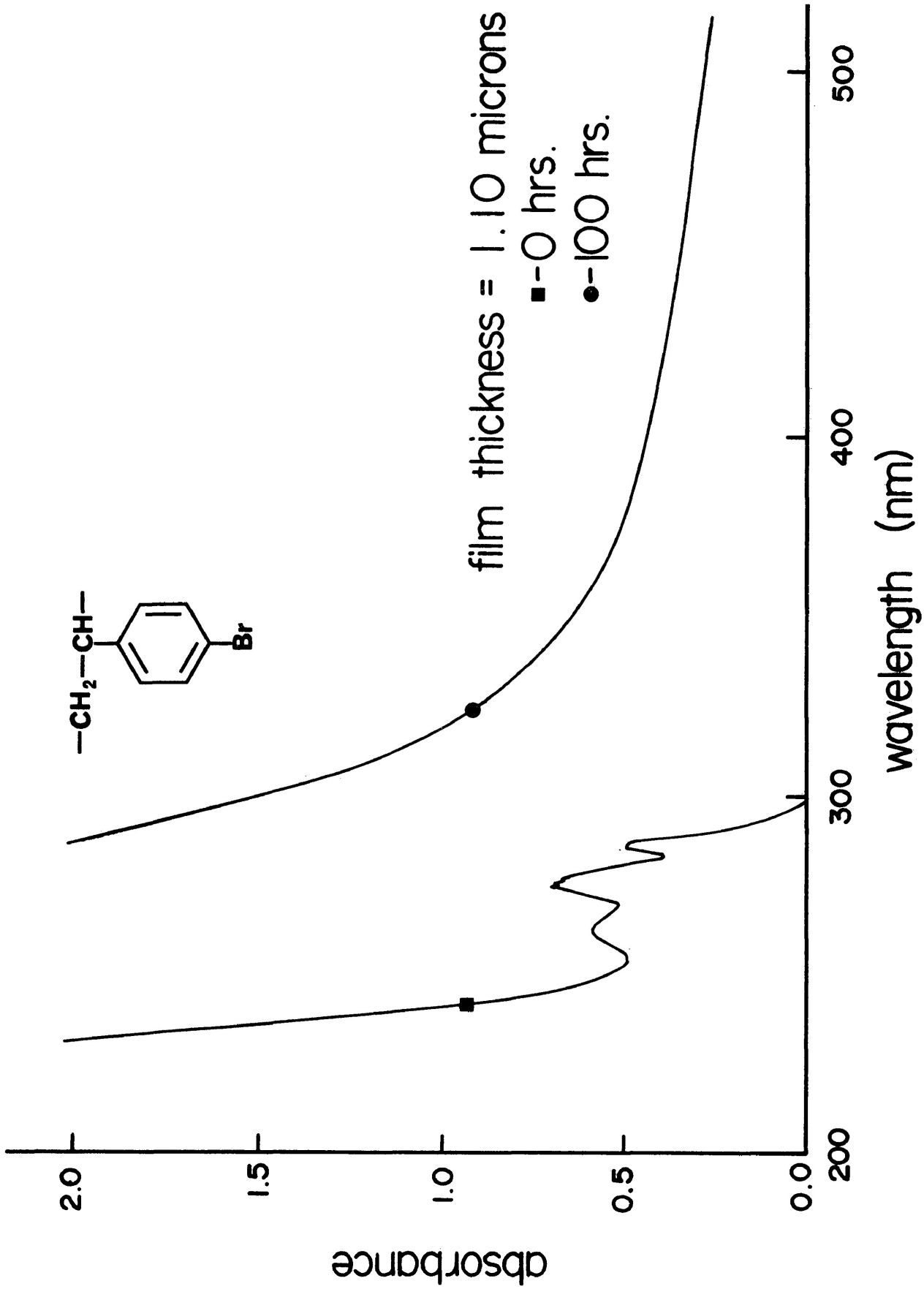


Figure 3.20 - U. V. Spectra of Poly(p-chlorostyrene) Film Before and After 100 Hours Irradiation:

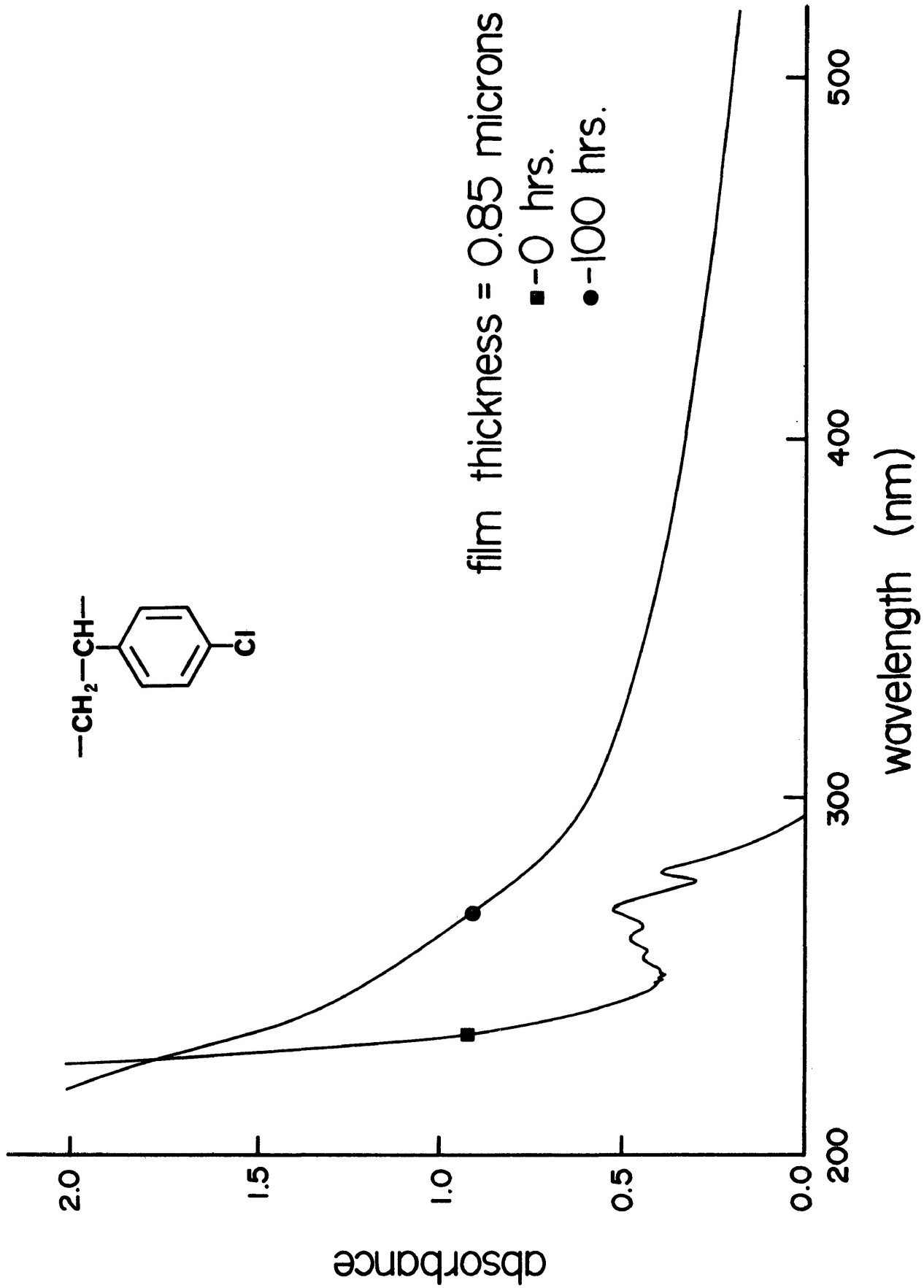


Figure 3.21 - U. V. Spectra of Poly(p-fluorostyrene) Film Before and After 100 Hours Irradiation:

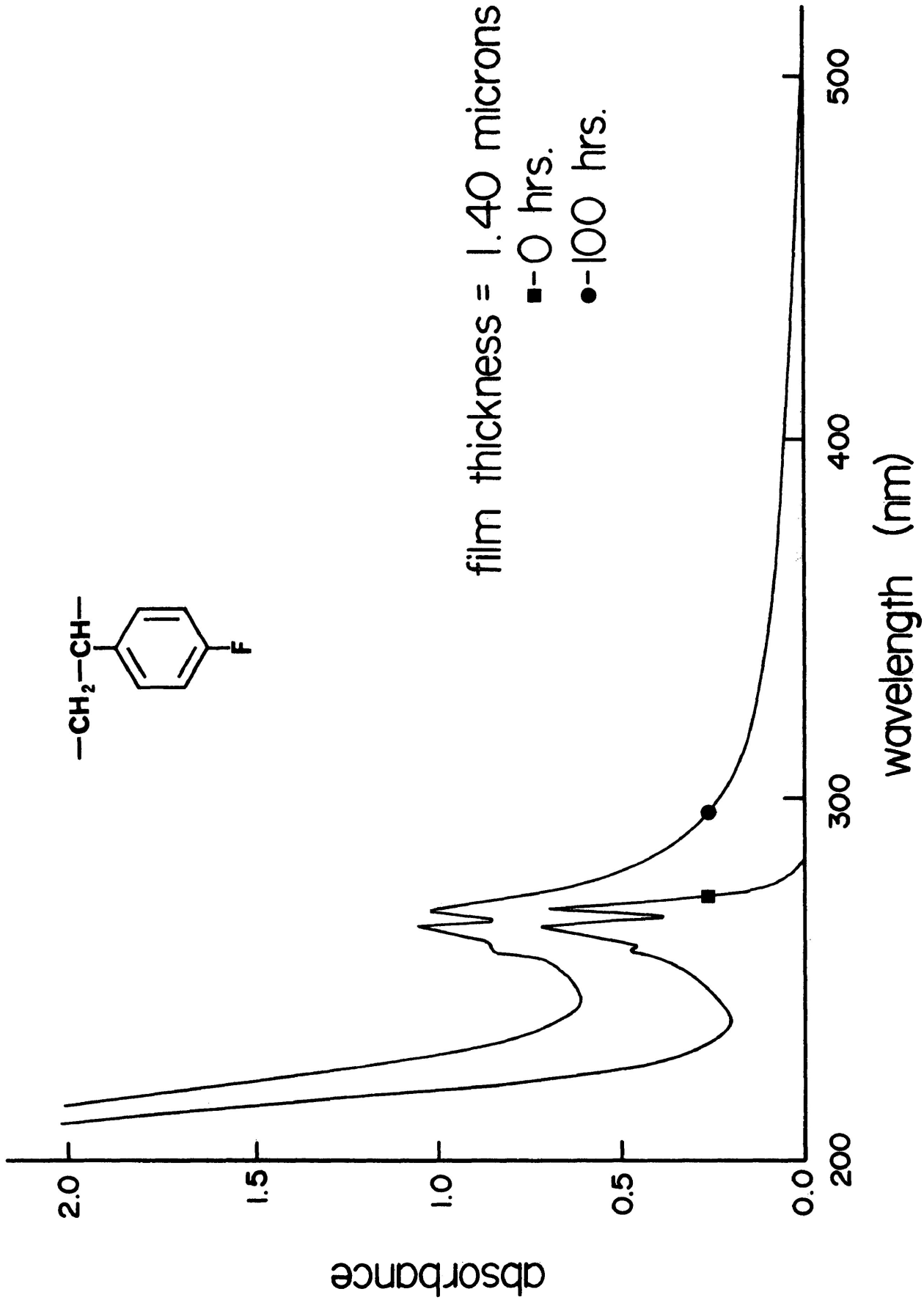


Figure 3.22 - U. V. Spectra of Poly(p-isopropylstyrene) Film Before and After 100 Hours Irradiation:

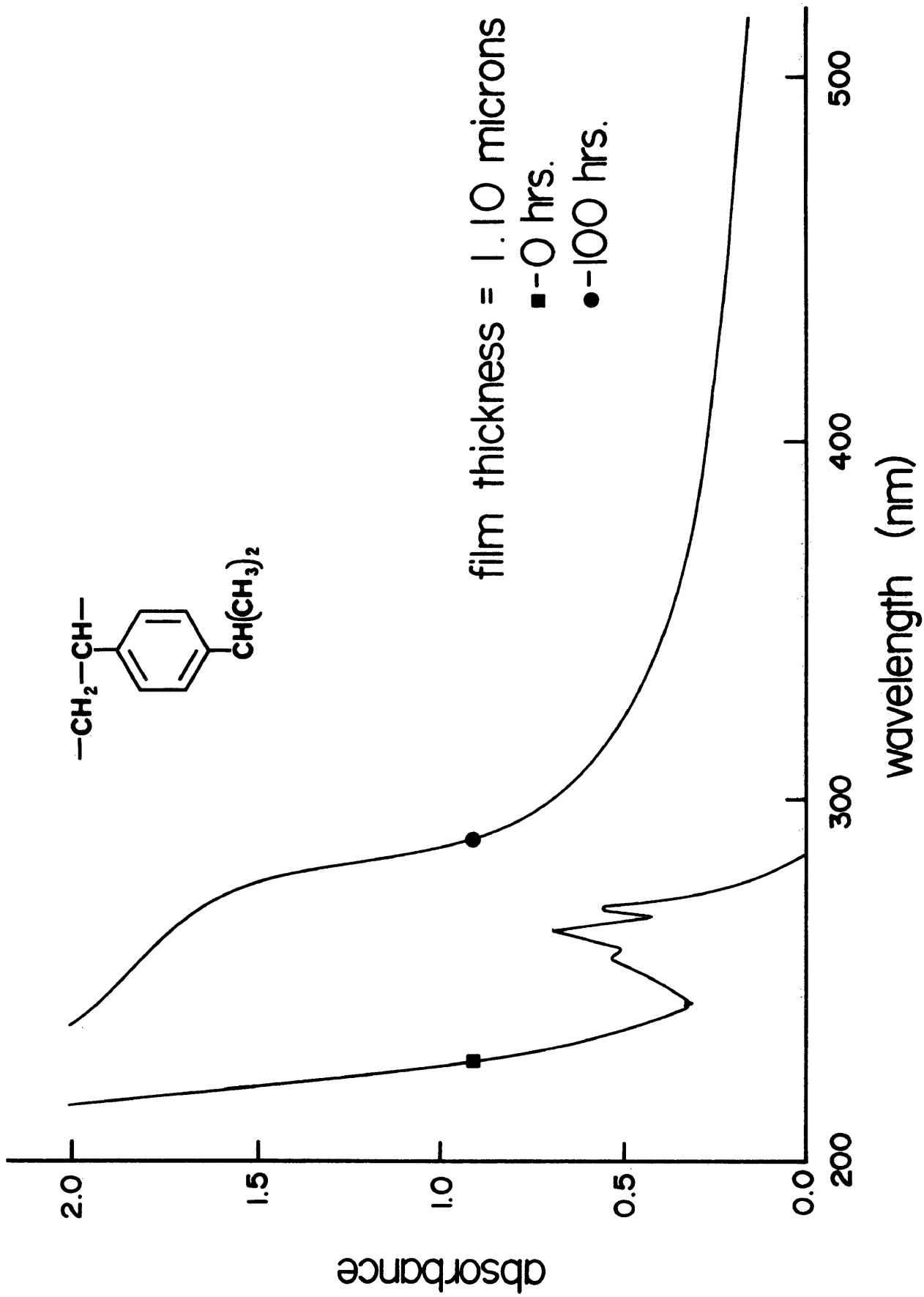


Figure 3.23 - U. V. Spectra of Poly(p-methoxystyrene) Film Before and After 100 Hours Irradiation:

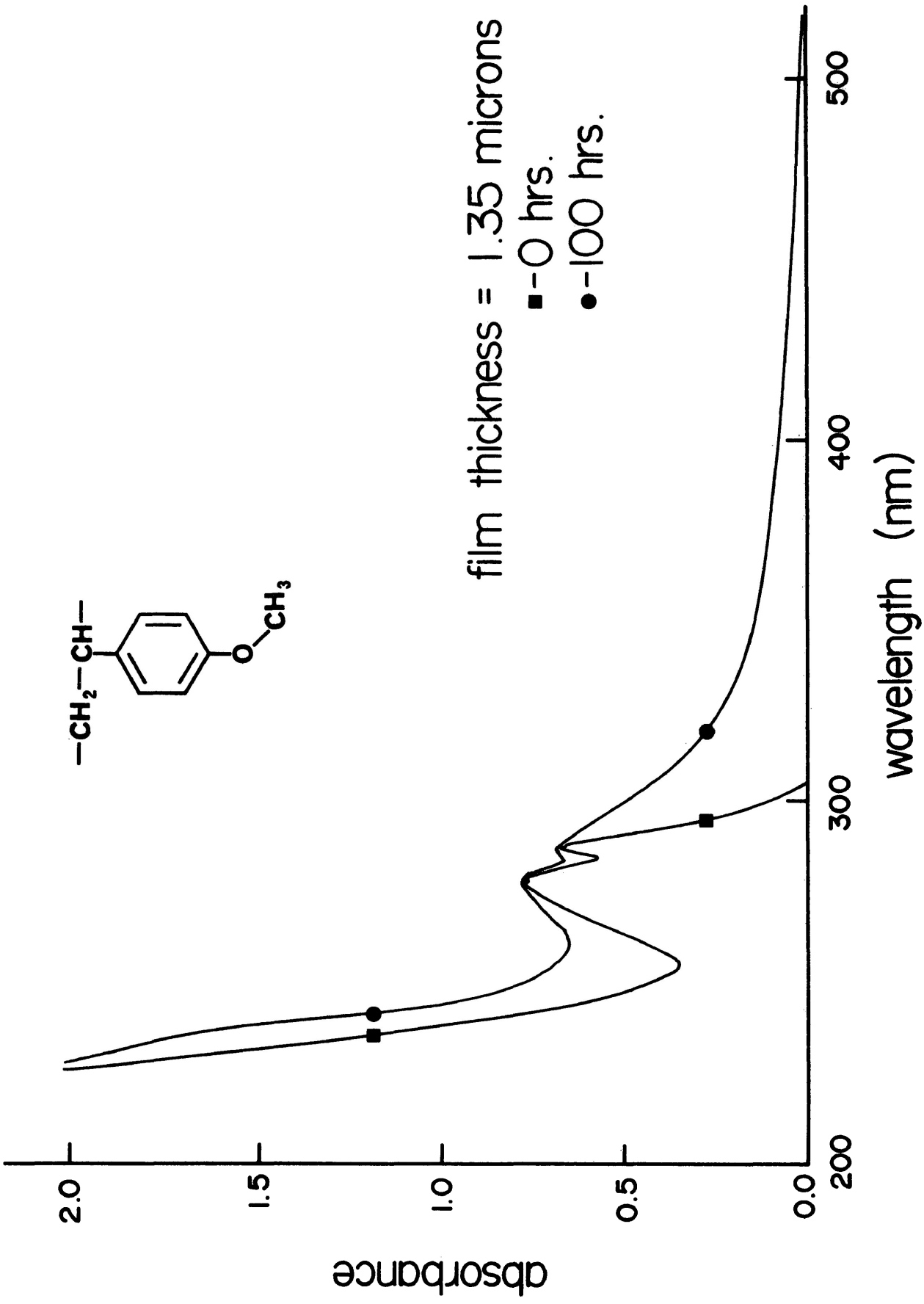


Figure 3.24 - U. V. Spectra of Poly(p-*tert*-butylstyrene) Film Before and After 100 Hours Irradiation:

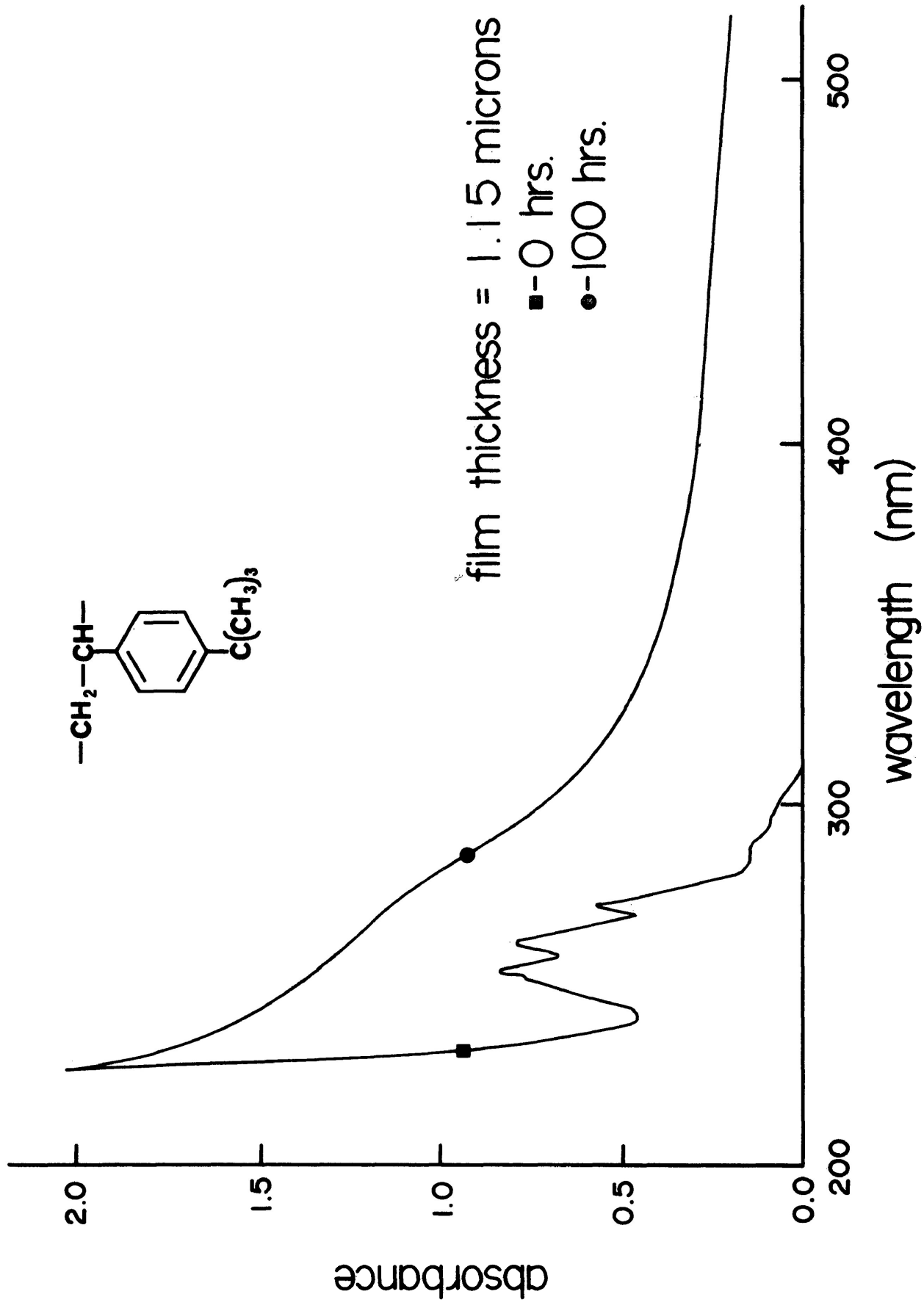


Figure 3.25 - Changes in Absorbance at 400nm for the Para-substituted Styrene Polymers:★

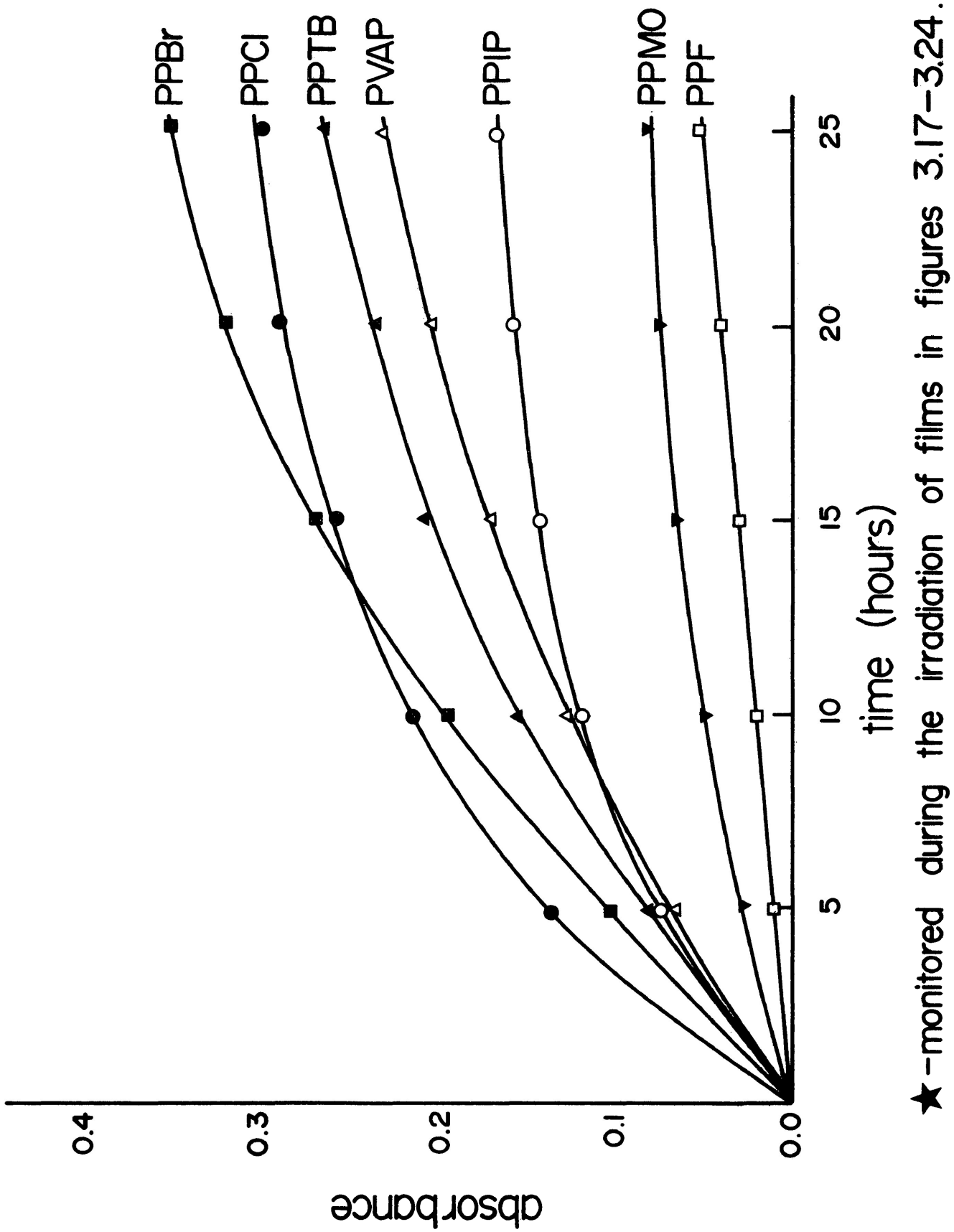


Figure 3.26 - Fluorescence Spectra of Poly(vinylacetophenone) Film Before and After 100 Hours Exposure to Short-wave Radiation:

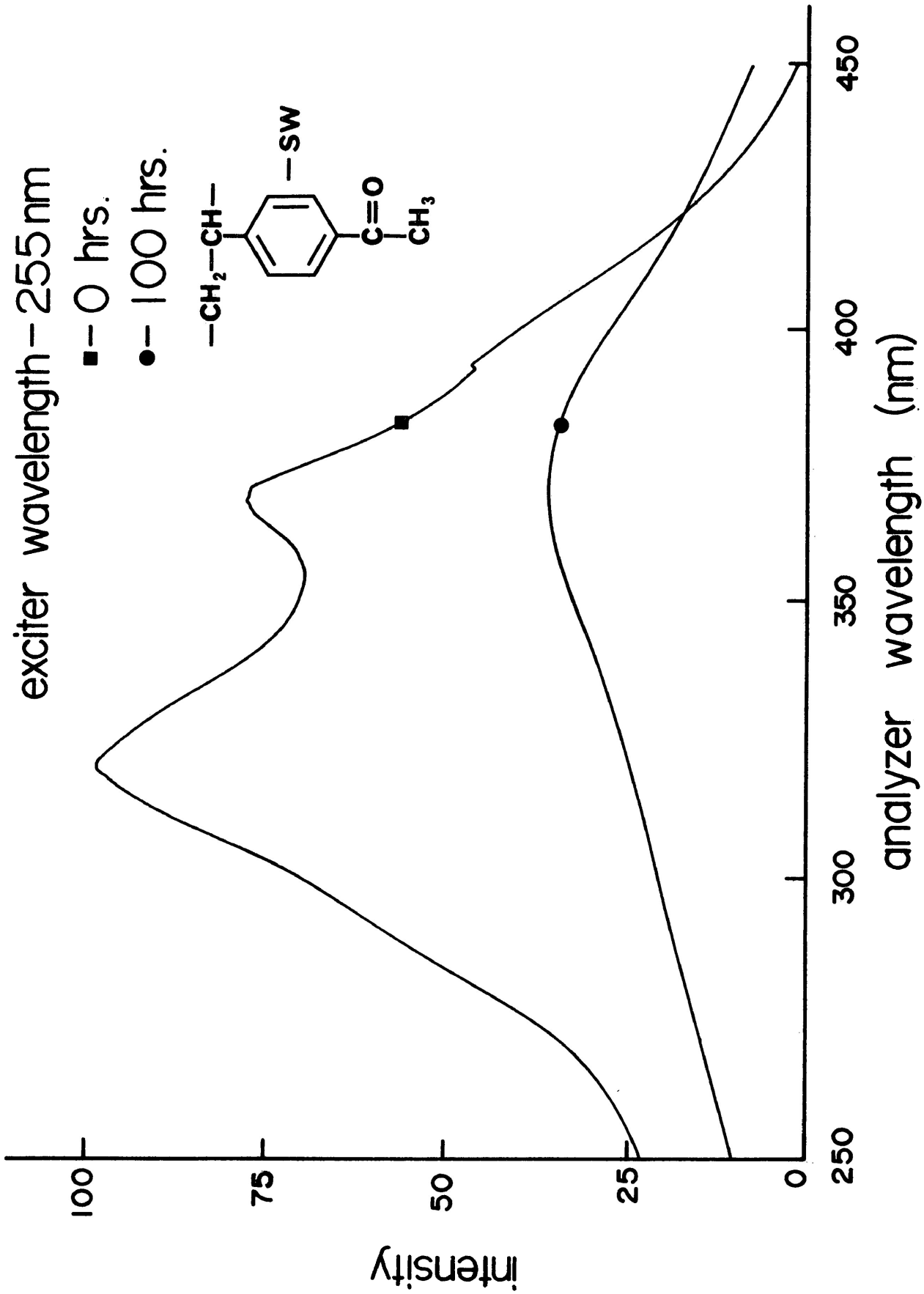


Figure 3.27 - Fluorescence Spectra of Poly(vinylacetophenone) Film Before and After 100 Hours Exposure to Long-wave Radiation:

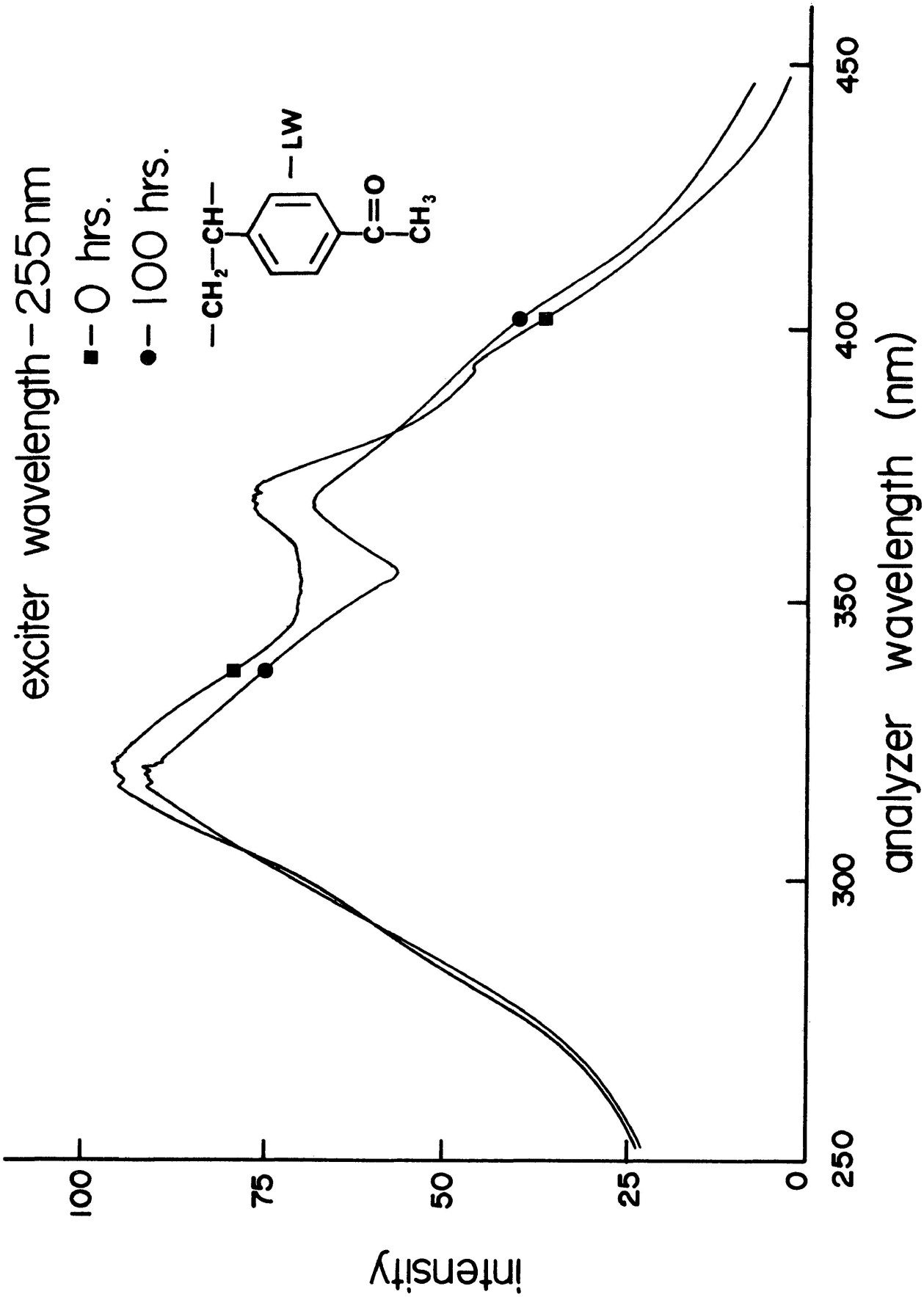


Figure 3.28 - Fluorescence Spectra of Poly(p-bromostyrene) Film Before and After 100 Hours Irradiation:

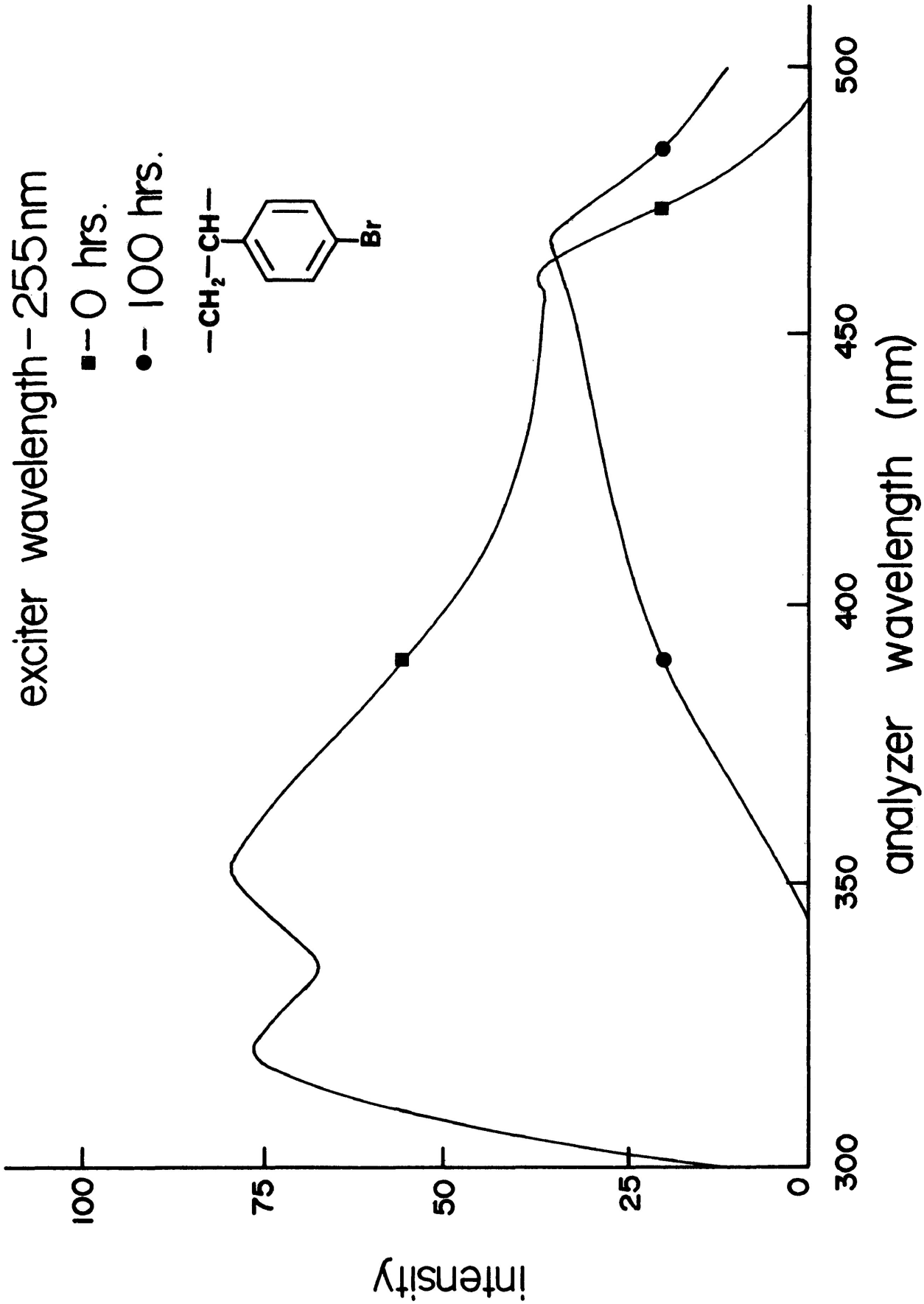


Figure 3.29 - Fluorescence Spectra of Poly(p-chlorostyrene) Film Before and After 100 Hours Irradiation:

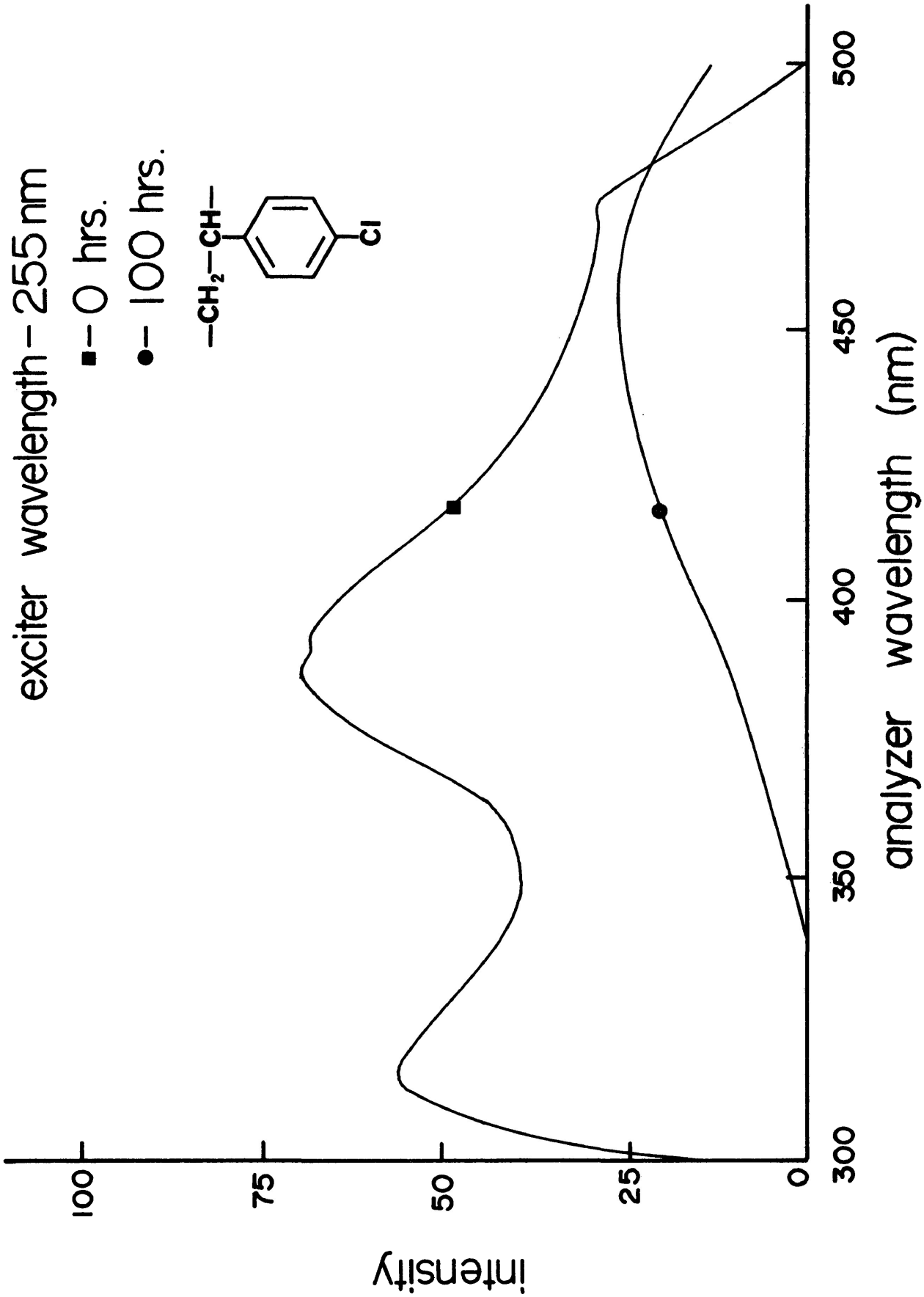


Figure 3.30 - Fluorescence Spectra of Poly(p-fluorostyrene) Film Before and After 100 Hours Irradiation:

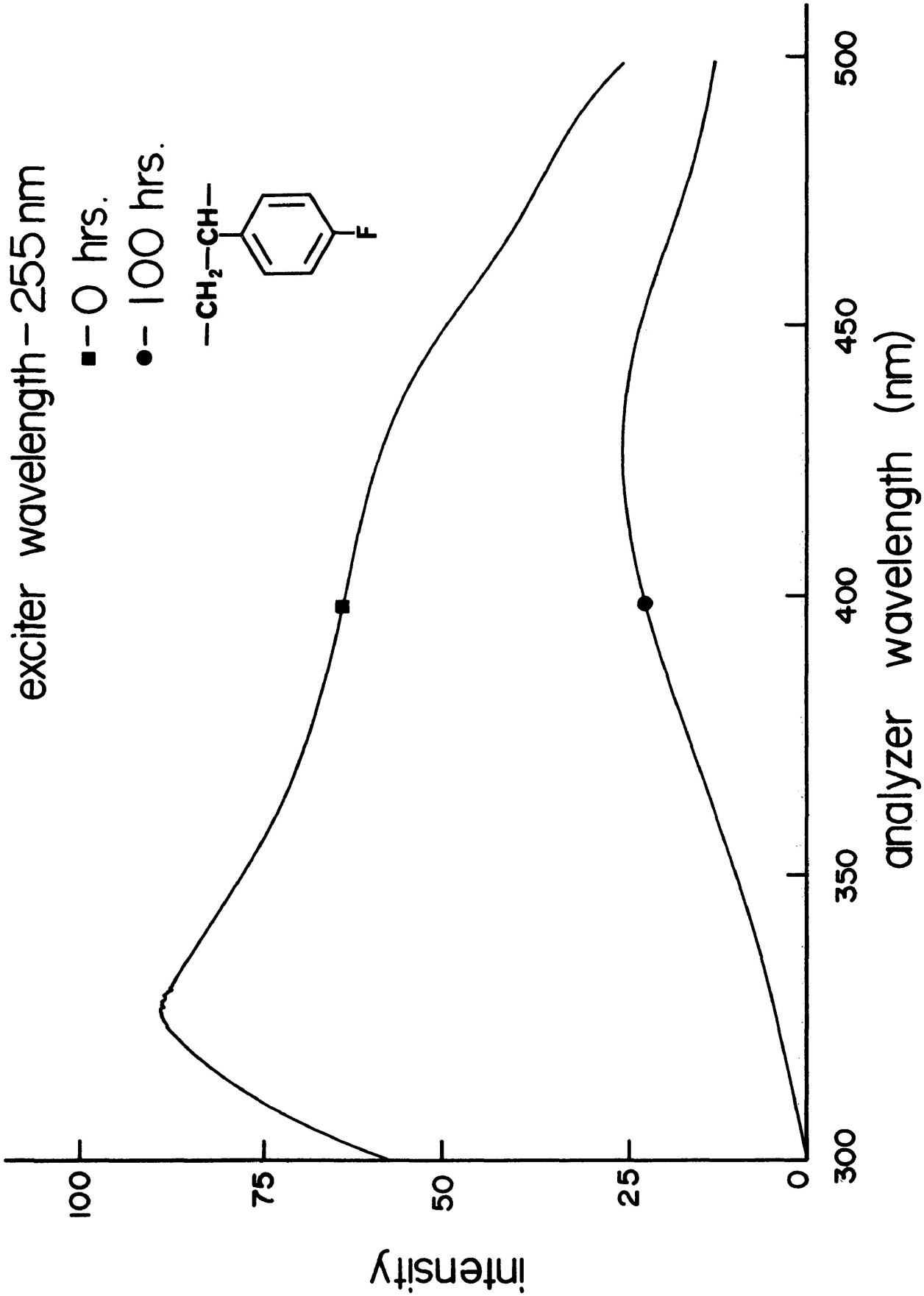


Figure 3.31 - Fluorescence Spectra of Poly(p-isopropylstyrene) Film Before and After 100 Hours Irradiation:

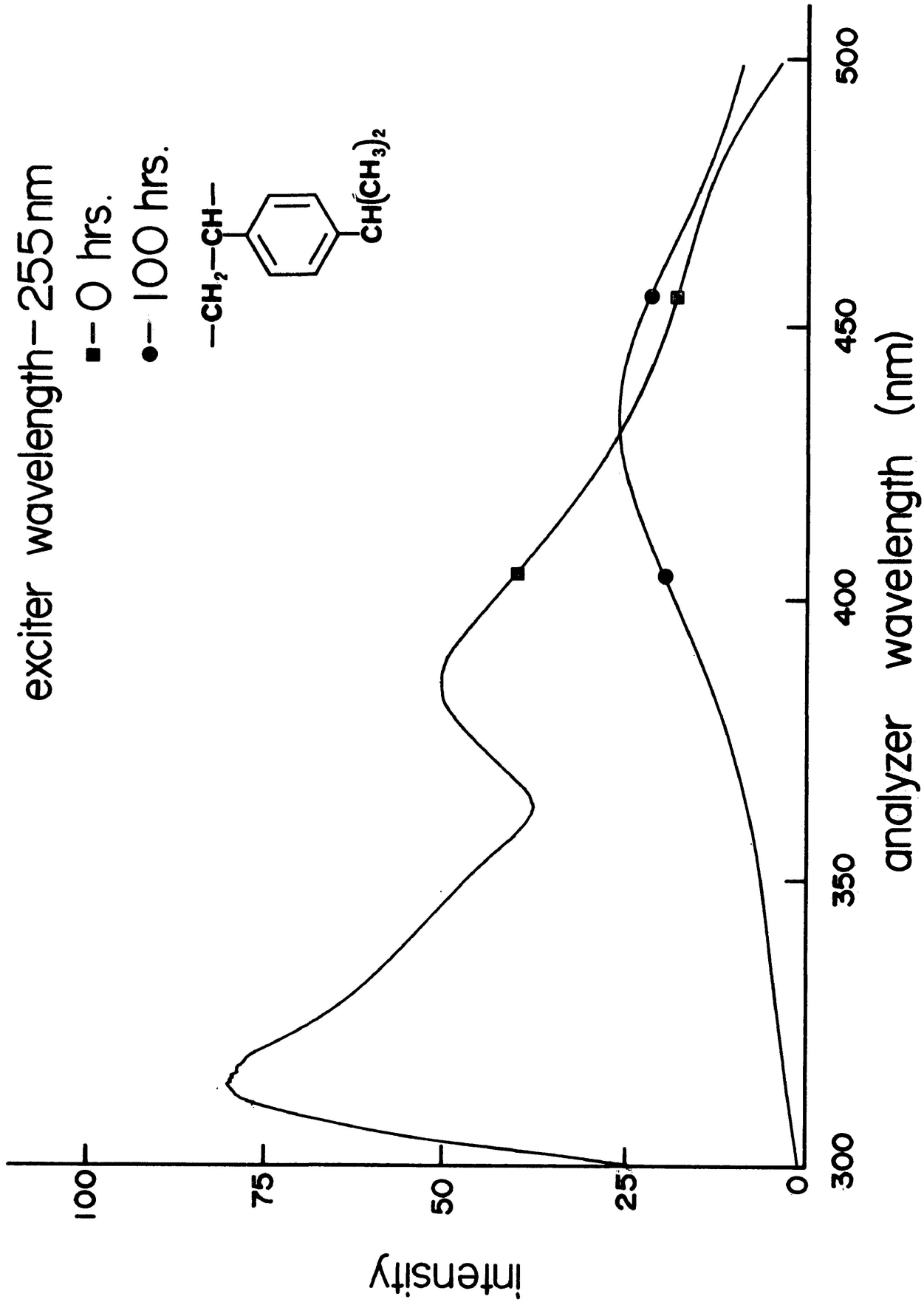


Figure 3.32 - Fluorescence Spectra of Poly(p-methoxystyrene) Film Before and After 100 Hours Irradiation:

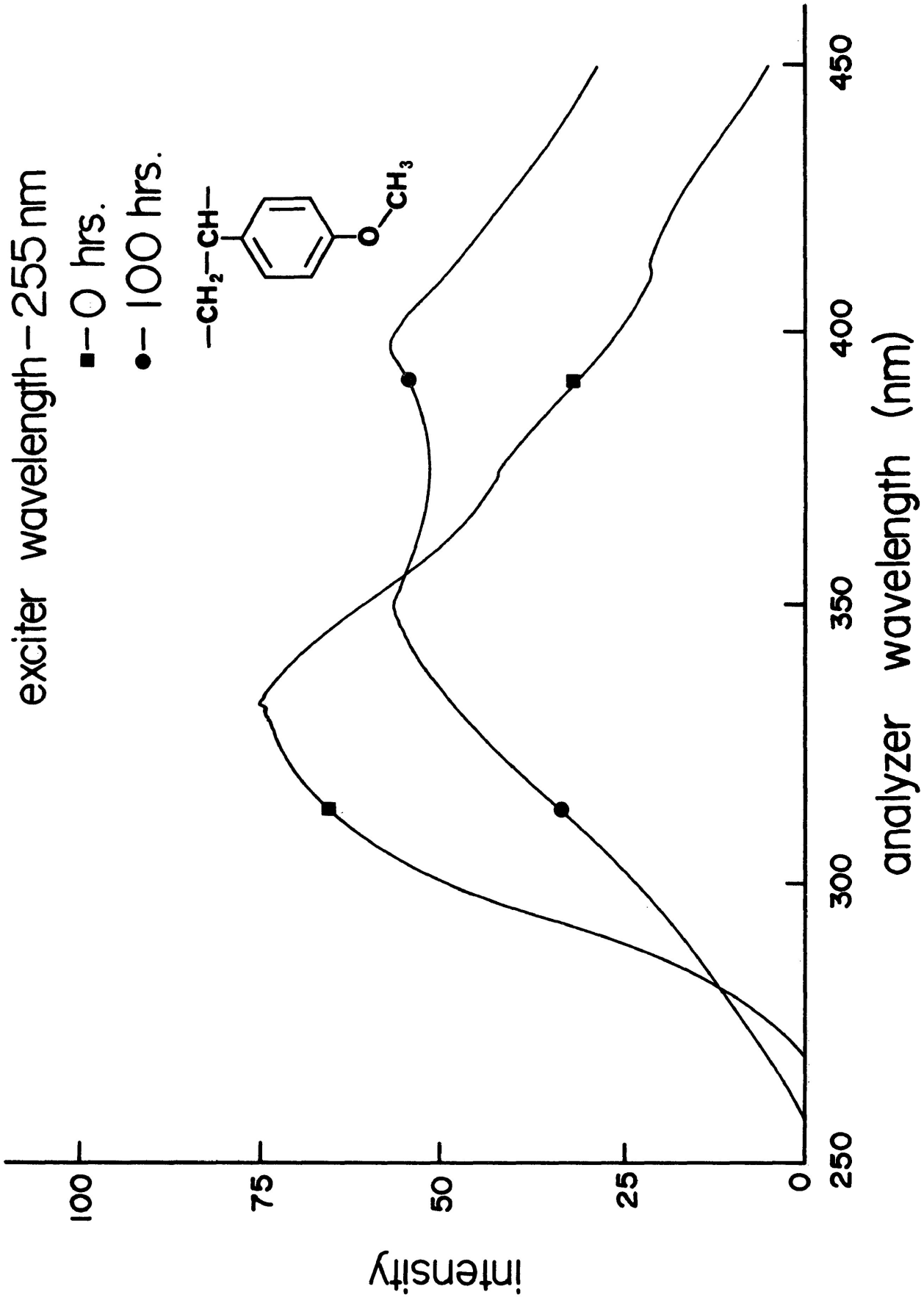


Figure 3.33 - Fluorescence Spectra of Poly(p-*tert*-butylstyrene) Film Before and After 100 Hours Irradiation:

