JACI Textbook | Learning from social practice cases that have received the GSC Awards

Green and
Sustainable
Chemistry

Introduction to GSC

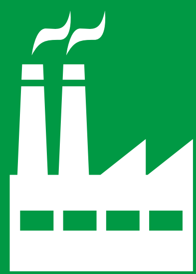
No.2 Revised Edition

Received the Minister of Economy, Trade and Industry Award of the 2nd GSC Awards (2002)

Novel Non-phosgene Polycarbonate Production Process Using By-product CO_2 as Starting Material

Asahi Kasei Corporation

Asahi Kasei Corporation has successfully produced a polycarbonate resin by using the by-product carbon dioxide, which has been emitted into the atmosphere until now, as a starting material.
This production process does not use toxic materials such as phosgene as a starting material, which suppresses generation of wastewater and waste products.
This is a breakthrough process with excellent environmental, social, and economic benefits.



Outline of the GSC Awards and the award-winning company

The GSC Awards are bestowed upon individuals and organizations for their contribution toward the advancement of Green and Sustainable Chemistry (GSC), and several awards are conferred each year. Innovations that contribute toward the development of sustainable industrial technology are awarded the Minister of Economy, Trade and Industry Award; those that contribute toward the development and promotion of science are awarded the Minister of Education, Culture, Sports, Science and Technology Award; those that contribute toward the overall reduction of environmental impact are awarded the Minister of the Environment Award; while small and medium-sized businesses that contribute toward the development of industrial technology are awarded the Small Business Award (established in 2015; renamed to Venture Company Award, Small and Medium-sized Company Award in 2018 and Venture, Small and Medium sized Company Award in 2022). Additionally, innovations that exhibit high potential for future development are awarded the Incentive Award.

Asahi Kasei Corporation is a diversified manufacturer centered on chemistry (headquarters: Chiyoda-ku, Tokyo) founded in 1887. Asahi Kasei's wide range of businesses includes chemicals, fibers, housing, building materials, electronics, pharmaceuticals and medicine.

Objective of the textbook series

Global issues, in areas such as resources and energy, global warming, water and food have increasingly become major and complicated concerns. Innovations for achieving both environmental conservation and economic development are needed in order to resolve these issues and realize the sustainable development of society, and expectations for GSC continue to rise. In this textbook series, technologies and products that have received the GSC Awards given to great achievements contributing to the progress of GSC are explained, so that everyone can understand "what is GSC?" and take responsibility for realizing a sustainable society.

*Please refer to The Statement 2015 at the end of the textbook.

What is GSC?

Acronym for Green and Sustainable Chemistry

Definition of GSC

Chemical sciences and technologies which are benign to both human health and the environment, and support the development of a sustainable society

Guidelines of GSC activities

- The chemistry community has been addressing future-oriented research and education, and development towards environmentally-benign systems, processes and products for the sustainable development of society.

- Specifically, in response to the Rio Declaration at the Earth Summit in 1992, the chemistry community has been working in a unified manner linking academia, industry and government to start up Green and Sustainable Chemistry and engage in its activities, in order to advance the pursuance of coexistence with the global environment, the satisfaction of society's needs, and economic rationality. These goals should be pursued with consideration for the environment, safety and health across the life cycles of chemical products, their design, selection of raw materials, processing, use, recycling and final disposal.

- Long-term global issues, in areas such as resources and energy, global warming, water and food, and demographics have increasingly become major and complicated concerns in the present century. Therefore, expectations are growing for innovations, based on the chemical sciences, as driving forces to solve such issues and to achieve the sustainable development of society with enhanced quality of life and well-being.

- The chemistry community will live up to these expectations by strongly advancing Green and Sustainable Chemistry through global partnership and collaboration and by bridging the boundaries that separate industries, academia, governments, consumers and nations.

Examples of GSC

- The general classification is expressed in terms of a combination of the intended social contribution and the means to achieve this goal. With regard to the objectives, the efforts to achieve them have extended in stages from social challenges to difficult long-term challenges, beginning with manufacturing or utilization, and common/basic categories have also been established -

Minimization of resource consumption and maximization of the efficiency of reaction processes for production with reduced environmental impact

1. Chemical technologies and products that lead to reduction in by-product formation and avoid the use of hazardous substances
2. Separation, purification and recycling technologies that reduce the generation and emission of greenhouse gases like CO_2 or toxic/hazardous substances, thus lowering environmental impact
3. Chemical technologies and products that reduce the generation and emission to the environment of greenhouse gases like CO_2 or toxic/hazardous substances
4. Catalysts and reaction processes that realize the saving of energy and resource and improvement in product yields

Risk reduction of chemical substances beneficial to safe and secure living environment

5. Chemical technologies, products and systems that reduce waste generation
6. Chemical technologies, products and systems that inhibit the generation and emission of hazardous substances and pollutants

Challenges to solve energy, resource, food and water issues

7. Chemical technologies, products and systems to utilize low-grade heat sources, non-conventional resources, and other similar alternatives
8. Chemical technologies, products and systems whereby un-utilized energy and resources can be converted into available energy, transported and stored
9. Chemical technologies, products and systems which decrease the dependence on exhaustible resources such as fossil fuels and scarce minerals and promote the shift to renewable energy and resources, including their storage
10. Chemical technologies, products and systems that contribute to the Three R's: Reduce, Reuse and Recycle
11. Chemical technologies, products and systems that promote the efficiency of production and supply of food, and utilization of water resources

