

SPECIFICATION

Polycarbonate resins and methods for preparing the same

Technical Field

The present invention relates to the polycarbonate resins and methods for preparing them, more particularly the polycarbonate resins reduced in content of volatile impurities such as phenols, and processes for producing such polycarbonate resins.

Background Art

The polycarbonate resins have excellent mechanical properties such as heat and impact resistance, as well as high dimensional stability and transparency, and have therefore been used for a wide variety of purposes.

For the preparation of polycarbonate resins, there are known, most popularly, melting method (ester exchange method) and phosgene method (interfacial polymerization method), but any of these methods is merely capable of producing a crude polycarbonate resin which contains volatile impurities such as unreacted starting materials, low-molecular weight products and reaction solvent. A typical example of the said low-molecular weight products is

phenols in the melting method. In the melting method, the phenols produced from the ester exchange reaction are evaporated away under reduced pressure, but as a result of equilibration between the liquid and gaseous phases of the reaction, phenols are left in the reaction solution and consequently contained in the produced polycarbonate resin.

The following methods have been known for producing the polycarbonate resins by removing the volatile impurities: a method in which when, for instance, a polycarbonate resin is melted and extruded into pellets, nitrogen or water is supplied to the material mixing section of the melt extruder to conduct treatment under reduced pressure (Patent Documents 1 and 2); a method in which a saturated aliphatic hydrocarbon or an aromatic hydrocarbon is added (Patent Documents 3 and 4); a method in which carbon dioxide is supplied in a pressurized state and the treatment is conducted under reduced pressure (Patent document 5); and a method in which by using a multi-stage vented melt extruder, a polycarbonate resin and water are mixed under a reduced pressure of 0.3 to 10 MPa to conduct treatment under reduced pressure (Patent Document 6).

Patent Document 1: Japanese Patent Application Laid-Open (KOKAI) No. 9-59367

Patent Document 2: Japanese Patent Application Laid-Open (KOKAI) No. 9-59368

Patent Document 3: Japanese Patent Application Laid-Open
(KOKAI) No. 9-67433

Patent Document 4: Japanese Patent Application Laid-Open
(KOKAI) No. 9-157375

Patent Document 5: Japanese Patent Application Laid-Open
(KOKAI) No. 2000-302879

Patent Document 6: Japanese Patent Application Laid-Open
(KOKAI) No. 2001-31753

Disclosure of the Invention

Problem to be Solved by the Invention

An object of the present invention is to provide the polycarbonate resins phenomenally reduced in content of volatile impurities such as phenols, and processes for producing such polycarbonate resins.

Means for Solving the Problem

In the course of studies for resolving the above problem, the present inventors came upon the surprising findings accounted below.

(1) In the production of polycarbonate resins in general, a polymer filter is provided at the exit of the melt extruder in the pelletization step for the purpose of removing the foreign substances such as fish eyes. In this step, on the other hand, phenols are regenerated in the

polymer filter. Such regeneration of phenols is associated with the catalytic action of the component metals of the polymer filter and the decomposition of the carbonic acid diesters or the polymer by shearing heat in the polymer filter. Therefore, even if a vented melt extruder is used for removing the volatile impurities, the polymer filter is incapable of fully performing its capacity in removing phenols which are left as volatile impurities in the product, making it hardly possible to produce a polycarbonate resin reduced in phenol content to a satisfactory level.

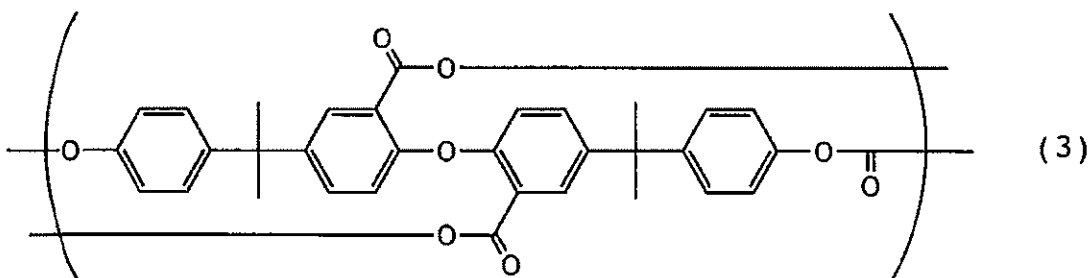
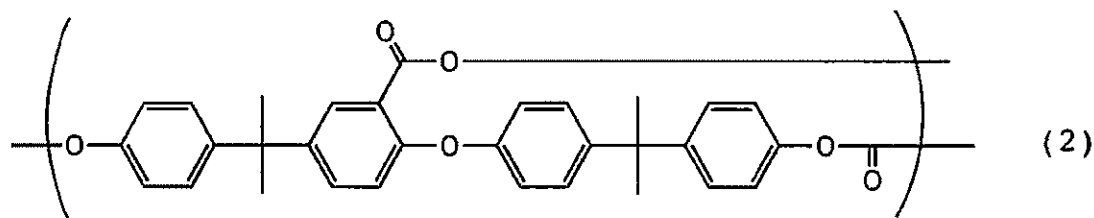
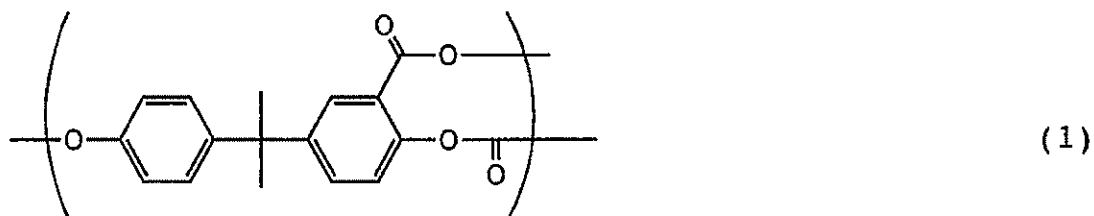
(2) In producing a polycarbonate resin from a dihydroxyl compound and a carbonic acid diester by an ester exchange method using a polycarbonate resin producing apparatus comprising at least one reactor and at least one extruder, if a specific temperature condition is employed for the extruder, it is possible to suppress the polycarbonate resin decomposition reaction to allow effective removal of volatile impurities, and moreover, there can be obtained a novel polycarbonate resin that has been unknown in the art to date.

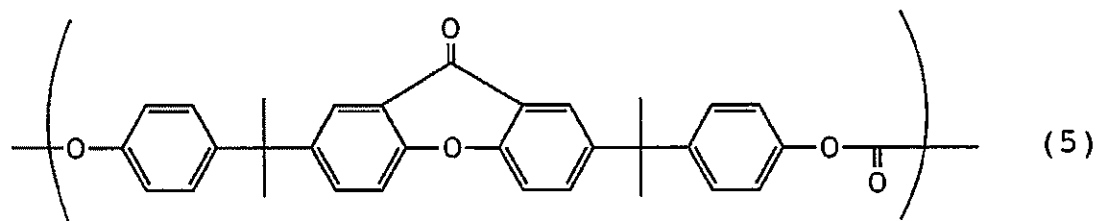
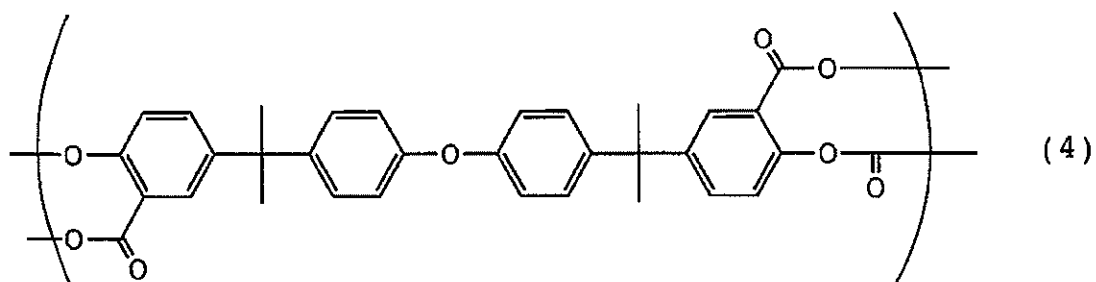
The present invention has been attained as a result of further studies on the basis of the above findings, and is embodied as follows.

In a first aspect of the present invention, there is provided an aromatic polycarbonate resin which is obtainable

from an ester exchange reaction of an aromatic dihydroxyl compound and a carbonic acid diester, and satisfies such the following conditions (1) to (3) that:

- (1) viscosity-average molecular weight is 13,000 to 30,000;
- (2) the amount of the residual aromatic monohydroxy compound and the amount of the residual aromatic dihydroxyl compound in the resin are each not more than 20 ppm; and
- (3) the resin contains at least one of the structural units of the following formulae (1) to (5), with the total amount of such structural units being 1,000 to 6,000 ppm:





In a second aspect of the present invention, there is provided a process for producing a polycarbonate resin reduced in content of volatile impurities by subjecting a polycarbonate resin containing volatile impurities to melt devolatilization, said melt devolatilization of the resin being carried out after it has been passed through a polymer filter.

In a third aspect of the present invention, there is provided a process for producing a polycarbonate resin from a dihydroxyl compound and a carbonic acid diester by an ester exchange method using a polycarbonate resin producing apparatus comprising at least one reactor and at least one extruder, in which when the extruder inlet resin temperature is represented by T1 (°C) and the extruder outlet resin temperature by T2 (°C), T2 is not higher than 370°C, and ΔT given by the following equation (I) is not higher than 70°C:

$$\Delta T = T_2 - T_1 \quad (I)$$

Effect of the Invention

According to the present invention, there are provided the polycarbonate resins which are extremely lessened in content of volatile impurities such as phenols, and the processes for producing such polycarbonate resins.

