POLYCARBONATES – SYNTHESIS, PROPERTIES AND ENVIRONMENTAL IMPACT

K. Wnuczek, B. Podkościelna

Maria Curie-Skłodowska University, Institute of Chemical Science, Faculty of Chemistry, Department of Polymer Chemistry, Gliniana 33, 20-614, Lublin, Poland

Abstract

In this work a synthesis of commercially available polycarbonates as well as selected applications of these unique polymers are discussed. A traditional method of synthesis using phosgene and Bisphenol A, as well as methods based on the transesterification of methyl carbonate and diphenyl carbonate are presented. The advantages and disadvantages of the above procedures are shown. The possibilities of replacing the phosgene technology, used by most polycarbonate manufacturers, with more environmentally friendly methods were assessed. In addition, the work includes general characteristics of polycarbonates and their wide application.

Keywords: polycarbonate, Bisphenol A, phosgene

Introduction

Polycarbonates are materials we encounter every day. It is a class of thermoplastic polymers that are formally esters of carbonic acid. They have a lot of advantages such as hardness, ductility, rigidity, transparency, toughness and excellent mechanical properties. These materials are amorphous and polar polymers (Hammani et al. 2012, Shu et al. 2019). Polycarbonate, as a commercial thermoplastic engineering plastic, has been widely applied in electronics, medical equipment, food packaging, automotive industries, aerospace because of its unique thermal, mechanical, electrical and optical properties (Hauenstein et al. 2016, Zhencai et. al 2020). Due to this set of favorable properties, polycarbonates have many applications. The most advantageous properties, compared to other thermoplastics, are as follows: high impact strength, good dielectric properties, good dimensional stability, wide operating temperature range, creep strength, low water absorption, and self-extinguishing tendency. In addition, most polycarbonates, are non-toxic, very hard, abrasion and chemical resistant materials (Schnell 1964, Tabell et al. 1959, Hubacher 1957).

A number of properties of this polymer depends on the chemical structure of a polycarbonate particle. Polycarbonate macromolecules are characterized by high stiffness, limited rotation of aromatic rings and relatively long segments without polar groups (Serini 2000, Distaso et al. 2006, Darensbourg et al. 2011). The general characteristics of polycarbonates have been well described in literature. The thermal properties of unmodified polycarbonate, which can operate in the temperature range from minus 100°C to plus 130°C, are well understood. The melting point is high and exceeds 220°C. The decomposition temperature is above 320°C but the polymer may start to decompose earlier due to additives (e.g. presence of water). Polycarbonate is considered to be a self-extinguishing material, i.e. one that ignites in a flame and tends to go out when the flame is removed (Schnell 1964, Christopher 1962).

To study the behavior of polycarbonates, thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) are used. Polycarbonate distinguishes itself from the thermoplastic polymers with exceptionally favorable mechanical properties. They depend on the average molecular weight. When it comes to the construction of polycarbonates, we include them among polyesters. So they are generally not resistant to alkaline substances that will cause the hydrolysis of ester bonds. These materials are resistant to acid substances (including organic acids) and neutral salt solutions (Wnuczek et al. 2021, Lee 1964).

Bisphenol A polycarbonate is the carbonic acid polyester derived from 2,2-bis(4-hydroxyphenyl)propane. It is the best known resin polycarbonic material of this type because of its good mechanical, thermal and electrical properties, as well as being made from easily available raw materials. Most of the commercially available polycarbonates have been synthesized using Bisphenol A. This compound is a precursor of important plastics, primarily certain polycarbonates and epoxy resins. Plastic materials based on Bisphenol A are clear and tough and are used to produce a variety of common consumer goods, such as plastic bottles, food storage containers, sports equipment. Epoxy resins derived from Bisphenol A are used to manufacture water pipes, serve as coatings on the inside of many food and beverage cans and thermal paper such as the one used in sales receipts. The use of Bisphenol A for products that will come into contact with food is still controversial and raises many concerns (Pivnenko et al. 2015). Bisphenol A is a minor skin irritant but not as much as phenol (Fiege et al. 2000). Bisphenol A is a xenoestrogen with hormone-like properties. Although the effect is very weak, the pervasiveness of Bisphenol A - based materials raises concerns. However, the multitude of advantages of these plastic materials is so great that in industrial applications, Bisphenol A is still irreplaceable. For this reason the search for new components for the synthesis of polycarbonates is very important (Thoene et al. 2020, Egan 2014)

