

Description

Title of Invention:

METHOD FOR PRODUCING POLYPHENYLENE ETHER

Technical Field

[0001]

The present invention relates to a method for producing a polyphenylene ether.

Background Art

[0002]

Polyphenylene ethers have excellent electrical insulation, heat resistance, hydrolysis resistance, and flame retardance. Thus, resin compositions including such a polyphenylene ether have been used in the fields of, for example, home electrical appliance, office automation (OA) apparatuses, and automobile components.

[0003]

Different methods for producing a polyphenylene ether by oxidatively polymerizing a phenolic compound have been conventionally disclosed. For example, Patent Literature 1 discloses a method for controlling the absolute pressure of the reaction system to 0.098 MPa or more and less than 0.392 MPa and controlling the oxygen partial pressure of an oxygen-containing gas to 0.0147 MPa or more and 0.0883 MPa or less with the use of the

specific catalyst, for the purpose of efficiently removing water generated in oxidative polymerization of a phenolic compound. Patent Literature 1 further discloses that the flow-through rate of the oxygen-containing gas is 0.5 NL/min to 15 NL/min based on 1 kg of the reaction mixture, and that allowing the flow-through rate to be relatively low in the early stage of polymerization and to be relatively high in the latter stage of polymerization achieves a preferred result.

[0004]

In contrast, common methods for producing a polyphenylene ether have a problem of occurrence of 10 to 30% by volume of foam based on the volume of the polymerization solution in the early stage of the oxidative polymerization. This is because a phenolic compound is oxidatively polymerized by allowing an oxygen-containing gas to flow through a polymerization solution. To solve this problem, for example, Patent Literature 2 discloses a method for suppressing foaming by adding an antifoaming agent in an amount of 0.000001 to 0.0001 parts by mass to a polymerization solution composed of 10 to 25 parts by mass of a phenolic compound, 75 to 90 parts by mass of an aromatic solvent, and 0.1 to 10 parts by mass of a catalyst.

Citation List

Patent Literature

[0005]

Patent Literature 1: Japanese Patent Laid-Open No. 2002-3597

Patent Literature 2: Japanese Patent Laid-Open No. 2010-270250

Summary of Invention

Technical Problem

[0006]

In the case of performing polymerization reaction with adding an antifoaming agent to a polymerization solution based on the technologies described in Patent Literature 2, however, a disadvantage such as a decrease in the oxidative polymerization activity may cause a concern. Thus, the technologies of Patent Literature 1 and Patent Literature 2 cannot sufficiently suppress foaming while maintaining the polymerization activity in production of a polyphenylene ether.

[0007]

The present invention has been made in consideration of the problem described above, and has an object to provide a method for producing a polyphenylene ether, the method enabling the polymerization time to be reduced while sufficiently suppressing foaming in the early stage of the oxidative polymerization.

Solution to Problem

[0008]

As a result of intensive studies in consideration of the object described above, the present inventors have found that increasing the absolute pressure of a gas phase in the reactor used for producing a polyphenylene ether can suppress foaming in the early stage of the reaction although the time to complete the reaction is increased. The present inventors thus have completed the present invention based on an idea of increasing the absolute pressure described above in the early stage of the reaction to suppress foaming and reducing the absolute pressure described above in the latter stage of the reaction to reduce the time to complete the reaction.

[0009]

That is, the present invention is as follows.

[1]

A method for producing a polyphenylene ether, comprising:

a polymerization step of oxidatively polymerizing a phenolic compound (M) by allowing an oxygen-containing gas (O) to flow through a polymerization solution comprising the phenolic compound (M), an aromatic solvent (A), and a catalyst (C) in a reactor,

wherein the polymerization step comprises:

a first polymerization step of performing polymerization by controlling an absolute pressure of a

gas phase in the reactor to a first pressure of more than 0.098 MPa and 0.392 MPa or less; and

a second polymerization step of performing polymerization by controlling the absolute pressure to a second pressure lower than the first pressure and of 0.098 MPa or more and less than 0.392 MPa after the first polymerization step.

