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Chemistry and Technology of Polymer Additives

Edited by

S. Al-Malaika

Aston University, Birmingham, UK

A. Golovoy

Ford Research Laboratory, Dearborn, USA

C.A. Wilkie

Marquette University, Milwaukee, USA

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Blackwell Wissenschafts-Verlag GmbH
Kurfürstendamm 57
10707 Berlin, Germany

Blackwell Science KK
MG Kodonmachi Building
7-10 Kodonmachi Nihombashi
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First published 1999

Set in 10/13 pt Times
by DP Photosetting, Aylesbury, Bucks
Printed and bound in Great Britain by
MPG Books Ltd, Bodmin, Cornwall

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A catalogue record for this title is available
from the British Library

ISBN 0-632-05338-0

Library of Congress
Cataloging-in-Publication Data
is available

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Preface

Additives continue to play a lead role in the steady growth and success of commercial plastics, elastomers, rubbers coatings and adhesives. As a result the additives market has remained healthy and buoyant even during the recent intense period of reorganisation and business realignment involving the major producers. Without additives, many polymers would have made few inroads into the consumer market. The demands of service requirements, the environmental concerns and regulatory constraints, as well as increased consumer demands and expectations of safe, high quality products, has put under the spot light the credentials of additives in controlling and modifying polymer properties to achieve target end-use applications. In particular, commercial hydrocarbon polymers are extremely susceptible to oxidation and to environmental factors such as heat, light, and pollutants, and to stress during service. High temperature fabrication of these polymers is therefore a primary source of problems for these materials in terms of their stability, durability, flammability, and ultimately their use. Without additives, many polymers would simply be of limited use as they would not have the appropriate balance of properties for the required application.

The chapters in this book are expanded versions of selected presentations given by academic and industrial experts at the Seventh International Conference, 'Additives '98', organised by Executive Conference Management, Plymouth, Michigan, USA, and held in Orlando, Florida, USA in February 1998. These chapters, however, do not represent the proceedings of the Conference. Each chapter was specially commissioned for this book to give an up-to-date overview of the chemistry and technology of speciality polymer additives, including antioxidants, polymer stabilisers and stabilisation, fire retardants and plastics flammability, and the important emerging field of nanocomposites. Since additives are essential ingredients of almost all commercially important polymers, the information in this book covering the chemistry, technology and industrial applications of polymer additives will be of vital interest to academics and industrialists, including polymer scientists, technologists, chemists and engineers, who are concerned with the underlying science of polymer additives as well as the design, fabrication, use and re-use of polymers in all areas of application.

We wish to express our thanks and appreciation to all the authors for contributing to this book which, we believe, will make a welcome addition to the scientific literature available on this subject. Our warm thanks to Paul Sayer for his interest and support in the initial stages of this project. We would like to acknowledge the opportunity that the publisher, Blackwell Science, has provided, with our special thanks and gratitude to Jon Walmsley who had made the publication of this book

possible, and for his help and dedication. Sincere thanks are due to all the editorial staff and, in particular, Shahzia Chaudhri, for their professional assistance and for working to a very tight production schedule.

Sahar Al-Malaika
Aston University
Birmingham
UK

Amos Golovoy
Ford Motor Company
Dearborn
USA

Charles A. Wilkie
Marquette University
Milwaukee
USA

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Chapter 1

The Good, The Bad and The Ugly in the Science and Technology of Antioxidant Grafting on Polymers

S. Al-Malaika

Polymer Processing and Performance Research Unit, Aston University, Aston Triangle, Birmingham B4 7ET, England, UK

ABSTRACT: Industrial hydrocarbon polymers, which normally undergo high temperature manufacturing and fabrication operations, are susceptible to oxidation throughout the different stages in their lifecycle. Stabilizers and antioxidants are therefore used to inhibit polymer oxidative damage which is ultimately responsible for the loss of physical properties, embrittlement and premature failure of polymer artifacts. Environmental awareness and health and safety considerations have given significant impetus to research into improving the safety and efficiency of antioxidants and stabilizer systems for polymers. An important breakthrough has come from the use of reactive antioxidants which can become chemically grafted on the polymer substrate resulting in efficient attachment of antioxidants, hence their permanence, without undermining their effectiveness. The chemistry, its problems and benefits, and the technology of antioxidant grafting is the subject of this chapter.