Overall, polycarbonates are a very promising group of polymers. Seeking new polycarbonates with special properties, combining mechanical and thermal resistance, as well as light construction, is still a challenge for scientists. In addition, ecological methods with the use of safe technologies are being searched for. That is why the production of polycarbonates would increasingly fit the term of "green chemistry".

Production

The main polycarbonate material is produced by the phosgene method by the reaction of bisphenol A and phosgene COCl₂ (carbon dichloride oxide,

dichloromethanal). Phosgene is an essential raw material for the synthesis of polycarbonate by the interfacial polycondensation method and for the synthesis of phenyl carbonate, which in turn is a raw material for the preparation of polycarbonate by the ester exchange method.



Figure 1. Scheme of reaction of bisphenol A and phosgene.

The first stage of the synthesis involves the treatment of Bisphenol A with sodium hydroxide which deprotonates the hydroxyl groups of Bisphenol A. The diphenoxide reacts with phosgene to form the chloroformate that is then attacked by another phenoxide (Serini 2000)

 $(C_{6}H_{4}(OH))CMe_{2} + 2NaOH \rightarrow [Na_{2}(C_{6}H_{4}O_{2})CMe_{2}] + 2 H_{2}O$ $[Na_{2}(C_{6}H_{4}O_{2})CMe_{2} + COCl_{2} \rightarrow [OC(C_{6}H_{4}O_{2})CMe_{2}] + 2NaCl$

Synthesis by direct phosgenation is performed either in a system of two solvents that are immiscible with each other (a kind of interfacial polycondensation) or in a single-phase system using pyridines. Pyridine acts as a solvent and hydrogen chloride acceptor. However, the traditional synthetic process of polycarbonates from Bisphenol A with phosgene or diphenyl carbonate face problems because phosgene is a highly toxic compound and Bisphenol A is also a toxic substance that affects the health of human beings, especially children (Zhencai 2020, Darensbourg et al. 2011, Christopher et al. 1962, Lee 1964, Ozyildiz et al. 2019, Dong et al. 2019, Samikannu et al. 2019). The traditional synthetic process of polycarbonates from Bisphenol A and phosgene contributes to environmental pollution due to toxic raw materials and large-scale use of dichloromethanal. The hydrochloric acid is scavenged with aqueous base. Therefore, the development of green non-phosgene routes for the synthesis of polycarbonates is urgently needed (Erythropel et al. 2018, Lounsbury et al. 2018, Clarke et al. 2018, Rogers et al. 2019, Anastas et al. 2010, He et al. 2013).

Transesterification of diphenyl carbonate with Bisphenol A is an ester exchange method, which is discussed for industrial application in the production of polycarbonate (next to the method of direct phosgenation in solvents). This method has a number of advantages. The polymer obtained by ester exchange is suitable for granulation because it is in molten state after the end of the process. In addition, this method does not use solvents, which allows for high yield. The waste product in transesterification is phenol, which can be used for other purposes (Schnel 1964, Tarbell 1959, Serini 2000). Unfortunately, phenol, a byproduct of the reaction, can only be removed under severe conditions (Clarke et al. 2018).

$$(C_6H_4(OH))CMe_2 + (C_6H_5O)_2CO \rightarrow [OC((C_6H_4)_2O)CMe_2] + 2C_6H_5OH_2O(C_6H_4)O(C_6H_4)O(C_6H_4)O(C_6H_4)O(C_6H_4)O(C_6H_4)O(C_6H_4)O(C_6H_4)O(C_6H_4)O(C_6H_4)O(C_6H_4)O(C_6H_4)O(C_6$$

$$n HO - (CH_3) - OH + 2n (CH_3) - OH +$$

Figure 2. Scheme of transesterification reaction of bisphenol A and diphenyl carbonate.