[2]

The method for producing the polyphenylene ether according to [1], wherein the second pressure is less than 90% of the first pressure.

[3]

The method for producing the polyphenylene ether according to [1] or [2], wherein the polymerization solution comprises 10 to 25 parts by mass of the phenolic compound (M), 75 to 90 parts by mass of the aromatic solvent (A), and 0.1 to 10 parts by mass of the catalyst (C), based on 100 parts by mass of a sum of the phenolic compound (M) and the aromatic solvent (A).

[4]

The method for producing the polyphenylene ether according to any of [1] to [3], wherein the phenolic compound (M) comprises 2,6-dimethylphenol or a mixture of 2,6-dimethylphenol and 2,3,6-trimethylphenol.

[5]

The method for producing the polyphenylene ether according to any of [1] to [4], wherein the aromatic

solvent (A) comprises at least one selected from the group consisting of toluene, xylene, and ethylbenzene.

[6]

The method for producing the polyphenylene ether according to any of [1] to [5], wherein the catalyst (C) comprises a copper compound, a bromine compound, and one or more selected from the group consisting of a diamine compound, a tertiary monoamine compound and a secondary monoamine compound.

[7]

The method for producing the polyphenylene ether according to any of [1] to [6], wherein the oxygen-containing gas (O) has an oxygen concentration of 5 to 25% by volume.

[8]

The method for producing the polyphenylene ether according to any of [1] to [7], wherein the oxygen-containing gas (O) comprises oxygen and nitrogen, and the oxygen-containing gas (O) has an oxygen concentration of 8 to 12% by volume.

[9]

The method for producing the polyphenylene ether according to any of [1] to [8], wherein the oxygen-containing gas (O) has an oxygen partial pressure of 0.0147 MPa or more and 0.0883 MPa or less.

Advantageous Effects of Invention

[0010]

The present invention can achieve a method for producing a polyphenylene ether, the method enabling the polymerization time to be reduced while sufficiently suppressing foaming in the early stage of the oxidative polymerization.

Description of Embodiments

[0011]

An embodiment to implement the present invention (simply referred to as "the present embodiment" hereinbelow) will be described hereinbelow in detail. The present invention is not intended to be limited to the following embodiment, but may be modified to be implemented in various ways within the scope of the gist thereof.

[0012]

[A method for producing a polyphenylene ether]

A method for producing a polyphenylene ether according to the present embodiment includes a polymerization step of oxidatively polymerizing a phenolic compound (M) by allowing an oxygen-containing gas (O) to flow through a polymerization solution containing the phenolic compound (M), an aromatic solvent (A), and a catalyst (C) in a reactor. Furthermore, the polymerization step described above of the method for producing a polyphenylene ether according to the present

embodiment includes a first polymerization step of performing polymerization by controlling the absolute pressure of the gas phase in the reactor to a first pressure of more than 0.098 MPa and 0.392 MPa or less and a second polymerization step of performing polymerization by controlling the absolute pressure to a second pressure lower than the first pressure and of 0.098 MPa or more and less than 0.392 MPa after the first polymerization step. Owing to the constitution, the method for producing a polyphenylene ether according to the present embodiment can reduce the polymerization time while sufficiently suppressing foaming in the early stage of the oxidative polymerization. That is, the method for producing a polyphenylene ether according to the present embodiment, which can suppress foaming of the polymerization solution without reducing the polymerization reaction activity, can achieve a reduction in the polymerization time.

