

**ENVIRONMENTAL ASSESSMENT  
FOR BISPHENOL-A AND POLYCARBONATE**

by

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## **Abstract**

Polycarbonate products have been used extensively world wide for decades because they are lightweight, shatter-resistant and considered to be safe. Polycarbonate is a thermoplastic that is used to make compact discs, phones, lenses, and food contact products such as water bottles, baby bottles and food storage containers.

For more than half century, there has been interest in polycarbonate (PC) products and the monomer bisphenol-A (BPA) because BPA can leach from food polycarbonate containers. The environmental fate for both chemicals in air, water and soil is of interest, also. To understand the fate of polycarbonate, its main degradation pathways, main degradation mechanisms and main products are reviewed. These pathways are thermal degradation, photo-degradation and hydrolysis under different conditions. Furthermore, key topics like PC degradation kinetics and PC chemical resistance are part of this comprehensive discussion.

The biodegradation of BPA has been thoroughly studied. About twelve lab methods for environmental fate are summarized and reviewed to understand the “big picture” for BPA degradation. This includes screening tests, which assess the ready and inherent degradability, to simulation tests for surface waters, soils and wastewater treatment systems. The testing of all methods is examined under conditions close to the real environment fate. Furthermore, the fate distribution for BPA based on the Equilibrium Criterion Model (EQC) model is reviewed.

Extensive research on polycarbonate and BPA has been conducted in the last fifty years. During this time, both chemicals have been studied and tested by industry and government agencies. The pharmacological test results from major studies indicate that consumer exposure to BPA at concentrations normally experienced in daily living does

not pose a risk to human health. On the other hand, minor toxicological studies indicate potential risks to human health. Research on health and safety are continuing.

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## CHAPTER 1 - INTRODUCTION

Polycarbonate is a commercial polymer that was discovered and developed by Dr. H. Schnell at Bayer Germany in 1953. Ever since, Bayer has produced the polymer resin under the name of Makrolon. Also at the same time, The General Electric Company in the USA developed a similar polycarbonate process. Bayer has been the largest polycarbonate producer in Europe and the second largest in the world after the General Electric Company (Bayer AG Plastics Business Group, 1999).

This polymer resin known as “plastic” had shown many versatile and key properties for many industrial applications. Some of the properties include transparency, breakage resistance, thermal stability, flame retardance, electrical insulation, low density, recyclability, and easy processability.

The total production capacity of all producers worldwide exceeded 2,000,000 tons in 2005 (American Plastics Council, 2006). Producers expect further growth on this capacity due to new applications arising in the market. Some of the applications are electrical (38 %), lightweight glazing (20 %), compact discs (13 %), automotive (10 %), packaging (3%), medicine (3%), spectacles (1%), optical lenses, material science applications, and other products (12%) (Bayer AG Plastics Business Group, 1999).

Polycarbonate is made by reacting Bisphenol-A with phosgene. It takes approximately one pound of Bisphenol-A and one half pound of phosgene to produce one pound of polycarbonate. The polymer chains are built by alternately connecting BPA molecules and the carbon monoxide portion of the phosgene molecule as observed in Figure 1 (All figures are at the end of each chapter).

Aromatic polycarbonates, like BPA polycarbonate, are not prepared by direct phosgenation of the aromatic compound, because this reaction is too slow to be of use

commercially. Instead of direct phosgenation, three viable processes have been developed to manufacture polycarbonate (Schnell et al., 1962; Schnell 1964).

**Transesterification Process** – BPA is reacted at elevated temperatures with diphenyl carbonate to form a polymer melt.

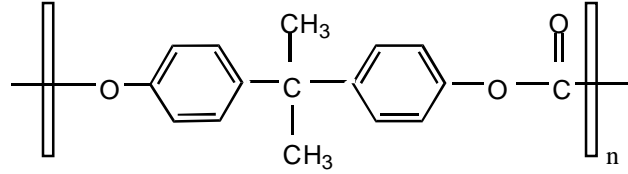
**Solvent Process** – BPA in a pyridine solution is reacted directly with phosgene.

**Interfacial Polycondensation** – Reaction of the sodium salt of BPA, in an aqueous phase, with phosgene, in an organic solvent phase, takes place (Figure 2). The reaction takes place at the phase boundary, with the polymer chains growing into the organic solvent phase. The reaction is normally run in a continuous system.

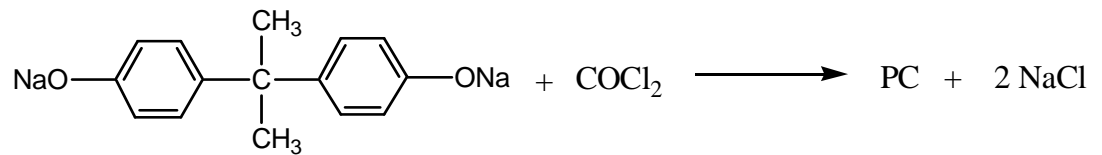
Besides BPA and phosgene, there is another type of compound that goes into the building of the polycarbonate chain called chain terminator. Chain terminator is added to cap the ends of the chains, limiting how long they can grow. By increasing chain terminator levels in the reactor, more chains will be formed. Each chain will be shorter in length or of lower molecular weight. By decreasing the levels, fewer chains will be formed, but each will be of longer length and higher molecular weight. The variations on the chain length and molecular weight can lead to different polymer applications and businesses.

Some manufacturers do not use phosgene for polycarbonate production. Phosgene is very toxic and not environmentally friendly. Instead of phosgene, they use diphenylcarbonate (DPC) which changes the nature of the polymer reaction.

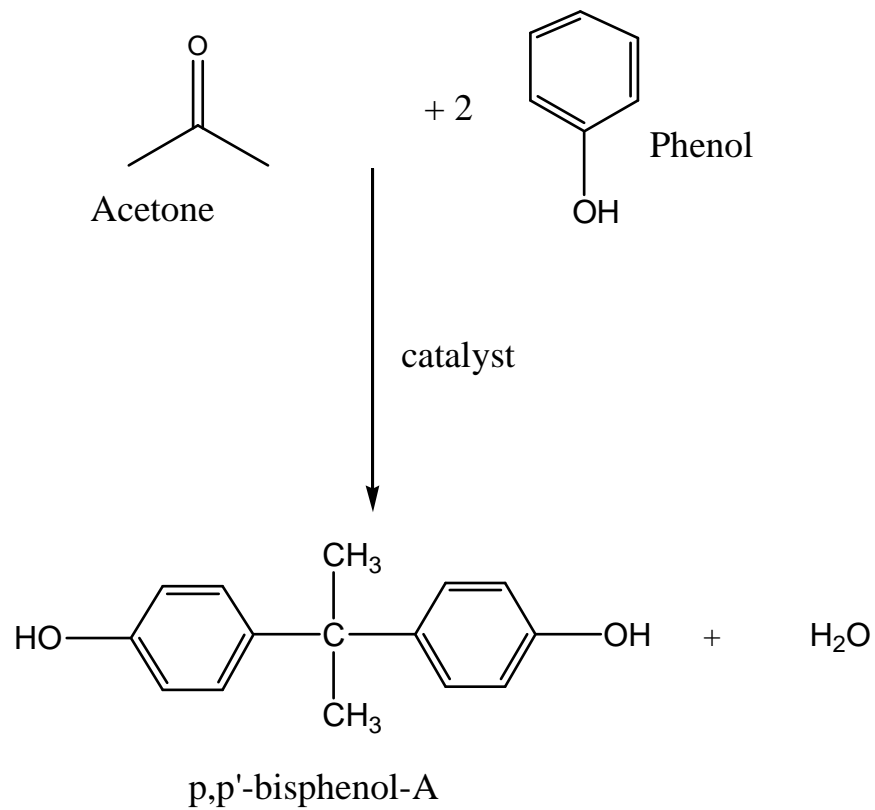
Bisphenol-A,  $C_{15}H_{16}O_2$ , is made from phenol and acetone as shown in Figure 3 (European Chemicals Bureau, 2003). In this exothermic reaction, catalyzed by acid, water is formed as a by-product.



**Figure 1. Repeating unit of BPA polycarbonate**



**Figure 2. Interfacial poly-condensation process; PC=polycarbonate**



**Figure 3. Synthesis of Bisphenol-A (BPA)**

## **CHAPTER 2 - PRELIMINARY SAFETY ASSESSMENT FOR POLYCARBONATE AND BISPHENOL-A**

The material safety data sheets for both BPA and polycarbonate chemicals are included in Appendix A and B, respectively. The MSDS information suggests that these chemicals are safe if they are used properly.

Most of the applications use the polycarbonate material with a service life of many years. In some cases, consumers come into direct contact with many products containing polycarbonate. As examples, consumers may interact with polycarbonate more intensively when the resin used in packaging bags where there is contact with food or in medical products where there is contact with medicine. There is a possible potential that the monomer Bisphenol-A can be released from the polycarbonate via hydrolysis or leaching.

In these cases, the potential exposure is subject to regulations. From the scientific literature, and government agencies, it has been shown that the amounts of Bisphenol-A (BPA) released from polycarbonate are very low (ppb levels) and may not be a threat to human health (American Plastics Council, 2006).

Environmental effects may occur with the application of polycarbonate sheeting or glazing outdoors. It is known that Bisphenol-A (BPA) is readily biodegraded in waterways and does not accumulate in any food chain. So far, the BPA concentrations, which are detected by very highly sensitive analytical methods, are far below the thresholds and toxicological limits that can cause harm to humans and animals in the environment (Bayer AG Plastics Business Group, 1999).

Bisphenol-A had been granted statutory approval in the USA (1967), Japan (1992) and Europe (1996) for polycarbonate production followed by food polycarbonate applications. Based on European requirements, the maximum amount of BPA allowed in food is 3000  $\mu\text{g}$  per kg of foodstuff. According to the US FDA, the amounts of BPA found vary from 0.2  $\mu\text{g}$  to 10  $\mu\text{g}$  per kg of foodstuff (European Chemicals Bureau, 2003).

The Environmental Protection Agency (EPA) had set the safe dose for life long daily intake of BPA by humans at 0.05 mg/kg per body weight. This amount is one thousandth of the dose that has an effect on animals (Gray and Cohen, 2004).

BPA does diffuse from polycarbonate utensils and containers. It is estimated that between 0.2  $\mu\text{g}$  and 5  $\mu\text{g}$  migrate per kg of food. These levels are about 1000 times less than the European limit of 3000  $\mu\text{g}/\text{kg}$  (Biles et al., 1997; Mountfort et al., 1997). According to these studies, the migration of residual BPA from polycarbonate containers or utensils into food is independent of residual BPA. It is believed that the cause of the increased residual BPA content is due to improper processing and coloring of polycarbonate granules.

The FDA found that the migration during long-term storage of water in polycarbonate bottles is only 0.2  $\mu\text{g}$  BPA per kg water after three weeks and only 4.7  $\mu\text{g}$  BPA per kg water after thirty-nine weeks (Biles et al., 1997). Both values obtained are well below the permitted limit. If tests conditions are exaggerated, like storing food in polycarbonate containers at 65 Celsius for weeks, the BPA migration increased to 18  $\mu\text{g}/\text{kg}$  or higher. A Japanese manufacturer group found similar BPA migration trends when polycarbonate resins were washed using strongly alkaline agents or at higher temperatures such as 80 Celsius (Polycarbonate Resin Manufacturers Group, 1998). In real life, people would never apply these conditions for storing food or washing polycarbonate containers.

On the other hand, home processes to clean baby bottles like sterilization with hypo-chlorite solution, boiling or dish-washing had no significant effect on BPA

migration into baby's food (Mountfort et al., 1997). Different researchers have conducted measurements with food standards such as whole milk, olive oil, water, alcohol and diluted acetic acid. The whole milk had indicated a BPA migration of less than 1 µg BPA per kg food (Howe and Borodinsky, 1998). The rest of the food standards showed small amounts of 3 to 5 µg BPA per kg food.

Polycarbonate resins are used in the production of medical technological equipment since the resins are biologically well tolerated. They can be easily sterilized and BPA migration is low.

Release or migration of BPA to foodstuff may occur either on contact of the foodstuff with polycarbonate resins or in long-term storage in polycarbonate containers. However, the amounts of BPA released are very low. The Scientific committee on food has concluded several times that the use of BPA is safe (SCF, 1998). There is no evidence of health hazards to humans (Böhme, 1998).

Although polycarbonate has been used regularly for a long time, there are still doubts with respect to safety and health. Recently, the city of San Francisco enacted ordinance banning bisphenol A (BPA) in children's products. The ban is being challenged in California state court on several legal grounds. The ordinance, which bans the manufacture, sale or distribution of toys and child care articles made with or containing BPA and intended for use by children under three years of age, appears to be both legally flawed and scientifically unsound.

## **CHAPTER 3 - THERMAL AND PHOTO-DEGRADATION OF POLYCARBONATE**

One of the goals for producing polycarbonate is to design more stable and durable systems that allow the reliable use of polycarbonate at the limits of its stability range. Therefore, many manufacturers have looked at the resistance of polycarbonate resins to hydrolytic, thermal, thermal oxidative and photochemical degradation. None of the mechanisms investigated lead to the formation of significant quantities of BPA.

The most important and overlooked aspect of polycarbonate stability is its vulnerability to react with water as observed in Figure 4. Hydrolysis of a polycarbonate may potentially yield BPA (monomer) and ultimately phenol under different media and temperature conditions.

This reaction is important during melt processing and in final applications when polycarbonate is exposed to water at high temperatures. The recommendations for minimizing hydrolysis are: a) removal of catalytic basic or acidic traces from the polycarbonate resin during production, b) decrease the water content of the resin to less than 0.05 % before melt processing by drying the resin, c) use of only stable and neutral stabilizers, d) employ a buffering agent to enhance hydrolytic stability.

BPA has been found to hydrolyze and leach from polycarbonate products under high heat and alkaline conditions. The amount of leaching increases as a function of use (Howdeshell et al., 2003). This research group examined whether new and used polycarbonate animal cages release slowly bioactive levels of BPA into water at room temperature and neutral pH. In their study, purified water was incubated at room temperature in new polycarbonate cages and used polycarbonate cages, as well as control (glass and used polypropylene) containers. The used polycarbonate cages were

discolored. The resulting water samples were analyzed by GC/MS and tested for estrogenic activity using a cell proliferation assay. The results indicated significant BPA amounts (estrogenic activity) were found in used polycarbonate animal cages (up to 310 µg/L). Lower levels of BPA were released from new polycarbonate cages (up to 0.3 µg/L). There was no BPA detected in water incubated in glass and used polypropylene cages. Findings suggest that laboratory animals living in polycarbonate cages are definitively exposed to BPA via leaching, with exposure reaching the higher levels in old cages.

The results are in agreement with the findings of a Japanese research group, who indicated an increased rate of leaching from polycarbonate plastic with age. Furthermore, there were higher levels of BPA migrating from the used polycarbonate cages than from the new polycarbonate cages. The used polycarbonate cages were under normal room temperature and undisturbed conditions using neutral pH water (Takao et al., 1999).

Another Japanese group from the National Institute of Environmental Studies had quantified the leaching of bisphenol-A into water. In their study, various samples of plastic waste were cut into small pieces, soaked in water for two weeks at room temperature in the dark, and the concentration of bisphenol-A in the water analyzed by gas chromatography/ mass spectrometry (GC/MS). The amount of BPA leached from the plastic wastes varied from non-detectable to 139 µg/g. The detection limit was 2 ng/g when 100 g of plastic waste was used for sample preparation (Yamamoto and Yasuhara, 1999).

As mentioned earlier, polycarbonate is a strong thermoplastic and copolymer that has ester linkages. Its strength comes from the rigid aromatic rings, and its flexibility is due to the ester C—O single bonds, which can rotate freely. Polycarbonate as an ester is susceptible to hydrolysis and base-catalyzed hydrolysis, at very high temperatures, while it remains resistant to hydrolysis at ambient temperatures (Thompson and Klemchuk, 1996). This applies to the new polycarbonate cages but as polycarbonate cages get older,



there will be discoloration and cracking. Therefore, chances of an increase in leaching of free BPA into water at room temperature are greater for older containers.

The solubility of liquid water in polycarbonate is low but vapor can dissolve in it when polycarbonate is immersed in hot water. After cooling polycarbonate surfaces exposed to hot water, the surfaces look hazy because small water droplets have formed and condensed within the matrix. There were no mechanical defects found when polycarbonate was immersed in water at room temperature for one year but a 16% material shrinkage is observed after 30 days at 40 Celsius, a 55% material shrinkage is observed after 30 days at 60 Celsius and total “tensile breakdown” is observed after 14 days at 80 Celsius (Ram et al., 1985).

Therefore, BPA can be formed from polycarbonate as a breakdown product when the polymer is treated under specific conditions, or it can leach as un-reacted monomer via the surface area increase of the cage interior as a result of wear.

The researchers found a decrease in the amount of BPA that was released from the used polycarbonate cages when examined multiple times in three leaching experiments. The first leaching experiment was run on cages that had been recently cleaned in the industrial sanitizing cage washer and then stored, thus allowing for the accumulation of free BPA on the surface of the cages. They used water rinse to remove the free BPA on the surface of the cages before continuing with the other two leaching experiments. Therefore, the initial amount of free BPA available to leach into the water was reduced in the second and third replicates relative to the first experiment with the used polycarbonate cages. The amount of BPA obtained after the first rinse for the first leaching experiment is the most representative one.

The most likely application of polycarbonate that can result in hydrolysis of the polymer is thought to be use in solid and multi-wall sheet in outdoor applications. Here weathering effects may lead to the breakdown of the polymer.

Because of the high aromatic structure, polycarbonate is one of the most stable polymers found in the market (Factor, 1996). Factor (1996) reports thermo-gravimetric weight loss only above 550 Celsius. In industry, polycarbonates are melt processed well below 550 Celsius. The actual melting temperature is between 230 and 340 Celsius. Heating polycarbonate above 340 Celsius can lead to molecular weight loss and gelation reactions. The gelation reaction occurs when diphenyl-carbonate (DPC) is used in manufacturing and yields o-phenoxybenzoid acids and esters.

The thermolysis of diphenyl-carbonate (DPC) at 360 Celsius can lead to different side products. DPC would convert to o-phenoxybenzoic acid, which in turn yields xanthone via self condensation, diphenyl ether via decarboxilation and phenyl o-phenoxybenzoate via trans-esterification (Schnell, 1964).

Polycarbonate is stable in air at a temperature of between 120 to 125 Celsius. However, the major issue found at these temperatures is yellowing. The discoloration is measured by changes in yellowness index which is sensitive to time, temperature and oxygen absorption.

Oxygen uptake studies indicated negligible oxygen absorption in polycarbonate after more than 625 days at 100 Celsius. Moreover, it was estimated that 6 mL of Oxygen absorbs in 1 gram of polycarbonate after 83 days at 140 Celsius and 4 mL of Oxygen absorbs in 1 gram of polycarbonate after 100 hours at 200 Celsius (Factor, 1996).

Polycarbonate can be auto-oxidized via the catalysis of free BPA and sodium salts. The reaction rate can be auto-accelerating above 240 Celsius. Kinetic and spectral studies suggested that the auto-oxidation of polycarbonate yields compounds such as ketones, phenols, o-phenoxybenzoic acid and unsaturated compounds. The key color forming reactions relate to the formation and subsequent oxidation of phenolic end groups. This pathway is described in Figure 5.

In a more detailed study (Factor, 1996), a sample of polycarbonate was kept in the oven at 250 Celsius for sixteen hours after base hydrolysis. The resulting solution was analyzed by liquid chromatography, IR, NMR, UV and mass spectrometry techniques. The BPA derived compounds in solution are displayed in Figure 6.

Proposed mechanisms for these products syntheses are described in Figure 7 (Factor, 1996).

According to the researcher, several reactions can occur at the same time. This includes but not limited to:

- the oxidation of the geminal methyl groups to yield p-hydroxyacetophenone, p-hydroxybenzoic acid, water.
- the acid catalyzed rearrangement to yield salicylate products.
- hydrolysis reaction of polycarbonate to yield free BPA end groups.
- oxidative coupling of the BPA end groups to yield dimer products.
- the cracking of BPA end groups to yield isopropenylphenol (IPP) which leads to the formation of IPP-BPA complexes (Factor, 1996).

