Photodegradation and Stability of Bisphenol A Polycarbonate in Weathering Conditions

PROEFSCHRIFT

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Voor Papa en Mama
## Contents

Summary i

1 General Introduction 1
   1.1 Introduction ................................................. 1
   1.2 Mechanisms of photodegradation ................................. 2
       1.2.1 Photolysis: Norrish I, Norrish II and photo-Fries reactions 3
       1.2.2 Photo-oxidation mechanism .................................. 5
   1.3 Stabilization .................................................... 7
       1.3.1 UV-absorbers (UVAs) ....................................... 7
       1.3.2 Hindered Amine Light Stabilizers (HALS) .................... 9
   1.4 Weathering tests ................................................. 10
       1.4.1 Outdoor weathering tests .................................... 11
       1.4.2 Indoor weathering tests ..................................... 11
   1.5 Polycarbonate .................................................... 12
   1.6 Objective of this thesis ......................................... 14
   1.7 Outline of this thesis ........................................... 14

2 Photodegradation of bisphenol A polycarbonate 19
   2.1 Introduction ..................................................... 20
       2.1.1 Photo-Fries rearrangement of BPA-PC .......................... 20
       2.1.2 Side chain oxidation of BPA-PC ............................... 21
   2.2 Experimental ................................................... 23
       2.2.1 Materials ................................................... 23
       2.2.2 Weathering .................................................. 23
       2.2.3 Characterization techniques ................................. 25
2.3 Results ................................................................. 25
  2.3.1 UV-spectroscopy analysis ....................................... 25
  2.3.2 Infrared spectroscopy analysis .................................. 27
  2.3.3 Chemiluminescence analysis ..................................... 28
  2.3.4 MALDI-TOF MS analysis ........................................ 29
  2.3.5 Fluorescence analysis ........................................... 31
2.4 Discussion ............................................................ 32
2.5 Conclusion ............................................................. 34

3 Photo-oxidative degradation of bisphenol A polycarbonate and its possible initiation processes 37
  3.1 Introduction .......................................................... 39
  3.2 Influence of photo-Fries rearrangement products on the photo-oxidation of BPA-PC .................................. 41
    3.2.1 Experimental ...................................................... 42
    3.2.2 Influence of photo-Fries rearrangement reactions in polypropylene ........................................... 43
    3.2.3 Influence of different irradiation spectra on photodegradation of BPA-PC ........................................ 45
    3.2.4 Relevance of photo-Fries rearrangements in BPA-PC .................................................. 47
  3.3 Influence of thermo-oxidation products on the photodegradation of BPA-PC ................................ 47
    3.3.1 Experimental ...................................................... 47
    3.3.2 Results and Discussion .......................................... 48
  3.4 Influence of oxygen on the photodegradation of BPA-PC ........ 51
    3.4.1 Experimental ...................................................... 52
    3.4.2 Formation of Charge Transfer Complexes ............................ 52
    3.4.3 Photodegradation under air pressure .............................. 54
  3.5 Conclusion ............................................................. 59

4 Influence of light intensity on the photodegradation of bisphenol A polycarbonate 61
  4.1 Introduction .......................................................... 62
  4.2 Experimental .......................................................... 64
    4.2.1 Materials ......................................................... 64
4.2.2 Weathering tests ........................................... 65
4.2.3 Analysis Techniques ........................................ 65
4.3 Results and Discussion ....................................... 66
4.4 Conclusion ................................................... 70

5 Photodegradation of bisphenol A polycarbonate with different
types of stabilizers ........................................... 73
5.1 Introduction .................................................. 74
  5.1.1 UV-absorbers (UVAs) ...................................... 74
  5.1.2 Hindered Amine Light Stabilizers (HALS) ............... 75
5.2 Experimental ............................................... 76
5.3 Influence of UVAs ........................................... 78
  5.3.1 Effect of UVA-containing top layer on BPA-PC ........ 83
5.4 Influence of HALS ........................................... 84
5.5 Conclusion .................................................. 87

6 Photostabilizing of bisphenol A polycarbonate by using UV-
absorbers and self protective block copolymers .................. 89
6.1 Introduction .................................................. 90
6.2 Experimental ............................................... 92
6.3 Photodegradation of BPA-PC with UV-absorbers and BPA-PC-
  ITR block copolymers ........................................ 93
6.4 Effectiveness of the stabilization method ..................... 99
6.5 Conclusion .................................................. 101

7 Outdoor and accelerated weathering studies of bisphenol A
polycarbonate ................................................ 103
7.1 Introduction .................................................. 104
7.2 Experimental ............................................... 105
  7.2.1 Materials ................................................ 105
  7.2.2 Weathering ............................................... 105
  7.2.3 Characterization techniques .............................. 106
7.3 Comparison of accelerated and outdoor exposure tests ....... 106
7.4 Outdoor weathering of BPA-PC with model compounds ....... 111
7.5 Conclusion .................................................. 112
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Samenvatting</td>
<td>115</td>
</tr>
<tr>
<td>Curriculum Vitae</td>
<td>119</td>
</tr>
<tr>
<td>List of Publications</td>
<td>120</td>
</tr>
<tr>
<td>Dankwoord</td>
<td>121</td>
</tr>
</tbody>
</table>
Summary

Photodegradation and stability of bisphenol A polycarbonate in weathering conditions

Polycarbonates, and especially bisphenol A polycarbonate (BPA-PC), are used in many fields of applications due to their excellent physical and mechanical properties, such as high impact resistance, ductility, and transparency. One major drawback of using polycarbonates in outdoor applications is that the polymer degrades under the influence of UV-light, humidity and oxygen. This undesired photodegradation process is initiated by the absorption of the terrestrial sunlight.

Although there has been quite a lot of published work on the degradation of BPA-PC, there is still no consensus on what is happening in outdoor weathering conditions, since most of these studies were performed under different (often accelerated) ageing conditions. The aim of this thesis is to get a more detailed knowledge about the degradation chemistry and the stabilization of bisphenol A polycarbonate in outdoor weathering conditions, which could lead to more stable polymers which will broaden their range of applications.

In the literature the chemistry underlying the photodegradation has been ascribed to two different mechanisms: i.e. photo-Fries rearrangement and photo-oxidation. The relative importance of the photo-Fries rearrangements and the photo-oxidation depends on the irradiation wavelengths used. It is known that the photolytic photo-Fries rearrangements take place at short wavelengths (<300 nm), whereas at longer wavelengths (>300 nm) only photo-oxidation reactions take place. The wavelength distribution of terrestrial sunlight starts around 300 nm, which implies that both degradation reactions can be present in outdoor weathering conditions.
In this thesis it is shown that when BPA-PC is exposed to outdoor weathering conditions, the photo-oxidation reaction is dominant. However, this reaction needs to be initiated by an initiating radical. Small amounts of free radicals can already be sufficient to initiate the autocatalytic photo-oxidation reaction. In the literature the source for initiating radicals is under debate. It was assumed that the initiating radicals were formed by photo-Fries rearrangements, however there was no convincing evidence.

In the first part of this thesis, possible initiation sources were explored and their influence on the photo-oxidation reaction was studied. It was shown by using different spectral analysis methods, such as UV-spectroscopy, FT-IR spectroscopy, and fluorescence spectroscopy, that photo-Fries rearrangement products were formed in accelerated outdoor exposure conditions, albeit in very low concentrations. Nevertheless, they do not act as initiators for the photo-oxidation reaction. Thermally produced hydroperoxides, which are known as photo-oxidation initiators for polyolefins also do not influence the photodegradation rate of BPA-PC.

The influence of oxygen was determined by degrading BPA-PC films at different oxygen pressures. It was found that charge transfer complexes were formed between oxygen and the polymer. The absorption of these complexes tails into the terrestrial sunlight wavelengths and might lead to photo-oxidation initiating radicals. It was also shown that at higher oxygen pressures the photo-Fries rearrangement reactions are quenched.

It was shown that small wavelength fluctuations in the onset of the irradiation spectra (starting from 290 to 300 nm) lead to different ratio between the photo-Fries and the photo-oxidation reaction. Though, in the second part of this thesis a linear relationship between the irradiation intensity and the photodegradation rate, according to the reciprocity law, was found. By retaining the wavelength distribution, the intensity has no effect on the degradation mechanisms.

In the third part of this work, different stabilizing techniques were studied. The action of conventional stabilizers and block copolymers based on resorcinol polyarylate, which rearrange themselves into a protective top layer, were compared. The best way to stabilize BPA-PC against photodegradation is to keep the light out by using UV-absorbers or protective coatings. The addition of hindered amine light stabilizers did not greatly affect the degradation rate.
In addition, the best results for stabilizing BPA-PC were obtained when the (harmful) UV light was absorbed by hydroxybenzophenones. Especially when a high concentration of UV absorbing species is located on top of the polymer film, i.e. by a secondary film or by a resorcinol polyarylate block copolymer.

In the last part of this thesis the results of the accelerated and outdoor tests were compared. Due to a different wavelength distribution of the spectra for the light used in the accelerated test and the terrestrial sunlight, a different ratio between the photo-Fries and the photo-oxidation reactions for accelerated and outdoor weathering was found. Due to this wavelength sensitivity of BPA-PC towards the lowest wavelengths of terrestrial sunlight, it is difficult to make a good lifetime prediction for BPA-PC used in outdoor applications with accelerated tests.
Chapter 1

General Introduction

1.1 Introduction

Over the past decades the production and consumption of polymeric materials has been increasing rapidly. Many of these polymers are used for outdoor applications, for example in automobiles, greenhouses, and fibers for ropes. Over the past years the list of demands for these applications have grown. To meet these requirements, new polymers can be developed, or the current polymers can be modified to improve their properties.

One of the disadvantages of using polymers, is that they degrade when they are used in high temperature conditions or in outdoor applications. When polymers are used in outdoor applications, the environment negatively influences the service life. This process is called weathering.\textsuperscript{1,2}

The weathering of polymers can be defined as an irreversible chemical process induced by environmental parameters that leads to undesired changes of properties of the polymers, such as discoloration and loss of mechanical properties.\textsuperscript{3,4} The degradation of polymers during their service life, especially when they are used in outdoor applications, can be caused by reactions of the polymer with and without oxygen induced by terrestrial sunlight. But also parameters as the humidity, temperature, geographic location, mechanical stresses, abrasion and biological attack can affect the degradation rate.\textsuperscript{5,6} It has been stated that, the (UV)-radiation is one of the most important factors determining the polymers lifetime. Degradation due to (UV)-radiation is called
Chapter 1

photodegradation. Chemical reactions (e.g. chain scissions, cross linking, and oxidation) influence the physical properties and thus the article’s lifetime.\(^7\)

Besides the service environment, other parameters, as the polymer itself and the use of stabilizers influence the rate of degradation. The most important polymer-related parameters for degradation are the type of polymer, (e.g. polyolefins, engineering plastics as polyamides or polycarbonates), the amount of branching, catalyst residues, or end groups.\(^8\)

Different techniques to stabilize polymers have been developed, e.g. adding different types of stabilizers, or applying a protective coating.\(^9\) In order to improve the polymer photostability there has been a very big effort over the last decades to understand the reaction mechanisms involved in photodegradation and environmental ageing of different polymers.

In the next paragraphs the different types of photodegradation reactions, stabilization methods, and weathering tests will be presented.

1.2 Mechanisms of photodegradation

When light is absorbed by a polymer, photochemical reactions can occur as a result of activation of a polymer macromolecule to its excited singlet or triplet states.\(^10\) If the energy of the absorbed UV light is higher than the bond energy, the chemical bond may break.

The most important mechanisms causing weathering of polymers are photolysis and photo-oxidation.\(^10,11\) If the absorption of light leads directly to chemical reactions causing degradation, this is called photolysis. Photo-oxidation is a result of the absorption of light that leads to the formation of radicals that induces oxidation of the material.

For polyolefins it is well known that photo-oxidation is the dominating mechanism.\(^10,12\) These polymers do not have an inherent absorption at wavelengths present in terrestrial sunlight (>290-300 nm) causing that photolysis can not play an important role. Nevertheless, irradiation of these polymers with terrestrial wavelengths results in accelerated degradation. This can be ascribed to impurities that are formed during storage and processing or to charge transfer complexes between the polymer and oxygen.\(^10,13,14\) Due to photolytic
reactions of these absorbing species, radicals are formed that initiate the photo-
oxidation reaction.

In contrast to polyolefins, the majority of engineering plastics do have
absorptions at wavelengths being present in terrestrial sunlight, so that for these
polymers photolysis can play an important role too.

For these polymers in principle there are three mechanisms that can describe
their light-induced degradation:¹⁵

- Photolysis; absorption as a result of the inherent polymeric structure results
  in chemistry causing changes in the molecular structure;

- Photo-oxidation initiated by photolysis reactions of the polymer itself as
  mentioned above;

- Photo-oxidation initiated by impurities not part of the inherent polymer
  structure.

In the next paragraphs these mechanisms will be briefly discussed.

1.2.1 Photolysis: Norrish I, Norrish II and photo-Fries reactions

Photolytic reactions occur when light is absorbed by the polymer and leads to
changes in structure. Important photolytic reactions for degradation are the
Norrish I and Norrish II reactions and the photo-Fries rearrangement. These
are described in more detail in the following sections.

Norrish I and Norrish II reactions

When light is absorbed by the polymer, Norrish reactions can occur, which lead to
changes in molecular structure resulting in degradation.¹⁰ The Norrish I reaction
leads to chain cleavage and radicals that might initiate the photo-oxidation. The
Norrish II reaction is a non-radical intramolecular process, in which hydrogen is
transferred, leading to chain cleavage. For polyamides and polyesters the most
important photolytic reactions are the Norrish I and II reactions. In Figure 1.1
both reactions are shown.
Chapter 1

Figure 1.1: Norrish I (top) and Norrish II (bottom) reactions for polyamides (X=NH) and polyesters (X=O).

The photo-Fries rearrangement

Engineering plastics containing phenyl ester groups, like polycarbonates, can undergo Fries rearrangements. When a phenyl ester rearranges, as a result of the absorption of UV-radiation, it is called the photo-Fries rearrangement. In Figure 1.2 the photo-Fries rearrangement of a phenyl ester is shown. The reaction involves three basic steps; 1) the formation of two radicals, 2) recombination, and 3) hydrogen abstraction.

The phenoxy radical is in equilibrium with two cyclohexadienone radicals. It may also be possible that the phenoxy radical reacts neighboring molecules by abstracting a hydrogen atom from the neighboring molecules to form phenol. It can also convert to one of the cyclohexadienone radicals and form one of the acylphenols through recombination with an acyl radical and abstraction of hydrogen. The formation of phenol is favored in non-polar solvents, the

Figure 1.2: The photo-Fries rearrangement of a phenyl ester.
rearrangement is favored in polar solvents. So this photo-Fries rearrangement reaction can be a concerted or radical process.\textsuperscript{16–17}

The rearrangement of the radical depends on substituents and temperature. At higher temperature the ortho isomer usually predominates.

### 1.2.2 Photo-oxidation mechanism

Polymers can undergo photo-oxidative reactions when they are exposed to (UV)light.\textsuperscript{10} The mechanism describing the photo-oxidation of polymers is shown in Figure 1.3.\textsuperscript{15}

In this figure different degradation steps can be considered:

1. Initiation step: The formation of free radicals, where R· is a polymer radical induced by hydrogen abstraction by other initiating radicals I·;

   \[
   I \rightarrow I^* \quad (1.1)
   \]

   \[
   I^* + R·H \rightarrow R^* + I-H \quad (1.2)
   \]

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{photo_oxidation_diagram.png}
\caption{Photo-oxidation mechanism of polymers RH most labile hydrogen.\textsuperscript{15}}
\end{figure}
2. Propagation step: The reaction of free polymer radicals with oxygen;

\[ R\cdot + O_2 \rightarrow R-OO\cdot \quad (1.3) \]

\[ R-OO\cdot + R-H \rightarrow R-OOH + R\cdot \quad (1.4) \]

3. Branching and Secondary Reactions: Rearrangements and chain scissions may occur;

\[ R-OOH \rightarrow R-O\cdot + \cdot OH \quad (1.5) \]

\[ R-O\cdot + R-H \rightarrow R\cdot + R-OH \quad (1.6) \]

\[ R-O\cdot \rightarrow R'=O + \cdot R' \quad (1.7) \]

\[ \cdot OH + RH \rightarrow R\cdot + H_2O \quad (1.8) \]

\[ R-OOH \rightarrow R'=O + H_2O \quad (1.9) \]

4. Termination step: The reaction of different free radicals with each other, which may result in crosslinking.

\[ R\cdot + R\cdot \rightarrow R-R \quad (1.10) \]

\[ R\cdot + R-OO\cdot \rightarrow R-OOR \quad (1.11) \]

\[ 2 \, R-OO\cdot \rightarrow R-OOOO-R \rightarrow R-OH + R'=O + O_2 \quad (1.12) \]

This last reaction can only occur when at least one of the radicals involved is a primary or a secondary radical.

The origin of the radical I\cdot as initiating radical for the chain reaction is very important and polymer dependent.

This autooxidative degradation process can be initiated by different sources.\textsuperscript{18–21} When a polymer contains chromophore groups in its repeating unit the initiation step can take place in each unit. However, if the polymer has no...
chromophoric groups in its repeating unit, other mechanisms are responsible for
the initiation. When the polymer contains structural defects, such as carbonyls
and hydroperoxides or other impurities originating from for example processing
conditions, these chromophores can be a source for initiating radicals. In addition
catalysts, solvent residues, and end groups can not be excluded as initiating
sources.

1.3 Stabilization

To prevent photodegradation reactions, there are several ways to stabilize the
polymer. One can stabilize polymers by keeping the light out, quench excited
states before photochemistry occurs, or trap free radicals. This can be achieved
by adding UV-absorbers, quenchers, radical scavengers, metal deactivators or
synergistic combinations to the polymer.\textsuperscript{1,9} In order to be a good stabilizer, it has
to be photostable itself and must not negatively influence the processability, i.e.
decrease the melt viscosity by molecular weight reduction. In the next paragraphs
the most important stabilizing groups are discussed.

1.3.1 UV-absorbers (UVAs)

To protect polymers from (UV)-radiation compounds that have the ability to
absorb UV radiation, can be applied; these compounds are called UV-absorbers
(UVAs). To become an effective UV-stabilizer UVAs must strongly absorb,
for polymers, harmful UV light. UVAs, like dihydroxybenzophenones, are
photostable because their excited states can dissipate the absorbed energy as
heat by a rapid internal hydrogen transfer.\textsuperscript{1,22} This mechanism is shown for a
\(\alpha\)-hydroxybenzophenone (HBP) in Figure 1.4. When photons are absorbed by the
HBP, it is excited to the first excited singlet state. UVAs with an intramolecular
hydrogen bridge, like HBP, can undergo an excited state intramolecular proton
transfer (ESIPT). The excited proton transferred product loses its energy by heat,
fluorescence, or phosphorescence, to form the ground-state proton transferred
product, followed by a proton shift, which leads to the UVA in the ground state.
For HBP it is also postulated that the deactivation of the tautomeric compound
can proceed by intersystem crossing (ISC) through a triplet state T1.\textsuperscript{1} The HBP
remains intact as long as intramolecular proton transfer can take place. In order to
be a good UV-stabilizer, the deactivation process has to be very effective, because even low quantum yields of destruction will result in an undesired reduction of stabilizer concentration.