1.1 Introduction

The damaging effects of polymer oxidation which occur during manufacture, fabrication and service can be controlled by the use of low levels of antioxidants normally incorporated during the processing stage. The quest for more efficient antioxidants has been spurred by the ever increasing demands placed on the performance of commercial polymers. The level of protection afforded by antioxidants to the host polymer is commensurate with its inherent antioxidant activity and its degree of permanence in the polymer artifact. It is important that a sufficient amount of antioxidant(s) remains in the polymer, both during processing and in-service, to control and inhibit the oxidation process, hence the importance of physical factors (volatility, extractability, compatibility and antioxidant distribution), besides chemical functionality, as additional indicators of antioxidant performance and efficiency.

To overcome the problem of physical loss normally encountered with lower molar mass antioxidants, e.g. BHT (AO1), higher molar mass counterparts, e.g. Irganox 1010 (AO2), Ethanox 330 (AO3), were developed commercially; these too were found to suffer physical loss by leaching out under aggressive service conditions. Further progress in this direction led to the commercialization of oligomeric and, to a lesser

extent, macromolecular antioxidants, e.g. the oligomeric HALS photostabilizers Tinuvin 622 (AO4) and Chimassorb 944 (AO5) [1], see Fig. 1.1 for structures. Macromolecular antioxidants are often more difficult to synthesize and characterize and are generally more expensive than their low molar mass analogues [2]. Indeed, the superior performance of such antioxidants which is ascribed to their greater retention in the polymer has been demonstrated [2–4] particularly when used in polymers under demanding conditions. However, the main drawback of these high molar mass antioxidants is that of reduced compatibility with the host polymer, especially in crystalline polymers.

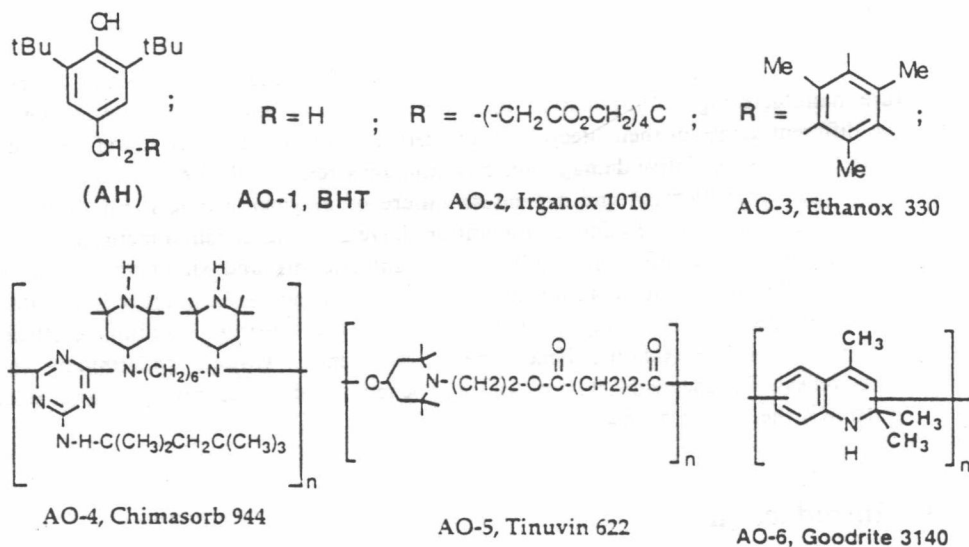


Fig. 1.1

An alternative route to producing antioxidants, which suffer minimum or no physical loss during fabrication and exposure to service conditions, involves the use of reactive antioxidants which could become an integral part of the macromolecular chain [5]. Reactive antioxidants may either be copolymerized with monomers during polymer synthesis or grafted on preformed polymers; this can be considered as a 'fool-proof' approach as such chemically attached antioxidants can only be lost from the polymer by breaking chemical bonds, hence offering the ultimate solution to antioxidant permanence. Although the copolymerization route has been successfully exploited [6–10], it has lacked major commercial development due, at least in part, to the high costs generally involved in the synthesis and production of tailor-made 'speciality' materials for specific applications. On the other hand, grafting of antioxidants on preformed polymers can offer a more flexible and versatile approach. Both routes, however, offer tremendous advantages in terms of the physical persistence of antioxidants in the polymer. In both cases, the process of chemical attachment (target reaction) of antioxidants onto the polymer backbone proceeds in

competition with other undesirable processes, hence full control of the reaction and process conditions is imperative.

