NEW ASPECTS OF ENERGY TRANSFER PHENOMENA IN HIGH POLYMER SYSTEMS INCLUDING
DEGRADATION PHENOMENA

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ABSTRACT

Energy transfer in solid polymers is favoured by strong interactions bet-
ween chromophores. It depends on the nature of these chromophores, and de-
creases with increasing distance between them. Orientation of the chains
and sample crystallinity improve its efficiency. Energy transfer is useful
to prevent polymer degradation. It can also be responsible for the initia-
tion of the photo-oxidation of polymers.

INTRODUCTION

Transfer of energy from one molecule or group in the excited state to another molecu-
le or group usually in the ground state : $D^* + A \rightarrow D + A^*$
can result either in sensitization of photochemical reactions of the acceptor A or in inhibi-
tion of photochemical reactions of the donor D. In polymers such a photophysical process can
be even more important than in most low molecular weight systems because migration of energy
often occurs prior to the transfer, making the transfer more efficient than expected. More-
over, initiation of the photodegradation of polymers is sometimes the consequence of energy
transfer from an absorbing impurity to a photoreactive group in the macromolecule. On the
other hand, transfer of energy also provides a useful method of preventing the deterioration
of polymeric materials during continued exposure to solar radiation or to artificial light
sources.

MIGRATION OF ENERGY IN POLYMERS

Migration of energy in polymers was demonstrated some years ago when it was discovered that
in polyvinylbenzophenone (PVB) the transfer of energy from the excited triplet state of the
benzophenone chromophore to naphthalene was much more efficient than in a glassy solution
of benzophenone and naphthalene [1]
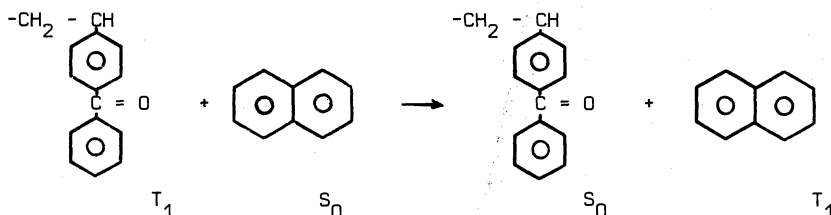
Such a process occurs by exchange interaction and its efficiency is expected to decrease ex-
ponentially with increased distance between donor and acceptor [2]. It can be characterized
by a critical transfer distance R_o between donor and acceptor at which the probabilities for
spontaneous deactivation and for energy transfer are equal [3]. In glassy solutions of low
molecular weight compounds R_o is usually 11 to 13, but in PVB it was found to be 36 Å. Such
a high value is strong evidence for extensive migration of energy between benzophenone chro-
mophores in the polymer prior to transfer to naphthalene when naphthalene is acting as the
final acceptor. Similar measurements were performed with polyphenylvinylketone (PPVK) [4]
and with polymethylvinylketone (PMVK) [5]

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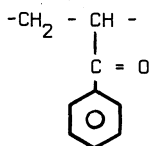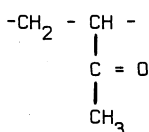
The results are summarized in Table 1.

TABLE 1. Triplet-triplet energy transfer to naphthalene

Polymer (film at 77°K)	R_0 experimental (Å)
Polyvinylbenzophenone	36
Polyphenylvinylketone	26
Polymethylvinylketone	11