Best Mode for Carrying out the Invention

A detailed account of the present invention is given below.

First, for the convenience of explanation, the processes for producing the polycarbonate resins according to the present invention are described.

In the present invention, a polycarbonate resin is produced by an ester exchange method from a dihydroxyl compound and a carbonic acid diester. Use of an ester exchange method makes it possible to obtain the polycarbonate resins regulated in the amount of terminal OH groups.

The dihydroxyl compounds that can be used as a starting material in the present invention include, for example, bis(hydroxyaryl)alkanes such as 2,2-bis(4-hydroxyphenyl)propane (aka bisphenol A), 2,2-bis(3,5-dibromo-4-hydroxyphenyl)propane (aka tetrabromobisphenol A),

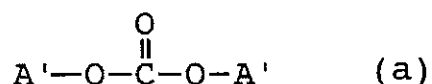
bis(4-hydroxyphenyl)methane, 1,1-bis(4-hydroxyphenyl)ethane, 2,2-bis(4-hydroxyphenyl)butane, 2,2-bis(4-hydroxyphenyl)octane, 2,2-bis(4-hydroxy-3-methylphenyl)propane, 1,1-bis(3-tert-butyl-4-hydroxyphenyl)propane, 2,2-bis(4-hydroxy-3,5-dimethylphenyl)propane, 2,2-bis(3-bromo-4-hydroxyphenyl)propane, 2,2-bis(3,5-dichloro-4-hydroxyphenyl)propane, 2,2-bis(3-phenyl-4-hydroxyphenyl)propane, 2,2-bis(3-cyclohexyl-4-hydroxyphenyl)propane, 1,1-bis(4-hydroxyphenyl)-1-phenylethane, bis(4-hydroxyphenyl)diphenylmethane, 2,2-bis(4-hydroxyphenyl)-1,1,1-trichloropropane, 2,2-bis(4-hydroxyphenyl)-1,1,1,3,3,3-hexachloropropane, and 2,2-bis(4-hydroxyphenyl)-1,1,1,3,3,3-hexafluoropropane; bis(hydroxyaryl)cycloalkanes such as 1,1-bis(4-hydroxyphenyl)cyclopentane, 1,1-bis(4-hydroxyphenyl)cyclohexane, and 1,1-bis(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane; bisphenols having a cardo structure such as 9,9-bis(4-hydroxyphenyl)fluorene, and 9,9-bis(4-hydroxy-3-methylphenyl)fluorene; dihydroxydiaryl ethers such as 4,4'-dihydroxydiphenyl ether, and 4,4'-dihydroxy-3,3'-dimethyldiphenyl ether; dihydroxydiaryl sulfides such as 4,4'-dihydroxydiphenyl sulfide, and 4,4'-dihydroxy-3,3'-dimethyldiphenyl sulfide; dihydroxydiaryl sulfoxides such as 4,4'-dihydroxydiphenyl sulfoxide, and

4,4'-dihydroxy-3,3'-dimethyldiphenyl sulfoxide;
 dihydroxydiaryl sulfones such as 4,4'-dihydroxydiphenyl
 sulfone, and 4,4'-dihydroxy-3,3'-dimethyldiphenyl sulfone;
 hydroquinone, resorcin, 4,4'-dihydroxydiphenyl, and the like.
 Of these compounds, bis(4-hydroxyphenyl)alkanes are
 preferred, and bisphenol A is especially preferred in terms
 of impact resistance. The compounds obtained by combining
 one or more tetraalkylphosphonium sulfonates with the above-
 mentioned dihydroxyl compounds can also be used for the
 purpose of improving flame retardancy. These dihydroxyl
 compounds may be used by combining two or more of them.

In the melting method, it is possible to obtain a
 branched polycarbonate resin by properly adjusting the
 reaction temperature and the amount of the catalyst used.
 Also, as part of the dihydroxyl compounds, there can be used
 the polyhydroxyl compounds such as fluoroglucine, 4,6-
 dimethyl-2,4,6-tris(4-hydroxyphenyl)heptene- 2,4,6-dimethyl-
 2,4,6-tris(4-hydroxyphenyl)heptane, 2,6-dimethyl-2,4,6-
 tris(4-hydroxyphenyl)heptene-
 3,1,3,5-tris(4-hydroxyphenyl)benzene, and 1,1,1-tri(4-
 hydroxyphenyl)ethane; 3,3-bis(4-hydroxyaryl)oxyindole (aka
 isatinbisphenol), 5-chloroisatin, 5,7-dichloroisatin, 5-
 bromoisatin and the like as a branching agent.

As the carbonic acid diesters to be used as another
 starting material, the compounds represented by the

following general formula (a) can be cited as examples.



In the above-shown formula (a), A' is a linear, branched or cyclic monovalent hydrocarbon group with a carbon number of 1 to 10, which may be substituted. The two A's may be identical or different from each other. Examples of the substituents of A' are halogen atoms, C₁₋₁₀ alkyl groups, C₁₋₁₀ alkoxy groups, phenyl groups, phenoxy groups, vinyl groups, cyano groups, ester groups, amide groups and nitro groups.

Exemplary of the carbonic acid diesters are diphenyl carbonate, substituted diphenyl carbonates such as ditolyl carbonate, and dialkyl carbonates such as dimethyl carbonate, diethyl carbonate and di-t-butyl carbonate. Among these diesters, diphenyl carbonate (which may hereinafter be abbreviated as DPC) and substituted diphenyl carbonate are preferred. These carbonic acid diesters may be used as a mixture of two or more of them.

The said carbonic acid diesters may be partially substituted with dicarboxylic acids or dicarboxylic acid esters at a rate of usually not more than 50 mol%, preferably not more than 30 mol%. Typical examples of the dicarboxylic acids and dicarboxylic acid esters are terephthalic acid, isophthalic acid, diphenyl terephthalate

and diphenyl isophthalate. When the carbonic acid diesters are substituted with these dicarboxylic acids or dicarboxylic acid diesters, polyester carbonates can be obtained.

In the ester exchange method, a dicarboxylic acid diester (which includes the above-mentioned substituted dicarboxylic acids and dicarboxylic acid esters, and this holds good throughout the following description) is used in excess of the dihydroxy compound. More definitely, the ratio (molar ratio) of the carboxylic acid diester to the dihydroxy compound is usually in the range from 1.00 to 1.30, preferably from 1.01 to 1.20, more preferably from 1.03 to 1.20. When this molar ratio is too small, there is seen a tendency for the terminal OH groups of the produced polycarbonate resin to increase, resulting in deterioration of thermal stability of the produced resin. On the other hand, if the said molar ratio is too high, there arises a decreasing tendency of the ester exchange reaction rate, making it hard to produce a polycarbonate resin having a desired molecular weight. Also, in this case, the residual amount of the carbonic acid diester in the resin increases, which may cause issuance of offensive smell during molding of the resin or after it was molded into a product.

Generally, it is possible to obtain a polycarbonate having a desired molecular weight and a desired amount of

terminal hydroxyl groups by adjusting the carbonic acid diester and dihydroxy compound mixing ratio and the degree of reduction of pressure in the reaction. As a more positive method, it is known to add a terminal stopper separately in the course of the reaction. As such a terminal stopper, monovalent phenols, monovalent carboxylic acids, carbonic acid diesters and the like can be used. The amount of the terminal hydroxyl groups exerts a great influence to thermal stability, hydrolytic stability, color tone and other qualities of the product polycarbonate. The amount of the terminal hydroxyl groups, although variable depending on the purpose of use of the product, is usually not more than 1,000 ppm, preferably not more than 700 ppm, for providing the product with practical properties.

Usually, an ester exchange catalyst is used in the ester exchange method. The ester exchange catalyst used in the present invention is not specifically defined, but the alkaline metal compounds and/or alkaline earth metal compounds are preferably used. It is also possible to use therewith the basic compounds such as basic boron compounds, basic phosphorus compounds, basic ammonium compounds and amine type compounds as an adjunct. Of these ester exchange catalysts, the alkaline metal compounds are preferred from the viewpoint of practicality. These ester exchange catalysts may be used as a combination of two or more of

them. The amount of the ester exchange catalyst(s) used in the present invention is in the range usually from 1×10^{-9} to 1×10^{-1} , preferably from 1×10^{-7} to 1×10^{-3} , more preferably from 1×10^{-7} to 1×10^{-5} .

The alkaline metal compounds usable as the ester exchange catalyst in the present invention include the inorganic alkaline metal compounds such as hydroxides, carbonates and hydrogencarbonates of alkaline metals, and the organic alkaline metal compounds such as salts with alcohols (or phenols) and organocarboxylic acids of alkaline metals. The alkaline metals referred to herein include, for instance, lithium, sodium, potassium, rubidium and cesium. Of these alkaline metal compounds, the cesium compounds, especially cesium carbonate, cesium hydrogencarbonate and cesium hydroxide are preferred.

The ester exchange reaction of a dihydroxy compound and a carbonic acid diester can be carried out according to the following process.