There are different groups of UVAs. The most important types which are commercially used are: hydroxybenzophenones, hydroxyphenyl benzotriazoles, cyanoacrylates, oxanilides, and more recently-commercialized hydroxyphenyl triazines. The UV-absorption of these molecules depends, besides on the type, also on their substitution. In order to be effective for transparent applications, these stabilizers should have a high absorption coefficient in the range of 250-400 nm to absorb UV-irradiation and not visible light.

**Efficiency of UV-absorbers**

An important aspect of the effectiveness of UVAs in the polymer is the amount of light which is absorbed at a certain depth in the polymer. The absorption of light by UVAs follows Lambert-Beer’s law, given in Equation 1.13,

\[ I_d = I_0 10^{-\varepsilon cd} \]  

where, \( I_d \) the intensity of the light at depth \( d \), \( I_0 \) the incident light intensity, \( \varepsilon \) is the extinction coefficient, and \( c \) is the concentration of the UVA. In Figure 1.5 the influence of the UVA concentration and relative light intensity as a function
of depth for a non-absorbing polymer is depicted. This figure clearly shows that UVAs mainly protect the bulk material, and are not very effective in preventing surface degradation.\textsuperscript{23} This means that blending of UVAs can be effective in preventing bulk degradation, but is not a very effective way to prevent degradation of thin articles or where the degradation only appears at the surface. High concentrations of UVAs are necessary to prevent degradation of thin articles, nevertheless, UVAs are used in many applications.

1.3.2 Hindered Amine Light Stabilizers (HALS)

In many polymers, hindered amine light stabilizers (HALS) are the most effective for preventing photodegradation.\textsuperscript{25}

Since the discovery of HALS, many studies on the mechanism of action have been performed and different mechanisms have been proposed, however at this moment, there is still no consensus. As the UV-degradation of polymers is circumstances dependent, the mechanism of action of HALS is that too. Therefore, the results of the mechanism of action can vary, e.g. with polymer type, and light sources used for the UV degradation.

A simplified mechanism of action that often is used, is the reaction of an alkyl radical with a nitroxy radical leading to the formation of a hydroxylamine ether.\textsuperscript{1}
Subsequently, this reacts with a peroxo radical, resulting in a peroxide and the reformation of the nitroxyl radical. This mechanism is shown in Figure 1.6. The mechanism of the nitroxyl radical formation from sterically hindered amines is still a controversial issue.

One advantage of the hindered amine light stabilizers is that no specific layer thickness or concentration limit needs to be reached to be effective. Even at low concentration the service life can be increased. Although HALS are very effective for polyolefins, they are generally less effective for aromatic polymers where the rate of initiation is high and the number of propagation steps in the cycle is small.\textsuperscript{11}

1.4 Weathering tests

To determine the lifetime of an article which is exposed to outdoor conditions, weathering tests need to be performed. The best way to test an article’s lifetime is to test it in its service life. The most suitable method to test the lifetime of a polymer is exposing the polymer in conditions as close as possible to its service environment.\textsuperscript{26} However, in many cases these tests are very time consuming.

To reduce the exposure time, different accelerated tests were developed. In general they can be divided into outdoor and indoor tests. In the next sections they will be briefly discussed.
1.4.1 Outdoor weathering tests

One way to reduce the exposure time is to weather the samples in extreme testing sites.\textsuperscript{2} At these sites there is often a high intensity of terrestrial light and high temperatures. There are several official testing sites, such as sites in Florida, Arizona and Sanary. However performing these tests can still be very time consuming.

Even though these tests are quite realistic, their correlation with the results of real situations is not trivial.\textsuperscript{27–29} The environment itself deviates throughout the year. For example, the irradiation times and irradiation intensity vary with the season and the total light intensity can also vary from year to year. This leads to complex interactions of the combination of weathering parameters in the material. Therefore testing times need to be long enough to find a relatively good correlation with the lifetime of applications in their service environment.

1.4.2 Indoor weathering tests

To reduce the time to test the lifetime of polymers, several indoor accelerated ageing tests were developed.\textsuperscript{2} The accelerated degradation process has to correspond to the real-time situation, which means that the conditions must be as close as possible to those used in practice, causing that the degradation can not be accelerated to much. However, the consequence is that this ageing still takes long periods. Therefore accelerated tests have to speed up the degradation process to come up with an acceptable testing time period.

Different test devices with artificial light sources were developed to accelerate the degradation. The light sources in these devices include filtered carbon arcs, filtered xenon arcs, and metal halide or fluorescent UV lamps. Although the light source is a critical factor in the weathering of materials, heat and moisture play a significant role in the effect of the environment on the materials as well.

The advantages of laboratory weathering tests is that the testing time can be reduced dramatically, since the samples can be irradiated at high intensity for 24 hrs a day. However the results can not always be correlated to outdoor results. There are different indoor testing devices, for example weatherometers, suntest XXL\textsuperscript{+}, and QUV. The main differences between the lamps are the emission spectra, intensity of irradiation, working temperature, lifetime, size and...
construction. Especially the irradiation with short UV wavelengths gives different results compared to outdoor tests. The best way to mimic outdoor conditions is to have irradiation spectra similar to the terrestrial wavelength spectra, which means that the preferred irradiation light contains wavelengths $> 295$ nm. In addition, in outdoor conditions, there is a lack of reproducibility since the ageing parameters are also varying each day. Therefore in most weathering tests, laboratory equipment is used to predict the articles lifetime and to study what is happening in outdoor conditions.

### 1.5 Polycarbonate

Polycarbonate is one of the most important engineering plastics due to its high toughness and clarity.\(^{30}\) It is used in many applications. The most common applications can be found in glazing and sheet applications, such as transparent panels for greenhouses, electrical and electronics applications, such as computers and, mobile phones, and optical media, such as compact discs. Moreover, they can also be used in medical and health care, bottles and packaging, leisure and safety, and automotive.

The most important polycarbonate is based on bisphenol-A. In general there are two different industrial routes for the synthesis of high molecular weight bisphenol A polycarbonate (BPA-PC), which were developed independently in the early 1960s, i.e. the interfacial synthesis and the melt synthesis.\(^{31-33}\)

![Figure 1.7: Industrial routes to bisphenol A polycarbonate, interfacial synthesis (left) and melt synthesis (right).](image)
The most widely used commercial process, involves the interfacial reaction between phosgene and the sodium salt of bisphenol-A (BPA) in a heterogeneous system, see Figure 1.7(left). The hydroxyl group of the BPA molecule is deprotonated by the sodium hydroxide. The deprotonated oxygen reacts with phosgene to form a chloroformate, which reacts with another deprotonated BPA. The molecular weight is regulated by the addition of phenol or phenolic derivatives to endcap the polymer chains.

The second industrial route to synthesize BPA-PC consists of a melt-phase transesterification between a bisphenol-A and diphenyl carbonate (DPC), see Figure 1.7(right). This process occurs typically in two stages. In the first stage the BPA, DPC and a catalyst are heated to 200 °C to form a low molecular weight polycarbonate and to remove most of the formed phenol. The second stage involves a heating of the remaining mixture to evaporate the remaining phenol and DPC to form an intermediate weight average molecular weight polycarbonate.

One of the major differences between the melt and the interfacially prepared BPA-PC, is that the melt prepared polycarbonate is typically not completely end-capped; some level of phenol-terminated polymer will usually be present. The polymer prepared with the melt process is exposed to high temperatures, which leads to instability and discoloration of the product. It is believed that the free hydroxyl groups of BPA are responsible for instability of the product.

Because of its good properties, BPA-PC is an ideal material for use in demanding applications where it is often exposed to environmental parameters. On extended exposures to (UV) light, BPA-PC slowly degrades, turning progressively more yellow eventually leading to a decrease in its physical properties. Over the past decades, there have been numerous studies of these degradation processes. However the chemistry underlying the degradation reactions is still under debate, since most of these studies were performed under different (often accelerated) exposure conditions.
Chapter 1

1.6 Objective of this thesis

Although the durability and reliability are of key importance for bisphenol A polycarbonate, the knowledge determining these factors is limited. The present knowledge on degradation and stabilization is mainly derived from research results on polyolefins, which resulted in the development of several new stabilizers that caused major breakthroughs in the stability of polyolefins. All improvements realized for engineering plastics are a spin off of the developments for polyolefins and are never based on scientific knowledge. For these polycarbonates there were no major breakthroughs, which is a result of a lack of scientific knowledge. The aim of this thesis is to get a more detailed knowledge about the degradation chemistry of polycarbonate in outdoor weathering conditions, which could lead to more stable polymers which will broaden their application.

1.7 Outline of this thesis

First, the photodegradation of bisphenol A polycarbonate in outdoor exposure conditions is studied in Chapter 2. In this chapter it is investigated which degradation mechanisms play a major role during the irradiation with wavelengths similar to the terrestrial sunlight. It is shown that photo-oxidation is the most important degradation mechanism, however, photo-Fries rearrangement products are also found indicating that both degradation reactions are present in outdoor exposure conditions.

Photo-oxidation reactions need to be initiated by initiating radicals. In Chapter 3 different radical sources are explored as initiating agents for the photo-oxidation. These possible sources are derived from the possible initiation sources for polyolefins. In this chapter, the influence of photo-Fries rearrangements and the influence of oxygen on the degradation of polycarbonate is studied.

In Chapter 4 the influence of the irradiation intensity on the photodegradation of polycarbonate is investigated to see if by changing the intensity the degradation mechanisms remain the same. In this chapter it is investigated if the degradation obeys the reciprocity law.

Chapter 5 gives an overview of the influence of different types of stabilizers on the photodegradation of polycarbonate. For an applied UVA, the degradation
rates of the stabilized polycarbonates are compared with the scaling factors derived in Chapter 4.

UV-absorbers, based on hydroxybenzophenones are compared with block copolymers based on polyarylates in Chapter 6. These block copolymers rearrange through a photo-Fries rearrangement to form a self protecting, UV-absorbing top layer.

To correlate our results obtained in Chapters 2-6, the results are compared to outdoor weathered samples in Chapter 7.

References

4. N. Billingham, Oxidative degradation of polymers: A tutorial on what we don’t know, 233rd ACS National Meeting, Chicago, United States, 2007
5. J.E. Pickett, Effect of environmental variables on the weathering of some engineering thermoplastics, Polymer Preprints, 2001, 42, 424-425


General Introduction


Chapter 2

Photodegradation of bisphenol A polycarbonate

Depending on the irradiation wavelengths used, bisphenol A polycarbonate can degrade by two different mechanisms, i.e. photo-oxidation and photo-Fries. The relative importance of these mechanisms in outdoor exposure conditions is still unknown. In this chapter bisphenol A polycarbonate is exposed to simulated weathering conditions. Different analysis techniques show that photo-oxidation is the most dominant degradation reaction. However, fluorescence spectroscopy shows that small amounts of photo-Fries rearrangement products are formed.

This chapter is partly reproduced from: M. Diepens, P. Gijsman, Polymer Degradation and Stability, **2007**, 92, 397-406
2.1 Introduction

When engineering plastics, like bisphenol A polycarbonate (BPA-PC), are used in outdoor applications, the polymer starts to show losses in mechanical properties and changes in aesthetical properties. Due to sunlight, humidity and oxygen this polymer degrades. To increase its lifetime, this undesirable degradation process needs to be overcome. Therefore, it is necessary to know what chemical degradation reactions occur and how these processes are initiated.

The chemistry of degradation processes in polycarbonates has been studied extensively over the past few decades, however, what is happening under outdoor exposures is still under debate, since most of these studies were done under different exposure conditions. In BPA-PC the chemistry underlying the photodegradation has been ascribed to two different mechanisms: photo-Fries rearrangement and photo-oxidation. The relative importance of these mechanisms depends on the irradiation wavelengths used. Lemaire et al. illustrated that the photo-Fries rearrangement reaction is more likely to occur when light with wavelengths shorter than 300 nm is used, whereas photo-oxidation reactions are more important when light of longer wavelengths ( > 340 nm) is used.

The major part of the natural sunlight spectrum contains wavelengths longer than 300 nm, although, sunlight can contain wavelengths down to 295 nm. This means that there is a possibility that both photo-oxidation and photo-Fries rearrangement take place under outdoor exposures. Therefore, it is important to investigate which mechanism is most important during the outdoor weathering of polycarbonate.

2.1.1 Photo-Fries rearrangement of BPA-PC

Irradiation of the polymer with short wavelengths causes the aromatic carbonate unit to rearrange itself into phenylsalicylate and dihydroxybenzophenone derivatives. This photo-Fries reaction can either be a concerted or a radical process. However, the opinions on which of these processes is dominating are divided.
In Figure 2.1 the photo-Fries rearrangement via radicals is represented. Photo-Fries products, like phenylsalicylate, are easily photooxidized, which makes it difficult to detect these products and to find evidence for the photo-Fries pathway.\(^5,6\)

### 2.1.2 Side chain oxidation of BPA-PC

In general, side chain oxidation reactions are dominating when light with wavelengths longer than 340 nm is used.\(^5\) For BPA-PC this mechanism is shown in Figure 2.2.

In this mechanism an initiating radical is required to start this autocatalytic oxidation process. Up till now, it is not clear where this radical originates from. For polyolefins, it is generally accepted that this radical results from light absorption by chromophoric impurities or by charge transfer complexes.\(^3-6,12-14\) For BPA-PC, it is suggested that during the initiation of the photodegradation process, the photo-Fries rearrangement reaction is the source for free radicals.\(^11,15,16\) However, at wavelengths longer than 340 nm this can not be the case, and the initiating radical have to originate from other reactions.\(^17\) At short wavelengths initiation through photo-Fries rearrangement might play a role. In the presence of oxygen, formed radicals lead to photo-labile oxidation
products such as hydroperoxides and aromatic ketones. The hydroperoxides can initiate new oxidation cycles causing autocatalytic photo-oxidation.

Factor\textsuperscript{15} characterized nearly 40 degradation products in a bisphenol A polycarbonate sample which was placed outdoors for 4 years. The products were predominately photo-oxidation products; although, small amounts of photo-Fries products were found too. In order to proof that photo-Fries rearrangement occurs in outdoor exposures, samples were placed outdoors under vacuum.\textsuperscript{16} Analyses by gas chromatography mass spectroscopy showed that small amounts of photo-Fries rearrangement products were formed. Without convincing evidence it was postulated that the radicals formed as intermediates in the photo-Fries rearrangement can act as initiators for the (autocatalytic) photo-oxidation. The same author also postulated other initiating reactions.\textsuperscript{11}

Andrady et al.\textsuperscript{17} showed that for wavelengths under 300 nm, the photo-Fries rearrangement is responsible for the discoloration of the polymer. Irradiation with longer wavelengths (310-350 nm) also resulted in yellowing of the samples, which was ascribed to impurities and defects in the polymer chain. From this result they concluded that the photo-Fries pathway is insignificant in outdoor exposures, since the wavelengths of solar radiation are longer than 300 nm.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.2.png}
\caption{Photo-oxidation of bisphenol A polycarbonate.\textsuperscript{4}}
\end{figure}
So first the degradation chemistry of bisphenol A polycarbonate is studied by focusing on which degradation mechanisms are present under simulated outdoor weathering conditions. This is achieved by irradiating the polycarbonate films in an accelerated testing device that simulates outdoor conditions. The samples are analysed by different spectral analysis techniques to detect if photo-Fries reactions and oxidation reactions are present in these conditions.

2.2 Experimental

2.2.1 Materials

Extruded films of unstabilized bisphenol A polycarbonate were supplied by General Electric (Lexan 145, synthesized by the interfacial process). The thickness of the films was approximately 0.2 mm. Model compounds for photo-Fries products were supplied by Aldrich and were used without any further purification. In Table 2.1 the chemical structures and abbreviations of these model compounds are given.

2.2.2 Weathering

The samples were irradiated in an Atlas Suntest (CPS) containing a borosilicate filtered xenon lamp, with an irradiance level of 0.5 W/m²/nm at $\lambda = 340$ nm at an average room temperature of 40 °C. The wavelength distribution of the irradiated light was measured using an Ultraviolet radiation spectroradiometer of type MSS 2040-UV. In Figure 2.3 the irradiation wavelength spectrum is shown. In this figure it can be seen that the irradiation wavelengths start below 300 nm.
Table 2.1: Chemical structures of model compounds of PC and photo-Fries rearrangement products.

<table>
<thead>
<tr>
<th>Model Compound</th>
<th>Abbreviation</th>
<th>Chemical structures</th>
</tr>
</thead>
<tbody>
<tr>
<td>diphenyl carbonate</td>
<td>DPC</td>
<td><img src="image" alt="Chemical structure" /></td>
</tr>
<tr>
<td>2,2'-dihydroxybiphenyl</td>
<td>DHB</td>
<td><img src="image" alt="Chemical structure" /></td>
</tr>
<tr>
<td>bisphenol A dimethyl ether</td>
<td>BPADME</td>
<td><img src="image" alt="Chemical structure" /></td>
</tr>
<tr>
<td>2,2'-dihydroxybenzophenone</td>
<td>DHBP</td>
<td><img src="image" alt="Chemical structure" /></td>
</tr>
<tr>
<td>phenylsalicylate</td>
<td>PS</td>
<td><img src="image" alt="Chemical structure" /></td>
</tr>
</tbody>
</table>

Figure 2.3: Irradiation wavelength spectrum emitted by the borosilicate filtered xenon lamp in the CPS.
2.2.3 Characterization techniques

UV-Vis spectra were recorded on a Shimadzu UV-3102PC UV-VIS-NIR scanning spectrophotometer. Infrared spectra were recorded using a BioRad FTS 6000 spectrometer in the attenuated total reflection (ATR) mode for 200 scans at a resolution of 4 cm$^{-1}$. The BioRad Merlin software was used to analyse the spectra.

Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were recorded on a Voyager-DE STR in the reflector mode from Applied Biosystems. The polycarbonate films were dissolved in tetrahydrofuran (THF). The matrix used was trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile and potassium as cation.

The chemiluminescence signal was measured in a ramp experiment. Around 50 mg of the films was put on an aluminium tray and then placed inside the chemiluminescence apparatus. After 20 minutes of flushing with nitrogen, the samples were heated linearly at a rate of 10 °C/min from 25 °C to 250 °C and at this point the temperature was maintained.

A Shimadzu RF-1501 spectrofluorophotometer was used to record fluorescence spectra. The irradiated polycarbonate samples were dissolved in dichloromethane (0.001 wt% PC in DCM). Emission spectra were recorded using an excitation wavelength of 310 nm. The second-order Rayleigh scattering peak (located at 622 nm) was used to scale the recorded fluorescence spectra.

2.3 Results

2.3.1 UV-spectroscopy analysis

UV-Vis spectrophotometric scans of polycarbonate films with different ageing times were measured in the range of 200-800 nm. Figure 2.4 shows that the absorbance for wavelengths below 400 nm is increasing with increasing irradiation times, however no clear absorbance bands can be observed.