[0013]

[Transition from the first polymerization step to the second polymerization step]

In transition from the first polymerization step to the second polymerization step, the absolute pressure of the reactor gas phase is changed from a first pressure of more than 0.098 MPa and 0.392 MPa or less to a second pressure of 0.098 MPa or more and less than 0.392 MPa. Increasing the pressure of the reactor gas phase in the

former stage of the oxidative polymerization of the phenolic compound in this manner can allow foaming of the polymerization solution to be suppressed. Alternatively, reducing the pressure of the reactor gas phase in the latter stage of the oxidative polymerization of the phenolic compound can prevent a reduction in the polymerization activity in the latter stage of the polymerization. It should be noted herein that the "former stage" refers to a period corresponding to a first polymerization step in the present embodiment and the "latter stage" refers to a period corresponding to a second polymerization step in the present embodiment. This production method enables the capacity of the reactor to be fully employed and the polymerization time to be reduced. The second pressure should be lower than the first pressure, and is preferably lower than the first pressure by 10% or more. In other words, the second pressure is preferably less than 90% of the first pressure. Additionally, it is more preferred to continue the oxidative polymerization under the second pressure lower than the first pressure by 15% or more, and it is still more preferred to continue the oxidative polymerization under the second pressure lower than the first pressure by 20% or more. It should be noted that the absolute pressure of the present embodiment can be measured by a procedure described in the examples described hereinbelow.

[0014]

In the former half (former stage) of the polymerization reaction, the height of foam, after increasing as the reaction progresses, sharply decreases. In the latter half (latter stage) of the polymerization reaction, the foam is eliminated. The timing of the change from the first polymerization step to the second polymerization step can be the time point at which the height of foam begins to decrease or later. The timing is preferably within 10 minutes before and after the time point at which the foam is completely eliminated. Specifically, the foam is completely eliminated about 10 minutes after the height of foam begins to decrease.

[0015]

The ratio of the polymerization time between the former stage and the latter stage of the polymerization (reaction) of the present embodiment is not particularly limited provided that the desirable effect of the present embodiment can be achieved. From the viewpoint of reducing the polymerization time in the latter stage, the polymerization time in the latter stage is preferably 92% or less of, more preferably 82% or less of, still more preferably 54% or less of the polymerization time in the former stage. For example, without limitation to the following, the cases where "the polymerization time in the former stage: the polymerization time in the latter

stage" is 55:45 or 65:35 can be said to be typically preferable aspects.

[0016]

The method for changing the absolute pressure of the reactor gas phase is not particularly limited. A method for changing the absolute pressure in the reactor with a pressure adjusting valve for the reactor gas phase is industrially easy to implement. In addition, the amount of the oxygen-containing gas (O) to flow through in the first polymerization step and the second polymerization step may be changed, and the amount of a nitrogen-containing gas and air to flow through may be changed.

[0017]

In controlling the first pressure to more than 0.098 MPa and 0.392 MPa or less and the second pressure to 0.098 MPa or more and less than 0.392 MPa, the partial pressure of oxygen contained in the oxygen-containing gas to flow through is preferably an absolute pressure of 0.0147 MPa or more and 0.0883 MPa or less. When the absolute pressure of the reactor gas phase is A (MPa), A is in a range of $0.098 \leq A < 0.392$. From the viewpoint of achieving the state of the reactor gas phase described above, it is preferred to use a value represented by $[(0.0147/A) \times 100]$ (%) as the lower limit of the oxygen concentration and a value represented by $[(0.0883/A) \times 100]$ (%) as the upper limit of the oxygen concentration in the oxygen-containing gas.

[0018]

[First polymerization step and second polymerization step]

In the present embodiment, a polymerization solution containing a phenolic compound (M), an aromatic solvent (A), and a catalyst (C) is prepared and placed in a reactor, and an oxygen-containing gas (O) is allowed to flow through the polymerization solution in the reactor to oxidatively polymerize the phenolic compound (M) to thereby provide a polyphenylene ether.

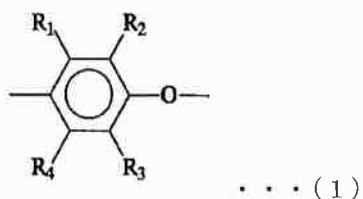
[0019]

<Polyphenylene ether>

The polyphenylene ether produced in the polymerization step of the method for producing a polyphenylene ether according to the present embodiment will be described hereinbelow. The polyphenylene ether produced in the polymerization step is specifically, but not particularly limited to, a homopolymer or a copolymer having repeating units represented by the following formula (1).