First, as a step for preparing the starting mixture, a mixed molten solution of the starting materials is prepared in an atmosphere of an inert gas such as nitrogen or argon by using the batch-type, half-batch-type or continuous agitators. When, for instance, bisphenol A is used as the dihydroxy compound and diphenyl carbonate as the carbonic acid diester, the melt mixing temperature is selected from

the range usually from 120 to 180°C, preferably from 125 to 160°C.

Then, as a step for polycondensation, an ester exchange reaction between a dihydroxy compound and a carbonic acid diester is carried out. This ester exchange reaction is conducted continuously, usually in two or more stages, preferably in a 3 to 7 multi-stage scheme. The specific reaction conditions for each agitator are 150 to 320°C, normal to reduced pressure (0.01 Torr, 1.3 Pa), and 5 to 150 minutes in average residence time.

In each multi-stage reactor, in order to efficiently remove phenols formed as a by-product with the progress of the polycondensation reaction out of the system, the temperature and the degree of vacuum are increased stepwise within the above-defined range of reaction conditions, with the final degree of vacuum reaching 2 Torr (266.6 Pa) or below. This makes it possible to carry out the melt polycondensation reaction while removing the by-products such as the aromatic hydroxyl compounds. For preventing degradation of quality such as hue of the produced polycarbonate resin, it is expedient to keep the temperature as low and residence time as short as they can be within the above-defined limitation.

As the deactivator of the catalyst in the polycarbonate obtained from the ester exchange reaction, the

compounds capable of neutralizing the catalyst used, for example, the sulfur-containing acidic compounds or their derivatives can be used. The catalyst-neutralizing compound is used in an amount of usually 0.5 to 10 equivalents, preferably 1 to 5 equivalents to the alkaline metal contained in the catalyst. Also, the ratio of the catalyst-neutralizing compound to the polycarbonate is in the range usually from 1 to 100 ppm, preferably from 1 to 20 ppm.

The viscosity-average molecular weight of the product polycarbonate resins, though not specifically defined, usually falls within the range from 13,000 to 30,000, preferably from 20,000 to 30,000, more preferably from 23,000 to 30,000. If the viscosity-average molecular weight exceeds 30,000, fluidity in the molding operation may deteriorate, and if it is less than 13,000, workability may be impaired. The viscosity-average molecular weight shown here is the value determined based on the solution viscosity measured at 20°C using methylene chloride as solvent.

<First production method>

The present invention provides a process for producing the polycarbonate resins with a reduced content of volatile impurities by subjecting the polycarbonate resins containing volatile impurities to melt devolatilization, characterized in that melt devolatilization is conducted after passing the polycarbonate resin through a polymer filter.

The polymer filter used in the present invention is a filter capable of removing the foreign substances existing in the polycarbonate resins. It is possible to use various known types of filter such as candle type, pleat type, leaf disc type, etc., but a leaf disc type polymer filter is especially preferred. The leaf disc type usually comprises one or more disc-shaped woven wire gauzes with various wire sizes and openings, said wire gauzes being placed one over another in layers. The types of weave usable in the present invention include, for instance, plain weave, twilling, plain dutch weave, and twilled dutch weave. The gauze may be nonwoven. As for the gauze material, usually stainless steel materials such as SUS-316 and SUS-316L are used, but it is also possible to use sintered metals and resins. The absolute filtration precision required in the present invention is usually 0.5 to 50 μm , preferably 0.5 to 20 μm .

The method for melt devolatilization is not specified in the present invention. Various methods are available for this operation, for example, a method using a vented melt extruder, a method using a thin-film evaporator and a method in which the starting materials are melted and agitated in an agitator. In this invention, it is preferred to employ the method using a vented melt extruder or the method using a thin-film evaporator, particularly the former.

As the vented melt extruder, there can be used, for

example, a vented single or multiple screw extruder, preferably an intermeshing double screw extruder. The screws may be revolved either in the same direction or in the opposite directions. Also, the number of the vents is not restricted, but usually it is properly selected within the range of 1 to 10. The resin temperature in the extruder is measured by the resin thermometers set in the center and at the exit of each barrel of the extruder. The resin thermometers are set to indicate the highest temperature registered in the operation. As the thermometer, a thermocouple or infrared contact type is preferably used. The resin supplied to the extruder may be either in a molten state or in the form of pellets.

In the present invention, a polycarbonate resin which has already been pelletized by a melt extruder provided with a polymer filter at its outlet may be used as the starting material, and it may be melt extruded for devolatilization before molding. It is, however, preferable to carry out melt extrusion for devolatilization by using a system having a polymer filter disposed between a pair of vented melt extruders connected in series to each other by piping. In this case, the location of the polymer filter is not restricted; it may be disposed, for example, at the outlet of the first vented melt extruder, halfway in the extruder-connecting pipe or at the inlet of the last vented melt

extruder.

It is preferable to use an extruder with its screws revolving in the same direction for the first vented melt extruder and an extruder with its screws revolving in the opposite directions for the last vented melt extruder. Basically, the type having the screws arranged to revolve in the same direction is designed for facilitating the mixing operation while the type having the screws arranged to revolve in the opposite directions is purported for giving priority to the kneading operation. However, from the viewpoint of removal of volatile impurities, that is, from the aspect of devolatilization effect, the opposite-direction screw revolution type extruder is preferred as it excels in surface renewability, especially a partially intermeshed screw type being said most preferable. Generally, however, since there are many cases where various types of additives need be added to the extruder, the same-direction screw revolution type extruder, which is smaller in variation of dispersibility or extrusion rate, is more convenient to use. Therefore, it is important to adopt a structure which makes best use of the characteristics of the respective types, and this makes it possible to obtain a high-quality product.

The molten resin temperature in the last vented melt extruder is preferably set lower than that in the first

vented melt extruder. The molten resin temperature is preferably as low as possible because it needs to suppress regeneration of phenols due to decomposition of the polymer or carbonic acid diester for effectively removing the volatile impurities. It is to be noted, however, that in case where a polymer filter is provided in the first vented melt extruder, if the resin temperature is lowered excessively, although it is possible to suppress decomposition of the polymer or carbonic acid diester, the pressure differential after passage through the polymer filter rises sharply, which may cause damage to the polymer filter. Also, in case where the additives are supplied to the extruder, a low resin temperature serves for worsening miscibility and/or dispersibility of the materials due to the increased resin viscosity. Accordingly, the molten resin temperature (T_1) in the first vented melt extruder is set at usually 200 to 400°C, preferably 250 to 380°C, while the molten resin temperature (T_2) in the last vented melt extruder is set at usually 200 to 350°C, preferably 220 to 330°C, with the difference between T_1 and T_2 being usually 1 to 100°C, preferably 1 to 50°C.

The molten resin residence time (θ_1) in the last vented melt extruder is preferably set shorter than the molten resin residence time (θ_2) in the first vented melt extruder. From the viewpoint of removal of volatile

impurities, a shorter residence time of the molten resin is more advantageous for the decomposition of the said polymer or carbonic acid diester. On the other hand, in case where various types of additives are supplied to the first vented melt extruder, a short residence time worsens dispersibility. It is therefore preferable not to supply any additives and to shorten the residence time in the last vented melt extruder so as to maximize the volatile impurity removal effect. The molten resin residence time (θ_1) in the first vented melt extruder is usually 0.1 to 60 minutes, preferably 1 to 30 minutes, while the molten resin residence time (θ_2) in the last vented melt extruder is usually 0.1 to 60 minutes, preferably 0.5 to 20 minutes, with the difference between θ_1 and θ_2 being usually 0.1 to 30 minutes, preferably 1 to 10 minutes. Residence time can be varied by changing the barrel length of the melt extruder.

The vent pressure in the last vented melt extruder is preferably set to be lower than that in the first vented melt extruder. It has been considered that a lower vent pressure was preferable for the removal of volatile impurities, that is, for the betterment of devolatilization efficiency. It was found, however, that the removal of phenols in particular is greatly dependent on the molten resin temperature, and even if the vent pressure is lowered in a state of high resin temperature, although the content

of carbonic acid diester can be lowered, the content of phenols is rather increased. Therefore, by lowering the molten resin temperature as well as vent pressure in the last vented melt extruder, it is possible to elevate the phenol removing efficiency. The vent pressure (P_1) in the first vented melt extruder is usually in the range from 0.01 to 100 kPa, preferably from 0.1 to 70 kPa, while the vent pressure (P_2) in the last vented melt extruder is usually in the range from 0.001 to 80 kPa, preferably from 0.01 to 50 kPa, with the difference between P_1 and P_2 being usually in the range from 0.01 to 100 kPa, preferably from 0.1 to 80 kPa.

In the present invention, it is preferable to use water as a devolatilization assistant. Water supplied to the extruder is not subject to any specific restrictions as far as it does not exert any influence to the quality of the produced polycarbonate resins, but use of water with a low electric conductivity is preferred. Electric conductivity of water used in the present invention is usually not higher than 1 mS/cm, preferably not higher than 1 μ S/cm. The primary object of introducing a devolatilization assistant is to expedite devolatilization while promoting diffusion of volatile impurities from the surface layer by the reduction of partial pressure of the volatile impurities incidental to the evaporation of the devolatilization assistant or its

azeotropic effect. It should be noted, however, that too small supply of the devolatilization assistant may prove unable to provide a satisfactory enhancement of devolatilization, while too much supply of the assistant may cause hydrolysis of the polymer to invite reduction of molecular weight of the polymer or deterioration of its hue. In the light of these facts, the amount of water to be supplied as a devolatilization assistant is usually in the range from 0.01 to 5% by weight, preferably from 0.05 to 2% by weight, based on the amount of the extruded resin. The devolatilization assistant may be supplied to either the first vented melt extruder or the last vented melt extruder, or to both of them.