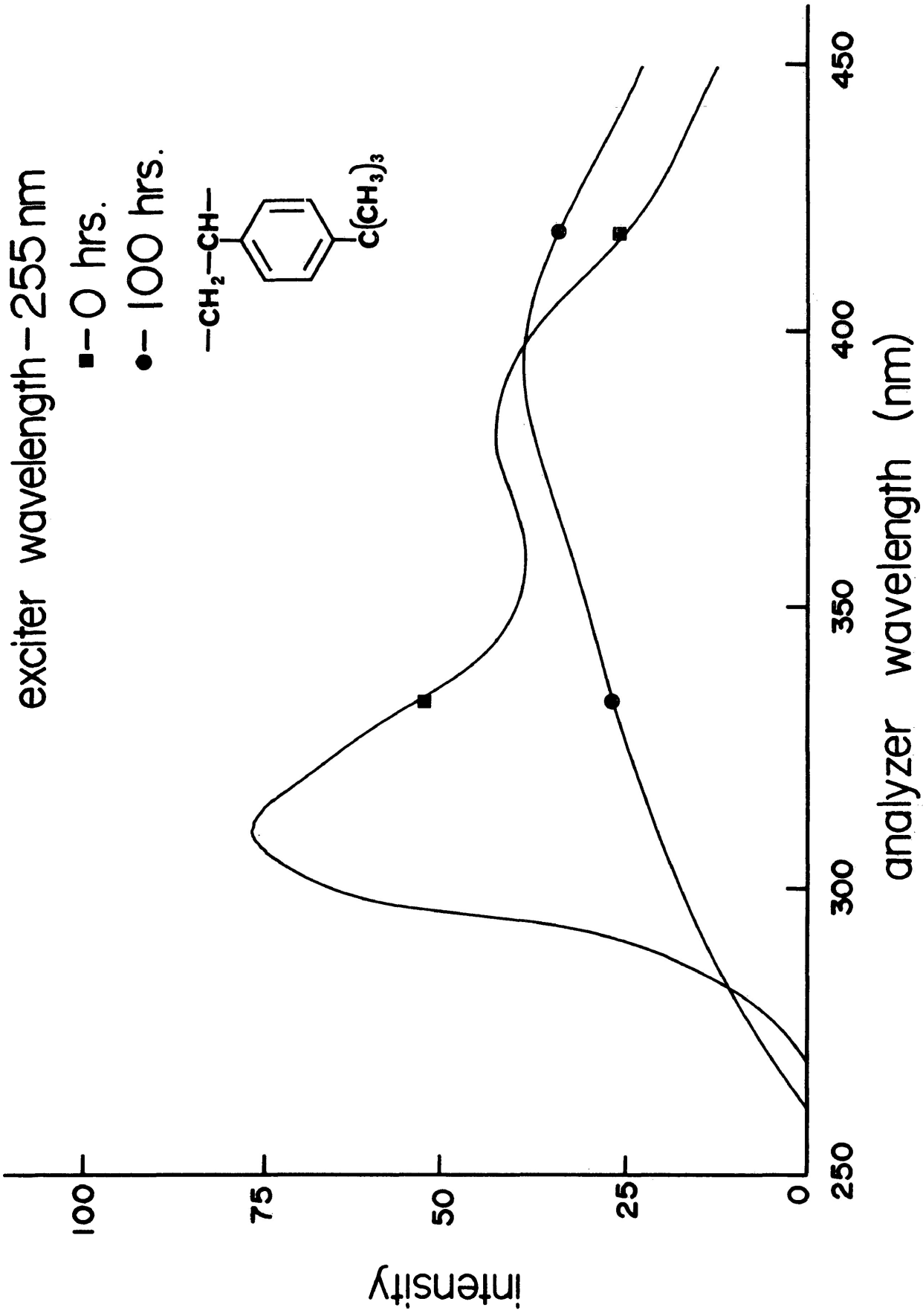


Figure 3.34 - Volatile Products from Poly(vinylacetophenone) as a Function of Short-wave Irradiation Time:

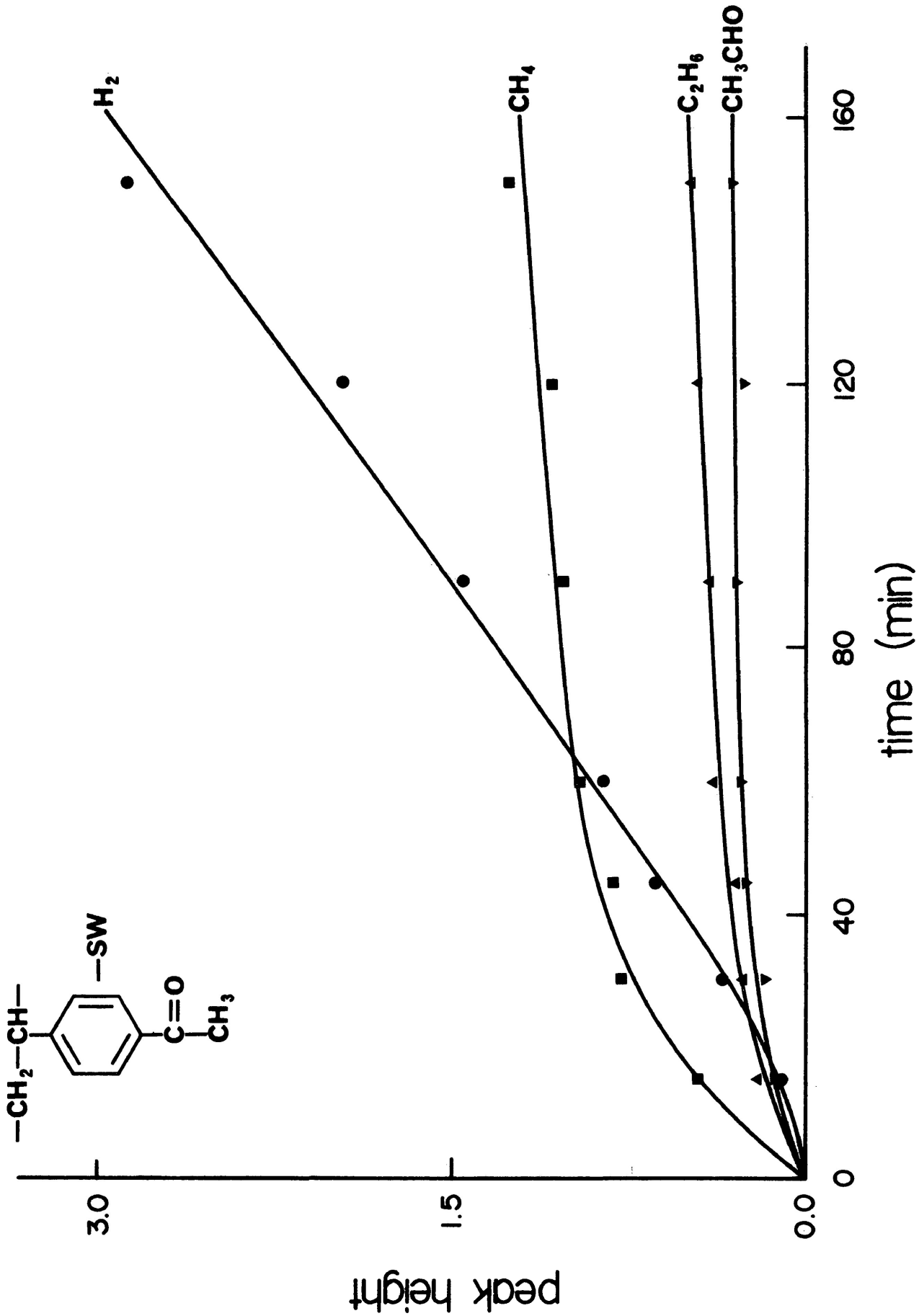


Figure 3.35 - Volatile Products from Poly(vinylacetophenone) as a Function of Long-wave Irradiation Time:

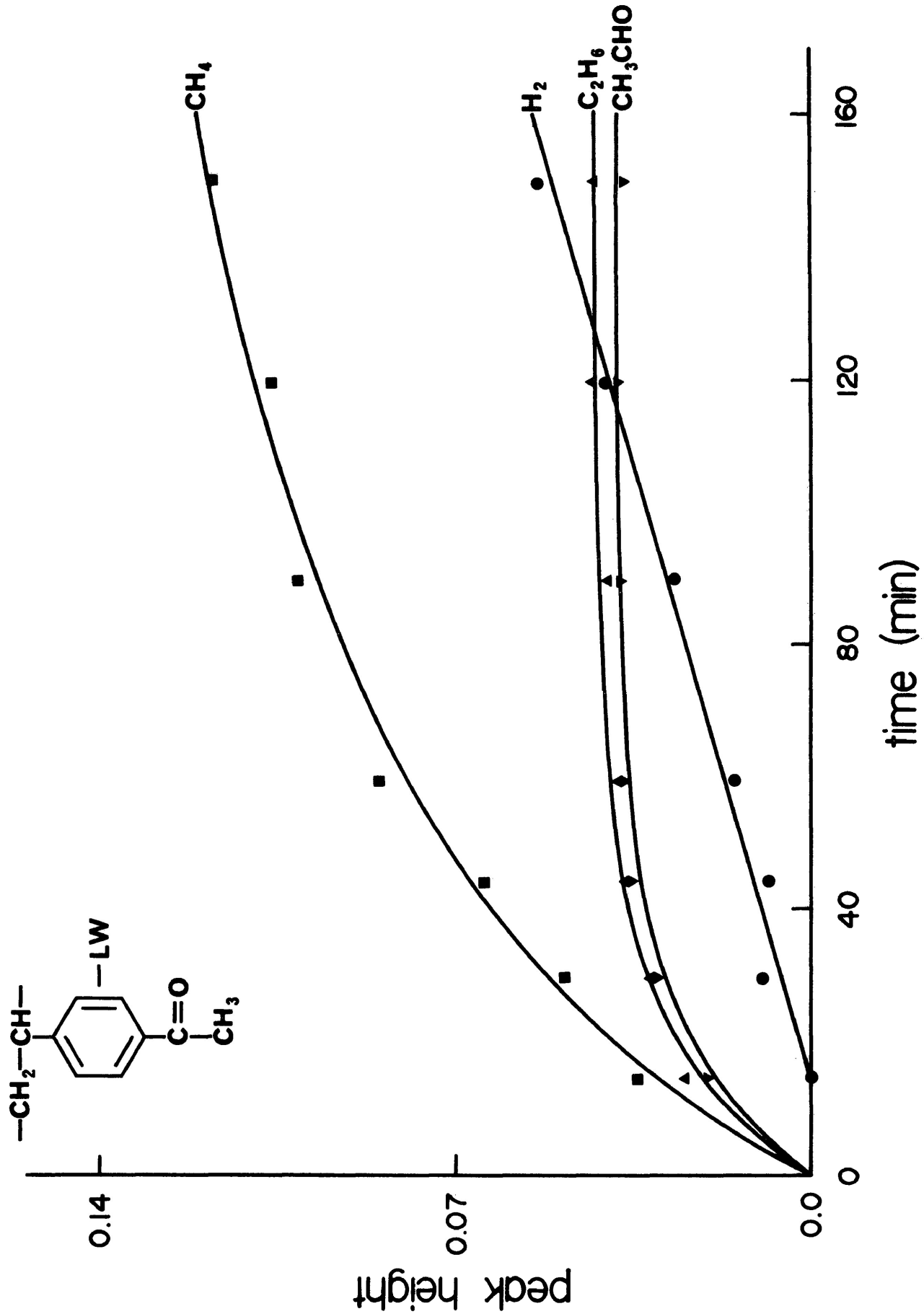


Figure 3.36 - Volatile Products from Poly(p-bromostyrene) as a Function of Irradiation Time:

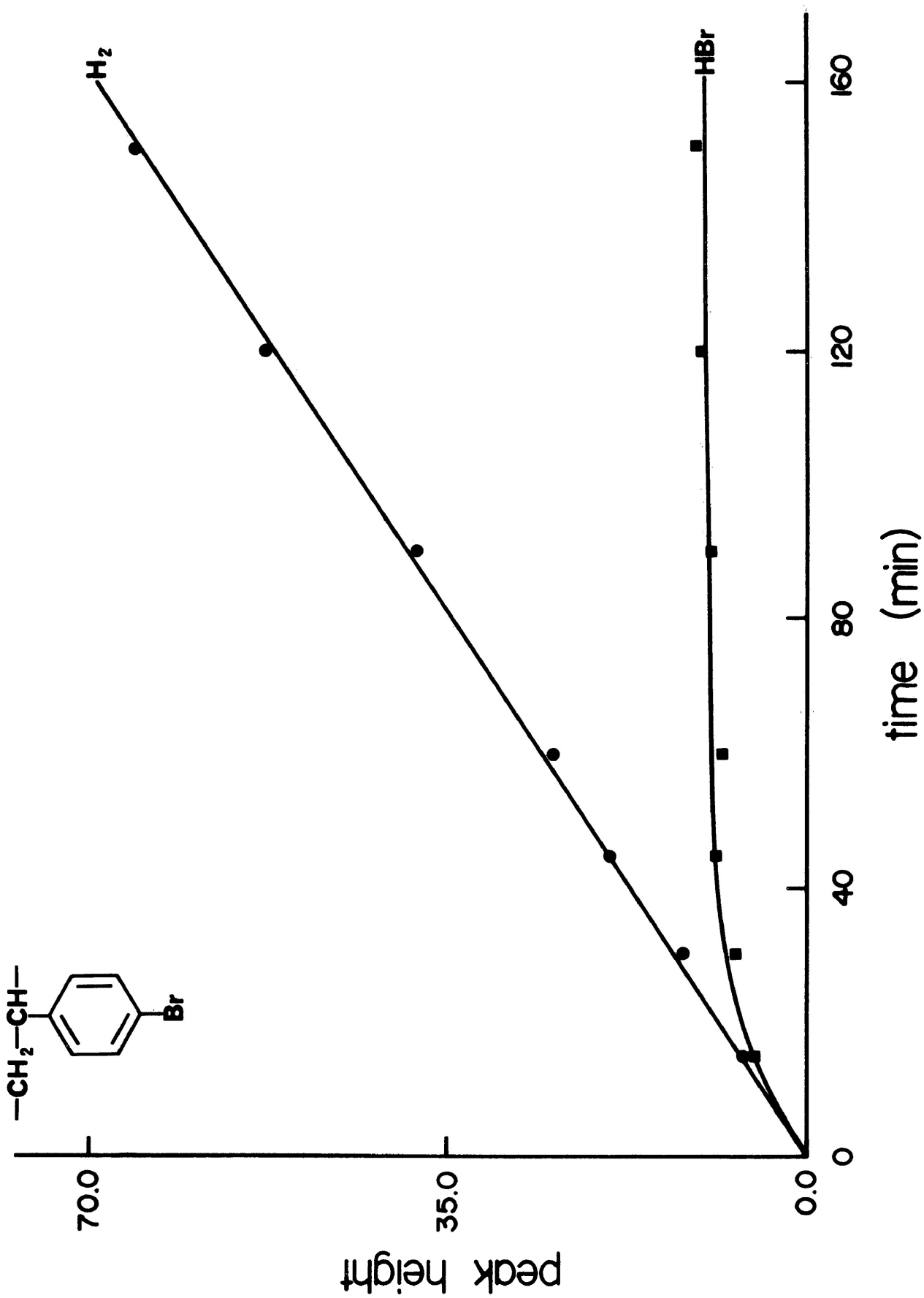


Figure 3.37 - Volatile Products from Poly(p-chlorostyrene) as a Function of Irradiation Time:

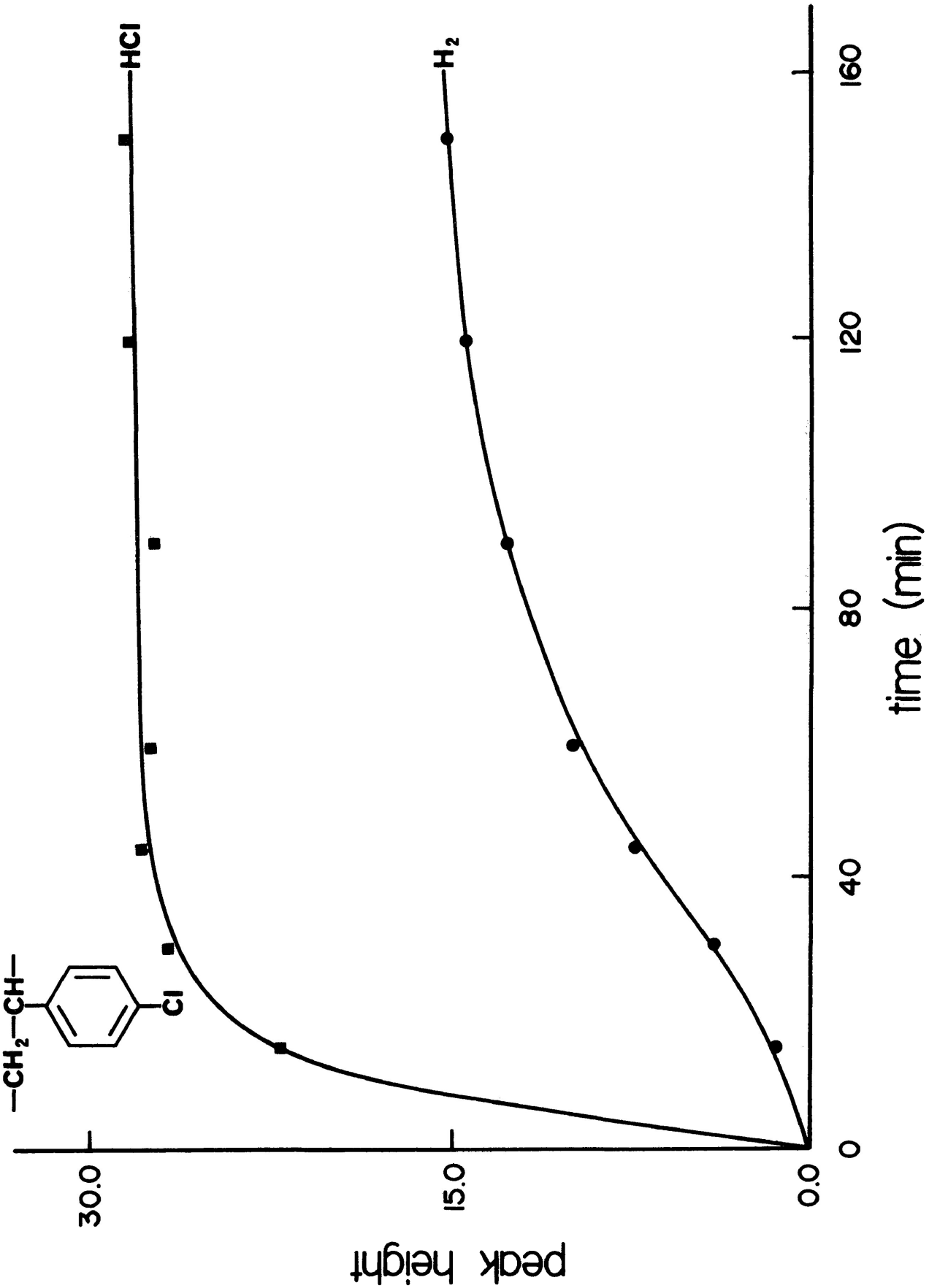


Figure 3.38 - Volatile Products from Poly(p-fluorostyrene) as a Function of Irradiation Time:

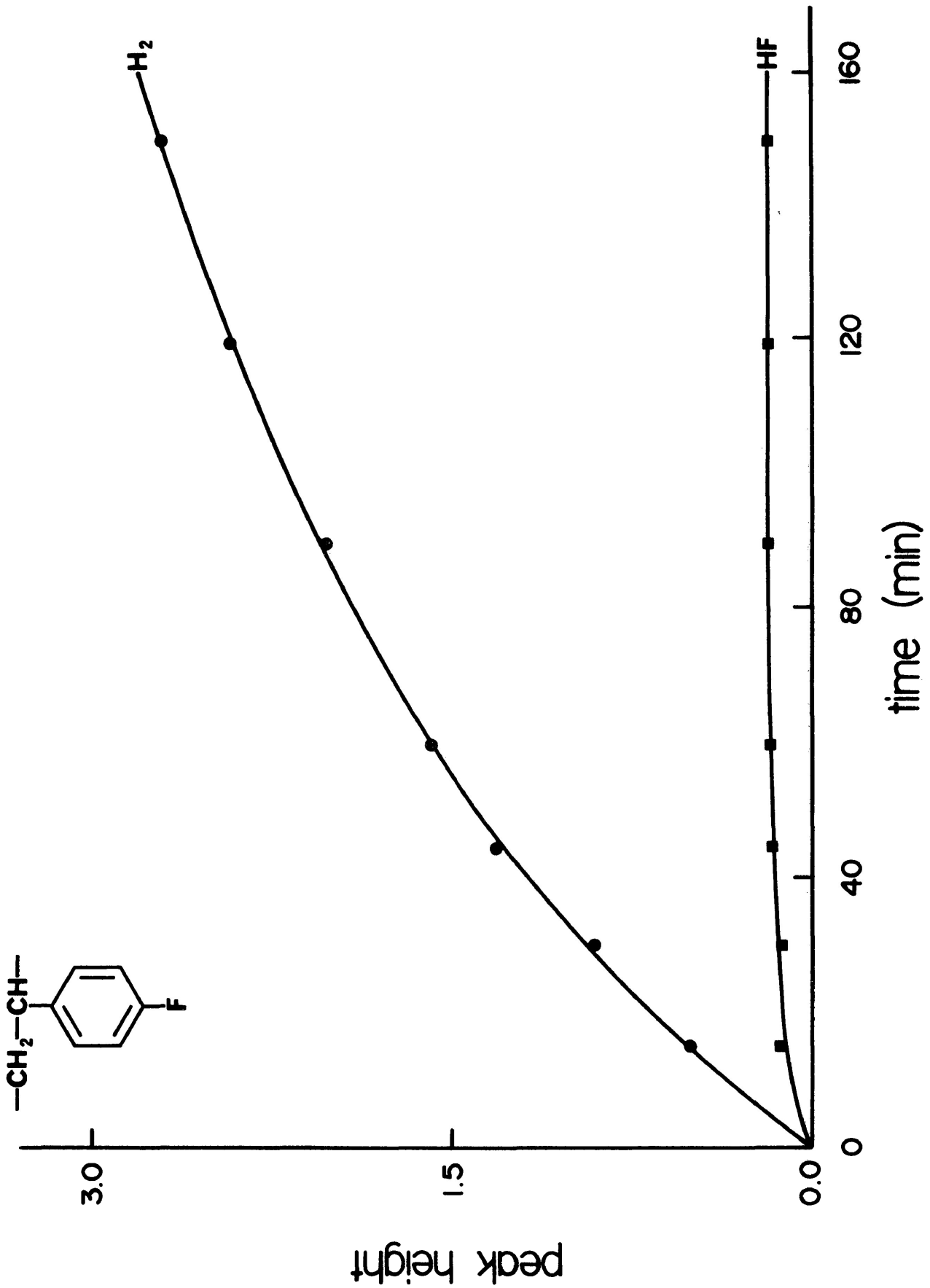


Figure 3.39 - Volatile Products from Poly(p-isopropylstyrene) as a Function of Irradiation Time:

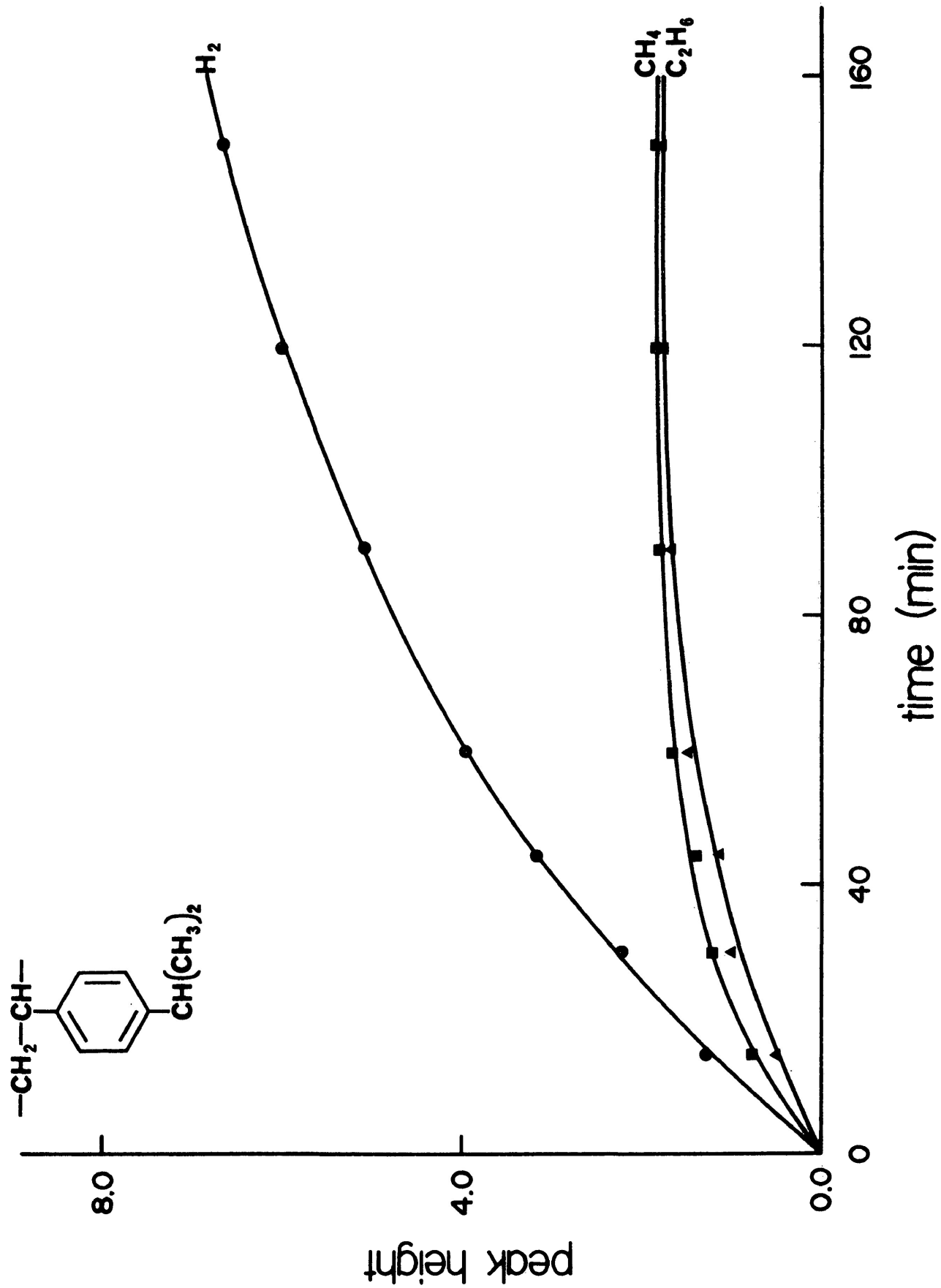


Figure 3.40 - Volatile Products from Poly(p-methoxystyrene) as a Function of Irradiation Time:

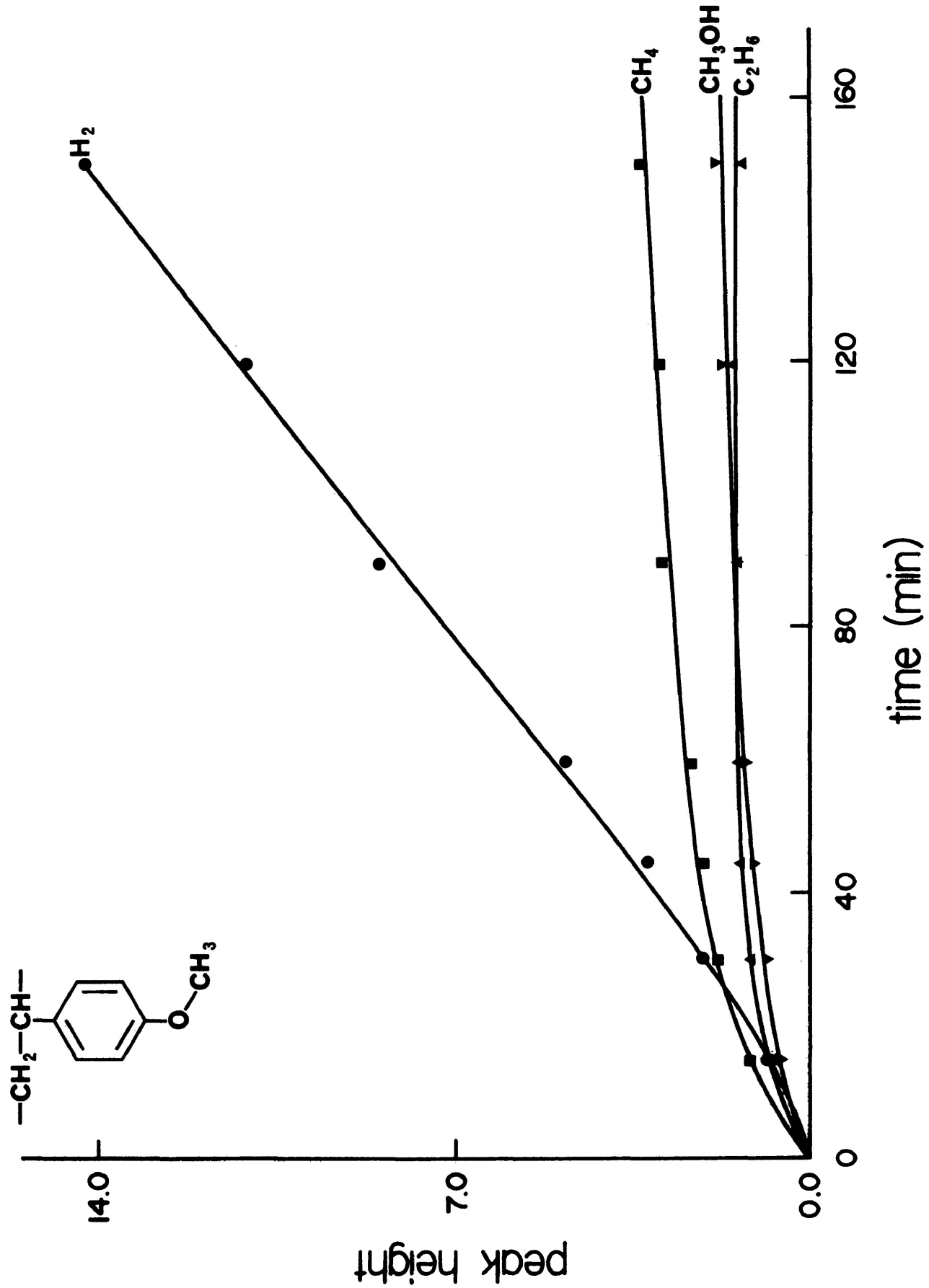


Figure 3.41 - Volatile Products from Poly(p-*tert*-butylstyrene) as a Function of Irradiation Time:

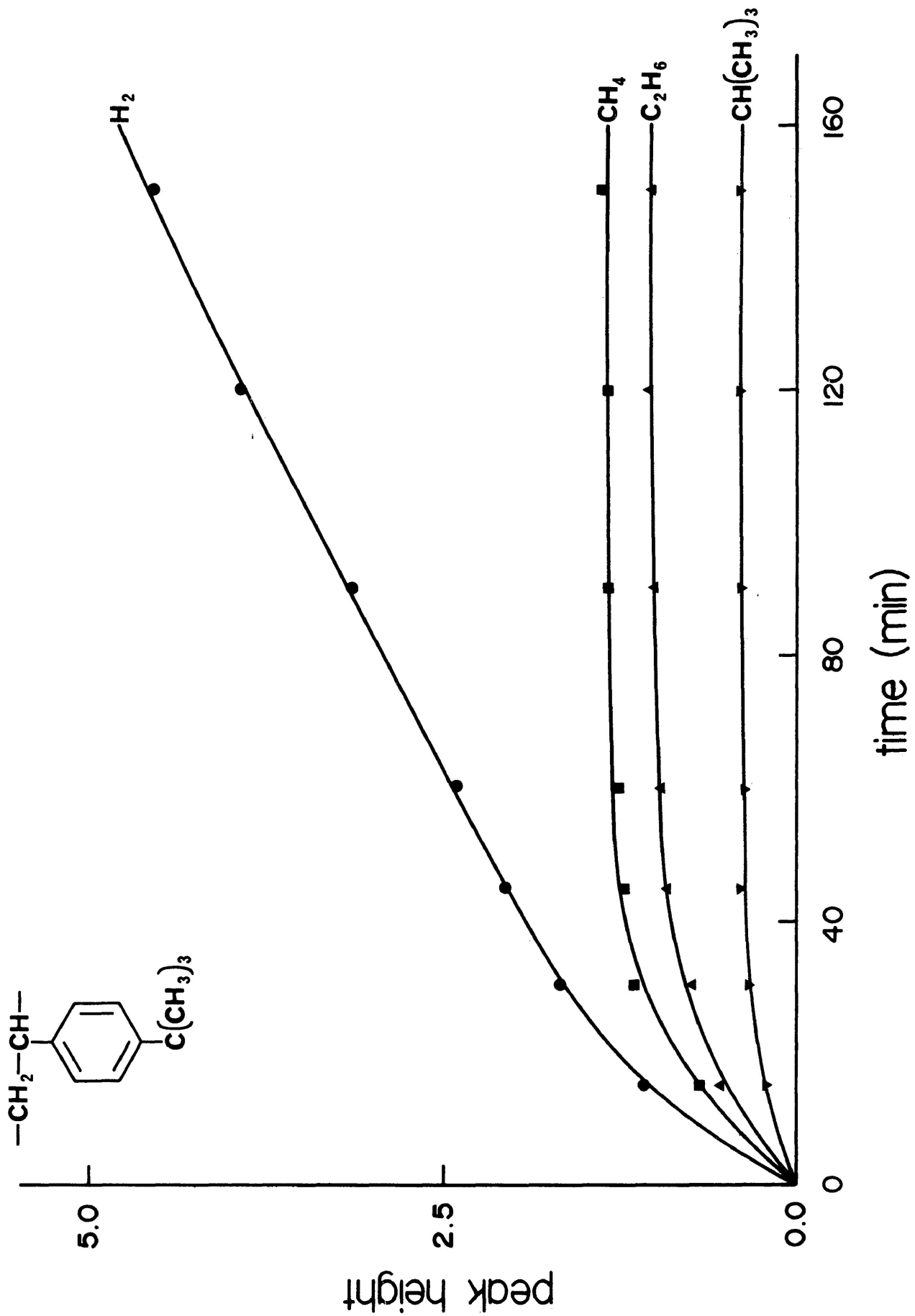


Figure 3.42 - Volatile Products from Poly(vinylacetophenone) as a Function of Temperature Following 2.5 Hours Exposure to Short-wave Radiation:

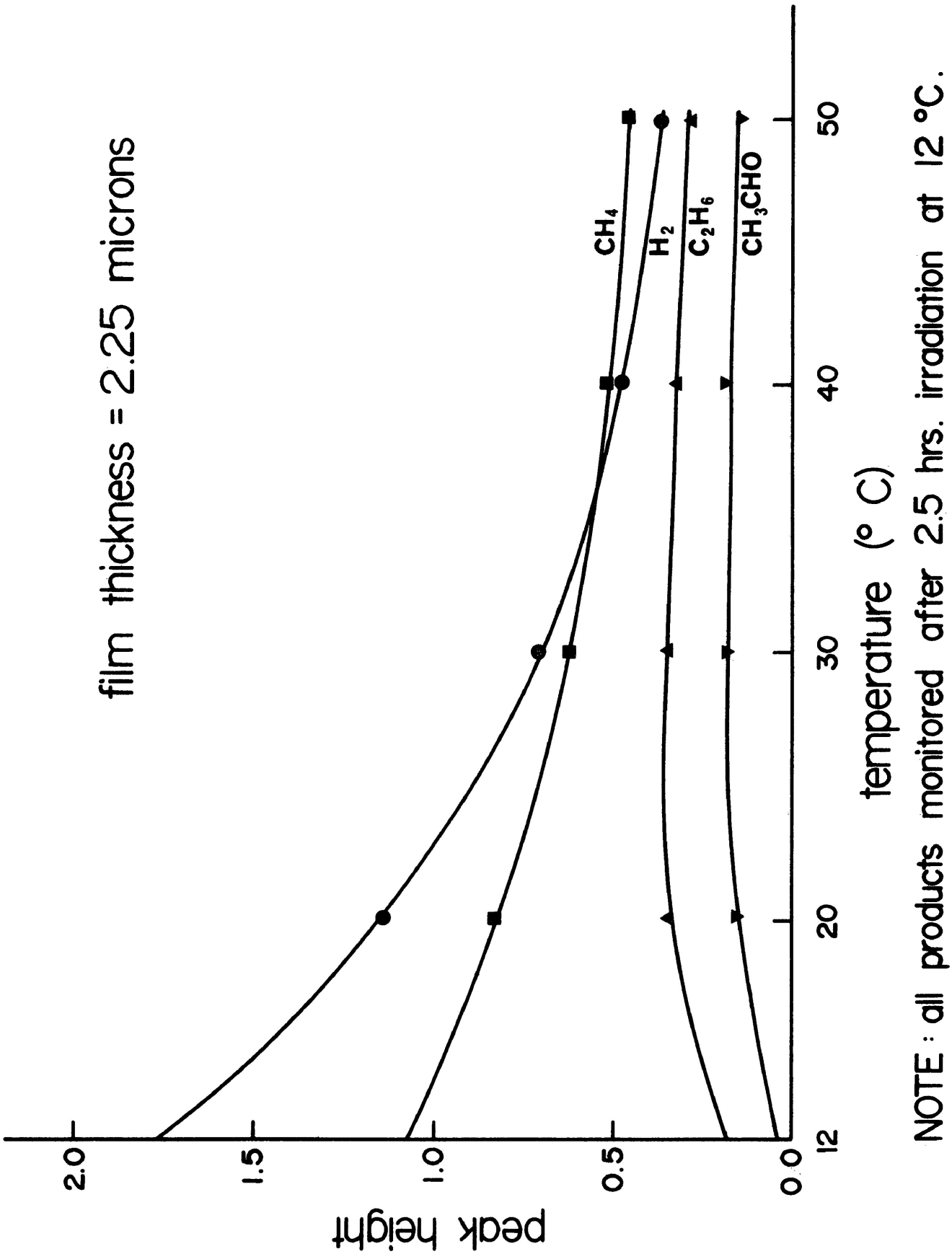


Figure 3.43 - Volatile Products from Poly(vinylacetophenone) as a Function of Temperature Following 2.5 Hours Exposure to Long-wave Radiation:

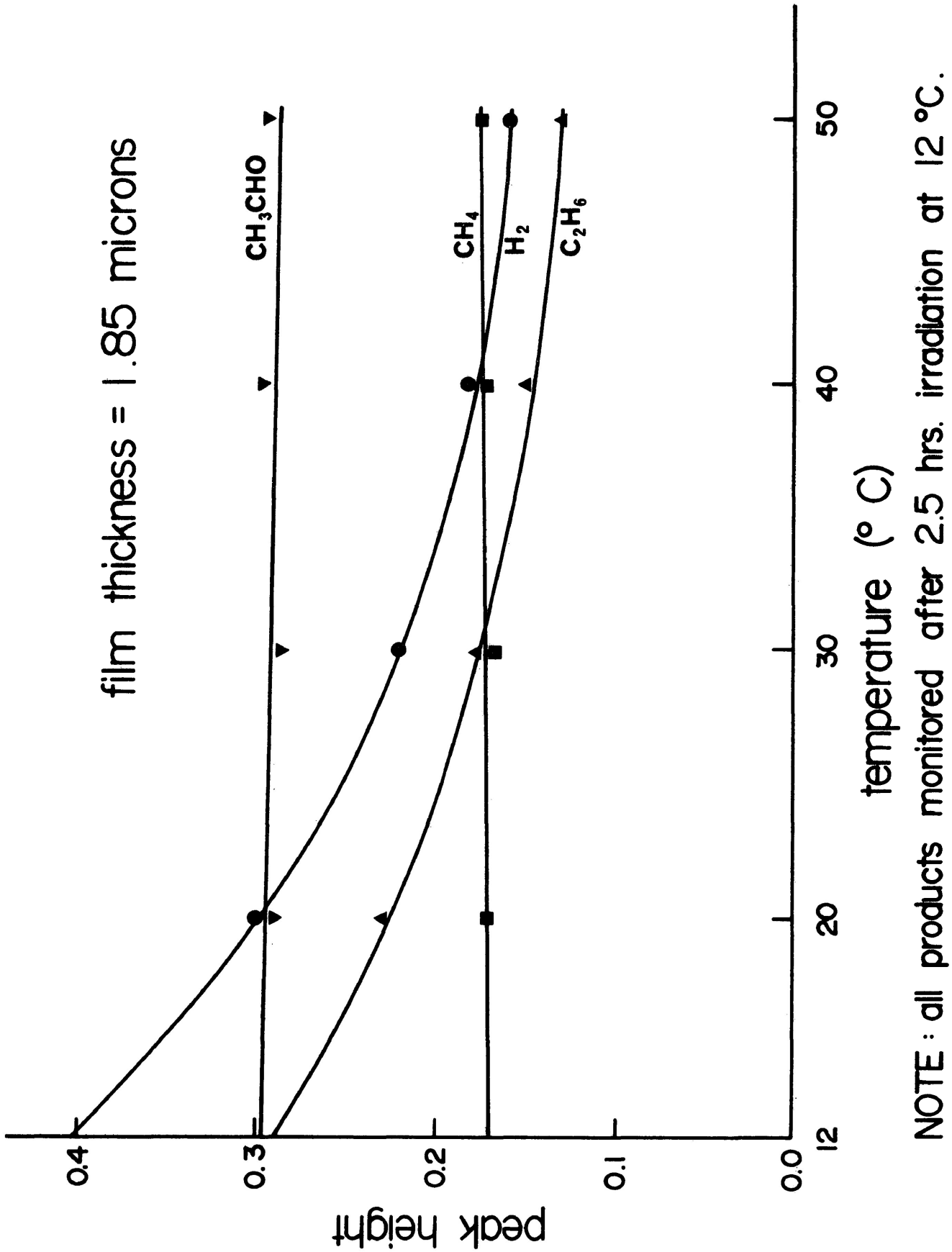


Figure 3.44 - Volatile Products from Poly(p-bromostyrene) as a Function of Temperature Following 2.5 Hours Irradiation:

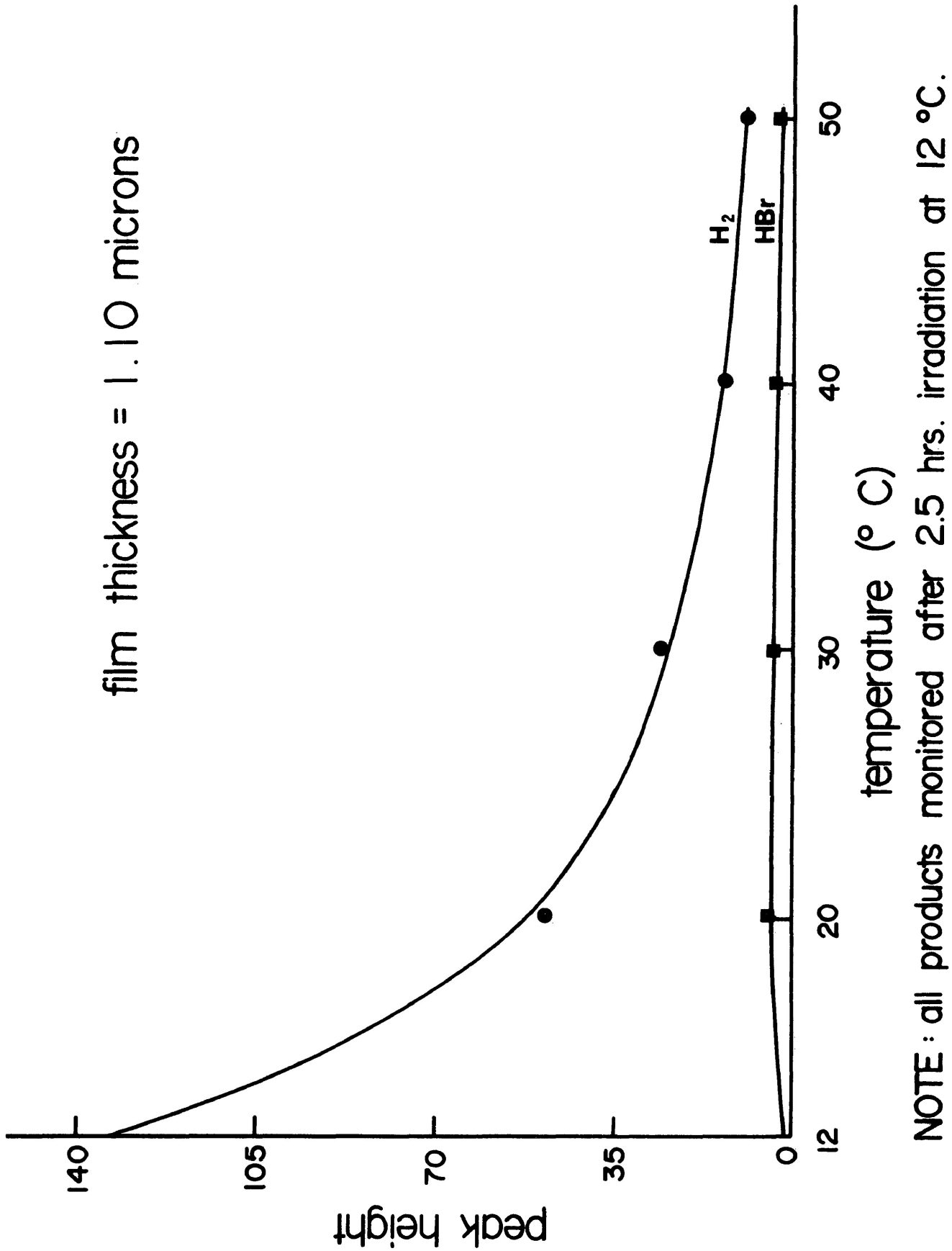


Figure 3.45 - Volatile Products from Poly(p-chlorostyrene) as a Function of Temperature Following 2.5 Hours Irradiation:

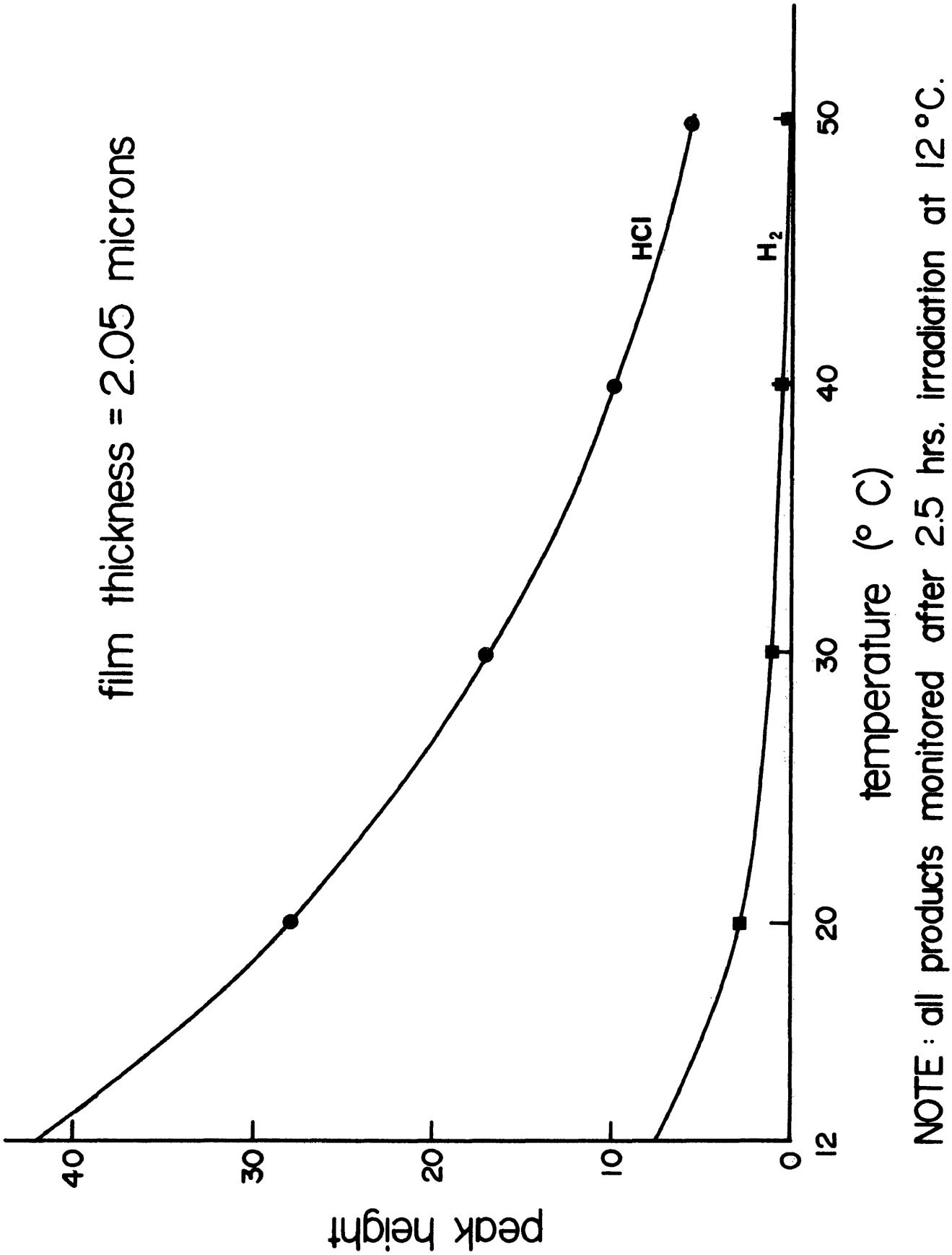


Figure 3.46 - Volatile Products from Poly(p-fluorostyrene) as a Function of Temperature Following 2.5 Hours Irradiation:

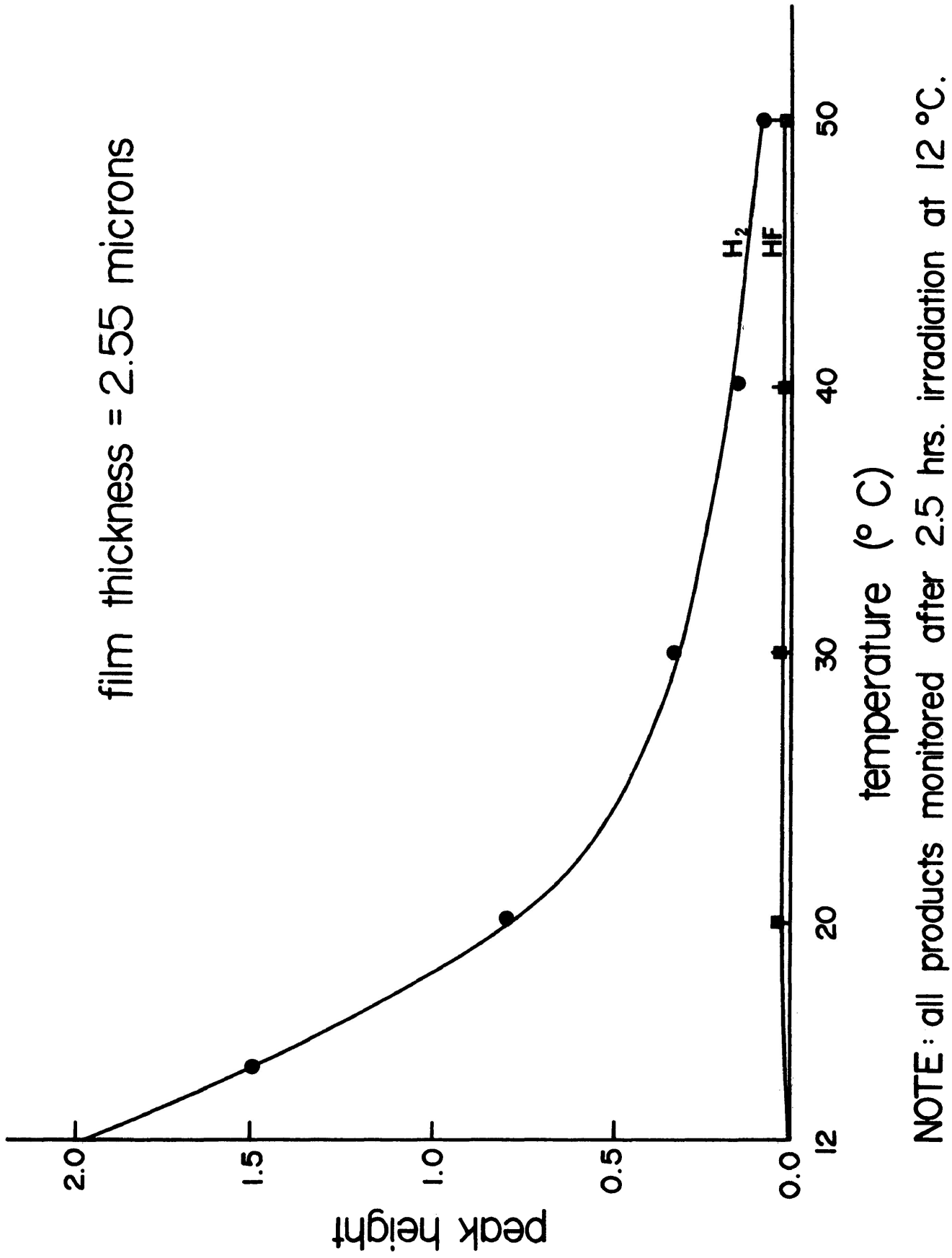


Figure 3.47 - Volatile Products from Poly(p-isopropylstyrene) as a Function of Temperature Following 2.5 Hours Irradiation:

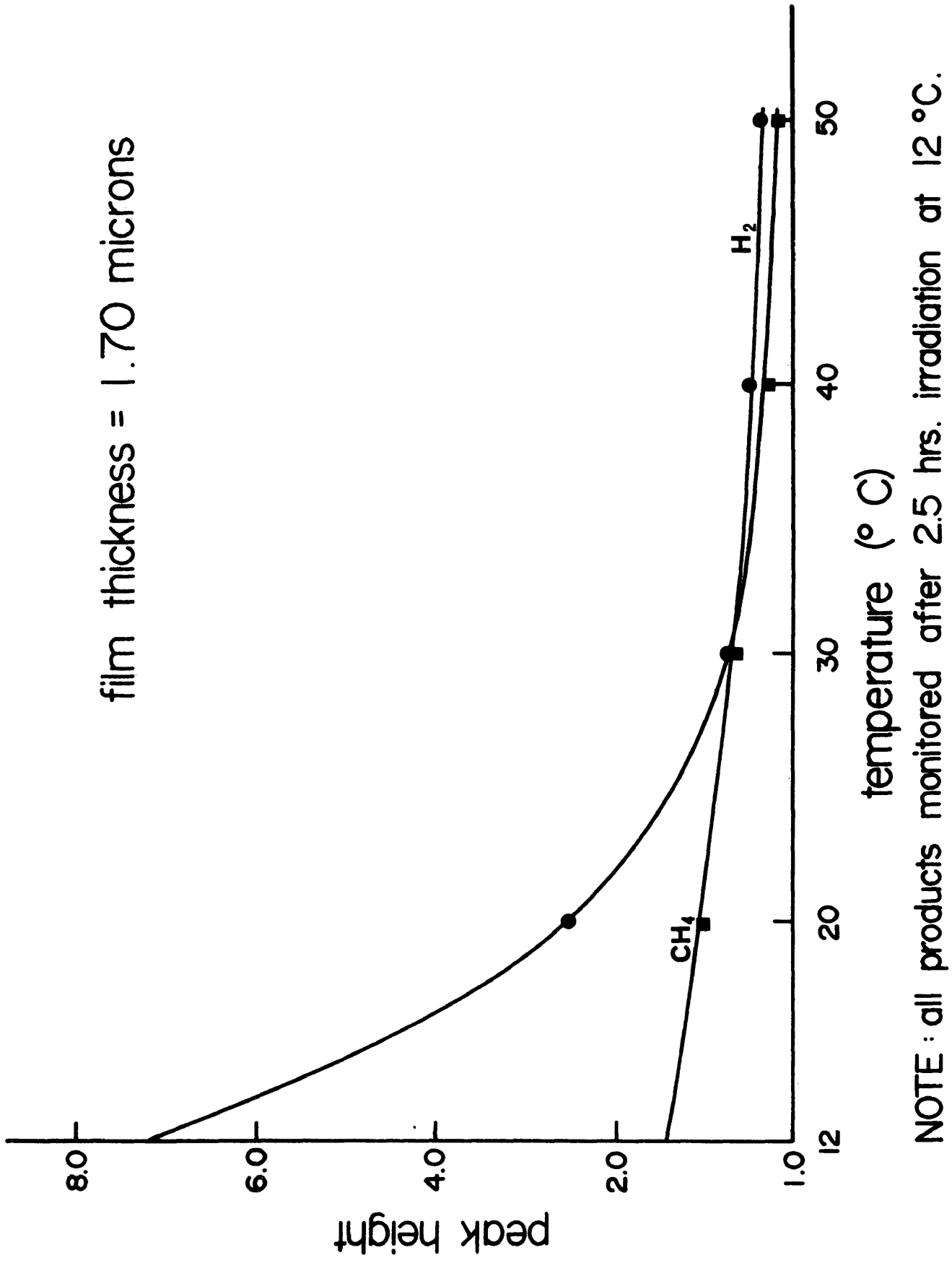


Figure 3.48 - Volatile Products from Poly(p-methoxystyrene) as a Function of Temperature Following 2.5 Hours Irradiation:

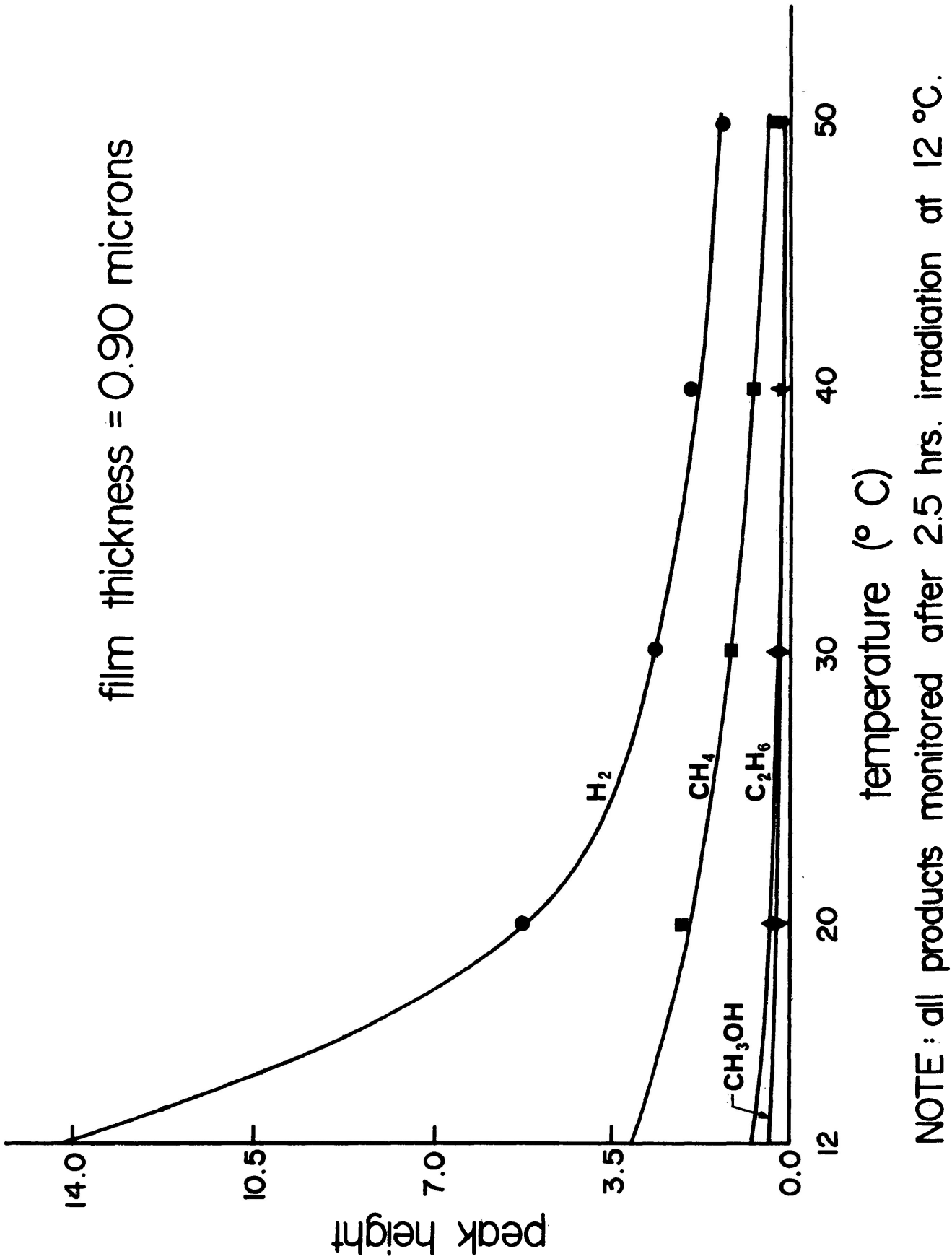


Figure 3.49 - Volatile Products from Poly(p-*tert*-butylstyrene) as a Function of Temperature Following 2.5 Hours Irradiation:

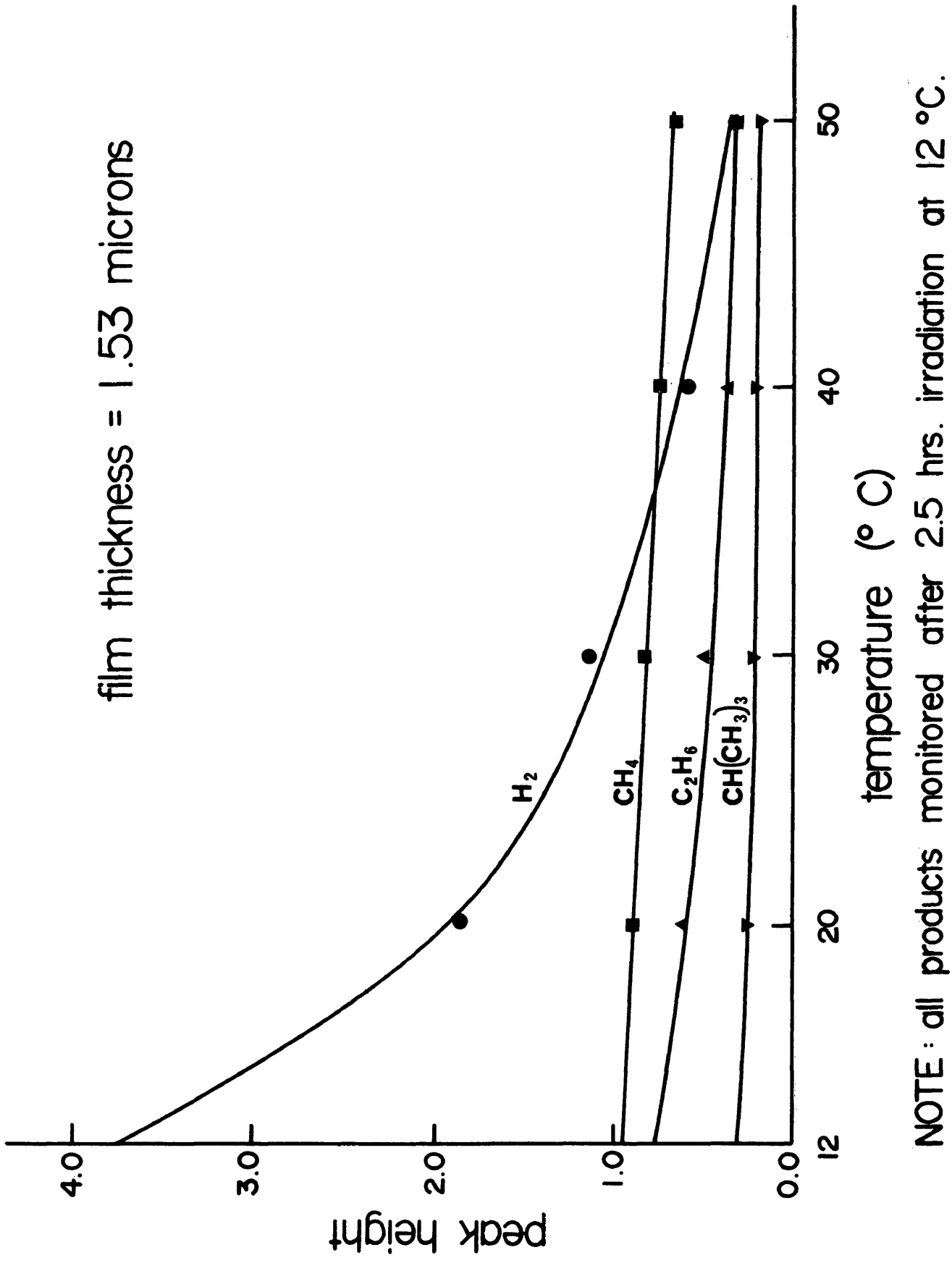


Figure 3.50 - Changes in Molecular Weight as a Function of Irradiation Time for the Para-substituted Styrene Polymers:

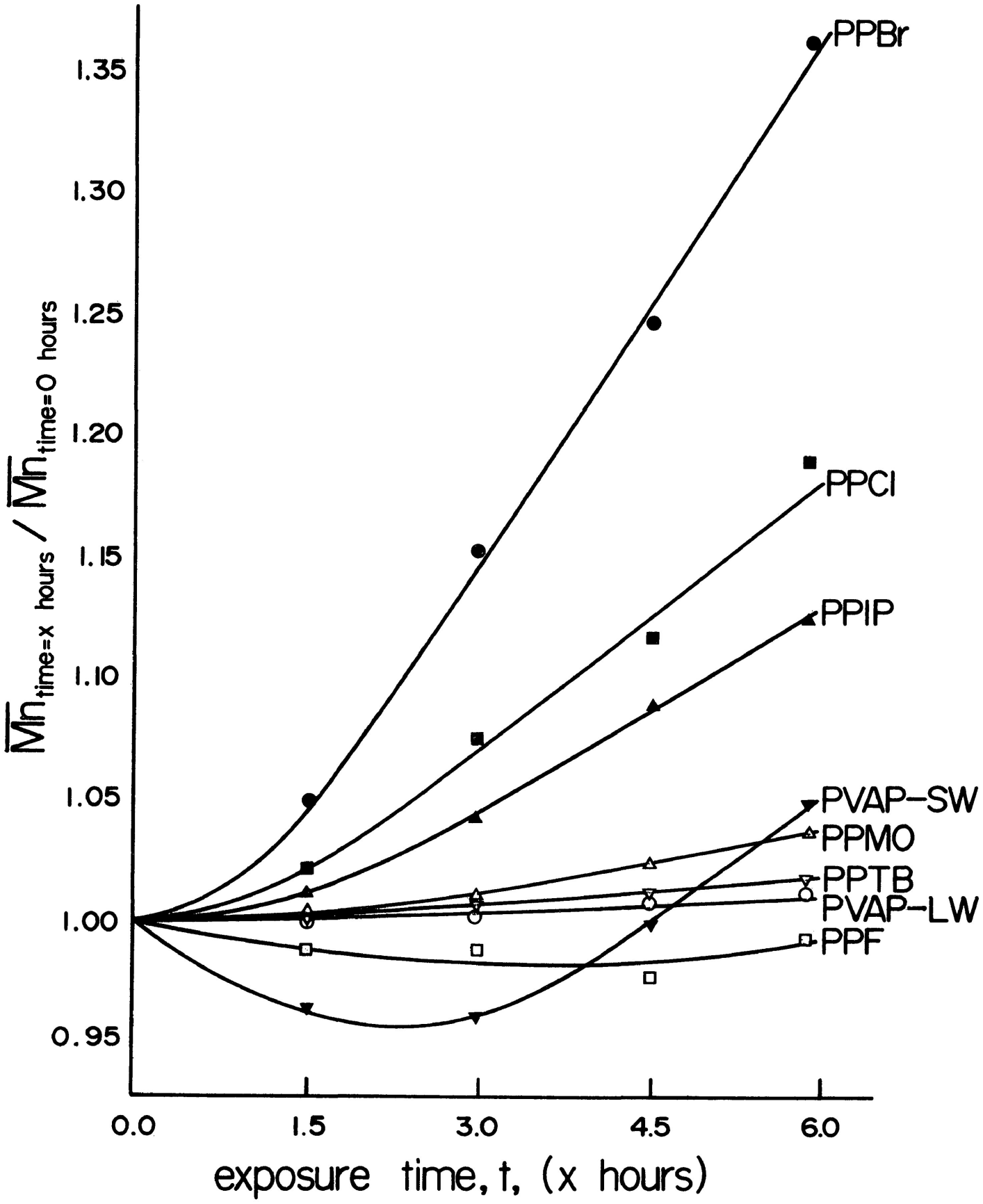


Table 3.1 - Dissociation Energies for Substituents in Benzene Compounds:

Compound	Dissociation Energy (kcal/mole)
$C_6H_5-COCH_3$	85 (54)
$C_6H_5CO-CH_3$	78 (55)
C_6H_5-Br	71 (55)
C_6H_5-Cl	86 (55)
C_6H_5-F	115 (55)
$C_6H_5-iC_3H_7$	85 (54)
$C_6H_5-OCH_3$	82 (54)
$C_6H_5-tC_4H_9$	85 (54)

Table 3.2 - Changes in Molecular Weight as a Function of Irradiation Time for the Para-substituted Styrene Polymers:

Polymer	Exposure Time (hrs.) 0	1.5	3.0	4.5	6.0
PVAP-SW	280,745	272,350	270,900	278,850	294,100
PVAP-LW	280,745	281,010	281,560	282,100	283,555
PPBr	54,700	57,435	62,900	67,990	74,600
PPCl	56,180	57,525	60,280	62,920	66,400
PPF	415,400	408,300	408,640	408,010	410,210
PPIP	38,060	38,940	39,870	41,160	44,070
PPMO	701,600	704,210	707,400	711,410	716,680
PPTB	101,500	102,310	102,880	103,140	103,140

Table 3.3 - Charlesby Data ($\overline{\alpha/\beta}$ Values) for the Para-substituted Styrene Polymers:

Polymer	α/β
PVAP-SW	0.24
PPBr	0.05
PPCl	0.13
PPF	0.77
PPIP	0.28
PPMO	0.26
PPTB	0.33

α/β = probability of chain scission / probability of crosslinking.

Table 3.4 - A Summary of the Results of the Secondary Reactions:★

Polymer	Chain Scission	Crosslinking	Coloration
PVAP-SW	3	5	4
PVAP-LW	1	2	1
PPBr	2	10	10
PPCl	3	8	8
PPF	10	1	1
PPIP	2	6	5
PPMO	4	4	2
PPTB	7	2	6

★ Each secondary reaction was assessed on a scale of 1 to 10 : the magnitude indicating the extent of the particular reaction.

CHAPTER 4

DISCUSSION

4.1 Introduction

4.1.1 Primary Reactions

The ultraviolet spectra of all para-substituted styrene polymers studied had broad absorbances extending from 245nm to 275nm (associated with the $\pi \rightarrow \pi^*$ transitions of the phenyl rings). Generally, absorption of energy will first lead to the excited singlet which may be deactivated by a number of photochemical and photophysical processes;

$$\text{polymer} \xrightarrow{h\upsilon} \text{polymer}^* \begin{cases} \rightarrow \text{photophysical processes} \\ \rightarrow \text{photochemical processes} \end{cases} \qquad (39)$$

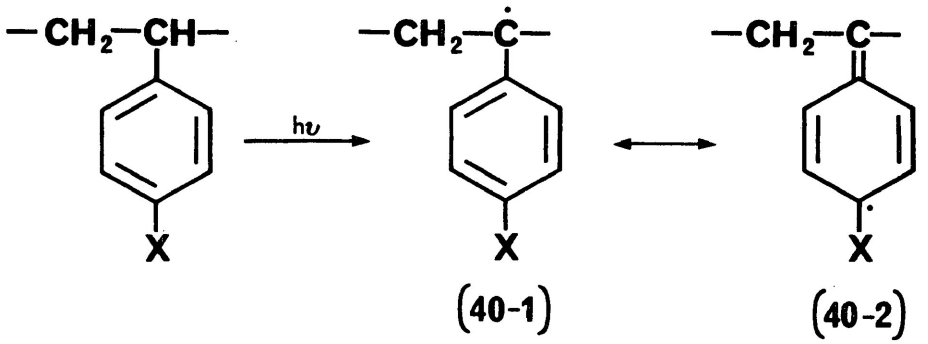
Photophysically, energy may be lost by the radiationless process of internal conversion, singlet fluorescence as well as the formation of the triplet and eximer.

Photochemically, energy may be transferred from the phenyl ring to initiate the fission of bonds in the main chain or para-

substituent. For main chain scission reactions a decrease in molecular weight will be observed. Side chain scission reactions will initially produce macro- and microradicals. Macroradicals may recombine and result in the formation of crosslinks (an increase in molecular weight will be observed). Microradicals may either recombine or abstract atoms from the polymer chain or side chain and result in the elimination of volatile products.

It has been reported that in polystyrene α-C-H cleavage on the main chain is the most probable reaction.(57) Apart from the para-substituent, it is reasonable to assume that all of the polymers studied here will behave similarly. The dissociation energy of the α-C-H bond will be influenced by the stability of the resulting radical. This depends on inductive, conjugative and steric factors associated with the para-substituent. Otsu(58) has observed correlations between inductive effects of para-substituents in copolymerization studies and has found that electron withdrawing groups (e.g., Br and Cl) destabilize the growing radical. Also, Inagaki et al.(59) have shown that para-substituents influence the thermal stability of para-substituted styrene polymers (i.e., electron repelling groups stabilize radicals and this leads to less depolymerization).

It is important to note that the delocalization of a radical throughout the π-electron system (i.e., increasing the stability of the radical thus formed) may be affected by steric factors. In particular, delocalization of radical (40-1) proceeds with the formation of a co-planar structure, (40-2):



(40-1) (40-2) (40)

However, if there is opposition to co-planarity, delocalization of the radical will be inhibited.

To account for the majority of volatile products observed during irradiation, partial or total para-substituent cleavage must be involved. Depending upon the nature of the substituent, this reaction may be energetically favoured over α-C-H fission.

4.1.2 Secondary Reactions

Macro- and microradicals formed as a result of the primary reactions may either recombine, abstract atoms from the polymer chain

or initiate crosslinking and chain scission, the extent of each dependent on the nature of the para-substituent.

With the exception of PVAP-LW and PPCl, hydrogen was the major gaseous product observed during photolysis. Hydrogen may be formed by direct combination of two atoms (in the presence of a third body), but on account of the reactivity of H atoms it is likely that most of the molecular hydrogen results from inter- and intramolecular abstraction reactions.(39) Abstraction may occur from either the α-position in a neighbouring chain or the β-position in the same polymer chain (i.e., adjacent to the initial C-H fission). The latter has been observed in polystyrene to account for main chain unsaturations and it is likely to be equally important for the polymers in this current study.

Other volatile products may be accounted for in a similar manner (i.e., recombination or abstraction). The formation of ethane would most likely arise from radical recombination since the abstraction of a methyl radical would be highly unlikely.

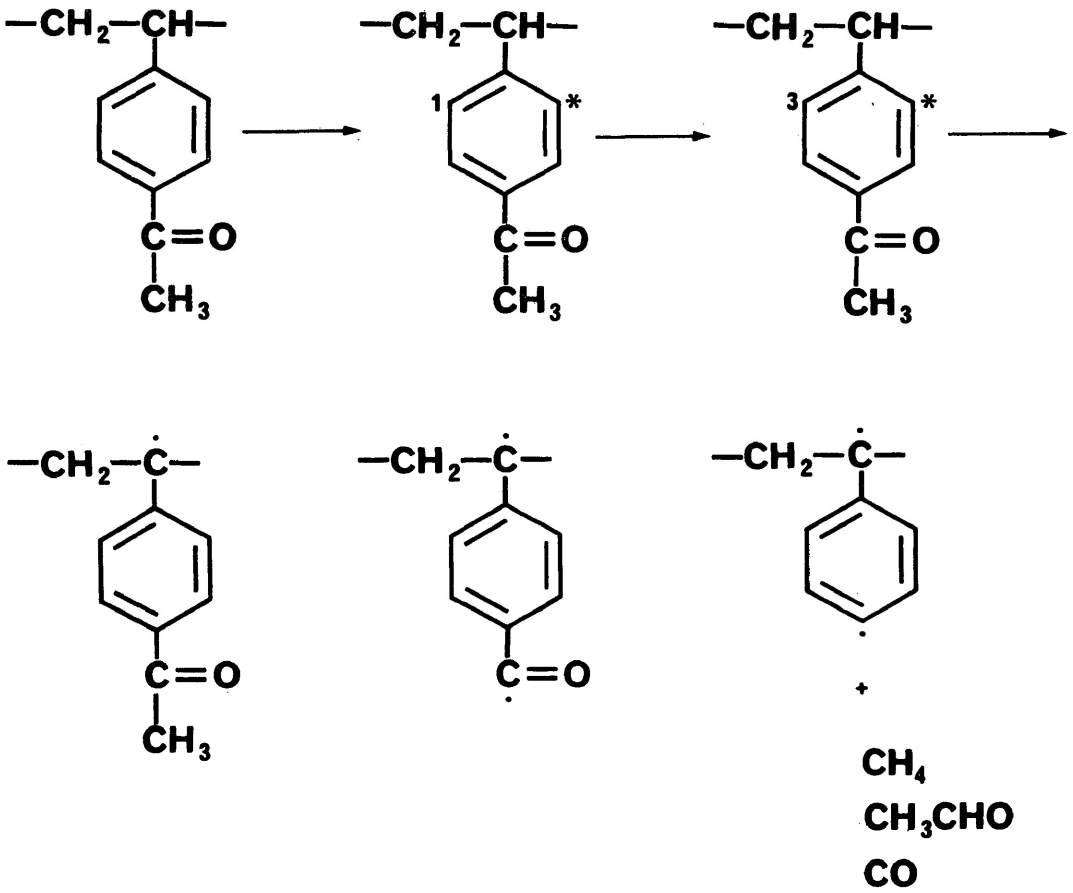
Crosslinking and main chain scission can be directly related to electronic and steric factors associated with the para-substituent.

4.2 Poly(vinylacetophenone)

4.2.1. Short-wave Photolysis

The short-wave photolysis of PVAP involves the absorption and subsequent distribution of energy by the phenyl ring and the carbonyl group in the para-substituent.