[0020]

[Formula 1]



[0021]

In the formula (1), R_1 and R_4 each independently represent any one selected from the group consisting of a hydrogen atom, a primary or secondary lower alkyl group, a phenyl group, an aminoalkyl group, and a hydrocarbonoxy group. Additionally, in the formula (1), R_2 and R_3 each independently represent any one selected from the group consisting of a hydrogen atom, a primary or secondary lower alkyl group, and a phenyl group.

[0022]

Examples of the polyphenylene ether homopolymer include specifically, but not particularly limited to, poly(2,6-dimethyl-1,4-phenylene)ether, poly(2-methyl-6-ethyl-1,4-phenylene)ether, poly(2,6-diethyl-1,4-phenylene)ether, poly(2-ethyl-6-n-propyl-1,4-phenylene)ether, poly(2,6-di-n-propyl-1,4-phenylene)ether, poly(2-methyl-6-n-butyl-1,4-phenylene)ether, poly(2-ethyl-6-isopropyl-1,4-phenylene)ether, poly(2-methyl-6-hydroxyethyl-1,4-phenylene)ether, and poly(2-methyl-6-chloroethyl-1,4-phenylene)ether. Of these, poly(2,6-dimethyl-1,4-phenylene)ether is preferred from the viewpoint of the inexpensiveness and availability of the starting material.

[0023]

A polyphenylene ether copolymer means a copolymer that having phenylene ether units as monomer units. Examples of the polyphenylene ether copolymer include specifically, but not particularly limited to, copolymers

of 2,6-dimethylphenol and 2,3,6-trimethylphenol, copolymers of 2,6-dimethylphenol and o-cresol, and copolymers of 2,6-dimethylphenol, 2,3,6-trimethylphenol, and o-cresol. Of these, copolymers of 2,6-dimethylphenol and 2,3,6-trimethylphenol are preferred from the viewpoint of inexpensiveness and availability of the starting material.

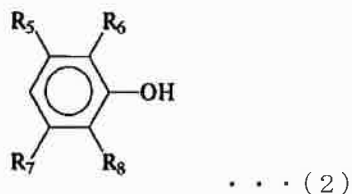
[0024]

<Phenolic compound (M)>

The polyphenylene ether described above can be produced by oxidatively polymerizing a phenolic compound (M) of the following formula (2).

[0025]

[Formula 2]



[0026]

In the formula (2), R₅ and R₇ each independently represent any one selected from the group consisting of a hydrogen atom, a primary or secondary lower alkyl group, a phenyl group, an aminoalkyl group, and a hydrocarbonoxy group. Additionally, in the formula (2), R₆ and R₈ each independently represent any one selected from the group consisting of a hydrogen atom, a primary or secondary lower alkyl group, and a phenyl group.

[0027]

Examples of the phenolic compound (M) include specifically, but not particularly limited to, 2,6-dimethylphenol, 2,3,6-trimethylphenol, 2-methyl-6-ethylphenol, 2,6-diethylphenol, 2-ethyl-6-n-propylphenol, 2-methyl-6-chlorophenol, 2-methyl-6-bromophenol, 2-methyl-6-isopropylphenol, 2-methyl-6-n-propylphenol, 2-ethyl-6-bromophenol, 2-methyl-6-n-butylphenol, 2,6-di-n-propylphenol, 2-ethyl-6-chlorophenol, 2-methyl-6-phenylphenol, 2,6-diphenylphenol, 2,6-bis-(4-fluorophenyl)phenol, 2-methyl-6-tolylphenol, and 2,6-ditolylphenol. These phenolic compounds (M) each may be used singly or may be used in combination of two or more. Alternatively, an aromatic solvent (A) used as a polymerization solution may substantially include a small amount of, for example, phenol, o-cresol, m-cresol, p-cresol, 2,4-dimethylphenol, or 2-ethylphenol as an impurity because such an impurity is consumed as a portion of the phenolic compound (M) by the polymerization reaction to be incorporated in the polyphenylene ether.