The polycarbonate resin discharged from the last vented melt extruder is usually made into pellets by a conventional method. In case of using cooling water in cooling and cutting of the discharged polycarbonate resin for pelletization, such cooling water is preferably one with a low electric conductivity, which is usually not higher than 1 mS/cm, preferably not higher than 1 μ S/cm as mentioned before. According to the present invention, it is possible to produce the polycarbonate resins remarkably reduced in content of volatile impurities such as phenols. For instance, the content of phenols in the produced polycarbonate resins according to the present invention is

usually not higher than 20 ppm, preferably not higher than 15 ppm, more preferably not higher than 10 ppm.

A preferred embodiment of the present invention employing an ester exchange process for producing a polycarbonate resin is a process featuring use of a polycarbonate resin producing apparatus comprising at least one reactor and at least one extruder, with at least one of the extruders being a vented melt extruder, and a polymer filter provided at the inlet side of the vented melt extruder (at the inlet side of the last vented melt extruder in case where two or more vented melt extruders are provided), wherein a hydroxyl compound and a carbonic acid diester are subjected to an ester exchange reaction in the reactor, and melt devolatilization for the removal of volatile impurities is carried out by the extruder.

<Second production method>

The present invention also provides a process for producing a polycarbonate resin from a dihydroxy compound and a carbonic acid diester by their ester exchange, by using a polycarbonate resin producing apparatus comprising at least one reactor and at least one extruder, characterized in that when the extruder inlet resin temperature is expressed by T_1 (°C) and the extruder outlet resin temperature by T_2 (°C), T_2 is not higher than 370°C, and ΔT given by the following equation (I) is not higher

than 70°C:

$$\Delta T = T_2 - T_1 \quad (I)$$

In the case of the producing apparatus comprising one extruder, T_1 and T_2 indicate the inlet resin temperature (final reactor outlet resin temperature) and the outlet resin temperature, respectively, of that one extruder, and in the case of the producing apparatus comprising two extruders, T_1 and T_2 indicate the first extruder inlet resin temperature (final reactor outlet resin temperature) and the second extruder outlet resin temperature, respectively.

When the extruder outlet resin temperature T_2 exceeds 370°C or ΔT is over 70°C, removal of the volatile components becomes difficult. This is considered attributable to the pyrolysis of the polycarbonate resin and/or decomposition of the starting materials. The extruder outlet resin temperature T_2 is preferably in the range from 250 to 350°C, and ΔT given by the above-shown equation (I) is preferably not higher than 50°C.

In the present invention, for the same reason as stated above, the difference between the maximum preset temperature ($T_{\max}$) and the minimum preset temperature ($T_{\min}$) of the barrel in the said extruder is one that satisfies the following equation (II):

$$T_{\max} - T_{\min} = 40 - 120^{\circ}\text{C} \quad (II)$$

In the above equation (II), $T_{\min}$ is preferably in the

range from 200 to 240°C, and the difference between the maximum preset temperature ($T_{\max}$) and the minimum preset temperature ($T_{\min}$) is preferably in the range from 60 to 120°C.

In the present invention, it is preferable that at least one of the extruders is a vented melt extruder, and it is more preferable that the final one of the extruders is a vented melt extruder. The type of the vented melt extruder is not specified; it may be a single screw or multiple screw type extruder, and it is also possible to employ a suitable screw revolution type such as opposite-direction screw revolution type, partially intermeshed opposite-direction screw revolution type, etc. The number of the vents is not restricted and may be properly selected from the range from 1 to 10.

For carrying out melt extrusion for devolatilization by using a vented melt extruder, the following two modes of practice (i) and (ii) are recommended.

(i) In case where no polymer filter treatment is conducted after devolatilization melt extrusion of the resin, devolatilization melt extrusion is carried out under the conditions that the extruder outlet resin temperature T_2 satisfies the formula (1), and that the peripheral speed (m/min) of the extruder screw satisfies the formula (2). The peripheral speed of the screw given in the formula (2)

is the peripheral speed at the largest outer diameter portion of the screw.

$$295 \times [\eta]^{0.1} \leq T_2 \leq 340 \times [\eta]^{0.1} \quad (1)$$

$$T_2/40 \leq V \leq T_2/5 \quad (2)$$

(In the above formula (1), $[\eta]$ indicates the intrinsic viscosity of the polycarbonate resin measured as a methylene chloride solution (polycarbonate resin concentration: 0.6 g/dL) at 20°C by an Ubbelohde viscometer.)

Formula (1) is an empirical formula which defines the extruder outlet resin temperature (molten resin temperature) used in the present invention by the extruder outlet resin temperature (molten resin temperature) and the intrinsic viscosity (a function of viscosity-average molecular weight) of the polycarbonate resin. This formula has the following significance.

The extruder outlet resin temperature needs to be properly selected in accordance with intrinsic viscosity of the molten resin flowing through the extruder. It has been generally considered that by setting the extruder outlet resin temperature so that it will become higher proportionally to the viscosity, it would be possible to better miscibility with the additives and to realize effective removal of the volatile components. The results of many experiments, however, revealed quite unexpectedly the fact that the removal of volatile components is rather

hindered when the extruder outlet resin temperature exceeds a certain mark. This is considered due to pyrolysis of the polycarbonate resin and/or decomposition of the starting materials. On the other hand, when the extruder outlet resin temperature is below a certain level, it not only becomes difficult to remove the volatile components as a result of a rise of melt viscosity of the resin, but there also takes place a hike of cylinder supply pressure or even crystallization. Thus, the above-shown formula (1) is an empirical formula indicating the optimal range of relation between the extruder outlet resin temperature and the intrinsic viscosity of the polycarbonate resins, which was elaborated on the basis of various phenomena such as mentioned above.

Formula (2) indicates that the peripheral speed V of the extruder screw needs to be properly selected in conformity to the extruder outlet resin temperature (T) defined by the formula (1). When the peripheral speed V of the extruder screw is below the range defined by the formula (2), it becomes difficult to remove the volatile components, while when it exceeds the range defined by the formula (2), the shearing stress exerted to the resin builds up exceedingly, resulting in a rise of resin temperature to cause pyrolysis of the polycarbonate resin and/or decomposition of the starting materials like in the previous

case, rather hindering removal of the volatile components.

In the case of (i) described above, the preferred range of extruder outlet resin temperature T_2 ($^{\circ}\text{C}$) is as defined by the following formula (10), and the preferred range of peripheral speed V (m/min) of extruder screw is as defined by the formula (20):

$$295 \times [\eta]^{0.1} \leq T_2 \leq 320 \times [\eta]^{0.1} \quad (10)$$

$$T_2/30 \leq V \leq T_2/5 \quad (20)$$

(In the above formula (10), $[\eta]$ has the same meaning as $[\eta]$ in the formula (1)).

(ii) In case where devolatilization melt extrusion of resin is carried out plus a treatment by a polymer filter, the extruding operation is conducted under the conditions that the extruder outlet resin temperature T_2 satisfies the following formula (3), and that peripheral speed V (m/min) of the extruder screw satisfies the formula (4):

$$295 \times [\eta]^{0.1} + 20 \leq T_2 \leq 340 \times [\eta]^{0.1} + 20 \quad (3)$$

$$T_2/40 \leq V \leq T_2/5 \quad (4)$$

(In the above formula (3), $[\eta]$ has the same meaning as $[\eta]$ in the formula (1)).

The technical meanings of the formulae (3) and (4) are the same as those of the afore-shown formulae (1) and (2). It is necessary to elevate the extruder outlet resin temperature for preventing the rise of pressure loss experienced in the polymer filter treatment, and naturally

the allowable conditions differ from those required in case where no polymer filter treatment is conducted.

In the case of (ii), the preferred range of extruder outlet resin temperature T2 (°C) is as defined by the following formula (30), and the preferred range of peripheral speed V (m/min) of the extruder screw is as defined by the formula (40):

$$310 \times [\eta]^{0.1} + 20 \leq T2 \leq 340 \times [\eta]^{0.1} + 20 \quad (30)$$

$$T2/30 \leq V \leq T2/5 \quad (40)$$

(In the above formula (30), $[\eta]$ has the same meaning as $[\eta]$ in the formula (1)).

The polymer filter used in the present invention is a filter capable of removing the foreign substances existing in the polycarbonate resins. It is possible to use various known types of filter such as candle type, pleat type, leaf disc type, etc., but a leaf disc type polymer filter is especially preferred. The leaf disc type usually comprises one or more disc-shaped woven wire gauzes with various wire sizes and openings, said wire gauzes being placed one over another in layers. The types of weave usable in the present invention include, for instance, plain weave, twilling, plain dutch weave, and twilled dutch weave. The gauze may be nonwoven. As for the gauze material, usually stainless steel materials such as SUS-316 and SUS-316L are used, but it is also possible to use sintered metals and resins. The

absolute filtration precision required in the present invention is usually 0.5 to 50 μm , preferably 0.5 to 20 μm .

In the present invention, water can be used as a devolatilization assistant. The water supplied to the extruder is not subject to any specific restrictions as far as it does not affect the properties of the polycarbonate resins, but use of water with a low electric conductivity, usually not higher than 1 mS/cm, preferably not higher than 1 $\mu\text{S/cm}$, is preferred. The amount of water to be supplied to the extruder is usually 5 to 5,000 ppm, preferably 5 to 3,000 ppm, more preferably 5 to 2,000 ppm, based on the polycarbonate resin.

