POLYMER
ADDITIVES

Edited by Jiri E. Kresta

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POLYMER SCIENCE AND TECHNOLOGY

Recent volumes in the series:

PREFACE

Ever since the beginning of the plastics and rubber industry,
it was realized that useful products could be produced only if cer-
tain additives were incorporated into polymers. With the help of
these additives, when physically dispersed in a polymer matrix,
it has been possible to improve stability against thermal, oxidative,
UV, hydrolytic and biological degradation, mechanical properties,
flammability, cost, and processibility of plastics. The enormous
growth of the volume of plastics consumed by modern society, and
new application areas for plastics, have created a demand for new,
better additives and better understanding of their functions in
polymer systems. As a result of these trends there is a need for
sharing of information on progress achieved in the area of polymer
additives among engineers and scientists of the plastics industry
and academia.

This book is based on expanded and updated papers originally
presented at the International Symposium on Polymer Additives, which
was held in Las Vegas, Nevada, and was sponsored by the American
Chemical Society, Division of Polymeric Materials Science and Engi-
neering. The book is divided into five parts which cover advances
in various areas of polymer additives. The first part is devoted
to the progress in understanding of UV degradation and stabilization
of various polymers. Oxidation degradation and stabilization of
plastic materials is covered in the second part. New developments
in the stabilization of PVC are presented in the third part. Prob-
lems associated with flame retardance and smoke suppression are dis-
cussed in the fourth part. The last section covers plasticizers,
fillers, fiber reinforcement and special additives.

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I would like to thank Mrs. Iris Glebe for her efforts in typing this book and for help with editing, and Dianne Lewis for her assistance in preparation of the index. Thanks is also due to the editors of Plenum Press for their patience and for helpfulness with the manuscript.

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April, 1984

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AND PHOTOSTABILIZATION OF POLYDIENES

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INTRODUCTION

Photooxidation reactions belong to the most important processes operating in the atmospheric aging of polydienes. Photooxidative degradation and/or crosslinking of polydienes is generally considered to proceed by reactions of free polymer alkyl-, alkylperoxy-, alkyl-oxy- and other free-radicals formed by photolysis or photoexcitation of internal (e.g., chromophoric groups such as carbonyl groups) and/or external impurities (e.g., traces of catalysts, initiators and other additives.[1-4]

Some recent publications on the photooxidative degradation and photostabilization of polydienes[5-20] have postulated the role of singlet oxygen ($^1O_2$) in the initial step of photooxidation in which allylic hydroperoxide groups are formed.

It is important to consider the fact that polymer hydroperoxides formed during photooxidation and/or singlet oxygen oxidation are not simple hydroperoxides but are most likely to have neighboring hydroxy, carbonyl, hydroperoxy groups and unsaturated bonds. These groups may be important in the photosensitized decomposition of hydroperoxide groups, formation of hydrogen bonds, charge transfer complexes and reaction with free radicals, etc.

The polymer alkyl radicals (P·) arising by the thermal and/or photoinduced initiation participate in a chain autooxidation reaction. In the propagation steps hydroperoxy groups are formed:

$$P\cdot + O_2 \longrightarrow POO\cdot \tag{1}$$

1

$$POO\cdot + PH \longrightarrow POOH + P\cdot \qquad (2)$$

The resulting hydroperoxide is decomposed in a monomolecular (3) or bimolecular (4) reaction:

$$POOH \longrightarrow PO\cdot + HO\cdot \qquad (3)$$

$$2\ POOH \longrightarrow PO\cdot + POO\cdot + H_2O \qquad (4)$$
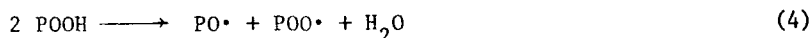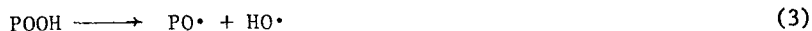
The perfect knowledge of individual degradation mechanisms and of their specific roles under given conditions and the optimum utilization of all aspects of the mechanism of the stabilizers' action are the conditions for the effective stabilization of polydienes.

In a pure photochemical process, the formation of polymer alkyl radicals (P·) can be considered as a result of a change in bond strength upon the redistribution of electrons in the excited state of a molecule and/or chromophoric groups in a macromolecule.