This chapter aims to highlight the unique advantages and benefits of grafted antioxidants and to discuss the underlying chemistry which underpins past and present endeavours in the technology of antioxidant grafting. The problems and pitfalls, both 'bad' and 'ugly', which would be encountered in the application of this technology are also delineated.

1.2 The process of antioxidant grafting

The process of free radical grafting has been exploited over the years for chemically modifying polymers by reactive modifiers either 'on the bench', in the presence of solvents, or *in situ* without solvents, e.g. in polymer melts [11]. The grafting process has been used mainly to functionalize polymers to promote property improvements, e.g. dyeability, adhesion, compatibility of immiscible polymers and, to a lesser extent, to stabilize polymers. The process of free radical grafting of antioxidants on polymers to achieve polymer stabilization is more complex than the process of blending of commercial antioxidants with polymers that is normally used for conventional stabilization. A typical grafting system comprises, at least, three components: polymer, initiator (often a peroxide) and reactive monomer (reactive antioxidant in this case). Figure 1.2 outlines some of the main reactions normally encountered in grafting of antioxidants on polymers.

Decomposition of the initiator (I) to free radicals (I[•]) gives rise to two competing reaction pathways: the first leads to the formation of macroradicals by hydrogen abstraction from the polymer which results in the target grafting reaction (route a), and the other leads to the undesirable process of homopolymerization of the reactive antioxidant monomer (route b). Homopolymerization of the reactive antioxidant is detrimental to the progress of the target graft reaction which result in lower grafting efficiency and loss of antioxidant performance as such homopolymers have been shown [12–14] to be inferior to their graft analogues, as well as their ease of loss from the polymer on contact with extractive solvents. It is important, therefore, to reduce or eliminate this undesirable and, sometimes, dominant reaction pathway to produce a polymer with highly grafted antioxidant functions. Other undesirable competing processes also involve polymer macroradicals (P[•]) initially formed in the process of free radical grafting. In addition to grafting reactions, these radicals can undergo chain scission (reaction d) or crosslinking (reaction e), both of which affect unacceptable changes in the mechanical properties of the polymer.

The final level of grafting of antioxidants, therefore, is a complex function of the physical nature, chemical structure and reactivity of the individual components in the system (as discussed later) and their dependence on reaction and process conditions. For example, the grafting reaction (Fig. 1.2, route a) will predominate if hydrogen transfer reactions, reactions a and h, outweigh the process of initiation for homopolymer formation, reaction b, and if the graft initiation reaction, reaction f, overshadows the monomer propagation reaction, reaction c. The overall outcome will generally depend on the relative reactivities of the initiator towards hydrogen-