The polycarbonate resin obtained from the process of the present invention is usually made into pellets by a conventional method. In case of using cooling water in cooling and cutting of the polycarbonate resin for forming its pellets, electric conductivity of such cooling water is preferably as low as possible, which, as in the previous case, is usually not higher than 1 mS/cm, preferably not higher than 1 $\mu\text{S/cm}$.

According to the present invention, it is possible to produce the polycarbonate resins which are remarkably reduced in content of volatile impurities. In these polycarbonate resins, most significantly, the content of aromatic monohydroxy compounds and the content of aromatic

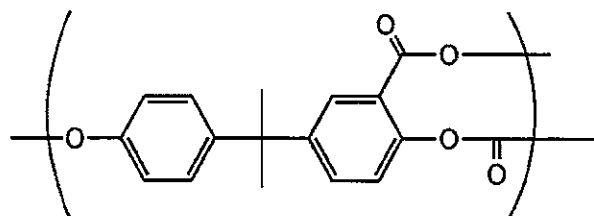
dihydroxy compounds are both usually not more than 20 ppm, particularly the former being preferably not more than 10 ppm.

<Aromatic polycarbonate resins>

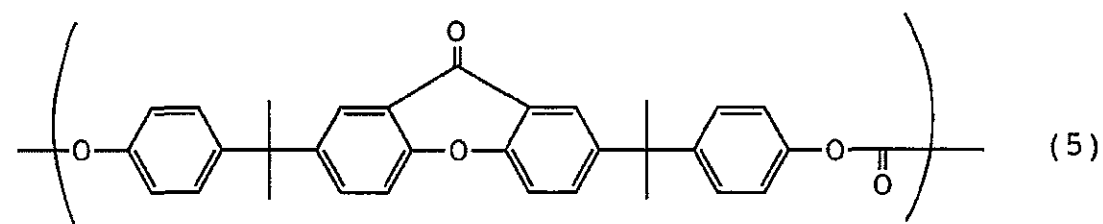
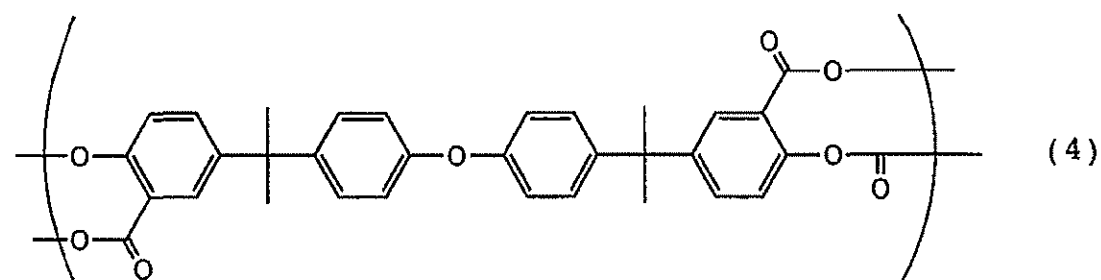
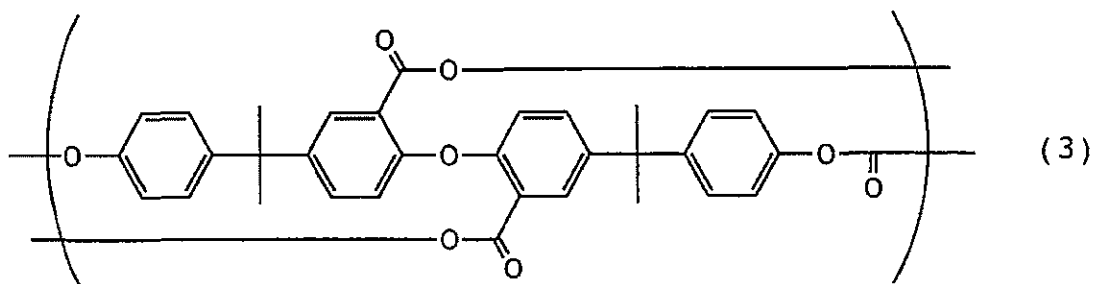
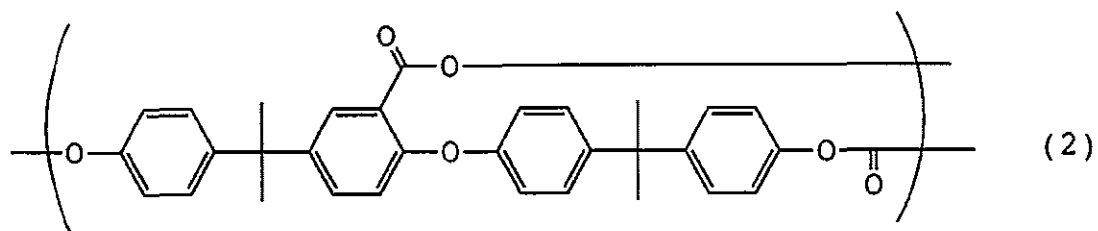
Now, the aromatic polycarbonate resins of the present invention are explained.

The aromatic polycarbonate resins of the present invention are produced by an ester exchange reaction of aromatic dihydroxy compounds and carbonic acid diesters, and satisfies such the following conditions that:

- (1) the viscosity-average molecular weight is 13,000 to 30,000;
- (2) the amount of the aromatic monohydroxy compound and the amount of the aromatic dihydroxy compound left in the produced resins are each not more than 20 ppm; and
- (3) they contain at least one of the structural units of the following formulae (1) to (5), with the total amount of such structural units being 1,000 to 6,000:



(1)



The viscosity-average molecular weight of the aromatic polycarbonate resins of the present invention is 13,000 to 30,000, preferably 20,000 to 30,000, more preferably 23,000 to 30,000. The method for determining the viscosity-average molecular weight and the meaning of the defined range of values are the same as stated before.

The residues of the aromatic monohydroxy compound and the aromatic dihydroxy compound in the resins are each not

more than 20 ppm, particularly the former is preferably not more than 10 ppm. With these conditions satisfied, the aromatic polycarbonate resins of the present invention are provided with good properties such as high thermal stability in molding.

The total amount of the said structural units in the aromatic polycarbonate resins of the present invention is 1,000 to 6,000 ppm, preferably 2,500 to 5,500, more preferably 3,000 to 5,500. When the total amount of the structural units is less than 1,000 ppm, there may take place, for instance, drooling in blow molding, and when it exceeds 6,000 ppm, the produced resins prove unsatisfactory in fluidity. The method for determining the said structural units will be explained in the Examples given later.

The aromatic polycarbonate resins of the present invention can be obtained by the above-described method using a polycarbonate resin producing apparatus comprising at least one reactor and at least one extruder.

The content of the said structural units in the aromatic polycarbonate resins of the present invention can be adjusted by properly selecting the conditions of the ester exchange reaction of an aromatic dihydroxy compound and a carbonic acid diester. The recommended conditions of the ester exchange reaction are as stated below.

The amount of the catalyst used in ester exchange and

the temperature (internal temperature) of the final reactor are the important factors in forming a specified amount of any of the structural units (1) to (5). The amount of the catalyst is selected from the range of usually 1×10^{-7} to 1×10^{-3} moles, preferably 1×10^{-7} to 1×10^{-5} moles, to one mole of the dihydroxy compound. The temperature of the final reactor is selected from the range of usually 260 to 300°C, preferably 270 to 290°C.

The obtained resin is supplied to an extruder and therein subjected to melt extrusion for removal of volatiles. By conducting this devolatilization melt extrusion at a specific temperature according to the present invention, it is possible to remove the volatile impurities alone, and the structural units formed in the ester exchange reaction can be maintained in the above-defined ranges of content without incurring any substantial damage.

In the polycarbonate resins according to the present invention, various known additives, such as other types of thermoplastic resin, flame retardant, impact resistance improver, antistatic agent, slip agent, anti-blocking agent, lubricant, anti-fogging agent, natural oil, synthetic oil, wax, organic filler, inorganic filler, etc., may be properly incorporated according to the purpose of use of the product resin.

The polycarbonate resins according to the present

invention find useful application to the construction materials such as sheeting, containers such as water bottle, head lamp lens for automobiles, optical lens for glasses, optical recording materials such as optical disc, photoconductive plates such as liquid crystal display, and such.

EXAMPLES

The present invention will be described in further detail with reference to the embodiments thereof, but it should be understood that the present invention is not limited to these embodiments but can as well be embodied in other forms without departing from the scope of the present invention. In the following Examples, those having the letter A affixed thereto, such as Example 1A, correspond to the first production method, and those having the letter B affixed thereto, such as Example 1B, correspond to the second production method. Analyses of the polycarbonate resins were made in the following way.

(1) Viscosity-average molecular weight (Mv):

Intrinsic viscosity $[\eta]$ was measured in a methylene chloride solution at 20°C using a Ubbelohde viscometer, and viscosity-average molecular weight (Mv) was determined according to the following equation.

$$[\eta] = 1.23 \times 10^{-4} \times (\text{Mv})^{0.83}$$

(2) Concentration of terminal hydroxyl groups:

0.1 g of resin was dissolved in 10 ml of methylene chloride, to which 5 ml of a 5% methylene chloride solution of acetic acid (special grade, produced by Wako Pure Chemicals Co., Ltd.) and 10 ml of a 2.5% methylene chloride solution of titanium tetrachloride (special grade, produced by Wako Pure Chemicals) to develop color, and the absorbance was determined at 546 nm using a spectrophotometer (Model UV160 mfd. by Hitachi Corp.). Separately from the above, extinction coefficient was determined using a methylene chloride solution of divalent phenol used in producing the resin, from which the concentration of OH groups in the sample was determined.