[0028]

Of these, as the phenolic compound (M), 2,6-dimethylphenol, or a mixture of 2,6-dimethylphenol and 2,3,6-trimethylphenol is preferred, and 2,6-dimethylphenol is more preferred.

[0029]

<Aromatic solvent (A)>

Examples of the aromatic solvent (A) that can be used include specifically, but not particularly limited to, solvents that dissolve the phenolic compound (M) having a low molecular weight and dissolve a portion or all of the catalyst (C).

[0030]

Examples of the aromatic solvent (A) include, but not limited to, aromatic hydrocarbons such as benzene, toluene, xylene, and ethylbenzene; halogenated aromatic hydrocarbons such as chlorobenzene, dichlorobenzene, and trichlorobenzene; and nitro compounds such as nitrobenzene. Of these, the aromatic solvent (A) is preferably at least one selected from the group consisting of toluene, xylene, and ethylbenzene, and is more preferably toluene.

[0031]

The aromatic solvent (A) can be mixed with a solvent having compatibility with water as required. Examples of the solvent having compatibility with water include specifically, but not particularly limited to, alcohols such as methanol, ethanol, and propanol; ketones such as acetone and methylethylketone; esters such as ethyl acetate and ethyl formate; amides such as dimethylformamide; and sulfoxides such as dimethylsulfoxide. These solvents can be used in mixture of one or more, and of additionally two or more as required.

[0032]

As the aromatic solvent (A) used in the polymerization step, solvents substantially incompatible with water can be preferably used. Preferred examples of the solvent substantially incompatible with water include aromatic hydrocarbon solvents such as toluene and xylene.

[0033]

Alternatively, the form of polymerization in the present embodiment depends on selection of a proportion of a good solvent and a poor solvent relative to the polyphenylene ether, which is a polymer obtained by oxidatively polymerizing the phenolic compound (M). Specifically, solution polymerization is used when the proportion of the good solvent is increased, whereas precipitation deposition polymerization, in which a polymer is deposited as particles in the reaction solvent as the reaction progresses, is used when the proportion of the poor solvent is increased. The form of polymerization in the present embodiment is not particularly limited. Adjusting the amount of the poor solvent added to the aromatic solvent (A), as required, allows a desired form of polymerization to be appropriately selected.

[0034]

<Catalyst (C)>

The catalyst (C) is an oxidative catalyst effective for producing a polyphenylene ether via efficient

oxidative polymerization of the phenolic compound (M) by allowing the oxygen-containing gas (O) to flow through a polymerization solution containing a phenolic compound (M), an aromatic solvent (A), and the catalyst (C).

[0035]

In specific examples of the catalyst (C), without particular limitations, a copper compound, a bromine compound, and one or more selected from the group consisting of a diamine compound, a tertiary monoamine compound and a secondary monoamine compound are preferably included. In specific examples of the catalyst (C), a copper compound, a bromine compound, a diamine compound, a tertiary monoamine compound and a secondary monoamine compound are more preferably included as essential components.

[0036]

Examples of the copper compound used as a component of the catalyst (C) that can be used include specifically, but not particularly limited to, cuprous compounds, cupric compounds, and mixtures thereof. Examples of the cuprous compound include specifically, but not particularly limited to, cuprous oxide, cuprous chloride, cuprous bromide, cuprous sulfate, and cuprous nitrate. Examples of the cupric compound include specifically, but not particularly limited to, cupric chloride, cupric bromide, cupric sulfate, and cupric nitrate. Preferred cuprous and cupric compounds of these are cuprous oxide,

cuprous chloride, cupric chloride, cuprous bromide, and cupric bromide. These copper salts may be synthesized in use from a copper oxide, a copper carbonate or a copper hydroxide with a halogen or acid corresponding to these. For example, mixing cuprous oxide with (a solution of) hydrogen bromide enables cuprous bromide to be provided. Preferred copper compounds are cuprous compounds. These copper compounds may be used singly or may be used in combination of two or more.