These values indicate that energy migration is also important in PPVK though less so than in PVB but that it does not occur, or only to a minor extent, in PMVK. This suggests that the extended conjugated system in the chromophore of PVB favours exchange interactions between side groups in that polymer and makes the migration of energy more efficient than in PPVK. In PMVK, the excitation is localized on the carbonyl group and migration does not occur. More recently, the efficiency of the energy transfer from benzophenone units to naphthalene has been studied in a series of styrene-vinylbenzophenone copolymers of various compositions (6).
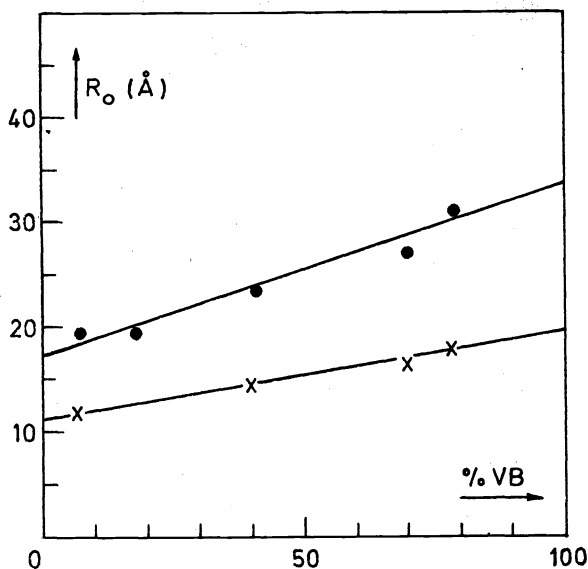

Fig. 1. Critical transfer distance to naphthalene at 77°K as a function of vinylbenzophenone content in styrene-vinylbenzophenone copolymers (● solid films, x glassy solutions).

Fig. 1 shows that increasing the mean distance between vinylbenzophenone units results in a decrease of the migration efficiency, as expected for a mechanism including exchange interactions.

Migration of energy is not typical of polymers : it is even more efficient in molecular crystals but polymers are soecially interesting because migration occurs also in amorphous samples. Their behaviour is thus intermediate between that of a completely disordered glass and that of an ordered lattice. This suggests that some kind of organization exists even in amorphous polymer samples and it is important to investigate whether the relative orientation of neighbouring units in the chain or the morphology of the sample has an influence on the efficiency of the migration. For that purpose the method used previously, based on the use of additive, is not suitable because the presence of an additive could change the morphology of the sample.

The emission spectra of vinylaromatic polymers and copolymers provide information concerning the structural factors involved in the migration of energy. In fluid solutions at room temperature most vinylaromatic polymers such as polystyrene, polyvinylnaphthalene, etc. exhibit beside normal fluorescence, which is the mirror image of the absorption spectrum, a broad structureless emission shifted to longer wavelengths due to excimer fluorescence. An excimer is a complex formed between an excited group and an identical group in the ground state during the life-time of the excited state. Formation of such a complex requires that the aromatic rings be parallel at a distance of about 3 Å. In fluid polymer solutions excimers

are formed intramolecularly since the emission spectrum is independent of concentration. In rigid glassy solutions, no excimer emission can be detected because the rigidity of the matrix restricts side group motion and prevents the attainment of the appropriate geometric configuration. However, in solid polymer samples at room temperature excimer fluorescence is emitted almost exclusively. Since light is absorbed at random, and since it is quite unlikely that any excited chromophore has one neighbouring group suitably oriented to allow the formation of an excimer, this clearly demonstrates that excitation can migrate until a pair of nearby groups forming an excimer site is reached.

When poly-1-vinylnaphthalene (PVN) is compared with polyacenaphthylene (PAcN) one can expect that formation of an excimer site will be easier in the former since rotation of the naphthalene ring around the single bond is possible and makes it more likely for two neighbouring groups to become parallel at a distance of about 3 Å than in PAcN where the naphthalene is rigidly linked to the polymer backbone

- CH$_2$ - CH -   - CH - CH -

PVN.   PAcN

Indeed, fig. 2 shows that in solution the ratio of normal to excimer fluorescence intensities is higher in PAcN than in PVN (7).
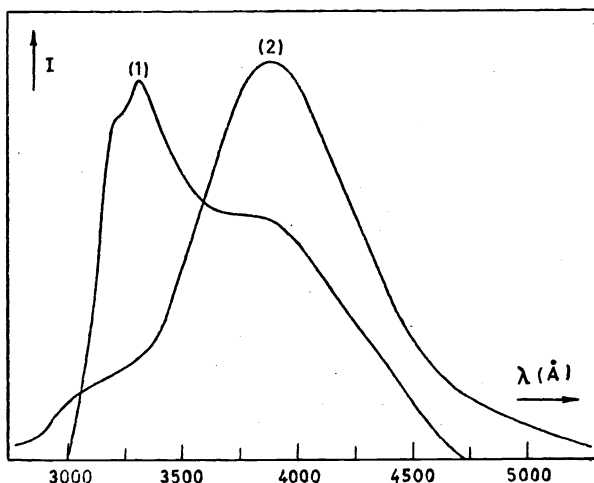

Fig. 2. Fluorescence spectra at room temperature of PAcN (1) and PVN (2) in 2-methyltetrahydrofuran (excitation at 3000 Å).