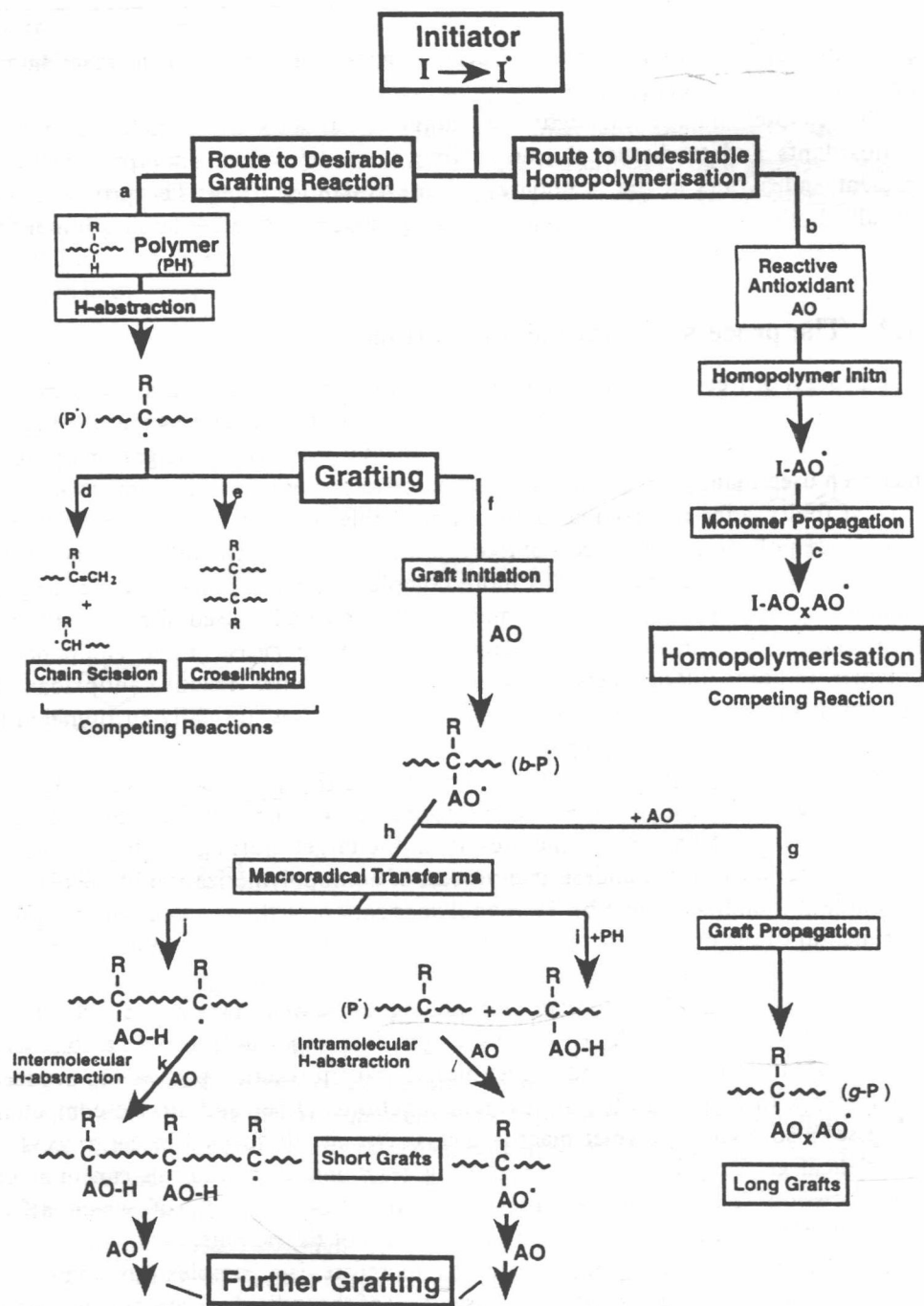


Fig. 1.2 Simplified outline of some of the main reactions involved in antioxidant grafting on polymers.

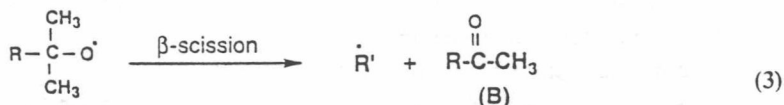
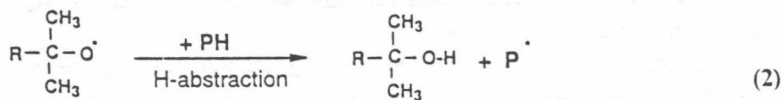
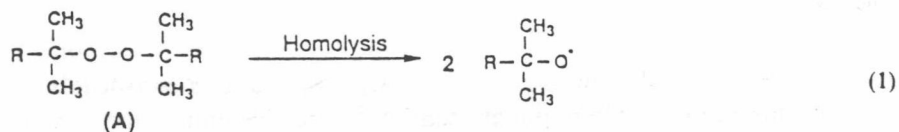
abstraction from the polymer and with the antioxidant, as well as the reactivity of the macroradicals formed towards the antioxidant. Furthermore, macroradical transfer reactions have a major role to play because they are able to mediate in the process of further graft formation that is crucial to the achievement of high levels of target graft reaction. The underlying chemistry which occurs during the antioxidant grafting reaction is clearly challenging especially when additional factors, such as viscosity and polymer heterogeneity, also become important when conducting *in-situ* melt grafting reactions at elevated temperatures.