The formation of p-hydroxyacetophenone and p-hydroxybenzoic acid occurs due to a re-arrangement reaction of an initial formed methyl radical to form a more stable benzylic radical followed by reaction with oxygen.

The thermal degradation of polycarbonate under nitrogen was studied as a function of mass loss (Nam Jang and Wilkie, 2004). The gases evolved during degradation were examined in situ by infrared spectroscopy. The evolved products were collected and analyzed by infrared spectroscopy, gas chromatography and mass spectrometry. The main thermal degradation pathways follow chain scission of the isopropylidene linkage, hydrolysis/alcoholysis and rearrangement of carbonate linkages. In the case of chain scission, it was proposed that methyl scission of isopropylidene occurs first, according to the bond dissociation energies. The presence of carbonate structures, 1,1#-bis(4-hydroxyl phenyl) ethane and bisphenol A in significant amounts, supports the view that chain scission and hydrolysis/alcoholysis are the main degradation pathways for the formation of the evolved products.

In the main region of degradation (480- 560 Celsius), the small molecules that evolved in nitrogen were similar to those obtained when polycarbonate thermally degraded under oxygen (Nam Jang and Wilkie, 2005). Compared to the thermal degradation of polycarbonate under nitrogen, oxygen may lead to branching as well as radical formation via the formation of peroxides. These peroxides may lead to dissociations and combinations that can produce aldehydes, ketones and some branched compounds in the early stages of degradation (Nam Jang and Wilkie, 2004).

A detailed study on the degradation kinetics of a linear (LPC) and a branched polycarbonate (BPC) was conducted recently (Polli et al., 2005). The linear (LPC) polycarbonate is synthesized from the main BPA isomer (p,p-BPA). In this study, the investigation was carried out using thermo-gravimetric analysis. The samples were heated from 30 to 900 Celsius in nitrogen atmosphere, with three different heating rates: 5, 10 and 20°C/min. The activation energy (E) for the thermal degradation process of LPC and BPC, was estimated by the Vyazovkin model-free kinetics method (Polli et al., 2005). These values were 193 +/- 7 kJ/ mol (BPC) and 177 +/- 10 kJ/ mol (LPC).

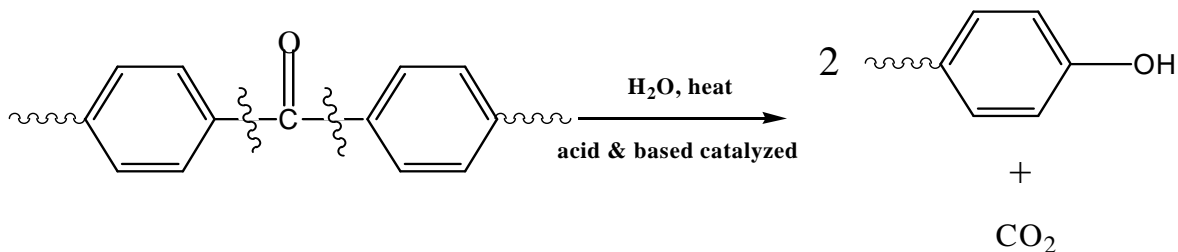
The activation energy for BPC is 10% higher than for LPC. This is in agreement with the fact that to mold some part in BPC, more temperature and energy is required to melt it, than for LPC. The LPC indicates that it starts degrading slightly over 350°C and the BPC starts degrading slightly over 400 °C. This shows that the BPC has more thermal resistance than LPC. Therefore the activation energy for BPC was higher. The thermo-gravimetric measurements provided a key link between the degradation temperature and thermal profiles for polycarbonate. The Vyazovkin model-free kinetics method (Polli et al., 2005) was also able to predict and estimate the temperature for the degradation process based on a conversion factor of 0 to 100 %. The temperature ranges from 349 Celsius to 565 Celsius as illustrated in Figure 8. For instance, for linear polycarbonate to achieve 10 % degradation, it is necessary to heat it at 433 Celsius for 10 minutes. For linear polycarbonate to achieve 90% degradation, it is necessary to heat it at 488 Celsius for ten minutes.

Photo-aging is another degradation route for polycarbonate. This happens when polycarbonate is exposed to UV light. The resin of the plastic would turn yellow and it would erode. This is a surface phenomenon and it may dig 25  $\mu\text{m}$  into the exposed surface (Factor and Chu, 1980). Depending on exposure conditions, the final byproducts are different. The three processes that lead to three different groups of byproducts are described in Figure 9. These processes are fries-photo rearrangement & fragmentation/couplings reactions, side-chain oxidation and ring oxidation. The nature of the components responsible for color formation is not all clear. The role of oxygen in the photo-aging process of polycarbonate surfaces is very important. Oxygen uptake experiments indicate the absorption of few  $\text{O}_2$  molecules thereby forming a thin monolayer on the polycarbonate surface (Factor and Chu, 1980). Therefore, most reactions occur within a thickness of 25  $\mu\text{m}$  of the polycarbonate surface.

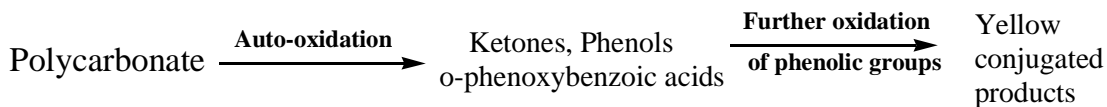
To search for key components, a research group (Factor et al., 1987) performed a reductive cleavage of four years old photo-aged polycarbonate with lithium aluminum hydride. The photo-aged process is a very complex one that involves all processes mentioned earlier. The resulting mixture was characterized via liquid chromatography/mass spectrometry techniques. About forty degraded products were found and characterized. The main degraded by-products are displayed in Figures 10 and 11. These by-products are grouped according to the most likely to take place mechanism. Most compounds are not very deeply colored but there are a few in the list such as the BPA resorcinol derivative and the ortho-coupled BPA that are formed via the reduction of very colored o-quinone and o-diphenoquinone compounds.

At the start of the photo-degradation process, the fries photo-reactions are the source for free radicals that yields photo-labile oxidation products such as hydroperoxides & aromatic ketones which would play a major role in the final autocatalytic stage polycarbonate photo-degradation.

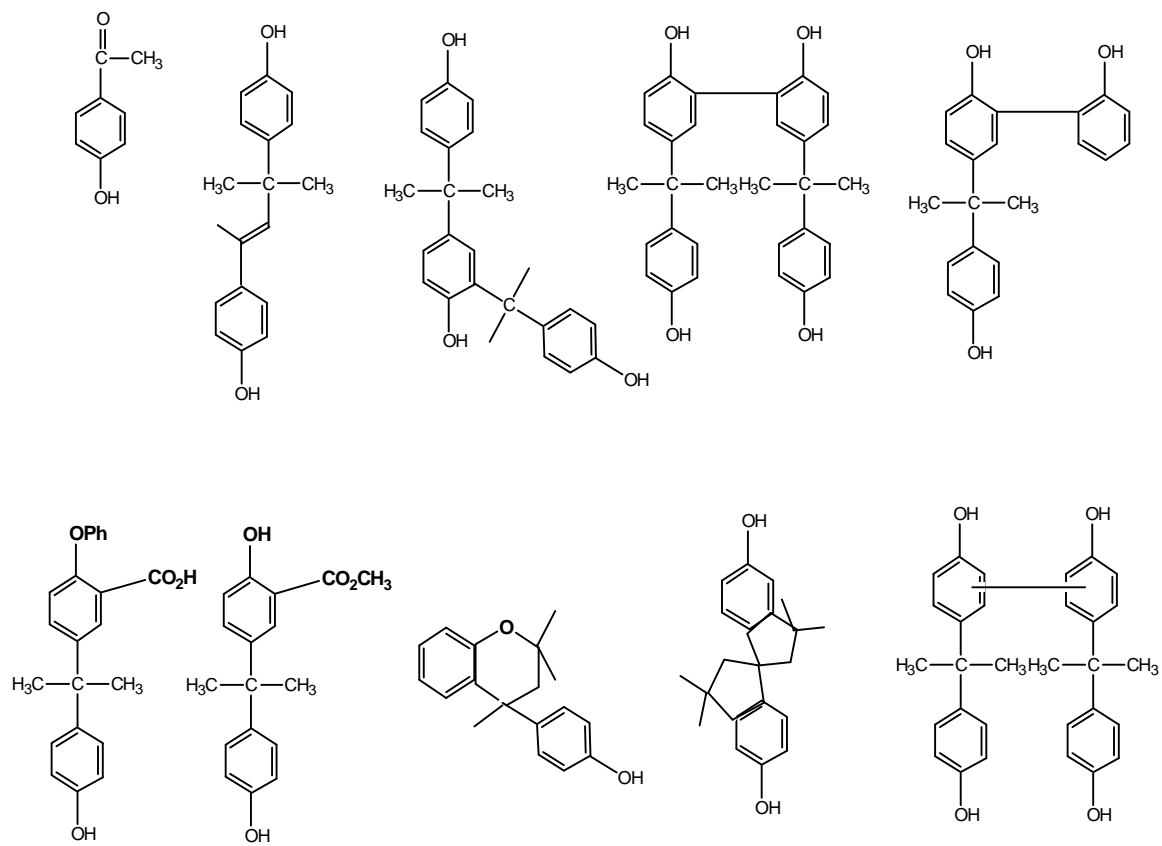
Other thoughts but not definitive (polymer durability), suggest that the photo-oxidation rather than the fries photo-reactions or direct-ring oxidation is the possible root source for polycarbonate photo-yellowing. This theory suggests that the actual compounds that are giving rise to color in polycarbonate are possibly not the compounds produced by direct photo-oxidation of the geminal dimethyl group in BPA, but rather are the products resulting from further oxidation of these compounds. For example, phenolic compounds produced by side-chain photo-oxidation may yield highly colored ring oxidation products in secondary oxidations.



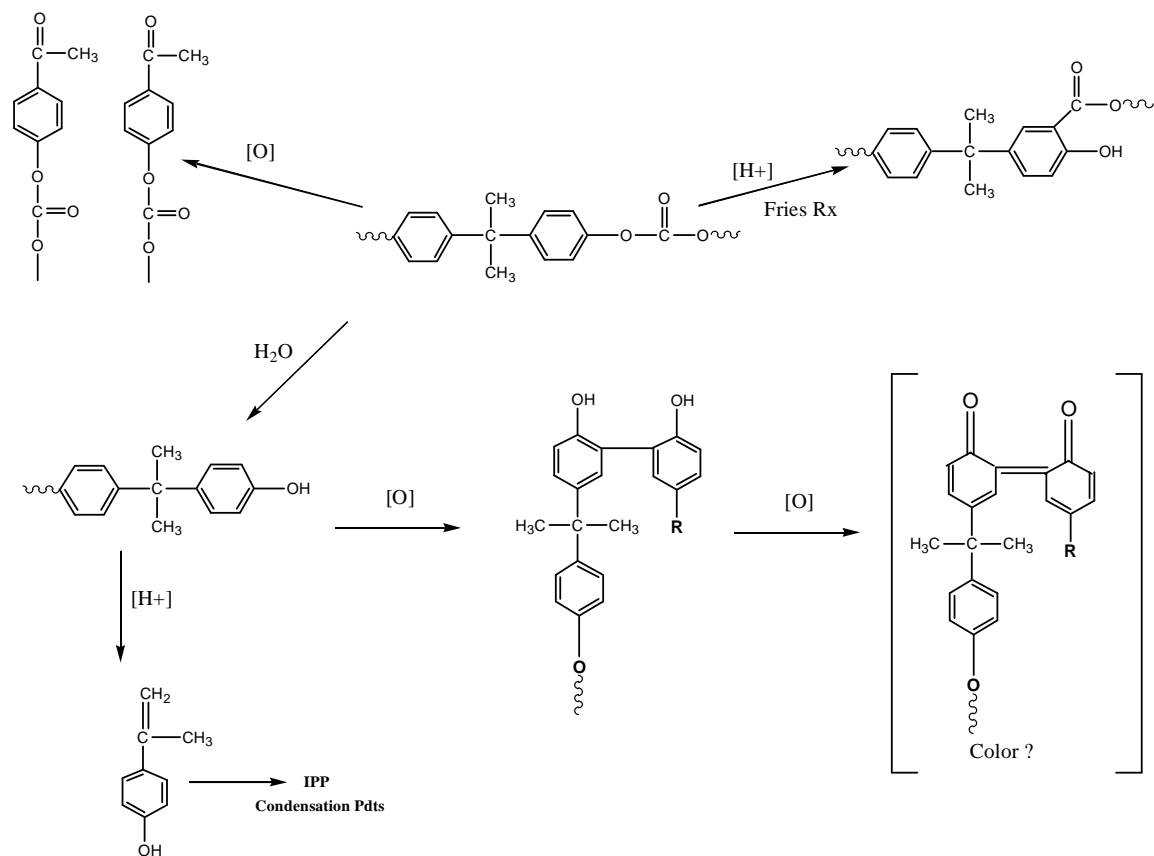
**Figure 4. Hydrolysis scheme of polycarbonate**



**Figure 5. An oxidative pathway for generating yellow conjugated products**

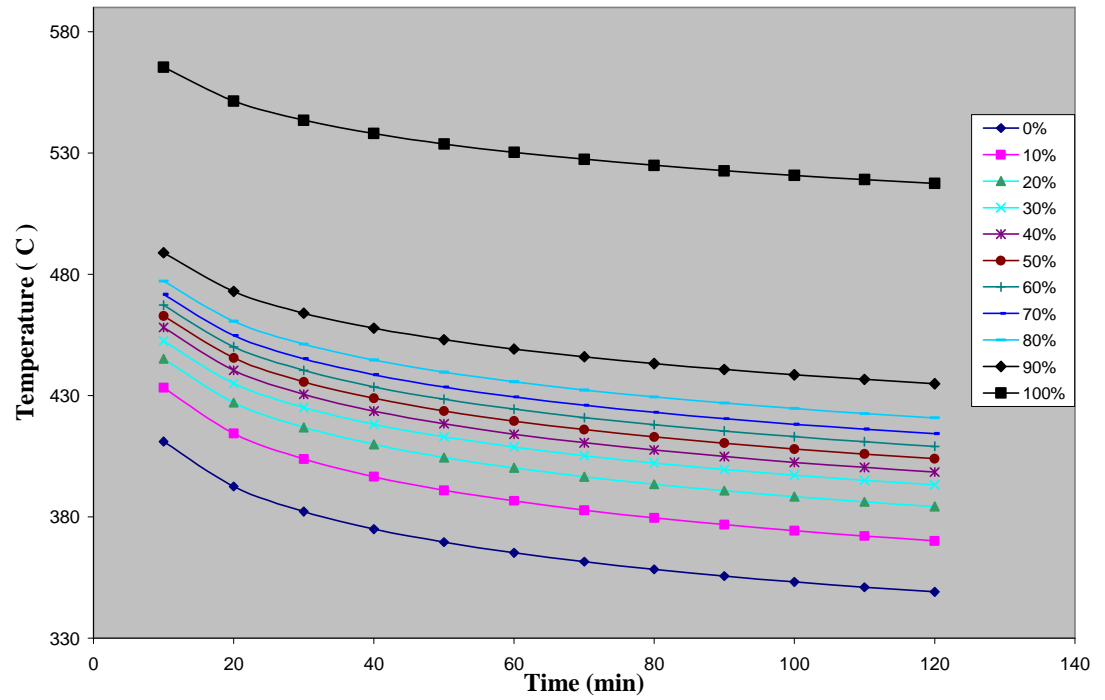


**Figure 6. Main products ( In addition to BPA) from the thermal oxidation of polycarbonate at 250 Celsius and sixteen hours (Factor, 1996).**

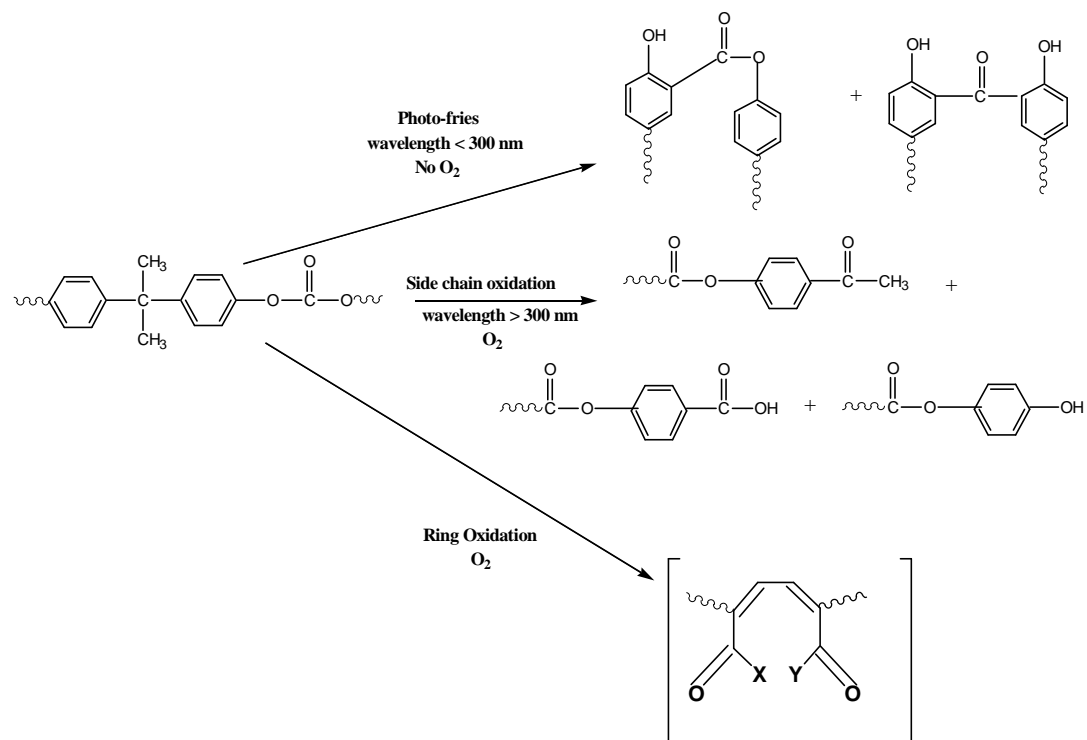


**Figure 7. Proposed mechanism of thermal oxidation of polycarbonate (Factor, 1996).**





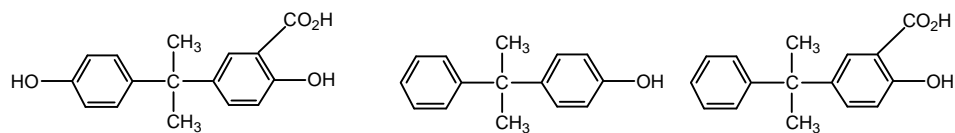
**Figure 8: Degradation curves (conversion) generated for LPC at different temperatures and times by the Vyazovkin model-free kinetics (Polli et al., 2005)**



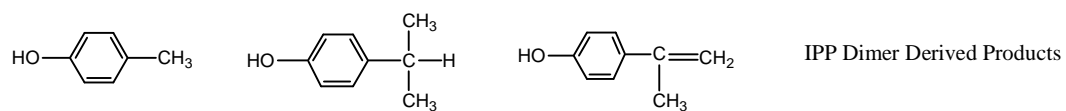
**Figure 9. Photochemical reactions of polycarbonate (Factor, 1996).**



Photo-Fries Products



Ring Attack Products



**Figure 11. Key products identified from the photo-fries and ring attack processes for aged polycarbonate (Factor et al., 1987).**

## **CHAPTER 4 - THE CHEMICAL RESISTANCE OF POLYCARBONATE**

General speaking, polycarbonate has been demonstrated to be resistant to many chemicals. But there are some chemicals that can attack polycarbonate and change its physical properties. For example, Table 1 (All tables are at the end of each chapter) displays the chemical resistance for the polycarbonate resin made by Bayer known as Makrolon at two different temperature conditions but the same exposure time. Key mechanisms that can change the properties of polycarbonate are swelling, stress cracking, and oxidative damage (Plastics Business Group, 1995).