In the solid state, however, only excimer fluorescence is observed in both cases (fig. 3). This shows that although the number of excimer sites is undoubtedly smaller in PAcN, migration is efficient enough for excitation to reach such a site. Stereochemical requirements for migration are thus less severe than for excimer formation. Moreover, this result indicates that in the solid state migration does not necessarily occur along the chain.

The influence of tacticity, orientation and crystallinity on the efficiency of energy migration has been investigated in polystyrene samples at 77°K (8).

TABLE 2. Ratio of normal to excimer fluorescence in polystyrene at 77°K

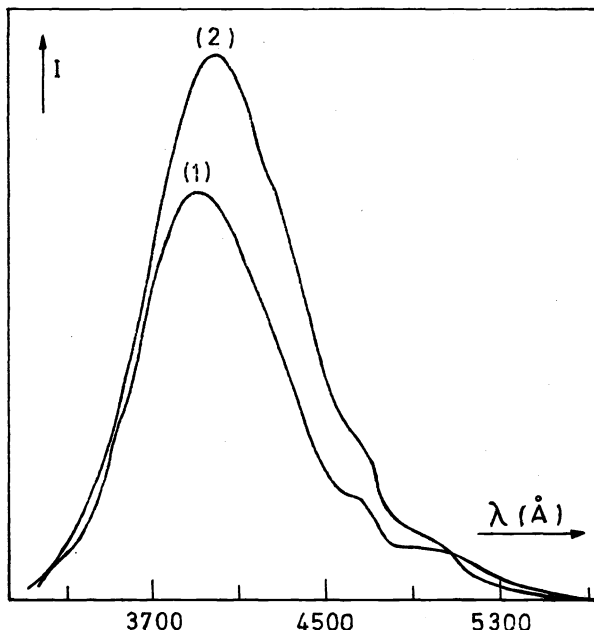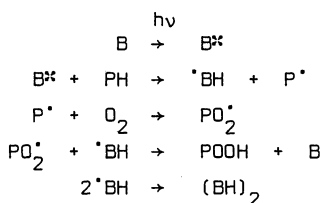| Polystyrene (film)	I_M/I_D
Atactic	0.70
Oriented (F = 0.07)	0.60
Oriented (F = 0.1)	0.48
Isotactic amorphous	0.28
Isotactic crystalline (25%)	0.10
Isotactic crystalline (35%)	0.01

Fig. 3. Fluorescence spectra at room temperature of PAcN (1) and PVN (2)
films (excitation at 3000 Å). Sensitivity is 1.6 times lower for PVN.

At 77°K in an amorphous film cast from a solution of atactic polystyrene normal and excimer
fluorescence are emitted with comparable intensities. When such films are stretched to a-
bout five times their original length the chains become oriented and the sample birefringent
(it can be characterized by an orientation factor F). This results in a decrease of the ratio
I_M/I_D. This ratio is even smaller in an isotactic sample and decreases further in crystalline
samples. This is not due to an increase of the number of excimer sites in crystalline poly-
styrene since in the threefold helices formed the distance between nearest parallel aromatic
rings is 6.5 Å (9) i.e. much too large to allow excimer formation. It can thus be conclu-
ded that excimer sites are probably trapped at crystalline and structural defects and that
the very low ratio I_M/I_D is the consequence of a more efficient energy migration in organi-
zed samples.