In the literature absorption bands at 320 nm and 355 nm are ascribed to phenylsalicylate and dihydroxybenzophenone respectively. Figure 2.5 shows that the absorbance at these wavelengths linearly increases with irradiation times. Since the absorptions at these wavelengths are ascribed to photo-Fries
rearrangement products, this indicates that photo-Fries rearrangement products can be present in outdoor weathering conditions. However, the UV spectra themselves do not clearly show peaks or shoulders at these wavelengths, which

Figure 2.4: UV absorption spectra of BPA-PC films for various irradiation times in CPS.

Figure 2.5: UV absorbance of BPA-PC films at 320 nm and 355 nm with increasing irradiation times.
makes it difficult to conclude from these spectra that photo-Fries rearrangements have taken place.

### 2.3.2 Infrared spectroscopy analysis

The degradation of polycarbonate is a surface phenomenon, which only extends about 25 $\mu$m into the exposed surface\textsuperscript{11,20} therefore the polycarbonate films were analysed with FT-IR in ATR mode. With this technique only the top layer of the films is examined for changes in chemistry during the degradation. In Figure 2.6 the IR spectra of samples with different irradiation times are shown. As the irradiation time increases, absorption bands are formed at different wavelengths.

The typical oxidation absorption band at 1713 cm\textsuperscript{-1} is ascribed to aliphatic chain-acids.\textsuperscript{6} In the literature,\textsuperscript{4,10} the phenylsalicylate and dihydroxybenzophenone bands are ascribed to the vibration band at 1689 cm\textsuperscript{-1} and 1629 cm\textsuperscript{-1} respectively. Furthermore a weak shoulder at 1840 cm\textsuperscript{-1} indicates the formation of cyclic anhydrides during the photo-oxidation.\textsuperscript{4}

When the spectra are normalized using the peak located at 1014 cm\textsuperscript{-1} the absorption as a function of irradiation time can be quantified, see Figure 2.7. This figure shows an increased absorption for the different wavelengths. Although

![Figure 2.6: FT-IR spectra of irradiated BPA-PC films in the carbonyl region for various irradiation times in CPS.](image-url)
absorption for the different bands is already present from the start of the experiment, it can be seen in this figure that after 400 hrs it is rapidly increasing. From the increase of the absorption at 1629 cm\(^{-1}\) and 1689 cm\(^{-1}\) it was suggested that photo-Fries products might be present in the irradiated films. However, it is also likely that the increase is due to band broadening of the oxidation band at 1713 cm\(^{-1}\).

2.3.3  Chemiluminescence analysis

When a chemiluminescence experiment was run in nitrogen, the total light intensity (TLI) was found to be proportional to the hydroperoxide concentration in the case of natural rubber\(^{21}\) and polypropylene.\(^{22}\) It was shown that chemiluminescence in nitrogen relates to oxygen uptake for several materials, even though this relation is polymer and degradation-environment dependent.\(^{23}\) This means that with chemiluminescence it is possible to detect the amount of hydroperoxides, and therefore identify how much the material was oxidized.

Irradiated BPA-PC films were examined using chemiluminescence in a nitrogen ramp experiment. The total light intensity (TLI) measured in ramp experiments in nitrogen as a function of irradiation time of the unstabilized polycarbonate films is shown in Figure 2.8. During the irradiation of the samples, the TLI increases for

---

**Figure 2.7:** Relative absorbance at different wavelengths for increasing irradiation times in CPS.
the first 400 hours. Hence, BPA-PC starts to oxidize from the beginning, without a distinct induction time. For longer irradiation times, the TLI stays constant. This means that during the first 400 hours the hydroperoxide concentration increases, after which the production and consumption of hydroperoxides are in equilibrium.

### 2.3.4 MALDI-TOF MS analysis

MALDI-TOF spectra of the undegraded and the aged polycarbonate films were recorded. In this study the samples were used without fractionation. The MALDI-TOF spectrum of a polycarbonate film irradiated in the CPS for 477 hrs is shown in Figure 2.9. The MALDI peaks are identified according to Montaudo et al.\textsuperscript{24–27} The results are depicted in Table 2.2. Peaks A, B and C were already present in the undegraded sample. Peaks D, E and F were formed during the irradiation of the sample. These products are formed by side chain oxidation. MALDI-TOF is a useful technique to show side chain oxidation products. Unfortunately this technique can not be used to detect photo-Fries products, since the photo-Fries products are rearrangements of the polymer backbone. This rearrangement does not result in a change in molecular weight, which makes it difficult to detect them using mass-spectroscopy. MALDI-TOF is only used to show that oxidation reactions did occur.
Figure 2.9: MALDI-TOF spectrum of bisphenol A polycarbonate film degraded for 477 hrs in CPS.

Table 2.2: Structural assignments of potassiated ions in the MALDI-TOF spectra according to Montaudo et al.\textsuperscript{26}

<table>
<thead>
<tr>
<th>Mass Series</th>
<th>Oligomers structures</th>
<th>n</th>
<th>M$^+\text{K}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td><img src="image" alt="Structure A" /></td>
<td>7</td>
<td>2033</td>
</tr>
<tr>
<td>B</td>
<td><img src="image" alt="Structure B" /></td>
<td>8</td>
<td>2073</td>
</tr>
<tr>
<td>C</td>
<td><img src="image" alt="Structure C" /></td>
<td>8</td>
<td>2167</td>
</tr>
<tr>
<td>D</td>
<td><img src="image" alt="Structure D" /></td>
<td>7</td>
<td>2046</td>
</tr>
<tr>
<td>E</td>
<td><img src="image" alt="Structure E" /></td>
<td>8</td>
<td>2209</td>
</tr>
<tr>
<td>F</td>
<td><img src="image" alt="Structure F" /></td>
<td>7</td>
<td>2090</td>
</tr>
</tbody>
</table>
2.3.5 Fluorescence analysis

Fluorescence spectroscopy can be used to detect photo-Fries rearrangement products in polycarbonates during the degradation. Hoyle et al.\textsuperscript{18,28} reported on the formation of a broad phenylsalicylate band when polycarbonate has been photolysed for short irradiation times.

Emission spectra of solutions of irradiated polycarbonate films in dichloromethane (DCM) were recorded and normalized to the second-order Rayleigh scattering peak at 622 nm, see Figure 2.10b. The normalized intensity is increasing with increasing irradiation times.

To investigate which products are responsible for the increasing signal (especially around 480 nm), emission spectra of some model compounds were recorded. These model compounds are possible photo-Fries rearrangement products and model compounds for polycarbonate. The chemical structures of the model compounds can be seen in Table 2.1. The fluorescence spectra of these model compounds were also normalized to the second-order Rayleigh scattering peak. The emission spectra of the model compounds are presented together with the spectrum of a 308 hrs degraded BPA-PC film in Figure 2.11.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure210.jpg}
\caption{Fluorescence of BPA-PC dissolved in DCM irradiated for different ageing times in the CPS, and the intensity at 480 nm for increasing irradiation times.}
\end{figure}
Figure 2.11: Fluorescence spectra of a 308 hrs irradiated BPA-PC sample compared with different model compounds (abbreviations can be found in Table 2.1. All spectra are normalized to the second-order Rayleigh scattering peak.

The model compound phenylsalicylate (PS) is the only compound which gives a signal at 480 nm. If we assume that the increase in signal at 480 nm is only due to PS, we can calculate the amount of PS units present in the degraded sample. Calculation shows that 1 gram of polycarbonate contains $4 \times 10^{-6}$ mol PS units when it was irradiated for 308 hours in the CPS. This means that approximately 1 phenylsalicylate unit is present in 1000 polycarbonate units. So very small amounts of photo-Fries rearrangement products are present after 308 hours of simulated weathering conditions in the CPS.

2.4 Discussion

It is clearly shown by different analysis techniques, i.e. infrared spectroscopy, chemiluminescence, and MALDI-TOF, that photo-oxidation has taken place in the aged BPA-PC samples, and is the dominant reaction under simulated outdoor exposure conditions. MALDI-TOF shows that different side chain oxidation products were formed.
Chemiluminescence results show that the oxidation starts from the beginning, it increases during the first 400 hours until a stationary level is reached, see Figure 2.8. Surprisingly an increase in absorption in the infrared signal at 1713 cm\(^{-1}\) is just observed when the luminescence signal does not change anymore, see Figure 2.7. It seems that the carbonyls were not formed from the beginning, but that they just were formed when the formation and consumption rate of hydroperoxides became in equilibrium.

In different studies\(^4\)\(^-\)\(^6\) clear IR bands at 1629 cm\(^{-1}\) and 1690 cm\(^{-1}\) were observed and were ascribed to dihydroxybenzophenone and phenylsalicylate derivatives. In our IR spectra an increase in signal is observed, however, this can also be caused by the band broadening of the oxidation peak at 1713 cm\(^{-1}\). UV spectroscopy shows an increase for the absorption at 320 nm and 355 nm, however, no absorption bands are clearly visible, like Rivaton et al.\(^4\)\(^,\)\(^10\) reported. In our UV and IR spectra no clear bands are present, which makes it difficult to conclude from these two techniques that in our case photo-Fries rearrangement reactions have taken place during the irradiation of the samples.

The fluorescence spectra show an increase in signal at 480 nm for increasing irradiation times. When the spectra of the model compounds are compared with the spectra of aged BPA-PC, the change in signal in aged BPA-PC can be caused by structures similar to the model compound phenylsalicylate, since this is the only compound which absorbs at 480 nm. If we assume that phenylsalicylate is the only structure responsible for this increase, we can calculate that in a 308 hrs irradiated BPA-PC sample 1 PS unit is present per 1000 PC units. It is impossible to calculate from these spectra the total amount of rearrangement reactions, since it is more than likely that the phenylsalicylate compounds have rearranged themselves further into dihydroxybenzophenone, which does not give a signal at 480 nm.\(^5\)\(^,\)\(^6\) It is difficult to detect DHBP, since its signal overlaps with other model compounds. Nevertheless, the fluorescence spectra show that PS is present, so photo-Fries rearrangement indeed has taken place when the polycarbonate has been irradiated in the suntest CPS.
2.5 Conclusion

In the past most degradation studies were performed under different exposure conditions, like irradiation with short wavelengths or high intensities, therefore it was under debate if photo-Fries rearrangement reactions take place in outdoor weathering. In this chapter it is shown, by different analysis methods used in this study that photo-oxidation is the dominant degradation reaction during the irradiation with simulated sunlight. However, fluorescence spectroscopy and UV spectroscopy show that small amounts of photo-Fries rearrangement products are formed during the irradiation in the suntest CPS.

References

4. A. Rivaton, Recent advances in bisphenol A polycarbonate photodegradation, Polymer Degradation and Stability, 1995, 49, 163-179
Photodegradation of bisphenol A polycarbonate


Chapter 3

Photo-oxidative degradation of bisphenol A polycarbonate and its possible initiation processes

During UV-degradation of bisphenol A polycarbonate (BPA-PC), photo-Fries rearrangements and photo-oxidation reactions take place. In outdoor exposure conditions the photo-oxidation reaction is dominant. To initiate this autocatalytic oxidation process, an initiating radical is required. In this chapter different sources for photo-initiation are explored, viz. photo-Fries rearrangement products, hydroperoxides and peroxides formed by thermal-oxidation, and charge transfer complexes between the polymer and oxygen. Model compounds for photo-Fries rearrangement products blended in isotactic polypropylene influence the photo-oxidation rate of the polymer. However, for BPA-PC, ageing in conditions causing an increased photo-Fries reaction rate does not result in a higher oxidation rate. This implies that in BPA-PC the photo-Fries reaction does not initiate its oxidation and thus does not proceed through oxidation initiating radicals.
Chapter 3

A comparison of the photo-degradation rate of thermo-oxidized and undegraded polycarbonate samples is made. In this chapter it is shown that the formed thermo-oxidation products in BPA-PC do not affect the photo-oxidation rate.

In this chapter it is also shown that charge transfer complexes (CTCs) between oxygen and polycarbonate are formed. The concentration of CTCs increases with oxygen pressure. The absorption of these complexes tails into the terrestrial sunlight wavelengths, which might lead to photo-oxidation initiating radicals. It is also shown that at higher oxygen pressures the rate of the photo-Fries reaction is decreased.

This chapter is partly reproduced from: M. Diepens, P. Gijsman, Polymer Degradation and Stability, 2007, 92, 397-406, and
M. Diepens, P. Gijsman, Polymer Degradation and Stability, 2008, 93, 1383-1388
Due to sunlight, humidity and oxygen bisphenol A polycarbonate (BPA-PC) degrades in outdoor applications.\(^1\) To increase its lifetime, this undesirable degradation process needs to be overcome. Therefore it is necessary to know what chemical degradation reactions occur. Over the past few decades the chemistry underlying photodegradation of BPA-PC has been studied extensively, however, it is still under debate what is occurring under outdoor exposure conditions, since most of these studies were done under different ageing conditions.

As already discussed in Chapter 2, the chemistry underlying the photodegradation of BPA-PC has been ascribed to two different mechanisms: photo-Fries rearrangement and photo-oxidation. The photo-Fries rearrangement reaction is a photolytic reaction, so that this reaction can only be important when the polymer absorbs the irradiating wavelengths. The photo-oxidation mechanism is a radical chain mechanism\(^2\)\(^−\)\(^4\) in which the absorption of the irradiated wavelengths leads to initiating radicals. The relative importance of the photo-Fries rearrangement and photo-oxidation reactions depends on the irradiation wavelengths used. The UV-spectrum of BPA-PC shows that absorptions below

![Figure 3.1: Solar spectrum measured at Sanary (France) at 1-06-2001 (—), and the UV absorption spectrum of an undegraded BPA-PC film (—).]
300 nm are present, see Figure 3.1, meaning that the photo-Fries rearrangement can take place when the polymer is irradiated with these wavelengths. At 340 nm such absorption is not present in undegraded BPA-PC implying that the photodegradation is only due to photo-oxidation and the photo-Fries rearrangement does not play a role. Terrestrial sunlight hardly shows intensity in the region in which BPA-PC absorbs (see Figure 3.1), which makes that the photo-Fries reaction due to terrestrial sunlight can only be very limited.

The photo-oxidation reaction is the dominant reaction in outdoor conditions, however it has to be initiated with radicals formed by absorption of the irradiating wavelengths. Because the amount of initiating radicals can be very small, in this case even a small absorption can lead to photo-oxidation. It was assumed that these initiating radicals were formed by photo-Fries rearrangements, however there was no convincing evidence.

For polyolefins, it is generally accepted that the initiating radical for photo-oxidation results from the absorption of chromophoric impurities that are formed by pre-oxidation of the polymer during processing or by charge transfer complexes (CTCs) between the polymer and oxygen. Pre-oxidation of the polymer leads to the formation of hydroperoxides and ketones that can absorb terrestrial sunlight wavelengths and can react to form radicals. Polyolefins do not absorb terrestrial sunlight wavelengths, however the absorption of its CTCs with oxygen is shifted its absorption to higher wavelengths which might result in absorption of terrestrial sunlight wavelengths, which can lead to the formation of radicals.

Both for the photo-oxidation of polyolefins assumed initiation reactions were explored for BPA-PC. During the production or during processing of BPA-PC high temperatures are used. At these high processing temperatures, 150-300 °C, polymers can be partially oxidized, as a result hydroperoxide and other peroxides can be formed. These labile intermediates can initiate the photo-oxidation reaction by the formation of macroalkoxy radicals which may abstract a hydrogen atom from the polymer matrix. This effect has been observed for polypropylene and low density polyethylene. Rufus et al. found that thermal treatment at temperatures of 250 °C of BPA-PC in air or oxygen gave rise to fluorescent structures, which were ascribed to the formation of dibenzofuran and phenyl-2-phenoxybenzoate. These samples were subsequently photolyzed using 300 nm broad-band lamps, and it was found that the presence of these structures would
not greatly affect the photodegradation of BPA-PC. However, in this case, the influence of thermal oxidation products on the rate of photo-oxidation was studied mainly with fluorescence spectroscopy, which is more specific for the determination of photo-Fries reactions than for photo-oxidation, so that nothing is learned about the influence of thermal oxidation products on the initiation of the photo-oxidation.

Another potential initiation source is the formation of CTCs as mentioned before. CTCs can play a role in the photo-oxidation of polyolefins, although their absorption of terrestrial sunlight wavelengths is very limited. Hydrocarbons show a red shift in their UV absorption spectra when oxygen is present. This is attributed to the formation of a transient complex on collision between oxygen and a CTC complex. Rabek et al. reported on the formation of a CTC between molecular oxygen and polystyrenes at high oxygen pressures, which absorbs terrestrial sunlight. It can be expected that the CTCs of aromatic polymers, like BPA-PC, and oxygen show absorption in terrestrial sunlight and can be a source of photo-instability of the polymer. Factor et al. showed by subtracting the spectrum of a thin PC film in oxygen with the spectrum of a thin film in nitrogen that charge transfer complexes are present that might play a role in the early stages of the photo-degradation of BPA-PC. Although oxygen BPA-PC CTCs were already mentioned in 1980, the possibility that these complexes are initiating the photo-oxidation of BPA-PC was neglected ever since.

In this chapter different sources for initiating radicals are explored.

### 3.2 Influence of photo-Fries rearrangement products on the photo-oxidation of BPA-PC

Previous results of the weathering of BPA-PC show that photo-oxidation is present and is, as expected, the dominant degradation reaction, see Chapter 2. However, small amounts of photo-Fries rearrangement reactions are also taking place in the accelerated weathering tests. In the next section it is investigated what the influence of these photo-Fries rearrangement reactions is on the photo-oxidation of isotactic polypropylene and on the photodegradation of BPA-PC.
3.2.1 Experimental

Materials

Extruded films of unstabilized bisphenol A polycarbonate were supplied by General Electric (Lexan 145). The thickness of the films was approximately 0.2 mm. Model compounds for photo-Fries products were supplied by Aldrich and were used without any further purification. In Table 2.1 the chemical structures of these model compounds (and their abbreviations) are depicted. Unstabilized isotactic polypropylene (iPP) was supplied by DSM. Blends of 1 wt% model compounds with PP were prepared by dissolving the model compounds in dichloromethane (DCM). The solution was mixed with the porous PP powder. After removal of the solvent, the PP was compression molded for 6 minutes at 180 °C.

Weathering

Two weathering tests with different wavelength ranges were performed. The first UV degradation experiments were carried out in an Atlas Suntest (CPS) containing a borosilicate filtered xenon lamp, with an irradiance level of 0.5 W/m²/nm at λ = 340 nm at an average temperature of 40 °C. The second set

![Figure 3.2: Comparison of the different irradiation wavelength spectra with the solar spectrum.](image-url)
of degradation experiments was carried out in an Atlas Suntest XXL+ (XXL+) containing a xenon lamp filtered by daylight filters. The irradiance level was 0.4 W/m²/nm at $\lambda = 340$ nm. The chamber and black standard temperature were set at 35 and 55 °C respectively and the relative humidity was set to 40%. In both suntesters the wavelength spectra were measured using an Ultraviolet radiation spectroradiometer of type MSS 2040-UV. These spectra were found to be different, see Figure 3.2. The main difference between the CPS and the XXL+ is the wavelength range between 290 and 300 nm. The CPS spectrum contains wavelengths below 290 nm, whereas in the XXL+ only wavelengths $> 298$ nm are present. This small difference can have an impact on the importance of the photo-Fries rearrangement.