(3) Amount of residual monomers:

1.2 g of resin was dissolved in 7 ml of methylene chloride, to which 23 ml of acetone was added with stirring to cause reprecipitation. The supernatant was subjected to liquid chromatography (LC-10AT mfd. by Shimadzu Corp.; column: MCI GEL ODS (5 μ m), 4.6 mmID x 150 mmL; detector: UV 219 nm; eluent: acetonitrile/water = 4/6 by volume) to determine the amount of residual phenol, the amount of residual bisphenol A (BPA) and the amount of residual diphenyl carbonate (DPC) in the resin.

(4) Amount of foreign matter:

The resin pellets were dried in a nitrogen atmosphere

at 120°C for more than 6 hours and worked into a 70 μ m thick film by a 30 mm single crew extruder (mfd. by Isuzu Chemical Industries Co., Ltd.). The 90 cm x 50 cm pieces (about 4 g per piece) were cut out from the film as samples, and they were observed under a stereo microscope, marking the transparent foreign matter (fish eyes) having no nucleus. The number of the fish eyes having a size of 10 μ m or greater was counted and shown as the number of foreign matter per gram of the resin.

(5) Determination of structural units (1) to (5):

0.5 g of polycarbonate was precisely weighed into a flask and dissolved in 5 ml of methylene chloride. To this solution, 45 ml of methanol and 5 ml of a 25 wt% sodium hydroxide solution were added, and the mixture was stirred at 70°C for 30 minutes while conducting dry distillation by a condenser. After allowing the solution to cool by itself, the condenser was washed with 5 ml of methanol and the washings were added into the above solution. The mixed solution was adjusted to a pH of about 2 with 7 ml of 6N hydrochloric acid and then pure water was added to make the total amount of the solution 100 ml in a 100 ml volumetric flask.

20 μ l of this solution was subjected to liquid chromatography (LC-10AD mfd. by Shimadzu Corp.; column: YMC-PackODS-AM AM-307-3, 4.6 mmID x 75 mmI; detector: UV 280 nm;

eluent: (A) 0.05% TFA solution/(B) methanol; gradient: 0 min (B = 40%) and 25 min (B = 95%)) to determine the amount of the structural units (1) to (5). Regarding the structural units (3) and (4), as it was impossible to make their perfectly independent determination because of overlapping of their peaks, they were determined as a combined content of the two.

Example 1A:

A 140°C molten mixture prepared by mixing bisphenol A and diphenyl carbonate at a fixed molar ratio (DPC/BPA molar ratio = 1.103) under a nitrogen gas atmosphere was supplied continuously into a first vertical stirring polymerizer controlled at 210°C and normal pressure under a nitrogen atmosphere, with the liquid level being maintained constant by controlling the opening of the valve provided in the polymer discharge line at the bottom of the polymerizer so that the average residence time would become 60 minutes. Synchronously with the start of the supply of the said starting materials, a cesium carbonate solution was supplied continuously as a catalyst at a flow rate of 0.5×10^{-6} mole to 1 mole of bisphenol A. The produced distillates such as phenols were liquefied continuously by a condenser provided in a distillation line of the polymerizer and recovered as such. The reaction solution discharged from the first

polymerizer was continuously introduced into the 2nd, 3rd and 4th vertical polymerizers and then into 5th horizontal polymerizer successively. The respective polymerizers were operated under the conditions shown below in a way that a higher temperature and a higher degree of vacuum would be provided in the succeeding polymerizers with the progress of the reaction.

Specifically, the operating conditions were 210°C, 13,300 Pa and 110 rpm for the 2nd polymerizer, 240°C, 1,995 Pa and 75 rpm for the 3rd polymerizer, 260°C, 67 Pa and 75 rpm for the 4th polymerizer, and 265°C, 67 Pa and 5 rpm for the fifth polymerizer. Throughout the reaction, the liquid level was controlled so that the average residence time in each polymerizer would become 60 minutes, and at the same time the by-product phenol was evaporated away. The polycarbonate resin yield was 50 kg/hr.

The molten polymer discharged from the 5th polymerizer was introduced into a double screw extruder-1 (screw diameter: 46 mm; screw type: partially intermeshed; both screws revolving in the same direction) having the 3-stage vent holes and 3-stage feed ports, and then butyl p-toluenesulfonate and tris(2,4-di-tert-butylphenyl) phosphate were supplied in amounts of 10 ppm and 1,000 ppm, respectively, based on the resin. After devolatilization through the vents, the molten product was passed through a

leaf disc type polymer filter (comprising 135 leaf discs made of woven wire gauzes with absolute filtration precision of 40 μm , the discs being mounted in layers on a center post; hereinafter referred to as P/F), then cooled with water and pelletized.

Then the pellets, after dried at 120°C for 6 hours, were introduced into a double screw extruder-2 (screw diameter: 46 mm; screw type: partially intermeshed; both screws revolving in the same direction) having a water inlet disposed between the two vent holes, thereby melted and kneaded, then after devolatilized through the vents, cooled with water and pelletized without passing through P/F. The operating conditions of extruder-1 and extruder-2 are shown in Table 1. Average residence time was determined from the time taken from addition of 0.5 g of a bluing agent through an extruder resin feed port till it is discharged from the die. The results of property evaluation of the P/F inlet resin and P/F outlet resin (pellets) of the double screw extruder-1 and the double screw extruder-2 outlet resin (pellets) are shown in Table 2.

Example 2A:

The same procedure as defined in Example 1A was conducted except that the pellets were formed by using a devolatilization extruder having a double screw extruder-1

(provided with P/F) and a double screw extruder-2 (no P/F) connected in series to each other by a pipe to produce an aromatic polycarbonate resin, and the properties of the obtained resin were evaluated. The operating conditions of the double screw extruder-2 and the results of property evaluations are shown in Table 1 and Table 2.

Example 3A and Example 4A:

The same procedure as defined in Example 2A was conducted except that the bisphenol A to diphenyl carbonate molar ratio (DPC/BPA molar ratio) was adjusted to 1.065, that the opening of P/F was made 40 μm , that the double screw extruder-2 was replaced by an "extruder having 3-stage vent holes and 2-stage feed ports" (screw diameter: 30 mm; screw type: partially intermeshed; two screws revolving in the opposite directions), and that the operating conditions of the double screw extruder-1 and double screw extruder-2 were changed as shown in Table 1 to produce the aromatic polycarbonate resins, and the properties of the obtained resins were evaluated. Average residence time was determined by adjusting the resin feed into the extruders. The results of property evaluation are shown in Table 2.

Comparative Example 1A and Comparative Example 2A

The same procedure as defined in Example 1A was conducted except that no double screw extruder-2 was used

and the operating conditions of the double screw extruder-1 were changed as shown in Table 1 to produce the aromatic polycarbonate resins, and their properties were evaluated. The results are shown in Table 2.

Comparative Example 3A:

The same procedure as defined in Example 2A was conducted except that no double screw extruder-2 was used and the operating conditions of the double screw extruder-1 were changed as shown in Table 1 to produce a polycarbonate, and its properties were evaluated, obtaining the results shown in Table 2.

Table 1

		Example 1A	Example 2A
Double screw extruder (1)	Resin temperature (°C)	320	320
	Residence time (min)	4.7	4.7
	Vent pressure (Pa)	370	370
	Amount of water supplied (wt%)	0	0
	Screw type	Partially intermeshed	Partially intermeshed
	Screw revolving direction	Same direction	Same direction
	P/F	Provided (20 μ m)	Provided (20 μ m)
Double screw extruder (2)	Resin temperature (°C)	330	320
	Residence time (min)	5.2	2.3
	Vent pressure (Pa)	400	50
	Amount of water supplied (wt%) (Electric conductivity of water: 0.5 μ S/cm)	0.1	0
	Screw type	Wholly intermeshed	Wholly intermeshed
	Screw revolving direction	Same direction	Same direction
	P/F	None	None

Table 1 (Continued)

		Example 3A	Example 4A
Double screw extruder (1)	Resin temperature (°C)	350	350
	Residence time (min)	4.7	4.7
	Vent pressure (Pa)	200	200
	Amount of water supplied (wt%)	0.2	0.2
	Screw type	Partially intermeshed	Partially intermeshed
	Screw revolving direction	Same direction	Same direction
	P/F	Provided (40 μ m)	Provided (40 μ m)
Double screw extruder (2)	Resin temperature (°C)	343	348
	Residence time (min)	2.3	1.9
	Vent pressure (Pa)	50	50
	Amount of water supplied (wt%) (Electric conductivity of water: 0.5 μ S/cm)	0	0.1
	Screw type	Wholly intermeshed	Partially intermeshed
	Screw revolving direction	Same direction	Opposite direction
	P/F	None	None

Table 1 (Continued)