To summarize the conclusions derived so far, one can say that migration of energy in solid
polymers, either to an additive or to an excimer site, is favoured by strong interaction bet-
ween chromophores; it decreases with increasing the mean distance between chromophores but
is not much dependent on their relative orientation. However orientation of the chains and
crystallization result in the creation of more or less organized regions in the sample which
makes the migration of energy more efficient. In fluid or glassy polymer solutions migration
of energy has also been demonstrated by using additives as energy acceptors (6), by measuring
the ratio of normal to excimer fluorescence (10) or by measuring depolarization of fluores-
cence and phosphorescence (11). As far as a comparison is possible, migration has always
been found more efficient in solid samples than in fluid or glassy solutions. This is impor-
tant with respect to photodegradation and photostabilization since polymers are most often
used as solid materials.

TRANSFER OF ENERGY IN DEGRADATION AND STABILIZATION OF POLYMERS

As a practical demonstration of the usefulness of energy transfer processes in the photo sta-
bilization of polymers we showed some years ago that both cross-linking of polyvinylbenzophe-
none (12) and main chain scission in polyphenylvinylketone (14) on irradiation at 3650 Å
could be very efficiently inhibited by naphthalene in agreement with the results mentioned
earlier in this paper. In natural weathering conditions the photodegradation of polymers
is complicated by the presence of oxygen and quite often photo-oxidation is initiated by
carbonyl groups present as impurities (14)(15). Aromatic ketones such as benzophenone or
acetophenone have been recently shown to initiate the photo-oxidation of polystyrene on irra-
diation at wavelengths higher than 3000 Å by a mechanism involving the excited triplet state
of the ketone (13) :

$$B \xrightarrow{h\nu} B^{*}$$

$$B^{*} + PH \rightarrow {}^{\cdot}BH + P^{\cdot}$$

$$P^{\cdot} + O_2 \rightarrow PO_2^{\cdot}$$

$$PO_2^{\cdot} + {}^{\cdot}BH \rightarrow POOH + B$$

$$2\,{}^{\cdot}BH \rightarrow (BH)_2$$

This process ultimately results in main chain scission and in a decrease of the ultimate tensile strength of the samples as shown on fig. 4.
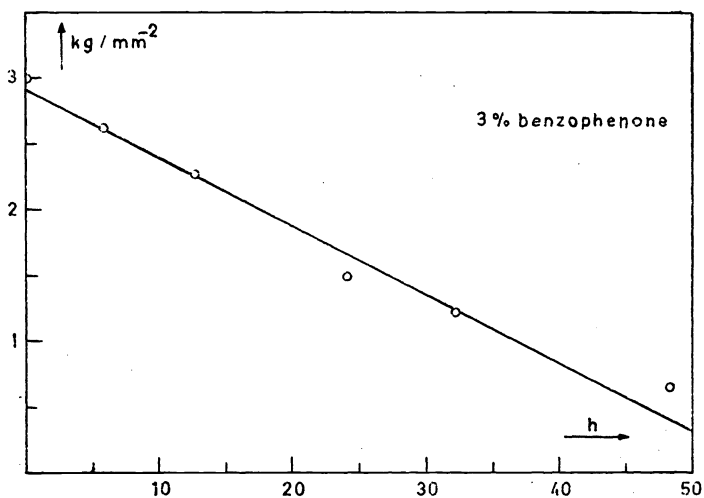

Fig. 4. Ultimate tensile strength of polystyrene samples (about 0.3 mm thick) containing 3 per cent by weight of benzophenone. Irradiation at 3650 Å in the presence of air.