1.3 The antioxidant grafting system


Each of the components of the grafting system discussed below play a key role in determining the outcome of the process of antioxidant grafting and the ultimate performance of the grafted antioxidant in the host polymer.

Initiators

Dialkyl peroxides are the main initiators used for antioxidant grafting reactions. Homolysis of the weak peroxide bond leads to the formation of highly reactive alkoxy radicals, reaction 1, which can readily abstract hydrogen from the polymer matrix, reaction 2, or undergo further decomposition (by β -scission) giving rise to further 'smaller' radicals (secondary radicals) and 'small' stable molecules, reaction 3. The chemical structure, reactivity and concentration of the peroxide, as well as its dependence on process variables and reaction conditions, affects the outcome of the grafting reaction [15, 16]. Several factors need to be considered, therefore, when choosing a peroxide for grafting reactions:



when $\text{R} = \text{CH}_3$; A = di-*t*-butyl peroxide (I) ; $\text{R}^\bullet = \dot{\text{C}}\text{H}_3$, B = acetone

When $\text{R} =$  ; A = dicumyl peroxide (II) ; $\text{R}^\bullet = \dot{\text{C}}\text{H}_3$, B = acetophenone

when $\text{R} = \text{CH}_3\text{-CH}_2$; A = di-*t*-amyl peroxide (III) ; $\text{R}^\bullet = \text{CH}_3\text{-}\dot{\text{C}}\text{H}_2$, B = acetone

- (1) The rate of peroxide decomposition. The initial process of decomposition to generate free radicals is strongly dependent on reaction conditions and process variables.
- (2) The reactivity of generated radicals towards hydrogen abstraction from polymer backbones. *t*-Butoxyl radicals abstract hydrogen efficiently, hence many of the peroxides used for grafting contain *t*-butyl groups within their structure, e.g. I, II, IV–VI in Fig. 1.3. The nature and reactivity of radicals formed from further decomposition of the alkoxyl radical are also important. For example, a methyl radical obtained by β -scission of the *t*-butoxyl radical (reaction 3, $R' = \dot{\text{C}}\text{H}_3$) is as reactive towards hydrogen abstraction as the *t*-butyl radical, whereas the more stable ethyl radical arising from the amyloxyl radical (reaction 3, $R' = \text{CH}_3\dot{\text{C}}\text{H}_2$) favours polymerization over hydrogen abstraction. Further, the stable molecule formed as a result of β -scission (reaction 3) should not lead to the sensitization of the polymer matrix under service conditions. For example, decomposition of dicumyl peroxide gives rise to the stable compound acetophenone which may sensitize the polymer upon UV exposure.