A new mechanism resulting from electronic-vibrational coupling should also be taken into consideration. In this mechanism reactions resulting from electronic-vibrational coupling leads to the excitation of specific molecular vibrations. Such coupling is strongest with high-energy stretching vibrations, and these vibrations are known to be the preferred energy acceptors in a radiationless relaxation process.[21-23]

The abundance of photochemical hydrogen abstraction reactions:

$$PH + h\nu \longrightarrow P\cdot + H\cdot \qquad (5)$$

can be explained by preferential electronic energy transfer to stretching vibrations involving hydrogen, which are of relatively high frequency. The quantum yield of this reaction is high when the rate of reaction of the vibrationally excited molecule exceeds the rate of vibrational relaxation.

In polydienes the most reactive atoms in a macromolecule are hydrogens in methylene groups (CH_2) which are involved in the high frequency molecular vibrations. When vibrations can be assigned to stretching modes of bonds and for bonds of similar vibrational frequencies, the lower the heat of formation of the bond or the more anharmonic the vibration, the more reactive the bond.[21]

The sigma electrons of carbon-hydrogen bonds in the methylene groups (CH_2) cannot be excited at wavelengths exceeding 2000 Å. Electron redistribution through polarization following excitation cannot be responsible for the reactivity of the sigma bonds of methylene groups, since sigma bonds involving hydrogen are among the least polarizable.

In the radiationless relaxation process (in which electronic energy is converted into vibrational energy[23-27]), the best energy accepting vibrations are the more anharmonic vibrations that approach most closely the electronic energies. These are usually anharmonic stretching vibrations with high vibrational energies that involve the stretching of the weaker bonds of carbon with hydrogen, the lightest atom.[22,23] In the electronic-vibrational coupling mechanism electronic energy flows preferentially to stretching vibrations involving hydrogen atoms whenever a radiationless relaxation takes place. This mechanism can be responsible for the formation of the polymer alkyl radicals (P·) in the photoinduced initiation step.

In further steps of photooxidation, hydrogen abstraction can be caused by excited ketone and/or aldehyde groups. Hydrogen abstraction by an excited carbonyl group ($C=O^*$) can be considered as a process of energy transfer from an electronically excited n,π^* state of a ketone or an aldehyde group to a stretching vibration involving a nearby hydrogen atom in the methylene group (CH_2). As a result of the transfer of energy, the vibration becomes highly excited. This allows the transfer of the hydrogen to oxygen of the carbonyl group to take place. Whether the reaction is intermolecular or intramolecular, the proximity of the electronically excited center and the hydrogen atom remain essential. Both n,π^* singlet and n,π^* triplets are expected to be reactive by the above mechanism, since either of the two can be an energy donor to a vibration.

The triplet state of carbonyl groups is also associated with formation of the ultimate biradical. The ultimate biradical possesses two independent electrons. The spin components of these two electrons are neither "paired" nor "unpaired"; they are independent. The electrons are spatially separated to such an extent that there is no overlap of their space wavefunctions. The total spin component of the system of two electrons is not defined; only that of each electron is defined. The ultimate biradical formed may abstract a hydrogen atom from the methylene group (CH_2) and produce a polymer alkyl radical (P·). The reactivity of n,π^* carbonyl triplets can also be explained by their biradical-like nature. Hydrogen abstraction reactions by carbonylic compounds have been observed with a large variety of substrates.[28]

The reaction of polymer alkyl radicals (P·) with molecular oxygen (Equation 1) is a very fast reaction. It is generally considered that under normal atmospheric pressure only polymer alkylperoxy radicals exist. They are stable even at room temperature and can be detected by ESR.[12,29] The polymer alkylperoxy radical can abstract hydrogen from the same or from another polymer molecule to form polymer hydroxyperoxides (POOH) (Equation 2).