[0037]

Examples of the bromine compound used as a component of the catalyst (C) include specifically, but not particularly limited to, hydrogen bromide, sodium bromide, potassium bromide, tetramethylammonium bromide, and tetraethylammonium bromide. These bromine compounds may be used in an aqueous solution or a solution including an appropriate solvent. These bromine compounds may be used singly or may be used in combination of two or more.

[0038]

A preferred combination of the copper compound and the bromine compound described above is cuprous oxide and an aqueous solution of hydrogen bromide. The amount of these compounds used is not particularly limited, and the molar amount of the bromine atom is preferably twice or more and 10 times or less the molar amount of the copper atom. The amount of the copper atom is preferably in the

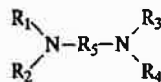
range of 0.02 mol to 0.6 mol based on 100 mol of the phenolic compound (M).

[0039]

Examples of the diamine compound used as a component of the catalyst (C) include specifically, but not particularly limited to, diamine compounds represented by the formula (3). Of the diamine compounds represented by the following formula (3), N,N'-di-t-butylethylenediamine is preferred. The amount of the diamine compound used can be, without particular limitations, 0.5 times molar amount or more based on the molar amount of the copper atom usually used, and the upper limit is not particularly limited.

[0040]

[Formula 3]



... (3)

[0041]

In the formula (3), R_1 , R_2 , R_3 , and R_4 each independently represent a hydrogen atom, or a linear or branched alkyl group having 1 to 6 carbon atoms, and not all of R_1 to R_4 represent a hydrogen atom at the same time. Additionally, R_5 represents a linear alkylene group having 2 to 5 carbon atoms or a methyl-branched alkylene group.

[0042]

Examples of the tertiary monoamine compound used as a component of the catalyst (C) include, but not particularly limited to, aliphatic tertiary amines including alicyclic tertiary amines. Examples of the tertiary monoamine compound include specifically, but not particularly limited to, trimethylamine, triethylamine, tripropylamine, tributylamine, triisobutylamine, dimethylethylamine, dimethylpropylamine, allyldiethylamine, dimethyl-n-butylamine, diethylisopropylamine, and N-methylcyclohexylamine. These tertiary monoamines may be used singly or may be used in combination of two or more. The amount of the tertiary monoamine compound used is, without particular limitations, preferably in the range of 0.1 mol to 15 mol based on 100 mol of the phenolic compound (M).

[0043]

Examples of the secondary monoamine compound used as a component of the catalyst (C) include specifically, but not particularly limited to, dimethylamine, diethylamine, di-n-propylamine, di-i-propylamine, di-n-butylamine, di-i-butylamine, di-t-butylamine, dipentylamines, dihexylamines, dioctylamines, didecylamines, dibenzylamines, methylethylamine, methylpropylamine, methylbutylamine, cyclohexylamine, N-(substituted or unsubstituted phenyl)alkanolamine, and N-hydrocarbon-substituted anilines.

[0044]

Examples of the N-(substituted or unsubstituted phenyl)alkanolamine include specifically, but not particularly limited to, N-phenylmethanolamine, N-phenylethanolamine, N-phenylpropanolamine, N-(m-methylphenyl)ethanolamine, N-(p-methylphenyl)ethanolamine, N-(2',6'-dimethylphenyl)ethanolamine, and N-(p-chlorophenyl)ethanolamine.

[0045]

Examples of the N-hydrocarbon-substituted aniline include specifically, but not particularly limited to, N-ethylaniline, N-butyraniline, N-methyl-2-methylaniline, N-methyl-2,6-dimethylaniline, and diphenylamine.

[0046]

These secondary monoamine compounds may be used singly or may be used in combination of two or more.

[0047]

The amount of the secondary monoamine compound used is generally, without particular limitations, in the range of 0.05 mol to 15 mol based on 100 mol of the phenolic compound (M).