Pioneering challenges to long-term issues aiming to realize a safe, secure and sustainable society with enhanced quality of life

12. Chemical technologies, new products and new operational systems that contribute to the introduction of new social systems, for instance based on ICT, and aimed at solving social issues such as energy and resource consumption, food and water security, disaster prevention and infrastructure improvements, transportation and logistics, medical and health care, education and welfare, and other mega-trends of society
13. Chemical technologies, new products and new operational systems that contribute to the improvement of social and individual comfort whilst reducing and preferably inhibiting environmental impact

Systematization, dissemination, enlightenment and education of GSC including its metrics to be established

14. Systematization of GSC practices and concepts
15. Dissemination, enlightenment and education of GSC practices and concepts
16. Establishment and dissemination of GSC metrics

(Definition from JACI GSCN Council
https://www.jaci.or.jp/english/gscn/page_01.html)

An internationally recognized, low-cost, environmentally benign polycarbonate production process that does not use toxic phosgene

Asahi Kasei Corporation

The Minister of Economy, Trade and Industry Award of the 2nd GSC Awards (2002) was bestowed upon the “Novel Non-phosgene Polycarbonate Production Process Using By-Product CO_2 as Starting Material“ developed by Asahi Kasei Corporation. Unlike conventional polycarbonate production processes, the proposed process does not utilize toxic phosgene as the starting material. The achievement of resource and energy conservation at the same time was epoch-making. At present, more than 10 years since its inception, this technology is internationally commercialized and recognized. It is the first technology developed by a Japanese company to receive the Heroes of Chemistry Award from the American Chemical Society (in 2014). Let us analyze the details of this world-renowned polycarbonate production process.

Picture 1: Plant (built in 2002) owned by "CHIMEI-ASAHI CORPORATION," a joint venture company of Asahi Kasei with Taiwan's Chi Mei Corporation, where the first non-phosgene polycarbonate was manufactured by Asahi Kasei.

1 The Path to Technology Development

~ What were the intentions that started development toward realizing the sustainable progress of society?

*1
Phosgene ($COCl_2$): A colorless gas. Phosgene is formed from carbon monoxide (CO) produced by incomplete combustion of coal, and chlorine (Cl_2) produced by electrolysis of salt (sodium chloride, NaCl). Phosgene exhibits asphyxiating properties and is extremely toxic; therefore, it was used as a poison gas during World War I. Furthermore, this highly reactive compound is used as a synthetic starting material for polyurethane and dye.

In general, several different types of resin are labeled "plastic" (Column①). Among them, polycarbonates are polymers that contain a carbonate group in the molecular structure (Fig. 1). Polycarbonate was developed in 1959 by Bayer in Germany and GE in the United States at about the same time, and in the 1970s it became widely used due to its excellent properties. The high impact resistance of polycarbonates (approximately 200 times greater than that of glass; polycarbonates show no breakage, even when struck by a hammer) makes them particularly suitable for the fabrication of construction-site helmets, protective goggles, and industrial parts. Moreover, their transparency and resistance to deformation enables their utilization as CD and DVD substrates (which can read and write data using laser beams). With an exponential increase in the demand for optical storage media in the 1990s, the production volume of polycarbonates increased significantly.

Polycarbonates are mainly (nearly 80%) produced by the phosgenation process that uses toxic phosgene ($COCl_2$)*1 and bisphenol A as starting materials (Fig. 2, Column②). Phosgene, with extremely high reactivity, undergoes facile reaction with bisphenol A to form a carbonate group (carbonate bond).

Although the synthesis of polycarbonates involves a simple one-step reaction of phosgene and bisphenol A, the actual synthesis process is extremely complex and problematic (from the viewpoint of GSC). First of all, the process uses toxic phosgene as a starting material.

Furthermore, methylene chloride, which is suspected to be carcinogenic, is used as a solvent. Methylene chloride is highly volatile (boiling point of 40°C) which makes its recovery difficult, and dissolves easily in water which makes its recovery from wastewater difficult. Moreover, a large amount of sodium chloride is produced as a byproduct. Impurities containing chlorine remain inside the synthesized polycarbonate resin, requiring the resin to be thoroughly washed if it is to be used as an optical material, which increases the amount of wastewater. The treatment for this wastewater results in tremendous environmental impact and costs.

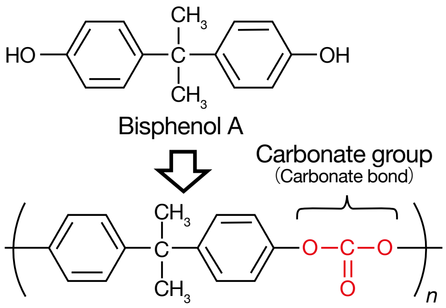


Fig. 1: Chemical formula of polycarbonates

Picture 2: Common products manufactured using polycarbonates (Photography in cooperation with the S. Nakamura Laboratory, Tokyo Institute of Technology).