UV-Vis spectra were recorded on a Shimadzu UV-3102PC UV-Vis-NIR scanning spectrophotometer. Infrared spectra were recorded using a BioRad FTS 6000 spectrometer in the attenuated total reflection (ATR) mode for 200 scans at a resolution of 4 cm$^{-1}$. The BioRad Merlin software was used to analyse the spectra.

### 3.2.2 Influence of photo-Fries rearrangement reactions in polypropylene

When isotactic polypropylene is irradiated with UV-light, this polymer degrades according to an autooxidation mechanism.$^{17}$ This degradation process can be accelerated by adding radical forming species to the polymer. The samples were prepared by adding small amounts of model compounds for photo-Fries products to unstabilized polypropylene. When these model compounds form radicals it can be expected that polypropylene shows earlier oxidation.

Films of unstabilized polypropylene and 1 wt% model compounds were made by compression molding and were irradiated in the Suntest XXL+. As a result of the irradiation the UV absorption of the PP containing diphenyl carbonate (DPC), the absorption below 500 nm increases, however, the DPC band at 280 nm becomes less pronounced, see Figure 3.3.a. The PP containing phenylsalicylate (PS) shows a more pronounced effect, Figure 3.3.b. The PS band at 320 nm is decreasing and a band at 355 nm is formed, which can be ascribed to dihydroxybenzophenone (DHBP). This indicates that PS has rearranged itself into DHBP.
Figure 3.3: a) UV absorption spectra of PP with diphenyl carbonate (DPC), and b) PP with phenylsalicylate (PS) for different irradiation times.

In Figure 3.4 the infrared absorbance at 1713 cm\(^{-1}\) for the different blends is shown. The pure PP sample shows a rapid oxidation reaction, however, blending the polypropylene with DPC causes the oxidation rate to increase. The increased oxidation rate for PP in the presence of DPC is due to the formation of radicals by

Figure 3.4: IR intensity at 1713 cm\(^{-1}\) for isotactic polypropylene blended with different model compounds for increasing irradiation times.
DPC. This means that the first photo-Fries rearrangement is initiating the photooxidation reaction of PP. When PS and DHBP are blended with the polymer, a reduction in the degradation rate is found. From this can be concluded that photo-Fries products stabilize against the photo-oxidation process for polypropylene, which is not that surprising because hydrobenzophenones are well known UV-stabilizers.¹

### 3.2.3 Influence of different irradiation spectra on photodegradation of BPA-PC

To investigate if the photo-Fries rearrangements, which are present in outdoor weathering conditions, have influence on the photo-oxidation of polycarbonate, the PC films were irradiated with two different suntesters with different irradiation wavelengths. The used suntesters have small differences in irradiation spectra, especially in the region below 300 nm, see Figure 3.2. The aged samples were analysed using different spectroscopic analysis techniques. The results are shown in Figure 3.5.

Figure 3.5.a. shows that the UV absorbance at 320 nm for samples irradiated with the CPS and the XXL⁺ are both linearly increasing with increasing irradiation time, however, the rate of degradation in the CPS is higher than in the XXL⁺. Also emission spectra of solutions of irradiated PC were recorded and normalized to the second-order Rayleigh scattering peak.

The change in fluorescent intensity at 480 nm is shown in Figure 3.5.b. This figure shows that the signal is increasing with increasing irradiation times. The CPS shows a more rapid increase at this wavelength than the XXL⁺ and this means that the CPS promotes the formation of photo-Fries products.

The infrared signal for a typical oxidation band at 1713 cm⁻¹ is shown in Figure 3.5.c. This figure shows that the signal for both suntesters overlaps. The spectra of the samples aged with the CPS and the XXL⁺ show the same behaviour for increasing irradiation times. This means that the wavelength differences don’t influence the oxidation behaviour.
Figure 3.5: Comparison of the results of irradiation of BPA-PC in suntest CPS and XXL+ with a) UV spectroscopy, b) fluorescence spectroscopy, and c) IR spectroscopy.
3.2.4 Relevance of photo-Fries rearrangements in BPA-PC

In the previous section it was shown that photo-Fries rearrangement products can initiate the photo-oxidation of polypropylene. It was also shown that photo-Fries reaction products are present when the BPA-PC films are irradiated with two different wavelength spectra.

Irradiation with the CPS results in higher concentrations of photo-Fries rearrangement products compared to the samples irradiated with the XXL+. This coincides with our expectations, since the CPS irradiation contains shorter wavelengths which can promote the presence of photo-Fries products. However the IR results show that the rate of oxidation is not changed when the samples are irradiated with different wavelength spectra. Thus, the higher amount of photo-Fries reactions in the CPS does not result in a higher oxidation rate. This means that the photo-Fries rearrangement reaction has no influence on the oxidation reaction in polycarbonate even though it influences the degradation of polypropylene. It is possible that the amounts of rearrangement reactions are too small or that other processes are more important in the initiation of polycarbonate.

3.3 Influence of thermo-oxidation products on the photodegradation of BPA-PC

Because the importance of photo-Fries rearrangement for the initiation of the photo-oxidation reaction is limited for polycarbonate, other initiating reactions have to be important. In this section it is investigated what the influence is of chromophoric impurities, formed at high temperatures, i.e. during processing, on the photo-oxidation of BPA-PC.

3.3.1 Experimental

Materials

Films of BPA-PC were prepared by solution casting and by film extrusion. The powder was heated in an oven at 170 °C for different ageing times. After thermal treatment the powder was dissolved in dichloromethane (20 wt% polymer in
DCM) and films were solvent cast on a glass plate and dried in a vacuum oven at 60 °C for 24 hrs. The samples had a thickness of 0.02 mm. For the film extruded samples (pcfe), the PC powder was extruded at 250 °C in a 16 mm Prism extruder. The residence time in the extruder was approximately 90 seconds. The extruded samples had a thickness of approximately 0.9 mm.

Weathering

The solution-cast and extruded films were placed in the Atlas Suntest XXL+. The chamber and black standard temperature were 40 and 60 °C respectively and the relative humidity was 50%. UV-Vis spectra were recorded on a Shimadzu UV-3102PC UV-Vis-NIR scanning spectrophotometer. Infrared spectra were recorded using a BioRad FTS 6000 spectrometer in the attenuated total reflection (ATR) mode for 200 scans at a resolution of 4 cm\(^{-1}\). The BioRad Merlin software was used to analyse the spectra.

3.3.2 Results and Discussion

To investigate whether chromophoric impurities, formed by pre-oxidation of the polymer during processing at high temperatures, influence the photo-oxidation

![Graph](image.png)

**Figure 3.6:** UV absorption spectra of pre-aged BPA-PC films in an oven of 170 °C for different heating times.
rate of BPA-PC, the samples were heated in an air venting oven with a temperature of 170 °C for 0, 95, and 250 hours. The set temperature is above the glass transition temperature (Tg) of BPA-PC which promotes oxygen diffusion, and the heating times were chosen not too long, to get reasonable amounts of oxidation products. Also film extruded samples were prepared at a high temperature to mimic processing. After the sample preparation the films were irradiated in the Suntest XXL⁺.

The influence of the pre-treatment was measured with UV-spectroscopy and IR-spectroscopy in the ATR mode. In Figure 3.6 the UV-absorption spectra for the oven-aged samples, normalized at 600 nm are shown. This figure shows that oven ageing results in a slightly increased absorption at wavelengths between 290 and 320 nm, and that longer heat exposures lead to a higher absorption in this region. This effect is also observed for the extruded BPA-PC sample. The UV-absorption results show that these treatments lead to the formation of thermal oxidation products and it shows that more oxidation products are formed for longer treatment times. Infrared spectroscopy in the ATR mode of the unirradiated samples was used to detect oxidation products (like hydroperoxides and carbonyls) at the surface of the films. The spectra of the different heat-

![Figure 3.7](image-url): IR absorption at 1713 cm⁻¹ for various irradiation times for the different pre-aged BPA-PC films (0, 95, and 250 hrs) and extruded BPA-PC (pcfe).
treated samples are comparable; no differences in oxidation bands were detected. This means that this spectroscopic technique is not very sensitive to oxidation in the first stages of the degradation, however, UV-spectroscopy showed that indeed oxidation reactions did occur when different heat treatments were applied.

The thermo-oxidized samples were exposed to outdoor weathering conditions in the Suntest XXL. After different irradiation times, the samples were evaluated with infrared spectroscopy to determine the oxidation degree of the exposed polymers. In Figure 3.7 the IR absorbance at 1713 cm\(^{-1}\), which is ascribed to an oxidation band,\(^{15}\) was plotted against irradiation times. This figure shows that the absorbance is increasing with increasing irradiation times. Especially in the first 400 hrs the IR absorbance at 1713 cm\(^{-1}\) of the unaged and pre-aged samples is comparable. After 500 hrs the data of the different samples start to deviate. After this irradiation time, all samples show a clear absorbance at 1713 cm\(^{-1}\), however there is no real trend between this absorbance and the thermal pre-aging time. The film extruded sample show a slightly lower absorption at higher irradiation times. A possible explanation for this effect can be attributed to an experimental error. The film extruded samples (pcfe) are much thicker than solvent cast samples. The ATR-crystal could be pushed deeper into these sample

![Figure 3.8: IR absorption at 1713 cm\(^{-1}\) plotted against UV absorption at 320 nm, for various irradiation times for the different pre-aged BPA-PC films (0, 95, and 250 hrs) and extruded BPA-PC (pcfe).](image-url)
and might crack the surface of the irradiated films and hence a lower absorption at 1713 cm$^{-1}$ could be observed. UV-absorption spectra were also taken at different irradiation times and these showed the same trend as the infrared spectra: increasing absorptions at wavelengths below 400 nm with increasing irradiation times.

The absorption at 320 nm in UV-spectroscopy was ascribed to photo-Fries rearrangement products, however, oxidation products can also be responsible for these absorptions, as is shown for the thermo-oxidative degradation (see Figure 3.6). In Figure 3.8 the IR absorbance at 1713 cm$^{-1}$ against the UV-absorbance at 320 nm is plotted. This figure shows that the relation between the above mentioned UV and IR absorbance is independent of the history of the sample, which again shows that pre-ageing has no influence on the degradation mechanism. Thus the products formed by thermal treatment (oven ageing or extruding) have no influence on the oxidation rate of BPA-PC. In contrast to polyolefins, the products formed by thermal treatment do not initiate the photo-oxidation of BPA-PC.

### 3.4 Influence of oxygen on the photodegradation of BPA-PC

As the main weathering mechanism of BPA-PC is photo-oxidation, it is clear that oxygen is important during weathering of polycarbonate. Oxygen is consumed during the autocatalytic photo-oxidation reactions. However, oxygen can play a role in other ways too. It is postulated that in polyolefins, oxygen can form a charge transfer complex with the polymer, which absorbs wavelengths in the terrestrial sunlight and might lead to the initiation of the oxidation of the polyolefin. Another known possible role of oxygen is quenching of photo-chemical reactions. In this way oxygen might interfere in the photo-Fries reaction and reduce its importance. In the next subsections these possible roles of oxygen are explored.
3.4.1 Experimental

Materials

BPA-PC films with a thickness of approximately 0.02 mm were prepared by solution casting of 20 wt% polymer in DCM on a glass plate. Also 0.02 mm thick BPA-PC films with 1 wt% phenylsalicylate (Aldrich) were prepared by solution casting a 20 wt% polymer in DCM. These samples were used to get a better insight in the possibility of reactions of phenylsalicylate during irradiation at different wavelengths at different air pressures. The films were dried in a vacuum oven at 60 °C for 24 hrs, to ensure the removal of solvent traces.

Experimental set-up

The films were placed in a specially designed sample holder in a high pressure reactor which was placed in a UV-Vis spectrometer, Spectronic Genesys 5 (THERMO). To investigate if CTCs were formed, different air and argon pressures, ranging from 1 to 30 bars, were applied to the sample and absorption spectra were collected between 250-800 nm. All spectra were shifted to 0 absorbance at 360 nm.

The influence of oxygen pressure on the photo-degradation was investigated by placing PC films in the high pressure reactor with a set air pressure. In between the measurements, the UV-Vis spectrometer was irradiating the sample with a pre-set wavelength. Absorption spectra were collected between 800-250 nm after different times in the spectrophotometer.

3.4.2 Formation of Charge Transfer Complexes

As already mentioned in the introduction, charge transfer complexes between oxygen and the polymers were mentioned for polystyrene and polyolefins. Although Factor et al. already in 1980 showed that CTCs can be present in BPA-PC its importance for the initiation of the oxidation was ignored since. Rabek showed that CTC complexes in polystyrene were formed at different oxygen pressures; at higher oxygen pressures more CTCs were formed. To get a better view of the possibility of the formation of oxygen BPA-PC CTCs, in this research a comparable experiment was done with undegraded BPA-PC films. These films
were placed in a reactor vessel under different air pressures and the influence of pressure on the UV-absorption spectra was determined. As a reference, the same experiments were conducted with comparable argon pressures. Every BPA-PC film was exposed to different air pressures, however, the order of the air pressure varied at random to investigate if the history of the pressure influences the absorption behavior. The spectra were taken directly after adjusting the pressure.

In Figure 3.9 difference spectra of BPA-PC at different air and argon pressures with the spectrum of BPA-PC at atmospheric pressure are shown. The absorption values below 280 nm are so high that subtraction spectra are not reliable, and thus are not taken into account. At wavelengths above 280 nm an increased absorption can be observed when higher air (and thus oxygen) pressures are applied. This is not the case at higher argon pressures; the absorption of BPA-PC with 5 bar of argon is considerably lower than at 5 bar air pressure. So not the applied pressure, but the oxygen concentration is responsible for the increased absorption above 280 nm. The increase in UV-absorption with higher air pressure shows the existence of oxygen-BPA-PC CTCs. The maximum of the subtraction spectra is found at 284 nm, but from Figure 3.9 it is also clear that the UV-spectra tails above 300 nm and thus into the terrestrial sunlight wavelengths (> 290 nm). The formation of the CTCs is instantaneous when higher air pressures are applied.
When the air pressure is decreased this absorption disappears, showing that it is due to a reversible process.

In Figure 3.10 the absorption at 284 nm is plotted against air pressure. This figure shows a linear relationship between the pressure and the absorption at 284 nm. From this we can conclude that CTCs are indeed formed; at the highest air pressures the amounts are the highest, but even at 1 bar air pressures they exist, although the concentration is low. Even though very small amounts of CTCs with an absorption that tails into the terrestrial sunlight wavelengths (> 290 nm) can lead to radicals that initiate the photo-oxidation of BPA-PC.

### 3.4.3 Photodegradation under air pressure

To determine the role of oxygen as a possible quencher for photolytic reactions, different oxygen pressures were applied to a BPA-PC film which was irradiated in a UV/Vis spectrophotometer with different wavelengths (i.e. 250, 300, and 320 nm). During the degradation in the spectrophotometer, UV-absorption spectra were recorded. In Figure 3.11 the absorption spectra of a BPA-PC film irradiated with a wavelength of 250 nm at 20 bar air pressure normalized at 360 nm for different irradiation times are shown. In this figure the formation of a band at 320 nm, during irradiation, can be clearly observed. This band is assigned to the formation of a phenylsalicylate moiety, which is formed by the first
Photo-oxidative degradation of bisphenol A polycarbonate and its possible initiation processes

photo-Fries rearrangement, as can be expected for irradiation of BPA-PC with wavelengths below 300 nm. Irradiation of BPA-PC with 300 and 320 nm did not lead to an increased absorption at 320 nm, which confirms that the photo-Fries rearrangement only takes place at wavelengths below 300 nm.

Another notable observation is that no band at 355 nm is formed. This band is assigned to a dihydroxybenzophenone moiety, which is the second rearrangement step in the photo-Fries rearrangement. The absence of this band shows that the phenylsalicylate moiety only rearranges when the irradiating wavelengths are absorbed by the moiety. In this case, when the BPA-PC is irradiated with a wavelength of 250 nm, only the first photo-Fries rearrangement step can take place. The photo-Fries rearrangement of the phenylsalicylate moiety is not observed, probably because at this wavelength most of the light is absorbed by the BPA-PC itself and not by the phenylsalicylate moiety.

BPA-PC samples were irradiated at different air pressures. As a function of irradiation time, the absorption at 320 nm was determined. At all oxygen pressures a lineair relation was found between the absorption at 320 nm and irradiation time, see Figure 3.12. During irradiation, the absorption at 320 nm

Figure 3.11: UV-absorption spectra for a BPA-PC sample at 20 bar air pressure measured for different irradiation times with a irradiation wavelength of 250 nm.
for 1 bar air and 5 bar argon increases faster than at higher air pressures. Since the UV-absorption band at 320 nm is ascribed to phenylsalicylate moieties, from the increase of this absorption in time, the change in the concentration of phenylsalicylate (being the slope of the curves) in Figure 3.12 at different air pressures can be calculated.

The plot of the slopes of these curves against air pressures are shown in Figure 3.13. The slope of the line in this figure is negative. There are two possible explanations for this effect. The rate of formation of phenylsalicylate reduces with air pressure (and thus higher oxygen concentrations), or at higher air pressures the formed phenylsalicylate decomposes. The formation of phenylsalicylate is due to the photo-Fries reaction, and a reduction of its formation rate with oxygen pressure can be ascribed to oxygen quenching. It is also possible that phenylsalicylate is sensitive to oxygen and light, leading to its rearrange into dihydroxybenzophenone or other degradation products.

To explore the reason for the decreased formation of a band at 320 nm at higher air pressures, further investigations have been performed. A BPA-PC film was irradiated during 332 hours in a Suntester, during this irradiation an absorption at 320 nm is formed. This absorption is ascribed to phenylsalicylate moieties as well as other oxidation products. This sample was irradiated with

![Graph showing absorbance at 320 nm vs. irradiation time for different air pressures.](image)

**Figure 3.12:** UV-absorption at 320 nm for different air pressures against irradiation time with a irradiation wavelength of 250 nm.
different wavelengths, i.e. 250 nm, 300 and 320 nm. The irradiation at 250 nm was done at different air pressures. Irradiation at 250 nm leads to an increase of the absorption at 320 nm, showing that phenylsalicylate still can be formed in an BPA-PC sample pre-aged in a Suntester.

This pre-aged sample was also irradiated with a wavelength of 300 nm or 320 nm, to see if species absorbing at 320 nm (phenylsalicylate moieties or oxidation products) could react further. There is no change in absorption at 320 nm and no formation of other bands. No indication of the presence of further reactions was observed.

To get a better insight in the possibility of decomposition of phenylsalicylate with air pressure during irradiation at 250 nm, some model experiments were conducted on a thin BPA-PC film that was doped with 1 wt% phenylsalicylate. In Figure 3.14 the UV-absorption spectrum of an unirradiated sample doped with phenylsalicylate is shown. This spectrum shows that the model compound has a maximum absorption located around 315 nm. When the phenylsalicylate is sensitive to oxygen and UV-light, a decreasing absorption at 320 nm is expected with increasing air pressures, since the concentration of phenylsalicylate moieties in BPA-PC is relatively high, even considering that only the top few microns are affected by the irradiation.