To account for the volatile products observed during photolysis, fission of both the α-C-H bond and the para-substituent must be considered:



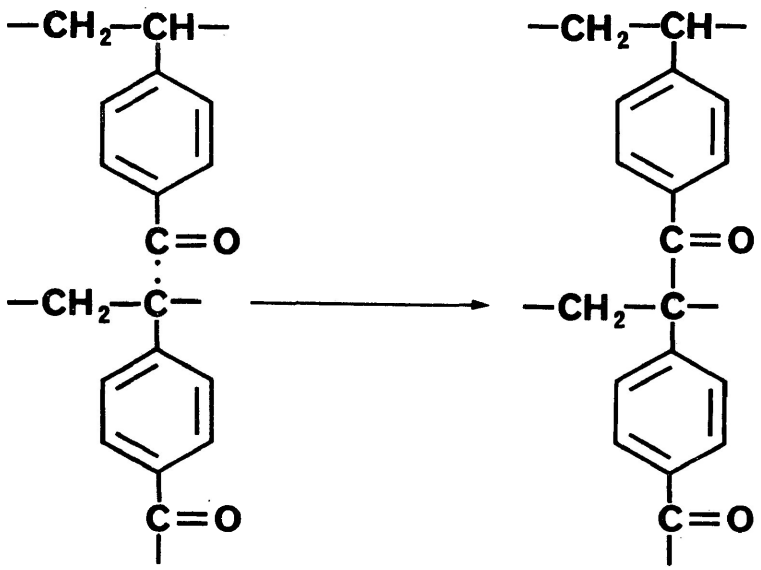
(41)

In addition, radicals formed on the main chain that use the phenyl ring for delocalization of charge, could be expected to have reduced stability in comparison to polystyrene and PPMS arising from the inductive effect (-I) associated with the para-substituent.

Since the radiation received by the polymer film during short-wave photolysis was not restricted to 255nm (see figure 2.3), the effect of the chromophore in the para-substituent should be considered. However, the effect of absorption and subsequent transfer of energy by this chromophore to initiate secondary reactions is rather small compared to the phenyl ring. For this reason, the participation of the carbonyl group to the overall mechanism of degradation will be discussed in the following subsection.

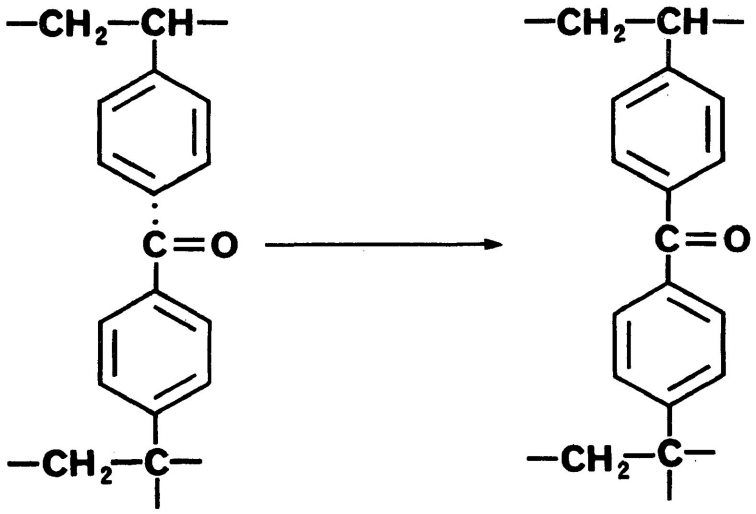
Radicals on the main chain, para-substituent or the phenyl ring may recombine with other macroradicals to form crosslinks. There are many types of crosslinks possible by simple recombination, a few of which can be envisaged by considering;

i) the recombination of a benzylic radical formed on the para-substituent by CO-CH_3 cleavage:



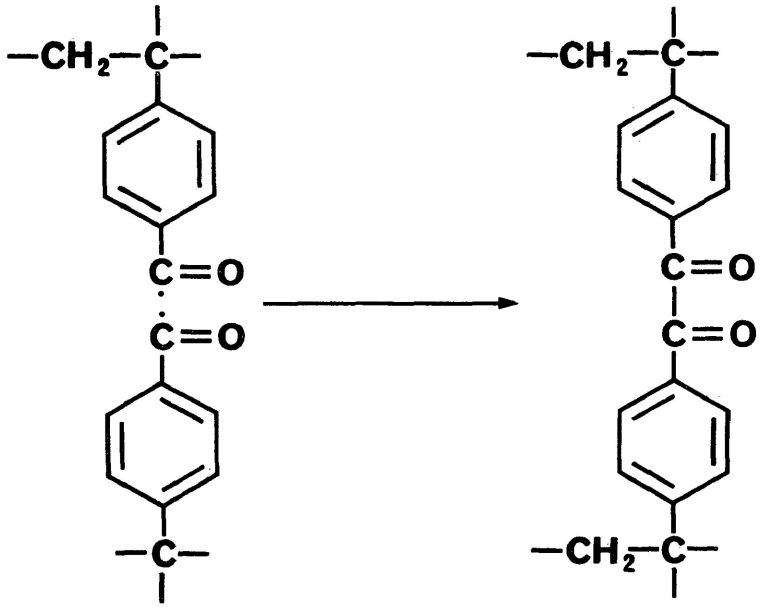
(42)

ii) the recombination of a phenyl radical and a radical formed on the para-substituent by CO-CH_3 cleavage:



(43)

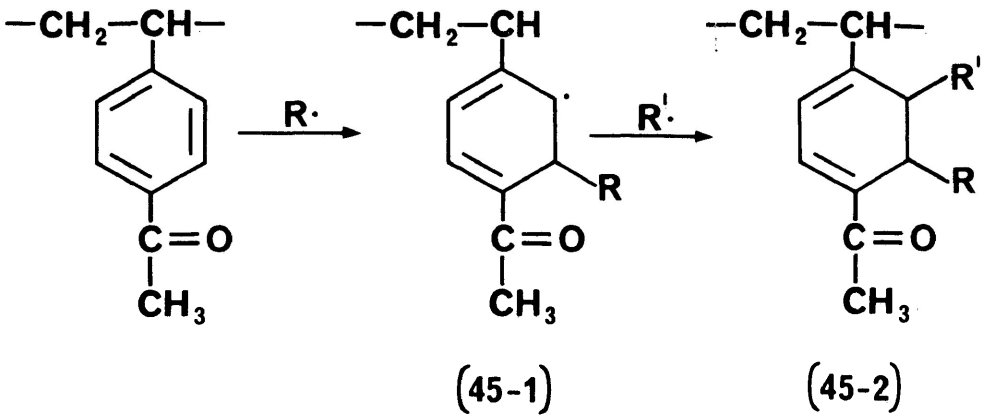
iii) the recombination of two radicals formed on the para-substituent by CO-CH_3 cleavage.



(44)

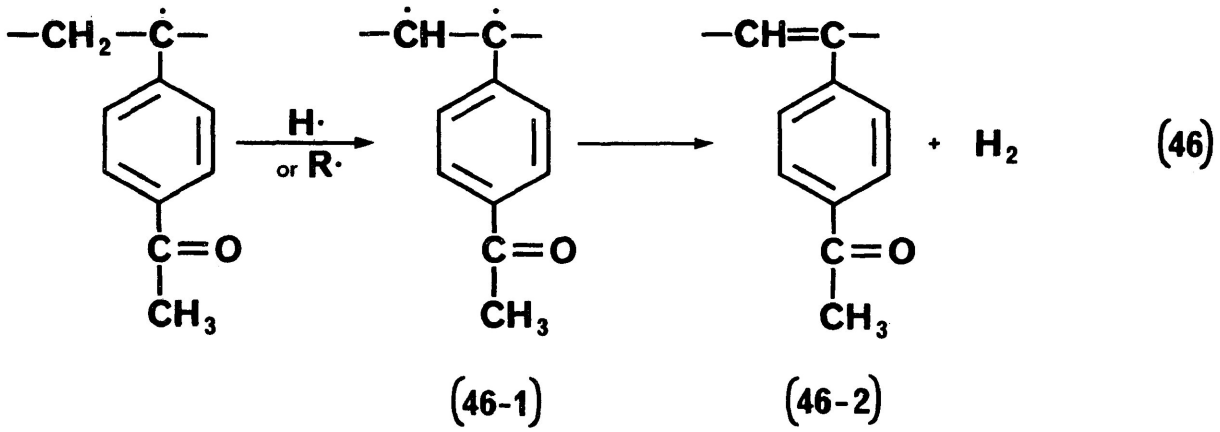
Absorptions in the infrared spectra (see figure 3.1 and 3.9) with particular attention to; new peaks recorded at 670cm^{-1} and 915cm^{-1}, the appearance of shoulders on the 815cm^{-1}, 1575cm^{-1}, and 1689cm^{-1} peaks as well as changes in intensities of the peaks in the 950cm^{-1} to 1110cm^{-1} region, are characteristic of olefins of the type: $CHR_1 = CH_2$ (1645-1640cm^{-1} and 915-905cm^{-1}), <u>cis</u>-$CHR_1 = CHR_2$ (1605-1635cm^{-1} and 730-665cm^{-1}) and <u>trans</u>-$CHR_1 = CHR_2$ (980-960cm^{-1}).(60) The Formation of structures containing these olefins can be rationalized by considering:

i) the addition of macroradicals to the phenyl ring resulting in the formation of a cyclohexadiene, **(45-2)**:



(45-1) (45-2) (45)

ii) the formation of main chain unsaturations by β-H abstraction in the main chain:



It is interesting to note that the increase in absorption at 400nm (see figure 3.25) is concomitant with the production of hydrogen, suggesting that conjugated main chain unsaturations, **(46-2)**, are largely responsible for the yellow coloration observed during irradiation. Evidence in support of this hypothesis does not however, rule out the possibility that photoisomers **(17-1)** and **(17-2)** contribute to the 'yellowing' as suggested by Ranby and Rabek.(21)

As reported earlier, radicals formed on the main polymer chain can initiate chain scission by disproportionation. Chain scission will lead to the formation of radicals very similar in structure to the growing radicals involved in polymerization. These could conceivably depolymerize, however, the absence of monomer in the

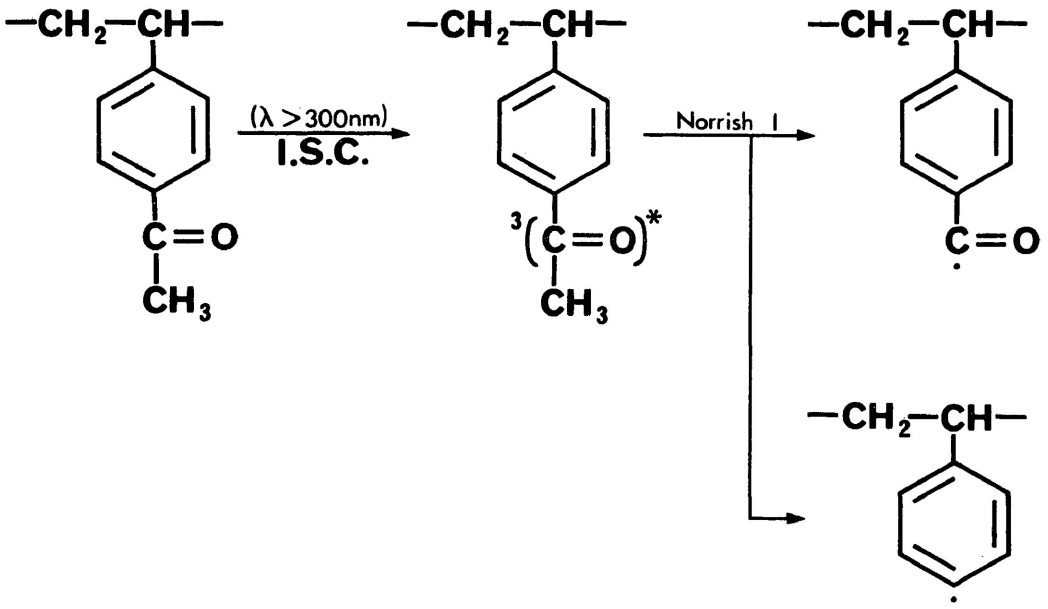
volatile products would suggest that depolymerization does not occur and this can be rationalized in terms of temperature (i.e., the reaction temperature being well below the ceiling temperature for the polymer).

Chain scission and crosslinking are competitive processes during irradiation, the latter becoming important during later stages of degradation (figure 3.50). This can be rationalized by considering the inability of macroradicals to separate once they are formed in an increasingly viscous (crosslinked) medium.

4.3.2 Long-wave Photolysis

The long-wave photolysis of PVAP deals specifically with those photochemical reactions arising from the absorption and subsequent transfer of energy from the carbonyl group as well as any impurity (peroxide) incorporated into the polymer during processing.

The energy associated with 295nm radiation is sufficient to cleave C-C bonds in the para-substituent provided that the transfer of energy is efficient:



(47)

The lack of major changes in the infrared, ultraviolet-visible and fluorescence spectra, indicates virtually no change in the macromolecular structure during irradiation (see figures 3.10, 3.18, and 3.27). Changes in molecular weight as well as the detection of trace quantities of volatile products indicate degradation is occurring, but to a very small extent. C-C bond fission is observed in the para-substituent (Norrish Type I reaction), reflected by very small amounts of methane, ethane and acetaldehyde (see figure 3.43). The observed hydrogen apparently arises from CH_2-H cleavage in the para-substituent since intramolecular energy transfer would not be expected to extend from the para-substituent to the main chain.

A slight increase in molecular weight during irradiation (see figure 3.50) indicates participation of the para-substituent in crosslinking. In particular, recombination between radical centres on adjacent phenyl segments and para-substituents is believed to constitute the majority of crosslinks formed.

It is not surprising that chain scission was not reflected in solubility measurements. The unlikely transfer of energy from the carbonyl group to the main chain would restrict scission reactions to impurities or radicals formed on the main chain by the abstraction of hydrogen.

The quantum yield for the reactions associated with the carbonyl group must be very small to account for the quantity of gaseous products and the lack of secondary reactions observed during irradiation. It is likely that photophysical processes are the major recipients of energy transfer processes.

Consistent with the observations of PVAP-LW, Hrdlovič et al.(61) have investigated the photolysis of benzophenone and copolymers with styrene and have found that the carbonyl group acts like an isolated chromophore and does not stabilize the polymer in a photophysical sense.

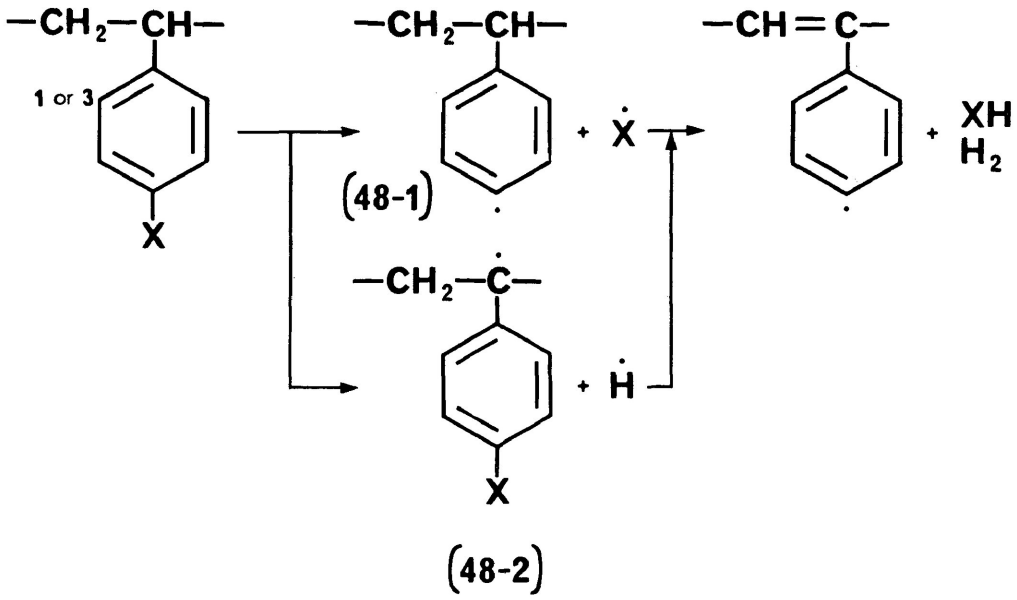
4.3 p-Halopolymers

Classified under this heading are the substituted styrene polymers having para-substituents of Br, Cl, and F. Since none of these groups absorb energy directly, photochemical reactions will occur as a result of intramolecular energy transfer processes associated with an electronically excited phenyl ring.

Changing the electronegativity of the para-substituent has the effect to alter the electronic environment about atoms on the main chain (arising from inductive effects associated with the substituent). The effect of the substituent may be assessed by examining the secondary reactions.

To account for the volatile products observed during irradiation (see figures 3.45, 3.46, and 3.47), cleavage of the para-substituent followed by either fission of C-H bonds or abstraction of hydrogen from the main chain must be occurring (see **(48)**) The formation of radicals **(48-1)** and **(48-2)** will depend on the dissociation energies, the efficiency of intramolecular energy transfer and inductive and conjugative effects of the para-substituent. To account for H_2 and HCl being the major products in PPBr and PPCl respectively, as well as noting that the quantity of HCl to HBr is

approximately 2:1, it must be concluded that electronic factors associated with the para-substituent play an important role in controlling the course of the reactions. One would expect however, on the basis of bond dissociation energies of benzene analogues (see table 3.1), that more HBr would be liberated than HCl or HF. This appears to be true for PPF compared to PPCl and PPBr, noting that H_2 production is low and HF formation is practically non-existent.



(48)

It is worth noting that neither Br_2, Cl_2, nor F_2 were detected in the volatile products during irradiation. The absence of these products is not indicative that the para-bond is not breaking, rather the halogen radicals formed abstract hydrogen, or possibly hydrogen radicals abstract halogen atoms. In addition, it is rather unlikely that electronically excited diatomic halogens would survive

vibrations on formation.

Major changes observed in the infrared spectra of the insoluble fraction (new peaks at 702cm^{-1} and 915 cm^{-1}; see figures 3.11, 3.12 and 3.13) as well as the ultraviolet-visible and fluorescence spectra (see figures 3.19, 3.20, 3.21, and figures 3.28, 3.29, 3.30 respectively), indicate significant changes are occurring in the macromolecular structure during irradiation.

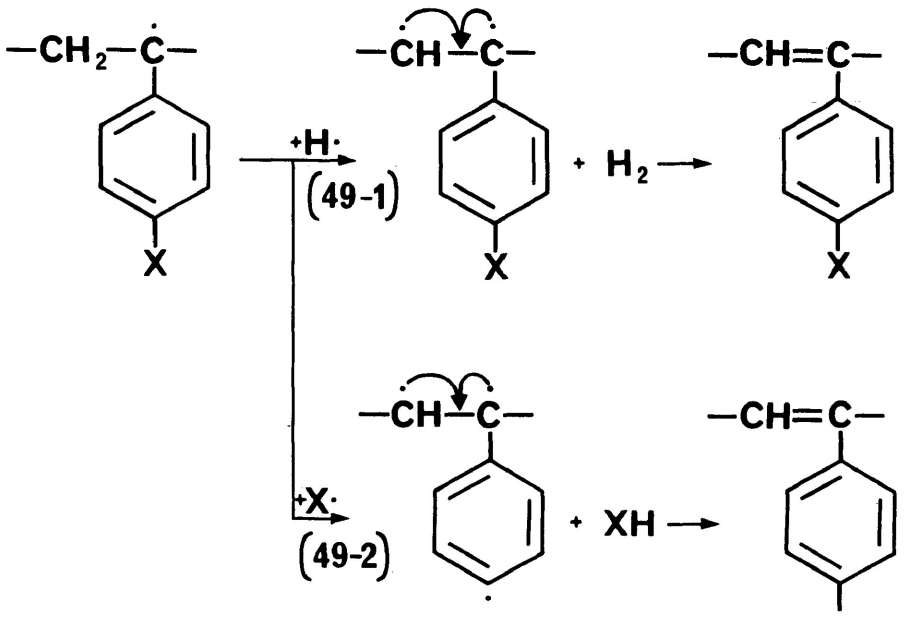
As with PVAP, radicals formed on the main chain or the phenyl ring may form crosslinks by recombining with other macroradicals or adding to the phenyl ring to yield a cyclohexadienyl structure, **(45-2)**.

The extent of crosslinking appears to coincide with the bond dissociation energy of the para-substituent. It must be noted, however valid this observation, that crosslinking is not restricted to those radicals formed by cleavage of the para-substituent, but also to radicals formed on the main polymer chain. Therefore, inductive and conjugative effects as well as dissociation energies must be considered as factors affecting crosslinking. A disscussion of electronic factors will be presented in section 4.6.1 of this thesis.

Chain scission appears to be prevalent in the early

stages of degradation for PPF, with some indication of crosslinking during later stages (see figure 3.50). PPF is the most degradation-resistant system in the overall series of polymers studied. This is reflected not only in molecular weight measurements but also in the lack of major changes in infrared, ultraviolet-visible and fluorescence spectra as well as the relatively low yield in volatile products. These results are not totally unexpected however, since the electron-withdrawing effect exhibited by the para-F would tend to destabilize the α-radical and lower the hydrogen yield as well as destabilize the radical formed by chain scission. Also, the strength of the C-F bond (approximately 115 kcal/mole; see table 3.1) would effectively inhibit loss of the para-substituent by abstraction or bond fission.

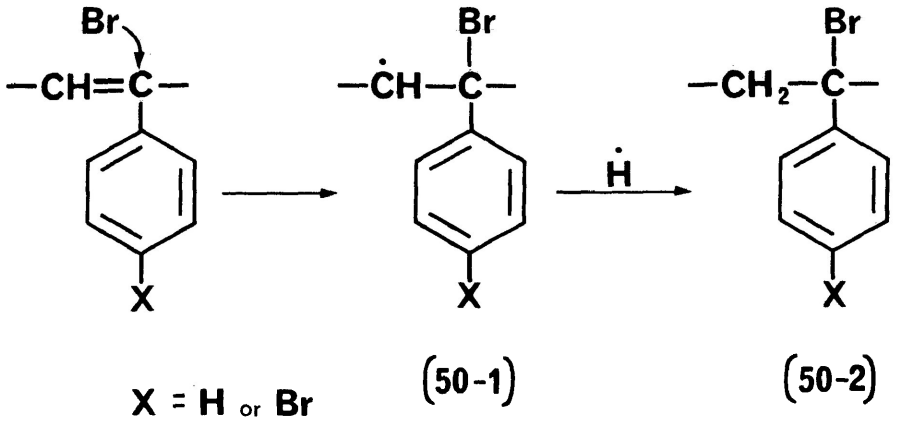
The yellow discoloration observed as a function of irradiation time (see figure 3.25) is concomitant with the evolution of hydrogen (see figures 3.36, 3.37, and 3.38); evidence in favour of the formation of conjugated main chain unsaturations. This can be rationalized by considering the abstraction of β-H on the main chain by the para-substituent or hydrogen radicals formed by α-C-H fission:



(49)

The intense discoloration associated with PPBr along with the relatively large quantity of H_2 liberated, can be explained in terms of reaction (49-1) with minor emphasis on reaction (49-2). The yellowing in PPCl could be accounted for primarily by reaction (49-2) with little emphasis on reaction (49-1). PPF on the other hand exhibited only slight discoloration during irradiation, accounted for primarily by reaction (49-1).

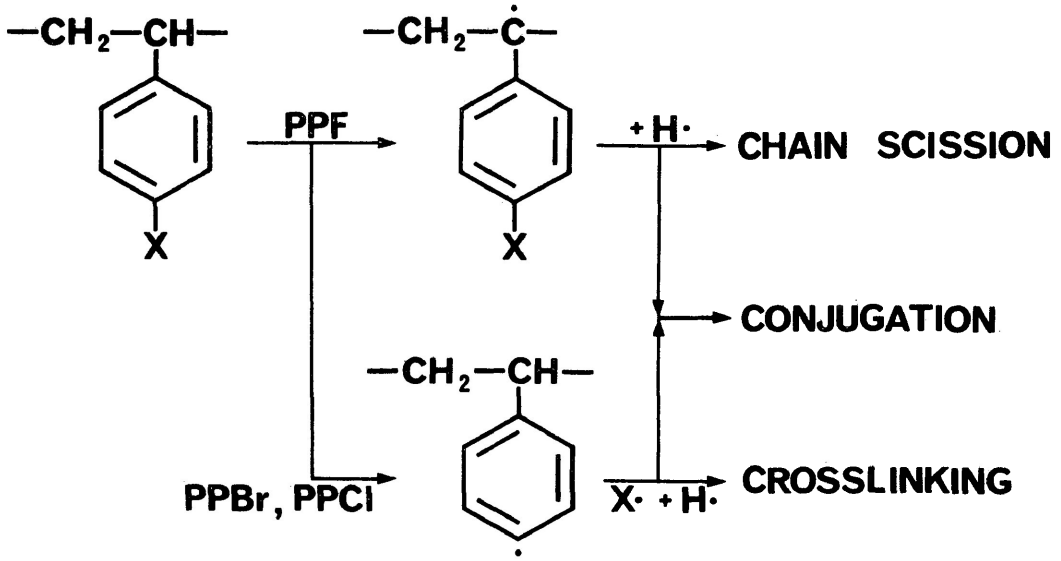
Since Br is not very reactive towards abstraction, it is likely that there may be 'free' Br atoms formed during photolysis that may diffuse throughout the polymer and react with double bonds (i.e., fulvene types and main chain unsaturations) according to:



X = H or Br (50-1) (50-2) (50)

The appearance of a band at 702cm^{-1} in the infrared spectra of the insoluble product (see figure 3.11) could account for structure (50-2).