During swelling, low-molecular, aromatic, halogenated and polar components can migrate into polycarbonate. It is expected that the damage can range from a tacky surface to complete dissolution of polycarbonate. Some examples are the dissolution of polycarbonate in mono-chlorobenzene and methylene chloride (Plastics Business Group, 1995).

In stress cracking, several chemicals in low concentrations can penetrate the surface slightly and cause a concentration gradient to develop in polycarbonate. This will reduce the bonding forces between molecules. Stresses prevailing in polycarbonate cause stress cracks to form. Stress cracks affect the appearance and physical look of molded polycarbonate products. Also they do lead to deterioration of many mechanical properties that are related to impact, flexural and tensile tests (Plastics Business Group, 1995).

Polycarbonate is relatively stable under exposure to oxidizing agents without stabilizers and at temperatures up to 100 Celsius compared to many commercial polymers. Oxidative damage can occur when polycarbonate is exposed for longer times (Plastics Business Group, 1995).

Makrolon is resistant to most of the industrial oils, greases and waxes tested over 6 days at 23 Celsius or over 6 days at 50 Celsius. The material resistance is achieved when polycarbonate products are free of low-molecular, aromatic and polar components and of other compounds that induce stress corrosion cracking. If polycarbonate is exposed to oils at high temperatures, the oils can decompose and form aggressive compounds that affect polycarbonate (Plastics Business Group, 1995).

Makrolon is not resistant to gasoline and diesel fuels. Low-molecular, aromatic hydrocarbons which are in the fuel, can cause cracking in polycarbonate surfaces that leads to stress (Plastics business group, 1995). Makrolon is resistant to many sealing compounds for 6 days at 23 Celsius and for 6 days at 50 Celsius when aggressive components, such as plasticisers or solvents, are present. This will avoid the migration out and attack of the aggressive components to polycarbonate.

Usually high-molecular weight plastics have an inert effect on Makrolon, but polycarbonate may be damaged by other compounds such as a migrating plasticiser, physical blowing agent and out-gassing amine (decomposed products from vulcanization accelerators in rubber or amines from aminoplastics). If polycarbonate is subjected to joint heat treatment with polyamide 6, the  $\epsilon$ -caprolactam compound may migrate from the polyamide to polycarbonate and cause degradation. Makrolon is resistant to a series of adhesives (Plastics Business Group, 1995).

When Makrolon is exposed to paints containing solvents, stress cracking or swelling may occur as a function of the solvent and the flash-off conditions. If solvent aggressiveness and flash-off conditions are tailored, it may be possible to develop paints that do not damage polycarbonate. The hardened paint may enhance the media compatibility. Makrolon is resistant to two-component paints if the individual components do not cause any damage in the short period between the application and the hardening of the paint. Makrolon is not resistant to turpentine or related products (Plastics Business Group, 1995).

Cleaning and washing agents are classified as products whose compositions may vary. Some of these agents may contain individual components to which Makrolon is not resistant. Makrolon is resistant to normal soaps but not to amines, ammonia, some solvent components, and a large quantity of high-gloss drying aids (Plastics Business Group, 1995).

Makrolon does not normally undergo any changes if it is contacted with foods and beverages under standard usage conditions. However, Makrolon is incompatible with a significant number of herbal and medicinal teas that incorporate etherial oils and spices. Cloves, nutmeg and pimento can damage Makrolon. It has been observed that brewed fennel tea produced from fruits may contain etherial oils in quantities that can cause polycarbonate to swell. Some cosmetics contain solvents or active ingredients that can damage Makrolon. Polycarbonate is incompatible with nail varnish remover and nail varnish (Plastics Business Group, 1995).

To improve the stress cracking resistance of polycarbonate, General Electric Advanced Materials was able to develop a polyester carbonate copolymer. This copolymer is part of their Lexan ® SLX resins which are comprised of ITR block and polycarbonate block. The ITR block is made from resorcinol and iso/terephthaloyl chloride while the PC block is polycarbonate of bisphenol-A (Li, 2005). The environmental stress cracking resistance (ESCR) performance of this polyester carbonate copolymer was studied. The ESCR is affected by a combination of material property and non-material factors. The non-material factors include molecular weight, residual stress of samples, temperature of the test, test duration, and most importantly the interacting solvent (Li, 2005).

The nature of the residual stress can reinforce or counteract the applied stress, resulting in an increase or a decrease in critical strain than that of zero residual stress sample. Annealing above the glass transition temperature can effectively reduce the effects of residual stress and orientation on ESC resistance. The ESCR does not show significant dependence on molecular weight with this copolymer in the range (20,000 - 28,000).

The copolymer was examined against thirty-eight chemicals which cover a wide range of polarity, from non-polar aliphatic hydrocarbons to highly polar formamide and water. The total solubility of the copolymer in the chemicals did not show a good correlation with ESCR performance; therefore, its application in predicting ESCR performance was not conclusive.

Lexan SLX products were generally found to perform much better than polycarbonate to environmental stress cracking.. They showed good ESCR performance against aliphatic hydrocarbons, siloxanes, aliphatic alcohols and chemicals of very high polarity and hydrogen bonding interactions such as formamide and water (Li, 2005).



**Table 1. Makrolon resistance to chemicals**

	6 days / 23 °C	6 days / 50 °C
+ resistant – non-resistant		
Acetic acid, 10 % in water	+	+
Hydrochloric acid, 10% in water	+	+
Sulphuric acid, 10 % in water	+	+
Nitric acid, 10 % in water	+	
Phosphoric acid, 1 % in water	+	–
Citric acid, 10 % in water +		
Sodium carbonate (soda), 10 % in water	+	– (70 °C)
Sodium chloride, saturated/aqueous solution	+	+
Sodium nitrate, 10 % in water	+	
Ammonium nitrate, 10 % in water/neutral	+	–
Iron(III) chloride, saturated/aqueous solution	+	+
Potassium hydroxide, 1 % in water	–	
Sodium hydroxide (caustic soda), 1 % in water	–	
Ammonia, 0.1 % in water	–	
Acetone	swells	
Benzine (free from aromatic compounds)	+	+
Benzene	swells	
Butyl acetate	–	
Chloroform	dissolves	
Dibutyl phthalate	–	
Diethyl ether	–	
Dimethylformamide	dissolves	
Diocetyl phthalate	–	
Dioxane	dissolves	
Ethanol (pure)	+	+
Ethylene glycol, 1:1 with water	+	+
Ethylene chloride	swells	
Ethyl acetate	swells	
Ethylamine	–	
Glycerin	reacts	
Isooctane (2,2,4-trimethyl pentane), pure	+	+
Isopropanol (pure)	+	
Hexane	+	+
Methanol	–	
Methylamine	reacts	
Methylene chloride	dissolves	
Methyl ethyl ketone	swells	
Ozone, 1 % in air	–	
Paraffin, paraffin oil, (Vaseline), pure/free from aromatic compounds	+	+
Perchloroethylene	–	
Perhydrol (hydrogen dioxide), 30 % in water	+	
Propane	+	+
n-propanol	– (30 °C)	
Styrene	–	
Silicone oil	+	+
Carbon tetrachloride	swells	
Tetrachloroethane	swells	
Trichloroethylene	swells	
Tricresyl phosphate	–	
Triethylene glycol	+	+
Xylene	swells	

**(Plastics Business Group, 1995)**

## **CHAPTER 5 - ENVIRONMENT FATE OF POLYCARBONATE AND ITS ASSESMENT**

There have been numerous studies that report that polycarbonate (PC) may degrade in the environment (water, air, landfills) under different special conditions. There are fewer studies reported that examine the degradation of polycarbonate in landfills.

In the past twenty years, many industries have focused their attention to plastics recycling. This is a way to improve manufacturing economics. Therefore it is meaningful to introduce recycling in the product design. Furthermore, increasing plastic consumption has lead to the accumulation of huge amounts of waste that pose serious environmental problems. Therefore, plastics waste needs to be treated.

There are several ways that polycarbonate can be recycled. These are thermal, mechanical, chemical and enzymatic recycling (Liu and Bertilsson, 1999). Thermal degradation of polycarbonate into low molecular weight compounds generally requires high temperatures and it may not lead to feasible energy balance. Chemical treatment can be rather expensive and does not apply to all polycarbonate grades. Enzymatic treatment of polycarbonate may be the environmental friendly approach, but it still needs more feasibility studies. Mechanical recycling of engineering plastics wastes such as polycarbonate can generate a key feedstock provided that degradation due to successive processing is properly characterized (Feller and Bourmaud, 2003).

A French group investigated the changes in rheological and calorimetric properties of polycarbonate (PC) as a function of eight recycling steps (Feller and Bourmaud, 2003). Dynamic mechanical analysis shows that in three point bending mode  $E'$  (storage modulus at 30 Celsius) increases from the first cycle to the fifth cycle and then remains constant up to eighth cycle. This observation may be related to molar mass decrease, certainly leading to an increase of yield strength and a decrease of the impact strength. The same stiffening is observed in tension mode in both longitudinal and

transversal directions. This suggests that macromolecular chains shortened by high shearing during injection can more easily align themselves during the process, leading to an increase of anisotropy in the sample (Feller and Bourmaud, 2003).

Differential calorimetric analyses indicate that the glass transition temperature ( $T_g$ ) of recycled polycarbonate decreases by about 3.5 Celsius after eight recycles. The glass transition temperature of polycarbonate is 150 Celsius. These observations confirm a stiffening of the material to a more brittle behavior.

Rheometry indicates that viscosity increases with decreasing temperature (from 280 Celsius to 240 Celsius) suggesting a molar mass decrease upon polycarbonate recycling. Viscosity is a measure of the resistance of a fluid to change under shear stress. The temperature dependence of liquid viscosity is the phenomenon by which liquid viscosity tends to decrease as its temperature increases. Colorimetric measurements after UV irradiation, shows a more rapid coloration for the recycled polycarbonate compared to non-recycled polycarbonate. All these results evidence a decrease of molar mass resulting from thermo-mechanical stress of polycarbonate during recycling (Feller and Bourmaud, 2003).

Polycarbonate is used in optical media storage devices as the substrate for CDs and DVDs in which silver or gold is also used as a thin reflective metal coating. Since huge amounts of CDs and DVDs are discarded in the environment, a Japanese research group had proposed to process these discarded discs with vegetable cooking oil (VCO). This approach treats the polycarbonate waste by thermal degradation and enhances the recovery of silver and gold (Mitan et al., 2007). Vegetable oils are biodegradable, nontoxic, and renewable materials.

The thermal degradation of waste DVDs, CDs and PC, at 450°C in a glass reactor gave about 40–50 wt% liquid products and 14–16 wt% gases, while 34–43 wt% remained as solid residue (Table 2). Liquid products contained mainly phenol derivatives (~75

wt%) but bisphenol (~10 wt%) and its derivatives were also present, all of them coming from fragmentation of the polycarbonate chain.

In the case of CD material, it gave liquid oil with a more complex composition than DVDs, oxygen-containing heterocyclic compounds being formed in the former case. The co-processing of PC, DVDs, and CDs with VCO enhanced the degradation of polycarbonate macromolecules by increasing the initial reaction rate. The composition of each mixture was 5 grams waste with 5 grams VCO. As we can see in Table 2, the liquid content increased to ~60 % while the solid residue contents decreased to ~ 20 %. Therefore, silver from DVDs and CDs became 2.5 times more concentrated in the solid residue compared to that of the initial materials (Mitan et al., 2007). In Table 2, the  $C_{np}$  is the average carbon number of the liquid. It varies from 12.7 to 14.2.

Table 3 displays the main compounds identified in the liquid products. The macromolecular backbone of polycarbonate may be degraded at the carbonate and bisphenol groups so that stable radicals are formed. Consequently, more than 75 wt% of the liquid product from the thermal degradation of all (PC, DVD, CD) with VCO consisted of phenol derivatives.

Polycarbonate may be degraded by repeated injection-molding cycles and by heating in air and nitrogen. Both these treatments narrow the molecular weight distribution and shift the mass fraction peak to a lower molecular weight value. The effect was more pronounced for the injection molding. The percentage by which the molecular weight was reduced increased linearly with the number of cycles (Gloekner, 1968).

BPA can leach significantly from polycarbonate (PC) tubes to water. In fact, researchers have examined the leaching from polycarbonate (PC) tubes to control water (BPA free), seawater and river water at 20 Celsius (Figure 12) and 37 Celsius (Figure 13) as a function of time (Sajiki and Yonekubo, 2003). BPA leached from PC tubes to all water samples increased with temperature and with the passage of time. The BPA

leaching velocity in seawater was the fastest among the three types of water. As we can extract from Figure 12 and Figure 13, the leaching rates of BPA from PC tubes was as follows; seawater (1.6 ng/mL/day at 20 °C and 11 ng/mL/day at 37 °C) > river water (0.2 ng/mL/day at 20 °C and 4.8 ng/mL/day at 37 °C) > control water (0.15 ng/mL/day at 20 °C and 0.8 ng/mL/day at 37 °C).

The seawater comes from the Pacific Ocean or Tokyo Bay (Japan). There was no difference in BPA concentrations leached from PC tube to either water source. The leaching velocity of BPA from PC also depends on the media pH. The more basic it is (pH 7 to 8 scale), the higher the leaching velocity. For example, the BPA leaching from PC tubes has been examined using Na<sub>2</sub>HPO<sub>4</sub> solutions. Change in the concentration of BPA leached from PC tubes to Na<sub>2</sub>HPO<sub>4</sub> solutions as a function of time is shown in Figure 14. We can observe that BPA concentration increased linearly in the three different dosed Na<sub>2</sub>HPO<sub>4</sub> solutions for 15 days. BPA leaching velocities to 1, 10, and 100 mM Na<sub>2</sub>HPO<sub>4</sub> solutions were 0.7, 7.1 and 33.6 ng/mL/day, respectively (Sajiki and Yonekubo, 2003).

Part of this study was conducted at 37 Celsius because significant amounts of BPA have been detected in commercial sera stored in plastic containers (Sajiki et al., 1999). Other research groups have found BPA leaching to blood and saliva when these human fluids are kept in PC tubes.

It has been found that BPA leaching velocities to sheep plasma and human serum from the same types of PC tubes at 37 Celsius were 41.4 ng/mL/day and 46.2 ng/mL/day, respectively (Sajiki et al., 1999). Therefore, BPA leaching velocity to seawater is about four times lower than that to sheep plasma or human serum. Based on these observations, the leaching velocity of BPA may be related to the concentration of phosphoric salts, but not to sulfuric or chloric salts. In addition, sodium ion was more effective than potassium ion in BPA leaching from PC tubes. This supports the fact that BPA leaching velocity to seawater was higher than river water since seawater contains three times more sodium.

Overall, the BPA leaching from PC tubes are attributed to a balance of minerals contained in water, in particular sodium and phosphorous.

In Chapter 3, polycarbonate hydrolysis was mentioned as one of the major ways that the polymer can be degraded. Polycarbonate was decomposed into phenol, bisphenol A, p-isopropenylphenol, and p-isopropylphenol by the reaction at 230 Celsius to 430 Celsius in water as pictured in Figure 15. These are the sub-critical and supercritical conditions. The study took place in a pressurized container. The decomposition reactions were accelerated by the addition of sodium carbonate, and the yields of identified products reached 67% even in the reaction at 300 Celsius for 24 hours (Tagaya et al., 1999).

It is well known that water under supercritical conditions is much less polar and this condition can homogenize substantial amounts of non-polar organic compounds. Water is less polar under these high temperatures because there will be less hydrogen bonding interactions among all molecules. Moreover, supercritical water is emerging as a medium that could provide the optimum conditions for a variety of chemical reactions, among them the destruction of hazardous waste (Tagaya et al., 1999). Therefore, treating polycarbonate with sub-critical and super-critical water is a technique for recycling polycarbonate.

A Xerox Corporation group had confirmed that polycarbonate undergoes molecular degradation if it is exposed to ozone. To minimize this molecular degradation, an enhanced anti-curl back coating has been developed (Yu, 2007). The coating comprises a liquid oligomer and contains little to no residual solvent. It shows improved resistance to wear and ozonolysis. It also shows increased lubricity to prevent static charge built-up. The anti-curl back coating solution was prepared to include Bisphenol A bisallyl carbonate monomer (HIRI®) which is commercially available from PPG industries. The goal is to form a coating layer of 17 micrometers on polycarbonate sheets.

To assess the extent of polycarbonate degradation as a result of ozone exposure, coated and non-coated polycarbonate sheets (8 inches x10 inches) were prepared and subjected to ozone exposure. There was a control reference in each case (Yu, 2007). The ozone was generated by turning on a charging device in an enclosed large glass tube operated under 700 micro-amperes and 8 kv conditions. The exposure test was accomplished by exposing the coated and non-coated polycarbonate sheet to ozone containing gaseous effluents generated by the charging device for 6 hours. All plastics sheets were then analyzed by gel permeation chromatography (GPC) for polycarbonate molecular weight distribution. Results indicate the extent of polycarbonate degradation due to ozone attack. The results obtained are included in Table 4.

As observed in Table 4, Mw is weight average molecular weight, Mn is number average molecular weight, and Mp is the peak molecular weight. The data (Table 4) suggested that molecular degradation of polycarbonate caused by ozone attack was very severe (lower Mw and Mp). But the degradation was minimized by using the coating (higher Mw and Mp). The control reference parameters (Mw, Mn, Mp) remain unchanged in both cases (Yu, 2007).

The levels of bisphenol A in hazardous waste landfill leachates collected in Japan in 1996 were determined by gas chromatograph/mass spectrometer (GC/MS). Bisphenol A was found in seven of ten sites investigated. All the hazardous waste landfills with leachates contaminated by bisphenol A were controlled. The concentrations of bisphenol-A ranged from 1.30  $\mu\text{g/L}$  to 17,200  $\mu\text{g/L}$  with a median concentration of 269  $\mu\text{g/L}$ . The source of bisphenol A in landfill leachates may be the waste plastics in the landfill. The leachates may be a significant source of bisphenol-A found in the environment (Yamamoto et al., 2001).