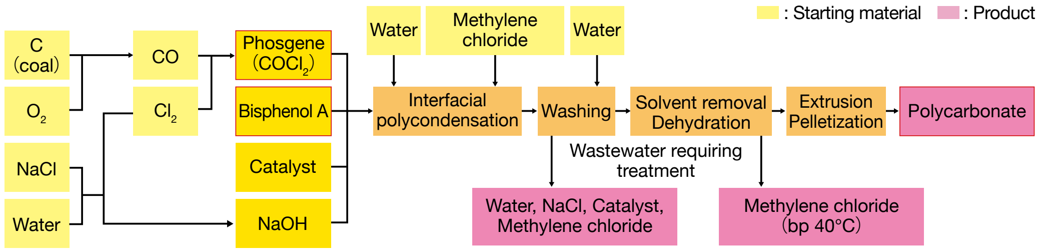


Fig. 2: Polycarbonate production by the phosgenation process

Column 1

Plastic

Plastics are macromolecular substances that can be molded into specific shapes in the presence of heat and pressure. Macromolecular substances can be categorized as natural resins (comprising hardened tree sap) and synthetic resins (derived from fossil fuels such as petroleum). Plastics are usually known as synthetic resins.

In Japan, naphtha is generally isolated from petroleum. Basic petrochemicals such as ethylene and propylene are formed from naphtha, and monomers are formed from these products to be used as a starting material for plastic. Low-molecular-weight monomers are polymerized*2 into macromolecular polymers. Various types of polymers have been synthesized using different starting materials and polymerization methods. After adding a compounding agent to polymers, the mixture can be molded into different plastic products.

Plastics can be categorized into thermoplastics (which soften upon heating, facilitating molding) and thermosetting-type plastics (which undergo irreversible structural changes on cooling after being heated, and no longer become soft). Thermoplastics include polyethylene and polystyrene, while thermosetting materials include phenol resin.

*2
Polymerization: A reaction in which a large number of monomers undergo bonding to form a polymer. A monomer is a molecule that is a unit for constituting the polymer.

Column 2

Polycarbonate production process (the conventional method)

There are two types of polycarbonate production processes: phosgenation and transesterification. In the phosgenation process, polycarbonate synthesis occurs via a polycondensation reaction*3 between bisphenol A and phosgene. This process can occur via interfacial polycondensation that involves polymerization in two phases (an organic solvent and water) or solution polycondensation that involves polymerization in a homogeneous solution. The interfacial polycondensation process is used for industrial purposes.

Phosgene is highly reactive and undergoes facile reaction with bisphenol A to form a carbonate group that is typically difficult to synthesize. Polycarbonate polymers are obtained by repeating this reaction.

In the actual synthesis, a reaction accelerator such as triethylamine and a molecular weight modifier such as t-butylphenol are added to a two-phase mixture of sodium hydroxide solution having bisphenol A dissolved thereinto and methylene chloride, and phosgene is blown into this mixture to carry out polymerization. Polymerization forms hydrogen chloride (HCl), which is neutralized by the addition of NaOH into the reaction mixture to form sodium chloride (NaCl). The formed polycarbonate dissolves in methylene chloride, so the methylene chloride is isolated and washed. Subsequently, the polycarbonate is precipitated from methylene chloride and pelletized. Moreover, a procedure for recovering the methylene chloride and sodium chloride is necessary.

This process allows polycarbonate having an arbitrary mean molecular weight to be produced under normal temperature and normal pressure, but the overall production process is very complex.

*3
Polycondensation: A reaction in which small molecules such as water (H_2O) are released from within the respective molecules which undergo polymerization. Molecules are linked to form chains while releasing small molecules to produce macromolecules.

5

Furthermore, it utilizes large amounts of toxic phosgene and methylene chloride (which are suspected carcinogens) and discharges large amounts of waste products (such as salts, catalysts, and wastewater containing organic substances such as methylene chloride), adversely affecting the environment.

The transesterification process involves polymerization via the transesterification of bisphenol A and diphenyl carbonate, which are heated and melted. It does not utilize toxic phosgene or solvents, eliminating the need for solvent recovery. After the development and initial utilization of the process, it gradually went out of use because of the poor quality of the polycarbonates generated. In later years, despite several reviews and improvements, it was never practically implemented.

2 Toward Resolution of Issues

~ What kind of technological challenges did the developers face, and how did they come up with solutions?

Non-phosgene polycarbonate production process developed by Asahi Kasei

It is extremely challenging to replace a mainstream process technology with a new alternative. Nevertheless, the expected increase in the demand for polycarbonates prompted several companies (including Asahi Kasei) to start developing alternative polycarbonate production processes without phosgene in the 1980s.

Each company strived to develop an environmentally-benign and low-cost production process. Asahi Kasei focused on "the reason why phosgene had to be used" while developing the new production process. Then, for the first time in the world, a polycarbonate production process in which carbon dioxide and ethylene oxide replaced phosgene and were reacted with bisphenol A was developed (Fig. 3).

In this process, ethylene carbonate is formed from carbon dioxide and ethylene oxide, which is then converted to diphenyl carbonate and polymerized with bisphenol A to produce polycarbonate. The byproduct ethylene glycol is the end product. This process does not use toxic phosgene or methylene chloride; instead, it utilizes carbon dioxide (discharged during the production of ethylene oxide) as the starting material. Furthermore, waste liquids and waste products are reduced so that the burden for their treatment is small, making the process an exceptional one from the viewpoint of GSC.