Dimethyl carbonate can react with Bisphenol A to prepare a precursor of polycarbonate. Transesterification of dimethyl carbonate with Bisphenol is ecological because dimethyl carbonate is qualified as a green reagent. Moreover, the byproduct methanol can be easily removed in low temperature. Dimethyl carbonate is not only a less toxic organic synthesis ingredient but also a raw material for the synthesis of diphenyl carbonate (Liang et al. 2019, Tong et al. 2007, Niu et al. 2007).



Figure 3. Scheme of transesterification reaction of bisphenol A and dimethyl carbonate.

Although well-developed and commercial, phosgene-free methods are complicated ones involving multiple reaction steps. Some of them are under severe equilibrium constraints (Kim et al. 2002, Tundo et al. 1988). The direct oxidative carbonylation of Bisphenol A into polycarbonate oligomers could be a promising method of non-phosgene polycarbonate synthesis because it converts CO and Bisphenol A directly to polycarbonate (Kim et al. 1999, 58-59, King 1999, Lago et al. 2016). The direct oxidative carbonylation of Bisphenol A has been reported with the use of homogeneous Pd catalysts (58).

Properties

Polycarbonates attract much attention because of their several interesting properties. There are some features that all polycarbonates have in common. They are unique in the polymer market owing to their excellent mechanical stiffness (2.0–2.4 GPa), electrical and optical properties, as well as self-extinguishing characteristics. This group is characterized by the unique high impact resistance and strength in a wide range of operating temperatures. Most polycarbonates are transparent (over 80% in visible spectrum, with a refractive index of 1.59) (58, King 1999, Lago et al. 2016). Polycarbonate, which has the advantages of ductility, rigidity, hardness, transparency, toughness and excellent mechanical properties, is an amorphous and polar thermoplastic polymer (Laurenti et al. 2016, Levchik et al. 2005, Eshaghi et al. 2014).

On account of the aromatic structure in macromolecular chains, polycarbonates show the capability of self-carbonation to some degree (Naik et al. 2012). Aliphatic polycarbonates, compared with traditional aromatic polycarbonates, have received little attention because of their worse thermal stability and high susceptibility to hydrolysis (Kuran et al. 2000). On the other hand, the aliphatic polycarbonates are getting more attention because of their biomedical application, e.g. the composition of biomedical implants and acting as drug delivery devices, due to their biodegradability, biocompatibility and low toxicity (Huang et al. 2015, Sun et al. 2016, Wnuczek et al. 2021).

Table 1. Properties of polycarbonates (Karazil et al. 2017). Table lists the mostcommonly quoted properties of PC. Table was collated from the mostrepresentative values found in different literature sources.

Property	Value
Refractive index	1.583-1.586
Transmittance [%]	89
Density [g/cm ³]	1.17-1.45
Thermal conductivity [W/m*°C]	0.19-0.21
Specific heat (J/g*°C]	1-1.2
Melting temperature [°C]	150
Glass transition temperature [°C]	147

Environmental impact

The use of Bisphenol A as a diol for the synthesis of polycarbonates is controversial. The detection of Bisphenol A in the environment and food products has been the subject of much recent research. Some studies prove that thermal treatment of any product containing Bisphenol A causes it to be released into food. Further, Bisphenol A is also found in other everyday objects, such as thermally printed paper receipts, medical devices, phones and sunglasses. It is estimated that over 100 tons of Bisphenol A are released into the environment every year (Vandenberg et al. 2009, Geens et al. 2012, Geens et al. 2011, Sun et al. 2016). Studies have shown that at temperatures above 70°C and at high humidity, polycarbonate is hydrolyzed to Bisphenol A (Bair et al. 1981).

Matrix/Reference	Concentration (µg/l or µg/kg)	
	Number of samples	Maximum
Baby bottles	6	15
Human breast milk	20	7.3
Tableware	3	2
Tap water and bottle water	>100	1
Canned food	Number of samples	Average
Fruit	70	9.8
Vegetables	305	32.4
Meat	70	69.8

Table 2. Occurrence data for Bisphenol A in food and beverages. Table sectionfrom WHO table (Raport of Joint FAO/WHO Expert Meeting 2010).

