Green and
Sustainable
Chemistry

Introduction to GSC

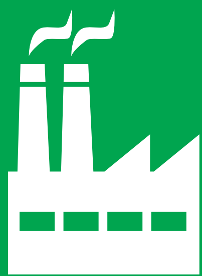
No.2

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 GSC Awards and award-winning company

The GSC Awards are given to individuals and organizations who have made great achievements which contributed to the advancement of Green and Sustainable Chemistry, and a number of Awards are conferred each year. Among the Awards, the Minister of Economy, Trade and Industry Award is given to contributions to the development of industrial technology; the Minister of Education, Culture, Sports, Science and Technology Award is given to contributions to the development and promotion of science; the Minister of the Environment Award is given to contributions to the overall reduction of environmental impact; and the Small Business Award (established in 2015) is given to small and medium-sized businesses that made contributions to the development of industrial technology. Moreover, the Incentive Award is given to achievements that are expected to lead to future developments.

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 co-existence 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 resources 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
http://www.jaci.or.jp/gscn/page_01.html)

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

ASAHI KASEI CORPORATION

The Minister of Economy, Trade and Industry Award of the 2nd GSC Awards (2002) was given to the “non-phosgene polycarbonate resin production process using by-product CO_2 as starting material” developed by 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?

Picture 1: Plant (built in 2002) owned by "CHIMEI-ASAHI CORPORATION," a joint venture company with Taiwan's Chi Mei Corporation. The very first polycarbonate production by the non-phosgene process developed by ASAHI KASEI took place here.

1 The path to technology development

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

In general, there are many different types of the resin that is referred to as "plastic" (Column ①). Among them, polycarbonate is a polymer that contains a carbonate group at the center of its molecular structure, as its name suggests (Fig. 1). Polycarbonate was developed by Bayer AG of Germany and General Electric Company of America around the same time in 1959, and became widely used in the 1970's for its excellent properties. Specifically, polycarbonate has an impact resistance which is said to be approximately 200 times that of glass and will not break even when struck by a hammer, and so it is used in helmets and protective goggles for construction sites as well as industrial parts. Its characteristics include being transparent and resistant to deformation, which makes it suitable as substrate materials for CDs and DVDs which perform reading and writing of data using laser beams. The demand for optical storage media grew rapidly in the 1990's, which resulted in the increased production volume of polycarbonate.

Nearly 80% of polycarbonates is produced by a phosgenation process which uses toxic phosgene ($COCl_2$)*1 and bisphenol A as starting materials (Fig. 2, Column ②). Phosgene has extremely high reactivity and reacts easily with bisphenol A to form a carbonate group (carbonate bond).

Although the synthesis reaction of polycarbonate is a simple, one-step reaction of phosgene and bisphenol A, the actual synthesis process is extremely complex and involves a number of issues 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 by-product. 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.

*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). It has asphyxiating properties and is extremely toxic, and was used as poison gas during World War I. Furthermore, it is highly reactive and is used as a synthetic starting material for polyurethane and dye.

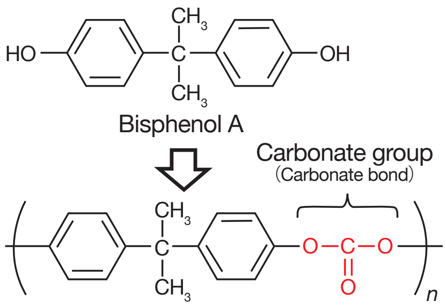


Fig.1: Chemical formula for polycarbonate

Picture 2:
Common products made of polycarbonate

(Photography in cooperation with: S. Nakamura Laboratory, Tokyo Institute of Technology)

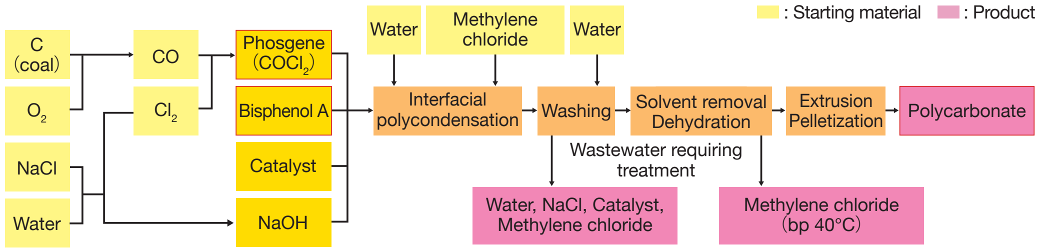


Fig. 2: Polycarbonate production process by phosgenation process

Column 1

Plastic

Plastic is a macromolecular substance which can be molded into an objective shape by applying heat and pressure. Macromolecular substances are categorized into natural resins formed by hardened tree sap and synthetic resins synthesized from fossil fuels such as petroleum. "Plastic" usually refers to synthetic resins.