**Figure 3.13:** Influence of air and argon pressure on the slope of the absorbance at 320 nm against irradiation time with irradiation with a wavelength of 250 nm.
When the doped sample was irradiated with a wavelength of 250 nm for different irradiation times at different air pressures, the band at 320 nm was still being formed independent of air pressure, showing that with increasing air pressure the rate of decomposition of phenylsalicylate is not increasing.

From the experiments with pre-aged and phenylsalicylate doped samples, it can be concluded that under the irradiation conditions applied, the phenylsalicylate moieties formed are stable and do not decompose. Thus the observed negative slope in Figure 3.13 (change in 320 nm absorption during irradiation versus air pressure) is not due to an increased decomposition of the formed phenylsalicylate moieties.

Therefore the most likely explanation of the above mentioned negative slope is a decrease in the formation rate of phenylsalicylate at higher air pressures. At higher air pressures more oxygen is present, which can prevent photolytic reactions from happening. In the present case, the photolytic photo-Fries rearrangement is quenched by oxygen, which might be an additional reason that the photo-Fries rearrangement reaction only plays a minor role in the photo-degradation of BPA-PC under outdoor exposure conditions.

**Figure 3.14:** UV-absorption spectrum of a solvent cast BPA-PC film doped with 1 wt% phenylsalicylate.
3.5 Conclusion

Since photo-oxidation is the dominant degradation reaction when BPA-PC is exposed to weathering conditions, the different possible sources for photo-initiation were studied.

In outdoor weathering conditions photo-Fries reactions are present. Even though the photo-Fries reactions can initiate the photo-oxidation of polypropylene, there is no indication that the photo-oxidation of BPA-PC is initiated by the photo-Fries rearrangement.

It was also shown that products formed by thermal treatment (oven-aged or extruded) have no influence on the photo-oxidation rate of BPA-PC. Thus, also the thermal oxidation products do not initiate the photo-oxidation of BPA-PC.

A more detailed investigation on the role of oxygen in the photo-degradation of BPA-PC shows that oxygen can play different roles. BPA-PC forms charge transfer complexes with oxygen in air. The absorption of these complexes tails into the terrestrial sunlight wavelengths (> 290 nm), and this absorption might lead to photo-oxidation initiating radicals.

A detailed investigation on the influence of oxygen on the photo-Fries reaction shows that oxygen is able to quench this reaction (see Figure 3.13), which might be an additional reason that the photo-Fries reaction only plays a very minor role during the photo-degradation of BPA-PC under outdoor exposure conditions.

References


Chapter 4

Influence of light intensity on the photodegradation of bisphenol A polycarbonate

In this chapter the influence of light intensity on the photodegradation rate and photodegradation mechanisms of an unstabilized BPA-PC film is described. This is studied by irradiating the BPA-PC samples with a wavelength distribution comparable to terrestrial sunlight by varying the irradiation intensities. The highest intensity used is comparable to maximum summer irradiance in Miami. The degradation rates and mechanisms are determined using IR, UV and fluorescence spectroscopy. A linear relationship between the irradiation intensity and the photodegradation rate, according to the reciprocity law, is found. It is also shown that the irradiation intensity has no influence on the overall degradation mechanisms.

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4.1 Introduction

Bisphenol A polycarbonate (BPA-PC) has excellent properties, such as high transparency and toughness; therefore it is used in many markets, ranging from architectural to automotive, digital recording, electrical, electronic and safety. One of the disadvantages of this polymer is that it degrades under the influence of sunlight, humidity and oxygen in outdoor applications. As a result, over the past decades much research has been done to get a better understanding of the degradation mechanism of BPA-PC. To be able to determine the mechanisms that are responsible for the degradation in outdoor applications, these studies should preferably be done in environmental conditions. However, outdoor testing times are often too time consuming to be practical. That is why the stability of polymers is mainly determined by using accelerated testing devices.

For BPA-PC it is known that the degradation mechanism depends on the wavelengths used to irradiate the polymer. As a result, to simulate outdoor ageing, accelerated degradation experiments are mostly done with a light source, like xenon lamps filtered by boro/boro silicate, that mimics the wavelengths present in terrestrial sunlight. Other light sources or filter systems are also being used. Another difference between outdoor and accelerated degradation is the intensity of the light; to decrease the exposure time in accelerated tests, the light intensity is often increased to higher levels than the average values present in outdoor conditions and dark periods are left out. To be able to translate results from accelerated ageing at high intensities to outdoor conditions it is necessary to know the dependence of the degradation mechanism and degradation rate on the light intensity.

Over the last decades investigations of the effect of irradiation intensity on the degradation rate of many polymeric materials have been performed. The relation between degradation rate and intensity normally obeys Schwarzschild’s law, which is given by Equation 4.1,

\[ k = A I^p \]  

where \( k \) is the reaction rate, \( A \) is a proportionality constant, \( I \) is intensity, and \( p \) is the Schwarzschild coefficient. The \( p \)-coefficient is material dependent and in some cases even irradiance range dependent. When \( p = 1 \), Schwarzschild’s law
becomes the reciprocity law. This law states that there is an inverse relationship between the intensity and duration of light that determines exposure of a light-sensitive material. For most (unstabilized, stabilized or pigmented) polymeric systems studied, the p-coefficient ranges between 0.5 and 1.0.\textsuperscript{9}

Chin et al.\textsuperscript{10} reported on a p-coefficient of 1 for a non-pigmented, unstabilized acrylic-melamine coating. The reciprocity law was verified for different photodegradation parameters, such as chain scission, oxidation and mass loss.

Christensen et al.\textsuperscript{11} found a p-coefficient of 0.5 for the rate of carbon dioxide generation in pigmented acrylic film. They suggested that the square root of the intensity dependence is a result of the concentration of radicals formed that lead to carbon dioxide, which would be the degradation rate determining step.

According to Kollmann and Wood et al.\textsuperscript{12} for unstabilized polypropylene the oxidation rate was nearly proportional to the square root of the irradiation intensity. These results were also found by Philippart et al.,\textsuperscript{13} who studied the influence of light intensity on the photo-oxidation of stabilized polypropylene by using a non-xenon light source. They found that the relative distribution of the oxidation photo-products was not dependent on the conditions of irradiation, and that the steady state rate of oxidation varies with the square root of the light intensity.

For high density polyethylene stabilized with phenolic antioxidants a coefficient of approximately 1 was found.\textsuperscript{14} This value is twice as high as expected, which was explained by the presence of an antioxidant in the HDPE. Moreover, the rate of light-induced dehydrochlorination of poly(vinyl chloride) (PVC) is also reported to have a p-coefficient of approximately 1.\textsuperscript{15}

In addition, most reciprocity experiments were conducted on commercial, stabilized or pigmented materials.\textsuperscript{9} This is also the case for BPA-PC. Jorgensen et al.\textsuperscript{16} found that a UV-stabilized PC sample follows a strict reciprocity even up to 100 times the solar intensity levels when irradiated with a wavelength distribution 290-475 nm. More recently Pickett et al.\textsuperscript{17} reported on the effect of irradiation conditions on the degradation of different pigmented polycarbonates. Using a Xenon arc weathering device filtered with CIRA/Sodalime filter combinations to irradiate BPA-PC and its blends, different irradiation intensities were obtained by using different quartz neutral density filter combinations. Possible disadvantages of using density filters are that the spectral distribution can vary and that
the filters themselves can be unstable upon prolonged exposures. Although quartz neutral density filters are not expected to affect the spectral distribution, instability of neutral density filters upon prolonged exposures has been reported.\textsuperscript{17}

For BPA-PC it was shown that its degradation mechanism depends on the irradiation wavelengths, so that it can degrade by different mechanisms.\textsuperscript{18–21} Pickett and Webb et al.\textsuperscript{6} showed that two different filter systems (boro/boro and CIRA/Sodalime) have different yellowing index behavior during exposures. Due to the influence of irradiation wavelengths on the photodegradation mechanism of BPA-PC, the wavelength cut-off is very important since the photo-Fries rearrangement reaction takes place at wavelengths below 300 nm.\textsuperscript{4,5,21} For systems, like BPA-PC, in which different photodegradation mechanisms play a role, a change in intensity might result in a change in relative importance of these mechanisms and thus in a change in the overall degradation mechanism.

In this chapter the influence of light intensity on the photodegradation mechanisms and degradation rate of an unstabilized BPA-PC film is studied by using a wavelength distribution comparable to the terrestrial spectrum. To make sure the spectral distribution for all experiments is the same, no neutral density filters are used. The samples are irradiated with an intensity up to maximum summer irradiance in Miami\textsuperscript{17} by using a flatbed accelerated testing device containing filtered xenon lamps. In this test the intensity was varied by changing the settings as well as changing the distance to the lamp so that the spectral distribution of the irradiation wavelengths was not changed. The degradation rates are determined using IR, UV, and fluorescence spectroscopy.

4.2 Experimental

4.2.1 Materials

Films of unstabilized bisphenol A polycarbonate (Lexan 145, Sabic Innovative Plastics) were prepared by solution casting. The powder, used without further purification, was dissolved in dichloromethane (20 wt\% polymer in DCM) and films were solvent cast on a glass plate and dried in a vacuum oven at 60 °C for 24 hrs. The samples had a thickness of 0.02 mm.
Influence of light intensity on the photodegradation of bisphenol A polycarbonate

Table 4.1: Irradiation intensity and scaling factors to superimpose the UV and IR spectra.

<table>
<thead>
<tr>
<th>Series</th>
<th>Place in suntester</th>
<th>Intensity [W/m²/nm at λ = 340 nm]</th>
<th>Scaling Factor UV [relative rate]</th>
<th>Scaling Factor IR [relative rate]</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2</td>
<td>high</td>
<td>0.73</td>
<td>1.8</td>
<td>2.1</td>
</tr>
<tr>
<td>H1</td>
<td>standard</td>
<td>0.49</td>
<td>1.35</td>
<td>1.4</td>
</tr>
<tr>
<td>N1</td>
<td>standard</td>
<td>0.35</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>L2</td>
<td>high</td>
<td>0.45</td>
<td>1.3</td>
<td>1.2</td>
</tr>
<tr>
<td>L1</td>
<td>standard</td>
<td>0.29</td>
<td>0.7</td>
<td>0.8</td>
</tr>
</tbody>
</table>

4.2.2 Weathering tests

The films were aged in an Atlas Suntest XXL⁺ containing xenon lamps filtered by daylight filters with a wavelength range starting from 298 nm. The chamber and black standard temperature were set to 40 and 60 °C respectively and the relative humidity was set to 50%. To determine the influence of irradiance intensity on the degradation of BPA-PC, experiments were performed at three different irradiance settings. To expose the material to two more intensities, a plateau closer to the lamp was installed in the suntester, on which the samples were degraded. Temperatures were measured at different levels in the suntest XXL⁺. The temperature in the suntester was not equally distributed; these differences (± 1-2 °C) have been neglected because of the low activation energy for photodegradation of BPA-PC (16-25 kJ/mol). All intensities were measured using a Multimeter (Cofomegra) with UV1131 (340 µm) sensor. For an overview of the used intensities, measured at λ = 340 nm, see Table 4.1.

4.2.3 Analysis Techniques

UV-Vis spectra were recorded on a Shimadzu UV-3102PC UV-Vis-NIR scanning spectrophotometer. Infrared spectra were recorded using a BioRad FTS 6000 spectrometer in the attenuated total reflection (ATR) mode for 200 scans at a resolution of 4 cm⁻¹. The BioRad Merlin software was used to analyse the spectra.
Chapter 4

A Shimadzu RF-1501 spectrofluorophotometer was used to record fluorescence spectra. The irradiated polycarbonate samples were dissolved in dichloromethane (0.001 wt% BPA-PC in DCM). Emission spectra were recorded using an excitation wavelength of 310 nm. The second-order Rayleigh scattering peak (located at 622 nm) was used to scale the recorded fluorescence spectra.

4.3 Results and Discussion

The chemical changes due to photo-oxidation were followed by infrared spectroscopy. An increased absorption at 1713 cm\(^{-1}\) was found with increasing irradiation times, see Figure 4.1a.

This absorption band at 1713 cm\(^{-1}\) is ascribed to aliphatic acids which are typical photo-oxidation products. The absorption increases with time. This effect is observed for the different irradiance intensities; as the irradiance intensity increases the absorption at 1713 cm\(^{-1}\) is increasing with irradiation time, see Figure 4.1a. To determine the influence of intensity on the degradation rate, all sets of data were visually superimposed on a reference graph by multiplying the time axis with a shift factor.

Figure 4.1: a) IR absorption at 1713 cm\(^{-1}\) of BPA-PC films irradiated with different irradiation intensities for different irradiation times. b) Data from 4.1a replotted by using the scaling factors shown in Table 4.1 to overlay series N1.
Influence of light intensity on the photodegradation of bisphenol A polycarbonate

The series N1 (with intensity of 0.35 W/m²/nm at λ = 340 nm) is used as a reference for the calculations. The scaling factors are shown in Table 4.1 and the results of the superposition can be seen in Figure 4.1b as well. For absorptions at 1713 cm⁻¹ up to absorbance values of 0.3, a good correlation was found. This suggests that no change in mechanism with intensity occurs. For higher carbonyl absorptions, the difference between the samples does not overlap that nicely. This effect is probably due to the differences in the samples themselves and differences in position within the suntester.

Besides IR-spectra, UV-Vis spectra were recorded too, see Figure 4.2. During exposure the absorption between 250 and 450 nm increases in time. The absorption at 320 nm and 355 nm are attributed in literature to phenylsalicylate and dihydroxybenzophenone respectively,⁵ which are typical photo-Fries rearrangement products. However, in Chapter 3, it was shown that these bands are probably due to oxidation.²⁵,²⁶ Although the origin of the bands at 320 and 355 nm is still under discussion, the absorption at these wavelengths increases with time, see Figure 4.3a. The absorption at 320 nm is linearly increasing with time. A higher increase in absorption at 320 nm is observed when higher intensities are used to irradiate the BPA-PC samples.

Similar as for the IR-spectra, scaling factors were determined to superimpose the data of the absorption of the UV-spectra. The scaling factors are depicted

![Figure 4.2: Normalized UV absorption spectra of BPA-PC films irradiated with 0.29 W/m²/nm at λ = 340 nm for different irradiation times.](image)
in Table 4.1 and the results of the superimposition are shown in Figure 4.3b. A good correlation is found between the different irradianced intensities, especially for the first 600 hrs. As for the IR absorption, after 600 hrs the results start to deviate.

To determine the presence of photo-Fries reactions, additional fluorescence spectroscopy was used to detect photo-products in polycarbonates during the degradation. Hoyle et al.\textsuperscript{23,25} reported on the formation of a broad phenylsalicylate band when polycarbonate had been photolyzed for short irradiation times. Emission spectra of solutions of irradiated polycarbonate films from series L2 in DCM were recorded and normalized to the second-order Rayleigh scattering peak at 622 nm, see Figure 4.4.

With increasing irradiation times an increased signal at 480 nm is observed. It was assumed that this intensity can only be caused by phenylsalicylate moieties.\textsuperscript{21} However, in the present study the increase of signal at 480 nm is only small, especially when compared to the results shown in Chapter 2 and 3, when shorter irradiation wavelengths were used to irradiate the BPA-PC films.\textsuperscript{21} So if photo-Fries products are formed at all, it is only a minute amount. Since the concentration of photo-Fries products is so small, the effect of irradiation intensity cannot be determined with reasonable accuracy.

\textbf{Figure 4.3:} a) UV absorption at 320 nm of BPA-PC films irradiated with different irradiation intensities for different irradiation times. b) Data from Figure 4.3a replotted by using the scaling factors shown in Table 4.1 to overlay series N1.
Influence of light intensity on the photodegradation of bisphenol A polycarbonate

Figure 4.4: Fluorescence spectra of PC (series L2, 0.45 W/m²/nm at λ = 340 nm) dissolved in DCM irradiated for different ageing times.

According to fluorescence spectroscopy small amounts of photo-Fries products are formed, however, this amount is so small that their contribution to the UV-absorption can be neglected.

Figure 4.5: UV absorption at 320 nm plotted against IR absorption of BPA-PC films for various irradiation times for different irradiation intensities.
Figure 4.6: Scaling factors, for UV and IR, plotted as a linear function of the irradiance intensity.

When the absorption at 320 nm for UV-spectroscopy is plotted against the IR absorption at $1713 \text{ cm}^{-1}$ an irradiation independent overlapping relation is found, see Figure 4.5. This indicates that the influence of intensity on the increase of the carbonyl absorbance and the UV-absorption at 320 nm is comparable, which might indicate that the mechanism of the degradation of BPA-PC is not changing with intensity. This is also confirmed by plotting the scaling factors for the UV- and for the IR-spectroscopy, see Figure 4.6, a linear relation is found for both techniques. When the irradiance intensity is doubled, a two times higher degradation rate is found without change in degradation mechanism. All these results are in accordance with the reciprocity law.

4.4 Conclusion

The influence of irradiance intensity on the degradation mechanism of BPA-PC was investigated by using the same wavelength spectral distribution, with different irradiation intensities. The unstabilized BPA-PC films were degraded for different ageing times at different intensity levels. The higher the irradiation intensity, the faster the increase in absorption for UV and IR spectroscopy. Combination of the absorption in UV and IR spectroscopy results in an overlapping linear relation. When the intensity is doubled, the photodegradation is doubled as well,
Influence of light intensity on the photodegradation of bisphenol A polycarbonate which is in accordance with the reciprocity law. There is no indication that the degradation mechanisms are changed when higher intensities with the same spectral distribution are used. Photo-Fries products are formed, however their presence is too small to influence a changed degradation mechanism with higher irradiation intensities. This justifies that, as long as the wavelength distribution is kept constant, high intensities can be used for accelerated weathering of BPA-PC without changing the degradation mechanism.

References

5. A. Rivaton, Recent advances in bisphenol A polycarbonate photodegradation, Polymer Degradation and Stability, 1995, 49, 163-179
When unstabilized bisphenol A polycarbonate is exposed to outdoor weathering conditions, it degrades due to irradiation, humidity and other parameters. To overcome this undesired degradation process BPA-PC can be stabilized. In this Chapter the influence of different types of stabilizers (i.e. UV-absorbers and hindered amine stabilizers) on the photodegradation of BPA-PC were compared. It is shown that the best way to stabilize polymers is to keep the harmful UV light out. Almost all stabilizers showed a decreased degradation rate, however the addition of UVAs to the polymer showed the best results. Although radical scavengers cause a decrease in degradation too. By applying a layer of UVA-stabilized BPA-PC on top of unstabilized BPA-PC the degradation mechanism was not changed. A decreased degradation rate that can be explained by a reduction of the irradiation intensity was observed.
5.1 Introduction

Because of its good physical and mechanical properties bisphenol A polycarbonate (BPA-PC) is used in many fields of applications. However, one of the main disadvantages of polycarbonate is that it degrades due to sunlight, humidity and oxygen.\textsuperscript{1} To increase the lifetime of BPA-PCs, the undesired photodegradation reactions (i.e. photo-Fries and photo-oxidation)\textsuperscript{2–5} need to be overcome.