In this case also naphthalene acting as a quencher of the excited triplet state of benzophe-none is a very efficient stabilizer : an almost complete inhibition of the photo-oxidation is obtained with concentration of the order of a few per cent by weight of the additive as shown on fig. 5. In fig. 5 the efficiency of the transfer f is defined as $\phi_{ox}^{o} - \phi_{ox}/\phi_{ox}^{o}$ where ϕ_{ox}^{o} and ϕ_{ox} are the quantum yields of oxygen absorption in polystyrene films containing 3 wt % benzophenone respectively in the absence and in the presence of naphthalene.
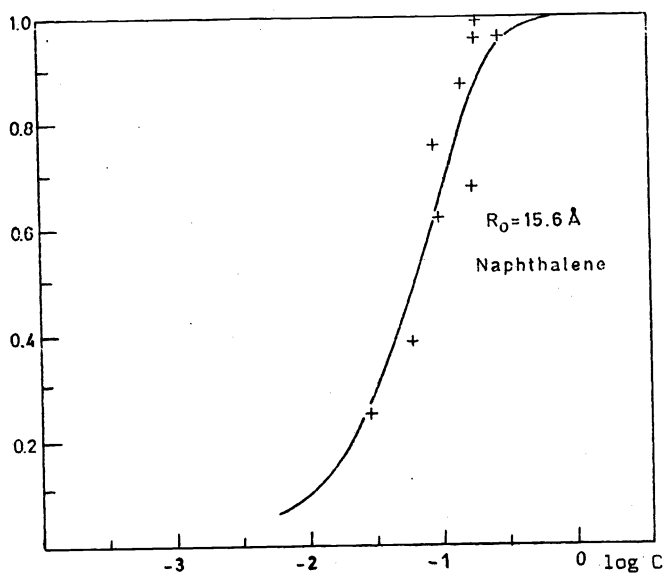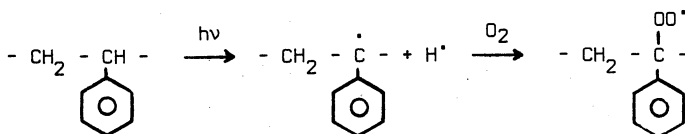

Fig. 5. Efficiency of energy transfer from benzophenone to naphthalene measured from the quantum yield of oxygen absorption. Irradiation at 3650 Å and 600 torr oxygen pressure.

The critical transfer distance determined in this case is in reasonable agreement with the value obtained by luminescence measurements (3). This indicates that fundamental energy transfer studies can be transposed quite easily and often quantitatively to practical applications.

Transfer of energy should not always be considered as a beneficial effect useful to prevent the deterioration of polymers. It can also be responsible for the initiation of the photodegradation. This is undoubtedly what happens in the photo-oxidation of polystyrene irradiated at 2537 Å i.e. in the absorption range of the phenyl chromophore. Under these conditions, the quantum yield of oxygen absorption has been measured to be $\phi_{O_2} = 2.7 \ 10^{-2}$ at a pressure of 600 torr oxygen. It is quite unlikely that the reaction is initiated according to

$$- CH_2 - \underset{\underset{\bigcirc}{|}}{CH} - \quad \xrightarrow{h\nu} \quad - CH_2 - \underset{\underset{\bigcirc}{|}}{\overset{\bullet}{C}} - \ + H^{\bullet} \quad \xrightarrow{O_2} \quad - CH_2 - \underset{\underset{\bigcirc}{|}}{\overset{\overset{OO^{\bullet}}{|}}{C}} -$$

since the quantum yield of hydrogen evolution in vacuum is only $\phi_{H_2} = 4.5 \ 10^{-5}$.

What reaction could be responsible for the formation of macroradicals which then react with oxygen ? Water is the major product formed in the photo-oxidation of polystyrene. It originates from the decomposition of hydroperoxides and is produced with a quantum yield $\phi_{H_2O} = 2.2 \ 10^{-2}$ very close to the quantum yield of oxygen absorption. This suggests that oxidation could be related to the photo-decomposition of hydroperoxides into free radicals which will abstract hydrogen atoms from the polymer chain. However, direct absorption of light by hydroperoxides is not important since their absorption coefficient is not higher than that of polystyrene at 2537 Å but energy absorbed by the polymer can be transfered to hydroperoxides. Such a mechanism is supported by luminescence measurements which show that excimer fluorescence of polystyrene disappears in the early stage of the photo-oxidation without being replaced by any new emission (fig. 6)
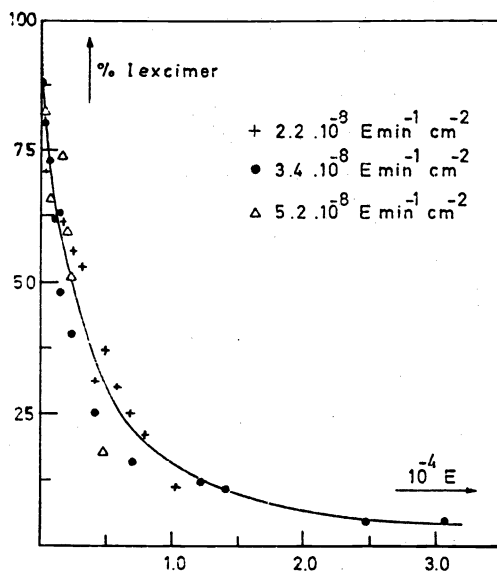