In Japan, generally naphtha is 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. The monomers having low molecular weight are polymerized*[2] to form polymers which are macromolecular compounds. Various types of polymers are formed according to different starting materials and polymerization methods. A compounding agent is added to the polymer and the mixture is molded to make plastic products.

Plastic is categorized into a thermoplastic type which becomes soft by being heated to allow easy molding, and a thermosetting type which undergoes an irreversible change in the structure once it is cooled after being heated and no longer becomes soft. Thermoplastic types include polyethylene and polystyrene, and thermosetting types include phenol resin.

*2
Polymerization: a reaction in which individual monomers bond in large numbers to form a polymer. A monomer is a molecule that is a unit for constituting the polymer.

Column 2

Polycarbonate production process (conventional method)

There are 2 types of polycarbonate production processes: the phosgenation process and the transesterification process. In the phosgenation process, synthesis is carried out by a polycondensation reaction*[3] between bisphenol A and phosgene. The process includes an interfacial polycondensation process which carries out polymerization in two phases, an organic solvent and water, and a solution polycondensation process which carries out polymerization in a homogenous solution. The interfacial polycondensation process is used for industrial purposes.

Phosgene is highly reactive and reacts easily with bisphenol A to form a carbonate group, which is difficult to synthesize. The polymer is 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. The polymerization forms HCl (hydrogen chloride), and by adding NaOH into the reaction, HCl is neutralized to form NaCl (sodium chloride). The formed polycarbonate dissolves in methylene chloride, so the methylene chloride is isolated and washed. Polycarbonate is precipitated from the 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. Furthermore, it poses environmental issues such as using large amounts of toxic phosgene and methylene chloride which is thought to be carcinogenic, and discharging a large amount of waste products such as salt and catalysts and wastewater containing organic substances such as methylene chloride.

The transesterification process carries out polymerization by transesterification of bisphenol A and diphenyl carbonate which have been heated and melted. It uses neither toxic phosgene nor solvents, therefore there is no need for any solvent recovery. However, this process was developed but gradually went out of use because it resulted in products with poor quality. In later years, the process was reviewed several times and improvements were made, but was never put to practical use.

*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.

2

Towards 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

When an established process technology has become mainstream, it is difficult to develop new technology to replace the existing one. Nevertheless, the expected increase in the demand for polycarbonates prompted many companies to start developing a polycarbonate production process without using toxic phosgene in the 1980's. ASAHI KASEI was one of these companies. While each company strived for an environmentally-benign and low-cost production process, ASAHI KASEI focused on "the reason why phosgene had to be used" and searched for a 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 by-product ethylene glycol is used as an end product. This process does not use toxic phosgene or methylene chloride, and the carbon dioxide that is discharged from the production of ethylene oxide is used as a 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.

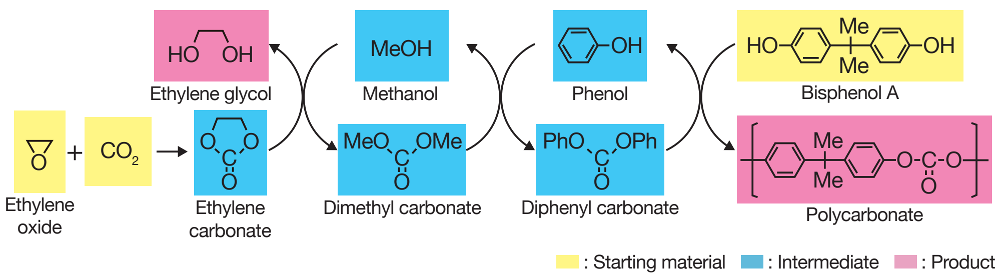


Fig. 3: Non-phosgene polycarbonate production process by ASAHI KASEI

Synthesis of diphenyl carbonate using carbon dioxide as 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 (Keyword ①), which produces polycarbonate and the by-product phenol. Since this reaction is an equilibrium reaction (Keyword ②), a mixture of starting materials must be heated to a high temperature, and the phenol must be continuously removed under reduced pressure while the reaction is taking place in order to obtain polycarbonate with a high degree of polymerization for use in industrial products.