There are several ways to stabilize polymers. One can stabilize polymers by keeping the light out, quench excited states before photochemistry occurs, or trap formed free radicals. This can be achieved by adding UV-absorbers, quenchers, radical scavengers, or synergistic combinations to the polymer respectively.\textsuperscript{6} In the next sections the most important types of stabilizers will be discussed.

5.1.1 UV-absorbers (UVAs)

To stabilize polymers against photodegradation, UV-absorbers can be used. An effective UV-stabilizer (UVA) must strongly absorb, UV light harmful for polymers, and dissipate this in a way harmless for the polymer. Another requirement for UVAs, especially when colorless, transparent polymers are used, UV-absorbers need to be colorless compounds and must not scatter light. UVAs, are photostable because their excited states can dissipate the absorbed energy as heat by a rapid internal hydrogen transfer.\textsuperscript{1,7} When photons are absorbed by the UVA, the UVA is excited to the first excited singlet state. UVAs with an intramolecular hydrogen bridge, can undergo an excited state intramolecular proton transfer (ESIPT), see Figure 1.4. The excited proton transferred product loses its energy by heat, fluorescence, or phosphorescence, to form the ground-state proton transferred product, followed by a proton shift, which leads to the UVA in the ground state.

There are different groups of UVAs.\textsuperscript{1} The most important groups are: hydroxybenzophenones, hydroxyphenyl benzotriazoles, cyanoacrylates, and the more recently-commercialized hydroxyphenyl triazines. The UV absorption of these molecules depends on their substitution as well as on the molecule type. In Figure 5.1 an overview of the hydrogen transfer mechanisms of some UVAs is given.
Photodegradation of bisphenol A polycarbonate with different types of stabilizers

\[
\begin{align*}
\text{(a) hydroxybenzophenone} & & \text{hv} & \rightarrow & \Delta \\
\text{(b) hydroxyphenylbenzotriazole} & & \text{hv} & \rightarrow & \Delta \\
\text{(c) cyanoacrylate} & & \text{hv} & \rightarrow & \Delta \\
\text{(d) hydroxyphenyl triazine} & & \text{hv} & \rightarrow & \Delta
\end{align*}
\]

Figure 5.1: Hydrogen transfer mechanism for the class of a) hydroxybenzophenones, b) hydroxyphenylbenzotriazoles, c) cyanoacrylates, and d) hydroxyphenyl triazines. 

5.1.2 Hindered Amine Light Stabilizers (HALS)

Hindered amine light stabilizers (HALS) absorb no light in the wavelengths between 300 and 400 nm, and act by catalyzing the termination step of the oxidation cycle. They can thus be active even at the surface of many polymers. This was already discussed in Chapter 1, see Figure 1.6. For polyolefins this process is very effective, however, it generally is less effective for aromatic polymers where the rate of initiation is high and the number of propagation steps in the propagation cycle of the auto-oxidation is small. HALS stabilizers can be basic. This basicity can be a concern with polycarbonate, because basic products can cause decomposition of PC upon processing and hydrolysis during weathering.
Chapter 5

It was previously shown that UVAs are more effective UV-stabilizers than HALS in stabilizing polycarbonate when accelerated tests were performed with lamps which irradiates wavelengths below (< 290 nm). In this chapter different types of stabilizers were added to bisphenol A polycarbonate and their stabilizing effect on the photodegradation rate was compared.

5.2 Experimental

Unstabilized bisphenol A polycarbonate (Lexan 145, Sabic Innovative Plastics) was used. To stabilize the BPA-PC samples, different types of stabilizers were added to a 20 wt% polymer in dichloromethane (DCM) solution. The used stabilizers are shown in Table 5.1. A concentration of 0.1 wt% of A1 relative to BPA-PC was used, the concentration of the other UV stabilizers was calculated so that the amount of functional groups was the same for each sample.

Films with a thickness of approximately 0.02 mm were prepared by solution casting the BPA-PC/stabilizer solution on a glass plate. The films were dried in a vacuum oven at 60 °C for 24 hrs.

The films were aged in an Atlas Suntest XXL+ containing xenon lamps filtered by daylight filters with a wavelength range starting from 298 nm. The spectrum of the irradiated light can be found in Figure 3.2. The chamber and black standard temperature were set to 40 and 60 °C respectively and the relative humidity was set to 50%. The irradiance level was approximately 0.49 W/m²/nm at λ = 340 nm.

UV-Vis spectra were recorded on a Shimadzu UV-3102PC UV-VIS-NIR scanning spectrophotometer. Infrared spectra were recorded using a BioRad FTS 6000 spectrometer in the attenuated total reflection (ATR) mode at 200 scans at a resolution of 4 cm⁻¹. The BioRad Merlin software was used to analyse the spectra. All spectra were normalized using the peak located at 1014 cm⁻¹.
Table 5.1: Schematic overview of stabilizers and their suppliers

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Photodegradation of bisphenol A polycarbonate with different types of stabilizers
5.3 Influence of UVAs

UV-spectra of the unirradiated BPA-PC films were measured. In Figure 5.2 the spectra of the unstabilized and stabilized BPA-PC samples are depicted. This figure shows that the UV-absorbers have no absorbance above 400 nm. This means that the samples are completely transparent and colorless. In the prepared solution of A4 in DCM, white particles were observed, showing that A4 was not completely soluble in DCM, however these particles were not observed in the final films. The absorption spectra shows that A4 was present in the BPA-PC film. The concentrations of UVA in BPA-PC were different, however the amount of functional groups was the same for each stabilized film. Comparing the absorption spectra, it can be observed that stabilizers A2, A3, and A8 have the highest absorbance at wavelengths below 400 nm, which suggests that these stabilizers will be the most effective in absorbing the harmful UV light.

The stabilized BPA-PC films were irradiated for different irradiation times and the UV absorption spectra were recorded. Some of the UV absorption spectra can be seen in Figure 5.3.

In Figure 5.3a, the absorption spectra of unstabilized BPA-PC for different irradiation times are shown. It can be seen that the absorption is increasing

**Figure 5.2:** UV absorption spectra of unirradiated stabilized BPA-PC films with different UVAs.
Figure 5.3: UV absorption spectra of a) unstabilized BPA-PC films and, BPA-PC stabilized with b) A1, c) A2, d) A4, and e) A5, as function of the irradiation time.
with irradiation times. The BPA-PC is already showing absorptions around 400 nm, indicating that the sample is beginning to show discoloration. Figure 5.3b shows that, even though A1 already has an initial absorption below 400 nm, with increasing irradiation times the absorption below 400 nm is increasing. The absorption around 400 nm is also increasing. However, this increase is limited, especially when compared to the increase found for unstabilized BPA-PC. Figures 5.3d and 5.3e show a similar behavior; increasing absorbance below 400 nm with irradiation time and limited increase above 400 nm. When BPA-PC was stabilized with A2, see Figure 5.3c, the absorption around 340 nm is decreasing whereas the absorption above 370 nm is increasing with increasing irradiation times. This indicates that the stabilizer is rearranged into another product.

To compare the effect of the added stabilizers, the yellowing index was calculated using the data from the UV absorption spectra. In Figure 5.4 the delta yellowing index is shown for all the stabilized BPA-PC samples. From this figure it can be observed that the BPA-PCs containing UV-absorbers show less yellowing than the unstabilized polycarbonate, except for sample A4. This is probably due to the unsuccessful blending in BPA-PC. Stabilizer A1 shows the least discoloration and thus the best results for stabilization against yellowing,

![Figure 5.4: Calculated yellowing index for increasing irradiation times. The lines serve as guides to the eye.](image-url)
but good results were also obtained for stabilizers A3 and A5.

To investigate the influence of UVAs on the photo-oxidation rate at the surface of the BPA-PC films, ATR infrared spectra were recorded. It was previously reported that the absorption band at 1713 cm$^{-1}$ is ascribed to aliphatic acids, which are typical oxidation products. In this study this band is used as a measure for the photo-oxidation rate. Figure 5.5 shows the infrared spectra of unirradiated BPA-PC and BPA-PC with A1. The spectra are almost similar. The absorption of A1 at 1713 cm$^{-1}$ is negligible, so that this band can be used as a measure of oxidation for the stabilized BPA-PC too. This was also observed for the other UVAs. When the samples were irradiated in the XXL$^+$ an increased absorbance at 1713 cm$^{-1}$ was observed. The delta absorbance at 1713 cm$^{-1}$ for all UVA containing samples is shown in Figure 5.6. For unstabilized BPA-PC the absorption is increasing with increasing irradiation times. When the BPA-PC was stabilized with UVAs, for the majority of the UVAs, a reduced oxidation rate was observed. However by adding A4 to BPA-PC the oxidation rate was increased. This means that the addition of A4 does not result in a good UV protection. Stabilizers A2 and A3 are showing the best results for stabilization against (surface)oxidation.

Figure 5.5: IR absorption spectra of BPA-PC, unstabilized and with A1.
In Figure 5.7a and 5.7b the yellowing index and the delta IR absorbance at 1713 cm$^{-1}$ after 870 hrs of irradiation are shown respectively. In this figure it is clear that the majority of the UVAs lead to a reduced degradation rate. As expected, stabilizer A2, A3, and A5, which have high UV absorbances below 400 nm, show good results. A1 is surprisingly effective against photodegradation. The UV absorbance of the unirradiated sample below 400 nm is not very high, especially compared to A2, however the addition of small amounts of A1 leads to a lower yellowing index and a lower carbonyl absorption.
The hydroxybenzophenone (A1) shows good results against yellowing. The hydroxyphenyl triazines (A2 and A3) show the best results for decreasing the oxidation rate, however, the differences between effectiveness of the two stabilizers is small. The benzotriazole (A5) also shows good results. The effectiveness of the cyanoacrylates (A6 and A7) is limited. A4 and A8 are not effective in stabilizing the BPA-PC against photodegradation.

When the different classes of stabilizers are compared, it is clear that the type of class is more important than the substitution of the stabilizer. In general, A1 shows the best results for stabilizing BPA-PC in the conditions used in this study.

### 5.3.1 Effect of UVA-containing top layer on BPA-PC

The effect of blending UVAs into BPA-PC films was also studied by applying a second film on top of the unstabilized BPA-PC. This second film was a stabilized BPA-PC film containing 0.1 wt% of A1 with a thickness of approximately 0.02 mm and was placed on top of the unstabilized film.

In Figure 5.8a it can be seen that the absorption at 320 nm for unstabilized BPA-PC is increasing with increasing irradiation times. When a UVA-stabilized film was placed on top of the unstabilized BPA-PC film, the increased absorption at 320 nm was dramatically reduced. The UV absorbance of the stabilized BPA-

![Figure 5.8](image-url)
PC top layer at 340 nm is 0.62, see Figure 5.2 A1. This means that at this wavelength only 24% of the incident light is transmitted to the underlying layer.

To determine the influence of this top layer on the actual degradation rate, the data for the BPA-PC with the top layer were visually superimposed on the unstabilized BPA-PC by multiplying the time axis with a shift factor. The results of this superimposition are also shown in Figure 5.8a. The shift factor was 0.25 used. This was also performed for the IR results and the same scaling factor was found. As a result of UV absorption by A1, only 24% of the light reaches the underlying BPA-PC film. The light intensity used was 0.49 W/m$^2$/nm at $\lambda = 340$ nm. As a result of the absorption, the underlying BPA-PC is only irradiated with an intensity of 0.1225 W/m$^2$/nm at $\lambda = 340$ nm. Since the photodegradation corresponds to the reciprocity law, a 75% reduction of the light intensity should cause a four times longer life time (shift factor = 0.25). This corresponds to the observed increase in life time. This means that by applying a UVA-stabilized top layer the degradation chemistry is not changed, but the overall rate of degradation is decreased.

Blending of UVAs through the bulk will increase the stability of BPA-PC, however there will always be a degradation layer formed at the surface. By blending UVAs over the whole sample, the UVAs which are located in the bulk do not contribute to a protection of the surface. Concentrating all UVA in a layer at the surface will lead to a better protection.$^{15,16}$ In this case the UV light is absorbed effectively in the regions where it is most destructive, which could lead to a better stabilization of the polymer.

### 5.4 Influence of HALS

As already discussed in the introduction, adding HALS to BPA-PC does not lead to an initial absorption in the wavelength regime of 300-400 nm. UV-absorption spectra were recorded after different irradiation times. In Figure 5.9a and 5.9b the spectra of BPA-PC containing H2 and H3 are shown.

After irradiation the absorption below 400 nm is increasing. In Figure 5.10a the increased absorption with irradiation times for the HALS-stabilized BPA-PCs is shown. In this figure it can be seen that the HALS-stabilize the BPA-PC. The samples with H3 and H4 show similar absorptions as unstabilized BPA-PC,
Photodegradation of bisphenol A polycarbonate with different types of stabilizers

![Graph](image)

**Figure 5.9:** UV absorption spectra of BPA-PC stabilized with a) H2, and b) H3, as a function of irradiation time.

However after 1000 hrs of irradiation these samples became very brittle and no absorptions could be measured. Because these types of stabilizers are not able to prevent the photo-Fries rearrangement, the decreased rate of absorption for H1 and H2 can only be attributed to the reduction of oxidation products formed.

![Graph](image)

**Figure 5.10:** a) UV absorption at 320 nm for BPA-PC stabilized with HALS, and b) IR absorption at 1713 cm$^{-1}$ for BPA-PC stabilized with HALS. The lines serve as guides to the eye.
Besides UV absorption spectra, ATR infrared spectra were recorded to measure the oxidation rate. As well as for the UVA-stabilized samples, no difference between the unirradiated BPA-PC and BPA-PC with HALS was observed. Thus this band can also be used as a measure for oxidation of the HALS-stabilized BPA-PC. With increasing irradiation times the oxidation band at 1713 cm\(^{-1}\) becomes more pronounced, see Figure 5.10b. By adding HALS stabilizers to the BPA-PC, the rate of oxidation at the surface of the film was reduced compared to an unstabilized BPA-PC film.

In Figure 5.11 an overview of the results for BPA-PC stabilized with HALS irradiated for 870 hrs is shown. Stabilizers H1 and H2 show the best results concerning yellowing and oxidation rate. The yellowing of the H3 and H4 stabilized samples is similar to that of unstabilized BPA-PC, and slightly better results were found for the oxidation rate. A major difference between H1+H2 and H3+H4 is the molecular weight of the HALS. H1 and H2 are oligomeric HALS types, whereas H3 and H4 are monomeric types. The substitution of the amine plays a minor role, the difference between the classes is more important.
5.5 Conclusion

In this chapter it is shown that by adding small amounts of UVAs and HALS to BPA-PC at room temperature, the degradation rate was decreased. When the results of the UVA- and the HALS-stabilized BPA-PC samples are compared (Figure 5.7 and 5.11) it is clear that the UV-absorbers show the best results for reducing the yellowing and the oxidation rate.

The best results for protecting BPA-PC from the harmful irradiation were obtained by adding hydroxybenzophenones or hydroxyphenyl triazines. The effectiveness of the stabilizer is more class dependent, than substitution dependent. Upon irradiating the BPA-PC stabilized with HALS, a reduced UV absorption at 320 nm is observed, which suggests that the increase at this wavelength is at least partly due to oxidation.

When a top layer with UVA was applied, the degradation rate of unstabilized BPA-PC was decreased. Due to the UV absorbance of 0.1 wt% UVA in BPA-PC, the irradiation intensity which reaches the underlying unstabilized BPA-PC sample was reduced by 76%. By superimposing the UV absorption at 320 nm, a scaling factor of 0.25 was found. Since these values correspond, it is clear that the degradation mechanism is not changed by applying a protective top layer. Only the irradiation intensity which reaches the surface of the unstabilized BPA-PC film was affected. Thus the stabilizing effect of UVAs is due to the reduction of harmful irradiation intensity.
Chapter 5

References

Chapter 6

Photostabilizing of bisphenol A polycarbonate by using UV-absorbers and self protective block copolymers

Bisphenol A polycarbonate degrades due to sunlight, humidity and oxygen. In this chapter two possible techniques to stabilize the polymer were compared, i.e. blending of UV-absorbers (UVAs) into the polymer or using block copolymers based on resorcinol polyarylates. Combination of different analysis techniques shows that the protection by UVAs is not as good as by the resorcinol polyarylate block copolymers. The block copolymer rearranges itself through a photo-Fries rearrangement within hours into a UV-absorbing top layer. Two different block compositions were studied, and the copolymer with the highest concentration of resorcinol polyarylate groups shows the best protection.

This chapter is submitted to *Polymer Degradation and Stability.*
6.1 Introduction

Polycarbonates are used in many fields of applications because of the excellent physical and mechanical properties such as high toughness and transparency. However, one of the main disadvantages of polycarbonate is that it degrades due to sunlight, humidity and oxygen.\textsuperscript{1}

In bisphenol A polycarbonate (BPA-PC) the chemistry underlying the photodegradation has been ascribed to two different mechanisms: photo-Fries rearrangement and photo-oxidation. The relative importance of these mechanisms depends on the irradiation wavelengths used.\textsuperscript{2-4} In Chapter 2 and 3, it is shown that when irradiation wavelengths which are present in terrestrial sunlight are used for degradation, the photo-oxidation reaction is the most important one and that photo-Fries rearrangements are irrelevant.\textsuperscript{5}

In order to increase the lifetime of BPA-PCs, these undesired photodegradation reactions need to be prevented. There are several ways to stabilize polycarbonates. One can stabilize polymers by keeping the light out, by quenching excited states before photochemistry occurs, or by trapping free radicals. This can be achieved by adding UV-absorbers, quenchers, radical scavengers or synergistic combinations to the polymer.\textsuperscript{6}

As already discussed in Chapter 1, the hydroxybenzophenones (HBP) are a well known group of UV-absorbers (UVAs). These absorbers are photostable because their excited states can dissipate the absorbed energy as heat by a rapid internal hydrogen transfer,\textsuperscript{1,7} see Figure 1.4.

In Chapters 1 and 5 it was also shown that UVAs mainly protect the bulk material, and are not very effective in preventing surface degradation, as shown in Figure 1.5. This means that blending of UVAs can be effective in preventing bulk degradation, but is not a very effective way to prevent degradation of thin articles or in case the degradation only appears at the surface.\textsuperscript{8} In this case high concentrations of UVAs are necessary to prevent degradation.

Another way of protecting the polymer is by applying a protective coating on the material, which can maintain the properties of the bulk by keeping the light out of the polymer. This can be achieved by applying a high concentration of UVA onto the polymer surface i.e. by co-extrusion of a thin film using the same substrate or other polymers, like PMMA, containing a high concentration of UV-
Photostabilizing of bisphenol A polycarbonate by using UV-absorbers and self protective block copolymers

absorber, or by impregnation of the polymers surface with a suitable UV-absorber solution, or by painting the polymers surface with a varnish containing UV-absorber.\textsuperscript{1} However, these techniques have some drawbacks. The most important drawback is the expensive secondary step during the production process. Another possible drawback is the adhesion between top layer and the matrix.