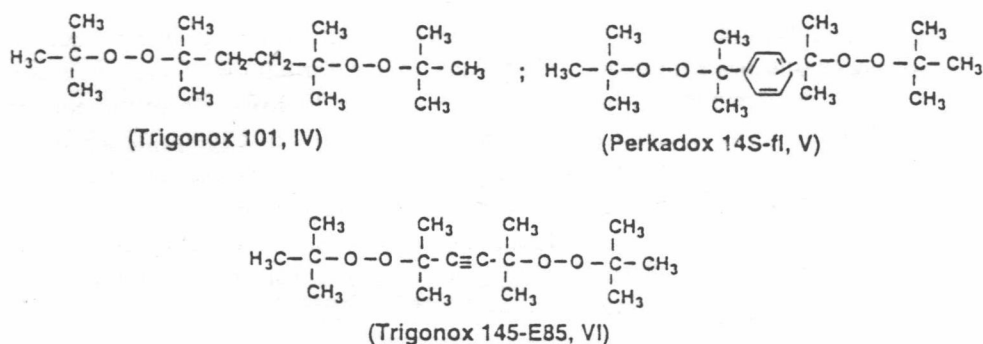


Fig. 1.3

- (3) The reactivity of initiating radicals towards the antioxidant leading to homopolymerization. Homopolymerization of reactive antioxidants increases with higher initiator reactivities for polymerization, resulting in lower levels of free radical grafting.
- (4) Peroxide half-life ($t_{1/2}$). This provides a measure of the decomposition rate of the peroxide under specific reaction conditions which include temperature, and the physical state of the polymer, e.g. liquid or solid, where viscosity and diffusion effects also become important.
- (5) The physical state of the peroxide. The physical state (liquid, solid, absorbed on solid carrier) of the peroxide can be very important for delivery and mixing regimes in addition to its physical characteristics (volatility, solubility), and its odour and toxicity.

Reactive antioxidants (the monomer)

These are compounds which contain one or more antioxidant functions (the anti-

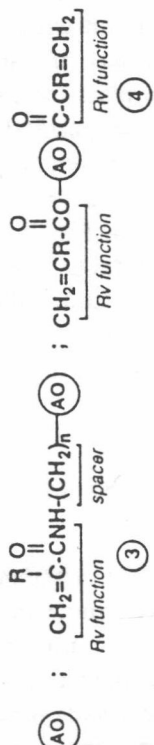
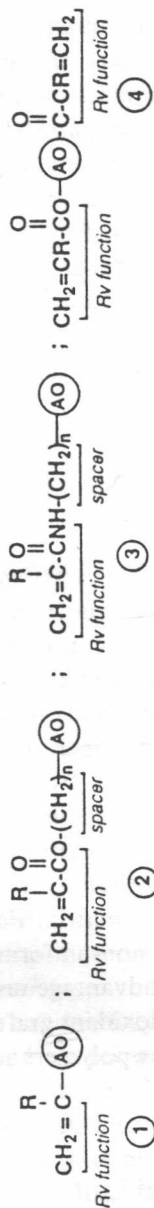
oxidant, AO, component) and one or more chemical functions capable of reacting either with monomers (same or different) or with polymers (the reactive, Rv, component). The AO function is based on any antioxidant moiety (e.g. VII–X in Fig. 1.4) whereas the reactive moiety can either be a polymerizable (e.g. Rv functions 1–4) or non-polymerizable (e.g. Rv functions 5–7) groups and may or may not contain a spacer (an inert flexible and short chemical link connecting the antioxidant moiety to the reactive function). It has been suggested that the presence of a spacer minimizes the influence of the main polymer chain and its characteristics on the activity of the antioxidant function [17] and that the chemical nature of the spacer affects the overall antioxidant activity and performance of the reactive antioxidant [18]. The extent of antioxidant grafting depends on both the structure and reactivity of the reactive function and the rate of combination with macroradicals. Physical effects of the antioxidant, e.g. solubility in polymer melt, are also important as this affects the state of 'mixedness' and hence the uniformity of the grafting reaction. Both antioxidant concentration and polymer viscosity (which affects diffusion rates) contribute to the extent of homopolymer formation, the major side reaction in antioxidant grafting procedures.

The chemical structure of polymers

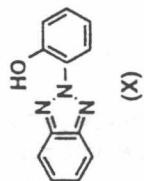
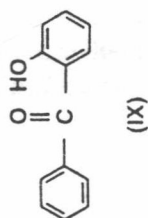
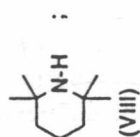
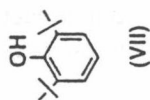
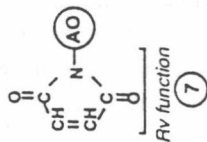
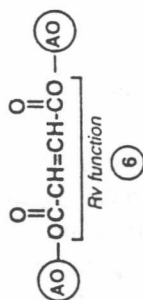
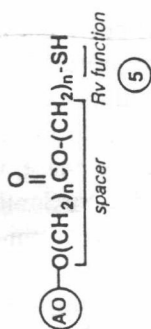
The ease of hydrogen abstraction, steric effects and stability of the polymer macro-radical formed are important chemical factors which determine the extent of the contributions of the different reactions occurring during the grafting process. For example, polyethylene (PE) and polypropylene (PP) affect the nature of the polymer side reactions differently: the more reactive secondary macroalkyl radicals derived from PE favour coupling reactions to give a crosslinked polymer, whereas the more stable tertiary macroalkyl radicals derived from PP fragments (by β -scission) yield a polymer with lower molar mass, see Fig. 1.5 [19]. Moreover, the physical, mechanical and morphological characteristics of polymers should not be altered significantly by the nature and extent of antioxidant grafts. Polymer morphology is a key factor in mediating the distribution of antioxidants throughout the matrix. For example, in polyolefins (semi-crystalline polymers) antioxidants are non-uniformly distributed and are concentrated in the amorphous phase, which is advantageous as the amorphous region is more sensitive to oxidation. Similarly, antioxidant grafts would occur predominantly in the amorphous regions of semi-crystalline polymers and should not, therefore, affect polymer crystallinity.