**Table 2. Material balance for individual degradation and co-processing of 10 g of polycarbonate (PC), DVDs, CDs and vegetable cooking oil (VCO) at 450 Celsius (Mitan et al., 2007)**

<b>Sample</b> <b>( Total 10 g)</b>	<b>Gas</b> <b>( wt %)</b>	<b>Liquid</b> <b>( wt %)</b>	<b>Residue</b> <b>( wt %)</b>	<b>Liquid Cnp</b>	<b>Liquid density</b> <b>(g/mL)</b>
PC	16.5	40.2	43.3	13.0	1.03
DVD	15.6	50.8	33.6	14.0	1.04
CD	13.7	47.1	39.2	12.8	1.02
VCO	15.6	77.7	6.7	12.5	0.84
PC/VCO	16.9	62.4	20.7	14.2	0.92
DVD/VCO	20.3	59.9	19.8	12.7	0.91
CD/VCO	19.6	59.4	21.0	12.9	0.90

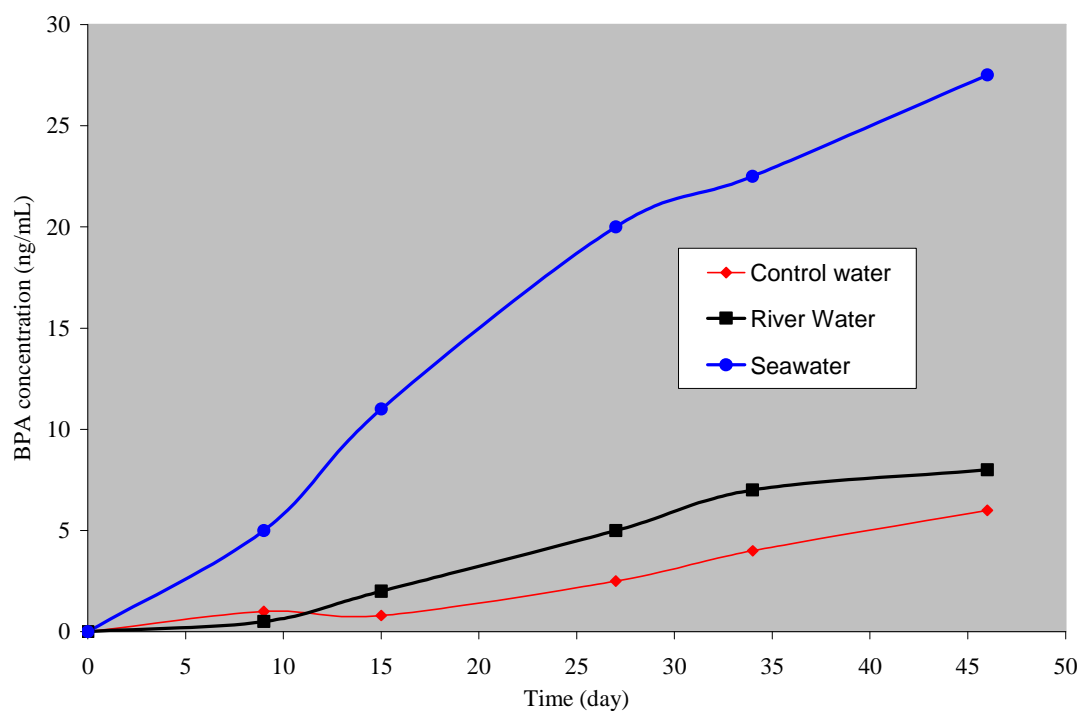


**Table 3. Main compounds identified in liquid products from the degradation of PC, DVDs, CDs and PC/VCO at 450 °C, % of GC-MS detector total peak area (Mitan et al., 2007).**

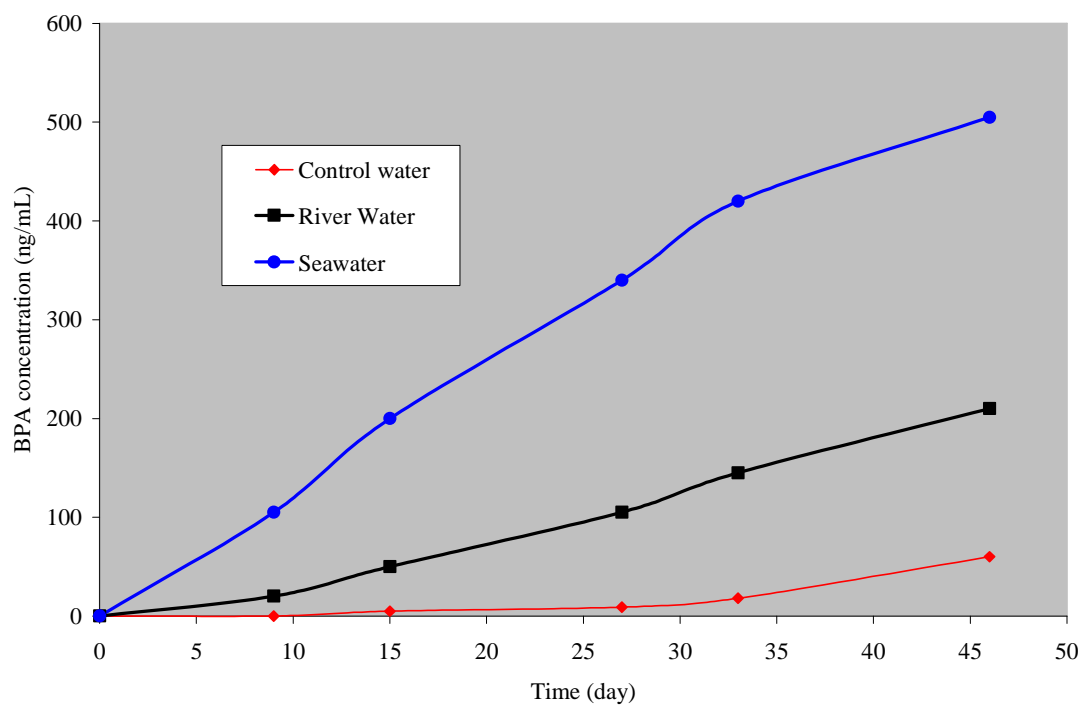
Compound name	Molecular formula	PC	DVD	CD	PC/VCO
Benzene	C <sub>6</sub> H <sub>6</sub>	0.09	0.10	0.03	–
Toluene	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	0.98	0.31	0.33	0.40
Ethylbenzene	C <sub>6</sub> H <sub>5</sub> C <sub>2</sub> H <sub>5</sub>	0.21	0.10	0.22	0.21
Dimethylbenzene	C <sub>6</sub> H <sub>4</sub> (CH <sub>3</sub> ) <sub>2</sub>	1.47	0.34	0.22	–
Ethylmethylbenzene	CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> C <sub>2</sub> H <sub>5</sub>	0.61	0.19	0.19	0.14
Phenol	C <sub>6</sub> H <sub>5</sub> OH	6.98	7.09	18.72	3.14
Diethylbenzene	C <sub>6</sub> H <sub>4</sub> (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	0.16	0.07	0.05	0.29
Methylphenol	HOC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub>	29.70	14.70	18.71	–
Ethylphenol	HOC <sub>6</sub> H <sub>4</sub> C <sub>2</sub> H <sub>5</sub>	18.07	10.31	14.49	0.20
Isopropylphenol	HOC <sub>6</sub> H <sub>4</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	4.18	5.76	14.69	–
Propylphenol	HOC <sub>6</sub> H <sub>4</sub> C <sub>3</sub> H <sub>7</sub>	0.43	0.50	1.03	–
Tert-butylphenol	HOC <sub>6</sub> H <sub>5</sub> C(CH <sub>3</sub> ) <sub>3</sub>	1.25	3.49	5.33	–
Butylphenol	HOC <sub>6</sub> H <sub>4</sub> C <sub>4</sub> H <sub>9</sub>	0.34	1.07	1.12	–
Methyldiphenylether	CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> OC <sub>6</sub> H <sub>5</sub>	0.16	0.13	0.17	–
Dimethylbiphenyl	CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub>	0.03	0.04	–	–
Dimethyldiphenylether	CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> OC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub>	0.51	0.31	0.15	–
Dimethyldiphenylethane	CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub>	0.25	0.06	–	–
Phenolisopropylbenzene	HOC <sub>6</sub> H <sub>4</sub> C(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	1.74	2.27	3.89	–
Phenoxyacetophenone	C <sub>6</sub> H <sub>5</sub> OC <sub>6</sub> H <sub>5</sub> COCH <sub>3</sub>	0.63	0.46	–	–
Biphenyl-2-ol, 5-tertbutyl	HOC <sub>6</sub> H <sub>3</sub> (C(CH <sub>3</sub> ) <sub>3</sub> )C <sub>6</sub> H <sub>5</sub>	2.08	1.45	0.12	–
Bisphenol A	HOC <sub>6</sub> H <sub>4</sub> C(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>4</sub> OH	10.64	12.55	5.77	8.71
Acetic acid	C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	–	–	–	0.79
Pentene	C <sub>5</sub> H <sub>10</sub>	–	–	–	0.33
Heptane	C <sub>7</sub> H <sub>16</sub>	–	–	–	0.95
Coumaranone	C <sub>8</sub> H <sub>6</sub> O <sub>2</sub>	–	–	–	0.14
Octanoic acid	C <sub>8</sub> H <sub>16</sub> O <sub>2</sub>	–	–	–	0.17
Nonanoic acid	C <sub>9</sub> H <sub>18</sub> O <sub>2</sub>	–	–	–	0.14
Nonane	C <sub>9</sub> H <sub>20</sub>	–	–	–	0.37
Propylbenzene	C <sub>9</sub> H <sub>12</sub>	–	–	–	0.09
Nonene	C <sub>9</sub> H <sub>18</sub>	–	–	–	0.28
Methylpropyl phenol	C <sub>10</sub> H <sub>14</sub> O	–	–	–	0.60
Decanoic acid	C <sub>10</sub> H <sub>20</sub> O <sub>2</sub>	–	–	–	1.60
Decene	C <sub>10</sub> H <sub>20</sub>	–	–	–	0.17
Decane	C <sub>10</sub> H <sub>22</sub>	–	–	–	0.15
Methylisopropylbenzene	C <sub>10</sub> H <sub>14</sub>	–	–	–	0.26
Undecene	C <sub>11</sub> H <sub>22</sub>	–	–	–	0.33
Undecane	C <sub>11</sub> H <sub>24</sub>	–	–	–	0.16
Undecanoic acid	C <sub>11</sub> H <sub>22</sub> O <sub>2</sub>	–	–	–	0.28
Dodecene	C <sub>12</sub> H <sub>24</sub>	–	–	–	0.18
Dodecane	C <sub>12</sub> H <sub>26</sub>	–	–	–	0.51
Tridecene	C <sub>13</sub> H <sub>26</sub>	–	–	–	0.21
Tridecane	C <sub>13</sub> H <sub>28</sub>	–	–	–	0.17
Tetradecene	C <sub>14</sub> H <sub>28</sub>	–	–	–	0.15
Pentadecane	C <sub>15</sub> H <sub>32</sub>	–	–	–	0.25
Hexadecanoic acid	C <sub>16</sub> H <sub>32</sub> O <sub>2</sub>	–	–	–	1.67
Oleic acid	C <sub>18</sub> H <sub>34</sub> O <sub>2</sub>	–	–	–	8.48
Heneicosane	C <sub>21</sub> H <sub>44</sub>	–	–	–	0.25

**Table 4. Molecular weight parameters for exposed coated and non-coated polycarbonate sheets (Yu, 2007).**

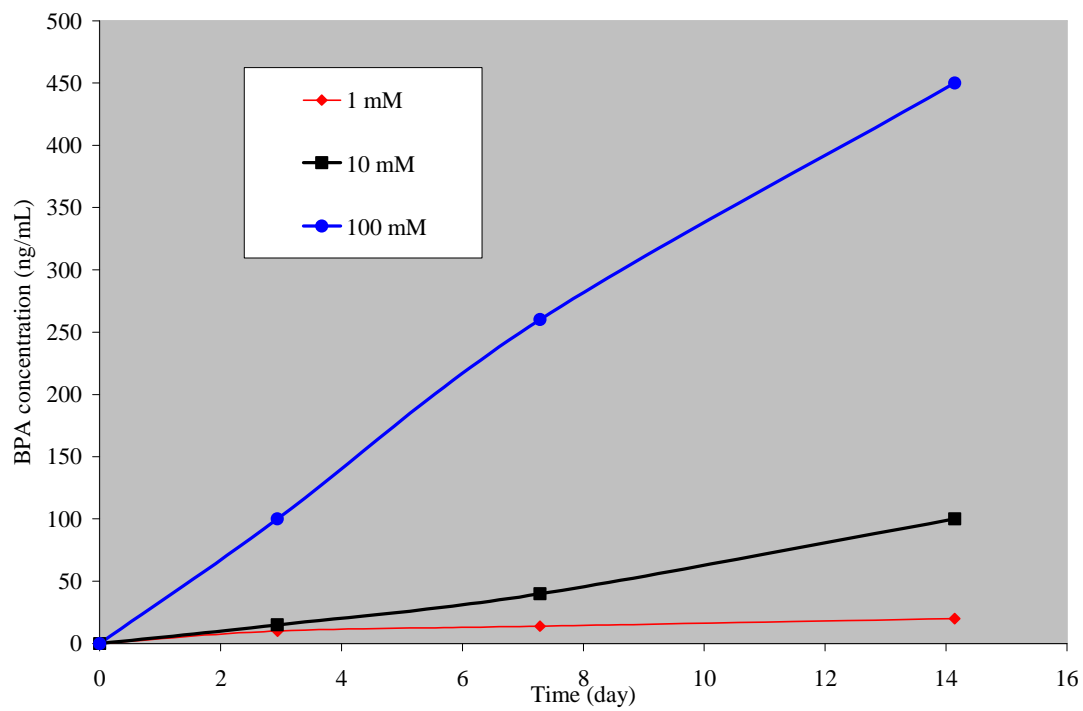
Sample ID	Mw (Kpse)	Mn (Kpse)	Mp (Kpse)
Coated sample exposed to O3	90.7	4.1	133
Control reference	163	37	146
Non-coated sample exposed to O3	30.1	4.9	37.6
Control reference	163	40	140



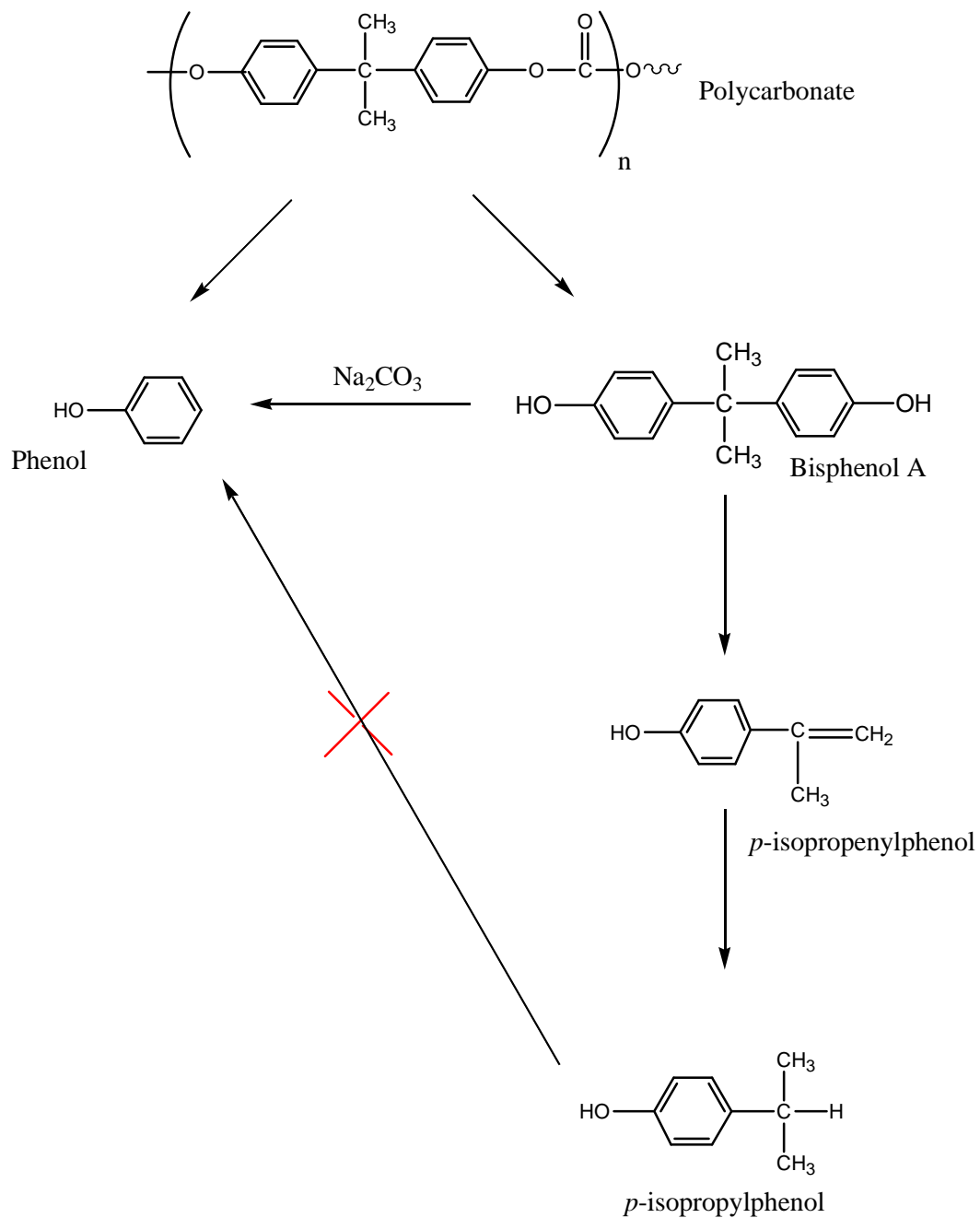
**Figure 12. Change of BPA concentration leached from PC tube to water samples at 20 Celsius as a function of time (Sajiki and Yonekubo, 2003).**



**Figure 13. Change of BPA concentration leached from PC tube to water samples at 37 Celsius as a function of time (Sajiki and Yonekubo, 2003).**



**Figure 14. Change of BPA concentration leached from PC tube for various concentrations of Na<sub>2</sub>HPO<sub>4</sub> solution (Sajiki and Yonekubo, 2003).**



**Figure 15. Decomposition reaction of polycarbonate in sub-critical and super-critical water (Tagaya et al., 1999)**

## **CHAPTER 6 - BPA ENTRY INTO THE ENVIRONMENT FROM POLYCARBONATE AND ITS ASSESSMENT**

It is believed that only small amounts of Bisphenol-A enter the environment during the production, processing, usage, recycling and disposal of polycarbonate.

Processing of polycarbonate may lead to an increase in residual BPA if the incorrect operating conditions are used, and this leads to polycarbonate degradation. The major causes of polycarbonate degradation during processing are water presence, high extrusion temperatures, and use of additives that promote degradation. To avoid these problems manufacturers provide information on proper processing conditions and handling information. If the guidelines are followed, BPA formation due to degradation is negligible (European Chemicals Bureau, 2003).

There are six key plants in Europe that produce BPA. The total amount of BPA produced was (700,000 tons/year) from 1997 through 1999. The data on their environmental releases is summarized in Table 5. The values presented are releases that took into account the production and processing of BPA.

For risk assessment purposes for all the site-specific scenarios, the largest emission to air estimated was 575 kg/year and the largest emission to receiving water was 277 kg/year (European Chemicals Bureau, 2003). A closer analysis of a particular plant indicates that it uses approximately 487,000 tons of BPA /year and it produces polycarbonate from BPA in a continuous wet process in a closed system. The plant operates for about 289 days/year. The release of BPA to air was estimated as 0.5 kg/24 hours based on their measurements. These data leads to a BPA release of about 144 kg/year. The release of BPA to water was estimated as 0.7 kg/24 hours based on analytical results. This leads to a yearly release of about 202 kg/year. Both air and water releases represents less than 0.0001 % of the BPA amount used for production (European Chemicals Bureau, 2003).

For example, the evolution of volatile organic compounds from polymers during extrusion and molding operations has been examined. In these studies, the blended polymers contained between 94-99.5% polycarbonate. For all blended polymers, BPA was not detected in the vent gases from the extrusion nor molding apparatus (European Chemicals Bureau, 2003).

During usage, migration of any residual BPA present in polycarbonate is retained very effectively in the polymer matrix. This leads to extremely low extractability by aqueous, alcohol or fat-containing media. Studies have been reported concerning migration of BPA into foodstuffs. Test results show very low levels of migration into food (European Chemicals Bureau, 2003).

Results from standard migration studies with water (Howe and Borodinsky, 1998) indicated no detectable migration of BPA following six hours extraction at 100 Celsius. The detection limit for the migration rate was  $7.8 \text{ ng/cm}^2$  of polycarbonate surface area. The results were acquired following these bottle conditions: the weight was 0.8 kg & total surface area was approximately  $8,194 \text{ cm}^2$ , the average bottle lifetime was two years and washing frequency was 25 times per year. There were a total of 8000 bottles.

The migration rate for the bottle washing scenario is  $<0.41 \text{ ng/cm}^2$ . For a surface area of  $1,270 \text{ in}^2$ , this is less than  $3.4 \text{ } \mu\text{g}$  per bottle per wash, and if there are 8,000 washings daily, there will be less than 27 mg BPA in water. In Europe, about 7,500 tons of polycarbonate is used for bottles each year at a weight of 0.8 kg per bottle. This corresponds to 9,375,000 bottles. Considering an average lifetime of two years, there are 18,750,000 bottles in use at one time. The release from one washing of one bottle was less than  $3.4 \text{ } \mu\text{g}$ , so for 25 washings per year the annual emission per bottle was  $85 \text{ } \mu\text{g}$ . Together with the total number of bottles this gives an estimated release from washing of 1.6 kg per year in Europe (European Chemicals Bureau, 2003).