A relatively new way to stabilize polymers is to incorporate moieties in the polymer chain that rearrange into UV-absorbers under the influence of sunlight.\textsuperscript{9} This can be done by incorporation of (block)polymers, such as polyarylates. These polymers can undergo a photo-Fries rearrangement which gives \( \alpha \)-hydroxybenzophenones which can act as a protective, UV blocking layer to the underlying resin. These resins have very good retention of gloss and mechanical properties, however, a major drawback is that the polymer rapidly turns yellow after the photo-Fries rearrangements.\textsuperscript{9}

Recently a polyarylate block copolymer based on blocks of polymer prepared with isophthaloyl chloride, terephthaloyl chloride and resorcinol (ITR) and BPA-PC was introduced, see Figure 6.1 for the chemical structure. By incorporation of these ITR blocks in BPA-PC chains, the undesired yellowing is reduced.\textsuperscript{10,11} Pickett et al\textsuperscript{10,11} showed that the gloss is retained during long exposure times, compared to unstabilized BPA-PC. The top layer of the samples erodes very uniformly, which makes gloss retention much better than for BPA-PC.

In this chapter a comparison is made between the degradation of unstabilized BPA-PC with a hydroxybenzophenone containing BPA-PC and hydroxyl benzophenone forming copolymers (ITR-BPA-PC). Two different compositions of

![Chemical structure of ITR-PC block copolymer and the photo-Fries rearrangement.](image)

\textbf{Figure 6.1:} Chemical structure of ITR-PC block copolymer and the photo-Fries rearrangement.
Chapter 6

ITR-BPA-PC were used, one with block ratio of 20-80% and one with 90-10% ITR and BPA-PC blocks respectively. Films were prepared by solution casting and were irradiated in an accelerated testing devise that simulates outdoor conditions. Samples with different irradiation times were analysed using MALDI-TOF, UV spectroscopy, infrared spectroscopy, and chemiluminescence.

6.2 Experimental

Unstabilized bisphenol A polycarbonate (Lexan 145) and the ITR-PC block copolymers (Lexan SLX2080 and SLX9010) were supplied by Sabic Innovative Plastics. The difference between SLX2080 and SLX9010 is the ratio between ITR and BPA-PC blocks. SLX2080 and SLX9010 contain 20% and 90% ITR blocks respectively. Films with a thickness of approximately 0.02 mm were prepared by solution casting of 20wt% polymer in dichloromethane (DCM) on a glass plate. BPA-PC samples containing 1 wt% 2-hydroxy-4-n-octoxybenzophenone (Cyasorb UV-531 from Cytec) were prepared by simultaneously dissolving the polymer and the stabilizer in DCM. The films were prepared by casting the 20 wt% polymer-DCM solution on a glass plate. All samples were dried in a vacuum oven at 60 °C for 24 hrs, to ensure the removal of the solvent traces.

The films were aged in an Atlas Suntest XXL+ containing xenon lamps filtered by daylight filters with a wavelength range starting from 298 nm. The chamber and black standard temperature were set to 40 and 60 °C respectively and the relative humidity was set to 50%. The irradiance level was approximately 0.4 W/m²/nm at λ = 340 nm.

Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were recorded in the reflector mode on a Voyager-DE STR from Applied Biosystems. The films were dissolved in tetrahydrofuran (THF). The matrix used was trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile and potassium as cation. The samples were used without fractionation.

UV-Vis spectra were recorded on a Shimadzu UV-3102PC UV-VIS-NIR scanning spectrophotometer. Infrared spectra were recorded using a BioRad FTS 6000 spectrometer in the attenuated total reflection (ATR) mode and a BioRad Infrared Excalibur 3000 in the transmission mode (200 scans at a resolution of 4 cm⁻¹). The BioRad Merlin software was used to analyse the spectra. All
Photostabilizing of bisphenol A polycarbonate by using UV-absorbers and self protective block copolymers

spectra were normalized using the peak located at 1014 cm$^{-1}$.

The chemiluminescence signal was measured in a ramp experiment. Around 50 mg of the films was put on an aluminium tray and then placed inside the chemiluminescence apparatus. After 20 minutes of flushing with nitrogen, the samples were heated linearly from 25 $^\circ$C to 250 $^\circ$C in 10 minutes, and at this point the temperature was maintained.

6.3 Photodegradation of BPA-PC with UV-absorbers and BPA-PC-ITR block copolymers

In Chapter 2 it was reported that MALDI-TOF spectroscopy is an useful technique to detect side chain oxidation products as a result of photodegradation of BPA-PC in outdoor weathering conditions, and it was shown that this technique cannot be used to detect rearrangements of the polymer backbone, such as photo-Fries rearrangements. The MALDI-TOF spectra of an unirradiated and

![Figure 6.2: MALDI-tof spectra of BPA-PC, unaged and aged for 477 hrs, and SLX2080, unaged and aged for 789 hrs in suntest XXL+](image)

Figure 6.2: MALDI-tof spectra of BPA-PC, unaged and aged for 477 hrs, and SLX2080, unaged and aged for 789 hrs in suntest XXL+.
irradiated BPA-PC sample are shown in Figure 6.2. In this figure it is clearly shown that some additional peaks appear when the BPA-PC is irradiated for 477 hours. These peaks can be ascribed to oxidation products.\(^5\)

When the SLX films were irradiated for 789 hours no additional peaks are observed, see Figure 6.2. The mass distribution remains the same and there is no clear sign that oxidation products were formed. So even if photo-oxidation products are formed, their amount both the SLX films is even after 789 hours exposure much smaller than for BPA-PC exposed for 477 hours.

UV-absorption spectra of unstabilized BPA-PC (a), BPA-PC stabilized with

**Figure 6.3:** UV absorption spectra of a) pure BPA-PC, b) stabilized BPA-PC film, c) SLX2080, and d) SLX9010 for various irradiation times.
1 wt% UV-531 (b), SLX2080 (c), and SLX9010 (d) for different irradiation times, are shown in Figure 6.3. As previously reported for unstabilized BPA-PC the absorption below wavelengths of 450 nm increases with increasing irradiation times, see Figure 6.3a.\textsuperscript{5,12–14} The absorptions at 320 and 355 nm are attributed in the literature to phenylsalicylate and dihydroxybenzophenone respectively,\textsuperscript{12} which are typical photo-Fries rearrangement products. However, we recently showed that the formation of broad bands between 300 and 400 nm is probably due to oxidation products.\textsuperscript{13,14}

The BPA-PC film, stabilized with UVA, already absorbs at a wavelength of 325 nm, which is due to the hydroxybenzophenone group, see Figure 6.3b. During irradiation the absorption is increasing, however, much slower compared to unstabilized BPA-PC. From the absorption at 400 nm it is clear that the stabilized sample shows little yellowing, since the absorption does not extend above 400 nm for these irradiation times. For the ITR-BPA-PC copolymers, the absorption spectra are shown in Figures 6.3c and 6.3d. These figures show that the absorbance at 340 nm is increasing with increasing irradiation time. The formation of this band is ascribed to the rapid photo-Fries rearrangement of the ITR block. In Figure 6.4 the absorption at 340 nm for different irradiation times for the two SLX polymers is depicted. It can clearly be observed that

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{absorption.png}
\caption{UV absorption at 340 nm of SLX2080 and SLX9010 irradiated for different irradiation times.}
\end{figure}
the absorption at this wavelength is increasing enormously from the beginning. Within 50 hrs the absorption band at 340 nm for the SLX9010 sample is so high that the change in absorption at this wavelength cannot be detected with good accuracy anymore. At the same exposure time, the absorption for SLX2080 is also quite high (absorbance > 1.5), which means that more than 97% of the UV-light in that range is already absorbed.

Since the degradation of BPA-PC only occurs in the first 25 microns of the surface,\textsuperscript{15,16} the films were analysed with FT-IR in ATR mode. This technique enables the examination of the top layer of the degraded films. In Figure 6.5 the

![Graphs of IR absorption spectra](image)

**Figure 6.5:** IR absorption spectra of a) pure BPA-PC film, b) stabilized BPA-PC film, c) SLX2080, and d) SLX9010 for various irradiation times.
Photostabilizing of bisphenol A polycarbonate by using UV-absorbers and self protective block copolymers

Figure 6.6: IR absorption at 1713 cm\(^{-1}\) of unstabilized and stabilized BPA-PC for different irradiation times. The lines serve as guides to the eye.

spectra of the samples, set to 0 absorbance at 2000 cm\(^{-1}\), for different irradiation times are shown. Figures 6.5a and 6.5b show the spectra of BPA-PC, unstabilized and stabilized with UVA. In the literature, the absorption band at 1713 cm\(^{-1}\) is ascribed to aliphatic chain-acids, which are typical oxidation products. The absorption at this band is increasing with irradiation time for both samples, however the stabilized BPA-PC sample is oxidizing slower than the unstabilized sample, see Figure 6.6.

The ITR-BPA-PC block copolymers have absorptions around 1738 cm\(^{-1}\), see Figure 6.5c and 6.5d. The band at this wavenumber is much higher for the copolymer with the highest concentration of ITR blocks, so the origin of this band is due to the phthalic ester group. When the samples are irradiated, a newly formed band at 1628 cm\(^{-1}\) can be observed within hours. This band can be ascribed to the benzophenone carbonyl group, which is the rearrangement product of the resorcinol unit. When the irradiation time increases the shoulder of the 1738 cm\(^{-1}\) peak is broadening. This indicates that the top layer of the films is oxidizing. It is difficult to determine the oxidation level from the absorbance at 1713 cm\(^{-1}\) for SLX2080 and SLX9010, since their phthalic group is also absorbing in this wavenumber range. Therefore another measure for oxidation was used, i.e. the change in absorbance in the hydroxyl region (3480 cm\(^{-1}\)), see Figure 6.7a.
This figure shows that the SLX9010 sample is oxidizing very fast at the surface, however after 500 hrs it is leveling off. For the other polymers an increased absorption can still be observed after this time.

Besides in the ATR mode, FT-IR spectra were also recorded in the transmission mode. In this case it is possible to see the formation of oxidation products at the hydroxyl region in the bulk and surface. The absorption at 3480 cm$^{-1}$ subtracted with the initial absorption is shown in Figure 6.7b. This figure shows that over the whole sample, the SLX9010 and SLX2080 samples have almost similar oxidation rates, whereas the oxidation for unstabilized BPA-PC is higher.

Chemiluminescence was used to follow the photo-oxidation of the samples. In Chapter 2 it was shown that chemiluminescence can be used for the identification of how much material was oxidized. Polycarbonate films irradiated for different times showed increased Total Light Intensity (TLI) for increasing irradiation times. Even after 700 hrs, this signal is still increasing, see Figure 6.8. Chemiluminescence experiments were performed on the ITR-BPA-PC block copolymers as well. The total light intensity (TLI) shows a different behavior, see Figure 6.8, especially for the copolymer with the highest concentration of resorcinol groups (SLX9010). This sample shows a high TLI in the beginning of
Photostabilizing of bisphenol A polycarbonate by using UV-absorbers and self protective block copolymers

Figure 6.8: TLI of BPA-PC, SLX9010 and SLX2080 films irradiated for different irradiation times. The lines serve as guides to the eye.

The irradiation. After approximately 50 hrs, the TLI drops to a lower value. As the TLI is believed to be due to the decomposition of peroxides present in the sample, this means that in the beginning of the irradiation many hydroperoxides are formed. After 50 hours a maximum hydroperoxide concentration is found followed by a decrease with irradiation time. The TLI of SLX2080 does not go through a maximum, however, within a few days the increase of the TLI levels off. From this time the hydroperoxide concentration is stationary; the production and consumption of hydroperoxides are in equilibrium.

6.4 Effectiveness of the stabilization method

Two different protection techniques were used to stabilize the BPA-PC, i.e. by blending of a UVA based on hydroxybenzophenone, and by incorporating a block which rearranges into a benzophenone-like group into the main chain of BPA-PC. Comparison of the results of the unstabilized and stabilized samples, shows that the unstabilized BPA-PC is degrading faster when exposed to weathering conditions.

The UV spectra of BPA-PC with stabilizer shows that the UVA is absorbing wavelengths below 380 nm, see Figure 6.3b. With increasing irradiation times,
the absorption at 400 nm is much less, compared to unstabilized BPA-PC (Figure 6.3a). This means that the undesired yellowing of BPA-PC is decreased with the UVA. However, infrared spectroscopy shows that the top layer of a stabilized BPA-PC is still oxidizing, but the oxidation rate is decreased compared to the unstabilized sample, see Figure 6.7a.

Chemiluminescence and infrared spectroscopy in the ATR mode show that the ITR-BPA-PC block copolymers show a very high oxidation rate in the beginning of the irradiation. In Chapter 2 it was showed that the photo-Fries reaction in BPA-PC does not lead to initiation of the oxidation. However the high oxidation rate of the ITR-BPA-PC in the beginning suggests that the photo-Fries rearrangement of the ITR block leads to oxidation-initiating radicals. The SLX9010 sample oxidizes much faster in the beginning of the irradiation than the SLX2080, therefore the more ITR-blocks present, the more oxidation products are formed. However, the MALDI-TOF spectra show no sign of additional oxidation peaks after 789 hrs of irradiation, however, UV spectroscopy shows that indeed a high concentration of UV-absorbing products is formed within short irradiation times. When these UV-absorbing rearrangement products are formed, they protect the material from further oxidation. Since TLI is a measure for hydroperoxides present a decrease of oxidation rate will result in a lowering of the TLI, as observed in Figure 6.8. The effectiveness against oxidation of the formed top layer can also be observed with infrared spectroscopy, see Figure 6.7a and 6.7b, where the rate of oxidation at the surface and the whole sample is shown. Even though the SLX9010 is oxidizing fast at the surface, this is not observed for the whole sample and therefore it can be concluded that only a thin top layer is degrading which protects the material from further oxidation.

The concentration of UV-absorbing groups, formed by the photo-Fries rearrangement, is much higher than when 1 wt % of UVA is blended with the BPA-PC. To achieve the same results for stabilizing BPA-PC with UVAs, a highly concentrated protective layer should be coated on the film, however to apply this layer costly secondary steps need to be involved. The advantage of the block copolymer is as the thin layer degrades more of the underlying ITR-blocks are exposed and subsequent rearrangement reactions occur to compensate for the property loss.
6.5 Conclusion

The most dominant photodegradation reaction in BPA-PC is the side chain oxidation. In this study two possible techniques to stabilize the polymer were explored, i.e. blending of UVAs, and using BPA-PC-based block copolymers based on resorcinol polyarylates which rearranges into a UV-absorbing group. Combination of the different analysis techniques shows that the lifetime of BPA-PC is increased by blending of hydroxybenzophenone groups. However, the protection by resorcinol type block copolymers is better than by blending of a UVA. The ITR block rearranges itself within hours into a UV-absorbing top layer. This rearrangement is accompanied by a high oxidation rate, however, MALDI-TOF, chemiluminescence, and infrared in transmission mode show that when this absorbing layer is formed, the oxidation rate of the whole sample is decreased. In this top layer a high concentration of UV-absorbing groups is formed, which protects the material from UV-light, because this layer is degrading uniformly the gloss retention is maintained. However, the block copolymers show an initial yellowing, which is still increasing for the irradiation times used. The higher the concentration of ITR-blocks, the faster the top layer is formed. In case of blending UVAs through the BPA-PC sample, the concentration of UVAs is much lower, especially at the surface, causing that the ITR-BPA-PC polymers are more effective in protecting the BPA-PC from oxidation than UVAs.

References

Chapter 6


Outdoor and accelerated weathering studies of bisphenol A polycarbonate

The degradation of unstabilized bisphenol A polycarbonate (BPA-PC) exposed to accelerated and outdoor weathering are compared. The degradation mechanisms in BPA-PC films exposed to different weathering conditions were studied by UV and IR spectroscopy. The results for the accelerated and outdoor tests were correlated by using scaling factors. The scaling factor derived for the UV spectroscopy does not coincide with the scaling factor derived for the IR spectroscopy, suggesting that the degradation mechanisms for accelerated and outdoor weathering are different. This is explained by a different wavelength distribution of the spectra for the light used in the accelerated test and the terrestrial sunlight. Blending of model compounds for photo-Fries products with BPA-PC, showed that the presence of photo-Fries reaction products in outdoor weathering does not lead to an increased photo-oxidation rate. The presence of dihydroxybenzophenone in BPA-PC leads to a stabilization against photo-oxidation.
7.1 Introduction

The chemistry of degradation processes in polycarbonates has been studied extensively over the past few decades, however, what is happening under outdoor exposures is still under debate, since most of these studies were done under different (often accelerated indoor) exposure conditions.\textsuperscript{1–6}

In BPA-PC, the chemistry underlying the photodegradation has been ascribed to two different mechanisms: viz. the photo-Fries rearrangement and the photo-oxidation. The relative importance of these mechanisms depends on the used irradiation-wavelengths.\textsuperscript{4–6} The photo-Fries rearrangement reaction is more likely to occur when light with wavelengths shorter than 300 nm is used, whereas photo-oxidation reactions are more important when light of longer wavelengths (> 340 nm) is used.

BPA-PC starts to absorb wavelengths shorter than 300 nm, see Figure 3.1, implying that the photolytic photo-Fries rearrangement can only take place when the polymer is irradiated with these wavelengths. At 340 nm such absorption is not present in undegraded BPA-PC, so that the photo-degradation with longer wavelengths is only due to photo-oxidation and the photo-Fries rearrangement does not play a role.\textsuperscript{4} The wavelengths in terrestrial sunlight hardly shows intensity in the region BPA-PC absorbs (see Figure 3.1), however wavelengths below 300 nm can be present. The intensities at these wavelengths are very limited, but depend on latitude, season and time of day.\textsuperscript{7}

In the previous chapters it was shown that small amounts of photo-Fries rearrangement products were found by exposing BPA-PC to wavelengths almost similar to the terrestrial light.\textsuperscript{8} However, the photo-oxidation reaction is the most prominent photodegradation reaction in these conditions.\textsuperscript{9}

Over the past decades many studies have been performed to find a good correlation between the accelerated and outdoor weathering tests.\textsuperscript{10,11} Because of the complex nature of the interaction of the different parameters of exposures (e.g. (UV)light, irradiation intensity, humidity, temperature differences, geographic location), there is no good correlation between accelerated and outdoor exposures at this moment.
In this chapter the influence of outdoor weathering on the degradation rate of unstabilized BPA-PC is investigated and compared to the results found for indoor accelerated weathering conditions.

7.2 Experimental

7.2.1 Materials

The BPA-PC films were prepared by dissolving unstabilized BPA-PC (Lexan 145, Sabic Innovative Plastics) in dichloromethane (20wt% polymer in DCM). The polymer solution was casted on a glass plate and films were dried in a vacuum oven at 60 °C for 24 hrs. The samples had a thickness of 0.02 mm. The films were placed in slide frames to facilitate sample handling. Blends of 1 wt% for photo-Fries products with unstabilized BPA-PC, were prepared by dissolving the model compounds in DCM. Phenylsalicylate and 2,2'-dihydroxybenzophenone were supplied by Aldrich and were used without any further purification. The chemical structures and abbreviations of these compounds can be found in Table 2.1.