Conventionally, the starting material diphenyl carbonate has been formed 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 (C_2). The reason for using phosgene is that it has the necessary structure for synthesizing polycarbonate and is highly reactive. The carbonate group being the main structure of the product originates from carbon monoxide, and the high reactivity of phosgene originates from chlorine which is a halogen, and both, although in different levels, are toxic. So they thought of using carbon dioxide, which also has the necessary structure, in place of carbon monoxide.

Carbon dioxide is inexpensive and easily available, but it is stable and will not react in its normal state. Thus the developers decided to synthesize ethylene carbonate from carbon dioxide by using ethylene oxide which is highly reactive but is far less toxic than phosgene. 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. Compared to the phosgenation process, there would be more steps involved in the reaction, but the aim was to "kill two birds with one stone" by eliminating the use of toxic phosgene, carbon monoxide and chlorine, and using the by-product carbon dioxide produced from ethylene oxide plants as a starting material after subjecting it to purification.

Synthesis of diphenyl carbonate using reactive distillation

In the actual production of diphenyl carbonate (monomer), using this new process turned out to be difficult. It is easy to write the chemical reaction formula, however, the equation represents an equilibrium state, which does not mean that the chemical reaction will proceed at a rate fit for practical use. In industrial manufacturing, reaction efficiency, or how much of a starting material is converted into a target substance, is important. This is why phosgene has been used until now. Phosgene has high reactivity, which enables efficient synthesis of polycarbonate. 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 is formed from non-active carbon dioxide, then this low reactive ethylene carbonate is used to sequentially form dimethyl carbonate and diphenyl carbonate with higher reactivity (Fig. 3). The transesterification used here is an equilibrium reaction (Keyword ②), where in both cases the starting material is more stable than the target substance, and thus the reaction will not proceed towards producing the target substance. Specifically, in the step of making diphenyl carbonate from dimethyl carbonate and phenol, methyl phenyl carbonate is formed during the step. This reaction has an equilibrium constant (Keyword ②), which represents how easily the reaction will proceed, of as extremely small as 10^{-3} to 10^{-4}, which means the reaction will hardly proceed by itself. 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.

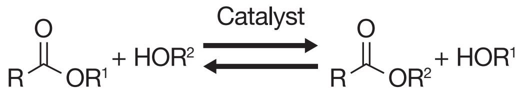
In order to make such an equilibrium reaction that will not react by itself proceed, removing a product from the reaction system, that is, returning the reaction to the state before equilibrium is achieved, is known to be a solution. For example, in the above reaction for making diphenyl carbonate, removing the by-product methanol would solve the issue. In order to do so, 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. Methanol can be evaporated and removed while carrying out transesterification, allowing the reaction to proceed efficiently. However, there had been very few cases in which this method was applied in industrial manufacturing, because this method 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. A number of chambers are stacked in ten or more layers inside the reactive distillation column, and reactions are carried out in each chamber. At the same time, the chambers are heated from below to evaporate the methanol. Developers back then say that developing the technology for this portion was the most difficult challenge.

A major contributor to the success of developing this technology was the computer simulation technology which progressed rapidly in this era.

Keyword

❶ Transesterification



Transesterification refers to a reaction in which an alkoxy group (OR^1) in the ester compound ($R(=O)OR^1$) is replaced by an alkoxy group (OR^2) originating from another alcohol (R^2OH) (see the equation above). An ester bond is formed from a dehydration reaction between carboxylic acid and alcohol. This reaction is an equilibrium reaction, and a reverse reaction takes place if water is present. If alcohol is present instead of water, the alcohol and ester react, and the alcohol in the ester bond is replaced. Generally, ester and alcohol are heated with a catalyst such as an acid or a base to carry out the reaction. The starting material for PET bottles, polyethylene terephthalate, is synthesized by applying the transesterification process.

❷ Equilibrium reaction and equilibrium constant

When a reversible chemical reaction approaches equilibrium, the forward reaction and the reverse reaction proceed at the same rate, and it will appear as though the reaction is not proceeding. At this time, the ratio between the product of the concentration of reactant substances and the product of the concentration of product substances will be a fixed value. This is called the equilibrium constant (K), which is an important indicator of the property of the reversible reaction. For example, for $A+B \rightleftharpoons AB$, $K = [AB] / [A][B]$.

If the equilibrium constant is large, the reaction will proceed towards the right side (product side), resulting in a large amount of the product.

