

**The Second Green and Sustainable Chemistry Award
Awarded by the Minister of Economy, Trade and Industry**

**Shinsuke Fukuoka, Isaburou Fukawa, Mamoru Kawamura,
Kyosuke Komiya, and Masahiro Tojo
Asahi Kasei Corporation**

***Novel Non-phosgene Polycarbonate Production Process
Using By-product CO₂ as Starting Material***

Polycarbonate is an engineering plastic with outstanding transparency, impact resistance, and heat resistance, which is used in a wide range of applications basic to the modern lifestyle including optical discs, automobiles, office equipment, and sheets. About 2.7 million tons of polycarbonate are produced annually worldwide, and until now all production used carbon monoxide (CO) as a starting material. The vast majority of polycarbonate is made in a process where CO and chlorine are combined to form phosgene, a toxic gas, as an intermediate material. The phosgene process entails a number of drawbacks in environmental terms including the toxicity of phosgene, the use of the low-boiling-point solvent methylene chloride to which exposure must be restricted, and the large quantity of waste water containing methylene chloride which must be treated. Many attempts have been made to overcome the environmental and cost disadvantages of the phosgene process, but faced with significant technological barriers, both for a production step for a safe monomer to replace phosgene and for a polymerization step to produce polycarbonate, success has been limited.

Based on a concept of green and sustainable chemistry which contributes to society, research and development for this new process spanned about twenty years, in an endeavor to develop new non-phosgene technology for the production of polycarbonate necessary for the modern lifestyle. In contrast to other existing processes, which use CO as a starting material, this is the world's first non-phosgene polycarbonate production process which uses CO₂ as a starting material.

This technology uses ethylene oxide, its by-product CO₂, and bisphenol-A as starting materials to produce high-quality polycarbonate and high-purity ethylene glycol at high yield. Because CO₂ has low chemical reactivity, it was considered to be difficult to incorporate it into the polycarbonate main chain. However, this technology successfully integrates all of the CO₂ used into the products through deft utilization of chemical reactions. The CO₂ used as starting material is a by-product generated in the production of ethylene oxide (generally used to make ethylene glycol for PET bottles and polyester fiber), and is usually released to the atmosphere.

This technology overcomes the problems of the phosgene process and additionally achieves high yield, resource conservation, and energy conservation while contributing to reduced CO₂ emissions (173 tons per thousand tons of product PC) in an expanse of benefits which embodies the spirit of green and sustainable chemistry.

This technology was commercialized at a plant of Chimei-Asahi Corporation, an Asahi Kasei affiliate, which entered commercial operation in June 2002. With lower plant construction costs and lower feedstock costs, it is anticipated that it will be widely adopted throughout the world as a non-phosgene polycarbonate production process.

**The Second Green and Sustainable Chemistry Award
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**Mr. Toshiro Yamada, Mr. Noriyasu Otsuki, Mr. Tatsuya Sugimoto,
and Mr. Kimiaki Tanaka
ZEON CORPORATION.**

**Mr. Akira Sekiya
The National Institute of Advanced Industrial Science and Technology**

***“The Development of the Manufacturing Technology of New Environment-friendly
Five-ring Fluorine Compounds”***

The curb of stratospheric ozone depletion and global warming is our major global environmental issue. To cope with this issue, we have already gained some good results, including the total abolishment of chlorofluorocarbon production among developed nations by the end of 1995. However, it still has been our urgent task to develop a new generation fluorine compound, which has no ozone depletion effect and low impact on global warming, due to the fact that most of the ever-developed alternative chemicals as countermeasures for ozone depletion have a profound impact on global warming.

The essence of this work, “the development of the manufacturing technology of new environment-friendly five-ring fluorine compounds,” is the practical application and manufacturing technology development of two unique fluorine compounds of a five-ring structure: heptafluorocyclopentane as a precision cleaning solvent; and octafluorocyclopentene as a dry etching agent for manufacturing semiconductor. These compounds have characteristics of zero ozone depletion effect and low impact on global warming. We have developed unique synthetic methods that shorten the manufacturing processes of these compounds. In the GSC view, the compounds prove their positive effects for potentially minimizing fluorinated wastes.

The main feature of this technology is compatibility of environmental suitability and high performance achieved by unique molecular design. Both products have high performance that responds to the cutting-edge realm owing to their innovative molecular structure featuring five-ring. One is being used worldwide as a dry etching agent for high integrated and leading-edge semiconductor manufacturing, and the other is used as a high precision cleaning agent for metal and electronic devices or used in polymer coating solvents. Both are making a significant social contribution for their higher performance than any other conventional fluorinated compound. The products, when reduced to practice, trickle down to etching equipment, cleaners, and the peripherals, thus contributing to the industry.

To date, many studies have been performed on expanded scope of the compounds developed through this work, their extended application as chemical materials, development of the next generation materials of environmental suitability and high performance using the accumulated manufacturing technologies, etc. Indeed, part of these is at its development stage toward practical application. Therefore, this work can be highly expected for its future expansibility.

**The Second Green and Sustainable Chemistry Award
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Science and Technology**

Kazuaki Ishihara, Graduate School of Engineering, Nagoya University

Highly Efficient Organic Syntheses Using Environmentally Benign Catalysts

To promote atom efficiency in synthesis and to avoid the generation of environmental waste, the use of stoichiometric amounts of condensing reagents or excess substrates should be avoided. In esterification, excess amounts of either carboxylic acids or alcohols are normally needed. Dr. Ishihara has found that hafnium(IV) or zirconium(IV) salts are highly effective as catalysts for the direct condensation of equimolar amounts of carboxylic acids and alcohols. This catalytic system can be applied to the direct polyesterification, the selective esterification of primary alcohols with carboxylic acids in the presence of secondary alcohols or aromatic alcohols, and may be suitable for large-scale operations.

On the basis of the same concept, he has found that 3,4,5-trifluorophenylboronic acid is a highly effective catalyst for the amide condensation of amines and carboxylic acids. Arylboronic acids bearing electron-withdrawing substituents at the aryl group behave as water-, acid-, and base-tolerant thermally stable Lewis acids, and can be easily handled in air. He has succeeded in applying this catalytic system to a direct thermal amide polycondensation to form not only aliphatic polyamides but also aromatic polyamides and polyimides. Furthermore, he has developed 3,5-bis(perfluorodecyl) phenylboronic acid which serves as a highly active and reusable catalyst by virtue of the electron-withdrawing effect and the immobility in the fluorous recyclable phase of the perfluorodecyl group. It is noteworthy that this fluorous catalyst is simply recovered by filtration without using any fluorous solvents. Simplification of product workup, separation, and isolation as well as reuse of solid catalysts can lead to an economical system. He has found that perchloric acid is an extremely active catalyst for dehydration of not only primary amides but also aldoximes to the corresponding nitriles. The reaction proceeds under essentially neutral conditions, and the catalyst is recoverable and reusable. He has succeeded in preparing polystyrene-bound super Brønsted acid which is effectively swollen by both polar and nonpolar organic solvents, and its catalytic activity for various organic reactions is superior to that of Nafion[®]-H. The resin-bound catalyst can be repeatedly reused in a batch system, and have been applied to a flow reaction system to avoid physical degradation of the resin beads. In addition, they have developed a fluorous super Brønsted acid catalyst, 4-(1*H*,1*H*-perfluorotetradecan-oxy)-2,3,5,6-tetrafluorophenyl-bis(trifluoromethanesulfonyl)methane, which can be recycled by using liquid/solid phase separation without fluorous solvents.

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