On the other hand, polycarbonate is used outdoors in huge amounts (tons). Some examples are roofs and automotive glazing. Many surfaces of roofs do include weather-

resistant coatings but atmospheric conditions such as rain, sunlight and other temperature changes could lead to some BPA migration from the surface. According to laboratory measurements ( Xenon Weatherometer), the BPA amounts released this way are in the order of few  $\mu\text{g}$  for each application (Bayer AG Plastics Business Group, 1999).

For example, Bayer Material Science reports that eight square kilometers of its polycarbonate sheets are installed yearly in Europe. It is calculated using laboratory results that 12 kg of BPA are released to the environment from the sheets yearly (Bayer AG Plastics Business Group, 1999).

Polycarbonate is suitable for recycling after it has been used. This is observed in industry for compact discs and bottles. The idea is to mix recycled material and virgin polycarbonate to yield new material that can be used later. The amount of BPA released to the environment due to recycling is very low. For example, compact discs are a popular polycarbonate product. Top polycarbonate producers recycle billions of discs per year. The incineration of polycarbonate waste leads to the formation of water and carbon dioxide. In addition, energy may be recovered (Mitan et al., 2007).

A European producer has conducted a study of the weathering of polycarbonate sheet samples. In the study, polycarbonate sample sheets were exposed to high UV and rainwater weathering conditions. More specifically, two hundred four samples of polycarbonate sheet with a total surface area of  $0.98 \text{ m}^2$ , a weight of 2.038 kg, and a residual BPA content of 6 ppm were exposed to different amounts of light, heat, and water in order to simulate different weather conditions (European Chemicals Bureau, 2003).

Samples of circulating water in the system were taken for BPA analysis. The results indicated that the BPA concentration released after 2000 hours of weathering to the circulating water was  $1.35 \text{ mg/m}^2$  exposed polycarbonate. This period of accelerated weathering may be equivalent to over 9 years in European climate conditions. Therefore, the yearly polycarbonate degradation is estimated



to be 0.15 mg/m<sup>2</sup>. Another top European producer reports that their polycarbonate production for sheets is 20,750 tonnes which yields a total surface area of 8.7 km<sup>2</sup>. Taking the release factor of 0.15 mg/m<sup>2</sup> this would result in a BPA release of 1.3 kg/year. This amount is small and it is within normal amounts compared to environmental releases of other industrial chemicals.

**Table 5. Summary of environmental releases data from BPA production sites (European Chemicals Bureau, 2003).**

Site	Air		Effluent (After wastewater treatment)		Receiving waters
	Measured levels	Release	Measured levels	Release	
1	<0.2 mg/Nm <sup>3</sup> (outlet)	< 0.012 kg/day <4.4 kg/year	<70 ug/L	0.76 kg/day <b>277 kg/year</b>	Flow rate 8.64E+6 m <sup>3</sup> /day
2	2.9 mg/Nm <sup>3</sup> (outlet)	0.00017 kg/day 0.0605 kg/year	0.69 ug/L	0.017 kg/day 6.1 kg/year	Flow rate 2.07E+8 m <sup>3</sup> /day
3	<1 mg/Nm <sup>3</sup> (dust)	< 1 kg/day(dust) <365 kg/year (dust)	~0005 mg/L	0.31 kg/day 113 kg/year	Flow rate 8.08E+07 m <sup>3</sup> /day
4		0.03 kg/day 10 kg/year		0.19 kg/day 70 kg/year	River estuary 2.49E+7 m <sup>3</sup> /day
5		1.58 kg/day (dust) <b>575 kg/year (dust)</b>	Up to 192 ug/L	2.14E-4 kg/day 0.08 kg/year	River estuary 2.59E+6 m <sup>3</sup> /day
6	10 mg/Nm <sup>3</sup> (dust)	0.08 kg/day (dust) 31.2 kg/year (dust)	Up to 30 ug/L	0.072 kg/day 25.8 kg/year	Sea Dilution factor 100

## CHAPTER 7 - ENVIRONMENT FATE OF BPA AND ITS ASSESSMENT

Bisphenol-A has been found in wastewater streams in very small amounts (100 ppb or less). These small amounts have not shown any adverse environmental impact because the low concentrations are non-toxic for aquatic species.

For example, BPA was analyzed in receiving waters upstream and downstream of five US manufacturers between 1996 and 1997 and processors in 1997 during seasonal low flow periods. The manufacturers included Assessment Technologies, Shell, Dow Chemical, Aristech Chemical Corporation, and GE Plastics.

BPA was not detected ( $<1 \mu\text{g/L}$ ) in any surface water sample in 1996 or at six of seven sites in 1997. The BPA concentrations at the seventh site ranged from 2 to  $8 \mu\text{g/L}$ . All surface water concentrations from this study were less than the freshwater predicted no effect concentration of  $64 \mu\text{g/L}$ . This suggests that BPA discharges from manufacturing and processing facilities to surface waters are not a threat to the environment (Staples et al., 1998; Staples et al. 2000).

Similarly, BPA has been analyzed in wastewater plants at manufacturing sites located in Europe and Japan. The BPA concentrations reported from Holland vary from  $0.004 \mu\text{g/L}$  to  $0.065 \mu\text{g/L}$  (Belfroid et al., 1998). The German Federal Environmental Agency has several monitoring programs for BPA in surface waters and wastewater streams. They report a low BPA content of within  $0.125 \mu\text{g/L}$  in their waters.

The Japanese Environmental Agency has conducted a study in which 56 points in their waterways are monitored for BPA. They found that no BPA is found in 41 points while 15 points indicated a BPA concentration that is 0.26 ppb or lower (Japanese Environment Agency, 1998).

All BPA concentrations found in waterways from key industrial countries are below the threshold concentrations for eco-toxic effects. Some key threshold examples are: 1170 ppb (no effect concentration for green algae), 3160 ppb (no effect concentration for Daphnids) and a range of 1000 to 20000 ppb for different variety of fish species (Staples et al., 1998 A).

The measured levels of BPA before and after wastewater treatment at chemical manufacturing plants and major users of BPA indicate a high level of removal. The possible removal mechanisms are adsorption to sludge and biodegradation; which may be the most likely based upon chemical properties and biodegradation experimental data.

BPA is readily biodegradable with a short period of adaptation and meets the ten day window according to the Organization of Economic Cooperation and Development (OECD) guidelines (Goodwin and West, 1997). The degradation in the environment has been approached through atmospheric, soil and aquatic routes. The aquatic route is the most studied. The resulting fate in a wastewater treatment plant as estimated by the European Union System for the Evaluation of Substances (EUSES) is 12% to water discharge, 6.2% to sludge, 81.9% degraded, and a negligible fraction to air.

The biodegradation of BPA which relates to fate and lifetime in the environment is well known. Table 6 summarizes results for different methods that support the present understanding. This includes screening tests, which assess the ready and inherent degradability, to simulation tests for surface waters, soils and wastewater treatment systems, which examines degradation in the laboratory under conditions close to the actual environment fate. Moreover, there are microorganisms that have the ability to use BPA as a carbon source for growth leading to metabolism pathways. The microorganisms have been isolated and characterized (Spivak et al., 1994; Ike et al., 2000; Kang and Kondo, 2002).

Results from several screening tests on the biodegradability of Bisphenol-A suggest that BPA meets the criteria for ready and inherent biodegradability. Preliminary

tests of ready biodegradability suggested that BPA did not meet the criteria. However, recent tests performed using OECD guidelines have shown that BPA meets the criteria. The recent findings are consistent with the conclusions of the European Union risk assessment (European Chemicals Bureau, 2003).

Ready biodegradability of BPA using the manometric respirometry (OECD 301F) test was examined (West et al., 2001). For this test, BPA of 99.7% purity was used. The theoretical oxygen demand (ThOD) of bisphenol-A was 2.52 mg O<sub>2</sub>/mg. The inoculum used in the study consisted of activated sludge mixed liquor from a municipal sewage treatment plant. The experimental section meets the criteria of good laboratory practice (GLP) standards for the test. The temperature used in the study was 27.1°C. This value indicates 2.1°C higher than the temperature set up at the OECD guidelines. Initial concentrations of BPA in the study were 7 ppm and 25 ppm. Oxygen consumption and carbon oxide evolution were determined over 28 days and removal of dissolved organic carbon from the biodegradation reactions was analyzed after 28 days. The time required for achieving 10% degradation of BPA varied from 5.6 days (7 ppm solution) to 6.1 days (25 ppm solution).

The additional time required to exceed 60% BPA degradation level after an additional 3.5 days (7 mg/L bisphenol-A) and 5 days (25 mg/L bisphenol-A). The biodegradation averages were 77.6% and 73.7% for the 7 ppm and 25 ppm solutions at ten days after the lag periods. The maximum degradation levels achieved were 84.6% and 81.7% (with respect to oxygen demand) for the 7 ppm and 25 ppm solutions after 28 days. Based on these degradation rates, BPA can be classified as “readily biodegradable”. The evolution of carbon dioxide coming from the mineralisation of BPA followed the oxygen consumption. In fact the maximum yields of carbon dioxide varied from 73.0% to 80.1% of the theoretical carbon dioxide thereby suggesting nearly complete conversion of the added BPA organic carbon to carbon dioxide.

The same study was repeated at 22.5°C to meet OECD guidelines for this test (West et al., 2001). The rest of the study conditions were unchanged. The degradation

rate results confirmed that BPA is classified as “readily biodegradable” according to the manometric respirometry test (OECD 301F). The time required to achieve 10% degradation for BPA varied from 4.7 days (7 ppm) to 5.2 days (25 ppm). The biodegradation averages were 92.3% and 77.1% for the 7 ppm and 25 ppm solutions at ten days after the lag periods. The maximum degradation levels achieved were 93.1% and 81.0% (with respect to oxygen demand) for the 7 ppm and 25 ppm solutions after 28 days. These results are consistent with values obtained similarly by other research groups (Mobil Oil Corporation, 1993).

Some studies indicated that BPA does not pass the biodegradability test easily. This is the case of those tests that involve a biological media. There are discrepancies between OECD and Chemical Inspection and Testing Institute (MITI, 1992) and those from the EPA. The discrepancies are due to differences in the microbial inoculum used in the studies. The majority of ready biodegradability tests conducted according to current guidelines (EPA) use freshly collected inoculum from municipal wastewater treatment plants. On the other hand, studies conducted by laboratories following the OECD 301C method, utilizes a mixed inoculum that has been pre-conditioned for 30 days on a medium containing glucose/peptone as the sole carbon source. This culturing of the inoculum on easily degraded substrates is considered to result in loss of microbial diversity originally present in the composite sample (Liu et al., 1997; Forney et al., 2001).

Because of this loss of microbial diversity, some researchers from Japan recently re-evaluated the ready biodegradability of Bisphenol-A in 2004 (CERI, 2004). The testing was performed according to OECD method 301F following Good Laboratory Practices utilizing an inoculum from a domestic sewage treatment plant. The maximum degradation achieved after twenty eight days averaged 89% based on oxygen consumption. This result suggested that BPA meets the criteria for ready biodegradability.

If the BPA biodegradation is conducted under anaerobic conditions, there is a great chance that the biodegradation will not be completed (Ike et al., 2006). As a second example, other scientists (Voordeckers et al., 2002) looked at the BPA fate in anaerobic media derived from estuarine sediments using samples taken in the USA. These samples were mixed with an inorganic anaerobic medium, with specific additions to promote methanogenesis, sulfate-, Iron (III)- or nitrate-reducing conditions. BPA amounts were added to each medium with a concentration of 200  $\mu\text{M}$ . After 162 days of monitoring, there was no significant loss of BPA observed in any of the live cultures or in autoclaved controls.

A research group at Shell Chemicals from England (Turner and Watkinson, 1986) approached BPA biodegradation using a modified semi-continuous activated sludge procedure. The microorganisms used in the test were obtained from a municipal wastewater treatment plant. The initial test concentration of BPA was 20 ppm. The BPA degradation was determined through the % dissolved organic carbon (DOC) and UV spectroscopy. After 24 to 30 days, the BPA removal was 87 to 95% as measured by changes in total organic carbon concentration. At the same time, UV spectroscopy indicated that the BPA signal had decreased. The lag phase before degradation of BPA was observed to be 13 to 17 days. All these results suggested BPA to be inherently biodegradable.

The biodegradability of organic substances in an activated sludge test using inocula from an industrial wastewater treatment plant had been examined (Matsui et al., 1988). The aeration conditions in the aeration unit were 2-3 g/L MLSS (mixed liquor suspended solids); air flow 150 mL/min and water temperature 25-30°C. The initial concentration of BPA in the sample was 58 ppm. During the study, two liters of wastewater were mixed with 0.5 liters of activated sludge. Later, the sample was aerated for 23 hours. After one-hour sedimentation, two liters of the supernatant solution were replaced by the sample water. The sludge was conditioned 24 hours before taking first samples. The biodegradability of BPA was determined from initial concentration and the concentration after 24 hours in terms of both COD and TOC. For BPA, the removal

efficiency was 72% based on COD and 57% based TOC. These results indicate that BPA is biodegradable.

The BOD test was presented by the US EPA. The test reports the following parameters for BPA: theoretical oxygen demand (ThOD) of 2.52 mg O<sub>2</sub>/mg; chemical oxygen demand (COD) with dichromate 2.31 mg O<sub>2</sub>/mg; COD with alkaline KMnO<sub>4</sub> 1.76 mg O<sub>2</sub>/mg; biological oxygen demand 0.66 mg O<sub>2</sub>/mg (after 5 days), 1.42 mg O<sub>2</sub>/mg (after 9 days) and 1.78 mg O<sub>2</sub>/mg (after 20 days). These results lead to a 5-day BOD/ThOD of 26% and a 20 day BOD/ThOD of 70.6%. The test meets the criteria for ready biodegradability (Alexander and Batchelder, 1984).

There are several studies on the degradation of BPA in natural waters. Removal seems to be rapid once the waters have become acclimated to BPA. The reported lag-phases before degradation are between three to eight days. After the lag phase period, the removal process was rapid with 50% removal in 1-2 days and nearly 100% removal in 2 to 17 days. These data confirm that natural waters BPA degradation meets the ten day window test.

One example of BPA degradation in natural waters is presented by a group at the Shell Westhollow Research Center. In this particular study, the waters samples were taken from the Houston Ship Channel near to a bisphenol-A manufacturing plant. Four types of samples were collected: 1. fresh water control; 2. chemical plant treated process effluent, 3. water taken 180 meters downstream of the effluent discharge and 4. water taken from ship channel further down stream (> 180 meters). Every water sample was spiked with 3.0 mg/L bisphenol-A, and aerated for 8 days. All samples were analyzed by liquid chromatography. It was observed that in the effluent water sample, BPA decreased after 24 hours with a 37% removal. BPA further decreased after 48 hours. And after 5 days the BPA concentration was lower than 0.1 mg/L. In samples taken downstream of the effluent outflow, BPA concentrations started decreasing after 48 hours and by 72 hours the BPA concentration was lower than 0.1 mg/L. In the ship channel sample, the BPA concentration started decreasing after 4 days and was below the detection limit after

8 days. In the case of control experiment no BPA removal was observed. BPA removal is quick after the system had been acclimated (Dorn et al., 1987).

The treatment of wastewater containing BPA by biological processes, activated carbon adsorption and pore resin adsorption had been studied (Furun et al., 1990). The biological wastewater treatment for degrading BPA was examined using the activated sludge treatment process. A synthetic wastewater feed of 200 mg/L BPA was used. The activated sludge used in this trial was taken from a plant treating petrochemical wastewater. The microorganisms were adapted to BPA over one week exposure. A removal rate of 99.7% BPA was achieved after two weeks exposure. Furthermore, this biological treatment experiment was also conducted on the effluent coming from a polycarbonate production plant. The wastewater contained about 100 mg/L of BPA, and small amounts of triethylamine (TEA). The acclimation stage of the activated sludge took two months. A removal rate of 99.4% was achieved in the effluent after an adaptation period.

Ready and inherent biodegradability tests are frequently used by regulatory agencies for assessing environmental fate and they are also used to estimate environmental half-lives. In the case of BPA, simulation tests have been also performed and they provide direct measurements of environmental lifetime. The fate of BPA in aquatic environments has been well studied. A major and recent study (Klecka et al., 2001), evaluated the biodegradation of <sup>14</sup>C-labeled BPA over a range of concentrations (0.05 to 5,500 micrograms/L) in seven different river waters collected on two large territories such as Europe and the United States. Bisphenol-A biodegradation in the river water samples was observed after a short period, with an average of 3.4 days. The average half-life after acclimation was 1.2 days. BPA was extensively mineralized to carbon dioxide during the experiments, with levels ranging from 59 % to 103 % of theoretical after less than eighteen days of incubation.

A similar study has been conducted in Japan (Kang and Kondo, 2002). In this study, river die away experiments were performed using fifteen surface water samples



taken from thirteen rivers in Japan. The degradation rates were shown to be a function of temperature and the amount of bacteria naturally present in the water. However, half-lives for BPA degradation in all water samples were in the range of four to seven days at 20 Celsius. This suggested that the bacteria were widely distributed in river waters.

The biodegradation of BPA by a gram-negative aerobic bacterium (Lobos et al., 1992) had been examined. Sludge from a wastewater treatment plant was enriched on BPA. The enriched sludge produced a microbial consortium capable of degrading a solution of 0.2% BPA after one week incubation. Gram-negative bacteria (strain MV1) were isolated to be ready and capable of degrading BPA. The growth of strain MV1 on BPA was achieved under aerobic conditions. Under normal experimental conditions, 60% of carbon in BPA was mineralized to carbon dioxide, 20% of the carbon was associated with the bacterial cells and 20% of the soluble organic carbon remained in the medium. The main metabolites obtained were 2,2-bis(4-hydroxyphenyl)-1-propanol, 4-hydroxyacetophenone and 2,3-bis(4-hydroxyphenyl)-1,2-propanediol with trace amounts of 4-hydroxybenzoic acid. The formation of metabolites was quick in the first 8 hours; then their concentrations decreased slowly. The concentration of 2,2-bis(4-hydroxyphenyl)-1-propanol was proportional to cell growth. The 2,3-bis(4-hydroxyphenyl)-1,2-propanediol was formed after 20 hours incubation. The pathways for the degradation of BPA by strain MV1 are described in Figure 16.

The mineralization of BPA by integrated ultrasound-UV-Iron(II) treatment (Torres et al., 2007) was performed. More specifically, the BPA degradation (118  $\mu\text{mol/L}$ ) under sono-chemical conditions of frequency (300 kHz) and electrical power (80 Watts) takes place in ninety minutes. But it was observed that at even longer ultrasound irradiation periods of ten hours, more than 50% of chemical oxygen demand (COD) and 80% of total organic carbon (TOC) remained in solution. This suggests that most BPA intermediates were recalcitrant toward ultrasonic action. Moreover, accumulation of hydrogen peroxide was observed.

To improve this treatment, the researchers experimented with several technique combinations such as ultrasound/UV (254 nm); ultrasound/Fe<sup>2+</sup> (100 μmol/L) and ultrasound/UV/Fe<sup>2+</sup>. The addition of Fe<sup>2+</sup> and UV radiation induced hydrogen peroxide dissociation, producing additional OH radicals and complete COD and TOC removal. Therefore the combination of ultrasound/UV/Fe<sup>2+</sup> was able to mineralize BPA with complete COD and TOC removal. The technique has become attractive for BPA wastewater treatment. Furthermore, the combination of ultrasound/UV/Fe<sup>2+</sup> together could eliminate BPA (118 μmol/L solutions) much faster than one or two combinations together as observed in Figure 17 (Torres et al., 2007).