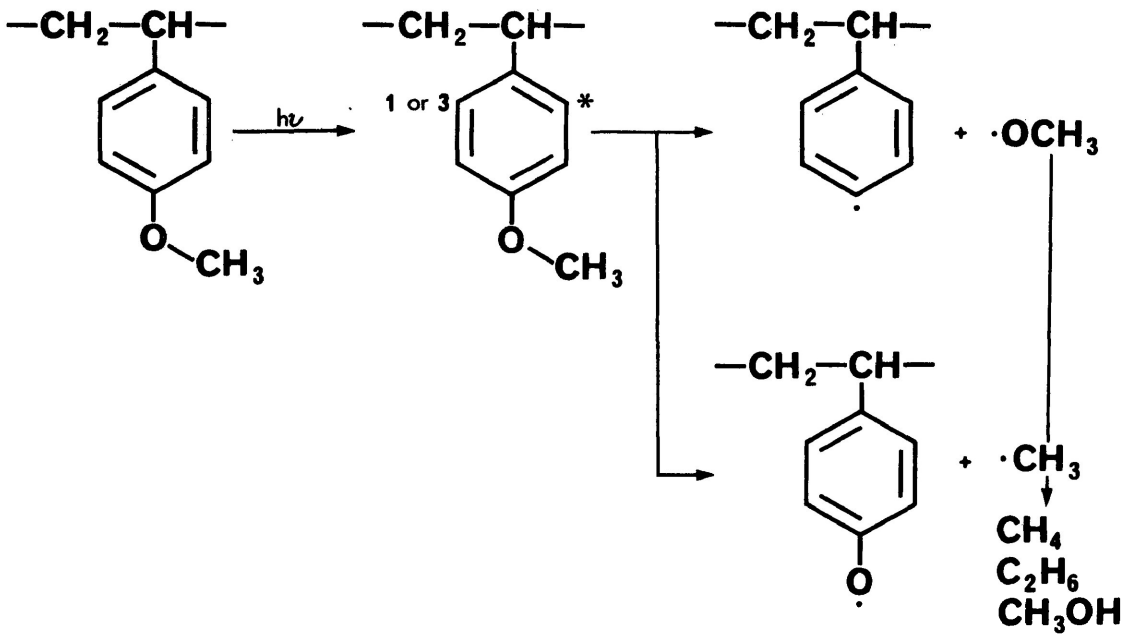
It is important to note that the volatile products obtained following the gamma irradiation of PPBr and PPCl(43) differ significantly from those observed following ultraviolet irradiation. For this reason, the radical chain reaction initiated by cleavage of the aromatic C-halogen bond (see (33)) does not seem likely after analyzing the results of this current study. The following scheme collectively presents a summary of the secondary reactions in PPBr, PPCl, and PPF following ultraviolet irradiation:



(51)

4.4 Poly(p-methoxystyrene)

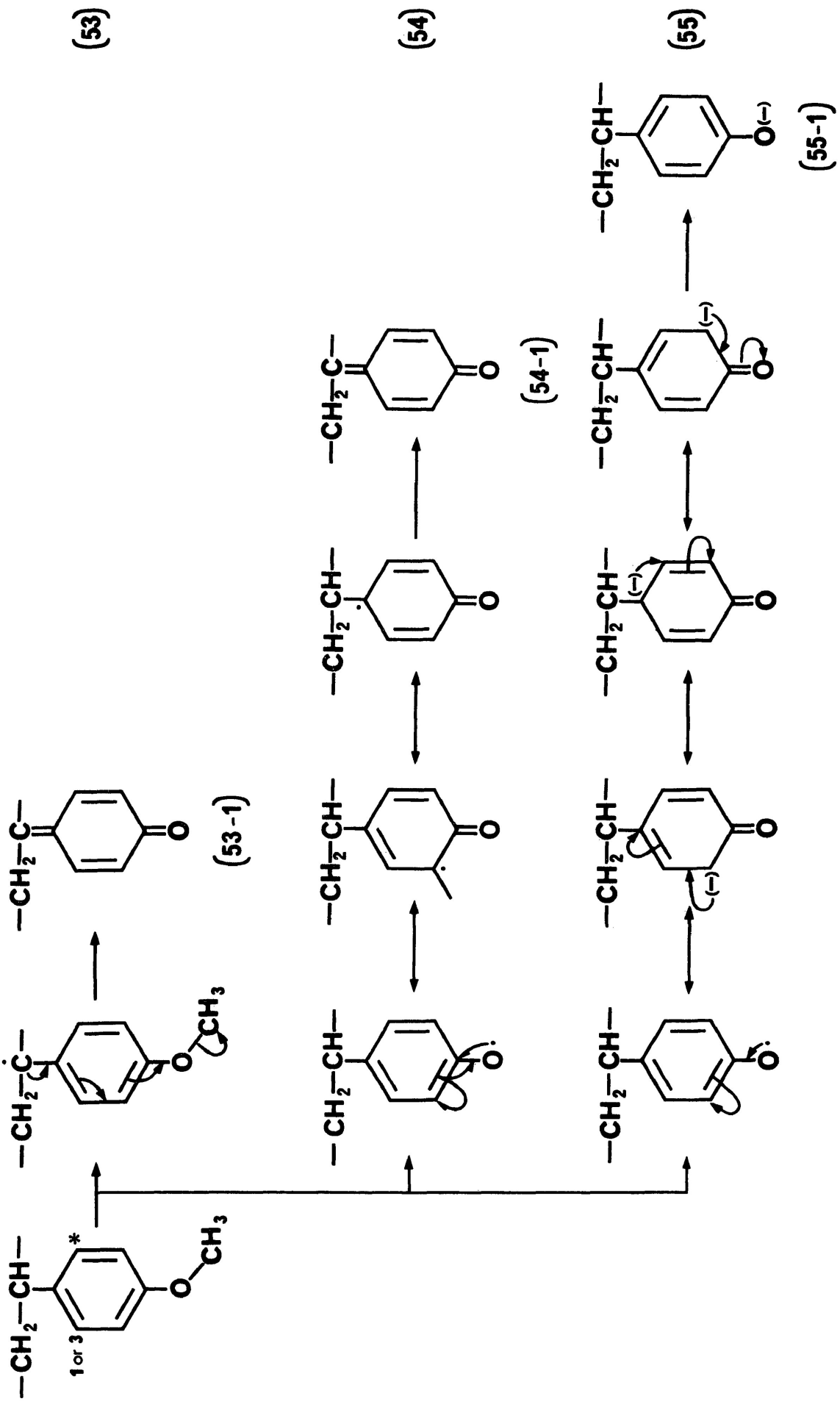
The origin of methane, methanol and ethane in the gases liberated during irradiation (see figure 3.40) can be explained in terms of partial or total cleavage of the para-substituent:



(52)

Hydrogen could be expected to be formed from radical recombination or abstraction following an initial α-C-H cleavage.

As with PVAP-SW and poly(p-halostyrenes), radical centres formed on the phenyl ring or main chain of PPMO could be expected to participate in chain scission or crosslinking. It is difficult to determine whether both of these processes are occurring simultaneously from the molecular weight data presented in figure 3.50. Certainly, crosslinking is important during the later stages of degradation, however, one would expect a more abrupt increase in molecular weight, reflecting the participation of two radical centres in the crosslinking mechanism. A plausible explanation to account for the rather gradual increase in molecular weight can be rationalized by considering reactions **(53)**, **(54)** and **(55)**. The reaction in **(53)** takes into account the stability of the intermediate radical formed (i.e., the delocalization of the unpaired electron on the α-C atom by resonance interaction with the para-substituent). The unpaired electron is delocalized through the π-electron system of the phenyl ring, which has the net effect to render it less available either for coupling with a radical site on an adjacent chain or initiating chain scission by disproportionation. It is important to note that quinones have been reported to be sensitizers in the photodegradation of polystyrene(62). In particular,


(53)
(54)
(55)
(53-1)
(54-1)
(55-1)
1 or 3

the absorption of energy by the quinone will lead to the production of the excited state that may abstract hydrogen from the polymer to produce radicals and possibly accelerate crosslinking. Formation of structure (53-1) or (54-1) would be photochemically unstable. It is more reasonable to consider an 'enol' structure, (55-1), which may abstract hydrogen and result in the formation of a substituted phenol. This would effectively eliminate the radical centre on the para-substituent and restrict any crosslinking to the α-position on the main chain or to additions in the phenyl ring.

As reported for PVAP, PPBr, $\overline{\text{PPCl}}$, and PPF, hydrogen production (see figure 3.40) is concomitant with the increase in absorbance at 400nm (see figure 3.25).

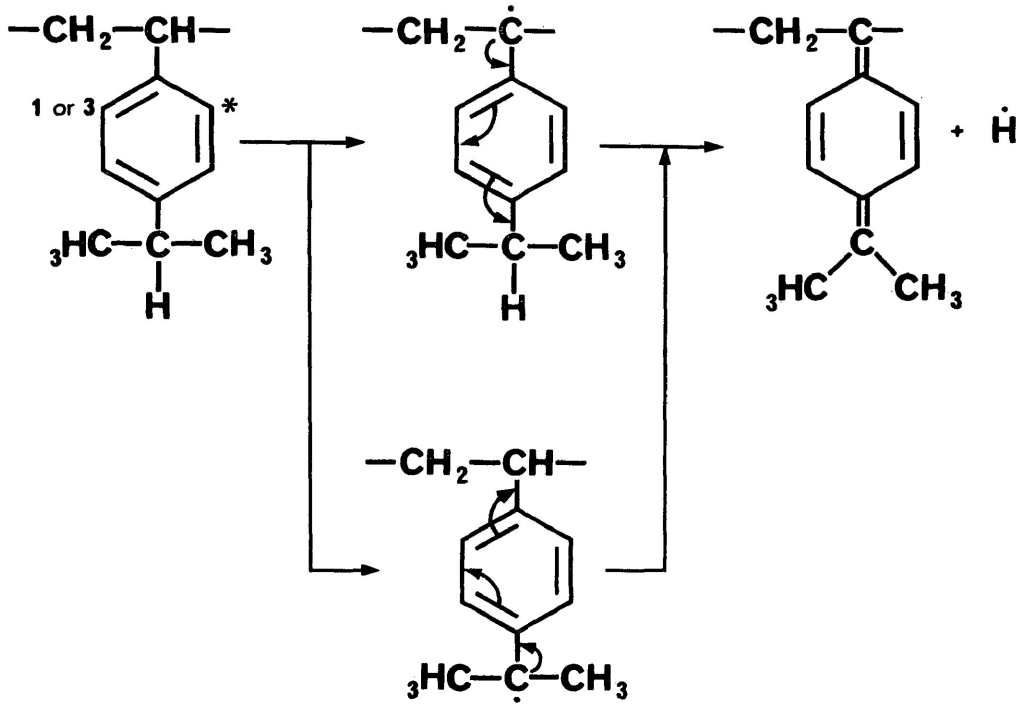
4.5 p-Alkylpolymers

PPIP and PPTB both contain relatively large alkyl substituents in the para-position of the phenyl ring.

The appearance of methane, ethane and isobutane during irradiation, can be accounted for by partial or total cleavage of the para-substituent followed by radical recombination. It is likely that hydrogen will be formed either by the recombination of radicals

from α-C-H fission or the abstraction of H atoms from the main chain.

For PPIP, two α-C-H groups are present, each being a potential source for hydrogen radicals (a possible explanation to account for approximately twice as much H_2 from PPIP than PPTB). Either radical may be delocalized throughout the π-electrons in the phenyl ring:



(56)

Due to the inductive effect, (+I), associated with the isopropyl group, α-C-H fission will be aided not in the para-substituent but on the α-position in the main polymer chain. However, because of

the possible delocalization as outlined in (56), radical centres can be formed on the para-substituent. Similar delocalizations have been noted for PPTB in the introduction to this thesis. (see (28)).

Significant changes in the infrared spectra of the insoluble product, with particular attention to the appearance of new peaks at 735cm^{-1} and 910cm^{-1} for PPTB and 735cm^{-1}, 915cm^{-1}, 1615cm^{-1}, and 1670cm^{-1} for PPIP, (see figures 3.14 and 3.16), reflect definite modifications in the macromolecular structure during irradiation. These absorptions are characteristic of olefins similar to those reported for PVAP.

Both PPIP and PPTB films yellow during irradiation and exhibit increases in the absorbance at 400nm (see figure 3.25) which is concomitant with the production of hydrogen (see figures 3.47 and 3.49). As previously noted throughout this discussion, this is evidence in support of the formation of conjugated main chain unsaturations.

Changes in molecular weight (see figure 3.50) indicates a significant degree of crosslinking in PPIP, which is practically non-existent in PPTB. This reflects the overwhelming participation of the para-substituent in crosslinking, with particular attention drawn to a rather labile proton in the isopropyl group. Undoubtedly,

radical centres formed on the para-substituent of PPIP delocalize throughout the phenyl ring, however, there is still sufficient localization to recombine with other macroradicals. The difference in reactivity towards crosslinking appears to be directly related to electronic (inductive and conjugative effects) rather than steric factors, since the removal of a hydrogen radical from the isopropyl group and methyl radical from the *tert*-butyl group leaves the same radical in the para-position of the phenyl ring.

Electronic factors must be considered in addition to steric factors as a possible influence in the formation of crosslinks to the phenyl ring (cyclohexadienyl structures) and across the tertiary carbon atom in the main chain. The inductive and conjugative effects associated with the isopropyl and *tert*-butyl groups will increase the electron density within the phenyl ring and tertiary main chain atoms. Since this effect will be greater with the tertbutyl group than the isopropyl group, cleavage of the α-C-H bond will be more probable in PPTB. Noting that the probability of forming tertiary radicals on the main chain is greater in PPTB than PPIP while more crosslinking is observed in PPIP than PPTB indicates more participation of the para-isopropyl group than the para-*tert*-butyl group in crosslinking.

The rather weak absorption at 400nm for PPIP compared

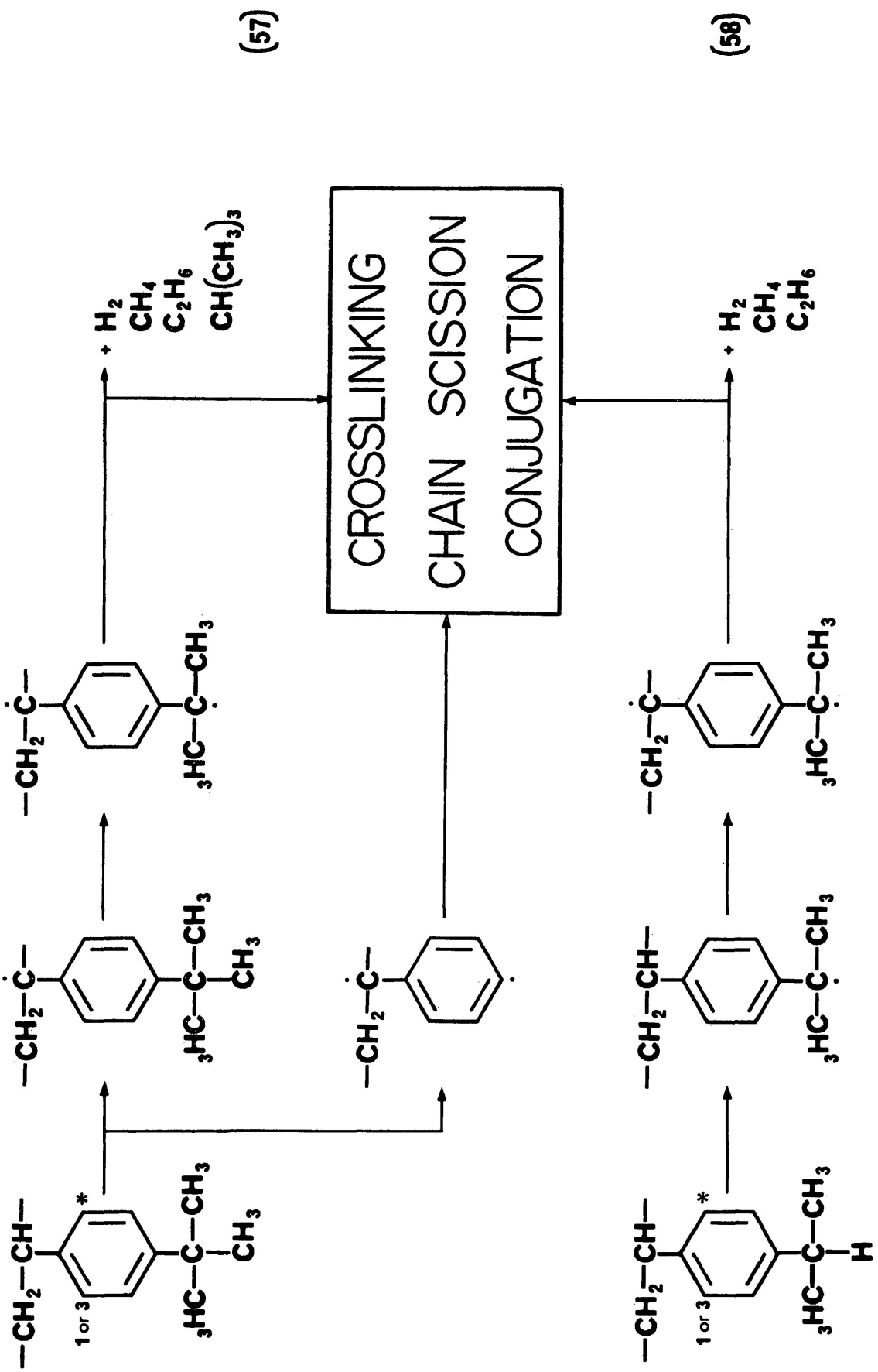
to a much more intense absorption observed for PPTB (see figure 3.25) is consistent with this theory since α-C-H cleavage followed by abstraction of an adjacent β-H is necessary for the formation of main chain unsaturations. Reactions (57) and (58) summarize the important details in the discussion of PPIP and PPTB.

4.6 Collective Considerations

4.6.1 Electronic Factors

In essence, the nature and extent of the secondary reactions observed in PVAP, PPBr, PPCl, PPF, PPIP, PPMO, and PPTB are directly related to the free energy of the radicals formed on the main chain, phenyl ring or the para-substituent. For example, benzylic radical formation on the main chain results in the α-carbon atom being electron defficient. Anything that assists in increasing the electron density at this location (i.e., the inductive and conjugative effects associated with the para-substituent), stablizes and lowers the free energy of the radical and also increases the probability of radical formation.

A measure of the electronic effects associated with a substituent in a phenyl ring can be assessed from Hammet σ-constants obtained from the Hammet equation (named for L. P. Hammet of Columbia University)(63):


(57)
(58)
CROSSLINKING
CHAIN SCISSION
CONJUGATION
+ H2
CH4
C2H6
CH(CH3)3
+ H2
CH4
C2H6
1 or 3
1 or 3

$$\log \frac{K}{K_0} = \rho \cdot \sigma \qquad (59)$$

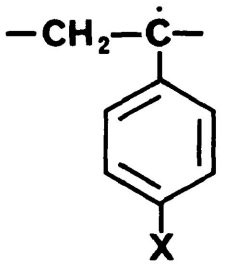
where: K refers to the reaction of a m- or p-substituted phenyl compound (e.g., ionization of a substituted benzoic acid)

K_0 refers to the same reaction of the unsubstituted compound

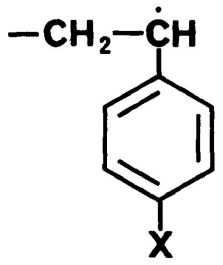
σ is the substituent constant which indicates the relative electron-withdrawing (positive value) or electron releasing (negative value) of a particular substituent

ρ is the reaction constant and is a measure of the susceptibility of the reaction to substituent effects.

It is important to note that the σ-constants are for reactions in solution and are not strictly comparable to reactions occurring in polymer films. The σ-values are presented however, in an attempt to provide a semi-quantitative measure of the effects of the para-substituents. Specifically, Hammet σ-constants may be used to evaluate the substituent effect on the two main radicals formed (i.e., benzylic radical, (60-1), or a radical formed by main chain scission (60-2)):



(60-1)



(60-2)

(60)

Electron withdrawing groups will reduce the stability of these radicals and therefore reduce the probability of formation.

Table 4.1 summarizes the inductive and conjugative effects as well as numerical values of Hammet σ-constants for the para-substituents involved in the styrene polymers. From the values listed, it may be predicted that the stability as well as the probability of main chain radical formation would follow a series such as:

$$\text{PPMO} > \text{PPTB} > \text{PPIP} > \text{PPF} > (\text{PPCl}, \text{PPBr}) > \text{PVAP} \qquad (61)$$

It is difficult to assess the activity of main chain radicals by taking into account the secondary reactions of chain scission, coloration and hydrogen production. In particular, it is difficult to separate and classify those reactions occurring in the main chain from those obtained from the system as a whole (i.e., para-substituent involvement).

On the basis of chain scission data from solubility and molecular weight measurements (assuming chain scission occurs by disproportionation rather than unzipping), the following series is suggested as an assessment of the activity of main chain (i.e., benzylic)

radicals:

$$PPF > PPTB > PPMO > (PPCl, PVAP) > (PPIP, PPBr) \quad (62)$$

A similar series is suggested on the basis of H_2 production:

$$PPBr > PPCl > PPMO > PPIP > PPTB > PVAP > PPF \quad (63)$$

A word of caution is in order with respect to this series, since para-substituents containing hydrogen atoms may contribute to the total amount liberated during photolysis. Also, all hydrogen radicals will not recombine with other hydrogen radicals or abstract hydrogen atoms since recombination with halogen and para-substituent radicals is observed.

The activity of the radical must be considered when evaluating its participation in any of the secondary reactions. It follows, that if the radical is stabilized by a +I effect (associated with the para-substituent) then involvement in crosslinking for example, will be much less than with radicals where such conditions do not exist. That is, the more stable the radical the less reactive it is as an isolated centre.

Considering series (61) and (62), there is a fair correlation between the ease of formation of a benzylic radical (reflected by Hammet σ-constants) and main chain scission. However, there does not appear to be a correlation between series (61) and (63), presumably due to mechanisms other than benzylic radical formation to account for hydrogen.

The lack of a better correlation with the Hammet series, (61), is partially due to the absence of experimentally observing a secondary reaction truly representative of the Hammet equation. In addition, it is worth noting that Hammet σ-constants are really applicable to solutions and not to reactions in a highly viscous media.

4.6.2 Steric Factors

The reactivity of the polymers cannot be discussed only in terms of inductive and conjugative effects. Steric factors must also be considered, with emphasis on both the para-isopropyl and para-*tert*-butyl groups.

For PVAP, PPBr, PPCl, PPF, and PPMO, partial or total cleavage of the para-substituent would leave the radical centre exposed, so that approach of another macroradical may result in the formation of a crosslink. However, in PPIP and PPTB, formation of

radical centres by partial cleavage of the para-substituent (i.e., fission of either C-CH_3 or C-H in PPIP and C-CH_3 in PPTB) would leave the radical centre 'shielded' by the remaining groups. In such a case, the approach and subsequent recombination with another macroradical would be sterically hindered.

It is also worth noting that cage effects imposed on large radicals may be important during the later stages of degradation. Isopropyl and *tert*-butyl radicals produced by complete cleavage of the para-substituent may not be able to escape such a cage and therefore be forced to recombine with the phenyl segment. Therefore, even though bonds are cleaved, radicals formed cannot participate in the crosslinking process.

4.6.3 Diffusion Controlled Reactions

During the initial stages of degradation, the production and subsequent liberation of products from thin polymer films may be diffusion controlled.

The importance of diffusion controlled reactions can be assessed by quantitatively measuring the amount of product produced as a function of temperature after receiving a dose of ultraviolet

radiation. Generally, two elementary observations may be made; either the amount of product increases (reflecting diffusion control) or remains constant with increasing temperature. In essence, as the temperature is increased the degassing process is monitored. From the data obtained (see figures 3.42 to 3.49), a decrease in product is observed with increasing temperature. Taking into account the method of detection, these results are consistent with the liberation of the product from the film during the period of analysis. In other words, what is actually observed at higher temperatures is the amount of product formed at 12°C less the amount which has diffused out and been analyzed. If diffusion control had been important, a gradual increase in products would have been noted. Instead, what is observed is the decrease in solubility of the gas with increasing temperature. This is a valid assumption since the same type of behaviour was observed for H_2, CH_4, C_2H_6, CO, and CO_2 during the calibration of the mass spectrometer (see figure 2.14). In each case a decay in relative peak height was observed in the amount of product detected, being directly proportional to the pressure (i.e., quantity) of sample.

Slight variations to this behaviour were observed in PPBr, PPF, PVAP-SW, and PVAP-LW. Both HBr and HF were entirely eliminated from the film at 20°C, beyond which a decrease was observed (see

figures 3.44 to 3.46). Similar behaviour was noted for ethane and acetaldehyde at 25°C in PVAP-SW (see figure 3.42). The slight increase in the production of ethane with increasing temperature for PVAP-LW (see figure 3.43) can be rationalized by considering the following. During long-wave irradiation, it is highly probable that radicals will be produced randomly (owing to the effective competition from photophysical processes). Since ethane must be formed by radical recombination, an increase in temperature will increase the mobility associated with the methyl radical and therefore increase the probability of recombination.

Considering an overall activation energy of 8 to 12 kcal/mole for the series of polymers studied, (4.8 kcal/mole reported for polystyrene(7)), as well as the temperature range covered during analysis, a significant increase in products should have been detected as a function of the diffusion process. However, from the present results it would appear that diffusion is not an important factor. In addition, Kilgoar and Van Oene(64), dealing with the photodegradation of automotive paints, have reported that with high absorption most of the reaction is on the surface and diffusion is not important.

4.7 Conclusions

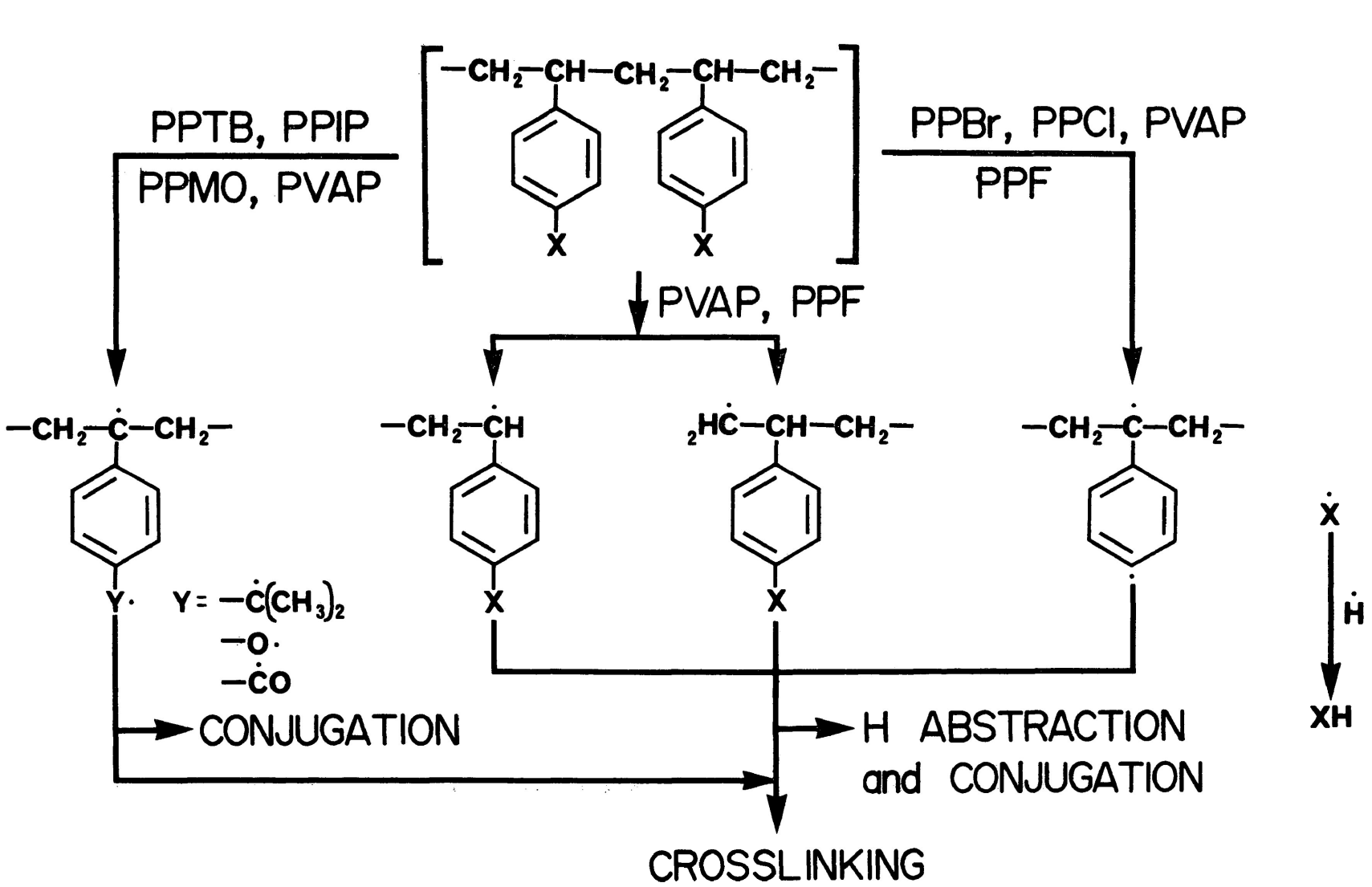
The data presented in this research project has shown that the nature and extent of the secondary photochemical reactions (chain scission, crosslinking, coloration and volatile product formation) are intimately related to the para-substitutent. Electronic (inductive and conjugative effects) and steric factors must be considered when evaluating the participation of the para-substituent in such reactions.