❸ Reactive distillation

Reactive distillation is a system capable of carrying out reaction, distillation and separation within a singe device. The production process of a chemical substance is composed of a combination of several steps of operations. In this system, instead of using a reaction vessel, the chemical reaction and distillation are carried out inside a distillation device, which improves reaction efficiency and saves energy required for the production process.

Development of unique polymerization device for improving degree of polymerization

In the synthesis of polycarbonate, diphenyl carbonate and bisphenol A are polymerized while phenol is continuously removed. When the degree of polymerization increases and the molecular weight becomes large, viscosity becomes high. As a result, the phenol becomes less likely to evaporate, and polymerization will cease to proceed. In such a case, the general solution is to agitate the mixture with an agitation apparatus and apply heat to evaporate the phenol. However, the conditions for production require the process to be carried out under reduced pressure, and so the polycarbonate will be discolored to yellow from the effect of oxygen in the atmosphere entering form the movable seal part of the agitation apparatus, and would not be suitable to be shipped out as the finished product.

Therefore, the developers took on the challenge of coming up with technology for a polymerization process to produce high-quality polycarbonate having a higher degree of polymerization.

As a result, they found that a porous crystal (solid state) can be obtained by immersing polycarbonate (prepolymer) with a low degree of polymerization and low molecular weight into acetone, and that heating this crystal prepolymer under reduced pressure further promotes the polymerization to produce polycarbonate with a high degree of polymerization (development of solid state polymerization method).

On the other hand, when producing polymers for industrial purposes, polymers in the liquid phase having high fluidity is easier to handle than polymers in the solid state. 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. A polymerization device was designed based on these principles and was finally successfully industrialized (gravity-based non-agitation melt-polymerization method).

Fig. 4 shows a device having a cylindrical container with wires therein stretched in a vertical direction. Under high-temperature, reduced-pressure conditions, the reaction mixture containing the prepolymer is allowed to drop by gravity along the wire. Then, the phenol foams and evaporates, and polymerization of diphenyl carbonate proceeds. This method does not require the mixture to be agitated, which means that air does not enter into the mixture, and the color of the finished product is not affected. 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.

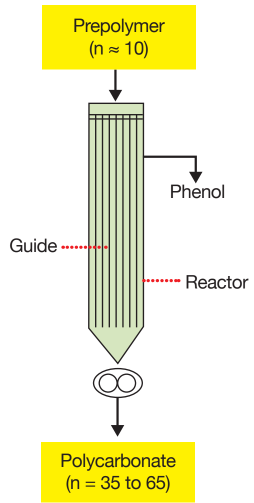


Fig. 4: Original polymerization apparatus

When the polymerization reaction of diphenyl carbonate and bisphenol A starts, the reaction mixture is made to flow along the wires in the polymerization device, resulting in producing polycarbonate with n = 35 to 65.

3 Contribution to Society

~ What kind of values were contributed to society by the new technology?

Through establishment of 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 complete the polycarbonate production process using carbon dioxide, ethylene oxide and bisphenol A as starting materials. 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 truly a Green and Sustainable process. 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, there were phosgene leakage accidents in the phosgene production plants. In order to prevent accidents, there is an increasing number of cases in which the non-phosgene polycarbonate production process is adopted. The polycarbonate produced by ASAHI KASEI's production process was 660,000 tons in 2012, which was 14% of the total amount of polycarbonates produced. Taking into account that approximately half of the newly established polycarbonate production plants have adopted this process, the production using this Green and Sustainable process is expected to continue to increase in the future.

Finally, the progress of further developments in new technologies is introduced. In the non-phosgene process developed by ASAHI KASEI, ethylene oxide and the by-product CO_2 formed during its production process are used as starting materials. Since ethylene oxide is difficult to transport, if there are no ethylene oxide production plants in the vicinity, ethylene carbonate or dimethyl carbonate which can be easily transported are produced near an ethylene oxide production plant, then transported to a polycarbonate production plant.

ASAHI KASEI has also developed a new process called the "dialkyl carbonate (DRC) process" for making diphenyl carbonate without using ethylene oxide (Fig. 5), and demonstration tests are already under way. The challenge for new technology still continues today.