After thirty minutes of treatment, 95% of BPA was degraded using the Ultrasound/UV/Fe(2+) combination, whereas 89% of BPA was degraded with Ultrasound/Fe(2+), 82% of BPA degraded with Ultrasound/UV, 77% of BPA degraded with Ultrasound and only 25% of BPA degraded with UV. For all processes after seventy five minutes, 100% of BPA was eliminated, except for UV treatment where about 50% of BPA remained in solution. In the last case, it took about two hundred forty minutes to degrade all BPA. This slow degradation obtained by UV treatment was due to the low BPA molar absorption coefficient at 254nm. The different combinations of techniques did indicate an enhancement in oxidation and mineralization of organic material (Torres et al., 2007).

It has been observed that BPA in water was degraded quickly in the presence of reactive oxygen species (ROS) such as the hydroxyl group at 20 Celsius. Moreover, BPA further degraded by an addition of physiological and environmental content of sodium chloride (0.9%–3%), possibly due to the formation of HOCl. On the other hand, ethanol inhibited the decrease in the BPA recovery (Sajiki and Yonekubo, 2002). In this study, BPA was not degraded easily in seawater but rather in control water. The reason why BPA could not be easily degraded by ROS in seawater compared to control water may be due to possible existing inhibitors in seawater. BPA does degrade in seawater under the presence of ROS and phytoplankton cells. The pH of seawater is between 7 and 8. It is

believed that BPA is degraded to BPA-quinone, probably via catechol followed by the formation of semiquinone in vivo (Sajiki and Yonekubo, 2003).

BPA-quinone is formed in the presence of ROS and it was more hydrophilic than BPA. Mass spectrometry analysis indicates that a base ion at 241 was found for BPA-quinone. This compound also showed other ions at 243, suggesting that BPA could be metabolized via the following reversible equilibration between BPA-o-quinone (MW 242) and BPA-o-catechol (MW 244) as described in Figure 18 (Sajiki and Yonekubo, 2003).

Fate of BPA in the aquatic environment and the safety for aquatic organisms are great concerns in the future because of a rapid increase in the distribution and abundance of plastic debris in the ocean around the world (Ogi et al., 1999).

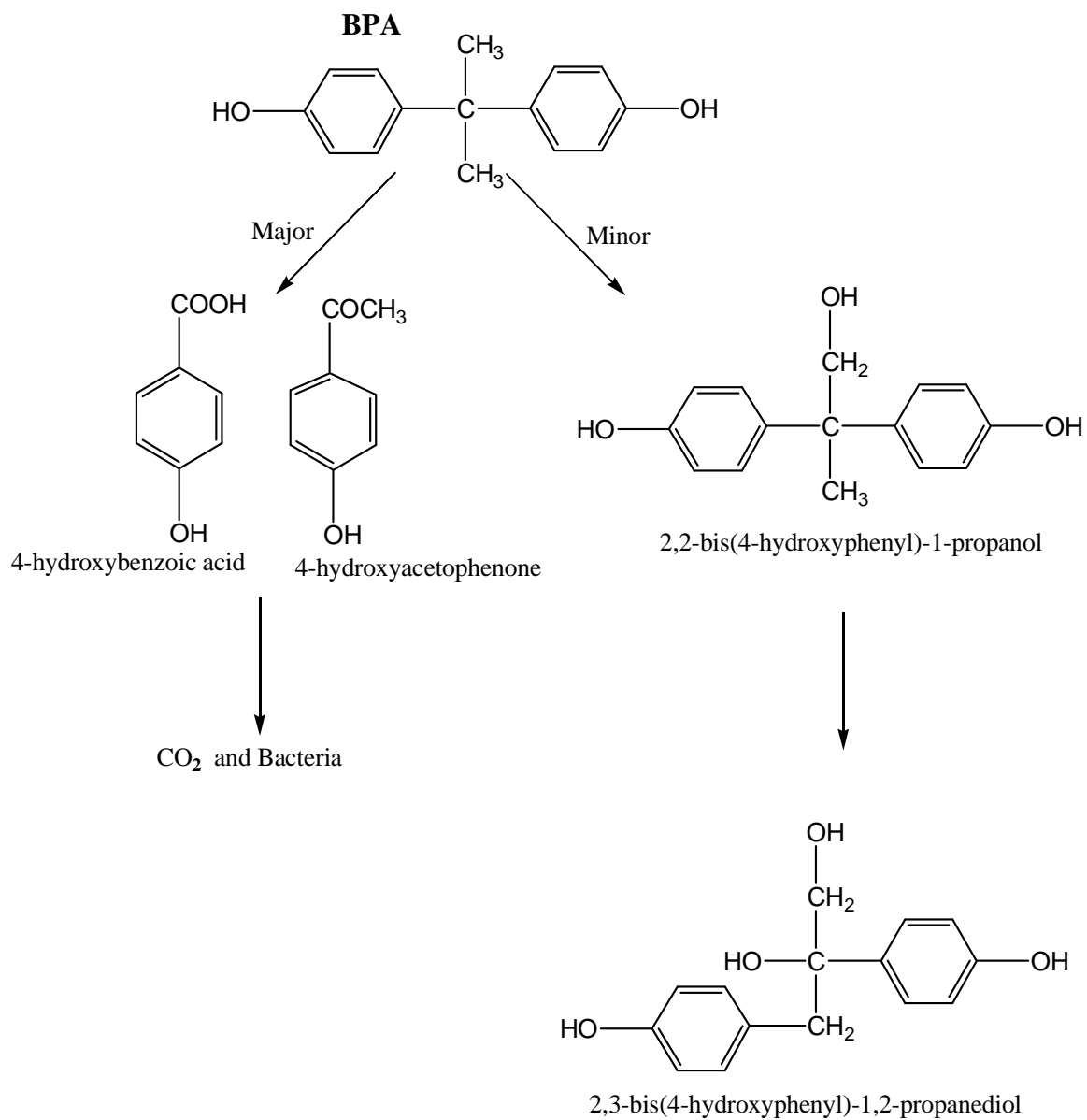
The fate of <sup>14</sup>C-labeled BPA in four different agricultural soils has already been evaluated (Fent et al., 2003). It was observed that BPA dissipated rapidly in soil. The chemical was not detected in soil after three days and it could not be recovered via extraction. These observations suggest that the half-life of BPA in soil is less than three days and they differ from the value obtained by the European Union System for the Evaluation of Substances (EUSES) of 30 days with a first order rate constant of 0.0231 d<sup>-1</sup>. It is believed that one mechanism of BPA dissipation in soil may be due to biologically mediated covalent bonding known as oxidative coupling and incorporation of Bisphenol-A into the organic fraction of the soil. Those reactions are commonly observed in studies examining the fate of phenolic substances in soil, and are in agreement with reactions catalyzed by soil microorganisms and naturally occurring soil enzymes (Dragun, 1988).

According to most tests presented in Table 6, BPA is expected to be rapidly degraded in aquatic and soil environments. These observations are in agreement with the report from the European Union (European Chemicals Bureau, 2003). As an average, the half-life for BPA in water and soil would be expected to be very short (1-5 days).

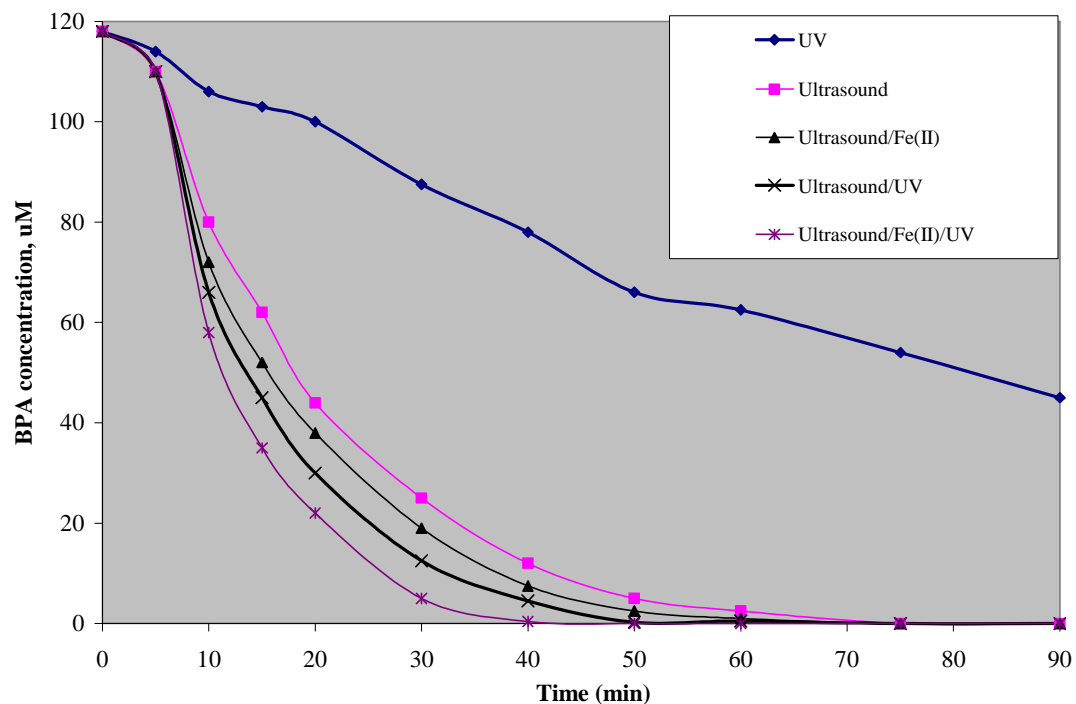
BPA does degrade in the atmosphere. It is believed that BPA reacts with radicals in the atmosphere. The reaction is classified as pseudo first-order and the rate has been estimated as  $3.48 \text{ d}^{-1}$  using kinetic programs (European Chemicals Bureau, 2003). With this rate constant, the half-life of the BPA reaction with radicals in air is 0.2 days.

**Table 6. Summary of Biodegradation Tests with BPA (Klecka and Staples, 2005).**

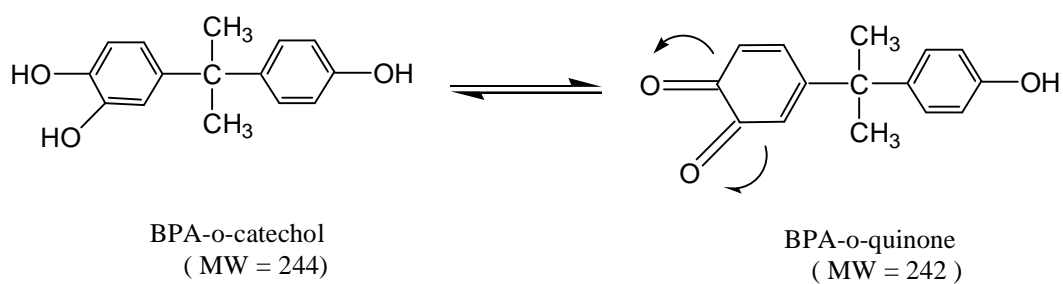
Reference	Study Type	GLP	Result	Conclusion
Ready Tests				
MITI, 1992	OECD 301C	Not specified	0 %	Does not meet ready biodegradability criteria
Alexander and Batchelder, 1984	BOD test	No	BOD 20 was 71% of theoretical oxygen demand	Meets criteria for ready biodegradability
Lobos, 1992	Degradation with gram (-) bacterium	Not specified	60% of carbon in BPA was mineralised to carbon dioxide, thus degradation observed	Meets ready biodegradability criteria
Mobil Oil Corporation, 1993	OECD 301B; EPA CG-2000 Shake Flask Method (560/6-82-003)	No	83.6% conversion to CO <sub>2</sub> in 28 days	Meets criteria for ready biodegradability
West et al, 2001	OECD 301F	Yes	81.7 to 84.6 O <sub>2</sub> consumed and 73.0 to 80.1% conversion to CO <sub>2</sub> in 28 days (27.1 C) 81.0 to 93.1% O <sub>2</sub> consumed in 28 days (22.5 C)	Meets criteria for ready biodegradability Passes ready test
CERI, 2004	OECD 301F	Yes	89% removal by BOD, 100% removal by HPLC and DOC analysis in 28 days	Meets criteria for ready biodegradability Passes ready test
Inherent Tests				
Turner and Watkinson, 1986	Modified SCAS Test	Not specified	87 to 95% degradation after 24 to 30 days	Meets criteria for inherent biodegradability
Matsui et al, 1988	Activated sludge test	Not specified	72% COD and 57% TOC reduction	Meets criteria for inherent biodegradability
Simulation Tests				
Furun et al, 1990	Activated sludge test	Not specified	99.7% removal in activated sludge simulation test	
Dorn et al, 1987	River die-away test (3 samples)	No	> 90% degradation within 4 days	Half-life < 4 days
Klecka et al, 2001	<sup>14</sup> C-River die-away test (7 rivers, 13 samples)	Yes	Lag period 3.4 days Complete degradation to <sup>14</sup> CO <sub>2</sub> within 18 days	Half-life range 0.5-3 days following short lag period (2-4 days)
Kang and Kondo, 2002	River die away test (13 rivers)	Not specified	BPA rapidly degraded in all samples; effects of bacterial count and temperature examined	Half-lives ranged from 4 to 7 days at 20 °C
Fent et al, 2003	<sup>14</sup> C-Soil degradation test (4 soils)	Yes	Complete disappearance within 3 days Majority incorporated into soil	Half-life < 3 days



**Figure 16. Degradation of BPA using bacteria (Lobos et al., 1992)**



**Figure 17. BPA (118  $\mu\text{mol/L}$ ) elimination by different oxidation processes applied to solutions saturated with  $\text{O}_2$ . Vol.:300 mL; pH: 3; T.: 20 $\pm$ 1  $^\circ\text{C}$ . Ultrasound: 300 kHz/80 W; UV irradiation: 254 nm;  $\text{Fe}^{2+}$ : 100  $\mu\text{mol/L}$  (Torres et al., 2007).**



**Figure 18. Possible reversible equilibrium between BPA-o-catechol and BPA-o-quinone (Sajiki and Yonekubo, 2003).**

## **CHAPTER 8 - FATE AND DISTRIBUTION OF BPA IN THE ENVIRONMENT**

The fate and distribution of a chemical in the environment depends on its physical and chemical properties. Adsorption, volatilization, precipitation and biodegradation are important and need to be considered.

As mentioned in the previous chapter, the treatment of wastewater containing BPA by activated carbon adsorption has been studied (Furun et al., 1990). Static and dynamic adsorption studies were carried out using activated carbon. In the static adsorption study 500 mg activated carbon was added to 100 mL BPA solution (347.6 mg/L). After shaking the solution for 2 hours the residual BPA concentration was determined and the average adsorption capacity of the activated carbon was calculated as 44.7 mg BPA/g carbon. The regeneration of the activated carbon was attempted using sodium hydroxide and it was found unsuccessful thereby suggesting that adsorption between BPA and carbon was strong. In the dynamic adsorption study activated carbon was packed into an adsorption column and then a BPA solution (100 mg/L) was pumped through it. The BPA concentration in the effluent was measured every hour. The average adsorption capacity of the activated carbon was 50 g BPA/L activated carbon. Similarly to the static study, the regeneration of the activated carbon using sodium hydroxide was also unsuccessful.

Extensive adsorption studies have been conducted using adsorption resins. Statically, the adsorption capacity varied from 7.5 to 21.0 mg BPA/g wet resin. Some resins were very efficient in adsorbing BPA after regeneration with sodium hydroxide. Derived partition coefficients have been determined based on TGD (Technical Guidance Document) methods. All values are reported in Table 7. The data suggests that BPA is adsorbed mildly to solids once BPA is released to the environment.

BPA is not volatile and it is relatively short lived in the atmosphere. Therefore, it is not likely to enter the atmosphere in huge amounts and neither will it be transported to



a far distance from an emission point. The chances to find BPA in rain water are very small.

The volatilization of BPA from surface water to air may be approached with the Henry's Law constant. This is estimated using by the European Union System for the Evaluation of Substances (EUSES) as  $4.03\text{E-}6 \text{ Pa}\cdot\text{m}^3\cdot\text{mol}^{-1}$  for BPA. The air-water partition coefficient ( $K$  air-water), also derived from the Henry's law constant, is estimated as  $1.7\text{E-}9 \text{ m}^3/\text{m}^3$  for BPA. Both values are very low and they suggest that volatilization is unlikely to be the removal mechanism for BPA from contaminated water streams.

Bisphenol-A has not been shown to accumulate in food chains. This has been demonstrated experimentally via different fish bio-concentration factors. Bioconcentration factors were determined for carp fish (*Cyprinus carpio*) exposed to bisphenol-A concentrations of  $15 \mu\text{g/L}$  and  $150 \mu\text{g/L}$  in a flow system for six weeks. At the  $15 \mu\text{g/L}$  exposure concentration, bioconcentration factors of less than 20 to 67.7 were obtained in a period of six weeks. At the  $150 \mu\text{g/L}$  exposure concentration, bioconcentration factors of 5.1 to 13.3 were obtained in a period of six weeks. Therefore, BPA was rated to have a low bioaccumulation potential.

The fishes used in the study were acclimated to the test conditions prior to the beginning of the study. The test length allows BPA, water and fish to reach steady state. BPA levels in fish varied from 0.79-1.94 ppm at the higher concentration and 0.21-1.05 ppm at the lower concentration. Bisphenol A has weak acute toxicity to aquatic organisms; LC50 or EC50 levels for fish and invertebrates range from 1.1 mg/L to 10 mg/L (Yamamoto and Yasuhara, 1999).

Rainbow trout was intentionally exposed to BPA (at  $100 \mu\text{g/L}$ ) in a flow-through system (Lindholst et al., 2001). Concentrations of BPA were determined in the blood plasma, liver and muscle tissues of the fish. Concentrations in blood plasma, liver and plasma reached a maximum level within forty eight hours. In addition, the bio-

concentration factors for all three fish were between 3.5 and 5.5. While the BPA level increased in the blood plasma, the Glucuronidated derivative metabolite increase was 2 to 2.5 times higher than that of BPA. It is easy for the metabolite to be excreted due to a lower partition coefficient.

As we can observe, BPA is distributed in air, water, soil and sediment in the environment. There are models that predict how much BPA can be distributed in each of these places. One of the models, known as Equilibrium Criterion (EQC) uses chemical-physical properties to quantify a chemical behavior in an evaluative environment of 100,000 km<sup>2</sup>. The environment is fixed to facilitate chemical-to-chemical comparison (Cousins et al., 2002).

There are three degrees of complexity in the Equilibrium Criterion model. The degrees are known as I, II and III. The degrees differ in physical conditions. Levels I and II assume that thermodynamic equilibrium is achieved; Level II includes advective and reaction processes. Level III is a non-equilibrium, steady-state assessment of chemical fate in the environment (Cousins et al., 2002).

The Equilibrium Criterion model may be useful in obtaining the general features of a new or existing chemical's behavior and it can also provide key information such as media into which the chemical will tend to partition, the primary loss mechanisms, and tendency for inter-media transport. Different emission scenarios may be modeled, also.

The level I EQC modeling of BPA indicates that under equilibrium conditions, most of the BPA (~98 %) will distribute between the soil (67.9%) and surface water (30.5%). Figure 19 presents the scheme, which includes this distribution.

Due to the low vapor pressure of BPA, only small amounts (<0.00003%) will be partitioning to the air. BPA is considered a moderately hydrophobic compound (KOW =103.4) and moderately soluble in water (300 mg/L ). Therefore the fugacity capacity in

soil (ZS:  $1.23 \times 10^7$  mol/m<sup>3</sup> Pa) is fifty times larger than in water (ZW : $2.48 \times 10^5$  mol/m<sup>3</sup> Pa).

Bisphenol-A is very rapidly metabolized in fish. This observation is consistent with its rapid biodegradation in the environment. The Level I model suggests equilibrium concentrations in sediment of 6.3 ng/g and in water of 153 ng/L, This yields a ratio of 0.041 L/g. These values are due to a high KOC (organic carbon-water partition coefficient) value of 715 (Table 3), which is consistent with KOC measurements for soils (Cousins et al., 2002).