		Comp. Example 1A	Comp. Example 2A	Comp. Example 3A
Double screw extruder (1)	Resin temperature (°C)	280	330	350
	Residence time (min)	4.7	4.7	4.7
	Vent pressure (Pa)	200	200	30
	Amount of water supplied (wt%)	0.2	0.5	0.2
	Screw type	Partially inter- meshed	Partially inter- meshed	Partially inter- meshed
	Screw revolving direction	Same direction	Same direction	Same direction
	P/F	Provided (20 μ m)	Provided (20 μ m)	Provided (40 μ m)
Double screw extruder (2)	Resin temperature (°C)	-	-	-
	Residence time (min)	-	-	-
	Vent pressure (Pa)	-	-	-
	Amount of water supplied (wt%) (Electric conductivity of water: 0.5 μ S/cm)	-	-	-
	Screw type	-	-	-
	Screw revolving direction	-	-	-
	P/F	-	-	-

Table 2

		Example 1A	Example 2A
Extruder (1)P/F inlet resin	Viscosity-average molecular weight	21,200	
	Terminal OH(ppm)	367	
	PhOH residue(ppm)	41	
	BPA residue(ppm)	10	
	DPC residue(ppm)	206	
Extruder (1)P/F outlet resin	Viscosity-average molecular weight	21,100	
	Terminal OH(ppm)	383	
	PhOH residue(ppm)	52	
	BPA residue(ppm)	14	
	DPC residue(ppm)	210	
	Foreign matter(pieces/g)	5	
Extruder (2)P/F outlet resin	Viscosity-average molecular weight	21,100	21,000
	Terminal OH(ppm)	380	377
	PhOH residue(ppm)	23	14
	BPA residue(ppm)	8	7
	DPC residue(ppm)	103	58
	Foreign matter(pieces/g)	5	6

Table 2 (Continued)

		Example 3A	Example 4A
Extruder (1)P/F inlet resin	Viscosity-average molecular weight	26,600	
	Terminal OH(ppm)	719	
	PhOH residue(ppm)	21	
	BPA residue(ppm)	24	
	DPC residue(ppm)	43	
Extruder (1)P/F outlet resin	Viscosity-average molecular weight	26,200	
	Terminal OH(ppm)	716	
	PhOH residue(ppm)	31	
	BPA residue(ppm)	33	
	DPC residue(ppm)	43	
	Foreign matter(pieces/g)	6	
Extruder (2)P/F outlet resin	Viscosity-average molecular weight	26,200	26,100
	Terminal OH(ppm)	710	711
	PhOH residue(ppm)	9	2
	BPA residue(ppm)	4	Undetected
	DPC residue(ppm)	21	8
	Foreign matter(pieces/g)	6	6

Table 2 (Continued)

		Comp. Example 1A	Comp. Example 2A	Comp. Example 3A
Extruder (1) P/F inlet resin	Viscosity-average molecular weight	21,000	21,000	26,300
	Terminal OH (ppm)	358	361	734
	PhOH residue (ppm)	34	38	46
	BPA residue (ppm)	9	10	20
	DPC residue (ppm)	169	229	21
Extruder (1) P/F outlet resin	Viscosity-average molecular weight	21,000	20,400	25,800
	Terminal OH (ppm)	360	388	751
	PhOH residue (ppm)	47	51	58
	BPA residue (ppm)	13	16	22
	DPC residue (ppm)	172	257	36
	Foreign matter (pieces/g)	5	8	11
Extruder (2) P/F outlet resin	Viscosity-average molecular weight	-	-	-
	Terminal OH (ppm)	-	-	-
	PhOH residue (ppm)	-	-	-
	BPA residue (ppm)	-	-	-
	DPC residue (ppm)	-	-	-
	Foreign matter (pieces/g)	-	-	-

Example 1B:

An aromatic polycarbonate resin was produced by a continuous production apparatus comprising four vertical stirring reactors and one horizontal stirring reactor which were operated under the conditions shown below:

First vertical stirring reactor: 220°C, 13.3 kPa

Second vertical stirring reactor: 240°C, 2 kPa

Third vertical stirring reactor: 270°C, 67 Pa

Fourth vertical stirring reactor: 270°C, 67 Pa

Fifth horizontal stirring reactor: 270°C, 67 Pa

First, in the starting material preparation step, bisphenol A (BPA) and diphenyl carbonate (DPC) were mixed at a specified molar ratio ($\text{DPC/BPA} = 1.030$) and heated at 140°C under a nitrogen gas atmosphere to obtain a mixed molten solution of starting materials. Then this solution was supplied continuously into the first stirring reactor through a starting material feed pipe heated to 140°C. The liquid level was maintained constant while controlling the opening of the valve provided in the polymer discharge line at the bottom of the reactor so that the average residence time would stay at 60 minutes. Simultaneously with start of the supply of said mixed solution of starting materials, a cesium carbonate solution was supplied continuously as a catalyst into the first vertical stirring reactor from a catalyst feed pipe at a rate of 1 μmol to one mole of bisphenol A.

The polymerization reaction solution discharged from the bottom of the first vertical stirring reactor was successively supplied into the second vertical stirring reactor, the third vertical stirring reactor, the fourth vertical stirring reactor and the fifth horizontal stirring reactor. During the polymerization reaction, the liquid level was controlled so that the average residence time in

each reactor would become 60 minutes, and the phenols formed as by-products in the polymerization reaction were evaporated away. The production rate of the aromatic polycarbonate resin was 15 kg/hr. The thus obtained aromatic polycarbonate resin had the following specificities: viscosity-average molecular weight = 25,800; content of bisphenol A = 24 ppm; content of diphenyl carbonate = 39 ppm; content of phenol = 33 ppm; content of structural unit (1) = 1,754 ppm; content of structural unit (2) = 1,286 ppm, total content of structural units (3) and (4) = 1,092 ppm; content of structural unit (5) = 145 ppm.

Then the above aromatic polycarbonate resin was supplied to an extruder connected to the fifth horizontal stirring reactor and subjected to devolatilization melt extrusion in the manner specified below.

The above aromatic polycarbonate resin was supplied to a double screw extruder JSW TEX30 mfd. by Japan Steel Works, Ltd. (the largest diameter portion of the screw: 30 mm) at a rate of 12.5 kg/hr and pelletized. The extruder operating conditions were as follows: extruder inlet (fifth horizontal reactor outlet) resin temperature = 270°C; extruder outlet resin temperature = 284°C; screw revolution = 100 rpm (peripheral speed = 9 m/min); degree of vacuum = 60 Pa. The strand of resin discharged from the extruder die was cooled and cut into pellets. The thus obtained resin pellets had a

phenol content of 4 ppm and a bisphenol A content of 18 ppm. The contents of the structural units (1) to (5) were the same as mentioned before.

The amount of the monomers was determined in the following way. 1.2 g of the polymer was dissolved in 7 ml of methylene chloride, to which 23 ml of acetone was added with stirring to cause reprecipitation, and the supernatant solution was subjected to liquid chromatography (LC-10AT mfd. by Shimadzu Corp.; column: MCI GEL ODS, 5 μ m, 4.6 mmID x 150 mmL; detector: UV 219 nm; eluent: acetonitrile/water = 4/6) to thereby determine the amount of phenol and the amount of bisphenol A in the polymer.

Example 2B:

The same procedure as defined in Example 1B was conducted except for the changes of the resin feed to the extruder to 15 kg/hr, extruder outlet resin temperature to 314°C, screw revolution to 150 rpm (peripheral speed: 14 m/min) and the degree of vacuum to 90 Pa. The phenol content and the bisphenol A content in the obtained resin pellets were 14 ppm and 17 ppm, respectively.

Comparative Example 1B:

The same procedure as defined in Example 1B was conducted except for the changes of the resin feed to the

extruder to 15 kg/hr, extruder outlet resin temperature to 342°C, screw revolution to 150 rpm (peripheral speed : 14 m/min) and the degree of vacuum to 90 Pa. The obtained resin pellets had a phenol content of 24 ppm and a bisphenol A content of 18 ppm.

The results of the above-described Examples 1B and 2B and Comparative Example 1B are shown collectively in Table 3 along with the melt extrusion conditions.

Table 3

	Example 1B	Example 2B	Comp. Example 1B
Extruder inlet resin temperature (°C)	270	270	270
Extruder outlet resin temperature (°C)	284	314	342
Range of temperature (°C) of formula (1) specified in the specification	279 - 321		
Temperature applied (°C)	284	314	342
Range of peripheral speed (m/min) of formula (2) specified in the specification	7 - 57	8 - 63	9 - 68
Peripheral speed applied (m/min)	9	14	14
Degree of vacuum (Pa)	60	90	90
Phenol content (ppm)	4	14	24
Bisphenol A content (ppm)	18	17	18
Content of structural unit (1) (ppm)	1754		
Content of structural unit (2) (ppm)	1286		
Total content of structural units (3) and (4) (ppm)	1092		
Content of structural unit (5) (ppm)	145		

Example 3B:

The same procedure as defined in Example 1B was conducted except that 4 pieces of leaf disc type polymer filter mfd. by Japan Pole Co., Ltd. (absolute filtration precision: 20 μ m) were set at the outlet of the extruder, that the resin feed was changed to 15 kg/hr, that the extruder outlet resin temperature was changed to 340°C, that the screw revolution was changed to 150 rpm (peripheral

speed: 14 m/min), that the degree of vacuum was changed to 60 Pa, and that water with an electric conductivity of 0.5 $\mu\text{S}/\text{cm}$ was supplied to the extruder as a devolatilization assistant in an amount of 2,000 ppm based on the resin. The obtained resin pellets had a phenol content of 19 ppm and a bisphenol A content of 24 ppm.