1.4 Polymer stabilization using grafted antioxidants

Thermoplastics, in particular polyolefins (especially PP), and elastomers including rubber-modified plastics (e.g. ABS) are the largest 'consumers' of commercial antioxidants and stabilizers [20]. This is directly related to the extreme sensitivity of these polymers to oxidation. These polymers are also increasingly being used in more demanding applications where they are required to perform in the presence of



where R = H ; R = CH₃ ; n = 0 - 4



Examples of AO functions:

Fig. 1.4

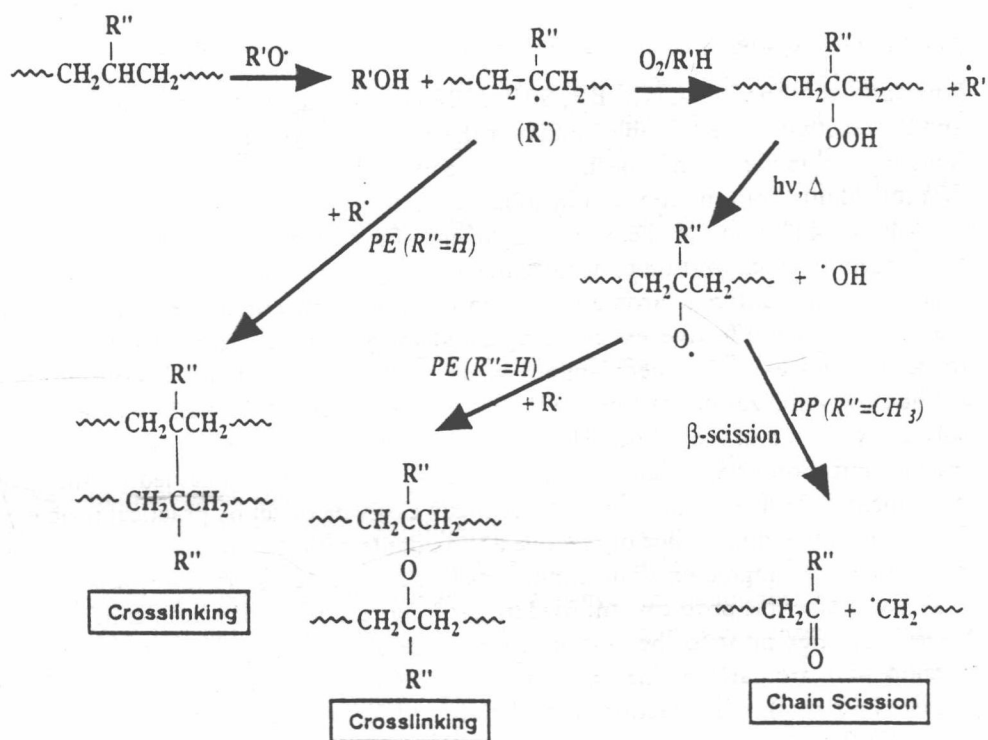


Fig. 1.5 Oxidative reactions of PE and PP.

aggressive and extractive environments, e.g. foodstuffs, oils, detergents, dry cleaning solvents and body fluids, hence the increased demands placed on greater efficiency and permanence of stabilizers. Much of the investigations reported in the literature on the grafting of antioxidants have, therefore, been carried out in these polymers.