Fig. 6. Intensity of excimer fluorescence measured at 3300 Å on polystyrene films irradiated at 2537 Å at 600 torr oxygen pressure.

This is the consequence of energy transfer from polystyrene to non-emitting oxidation products which are most likely hydroperoxides. Indeed, fig. 7 shows that cumene hydroperoxide, a model for polystyrene hydroperoxides, quenches the excimer fluorescence of polystyrene.

It can thus be concluded that transfer of energy from polystyrene to hydroperoxides becomes more and more efficient as their concentration increases until transfer becomes complete. At that time, decomposition of hydroperoxides into free radicals becomes the major mechanism responsible for the absorption of oxygen. This conclusion is supported by the fact that in polystyrene films containing cumene hydroperoxide transfer of energy is very efficient from the very beginning of the reaction and results in a high initial rate of oxidation (fig. 8). When cumene hydroperoxide has been decomposed (as measured by infra-red spectroscopy) photo-oxidation proceeds at the usual rate through the decomposition of polystyrene hydroperoxides.
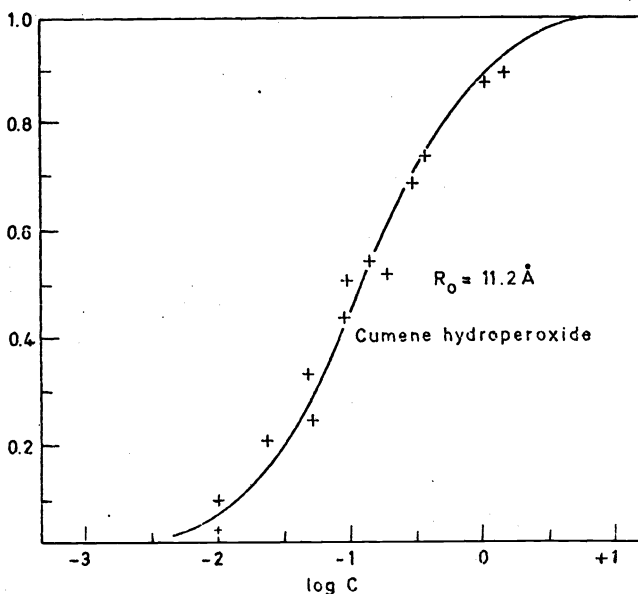
Fig. 7. Efficiency of energy transfer from polystyrene (excitation at 2537 Å) to cumene hydroperoxide. $f = I_o - I/I_o$, where I_o and I are the intensities of excimer fluorescence at 3300 Å, respectively in the absence and in the presence of the additive.
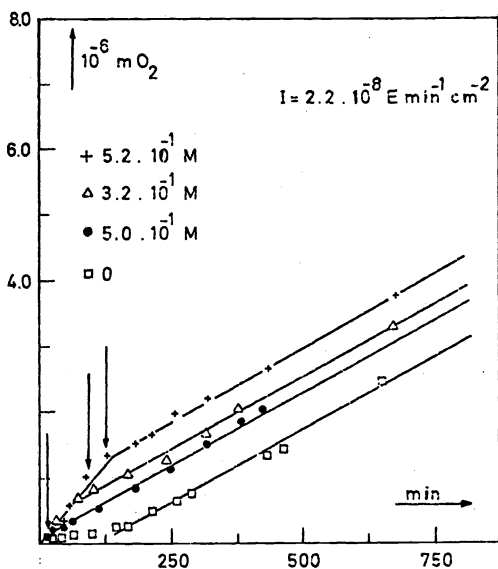

Fig. 8. Absorption of oxygen by polystyrene films containing various concentrations of cumene hydroperoxide. (The arrow indicates when cumene hydroperoxide is completely decomposed). Irradiation at 2537 Å and 600 torr oxygen pressure.