Comparative Example 2B

The same procedure as defined in Example 1B was conducted except that 4 pieces of leaf disc type polymer filter mfd. by Japan Pole Co., Ltd. (absolute filtration precision: 20 μm) were set at the extruder outlet, that the resin feed was changed to 15 kg/hr, that the extruder outlet resin temperature was changed to 355°C, that the screw revolution was changed to 150 rpm (peripheral speed: 14 m/min) and that the degree of vacuum was changed to 90 Pa. The obtained resin pellets had a phenol content of 27 ppm and a bisphenol A content of 30 ppm.

The results of the above-described Example 3B and Comparative Example 2B are shown collectively in Table 4 along with the melt extrusion conditions.

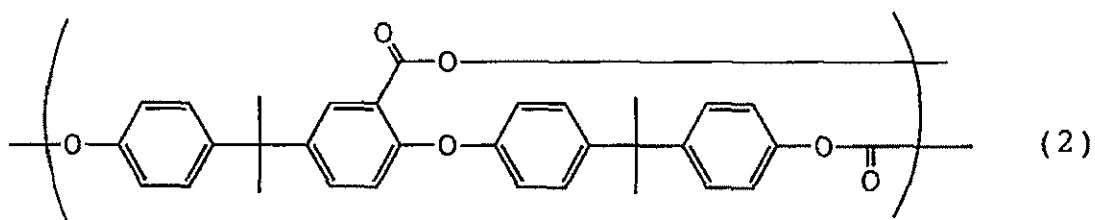
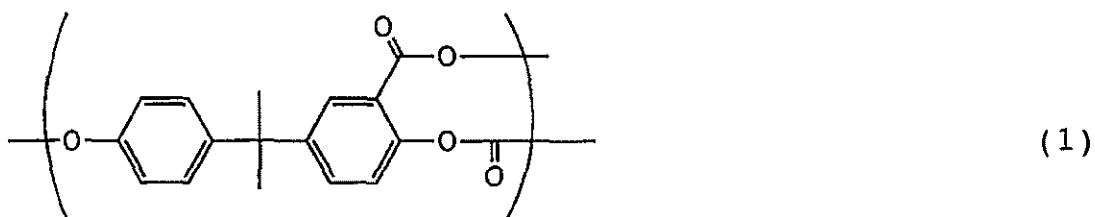
Table 4

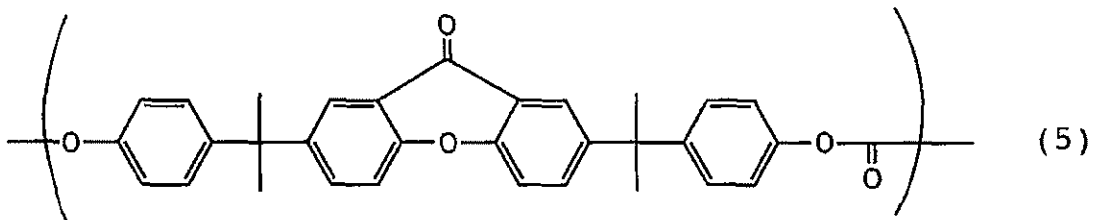
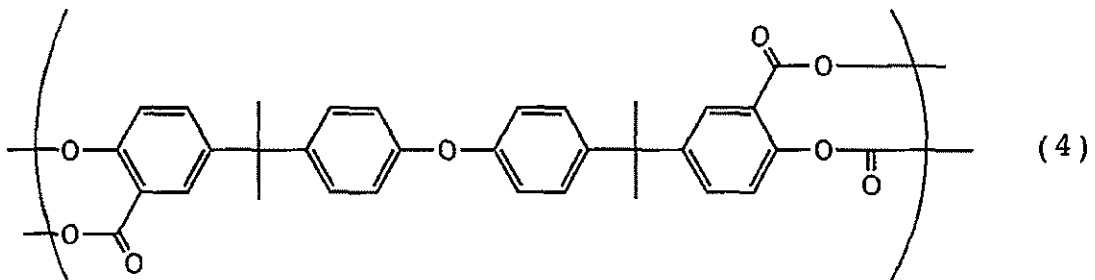
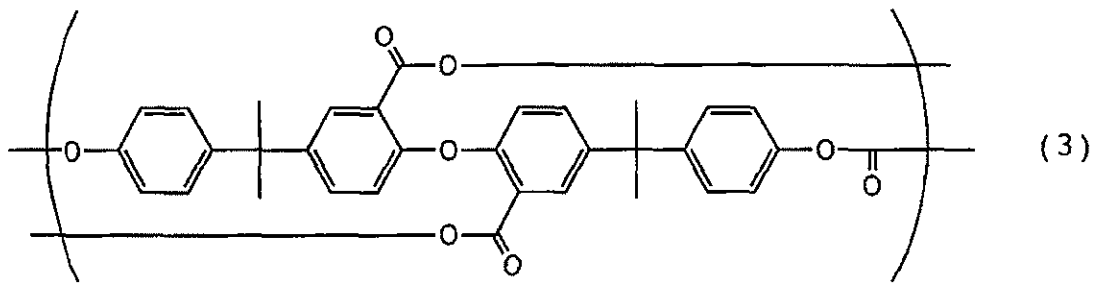
	Example 3B	Comp. Example 2B
Extruder inlet resin temperature (°C)	270	270
Extruder outlet resin temperature (°C)	340	355
Range of temperature (°C) of formula(3) specified in the specification	299 - 341	
Temperature applied (°C)	340	355
Range of peripheral speed (m/min) of formula (4) specified in the specification	9 - 68	9 - 71
Peripheral speed applied (m/min)	14	14
Degree of vacuum (Pa)	60	60
Phenol content (ppm)	19	27
Bisphenol A content (ppm)	24	30
Content of structural unit (1) (ppm)	1754	
Content of structural unit (2) (ppm)	1286	
Total content of structural units (3) and (4) (ppm)	1092	
Content of structural unit (5) (ppm)	145	

WHAT IS CLAIMED IS:

1. An aromatic polycarbonate resin which is obtainable from an ester exchange reaction of an aromatic dihydroxy compound and a carbonic acid diester, and satisfies such the following conditions (1) to (3) that:

- (1) viscosity-average molecular weight is 13,000 to 30,000;
- (2) the amount of the residual aromatic monohydroxy compound and the amount of the residual aromatic dihydroxy compound in the resin are each not more than 20 ppm; and
- (3) the resin contains at least one of the structural units of the following formulae (1) to (5), with the total amount of such structural units being 1,000 to 6,000 ppm:





2. A process for producing a polycarbonate resin reduced in content of volatile impurities by subjecting a polycarbonate resin containing volatile impurities to melt devolatilization, said melt devolatilization of the resin being carried out after it has been passed through a polymer filter.

3. The process according to Claim 2, wherein melt devolatilization is carried out by using an apparatus having a polymer filter disposed between at least two vented melt extruders connected in series to each other.

4. The process according to Claim 2 or 3, wherein an extruder with screws revolving in the same direction is used for the first vented melt extruder, and a partially intermeshed oppositely revolving screw type extruder is used for the last vented melt extruder.

5. The process according to any one of Claims 2 to 4, wherein the molten resin temperature in the last vented melt extruder is lower than that in the first vented melt extruder.

6. The process according to any one of Claims 2 to 5, wherein the residence time of the molten resin in the last vented melt extruder is shorter than that in the first vented melt extruder.

7. The process according to any one of Claims 2 to 6, wherein the vent pressure in the last vented melt extruder is lower than that in the first vented melt extruder.

8. The process according to any one of Claims 2 to 7 using a devolatilization assistance in the extruders.

9. The process according to any one of Claims 2 to 8

using a polycarbonate resin producing apparatus comprising at least one reactor and at least one extruder, at least one of the extruders being a vented melt extruder, and a polymer filter provided at the inlet side of the vented melt extruder (inlet side of the last vented melt extruder in case where two or more vented melt extruders are provided), wherein a dihydroxy compound and a carbonic acid diester are ester exchanged in the reactor, and melt removal of volatile impurities is carried out by the extruder.

10. The process according to any one of Claims 1 to 8, wherein the viscosity-average molecular weight of the polycarbonate resin is 13,000 to 30,000.

11. A process for producing a polycarbonate resin from a dihydroxy compound and a carbonic acid diester by an ester exchange method using a polycarbonate resin producing apparatus comprising at least one reactor and at least one extruder, in which when the extruder inlet resin temperature is represented by T_1 ($^{\circ}\text{C}$) and the extruder outlet resin temperature by T_2 ($^{\circ}\text{C}$), T_2 is not higher than 370°C , and ΔT given by the following equation (I) is not higher than 70°C :

$$\Delta T = T_2 - T_1 \quad (\text{I})$$

12. The process according to Claim 11, wherein the

difference between the maximum preset temperature (Tmax) and the minimum preset temperature (Tmin) of the extruder barrel satisfies the following equation (II):

$$T_{\max} - T_{\min} = 40 \text{ to } 120^{\circ}\text{C} \quad (\text{II})$$

13. The process according to Claim 12, wherein Tmin is 200 to 240°C.

14. The process according to any one of Claims 11 to 13, wherein at least one of said extruders is a vented melt extruder.

15. The process according to Claim 14, wherein the last one of said extruders is a vented melt extruder.

16. The process according to any one of Claims 11 to 15 using a devolatilization assistant in the extruders.

17. The process according to any one of Claims 11 to 16, wherein the viscosity-average molecular weight of the polycarbonate resin is 13,000 to 30,000.