Since the sediment samples are difficult to obtain, the reported sediment concentrations at level I may not be truly representative of the environment. Because of these sampling difficulties, there might not be a validated method for sediment analysis. Furthermore, the data may be biased toward overestimation of sediment concentrations because most of the data might be collected immediately downstream of wastewater outfalls.

Aromatic compounds may have a strong binding to sediments (Accardi-Dey and Gshwend, 2002). BPA in the sediment is not present in free molecular form, but it is present in another matrix. It is released and measured during analysis because aggressive solvent extraction releases the compound from the matrix. Furthermore, BPA may have been strongly bound to the matrix when it was released to the environment. The approach to equilibrium partitioning conditions may be slow (Cousins et al., 2002).

The level II EQC model includes the estimated environmental half-lives for air (4 hours), water (108 hours), soil (108 hours), and sediment (7200 hours). Under equilibrium partitioning and steady state conditions, the major loss routes for BPA will be reaction in water (29.6%) and soil (65.8%). The advection from the model world in water accounts for (4.6%). Figure 20 shows the Level II EQC modeling diagram.

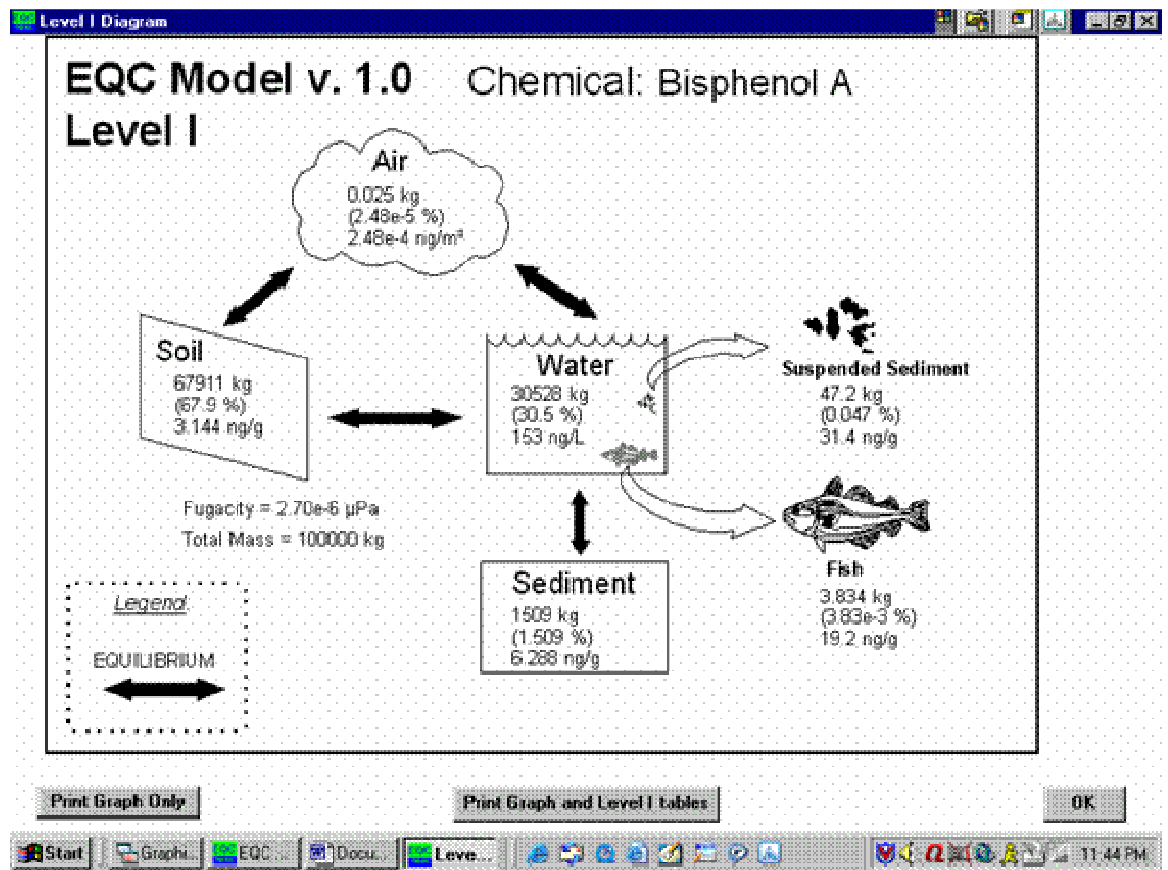
The level II EQC model predicts an overall residence time of 151 hours (6.3 days), reaction residence time of 158 hours (6.6 days) and advection residence time of 3272 hours (136 days). BPA is not predicted to be persistent in the environment and its dominant transformation is driven by reaction. The potential for atmospheric transport is very low while the potential for water transport is much greater.

The Level III modeling is useful in indicating how the media into which the chemical is released affects the overall environmental fate. The fugacity at this level allows non-equilibrium conditions to exist between connected media at steady state. The level III illustrates important transport and transformation processes, which are considered to be the most realistic approach that can be modeled with the EQC criterion. The trends of chemicals to migrate between media may be obtained by modeling emissions to each individual medium and determine the amount present at steady state.

Simultaneous emissions of 1000 kg/h to air, water, and soil are described in Figure 21. If the emission is to air, BPA partitions to atmospheric aerosols and it deposits to soil and water. The soil will accumulate a larger percentage of BPA because the soil compartment in EQC has a larger surface area for atmospheric deposition. If the emission is to water or soil, the model predicts that BPA will remain in the compartment where it is emitted. Furthermore, there is some transfer to bottom sediments when the emission is to water. The relative amounts emitted to different environmental media therefore have a large effect on environmental fate and exposure (Cousins et al., 2002).

**Table 7. Partition coefficients obtained for BPA from adsorption studies (Furun et al. 1990).**

Partition coefficient	Symbol	Values	Units
Organic Carbon-Water	KOC	715	L/kg
Solids-Water in soil	Kpsoil	14.3	L/kg
Solids-Water in sediment	Kpsed	35.8	L/kg
Solids-Water in suspended matter	Kpsusp	71.51	L/kg
Suspended matter- Water	Ksusp-water	18.18	m3/m3
Soil-Water	Ksoil-water	21.7	m3/m3
Sediment- Water	Ksed-water	18.7	m3/m3



**Figure 19. Level I, Equilibrium Criterion (EQC) modeling diagram (Cousins et al., 2002).**

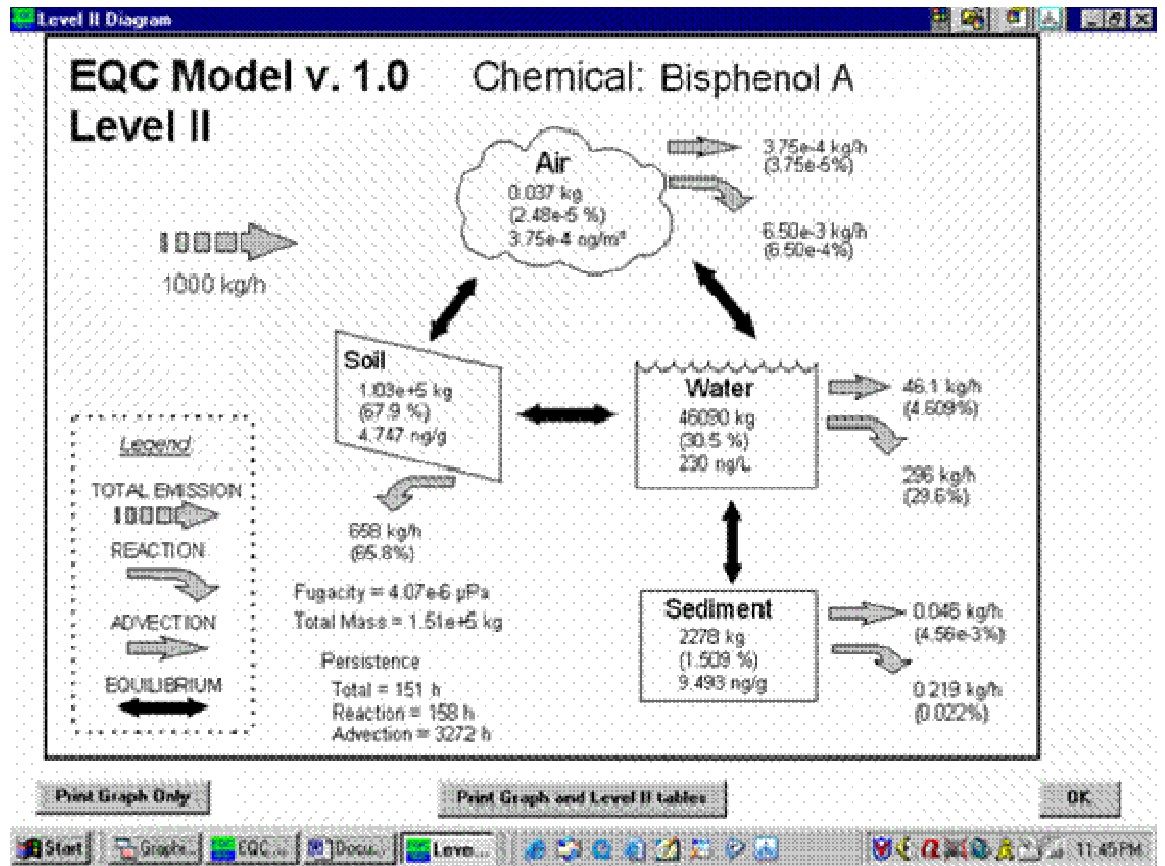


Figure 20. Level II, Equilibrium Criterion (EQC) modeling diagram (Cousins et al., 2002).

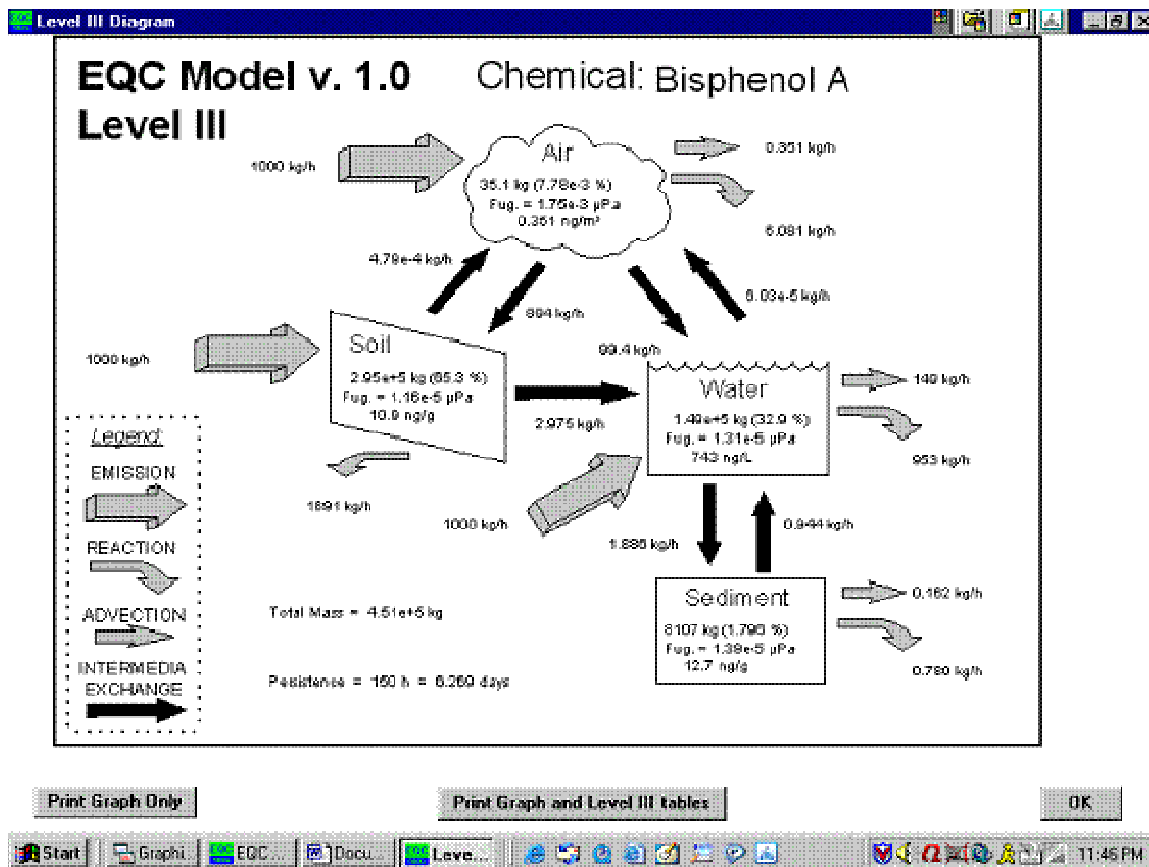


Figure 21. Level III, Equilibrium Criterion (EQC) modeling diagram (Cousins et al., 2002).

## **CHAPTER 9 - ENDOCRINE EFFECTS OF BISPHENOL-A**

Bisphenol-A has been considered an industrial chemical that may have endocrine effects in humans or animals. These effects happen when a change occurs in the body's hormone regulation system. The change leads to harmful effects on physical & mental development and reproduction capability.

In addition to the electrical control of the nervous system, the activity of several organs and tissues in the body are controlled by hormones and endocrine system. It is possible that BPA can create an endocrine disruption. This particular harmful effect may cause a disturbance that can not be compensated in the hormonal system with effects on the reproductive capability.

International organizations such as the European Union Scientific Committee on Food (SCF), UK Department of Health have determined that at low concentrations, BPA has very small or no potential for hormone like effects based on results from different investigations (American Plastics Council, 2006 A).

During the decade of 1930s, pharmacological search was conducted to look for substances that are able to replace human estrogenic hormones. For this purpose, the list of compounds searched was composed of hundreds of chemicals but BPA was not in the list because it showed very light estrogen-like effect even when very high doses were injected into the abdominal cavity and under the skin of rats (Dodds and Lawson, 1936). This observation prompted careful attention on BPA effects in all toxicological investigations since then. Table 8 summarizes the different toxicological studies and results through time. Major findings indicate that BPA, in contrast to natural human estrogen, does not cause cancer, does not destroy embryos nor affect fertility. Furthermore, animal based toxicological investigations have shown that BPA does not accumulate in the body but instead is excreted rapidly (Knaak and Sullivan, 1966; Pottenger et al., 1997).



Discussions on toxicological effects of BPA have been mixed. There are always differences in response and errors in the process of gaining scientific knowledge.

As an example, the hypothesis that BPA was harmful at a low dose was reported (Nagel et al., 1997). The researchers conducted a study with thirty nine mice in total. Fourteen mice were fed with BPA in ratios of 2  $\mu\text{g}$  BPA/kg through 20  $\mu\text{g}$  BPA/kg. Eleven mice without feeding BPA were used as comparison. Some effects were observed on prostate weight and semen production of male mice. These researchers thought that the effects might be applicable for humans if humans do ingest Bisphenol-A.

However, the effects were re-evaluated and followed up by other research groups later. The follow-up studies did not confirm any harmful effect at low BPA dose (Ashby and Tinwell, 1998; Cagen et al., 1999).

In a larger scale study, the feeding tests included a total of 568 mice. More than 386 mice were given BPA in concentration ratios of 0.2  $\mu\text{g}$  BPA/kg through 200  $\mu\text{g}$  BPA/kg. Twenty eight mice were used as control. The effect on prostate weight and semen production of male mice could not be confirmed.

In a most recent development in 2005, it was claimed that BPA leaching from polycarbonate can modify the developing brains of female mice so that they behave more like their male brethren (Thacker, 2006).

Researchers at Tufts University installed very small pumps into female mice during their pregnancy. From the eighth day of pregnancy until the sixteenth day of nursing, the pumps released doses of BPA. At the eighth day of development, mice embryos started growing and generating neurons in a part of the brain that is focus for sexual behavior. A set of female pregnant rats was exposed to 250 ng/kg/day of BPA while the other set was exposed to a lower amount of 25 ng/kg/day of BPA.

These levels of BPA released by these pumps were within the concentrations estimated to be found in humans. In 2005, the Centers of Disease Control and Prevention reported that 95 % of Americans excrete greater or equal to 100 ppt of BPA in the urine (Calafat et al., 2005).

The brains and behavior of the mice were evaluated. Female mice usually have 2 to 3 times as many neurons as male mice in the section of the brain that controls the sexual cycle. However, female mice that were exposed to BPA, showed fewer neurons in this part of the brain. According to the scientists, female mice are usually more active than male mice but female mice exposed to Bisphenol-A had less activity so that they were nearly equal to the male mice's activity level.

In another brain study, it was reported that rat brains may be affected by BPA at doses below 1 ppt (Belcher et al., 2005). Although these results might be a concern for humans, the American Plastics Council indicated that a more detailed and extensive study is needed to confirm these observations and see if BPA is harmful to human brains.

It was reported by 2006 that over six-billion pounds of BPA were used to make polycarbonate and other related products yearly (vom Saal and Welsons, 2006). By July 2005, there were 109 published studies that indicated significant effects of low doses of BPA in experimental animals including adverse effects at blood levels in animals within and below the average levels in human bloods. Furthermore, forty studies indicated effects below the reference dose of 50 $\mu$ g/kg/day. Agencies like the United States FDA and EPA consider that this dose is safe for the public.

Many studies had indicated concern on BPA at low dosage concentrations. While only several published studies, all funded by the chemical industry suggested that BPA has no significant toxicological effects.

Many studies have indicated that BPA is a chemical with a much higher estrogenic potential than previously reported by corporations and regulatory agencies.

Furthermore, BPA may cause some unique types of toxic effects that involve molecular mechanisms. BPA has the paradoxical effect to block the beneficial effects of estradiol on neuronal synapse formation (MacLusky et al., 2005). BPA has the potential to disrupt thyroid hormone action (Zoeller et al., 2005).

Very low dosage of BPA (in the order of ppt) can cause proliferation of human prostate cancer cells via binding to a mutant form. However, higher dosage (in the order of ppb) has shown no effect (Wetherill et al., 2002).

The National Toxicology Program (NTP) review panel believed that there was credible evidence for effects of BPA in the low dose range. Cautiously, the NTP panel recommended that the current testing paradigm utilized for monitoring reproductive and developmental toxicity should be reviewed if changes are necessary for dose selection, animal model selection, animals' age and endocrine active agents (NTP, 2001).

The US-EPA ignored this recommendation and stated that more research is needed. Furthermore, there is no regulatory action against Bisphenol-A since toxicological models and mechanisms are not well understood (EPA, 2002).

It has been suggested that all toxicological studies be conducted by regulatory agencies (vom Saal and Welshons, 2006). More specifically, this should examine the use of BPA in foods & beverages and the regulation of BPA containing products in the landfill. It has been found that the blood levels of BPA in human fetuses are greater than those BPA levels in mice due to maternal administration. Since these BPA blood levels can cause adverse effects in mice, then the same trend may be expected for humans (Zalko et al., 2003). In a similar study (Thacker, 2006), researchers exposed fetal rats to BPA based on similar levels found in humans. Later, they found that the male rats had a modified DNA where the methylation pattern changed. This changed pattern leads to greater chances of developing prostate cancer.

Studies conducted in Japan and in the United States suggested that BPA has significant toxicological effects. In both studies, the researchers indicated that BPA accounts for most of the estrogenic activity that leaches from soil to the environment (vom Saal and Welshons, 2006).

Although there are not many published studies on human health effects due to BPA exposure, there are only two epidemiological studies that potentially link BPA blood levels with ovarian diseases and pregnancy-miscarriages (Sugiura-Ogasawara et al., 2005).

Many industrial scientists believe that human exposure to BPA is 100 to 1000 times lower than the levels allowed by the government (vom Saal and Welshons, 2006). Human exposure levels are one million times lower than those levels showed to be safe in experiments related to multiple generations of lab animals.