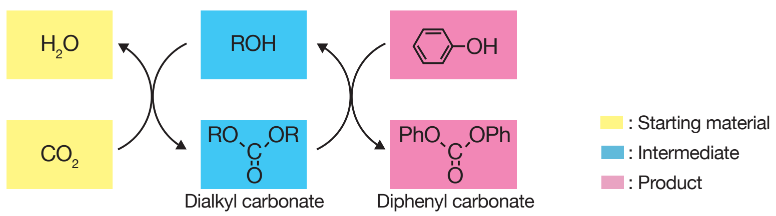


Fig. 5: "DRC process, " a new diphenyl carbonate synthesis process by ASAHI KASEI

The monomer, diphenyl carbonate, is produced by using 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 starting material

Diphenyl carbonate is formed from CO_2 and ethylene oxide, then the diphenyl carbonate and bisphenol A are polymerized to produce polycarbonate (Fig. 3).

❶ Ethylene carbonate is formed by reacting inactive carbon dioxide with highly reactive ethylene oxide.

❷ Dimethyl carbonate is formed from the ethylene carbonate and methanol. Ethylene glycol is formed at this time, which is used as a starting material for plastic and synthetic fibers.

❸ 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.

❹ Polycarbonate is synthesized by polymerizing diphenyl carbonate and bisphenol A.

❶ to ❹ are transesterification processes. By repeating transesterification, the sequential transformation of ethylene carbonate is carried out to obtain carbonate having high reactivity, and 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, since in all reactions the starting material side is more stable than the product side, the equilibrium is inclined towards the starting material side (reactants), which makes it difficult to carry out the reaction. In the transesterification to phenol ester in particular, the equilibrium is heavily inclined towards the starting material side, since phenol is more strongly acidic than alcohol. Therefore, the equilibrium constant of the reaction from dimethyl carbonate to methyl phenyl carbonate is as significantly small as 10^{-3} to 10^{-4}, and the rate of reaction is slow, hence the synthesis of diphenyl carbonate was thought to be almost impossible.

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 is carried out in the layer in the center portion of the distillation column, and the product, methyl phenyl carbonate having a high boiling point, is extracted from the column bottom. The product, methanol having a low boiling point, is gasified and removed from the column top. As the reaction progresses in each layer of the distillation column, each product continuously moves up and down, and thus the equilibrium shifts towards the product side to make the reaction proceed. Reaction and distillation progress simultaneously in the same distillation column, and the reaction progresses efficiently.

When a prepolymer having a low degree of polymerization formed by melt polycondensation of diphenyl carbonate and bisphenol A is immersed in acetone, a porous crystalline polymer is formed.

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, applying heat advances polymerization (solid state polymerization method). Polycarbonates having extremely high molecular weight can be formed by this process.

On the other hand, 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 phenol can be easily removed and the polymerization temperature can be lowered. Various grades of products from low molecular weight to high molecular weight can be produced. The melted polymer is continuously taken out from the device and pelletized as is to form the product (gravity-based non-agitation melt-polymerization method).

Questions

For deeper understanding

Please use this case study of ASAHI KASEI CORPORATION to discuss the questions below from the viewpoint of GSC.

Q1 Please discuss which Example of GSC best matches ASAHI KASEI's technology and product and why.

Q2 GSC is complete only after being implemented in society. To do so, the three aspects of co-existence with the global environment, satisfaction of society's needs and economic rationality must be fulfilled simultaneously.
Please summarize how the case study in this teaching material devised ways to satisfy these three aspects.
Please make a comparison to the "phosgenation process" and the "DRC process."

Q3 Search for products containing polycarbonate resin in your daily life. Why is polycarbonate used in that product?

Q4 Describe the state of a chemical reaction "reaching equilibrium."

Q5 The properties of a material, whether organic or inorganic, 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."
Please fill in the parentheses.

Q6 The higher the activity of the source material, the larger influence it has on living organisms. On the other hand, materials with low activity inhibit the reaction from being carried out, and the productivity of the final object is decreased. Realizing high productivity while using materials with low activity is the social value of "technology."
What kind of technologies were used in the non-phosgene process? Furthermore, please summarize the aim of these technologies and the reasons why they can be realized.

Q7 Look for products that use carbon dioxide as a starting material, aside from this case study.

Introduction of literature

Helpful materials:

"Polycarbonate Resin Handbook" by Seiichi Honma (Nikkan Kogyo Shimbun, Ltd.)
"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.)
"Introduction to New Polymer Chemistry" (Shin Kobunshi Kagaku Joron in Japanese) by Norio Ise, Sueo Kawabata, Toshinobu Higashimura (Kagaku-Dojin Publishing Company, INC)
Masahiro Tojo, Chemical industrial economy, 61(8), p.26 (2014)
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

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