RESULTS AND DISCUSSION

In order to stabilize a photooxidation process in polydienes it is very important to scavenge the $P\cdot$, $POO\cdot$ and $PO\cdot$ radicals. Our recent studies in our Institute of Polymer Technology, Royal Institute of Technology, Stockholm, were mainly devoted to these problems. Two groups of chain-breaking compounds, i.e., hindered phenols and hindered piperidines, were examined.
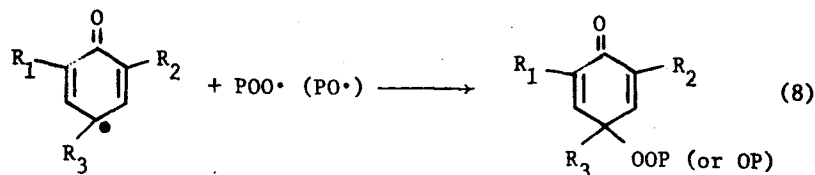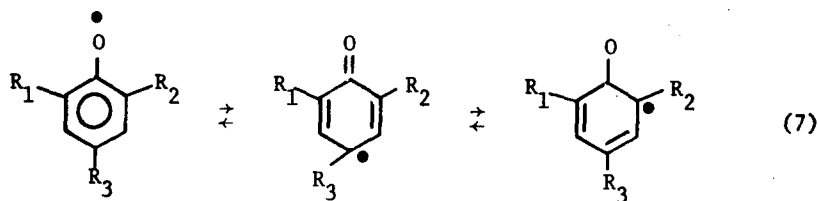
Hindered phenols stabilize polymer systems by interacting with free radicals formed in the thermal and/or photooxidation processes and with singlet oxygen formed in the polymer matrix.[30-32] Hindered phenols were previously examined as antioxidants in thermal oxidation of elastomers.[33,34] Hindered phenols react with free radicals forming a non-radical substrate and a phenoxy radical by donation of a hydrogen atom from the -OH group to the free radical:

$$R_1\text{---}\underset{R_3}{\overset{OH}{\bigcirc}}\text{---}R_2 + POO\cdot \text{ (or } PO\cdot) \longrightarrow R_1\text{---}\underset{R_3}{\overset{O\cdot}{\bigcirc}}\text{---}R_2 + POOH \text{ (or } POH) \quad (6)$$
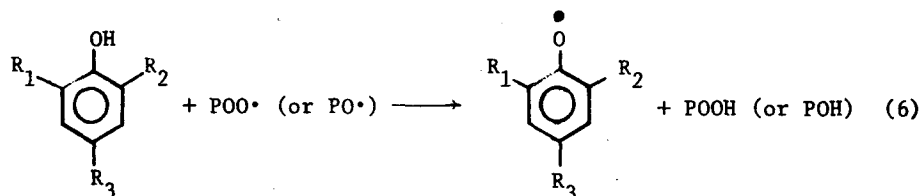
In our research hindered phenols with the following groups were examined:

$$R_1 = R_2 = CH_3, \ C(CH_3)_3 \text{ and } R_2 = H, \ CH_3, \ C(CH_3)_3$$
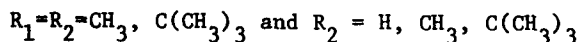
If the resulting phenoxy radical is well stabilized, or sterically prevented from further reactions, it will not participate in the hydrogen abstraction from methylene groups (CH_2) in polydienes. It may react with a second $POO\cdot$ or $PO\cdot$ radical in the polymer matrix:

$$\underset{R_3}{\overset{O\cdot}{\bigcirc}} \ \rightleftarrows \ \underset{\overset{|}{R_3}}{\overset{O}{\bigcirc}} \ \rightleftarrows \ \underset{R_3}{\overset{O}{\bigcirc}} \quad (7)$$

$$\underset{\overset{\bullet}{R_3}}{\overset{O}{\bigcirc}} + POO\cdot \ (PO\cdot) \longrightarrow \underset{R_3 \quad OOP \ (or \ OP)}{\overset{O}{\bigcirc}} \quad (8)$$