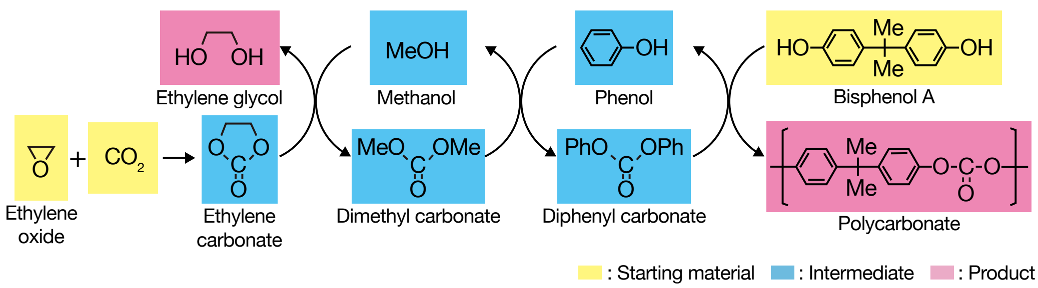


Fig. 3: Non-phosgene polycarbonate production process by Asahi Kasei

Synthesis of diphenyl carbonate using carbon dioxide as the starting material

A reaction in which diphenyl carbonate is used in place of phosgene and polymerized with bisphenol A to produce polycarbonate has been known. This reaction is called transesterification (Keyword①), which produces polycarbonate and the by-product phenol. However, this process is an equilibrium reaction (Keyword②). Therefore, to manufacture polycarbonates with a high degree of polymerization (suitable for industrial use), the mixture of starting materials is heated to a high temperature and phenol is continuously removed under reduced pressure during the process.

Conventionally, the starting material (diphenyl carbonate) is synthesized from phenol and phosgene. The use of phosgene would mean that the new process would be no different from the conventional phosgenation process. The developers once again considered the fact that phosgene ($COCl_2$) is formed of carbon monoxide (CO) and chlorine (Cl_2). Phosgene is used for polycarbonate synthesis owing to its structure and high reactivity. The main structural feature of polycarbonates is the carbonate group (which originates from carbon monoxide), and the high reactivity of phosgene originates from chlorine, which is a halogen. Both, carbon monoxide and halogens are toxic.

Therefore, they thought of using carbon dioxide, which also has the necessary structure, in place of carbon monoxide.

Carbon dioxide is inexpensive and readily available; however, it is stable and typically unreactive. Thus, ethylene oxide (which is highly reactive, but significantly less toxic than phosgene) was used to synthesize ethylene carbonate from carbon dioxide. However, the ethylene carbonate is not highly reactive. Thus they tried to obtain the final object through sequential conversions by transesterification towards a more highly reactive substance. Although the proposed synthetic strategy involved a larger number of steps than the phosgenation process, it aimed to "kill two birds with one stone" by eliminating the use of toxic materials (phosgene, carbon monoxide, and chlorine) and ensuring the utilization of carbon dioxide (the byproduct generated in ethylene oxide plants) as a starting material after purification.

Synthesis of diphenyl carbonate using reactive distillation

It is difficult to use this new process for the production of diphenyl carbonate monomers.

Although the chemical reaction appears simple on paper, the equation represents an equilibrium state; therefore, the reaction might be too slow to be practicable. In industrial manufacturing, a high reaction efficiency (which indicates the amount of starting material that is converted into the target substance) is vital. This is why phosgene has been used until now. Phosgene exhibits high reactivity, enabling the efficient synthesis of polycarbonates. On the other hand, phosgene also reacts easily with biological components, which causes it to be highly toxic.

In the newly developed process, ethylene carbonate (formed from the typically unreactive carbon dioxide) is sequentially converted to dimethyl carbonate and diphenyl carbonate with higher reactivity (Fig. 3). The transesterification is an equilibrium reaction (Keyword②) in which the starting material is more stable than the product; thus, the reaction does not spontaneously proceed toward the target substance. For example, methyl phenyl carbonate is generated during the synthesis of diphenyl carbonate from dimethyl carbonate and phenol. However, the equilibrium constant of this reaction (Keyword ②), which indicates how easily the reaction will proceed, is extremely small (in the order of 10^{-3} to 10^{-4}). The reason why the developers took on the challenge of this seemingly impossible reaction is that they believed that developing a new process will not only contribute to the environment, but also become an outstanding technology that would change society.

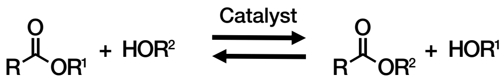
Continuously removing a product from the reaction system facilitates the progress of a non-spontaneous equilibrium reaction toward the product side. Therefore, continuously removing the byproduct methanol could facilitate the production of diphenyl carbonate. Consequently, a production process using the "reactive distillation method" (Keyword ③) was developed. In this method, reaction and distillation are simultaneously carried out in a single reaction vessel. Therefore, methanol can be evaporated and removed during transesterification, enabling the forward reaction to proceed efficiently. However, this method has been rarely applied in industrial manufacturing because it is difficult to control.

Many studies were patiently conducted in the laboratory regarding optimum conditions for carrying out reactive distillation, and the results were reflected in a large-scale "reactive distillation column" having a refined structure fit for industrialization. The newly developed reactive distillation column comprised several chambers (stacked in 10 or more layers) where reactions occurred; these chambers were heated from below (to evaporate methanol). According to the developers, this technology was the most difficult to develop.

Computer simulations, which have progressed rapidly in this era, contributed significantly toward the development of this technology.