Grafting of antioxidants has been investigated both on polymer surfaces and in polymer bulk. Surface grafting on polymer films and fibres has been used mainly to protect coatings and fibres from the damaging effect of UV light. Surface grafting of photostabilizing functions has been achieved, in the presence of photosensitizers (e.g. benzophenone), either by UV light or by high energy radiation, e.g. γ -irradiation. In both cases, the grafting method often involves the exposure of polymer films or fibres immersed in solvents containing the antioxidant and initiator [14, 21–25]. Surface grafting was shown to occur predominantly in solvents which did not swell the polymer appreciably and, generally, surface-grafted antioxidants have been shown to offer superior photostabilization compared with their use as conventional antioxidants. Antioxidant grafting in the bulk, and particularly melt grafting has, however, attracted much more attention than surface grafting and both thermal- and photo-antioxidant functions have been grafted *in situ* on a variety of polymer backbones by this method. Different approaches have been employed to achieve grafting of reactive antioxidants on preformed commercial polymers depending on the type of polymer system used.

Functional polymers

Unsaturated rubbers (e.g. NR, BR, SBR, NBR) are examples of functional polymers, and the reactivity of the double bonds (or the active methylene group attached to the double bond) in the polymer backbone can be utilized to achieve chemical attachment of antioxidants both in latex and in solid rubbers.

Early work [27] on the chemical attachment of antioxidants on rubbers exploited the concept of vulcanization to achieve the grafting of phenylenediamine and nitron functions using different aromatic nitroso compound precursors, e.g. 4-nitrosodiphenylamine. The effectiveness of these grafted antioxidant functions were shown [27] to be as good as the diphenylamines when used as antioxidants in conventional methods of stabilization but, unlike the latter, they retained their effectiveness after solvent extraction of the rubber. However, the process of antioxidant grafting during the vulcanization process has enormous pitfalls; the advantages gained by the high permanency of rubber-grafted antioxidants can easily be offset by practical problems arising from the interference of reactive antioxidants with the vulcanization process, both in terms of ingredients and conditions [26, 27], hence its limited appeal.

To overcome this problem, antioxidant grafting reactions have been conducted in the rubber latex prior to the vulcanization process. A number of reactive hindered phenols and aromatic amines have been successfully grafted in this way (using radical initiators), e.g. reaction 4, to produce effective stabilization [28–31]. For example, the performance of a latex-grafted antioxidant, e.g. DBBA (AO7) was shown to be superior to that of the control as well as that of a homopolymer antioxidant, poly-DBBA [26, 31], see Table 1.1. The reason for the low activity of poly-DBBA was attributed to unfavourable distribution of the antioxidant and limited compatibility.

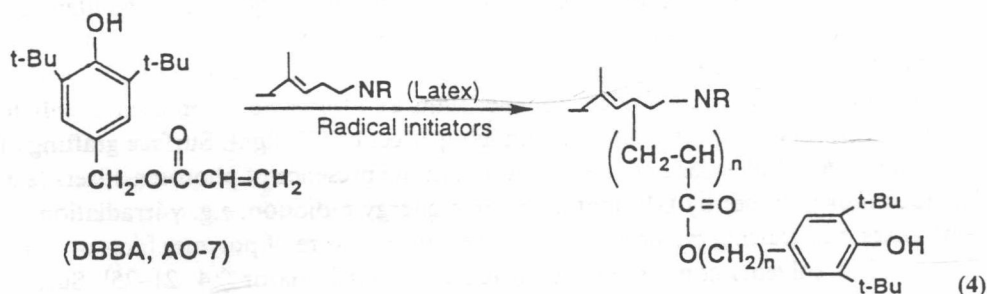


Table 1.1 The thermal stabilizing effect of latex-grafted antioxidant (2 phr) and its homopolymer after extraction in vulcanized natural rubber.

Antioxidant	Time to absorb 10 cm ³ O ₂ at 70°C (h)
Control, no antioxidant	32
DBBA, latex grafted	145
Poly-DBBA	42