Bisphenol A is the subject of well-developed medical research. It is a known endocrine-disrupting compound. Its structural form is similar to natural hormones such as estradiol and diethylstilbestrol. It can affect the functions of the hormone estrogen by binding to estrogen receptors (Sun et al. 2016). It has been demonstrated that even in very low doses (even in concentration on picogram levels) Bisphenol A could have an impact on physiological functions of the brain, endocrine pancreas, ovaries, and reproductive organs, as well as the immune system (Cabaton et al. 2011). Recently, some new studies have suggested that Bisphenol A is associated with global diseases such as obesity, diabetes and also cardiovascular diseases, neurotoxicity and behavioral problems (Michałowicz et al. 2014). The large production of plastics, including polycarbonates, creates a worldwide problem with waste disposal. Research on the degradation of polycarbonates by bacteria has been carried out since the 1990s. Soil bacteria are capable of degrading aliphatic polycarbonates such as polyhexamethylene carbonate and polyethylene carbonate (Suyama et al. 1998). When it comes to thermal degradation, polycarbonate decomposes in high temperatures. The polycarbonate waste decomposes to form solid, liquid and gaseous pollutants (Collin et al. 2012). In the presence of UV light, oxidation of polycarbonates can occur, leading to the formation of compounds such as phenols, ketones and other unsaturated compounds.

Application

The use of polycarbonates is very wide. We can really meet them anywhere. They are present in every aspect of our lives. Their unique properties mean that they dominate many industries. Generally, polycarbonates are used wherever transparency, thermal resistance and high impact strength is required (Wnuczek et al. 2021).

Polycarbonates are widespread in the household both in construction and in everyday use items. Currently, polycarbonate is increasingly replacing glass and is successful in various areas of construction. Polycarbonate is used to make the layers of panes resistant not only to breaking, but also to fire. In the construction industry these compounds are applied to manufacture glazing, roofing sheets and sound walls. In addition polycarbonate can also be found in relays, contacts, housings and elements of household appliances (60, Andrzejewski et al. 2018).

Electrical devices also contain polycarbonate in mounting frames. Polycarbonate is mainly used for electronic appliances to ensure their safety. Being a good electrical insulator and having heat-resistant and flame-retardant properties, it is used in various products associated with electrical and telecommunications hardware. Some major smartphone manufacturers use polycarbonate for finishing their products (Serini 2000, King 1999).

A major application of polycarbonate is the production of Compact Discs (CD), Digital Video Discs (DVD) and Blu-ray Discs. These discs are produced by injection molding polycarbonate into a mold cavity with two sides. One has a metal stamper containing a negative image of the disc data, while the other side is a mirrored surface (Suna et al. 2016).

Pure polycarbonate is used in such places as airplanes, astronaut helmets, or even in advertising panels, oil pumps, filters, lamp shades, control devices and security components (Feng et al 2012). In the streets there are large products such as: street letter boxes, switch cabinets, mounting plates, lamp posts, which are made from polycarbonates (Andrzejewski et al. 2018). Research is ongoing on the use of polycarbonates for medical applications (Feng et al 2012) and a variety of healthcare products such as dental sealants and tooth coatings (Li et al. 2015). The second largest consumers of polycarbonates are the manufacturers of food packing, drink bottles, water supply pipes (Zhu et al. 2018).

Conclusions

In summary, due to the prevalence of polycarbonates, research on synthesis as well as preparation of new materials based on polycarbonates and their use is very promising. Thanks to their excellent properties, this polymer group has many applications, both in daily life and in many sectors of industry. To conclude, these plastics have excellent mechanical and thermal properties (in particular impact resistance) which makes them very versatile. However, their most important feature is that they are transparent and durable. Polycarbonate is used in every place where a transparent material with extremely high mechanical parameters is needed. All in all, polycarbonates are a promising group of polymers that should be further developed with a special focus on improving its environmental performance.

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