Keyword

❶ Transesterification



Transesterification is a reaction in which the alkoxy group (OR^1) of an ester compound ($R(=O)OR^1$) is replaced by an alkoxy group (OR^2) of an alcohol (R^2OH) (as shown in the equation above). An ester bond is generated by the dehydration reaction between a carboxylic acid and alcohol. This is an equilibrium reaction, and the reverse reaction occurs in the presence of water. In the presence of an alcohol (instead of water), the ester reacts with the alcohol, replacing the alcohol in the ester bond. Generally, to facilitate this reaction, esters and alcohols are heated with a catalyst (such as an acid or base). The starting material for PET bottles (polyethylene terephthalate) is synthesized by transesterification.

❷ Equilibrium reaction and equilibrium constants

When a reversible chemical reaction approaches equilibrium, the forward and reverse reactions proceed at the same rate, therefore it will appear as though the reaction is not proceeding. At this point, the ratio between the product of the concentration of the reactants and the product of the concentration of the products is a fixed value. This is called the equilibrium constant (K), which is an important indicator of the reversibility of the reaction. For example, for $A + B \rightleftarrows AB$, $K = [AB] / [A][B]$.If the equilibrium constant is large, the reaction proceeds toward the right-hand-side (product side), generating a large amount of product

❸ Reactive distillation

Reactive distillation (RD) involves reactions, distillation, and separation within a single device (simultaneously). Typically, the production of chemical substances requires several steps. In this system, instead of using a reaction vessel, chemical reactions and distillation are carried out inside a distillation device. This improves the reaction efficiency and saves energy.

Development of a unique polymerization device for improving the degree of polymerization

Development of a unique polymerization device for improving the degree of polymerization

The synthesis of polycarbonates involves the polymerization of diphenyl carbonate and bisphenol A along with the continuous removal of phenol. With the progress of the reaction, the degree of polymerization and molecular weight increase, increasing the viscosity of the reaction mixture. Consequently, phenol gradually becomes less likely to evaporate, and polymerization ceases. In such cases, an agitation apparatus is used to agitate the mixture, which is heated to facilitate the evaporation of phenol. However, the polycarbonate production process requires low-pressure conditions. Using an agitation apparatus would discolor the polycarbonate product (to yellow) owing to the effect of atmospheric oxygen, making it unsuitable for final products.

Therefore, developers formulated a new polymerization technology to produce high-quality polycarbonates with a high degree of polymerization.

Immersing a polycarbonate (pre-polymer) with a low degree of polymerization and low molecular weight into acetone generates a porous crystal (in the solid state). Heating this crystal pre-polymer under reduced pressure promotes polymerization, generating polycarbonates with a high degree of polymerization (through solid-state polymerization).

However, liquid-phase polymers with high fluidity, which are easier to handle than solid-state polymers, are preferred for industrial applications. Thus, the developers considered several methods for realizing a state having large specific surface area in the molten state without mechanical agitation, similar to the porous pre-polymer crystal in the solid state polymerization. In the end, they found that by heating and melting the prepolymer under reduced pressure and allowing it to drop by gravity into a stringlike form, the produced phenol was removed by foaming and evaporation, and at the same time, the foaming action caused the polymer to be agitated so that the reaction would proceed effectively. The developers were certain that high-quality polycarbonate could be formed by using this method. Subsequently, a polymerization device based on these principles (the gravity-based non-agitation melt polymerization method) was designed and industrialized.

Fig. 4 shows the device comprising a

cylindrical container and wires (stretched in the vertical direction). Under high-temperature and reduced-pressure conditions, a reaction mixture containing the pre-polymer was allowed to drop (by gravity) along the wires. Then, the phenol foams and evaporates, and polymerization of diphenyl carbonate proceeds. This method did not require the agitation of the mixture, thereby preventing the entry of air into the mixture, enabling the final product to retain its original color. Furthermore, the conditions for the polymerization can be easily controlled, and various types of polycarbonates having low molecular weight to high molecular weight can be produced with high quality.

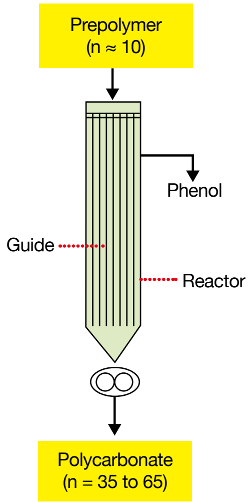
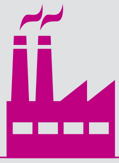


Fig. 4: Original polymerization apparatus
When the polymerization of diphenyl carbonate and bisphenol A begins, the reaction mixture flows along the wires in the polymerization device, generating polycarbonates with n = 35–65.



3 Contribution to Society

~ What is the contribution of this novel technology to society?

By developing the "process for synthesizing monomers (diphenyl carbonate) using reactive distillation" and the "process for synthesizing polymers (polycarbonate) with a new polymerization device," Asahi Kasei became the first company in the world to manufacture polycarbonates from carbon dioxide, ethylene oxide, and bisphenol A. More than 20 years had passed before the first plant started operation in 2002. It can be presumed that cooperation bridging the boundaries among technology experts responsible for developing the reactions, processes and devices, and their extraordinary enthusiasm and tenacity to resolve the continuously arising issues one by one provided the background for accomplishing this great achievement.