7.2.2 Weathering

Accelerated weathering parameters

For the accelerated weathering tests, the BPA-PC films were exposed to simulated outdoor weathering parameters in an Atlas Suntest XXL\(^+\) containing xenon lamps filtered by daylight filters with a wavelength range starting from 298 nm, see Figure 3.2. The chamber and black standard temperature were 40 and 60 °C respectively and the relative humidity was 50%. The irradiance level was approximately 0.49 W/m\(^2\)/nm at \(\lambda = 340\ nm\), which corresponds (according to the Suntest XXL\(^+\)) to an hourly UV dosage between 300 and 400 nm of approximately 0.23 MJ/m\(^2\).
Outdoor weathering parameters

The samples were sent to France to test the weatherability according to ASTM G7-05. The outdoor exposures were unbacked, and 45° south-facing at the Atlas Sanary sur Mer Test Service Site (France). The wavelength spectrum of the terrestrial light at this testing site was measured in 2001. The results can be found in Figure 3.2. The outdoor exposure tests took place from May 2007 to July 2008. Samples were taken at different time intervals, see Table 7.1. The average maximum temperature and the average maximum black standard temperature in 2007 were 22 °C and 40 °C. One year of outdoor exposure in Sanary sur Mer corresponds to a UV dosage between 300 and 400 nm of approximately 340 MJ/m².

Table 7.1: UV dosage (MJ/m² (300-400 nm); 45° S) at Sanary sur Mer for various interval times in the exposure periods May 2007 to July 2008.

<table>
<thead>
<tr>
<th>Exposure time in months</th>
<th>0</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>14</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dose [MJ/m²]</td>
<td>0</td>
<td>78</td>
<td>173</td>
<td>224</td>
<td>423</td>
</tr>
</tbody>
</table>

7.2.3 Characterization techniques

UV-Vis spectra were recorded on a Shimadzu UV-3102PC UV-Vis-NIR scanning spectrophotometer. The absorbance at 600 nm was set to 0 for all recorded spectra. Infrared spectra were recorded using a BioRad FTS 6000 spectrometer in the attenuated total reflection (ATR) mode for 200 scans at a resolution of 4 cm⁻¹. The BioRad Merlin software was used to analyse the spectra.

7.3 Comparison of accelerated and outdoor exposure tests

The comparison between the accelerated and outdoor test, the radiant exposure dosage is used as a standard instead of the irradiation time which was used in the previous chapters. UV absorption spectra were recorded for the accelerated and
outdoor degraded BPA-PC films. The UV-absorption spectra for the accelerated experiments were already shown and discussed in Chapter 5, see Figure 5.3a. The outdoor weathered samples show similar behavior; with increasing irradiation time, the absorption below 400 nm is increasing.

In Figure 7.1a, the UV absorption at 320 nm is shown for different exposure dosages. The increased absorption at 320 nm, is attributed to the formation of oxidation products. However, in literature it is also ascribed to the formation of phenylsalicylate moieties, which are typical photo-Fries rearrangement products. Figure 7.1a shows that the absorption at 320 nm is increasing faster for the BPA-PC films irradiated in the XXL+ than for the outdoor exposed samples.

To find a correlation between the outdoor and accelerated weathering tests, the UV absorption data for the outdoor exposed samples were visually superimposed on the data for the accelerated tests, by multiplying the exposure axis with a shift factor. A shift factor of 0.67 gave the best results, see Figure 7.1b. From these results it was calculated that the increased UV-absorbance at 320 nm of 1 year exposure (341 MJ/m²) in Sanary, corresponds to approximately 230 MJ/m² irradiation in the suntest XXL+, which corresponds to 980 hrs irradiation in the accelerated conditions used.
The chemical changes due to photo-oxidation were followed by infrared in the ATR mode. For both accelerated and outdoor weathered samples an increased absorption at 1713 cm\(^{-1}\) was found with increasing irradiation times, see Figure 7.2a. This absorption band at 1713 cm\(^{-1}\) is ascribed to aliphatic acids which are typical photo-oxidation products.\(^5\) The absorption increases with time for both exposure series; as the irradiation dosage increases, the absorption at 1713 cm\(^{-1}\) increases. To find a correlation between the outdoor and accelerated weathering tests, the IR absorption data for the outdoor exposed samples were visually superimposed on the data for the accelerated test, by multiplying the dosage axis with a shift factor. A shift factor of 0.43 gave the best fit, see Figure 7.2b. From these results it was calculated that the increased IR-absorbance at 1713 cm\(^{-1}\) after 1 year exposure in Sanary (with an annual dosage of 340 MJ/m\(^2\)), corresponds to approximately 630 hrs irradiation in the suntest XXL\(^+\).

In Chapter 4, a linear relation was found for the scaling factors derived for UV absorption and IR absorption with different irradiation intensities.\(^{13}\) Therefore it was expected that for the same dosage in the accelerated and in the outdoor weathering test a comparable amount of degradation would be found. However, in this study, the scaling factors found for UV absorption (0.67) and IR absorption
(0.43) are below 1. This means that the degradation rate in the XXL+ is faster than in outdoor weathering. A possible explanation for this increased effect is the degradation temperature. During the outdoor exposure, the temperature of the samples is often much lower than the temperature in the suntest XXL+.

The influence of temperature on the degradation rate can be calculated with the following formula:\textsuperscript{14}

\[
\frac{k_2}{k_1} = \exp \left( \frac{E_a(T_2 - T_1)}{R(T_2 \times T_1)} \right)
\]

(7.1)

where \( k_1 \) and \( k_2 \) are the relative degradation rates at temperature \( T_1 \) and \( T_2 \) respectively, \( R \) the gas constant, and \( E_a \) is the activation energy. For BPA-PC the activation energy is 21 kJ/mol.\textsuperscript{14} When for the outdoor ageing temperature the daily average maximum ambient temperature (22 °C) in Sanary, and for the accelerated degradation the chamber temperature (40 °C) is taken, according to Equation 7.1 the degradation rate during accelerated ageing is 0.61 times the degradation rate outdoors. This corresponds well to the scaling factor found for the UV absorption, suggesting that the reduced outdoor degradation rate is indeed due to the difference in degradation temperatures. The difference in scaling factor for the UV and IR results suggests that the ratio of the mechanisms of degradation in the accelerated and outdoor ageing is changed.

If the IR absorption at 1713 cm\(^{-1}\) is plotted against the UV absorption at 320 nm, relations are found for the accelerated and outdoor tests, see Figure 7.3. The results from the Suntest CPS, which were previously discussed in Chapter 3, are also included in this figure. It can be observed that slopes in Figure 7.3 depend on the weathering tests.

In Chapter 3 it was shown that by irradiating the unstabilized BPA-PC films in the Suntest CPS, the ratio between the UV absorption at 320 nm and the IR absorption at 1713 cm\(^{-1}\) was higher than for ageing in the XXL+. This was ascribed to the presence of shorter wavelengths in the CPS leading to more photo-Fries rearrangement reactions. It was also shown that the formation of these photo-Fries moieties does not affect the oxidation rate.\textsuperscript{8} In Figure 7.3, the data for the CPS show the largest ratio between the UV absorption at 320 nm an the IR absorption at 1713 cm\(^{-1}\), followed by the outdoor exposed samples, and the samples exposed in the XXL+. This result suggests that for the XXL+
the formation of photo-Fries moieties is smaller than for outdoor exposures. This means that the mechanism of the photodegradation is different in the XXL⁺ compared to outdoor exposures. The most likely explanation for this effect is the difference in irradiation spectra. The irradiation wavelengths of the XXL⁺ start around 298 nm. During the indoor exposure, these wavelength spectra do not vary during the irradiation times. However, the wavelength distribution in the terrestrial sunlight varies throughout the year. The distribution depends on latitude, season, and time of day. Therefore it is possible that wavelengths shorter than 295 nm were irradiating the sample during the outdoor exposure.⁷ Although the intensity for these low wavelengths is very limited, because of their high energy, this could already result in an increased formation of photo-Fries products.

It was observed that the outdoor weathered samples after a outdoor dosage of 224 MJ/m² became very brittle. Samples with longer outdoor exposure times could not be measured with the analysis methods since the samples were already broken or were too brittle to measure the UV, and FTIR spectra. The reason for this brittleness has not been investigated, however, weathering parameters such as stresses due to varying temperatures, (acid) rain cannot be excluded.¹⁰,¹⁵
7.4 Outdoor weathering of BPA-PC with model compounds

It was already shown that small concentrations of model compounds of photo-Fries products influence the degradation rate of isotactic polypropylene, however, this effect was not observed for BPA-PC. To investigate the influence of photo-Fries rearrangements on the outdoor degradation of BPA-PC, small amounts of model compounds for photo-Fries rearrangement products were mixed with unstabilized BPA-PC. The samples were exposed to outdoor weathering in Sanary. After different exposure times the oxidation was followed using the IR absorption band at 1713 cm$^{-1}$. Most samples were very brittle after 6 months and could not be measured after longer exposure times. In Figure 7.4 the IR absorption for the different BPA-PC blends for different outdoor exposures are shown.

With increasing outdoor weathering exposures the IR absorbance at 1713 cm$^{-1}$ is linearly increasing. The oxidation rates of BPA-PC and BPA-PC with 1 wt% PS were similar. However by adding DHBP to the unstabilized BPA-PC a reduction of the oxidation rate was found, which is not that surprising because hydroxybenzophenones are well known UV stabilizers.

![Figure 7.4: IR absorption at 1713 cm$^{-1}$ of BPA-PC with and without model compounds for different outdoor exposures.](image-url)
So although the relative amount of photo-Fries products during outdoor testing is higher than when the BPA-PC was irradiated in the XXL\(^+\), the formation of photo-Fries products does not influence the degradation rate and even leads to a stabilizing effect on the photo-oxidation.

### 7.5 Conclusion

Correlations of the accelerated weathering tests and outdoor exposures in Sanary are not trivial. By comparing the dosages of the different testing techniques, scaling factors were derived for correlating the UV absorption and the IR absorption. The difference between the scaling factor for the accelerated en outdoor tests could be explained by the lower degradation temperature. It was found that 1 year of outdoor exposure in Sanary, corresponds to 980 hrs irradiation in the suntest XXL\(^+\) for correlating the UV absorption at 320 nm. In addition, for correlating the IR absorbance at 1713 cm\(^{-1}\), 1 year outdoor corresponds to 630 hrs in the suntest XXL\(^+\). These derived scaling factors do not coincide with each other, suggesting that the ratio between the photo-oxidation and the photo-Fries rearrangement is different. More photo-Fries rearrangement products are formed when the samples were irradiated by the terrestrial sunlight. Due to the presence of shorter irradiation wavelengths, which can be present in the terrestrial sunlight, the formation of photo-Fries products was promoted, however the presence of these photo-Fries rearrangement did not result in an increased photo-oxidation rate. Even though many of the variables, like temperature, rain and dark cycles, which can influence the degradation rate were not taken into account, a correlation was found.

By adding model compounds for photo-Fries rearrangement products the oxidation rate of BPA-PC in outdoor weathering was changed. By adding small amounts of DHBP, the oxidation rate of BPA-PC was reduced.
References

Chapter 7
Fotodegradatie en stabiliteit van bisphenol A polycarbonaat in buiten verouderingscondities

Polycarbonaten, en met name bisphenol A polycarbonaat (BPA-PC), worden vanwege hun hoogwaardige fysische en mechanische eigenschappen, zoals hoge slagvastheid, taaiheid en transparantie, in verschillende toepassingen gebruikt.

Een van de belangrijkste nadelen bij het gebruik van polycarbonaten in buiten toepassingen, is dat het polymeer degradeert door de invloeden van UV-licht, (lucht)vochtigheid en zuurstof. Dit ongewenste degradatie proces wordt geïnitieerd door de absorptie van zonlicht.

Ondanks dat er in het verleden veel onderzoek is gedaan naar de degradatie van BPA-PC, is er nog steeds geen eenduidigheid over wat er daadwerkelijk gebeurt tijdens het verouderingsproces van BPA-PC tijdens de buiten veroudering, omdat de meeste studies onder verschillende (en vaak versnelde) verouderingscondities zijn uitgevoerd. Het doel van het proefschrift is het verkrijgen van een beter inzicht in de degradatie chemie van BPA-PC tijdens buiten verouderingscondities. Deze kennis kan worden toegepast om BPA-PC te stabiliseren, wat (uiteindelijk) kan leiden tot stabielere polymeren zodat de levensduur en het toepassingsgebied van dit polymeer kan worden verbreed.

In de literatuur wordt de chemie die ten grondslag ligt aan de fotodegradatie beschreven als twee verschillende mechanismen: i.e. de foto-Fries omlegging en de foto-oxidatie reactie. Afhankelijk van de gebruikte bestralingsgolflengten vinden er foto-Fries omleggingen of foto-oxidatie reacties plaats. Het is bekend dat de fotolytische foto-Fries omlegging plaatsvindt bij kortere golflengtes (<300 nm), terwijl bij langere golflengtes (>300 nm) alleen foto-oxidatie reacties plaatsvinden.
vinden. De golflengtes van het zonlicht die de aarde bereiken starten rond de 300 nm. Dit impliceert dat beide degradatie reacties aanwezig kunnen zijn tijdens de buiten verouderingscondities.

Het proefschrift laat zien dat wanneer BPA-PC blootgesteld wordt aan buiten verouderingscondities, beide fotodegradatie reacties aanwezig zijn, maar dat de foto-oxidatie reactie dominant is. Om deze reactie te initiëren moet er een vrij radicaal aanwezig zijn. Zelfs een kleine vrije radicalen concentratie kan al genoeg zijn om de autokatalytische foto-oxidatie reactie te initiëren. In de literatuur staat de bron voor de initiërende radicalen ter discussie. Er werd aangenomen dat de initiërende radicalen worden gevormd tijdens de foto-Fries omlegging, echter, hiervoor was er geen overtuigend bewijs aanwezig.

In het eerste gedeelte van het proefschrift worden verschillende initiatie bronnen verkend en is onderzocht wat hun invloed is op de foto-oxidatie reactie. Door middel van verschillende spectrale analyse methoden, zoals UV-spectroscopie, FT-IR spectroscopie en fluorescentie spectroscopie, is aangetoond dat foto-Fries omleggingproducten worden gevormd wanneer BPA-PC films worden blootgesteld aan versnelde buiten verouderingscondities, weliswaar in lage concentraties. Ondanks dat ze in lage concentratie aanwezig zijn, hebben ze geen invloed op de initiatie reactie voor de foto-oxidatie. Ook de voor polyolefinen bekende photo-oxidatie initiatoren zijn onderzocht, zoals thermisch gevormde hydroperoxiden, maar ook zij beïnvloeden de degradatie snelheid van BPA-PC niet.

Het is bekend dat zuurstof verschillende invloeden kan hebben op de degradatie. De invloed van zuurstof is bepaald door BPA-PC films te degraderen bij verschillende partiële zuurstof drukken. Ladingsoverdracht complexen tussen zuurstof en het polymer zijn experimenteel aangetoond. De absorptie van deze complexen reikt tot in de golflengtes die in het aardse zonlicht voorkomen, wat kan leiden tot de vorming van foto-initiërende radicalen.

Daarnaast is het aangetoond dat wanneer BPA-PC wordt bestraald met lage golflengtes (250 nm) en bij hoge partiële zuurstof drukken, de foto-Fries omleggingreacties onderdrukt worden.

In het tweede gedeelte van het proefschrift wordt beschreven dat kleine fluctuaties van de laagste golflengtes van het (artificiële) zonlicht (startend van 290 tot 300 nm) invloed hebben op de verhouding tussen de foto-Fries
en de foto-oxidatie reacties. Ook is er een lineair verband gevonden tussen de bestralingsintensiteit en de foto-degradatie snelheid. Zo lang de golflengte distributie van het artificiële licht gehandhaafd wordt, heeft de intensiteit geen effect op de verhouding tussen de degradatie mechanismen.

Er zijn verschillende manieren om polymeren te stabiliseren. In het derde gedeelte van dit proefschrift worden verschillende stabilisatie methodes toegepast en hun invloed op de degradatie bestudeerd. De beste manier om BPA-PC te stabiliseren tegen fotodegradatie is door het licht te absorberen door middel van het mengen van UV-absorberende verbindingen of het aanbrengen van een beschermende toplaag. Een vergelijking wordt gemaakt tussen de werking van conventionele stabilisatoren en blok copolymeren gebaseerd op resorcinol polyaryaalat, welke zichzelf kunnen herrangschikken in een beschermende toplaag. De toevoeging van “hinderend amine light” stabilisatoren heeft geen groot effect op de degradatie snelheid. De beste resultaten voor BPA-PC stabilisatie worden verkregen wanneer het (schadelijke) UV-licht wordt geabsorbeerd door hydroxybenzophenones; met name wanneer een hoge concentratie van UV absorberende substanties wordt gepositioneerd op de toplaag van het polymer, i.e. door middel van een tweede toplaag of bij een copolymeer bestaande uit resorcinol polyaryaalat blokken.

In het laatste gedeelte van dit proefschrift wordt een vergelijking gemaakt tussen de versnelde en de buiten verouderingstesten. Doordat de golflengte distributie van het licht gebruikt in de versnelde testen en het zonlicht variëren, worden er verschillende ratios tussen de foto-Fries en de foto-oxidatie reacties gevonden.

Concluderend, vanwege de grote gevoeligheid van BPA-PC voor de lage golflengtes die in het zonlicht kunnen plaatsvinden, is het moeilijk om een goede voorspelling voor de levensduur voor een BPA-PC toepassing in buiten verouderingscondities te maken met versnelde testen, omdat deze testen andere (constante) golflengte verdelingen hebben dan het zonlicht en dus ook tot andere verhoudingen tussen de foto-Fries en de foto-oxidatie reacties kunnen leiden.
Marjolein Diepens was born on 14th of October in Tilburg. In 1998 she obtained her “VWO” diploma at the Theresia Lyceum, a grammar school in Tilburg, and decided to continue her education at the department of Chemical Engineering and Chemistry at Eindhoven University of Technology. After an internship at the university on the topic toughness enhancement in amorphous polymer systems, and an internship of 3 months at the Australian Nuclear Science and Technology Organisation (Sydney, Australia) in the field of sheer induced crystallization of isotactic polypropylene, she started her MSc project in August 2003 within the Polymer Technology group of prof.dr. Piet Lemstra. The title of the master thesis was “Influence of in-situ formed nanosilica on the crystallization of isotactic polypropylene”. She graduated in June 2004 and decided to continue working as a PhD-student within the same group under supervision of prof.dr. Piet Lemstra and dr. Pieter Gijsman. During her PhD study, she successfully completed all the modules of the postgraduate course Register Polymer Science (RPK) of the National Dutch Research School PTN. The modules comprise; A - Polymer Chemistry, B - Polymer Physics, C - Polymer Properties, D - Rheology, E - Polymer Processing, and π - Polymer Innovations. The most important results of her PhD work are reported in this thesis.
List of Publications

- M. Diepens, P. Gijsman, *Photodegradation of bisphenol A polycarbonate with different types of stabilizers*, In Preparation

Parts of this work have been presented at the following conferences:

- Polymer Modification, Degradation and Stabilisation (MoDeSt2006), San Sebastián, Spain, 10th-14th September 2006.
- National ACS meeting, Chicago, United States of America, 25th-30th March, 2007
- Dutch Polymer Days, Lunteren, the Netherlands, 4th-5th February, 2008
- Polymer Modification, Degradation and Stabilisation (MoDeSt2008), Liège, Belgium, 7th-11th September, 2008
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Marjolein