In the case where the R_3 substituent is a hydrogen atom, hindered quinones may also be formed:

$$R_1 \diagdown \diagup R_1 \quad \longrightarrow \quad R_1 \diagdown \diagup R_2 \quad + \quad HOP \qquad (9)$$
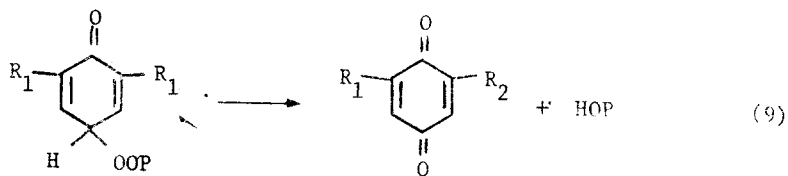
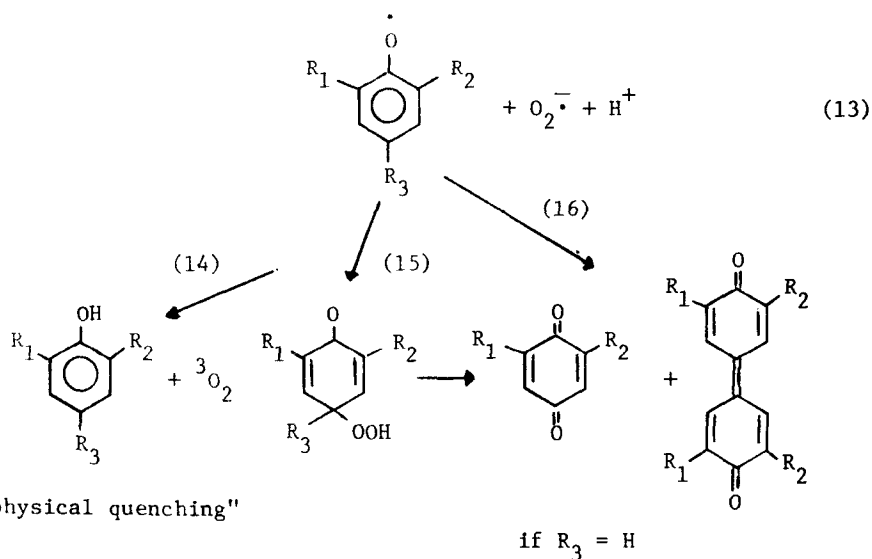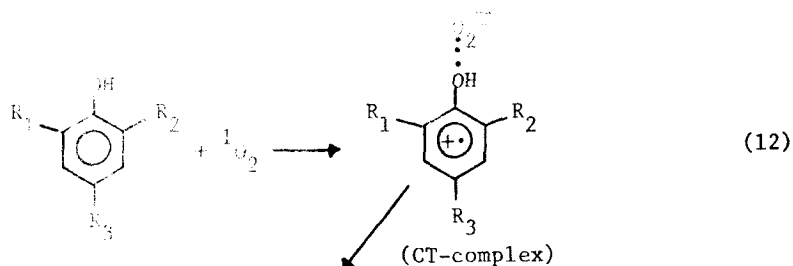Phenoxyl radicals undergo chemical transformations and may react either as O-radicals (phenoxy radicals) or C-radicals (cyclohexadienonyl radicals).[8] The stability and reactivity of phenoxyl radicals are determined by steric effects of substituents in the "ortho" position (R_1 and R_2).[33,35-37] In a series of phenoxyl radicals, lifetimes increase as steric hindrance in the "ortho" and "para" positions increases:

$$(10)$$

$$\underrightarrow{\text{Radical life time}}$$

$$\overleftarrow{\text{Radical reactivity}}$$
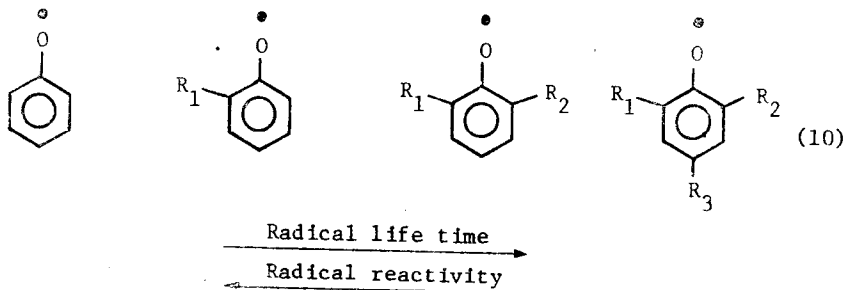
The stabilizing effectiveness of the hindered phenols examined in our research program was as follows:

$$(11)$$

II   I   III   IV
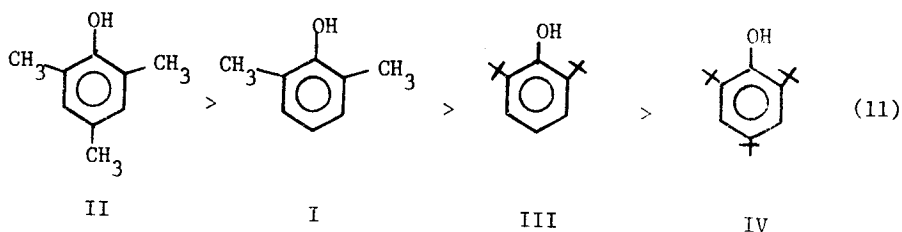
Hindered phenols are also capable of both reacting with and quenching singlet oxygen ($^1O_2$), depending both on their substituents (R_1, R_2 and R_3) and reaction conditions.[38,39] Based on the rate effects and the detection of the phenoxy radicals, the following mechanism of singlet oxygen oxidation of hindered phenols has been proposed:[39-41]

$$\text{(12)}$$

$$\text{(CT-complex)}$$

$$+ \; O_2^{-\cdot} + H^+ \qquad \text{(13)}$$

(16)

(14)   (15)

"physical quenching"

if $R_3 = H$

This complete mechanism considers formation of a charge-transfer (CT) but not a complete electron-transfer complex (Equation 12).

Our results show that hindered phenols decrease formation of hydroperoxy groups (OOH) (Figure 1, UV initiated, and Figure 3, singlet oxygen initiated) and carbonyl groups (Figure 3, UV initiated). They also decrease chain scission reactions (Figure 4, relative viscosity change). Other results are presented in the original paper.

Hindered phenols can be successfully used in stabilizers against free radical and/or singlet oxygen oxidation of polydienes. The main disadvantage is that they are not very compatible with non-polar polydienes and will tend to form crystalline aggregates in the polymer matrix, leaving large volumes of unstabilized material. Since the centers of antioxidant activity are, in general, polar
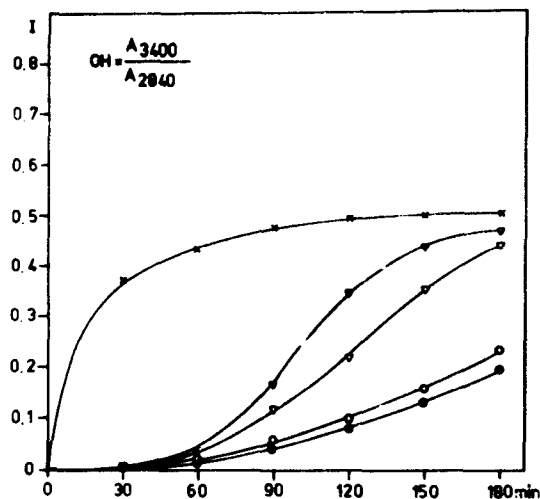
Figure 1.   Kinetics of formation of OOH/OH groups in PH after UV
            irradiation in the presence of hindered phenols $(10^{-3}$ M):
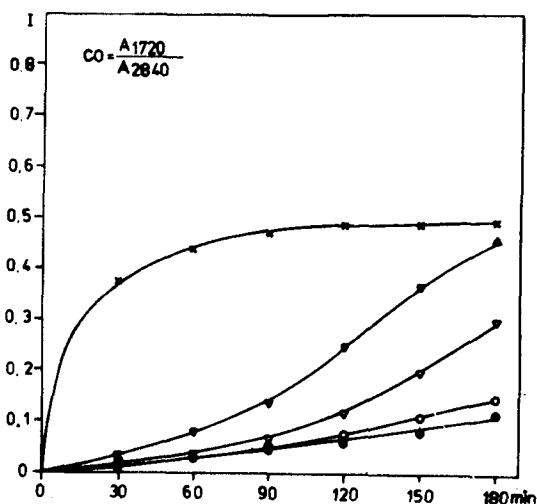   (O) I; (●) II; (∇) III; (▼) IV; and (X) without.

Figure 2.   Kinetics of formation of CO groups in PB after UV irradi-
            ation in the presence of hindered phenols (10^{-3}):
            (O) I; (●) II; (∇) III; (▼) IV; and (X) without.