Upon taking a closer look at this process, it is apparent that the carbon dioxide emissions into the atmosphere which is the byproduct of ethylene oxide synthesis can be suppressed because the carbon dioxide formed during the production of ethylene oxide is used as the starting material. Furthermore, the methanol and phenol which are added during the reaction are circulated within the system and reused. Ethylene glycol, another end product, is used as starting material for polyester fibers and is not disposed. Moreover, ethylene glycol can be produced with less energy as compared to the conventional method.

The non-phosgene polycarbonate production process developed by Asahi Kasei is green and sustainable. The cost for equipment for this process is one-half compared to that of the phosgenation process because the overall process is simple: toxic substances requiring strict control and handling are not used, treatment for by-products, waste products and impurities are reduced, and continuous production is possible. Thus, costs for starting materials and electricity can also be suppressed. In the past, phosgene leakage accidents have occurred in phosgene-producing plants. The adoption of the non-phosgene polycarbonate production process could significantly reduce such accidents. The Asahi Kasei production process was used to manufacture 660,000 tons of polycarbonate in 2012, which is 14% of the total amount of polycarbonates produced globally. As approximately half of the newly established polycarbonate production plants have adopted this process, polycarbonate production using this green and sustainable process is expected to increase significantly in the future.

After commercialization, the developers have continued to improve this new technology. In the non-phosgene process developed by Asahi Kasei, ethylene oxide and the byproduct CO_2 are used as starting materials. Ethylene oxide is difficult to transport. Therefore, in the absence of ethylene oxide production plants in the vicinity, ethylene carbonate or dimethyl carbonate (which can be easily transported) are produced and transported to polycarbonate production plants.

Asahi Kasei has also developed a new process called the "dialkyl carbonate (DRC) process" for manufacturing diphenyl carbonate without ethylene oxide (Fig. 5); demonstration tests are currently underway. The challenge for new technology still continues today.

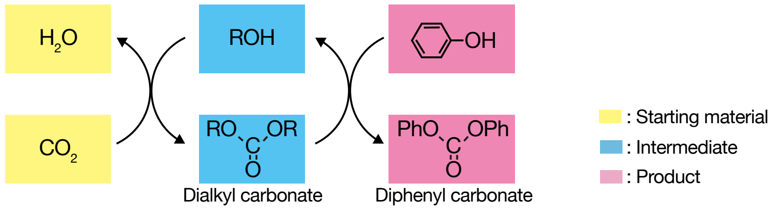


Fig. 5: "DRC process," a new diphenyl carbonate synthesis process developed by Asahi Kasei
The monomer, diphenyl carbonate, is produced from dialkyl carbonate, which is directly produced from alcohol (ROH) and CO_2 using a specific catalyst.

In more detail

Polycarbonate production process using CO_2 as the starting material

Diphenyl carbonate (formed from CO_2 and ethylene oxide) undergoes polymerization with bisphenol A to generate polycarbonates (Fig. 3).

1. Ethylene carbonate is formed by the reaction of carbon dioxide (typically unreactive) with ethylene oxide (highly reactive).
2. Dimethyl carbonate is formed from ethylene carbonate and methanol. Ethylene glycol is formed at this time, which is used as a starting material for plastic and synthetic fibers.
3. Diphenyl carbonate is formed from dimethyl carbonate in two steps. Methyl phenyl carbonate is synthesized from dimethyl carbonate and phenol. Diphenyl carbonate and dimethyl carbonate are synthesized from the 2 molecules of methyl phenyl carbonate.
4. Polycarbonates are synthesized by polymerizing diphenyl carbonate and bisphenol A.

1 to 4 represent transesterification. By repeating transesterification, ethylene carbonate is sequentially transformed into a carbonate with high reactivity. Finally, the resulting diphenyl carbonate and bisphenol A are polymerized. Methanol and phenol are circulated and used repeatedly.

Transesterification (Keyword ①) is an equilibrium reaction which requires the addition of large amounts of methanol and an acid catalyst to form a methyl ester such as dimethyl carbonate. However, the higher stability of the starting materials compared to that of the products in all these reactions makes the reactions non-spontaneous in the forward direction (toward the product side). For example, during the formation of phenol esters by transesterification, the equilibrium is heavily inclined toward the starting material because phenol is more strongly acidic than alcohol. Therefore, the equilibrium constant of the reaction from dimethyl carbonate to methyl phenyl carbonate is extremely small (in the order of 10^{-3} to 10^{-4}), and the rate of reaction is slow, making the synthesis of diphenyl carbonate impractical.

The interior of the distillation column used for reactive distillation is divided into several layers, and in the synthesis of methyl phenyl carbonate, the starting material phenol and a catalyst are supplied to the top layer, and the starting material dimethyl carbonate is supplied to the bottom layer. An esterification reaction was carried out in the central layer of the distillation column, and the product with a high boiling point (methyl phenyl carbonate) was extracted from the bottom of the column. The product with a low boiling point (methanol) was gasified and removed from the top of the column. As the reaction progressed in each layer of the distillation column, the products continuously moved up and down. Thus, the equilibrium shifted toward the product side, enabling the reaction to proceed in the forward direction. The reaction and distillation occurred simultaneously in the same distillation column, enabling the reaction to progress efficiently.

The immersion of a pre-polymer with a low degree of polymerization (formed by the melt polycondensation of diphenyl carbonate and bisphenol A) in acetone generates a porous crystalline polymer. Polycarbonate is a typical amorphous polymer. A polymer having low molecular weight swells in acetone, the glass transition temperature falls below room temperature, the molecular chain moves, and crystallization occurs. In this porous crystalline polymer, heat promotes polymerization (through solid-state polymerization). Therefore, polycarbonates with extremely high molecular weights can be formed using this process.