**Table 8. History of different events related to the development of BPA toxicology (Bayer AG Plastics Business Group, 1999).**

Study or event	Results	reference
Estrogen like effect: on injection of high doses under the skin or into the abdomen	Oestrogenic effect	Dodds and Lawson, 1936
fertility study: multiple oral doses	No oestrogenic effect	Bayer AG Plastics Business Group, 1999
Oral kinetics study	rapid metabolism and excretion	Knaak and Sullivan, 1966
Fertility studies: oral doses	No oestrogenic effect	Bayer AG Plastics Business Group, 1999
Fertility studies: oral doses	No fertility impairment	Bayer AG Plastics Business Group, 1999
Carcinogenicity study: oral doses	No oestrogenic effect	Bayer AG Plastics Business Group, 1999
Carcinogenicity study: oral doses	No Carcinogenic effect	Bayer AG Plastics Business Group, 1999
Teratogenicity studies: oral doses	No oestrogenic effect	Bayer AG Plastics Business Group, 1999
Teratogenicity studies: oral doses	No teragenic effect	Bayer AG Plastics Business Group, 1999
Multigeneration study: oral doses	No fertility impairment	Bayer AG Plastics Business Group, 1999
Kinetics study: high oral doses, scarcely any free BPA in the body	rapid excretion	Pottenger et al., 1997
One-generation study: " Estrogen effects" with 2 and 20 ug/kg/d oral	Oestrogenic effect	Nagel et al., 1997
One-generation study: comprehensive follow up	No oestrogenic effect	Ashby and Tinwell, 1998; Cagen et al., 1999
Chemical exposure to rats a low dosage up to 250 ng/kg/day	Leaching BPA can alter female brains	Thacker, 2006
Review: Fourty toxicological studies indicated effects below 50 ug/kg/day	EPA/FDA considers safe for public	vom Saal and Welshons, 2006

## CHAPTER 10 - CONCLUSIONS

Based on preliminary safety assessment, polycarbonate is safe if used properly and under daily normal conditions. These normal conditions exclude polycarbonate exposure to strong acid/basic media and high temperatures.

Hydrolysis is the most common degradation pathway for polycarbonate in which higher content of byproducts is obtained. The thermal and photo degradation of polycarbonate are more complex processes in which a lower yield of complex products is obtained.

Polycarbonate shows resistance to a variety of chemicals, industrial oils, greases, waxes and adhesives. This property makes it attractive for food and medicine storage applications.

A combination of thermal and mechanical recycling is the ideal way to treat polycarbonate waste. Many industries would develop or improve new technologies for polycarbonate recycling combining these two principles.

Phosphoric sodium salts are probably the most effective ones used in a basic aqueous media for BPA leaching (nanogram range) from polycarbonate. Therefore, human fluids are also effective for BPA leaching from polycarbonate since these salts are found in human serum.

The literature indicates that small amounts of BPA can enter the environment from many sources such as manufacturing, use, recycling and disposal of polycarbonate. Microbial biodegradation is found in water and soil, and this leads to lower concentrations of BPA.

The environmental concentrations are almost always below the known thresholds for harmful effects on humans and the environment based on test protocols and current regulatory concentrations.

Most ready, inherent and simulation tests for environment fate assessment are indicating that BPA is highly biodegradable to carbon dioxide thanks to existence of natural organisms that can digest BPA.

The EQC model indicates that BPA would be more distributed to soil than water under equilibrium and non-equilibrium conditions. Air would be always the compartment with least BPA distribution. Furthermore, most BPA present in soil or water would start biodegrading in a period of 10 days.

Relevant European environmental agencies and advisory committees have classified BPA as a compound with no hormonal effects and overall not being a health hazard if the thresholds are complied with. This is on the basis of the extensive data available.

Animal pharmacological studies indicated no estrogen-like effects, during life oral intake of high dosages of BPA. Suspected endocrine effects in humans and their harmful consequences have not been verified, even in the lowest dose range.

Based on the current scientific knowledge, BPA is not a potential hazard to humans and the environment to the extent that the manufacturing, processing and usage of BPA should be discontinued.

BPA was selected together with natural and synthetic estrogens for health and safety studies because it is known to show a positive effect in the in vitro tests used for reproductive studies that are of concern to several governmental agencies.

Extensive research conducted for half century indicates that there are no human health concerns from exposure to low dosages of BPA that are associated with current products.



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## **Appendix A - BISPHENOL- A MSDS**

Bisphenol A (BPA)

Material Safety Data Sheet (Hexion Specialty Chemicals, 2005)

Version 12.2 Print Date 07/01/2005, Revision Date 06/25/2005

### **SECTION 1. IDENTIFICATION OF THE SUBSTANCE/PREPARATION AND OF THE COMPANY/UNDERTAKING**

Trade name : Bisphenol A - 157

Product code : U8926

MSDS Number : 304

Product Type : Chemical intermediate.

Company : Hexion Specialty Chemicals, Inc.

P. O. Box 4500

Houston, TX 77210

USA

Telephone : (832) 486-6700

Emergency telephone number

CHEMTREC US Domestic (800) 424-9300

CHEMTREC International (703) 527-3887

### **SECTION 2. COMPOSITION/INFORMATION ON INGREDIENTS**

Product Group: Phenol derivative.

**Chemical Name CAS-No. Weight %**

4,4'-Isopropylidenebisphenol 80-05-7 100 %

### **SECTION 3. HAZARDS IDENTIFICATION**

#### **Emergency Overview**

Human health hazards: Irritating to eyes, respiratory system and skin. May cause

sensitization by skin contact.

Safety hazards : Danger of dust explosion when ground to a small particle size.

#### **SECTION 4. FIRST AID MEASURES**

Inhalation: Remove to fresh air.

Skin contact : Remove contaminated clothing. Wash skin with water using soap if available. If persistent irritation occurs, obtain medical attention.

Eye contact : DO NOT DELAY. Flush eye with water. OBTAIN MEDICAL ATTENTION IMMEDIATELY.

Ingestion: Do not induce vomiting. If rapid recovery does not occur, obtain medical attention.

#### **Notes to physician**

Symptoms : Irritation of the skin, eyes and respiratory tract

Treatment : Dermatitis may result from prolonged or repeated exposure. If skin sensitisation has developed and a causal relationship has been confirmed, further exposure should not be allowed.

#### **SECTION 5. FIRE-FIGHTING MEASURES**

Unsuitable extinguishing media

: Water in a jet.

Suitable extinguishing media

: Foam, water spray or fog. Dry chemical powder, carbon dioxide, sand or earth may be used for small fires only. Specific hazards during fire fighting

: Not classified as flammable but will burn. Hazardous combustion products may include carbon monoxide Explosive dust clouds may be produced.

Special protective equipment for fire-fighters

: Full protective clothing and self-contained breathing apparatus.

#### **SECTION 6. ACCIDENTAL RELEASE MEASURES**

Personal precautions : Avoid raising a dust cloud.

Avoid contact with skin, eyes, clothing. Do not breathe dust

Environmental precautions : Prevent from entering into drains, ditches or rivers.

Inform the local authorities if this cannot be prevented.

Clean-up methods – small spillage

: Shovel up and place in a labelled, sealable container for subsequent safe disposal.

Clean-up methods – large spillage

: Transfer to a labelled container for product recovery or safe disposal.

Additional advice : Notify authorities if any exposures to the general public or environment occurs or is likely to occur.

See Section 13 for information on disposal.

## **SECTION 7. HANDLING AND STORAGE**

### **Handling**

Advice on safe handling: Avoid contact with skin, eyes and clothing. Do not breathe dust. Avoid generation or accumulation of dusts. Earth all equipment.

Take precautionary measures against static discharges.

### **Storage**

Requirements for storage areas and containers

: Use nitrogen blanketing or tank air/desiccant dryers.

Storage temperature :  $\leq 60\text{ }^{\circ}\text{C}$  ( $\leq 140\text{ }^{\circ}\text{F}$ )

## **SECTION 8. EXPOSURE CONTROLS / PERSONAL PROTECTION**

Protective measures : Wear dust-tight monogoggles, PVC gloves, gauntlet type, disposable one-piece uncoated overall without integral hood, safety shoes or boots - chemical resistant

If there is a risk of inhalation of dusts, wear a NIOSH approved respirator with P100 filters.

Engineering measures: Use local exhaust ventilation.

### **Exposure Guidelines**

Components with workplace control parameters

Regulation Exposure time Value Remarks

4,4'- Isopropylidenebisphenol

ACGIH None established.

DUST, RESPIRABLE

DUST

OSHA PEL 5 mg/m<sup>3</sup>

ACGIH TLV 5 mg/m<sup>3</sup>

DUST, TOTAL DUST OSHA PEL 15 mg/m<sup>3</sup>

ACGIH TLV 10 mg/m<sup>3</sup>

## **SECTION 9. PHYSICAL AND CHEMICAL PROPERTIES**

Form : Flake Solid

Colour : White

Odour : Mild Phenolic

Melting / freezing point : 153 - 156 °C (307 - 313 °F)

Boiling point : 220 °C (428 °F)

Flash point : 207 °C (405 °F) (COC)

Vapour pressure : 27 Pa at 170 °C (338 °F)

Density : 1,170 g/cm<sup>3</sup> at 25 °C (77 °F)

Solubility in water: Slightly soluble.

## **SECTION 10. STABILITY AND REACTIVITY**

Conditions to avoid : None known.

Materials to avoid : None known.

Hazardous decomposition products

: None expected under normal use conditions.

Hazardous reactions : Stable under normal use conditions.

## **SECTION 11. TOXICOLOGICAL INFORMATION**

Acute oral toxicity : LD50 - > 2,000 mg/kg (Rat)

Low toxicity, LD50 > 2000 mg/kg.

Acute dermal toxicity : LD50 - > 2,000 mg/kg (Rabbit)

Low toxicity, LD50 > 2000 mg/kg.

Acute inhalation toxicity : LC50 - > 170 mg/m<sup>3</sup> (Rat)

Low toxicity, LC50 > 5 mg/l., Irritant.

### **Chronic Health Hazard**

Components Concentration Regulation Value Remarks

4,4'-Isopropylidenebisphenol

100 % US. IARC Monographs on Occupational Exposures to Chemical Agents

This component has not been classified by the International Agency for Research on Cancer (IARC).

Eye irritation : Slightly irritating to the eyes.

Skin irritation : Slightly irritating to the skin.

Sensitization : May cause skin sensitization.

Repeated dose toxicity : Repeated exposure affects the respiratory system.

Effects were seen at high doses only.

Carcinogenicity : Not a carcinogen.

Toxicity to reproduction : Does not impair fertility.

Mutagenicity : Not mutagenic.

Human effects : May cause skin sensitization.

See Section 4 for information regarding acute effects to humans.

Development toxicity : Development toxicity

Basis for assessment : Information given is based on product data.

### **Potential Health Effects**

Skin : May cause sensitization by skin contact.

## **SECTION 12. ECOLOGICAL INFORMATION**

### **Elimination information (persistence and degradability)**

Biodegradability : Readily biodegradable.

Bioaccumulation : Does not bioaccumulate significantly.

### **Ecotoxicity effects**

Toxicity to fish : Toxic,  $1 < LC/EC/IC\ 50 \leq 10$  mg/l .

Toxicity to algae : Toxic,  $1 < LC/EC/IC\ 50 \leq 10$  mg/l .

Acute toxicity - invertebrates

: Toxic,  $1 < LC/EC/IC\ 50 \leq 10$  mg/l .

Sewage treatment : Slightly toxic,  $10 < LC/EC/IC\ 50 \leq 100$  mg/l .

Basis for assessment : Information given is based on product data.

### **SECTION 13. DISPOSAL CONSIDERATIONS**

Product disposal : If this material becomes a waste, it would not be a hazardous waste by RCRA criteria (40 CFR 261). Place in an appropriate disposal facility in compliance with local and federal regulations.

### **SECTION 14. TRANSPORT INFORMATION**

#### **CFR\_RAIL**

NOT REGULATED FOR TRANSPORT

#### **CFR\_ROAD**

NOT REGULATED FOR TRANSPORT

#### **IATA\_C**

NOT REGULATED FOR TRANSPORT

#### **IMDG**

NOT REGULATED FOR TRANSPORT

### **SECTION 15. REGULATORY INFORMATION**

The regulatory information is not intended to be comprehensive. Other regulations may apply to this material.

#### **Notification status**

AICS : y

DSL : y

INV (CN) : y

ENCS (JP) : y

TSCA : y

EINECS : y

KECI (KR) : y

PICCS (PH) : y

**US. EPA CERCLA Hazardous Substances (40 CFR 302)**

4,4'-Isopropylidenebisphenol No RQ

**US. EPA Emergency Planning and Community Right-To-Know Act (EPCRA)**

**SARA Title III**

**Section 313 Toxic Chemicals (40 CFR 372.65) - Supplier Notification Required**

4,4'-Isopropylidenebisphenol De minimis concentration: 1.0 %

The mixture or trade name product contains a toxic chemical or chemicals subject to the reporting requirements of Section 313 of Title III of the Superfund Amendments and Reauthorization Act of 1986 and 40 CFR part 372.

**US. EPA Emergency Planning and Community Right-To-Know Act (EPCRA)**

**SARA Title III**

**Section 302 Extremely Hazardous Substance (40 CFR 355, Appendix A)**

4,4'-Isopropylidenebisphenol Threshold Planning Quantity: No TPQ

4,4'-Isopropylidenebisphenol Reportable quantity: No RQ

**New Jersey Right-To-Know Chemical List**

4,4'-Isopropylidenebisphenol Listed.

**Pennsylvania Right-To-Know Chemical List**

4,4'-Isopropylidenebisphenol Environmental hazard.

**Massachusetts Right-To-Know Chemical List**

4,4'-Isopropylidenebisphenol Not Listed

**HMIS Rating** : Health:

Fire:

Reactivity:

2

1

0

**SECTION 16. OTHER INFORMATION**

The information provided in this Safety Data Sheet is correct to the best of our knowledge, information and belief at the date of its publication. The information given is designed only as a guidance for safe handling, use, processing, storage, transportation, disposal and release and is not to be considered a warranty or quality specification. The information relates only to the specific material designated and may not be valid for such material used in combination with any other materials or in any process, unless specified in the text. A vertical bar ( | ) in the left margin indicates an amendment from the previous version.



## **Appendix B - POLYCARBONATE MSDS**

POLYCARBONATE

MATERIAL SAFETY DATA SHEET (Bayer Material Science, 2006)

### **I. PRODUCT IDENTIFICATION**

**PRODUCT NAME:** Polycarbonate

**PHONE NUMBERS:**

BAYER EMERGENCY: (412) 923-1800

BAYER INFORMATION: 1-800-628-5084

CHEMTREC: 1-800-424-9300

### **II. PHYSICAL AND CHEMICAL PROPERTIES**

**APPEARANCE:** Solid tint

**ODOR:** Slight

**PERCENT VOLATILES:** N/A

**MELTING POINT:** 428 – 446°F (220-230°C)

**SOLUBILITY IN WATER:** Insoluble

**SPECIFIC GRAVITY:** 1.2

### **III. STABILITY AND REACTIVITY**

**STABILITY:** Stable

**MATERIALS TO AVOID:** None known

### **IV. EXPOSURE CONTROLS/PERSONAL PROTECTION**

**VENTILATION:** Provide natural or mechanical ventilation to control exposure levels below airborne exposure limits. Local mechanical exhaust ventilation should be used at sources of air contamination, such as open process equipment, or during purging operations, to capture gases and fumes that may be emitted. Standard reference sources regarding industrial ventilation should be consulted for guidance about adequate ventilation. In the event of thermal decomposition from overheating the product, evacuate the work area, shut down equipment and

provide general ventilation to the room prior to reoccupying.

#### **PROTECTIVE EQUIPMENT**

**SKIN:** None required but fabric gloves are recommended when handling molten material

#### **IV. EXPOSURE CONTROLS/PERSONAL PROTECTION**

**EYE:** Safety glasses are recommended as a good industrial hygiene and safety practice.

**RESPIRATOR:** NIOSH/MSHA – approved dust respirator recommended if the airborne dust concentration is near or exceeds the nuisance dust exposure limits.

#### **ADDITIONAL PROTECTIVE MEASURES:**

The greatest potential for injury occurs when working with molten polymeric resins. During this type of operation it is essential that all workers in the immediate area wear eye and skin protection as protection from thermal burns. Purgings should be collected as small flat thin shapes or thin strands to allow for rapid cooling. Precautions should be taken against auto-ignition of hot, thick masses of the plastic. Quench with water. Grinder dust is an exposure hazard.

#### **EXPOSURE GUIDELINES:**

##### **INGREDIENT AGENCY VALUE**

Nuisance Dust OSHA-PEL 15mg/m<sup>3</sup>

Respirable Dust OSHA-PEL 5mg/m<sup>3</sup>

#### **V. HEALTH HAZARDS IDENTIFICATION**

##### **ACUTE OR IMMEDIATE EFFECTS**

**SKIN:** Contact with hot material will cause thermal burns

**EYES:** Mechanical irritation to the eyes may occur due to exposure to fines. Eyes may become red and scratchy and may tear.

**INHALATION:** Toxic gases/fumes given off during burning or thermal decomposition cause respiratory irritation

**CHRONIC/CARCINOGENICITY:** Not listed as a carcinogen

## **VI. FIRST AID MEASURES**

**SKIN:** Wash affected areas with soap and water. See a physician if thermal burn occurs

**EYES:** Flush with plenty of lukewarm water. See a physician or ophthalmologist for follow-up if irritation is present and persists

**INHALATION:** Move to an area free from risk of further exposure. Give oxygen or artificial respiration as needed. Obtain medical attention

## **VII. FIRE FIGHTING MEASURES**

**AUTOIGNITION TEMPERATURE:** Above 842°F (450°C) ASTM D-1929B

## **VII. FIRE FIGHTING MEASURES**

### **HAZARDOUS PRODUCTS OF COMBUSTION:**

Carbon monoxide, carbon dioxide, bisphenol A, diphenyl carbonate, phenol and phenol derivatives. Traces of aliphatic and aromatic hydrocarbons, aldehydes and acids.

**EXTINGUISHING MEDIA:** Water; carbon dioxide, dry chemical, foam

### **SPECIAL FIRE FIGHTING INSTRUCTIONS/PRECAUTIONS:**

Full emergency equipment with self-contained breathing apparatus must be worn by Firefighters.

## **VIII. ACCIDENTAL RELEASE MEASURES**

### **SPILL OR RELEASE:**

If molten material is spilled, allow it to solidify. Remove material mechanically by a method which minimizes the generation of airborne dust and place in appropriately marked containers.

## **IX. HANDLING AND STORAGE**

### **HANDLING:**

When handling flaked material or during secondary operations, vent storage bins, conveyors, dust collectors, etc. ground handling equipment, keep open flames, sparks and

heat away from dusty areas. Maintain highest standards of housekeeping to prevent accumulation of dust.

**STORAGE:**

Max 200°F (93°C) material should be stored in a clean, dry environment in sealed containers. Material must be dried before processing

**X. DISPOSAL CONSIDERATIONS**

**DISPOSAL:** Material may be incinerated or landfilled in compliance with Federal, State, Provincial and Local environmental control regulations.

**XI. DISCLAIMER OF EXPRESSED AND IMPLIED WARRANTIES**

The information presented in the Material Safety Data Sheet is based on data believed to be accurate as of the date this Material Safety Data Sheet was prepared. HOWEVER, NO WARRANTY OF MERCHANTABILITY, FITNESS FOR ANY PARTICULAR PURPOSE, OR ANY OTHER WARRANTY IS EXPRESSED OR IS TO BE IMPLIED REGARDING THE ACCURACY OR COMPLETENESS OF THE INFORMATION PROVIDED ABOVE, THE RESULTS TO BE OBTAINED FROM THE USE OF THIS INFORMATION OR THE PRODUCT, THE SAFETY OF THIS PRODUCT, OR THE HAZARDS RELATED TO ITS USE. No responsibility is assumed for any damage or injury resulting from abnormal use or from any failure to adhere to recommended practices. The information provided above, and the product, are furnished on the condition that the person receiving them shall make their own determination as to the suitability of the product for their particular purpose and on the condition that they assume the risk of their use. In addition, no authorization is given nor implied to practice any patented invention without a license.