The results obtained so far demonstrate that transfer of energy to hydroperoxides plays a major role in the photo-oxidation of polystyrene. It can be suggested that such a conclusion is of general significance and is applicable to the photo-oxidation of other polymers such as polyethylene or polypropylene exposed to solar radiation. In those polymers indeed, the photolysis of carbonyl groups is believed to be the main cause of deterioration in the absence of air but hydroperoxide decomposition is considered to be responsible for backbone scission and alteration of the mechanical properties in natural weathering conditions (15). Hydroperoxides, however, have a lower absorption coefficient than ketones in the solar ultra-violet range and their photo-decomposition through direct absorption of light is expected to be very inefficient. But, since they are produced in close vicinity to the carbonyl groups, the transfer of energy from ketones to hydroperoxides is very probable and the sensitized decomposition of hydroperoxides becomes the major source of free radicals responsible for the oxidation.

The sensitized decomposition of hydroperoxides provides a satisfactory explanation to the
fundamental difference between autoxidation and photo-oxidation of polymers (fig. 9).
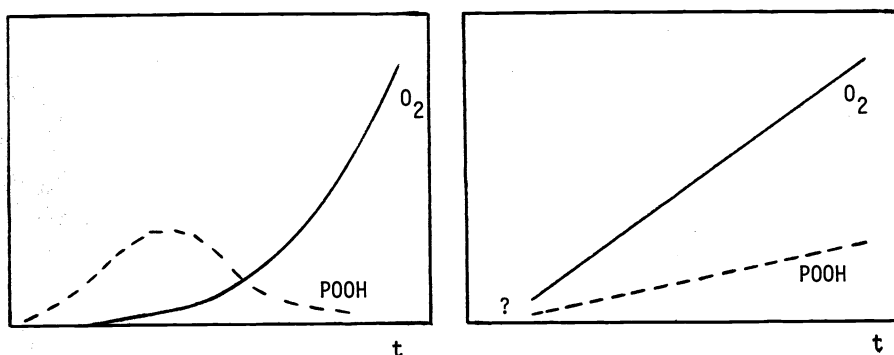

Fig. 9. Comparison of the total amount of oxygen absorbed and evolution
of hydroperoxide concentration during autoxidation (A) and photo-oxida-
tion (B).

Autoxidation is well known to be an autocatalytic process in which hydroperoxides are pro-
gressively decomposed faster than they are produced (16). On the other hand, photo-oxida-
tion proceeds at a constant rate and hydroperoxides accumulate. In the photo-oxidation a
short induction period is sometimes observed although it is usually difficult to measure
since it corresponds to absorption of minute amounts of oxygen. Moreover, the mechanism of
that early stage can be different from one polymer to another and even from one sample to
another because of the influence of impurities such as carbonyl groups on the initiation of
the photo-oxidation. This induction period is required for the building up of a sufficient
amount of hydroperoxides which results in an increasing efficiency of energy transfer from
the actual chromophores to hydroperoxides. As soon as the transfer becomes complete a sta-
tionary situation is reached since the rate of hydroperoxide decomposition and hence the ra-
te of oxygen absorption cannot increase further. Since hydroperoxides decompose into two
radicals which are both susceptible to produce a new hydroperoxide their concentration re-
gularly increases.

CONCLUSION

Transfer of energy can be more efficient in polymers than in most low molecular weight sys-
tems because migration often occurs prior to the transfer. Such a process sometimes provi-
des a useful method of preventing the photodegradation of polymers but it can also play a
major role in the degradation mechanism especially in the photo-oxidation.

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