In contrast, in a polymerization device for producing general-purpose grade polycarbonate, the prepolymer which is heated and melted under reduced pressure is dropped by gravity into several stringlike forms to advance polymerization. The phenol foams, which not only makes it automatically evaporate from the polymer surface to advance the reaction, but also eliminates the need for agitation, which prevents oxidative deteriorations (such as coloring) caused by air leakage. Moreover, the facile removal of phenol lowers the polymerization temperature. Various grades of products with low to high molecular weights can be produced using this technology. The melted polymer is continuously removed from the device and pelletized to form a product (by gravity-based non-agitation melt polymerization).

Questions

For deeper understanding

Through this case study, discuss the following questions from the viewpoint of GSC (Green and Sustainable Chemistry).

Q1 Discuss which of the GSC cases best applies to the technologies and products of this teaching material, along with the reasons.

Q2 Implementation in society is vital for any technology to meet the goals of GSC. This involves the simultaneous fulfillment of coexistence with the global environment, the satisfaction of society's needs, and economic rationality.
In the examples of technologies and products in this teaching material, summarize what measures have been taken to meet not only environmental and social satisfaction but also economic rationality.
In addition, compare the "phosgenation process" with the "DRC process."

Q3 Identify products containing polycarbonate resins in daily life.
Why are polycarbonates used in these product?

Q4 Describe the state of a chemical reaction on “reaching equilibrium.”

Q5 The properties of an organic/inorganic material are determined by its structure.
The properties of the polycarbonate introduced in this teaching material can be described as "having a structure spreading in three dimensions in a (   ) manner (amorphous), and high transparency.
The iso (   ) group gives it low moisture absorption and flexibility."
Fill in the parentheses.

Q6 Source materials with higher reactivity exhibit a greater influence on living organisms.
On the other hand, materials with low reactivity exhibit slow reactions, decreasing the productivity of the process.
Ensuring high productivity with low-reactivity materials comprises the social value of "technology."
What technologies are used in the non-phosgene process?
Furthermore, please summarize the aim of these technologies and the reasons why they can be realized.

Q7 Apart from this case study, please identify some products that use carbon dioxide as the starting material.

Introduction of literature

Helpful materials

1) "Polycarbonate Resin Handbook" by Seiichi Honma (Nikkan Kogyo Shimbun, Ltd.)
2) "CHEMISTRY TODAY, Special Issue 25 Carbon Dioxide" (Gendai Kagaku Zokan in Japanese) edited by Shohei Inoue, Katsura Izui, Koji Tanaka (Tokyo Kagaku Dojin Co. Ltd.)
3) "Introduction to New Polymer Chemistry" (Shin Kobunshi Kagaku Joron in Japanese) by Norio Ise, Sueo Kawabata, Toshinobu Higashimura (Kagaku-Dojin Publishing Company, INC)
4) Masahiro Tojo, Chemical industrial economy, 61(8), p.26 (2014)
5) Nobuhisa Miyake, Expected materials for the future, 5(6), p.46 (2010)

"The Statement 2015" declaring global partnership towards implementing GSC was adopted at the 7th International GSC Conference (GSC-7) held in 2015, 12 years after the previous Conference in Tokyo.

(See JACI Website: http://www.jaci.or.jp /images/The_statemant_2015_final_20151118.pdf)

The Statement 2015

We, the participants of the 7th International GSC Conference Tokyo（GSC-7）and 4th JACI/GSC Symposium make the following declaration to promote “Green and Sustainable Chemistry（GSC）” as a key initiative in the ongoing efforts to achieve global sustainable development.

The global chemistry community has been addressing future-oriented research, innovation, education, and development towards environmentally-benign systems, processes, and products for the sustainable development of society.

In response to the Rio Declaration at the Earth Summit in 1992 and subsequent global Declarations, the global chemistry community has been working on challenges in a unified manner linking academia, industry, and government with a common focus to advance the adoption and uptake of Green and Sustainable Chemistry. The outcomes include the pursuance of co-existence with the global environment, the satisfaction of society’s needs, and economic rationality. These goals should be pursued with consideration for improved quality, performance, and job creation as well as health, safety, the environment across the life cycles of chemical products, their design, selection of raw materials, processing, use, recycling, and final disposal towards a Circular Economy.

Long-term global issues, in areas such as food and water security of supply, energy generation and consumption, resource efficiency, emerging markets, and technological advances and responsible industrial practices have increasingly become major and complicated societal concerns requiring serious attention and innovative solutions within a tight timeline. Therefore, expectations are growing for innovations, based on the chemical sciences and technologies, as driving forces to solve such issues and to achieve the sustainable development of society with enhanced quality of life and well-being.

These significant global issues will best be addressed through promotion of the interdisciplinary understanding of Green and Sustainable Chemistry throughout the discussion of “ Toward New Developments in GSC. ”

The global chemistry community will advance Green and Sustainable Chemistry through global partnership and collaboration and by bridging the boundaries that traditionally separate disciplines, academia, industries, consumers, governments, and nations.