In the case of PVAP, the chromophore in the para-substituent does not particpate to any great extent in initiating photochemical reactions. The majority of the reactions are associated with intramolecular energy transfer processes following the absorption of ultraviolet light by the phenyl ring.

Volatile products measured as a function of temperature (12 to 52°C) following irradiation, suggest that diffusion is not important in the series of polymers studied.

A general reaction mechanism (a modified version of that originally suggested by Weir(39)) is presented in **(64)** to summarize the important reactions and preferred pathways for the para-substituted styrene polymers studied.

THE REACTION MECHANISM :



(64)

4.8 Suggestions for Future Work

This study on the vacuum photolysis of para-substituted styrene polymers has provided a considerable amount of information on their mechanisms of degradation.

There is however, other experimental data which should be obtained in order to provide a more comprehensive understanding into the nature of the photochemical reactions occurring in these styrene polymers.

In particular, fluorescence spectra obtained at lower temperatures (i.e., 77 K) can provide further insight into changes in the eximer prior to and during irradiation. Low temperature studies may also reveal carbonyl fluorescence or phosphorescence (associated with the carbonyl group in PVAP) which, when monitored as a function of exposure time, may reflect its participation in the formation of crosslinks.

As previously noted, the infrared spectra of polymer films following irradiation did not exhibit any major changes. This is not unexpected however, since the bulk of the polymer film would mask any changes occurring within the surface layers. A more detailed infrared spectra of the degraded polymer may be obtained by using

the technique of attenuated total internal reflectance (A.T.I.R.). This method essentially records the infrared spectra of the surface layers and may provide a greater examination of changes occurring in the macromolecular structure during irradiation.

The data obtained from the investigation into the possibility of diffusion controlled reactions is not conclusive evidence against this process. A more detailed study would be required in order to make a more definite conclusion. In particular, volatile products should be monitored as a function of film thickness after receiving dose of ultraviolet radiation.

Photooxidation should be performed on the series of polymers in order to evaluate the short and long term stability in typical environmental applications as well as to observe how the mechanism of photooxidation differs from that presented in this thesis.

Table 4.1 - Electronic Factors (Hammet σ-constants (63)) for the Para-substituents, Relative Hydrogen Yield and Relative Chain Scission Values for the Para-substituted Styrene Polymers:

p-substituent	Relative[1] H_2 Yield	Relative[1] Chain Scission	Inductive Effect[2]	Conjugative Effect[2]	Hammet σ-Constant[3]
$-COCH_3$	1^{-SW}	3^{-SW}	−	−	0.50
−Br	10	2	−	+	0.23
−Cl	7	3	−	+	0.23
−F	1	10	−	+	0.06
$-CH(CH_3)_2$	3	2	+	+	-0.15
$-OCH_3$	5	4	−	+	-0.27
$-C(CH_3)_3$	2	7	+	+	-0.20

1 – relative values are on a scale from 1 to 10 : the magnitude indicating the extent of the process.

2 – by convention, inductive and conjugative effects are − for electron withdrawl and + for electron donation.

3 – by convention, Hammet σ-values are + for electron withdrawl and − for electron donation.

CHAPTER 5

APPENDICES

5.1 Appendix A

```
*JOB
C
C     ************************************************************************
C     *                                                                      *
C     * VISCOSIMETRIC MOLECULAR WEIGHTS :                                    *
C     *                          A PROGRAM FOR EXPERIMENTAL DATA ELABORATION *
C     *                                                                      *
C     * THIS PROGRAM WAS WRITTEN BY A.PENATI, G.PAGANI, G.LOCATI AND F.BRACCO *
C     * OF THE INSTITUTE OF INDUSTRIAL CHEMISTRY, SECTION OF APPLIED CHEMISTRY *
C     * AND MATERIALS, POLYTECHNIC OF MILAN, ITALY.                          *
C     * REPRINTED FROM THE JOURNAL OF APPLIED POLYMER SCIENCE, VOLUME 19, PP. *
C     * 2583-2599, (1975).                                                   *
C     * THE PROGRAM HAS BEEN MODIFIED BY T.H.MILKIE, DEPARTMENT OF CHEMISTRY, *
C     * LAKEHEAD UNIVERSITY, AUGUST 12, 1976.                                *
C     *                                                                      *
C     * VARIABLES USED IN THIS PROGRAM :                                     *
C     * MN- IS THE NUMBER OF COMPLETE DATA SETS INPUT AS DATA.  EACH SET OF  *
C     *      DATA IS INDICATED BY A NUMERIC 1 IN COL 3 ON THE FIRST AND LAST *
C     *      CARD OF THE DATA SET                                            *
C     * ANI- NUMERICAL VALUES OF THE T-COEFFICIENT WITH REFERENCE TO A.H.BOWKER *
C     *      AND G.J.LIEBERMAN, ENGINERING STATISTICS, PRENTICE HALL, N.J.   *
C     * IPERC- IS THE CONFIDENCE INTERVAL                                    *
C     * AKA- IS THE CONSTANT 'K'                                             *
C     * AC- IS THE CONSTANT 'A'                                              *
C     * NN- IS THE NUMBER OF DILUTIONS MADE DURING EXPERIMENTATION           *
C     * AKK- IS THE VISCOMETER CONSTANT                                      *
C     * ROSOLV- IS THE SOLVENT DENSITY                                       *
C     * ROPOLY- IS THE POLYMER DENSITY                                       *
C     * TS- IS THE EFFLUX TIME OF PURE SOLVENT                               *
C     * T- IS THE EFFLUX TIME OF THE POLYMER-SOLVENT SYSTEM                  *
C     * WEIGHT- IS THE POLYMER WEIGHT IN GRAMS                               *
C     * CC- IS AN ARRAY OF WHICH THE FIRST ELEMENT IS THE INITIAL SOLVENT    *
C     *      VOLUME IN MLS. ; THE REMAINDER OF ELEMENTS LIST THE SOLVENT VOLUME *
C     *      ADDED AT EVERY DILUTION                                         *
C     *                                                                      *
C     * NOTES :                                                              *
C     * 1) DATA INPUT MUST BE CORRECTLY FORMATTED                            *
C     * 2) IF A NEGATIVE NUMBER IS INPUT FOR THE CONSTANT AKA, THE PROGRAM DOES *
C     *    NOT CALCULATE THE MOLECULAR WEIGHT                                *
C     * 3) IF A NEGATIVE NUMBER IS INPUT FOR THE CONSTANT AKK, DATA IS OUTPUT *
C     *    WITHOUT DENSITY AND KINETIC ENERGY CORRECTIONS                    *
C     *                                                                      *
C     * INPUT FORMAT :                                                       *
C     * CARD # :                                                             *
C     *   1 - COL 3 ; # OF DATA SETS (1D)                                    *
C     *   2 - COL 1 ; A MAXIMUM OF 80 CHARACTERS (80C)                       *
C     *   3 - COL 1 ; STUDENTS T DISTRIBUTION                                *
C     *       COL 11 ;                                                       *
C     *       COL 21 ;                                                       *
C     *       COL 31 ;                                                       *
C     *       COL 41 ;                                                       *
C     *       COL 51 ;                                                       *
C     *       COL 62 ; CONFIDENCE INTERVAL (COMMENCE IN COL 61 IF THIS IS A  *
C     *                THREE DIGIT NUMBER)                                   *
C     *   4 - COL 1 ; CONSTANT 'A' (3D)                                      *
C     *       COL 13 ; CONSTANT 'K'                                          *
C     *   5 - COL 3 ; NUMBER OF EXPERIMENTAL DILUTIONS (1D)                  *
C     *       COL 4 ; VISCOMETER CONSTANT (6D)                               *
C     *       COL 19 ; SOLVENT DENSITY (GMS/ML)                              *
C     *       COL 34 ; POLYMER DENSITY (GMS/ML)                              *
C     *   6 - COL 1 ; SOLVENT EFFLUX TIME (4D)                               *
C     *       COL 9 ; EXPERIMENTAL POLYMER-SOLVENT EFFLUX TIMES (4D)         *
C     *       COL 17 ;                                                       *
C     *       COL 25 ;                                                       *
C     *       COL 33 ;                                                       *
C     *   7 - COL 1 ; WEIGHT OF THE POLYMER IN GMS (6D)                      *
C     *       COL 11 ; VOLUME OF SOLVENT ADDED INITIALLY IN MLS.             *
C     *       COL 18 ; VOLUME OF SOLVENT ADDED FOR A DILUTION, IN MLS.       *
C     *       COL 25 ;                                                       *
C     *       COL 32 ;                                                       *
C     *   8 - COL 3 ; DIGIT 1                                                *
C     *                                                                      *
C     ************************************************************************
```

```
      1          DIMENSION T(100),X(100),Y(100),ANI(10),VOLSOL(100),
     1WEIGHT(100),ROPOLY(100),ROSOLV(100),CC(100)
      2          CHARACTER*80 TITLE                                              002100
      3       83 READ(5,80)MN                                                    003000
      4       80 FORMAT(I3)                                                      004000
      5          DO 63 I=1,MN                                                    005000
      6          READ(5,60) TITLE                                                006000
      7          WRITE(6,59) TITLE                                               007000
      8       60 FORMAT(A80)                                                     008000
      9       59 FORMAT('1',A80)                                                 009000
     10          READ(5,2)(ANI(K),K=1,6),IPERC                                   010000
     11        2 FORMAT(6F10.3,I3)                                               011000
     12          READ(5,61) AC,AKA                                               012000
     13       61 FORMAT(F10.4,F10.3)                                             013000
     14       62 READ(5,8)NN,AKK,ROSOLV,ROPOLY                                   014000
     15        8 FORMAT(I3,3F15.8)                                               015000
     16          IF(NN.LE.1)GOTO163                                              016000
     17          READ(5,9)TS,(T(I),I=1,NN)                                       017000
     18        9 FORMAT(10F8.3)                                                  018000
     19          READ(5,99)WEIGHT,(CC(I),I=1,NN)                                 019000
     20       99 FORMAT(F10.7,10F7.4)                                            020000
     21          SUMCC=0.0                                                       021000
     22          DO77M=1,NN                                                      022000
     23          SUMCC=SUMCC+CC(M)                                               023000
     24          VOLSOL(M)=SUMCC                                                 024000
     25          X(M)=WEIGHT*100.0/SUMCC                                         025000
     26       77 CONTINUE                                                        026000
     27          SUMX=0.0                                                        027000
     28          SUMY=0.0                                                        028000
     29          SUMXY=0.0                                                       029000
     30          SUMXO=0.0                                                       030000
     31          DO 7 M=1,NN                                                     031000
     32          IF(AKK.LT.0.0)GOTO444                                           032000
     33          VOLPOL=WEIGHT/ROPOLY                                            033000
     34          WESOL(M)=VOLSOL(M)*ROSOLV                                       034000
     35          ROSOLV(M)=(WEIGHT+WESOL(M))/(VOLPOL+VOLSOL(M))                  035000
     36          Y(M)=ROSOLV(M)*T(M)*(1.0-AKK/T(M)**2)/((ROSOLV*TS*X(M))*(1.0-AKK/T
     1S**2))-1.0/X(M)                                                           037000
     37      444 IF(AKK.LT.0.0)Y(M)=(T(M)-TS)/(TS*X(M))                         038000
     38          SUMX=SUMX+X(M)                                                  039000
     39          SUMY=SUMY+Y(M)                                                  040000
     40          SUMXY=SUMXY+X(M)*Y(M)                                           041000
     41          SUMXO=SUMXO+X(M)*X(M)                                           042000
     42        7 CONTINUE                                                        043000
     44       19 FORMAT(///,1X,' LIST OF MEASURES ',/)                           045000
     45          IF(AKK.LT.0.0)GOTO666                                           046000
     46          WRITE(6,667)TS                                                  047000
     47      667 FORMAT(//,2X,'TS =',F7.2,5X,' WITH DENSITY AND KINETIC-ENERGY CORR 048000
     1ECTIONS ',//)                                                             049000
     48          IF(AKK.GT.0.0)GOTO777                                           050000
     49      666 WRITE(6,668)TS                                                  051000
     50      668 FORMAT(//,1X,' TS =',F7.2,5X,' WITHOUT CORRECTIONS ',//)        052000
     51      777 NOBS=NN                                                         053000
     52          C=NN                                                            054000
     53          XMED=SUMX/C                                                     055000
     54          NI=NN-2                                                         056000
     55          B=(SUMXY-XMED*SUMY)/(SUMXO-C*XMED**2)                           057000
     56          A=SUMY/C-B*XMED                                                 058000
     57          PK=B/A**2                                                       059000
     58          XO=0.0                                                          060000
     59          QMIN=0.0                                                        061000
     60          DO30 M=1,NOBS                                                   062000
     61          Y1=A+B*X(M)                                                     063000
     62          QMIN=QMIN+(Y1-Y(M))**2                                          064000
     63          XO=XO+(X(M)-XMED)**2                                            065000
     64          WRITE(6,20)M,T(M),X(M),Y(M),Y1                                  066000
     65       20 FORMAT(1X,I2,2X,' TIME(SEC)=',F7.2,2X,' X(G/DL)=',F7.4,2X,' Y=',F7 067000
     1.4,2X,' Y1=',F7.4,/)                                                      068000
     66       30 CONTINUE                                                        069000
     67          SYX=SQRT(QMIN/(C-2.0))                                          070000
     68          ALIMB=ANI(NI)*(SYX/SQRT(XO))                                    071000
     69          ALIMA=ANI(NI)*SYX*SQRT(1.0/C+XMED**2/XO)                        072000
     70          WRITE(6,21)SYX                                                  073000
     71       21 FORMAT(//,'  STANDARD DEVIATION=',F7.4)                        074000
     72          WRITE(6,39)IPERC                                                075000
     73       39 FORMAT(///,'  CONFIDENCE INTERVAL =',I3)                       076000
     74          WRITE(6,5)A,ALIMA                                               077000
     75        5 FORMAT(//,'  INTERCEPT(=INTRINSIC VISCOSITY)=',F6.3,3H +-,F5.4,//) 078000
     76          WRITE(6,69)B,ALIMB                                              079000
     77       69 FORMAT(1X,' SLOPE=',E10.4,3H +-,E10.4,/)                        080000
     78          BMAX=B+ALIMB                                                    081000
     79          BMIN=B-ALIMB                                                    082000
     80          AMAX=A+ALIMA                                                    083000
     81          AMIN=A-ALIMA                                                    084000
     82          PKMAX=BMAX/AMIN**2                                              085000
     83          PKMIN=BMIN/AMAX**2                                              086000
     84          WRITE(6,233)PK,PKMAX,PKMIN                                      087000
     85      233 FORMAT(/,'  HUGGINS CONSTANT=',F7.4,2X,' MAX=',F7.4,2X,' MIN=',F7. 088000
     14)                                                                        089000
     86          IF(AKA.LT.0.0)GOTO73                                            090000
     87          AO=A/AKA                                                        091000
     88          RA=1.0/AC                                                       092000
     89          AL=ALOG(AO)                                                     093000
     90          AOA=(A+ALIMA)/AKA                                               094000
     91          AOM=(A-ALIMA)/AKA                                               095000
     92          ALA=ALOG(AOA)                                                   096000
     93          ALM=ALOG(AOM)                                                   097000
     94          ARG=RA*AL                                                       098000
     95          AM=EXP(ARG)                                                     099000
     96          AMA=EXP(RA*ALA)                                                 100000
     97          AMI=EXP(RA*ALM)                                                 101000
     98          WRITE(6,79)AC,AKA                                               102000
     99       79 FORMAT(//,1X,' A=',E10.4,4X,' K=',E10.4,///)                    103000
    100          WRITE(6,6)AM,AMA,AMI                                            104000
    101        6 FORMAT(1X,' AVERAGE MOL WEIGHT=',E10.4,2X,' MAX=',E10.4,2X,' MIN='  105000
     1,E10.4,//1H0)                                                             106000
    102       73 GOTO 62                                                        107000
    103      163 CONTINUE                                                       108000
    104       26 STOP                                                          109000
    105          END                                                           110000
      $ENTRY
```

5.2 Appendix B

The values of k and α for poly(vinylacetophenone) were not listed in conventional tables and therefore had to be determined experimentally.

Since two different molecular weight samples of the polymer were originally prepared, it was a matter of obtaining values of intrinsic ciscosity for each sample and calculating the constants on the basis of the Mark-Houwink equation(48):

$$\{\eta\} = k \cdot M^{\alpha}$$

where: $\{\eta\}$ is the intrinsic viscosity
$= \lim_{c \to o} [\eta_{sp}/c]$

η_{sp} is the specific viscosity
$= (ts-to)/to$

ts is the efflux time for solution

to is the efflux time for pure solvent

c is the concentration in units of weight fraction

M is the molecular weight

k and α are constants which depend on the solvent, polymer and temperature.

From the data obtained:

	M.Wt.	$\{\eta\}$
Sample 1	2.80×10^5	1.10
Sample 2	1.54×10^5	0.73

Using:

$$\{\eta\}_1 = k \cdot M_1^{\alpha} \quad (1)$$

$$\{\eta\}_2 = k \cdot M_2^{\alpha} \quad (2)$$

$$k = \{\eta\}_2 / k \cdot M_2^{\alpha} \quad (3)$$

$$\{\eta\}_1 / \{\eta\}_2 = (M_1/M_2)^{\alpha} \quad (4)$$

where:

$$c = M_1/M_2 = 0.55$$

$$d = \{\eta\}_1/\{\eta\}_2 = 0.66$$

$$\alpha = \log_c d \quad (5)$$

$$\alpha = \frac{\log_{10} d}{\log_{10} c} = 0.70$$

by substituting α into equation (1): $k = 2.79 \times 10^{-4}$.

5.3 Appendix C

Values of intrinsic viscosity and corresponding molecular weights (by light scattering) for poly(p-fluorostyrene) have been reported by Baysal et al.(65):

	M.Wt.	$\{\eta\}$
Sample 1	6.90×10^4	0.20
Sample 2	1.20×10^5	0.28

As with poly(vinylacetophenone), constants k and α were calculated using the Mark-Houwink equation(48):

$$\{\eta\} = k \cdot M^{\alpha} \qquad (1)$$

Using:
$$\{\eta\}_1/\{\eta\}_2 = (M_1/M_2)^{\alpha} \qquad (2)$$

where:
$$c = M_1/M_2 = 0.58$$

$$d = \{\eta\}_1/\{\eta\}_2 = 0.71$$

$$\alpha = \log_c d \qquad (3)$$

$$\alpha = \frac{\log_{10} d}{\log_{10} c} = 0.63$$

by substituting α into equation (1): $k = 1.79 \times 10^{-4}$.

REFERENCES

1. R. B. Fox, Polym. Prepr., 16, 177 (1975).

2. J. G. Calvert and J. N. Pitts, Jr., "Photochemistry", Wiley, New York (1966).

3. H. Morawetz, "A.C.S. Symposium on Ultraviolet Light Induced Reactions in Polymers", Series 25, (Ed. S. S. Labana), Amer. Chem. Soc., Washington (1976), p. 188.

4. G. Geuskens, "Degradation and Stabilization of Polymers", Wiley, New York (1975).

5. B. P. Straughan and S. Walker, "Spectroscopy", Vol. 3, Wiley, New York (1976).

6. W. Klopffer, Europ. Poly. J., 11, 203 (1975).

7. R. F. Reinisch, H. R. Gloria and G. M. Andros, "Photochemistry of Macromolecules", (Ed. R. F. Reinisch), Plenum Press, New York (1970), p. 185.

8. R. B. Fox, L. G. Isaacs, F. E. Saalfield and M. V. McDowell, U. S. Naval Research Lab. Rept., No. 6284 (1964).

9. N. Grassie and N. A. Weir, J. Appl. Polym. Sci., 9, 987 (1965).

10. S. W. Benson, "Thermochemical Kinetics", Wiley, New York (1969).

11. E. E. Schneider, Disc. Faraday Soc., 19, 158 (1955).

12. B. J. Abraham and D. H. Whiffen, Trans. Faraday Soc., 54, 1291 (1958).

13. R. E. Florin and L. A. Wall, Trans. Faraday Soc., 56, 1305 (1960).

14. H. Fischer, K. H. Hellwege and U. Johnson, Kolloid-Z., 170, 61 (1960).

15. S. Ohnishi, T. Tanei and J. Nitta, J. Chem. Phys., 37, 2402 (1962).

16. R. E. Florin, L. A. Wall and D. W. Brown, J. Polym. Sci., A-1, 1521 (1963).

17. L. A. Wall and R. B. Ingalls, J. Chem. Phys., 41, 1112 (1964).

18. H. Fischer, J. Chem. Phys., 37, 1094 (1962).

19. L. A. Wall and D. W. Brown, J. Phys. Chem., 61, 129 (1957).

20. N. A. Slovokhota, Z. F. Il'icheva and V. A. Kargin, Polym. Sci., U.S.S.R., 3, 54 (1962).

21. B. Ranby and J. F. Rabek, "Photodegradation, Photo-oxidation and Photostabilization of Polymers", Wiley, New York (1975).

22. N. Grassie and N. A. Weir, J. Appl. Polym. Sci., 9, 999 (1965).

23. J. B. Lawrence and N. A. Weir, unpublished work (1970).

24. J. B. Lawrence and N. A. Weir, J. Polym. Sci., 11, 105 (1973).

25. G. A. George and D. E. Hodgeman, Europ. Polym. J., 13, 63 (1977).

26. J. A. Kerr, Chem. Rev., 66, 466 (1966).

27. P. J. Burchill and G. A. George, J. Polym. Sci., Polym. Lett. Ed., 12, 497 (1974).

28. G. A. George, J. Appl. Polym. Sci., 18, 419 (1974).

29. B. Ranby and J. F. Rabek, J. Polym. Sci., 12, 282 (1974).

30. N. A. Weir, personal communciation (1976).

31. J. B. Birks, "Photophysics of Aromatic Molecules", Wiley, New York, (1970).

32. J. F. Rabek, "Comprehensive Chemical Kinetics", (ed. C. H. Bamford and C. F. Tipper), Vol. 14, Elsevier, Oxford (1974), p. 265.

33. T. Takeshita, K. Tsuji and T. Seiki, J. Polym. Sci., 10, 2315 (1972).

34. K. Tsuji, T. Seiki and T. Takeshita, J. Polym. Sci., 10, 3119, (1972).

35. R. H. Partridge, J. Chem. Phys., 45, 1679 (1966).

36. I. Boustead and A. Charlesby, Europ. Polym. J., 3, 459 (1967).

37. H. Monig and H. Z. Kriegel, Z. Naturforsh, 15, 333 (1960).

38. R. B. Fox and T. R. Price, J. Appl. Polym. Sci., 11, 2373 (1967).

39. N. A. Weir, J. Appl. Polym. Sci., 17, 401 (1973).

40. D. Nicholas, unpublished work (1975).

41. J. K. Chernova, V. P. Golikov, S. S. Leshchenko, V. I. Muromtsev and V. L. Karpov, Khimiya Vysokikh Energii, 8, 3, 265 (1974).

42. A. Charlesby, "Atomic Radiation of Polymers", Pergamon Press, Oxford (1960).

43. W. Burlant and J. Neerman, J. Polym. Sci., 58, 491 (1962).

44. N. Pravednikov and S. S. Mendelev, Dokl. Akad. Nauk SSSR, 122, 254 (1958).

45. A. Cox and T. J. Kemp, "Introduction to Photochemistry", McGraw-Hill, New York (1971).

46. H. C. Beachell and L. H. Smiley, J. Polym. Sci., 5, 1635 (1967).

47. D. Braun, H. Cherdron and W. Kern, "Techniques of Polymer Synthesis and Characterization", Wiley, New York (1971).

48. F. W. Billmeyer, Jr., "Textbook of Polymer Science", Wiley-Interscience, New York (1966).

49. J. Brandrup and E. H. Immergut, "Polymer Handbook", Wiley-Interscience, New York (1966).

50. U. V. Atlas of Organic Compounds, Butterworths, London (1968), D8/7.

51. N. Grassie and N. A. Weir, J. Appl. Polym. Sci., 9, 999 (1965).

52. F. Hirayama, J. Chem. Phys., 42, 3162 (1965).

53. E. A. Chadros and C. J. Dempster, J. Amer. Chem. Soc., 92, 3568 (1970).

54. R. T. Sanderson, "Chemical Bonds and Bond Energy", 2nd ed., Academic Press, London (1976).

55. V. I. Vendenevev, L. V. Gurvich, V. N. Kondrat'yev, V. A. Medvedev and Ye. L. Frankevich, "Bond Energies Ionization Potentials and Electron Affinities", St. Martin's Press, New York (1966).

56. R. T. Morrison and R. N. Boyd, "Organic Chemistry", 3rd ed., Allyn and Bacon, Boston (1974).

57. N. Grassie and N. A. Weir, J. Appl. Polym. Sci., 9, 975 (1965).

58. T. Otsu, "Progress in Polymer Science", Japan, Vol. 1, Kodansha, Tokyo (1971).

59. N. Inagaki, Y. Takagi and K. Katsuura, Europ. Polym. J., 13, 433 (1977).

60. A. D. Cross and R. A. Jones, "An Introduction to Practical Infrared Spectroscopy", 3rd ed., Butterworths, London (1969).

61. P. Hrdlovic, J. Danecek, D. Berek and I. Lucac, Europ. Polym. J., 13, 123 (1977).

62. J. F. Rabek and B. Ranby, J. Polym. Sci., 12, 295 (1974).

63. C. D. Johnson, "The Hammet Equation", Cambridge University Press, London (1973).

64. P. C. Killgoar, Jr. and H. Van Oene, "A.C.S. Symposium on Ultraviolet Light Induced Reactions in Polymers", Series 25, (Ed. S. S. Labana), Amer. Chem. Soc., Washington (1976), p. 407.

65. B. Baysal, B. A. Lowry, H. Yu and W. H. Stockmayer, in "Dielectric Properties of Polymers", (Ed. F. E. Karasz), Plenum Press, New York (1972), p. 329.