July 8, 2015
Kyohei Takahashi
on behalf of Organizing Committee
Milton Hearn AM, David Constable,
Sir Martyn Poliakoff, Masahiko Matsukata
on behalf of International Advisory Board
of 7th International GSC Conference Tokyo (GSC-7),
Japan July 5-8, 2015

JACI Textbook: Introduction to GSC ~ Learning from the social practice cases that have received the GSC Awards, No.1
Issued March 2024 (Japanese version issued March 2016, English version (1st edition) issued October 2019)
Planning/Editorial: Working Group for Teaching Materials, GSCN Dissemination and Enlightenment Group, Japan Association for Chemical Innovation
Issued by Japan Association for Chemical Innovation
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https://www.jaci.or.jp/english/
Acknowledgement : We would like to thank Editage (https://www.editage.jp/) for English language

GSC : Green and Sustainable Chemistry

Chemical sciences and technologies
which are benign to both human health and the environment,
and support the development of a sustainable society.

Introduction to GSC

Learning from social practice cases that received the GSC Awards

Global issues, in areas such as resources and energy, global warming, water and food have increasingly become major and complicated concerns. Innovations for achieving both environmental conservation and economic development are needed in order to resolve these issues and realize the sustainable development of society, and expectations for GSC continue to rise. In this textbook series, technologies and products that have received the GSC Awards given to great achievements contributing to the progress of GSC are explained, so that everyone can understand "what is GSC?" and take responsibility for realizing a sustainable society.

Special Edition

"Introduction to SDGs" Sustainable Development Goals GSC plays a driving role in SDGs

Let's change the world towards a sustainable future!

The SDGs are global goals adopted by the United Nations, and it is essential to harmonize the three elements of economy, society, and the environment in order to achieve sustainable development. This way of thinking is shared with the GSC, which aims to achieve both environmental conservation and economic development for the sustainable development of society. As a special issue, this text aims to explain the SDGs from the perspective of the GSC and encourage everyone to think about and put them into practice.

No.1

New laundry proposal for pioneering a sustainable society

Kao Corporation

The "new laundry proposal for pioneering a sustainable society" of Kao Corporation, which received the Minister of Economy, Trade and Industry Award of the 12th GSC Awards (2012), is characterized by the introduction of Life Cycle Assessment (LCA) into the development of laundry detergents, and the proposal to reduce laundry-related environmental impacts together with consumers by using just one rinse cycle in laundry. How was this innovation generated that simultaneously satisfies environmental friendliness, social contribution and economic rationality?

No.2

Novel Non-phosgene Polycarbonate Production Process Using By-product CO_2 as Starting Material

Asahi Kasei Corporation

The great success of this technology is that unlike the conventional polycarbonate production process, it does not use toxic phosgene as a starting material. At the same time, the technology was revolutionary because it achieved saving of both resources and energy. More than 10 years have passed, and the technology has been widely commercialized all over the world. This worldwide use was highly regarded, and the process became the first technology by a Japanese company to receive the Heroes of Chemistry Award from the American Chemical Society in 2014. What kind of technology is involved in this world-renowned polycarbonate production process?

No.3

Development of Carbon Fiber Composite Materials for Lightweight Commercial Airplanes

Toray Industries, Inc.

TORAY's carbon fiber reinforced plastic developed through over 40 years of research and development has features of high toughness (material tenacity) in combination with light weight and flexibility. The high toughness carbon fiber reinforced plastic (high toughness CFRP) realizes weight reduction of airplanes which is effective in improving fuel consumption, and makes a substantial contribution to reducing environmental impact.

No.4

Development and Commercialization of High Performance Transparent Plastics Derived from Plant-Based Raw Material

Mitsubishi Chemical Corporation

"DURABIOTM", the transparent engineering plastic made from renewable resources developed by the company, not only contributes to the reduction of environmental impact, but also realizes performance exceeding that of conventional engineering plastics in terms of optical characteristics, weathering resistance, etc.

No.5

Development of High-Performance Reverse Osmosis Membrane Contribution to the solution of global water issues

Toray Industries, Inc.

This reverse osmosis membrane can be used in not only seawater but also river water, sewage wastewater, and various other water treatment systems, providing high quality water while saving energy.

No.6

Development of Low Environmental Load Battery for Idling-Stop System Vehicle with High Charge Acceptance and High Durability

Hitachi Chemical Co., Ltd.
(Currently Energywith Co., Ltd.)
Hitachi, Ltd.

Idling-stop systems heavily burden on the battery, causing existing batteries to rapidly degrade, with short battery lifetimes. This technology resolves this problem and contributes to the reduction in CO_2 emissions.

No.7

Development of Water-based Inkjet Ink for Food Package

Kao Corporation

Kao Corporation developed a "water-based inkjet ink" for printing on the plastic films used for packaging daily commodities and food.
The ink maintains a high image quality and has lower volatile organic compound emissions, thereby reducing its environmental impact.

No.8

Development and Commercialization of a New Manufacturing Process for Propylene Oxide Utilizing Cumene Recycling

Sumitomo Chemical Co., Ltd.

Sumitomo Chemical Co., Ltd. developed a new manufacturing process for propylene oxide, which is used as a raw material for polyurethane and other materials.
The new process enables high yields of propylene oxide while reducing its environmental impact.

You can read them in "PDF" and "HTML" that is easy to read on mobile phones.

Please take a look!

https://www.jaci.or.jp/english/gscn/GSCgs/spmenu/page_19_01_sp.php

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