[0048]

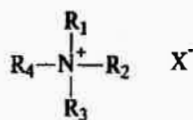
<Other materials>

In the method for producing a polyphenylene ether according to the present embodiment, examples of other materials that may be included in the polymerization solution include, but not limited to, at least one selected from the group consisting of tetraalkylammonium

salt compounds, polyethylene glycol group-containing alkylamines, and polyethylene glycol group-containing alkylammonium salt compounds. The content of the other materials described above is preferably in the range of not more than 0.1% by mass from the viewpoint of improving the efficiency of the polymerization reaction. Specific examples of the other materials described above include compounds having a structure represented by the following formula (4), (5), or (6).

[0049]

[Formula 4]



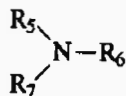
... (4)

[0050]

In the formula (4), R_1 , R_2 , R_3 , and R_4 each independently represent a linear or branched alkyl group having 1 to 22 carbon atoms, and X represents a negative counter ion, preferably a negative ion selected from Cl^- or Br^- .

[0051]

[Formula 5]



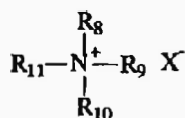
... (5)

[0052]

In the formula (5), R_5 represents a linear or branched alkyl group having 1 to 22 carbon atoms, R_6 may represent a group represented by $-(CH_2CH_2O)_n-H$ [n represents an integer of 1 to 40] in addition to the group defined in R_5 , and R_7 represents a group represented by $-(CH_2CH_2O)_n-H$ [n represents an integer of 1 to 40].

[0053]

[Formula 6]



... (6)

[0054]

In the formula (6), R_8 and R_9 represent a linear or branched alkyl group having 1 to 22 carbon atoms, R_{10} may represent a group represented by $-(CH_2CH_2O)_n-H$ [n represents an integer of 1 to 40] in addition to the group defined in R_8 , R_{11} represents a group represented by $-(CH_2CH_2O)_n-H$ [n represents an integer of 1 to 40], and X represents a negative counter ion, preferably a negative ion selected from Cl^- or Br^- .

[0055]

In the method for producing a polyphenylene ether according to the present embodiment, more specific examples of the other materials described above preferably used include trioctylmethyammonium chloride known as the product name such as Aliquat 336

(manufactured by Henkel Corporation) and Capriquat (manufactured by DOJINDO LABORATORIES).

[0056]

<Preparation of a polymerization solution>

In preparing a polymerization solution, the components, that is, the phenolic compound (M), the aromatic solvent (A), and the catalyst (C) may be each separately introduced into a reactor, or the phenolic compound (M) and the catalyst (C), after each dissolved in the aromatic solvent (A) in advance, may be introduced into a reactor. However, a preferred method is to introduce the catalyst (C) dissolved in advance in a portion of the aromatic solvent (A) into a reactor followed by introducing the phenolic compound (M) dissolved in the residual aromatic solvent (A) into the reactor.

[0057]

The temperature of the polymerization solution in the step of polymerizing polyphenylene ether is preferably adjusted to 0 to 80°C, more preferably to 10 to 60°C, still more preferably to 20 to 50°C from the viewpoint of the progress of the reaction and the catalyst activity. The temperature is preferably set to a relatively low level in the former half of the polymerization step and to a relatively high level in the latter half of the polymerization step. Accordingly, the

progress of the polymerization reaction tends to be further facilitated.

[0058]

The polymerization solution is preferably prepared in an amount blended of 10 to 25 parts by mass of the phenolic compound (M), 75 to 90 parts by mass of the aromatic solvent (A), and 0.1 to 10 parts by mass of the catalyst (C). Total parts by mass of the phenolic compound (M) and the aromatic solvent (A) herein equals to 100 parts by mass. By use of such an amount blended, the effect of stabilizing the control of the polyphenylene ether polymerization tends to be achieved. It should be noted that the amounts of the phenolic compound (M), the aromatic solvent (A), and the catalyst (C) in the polymerization solution correspond to the mass ratio of the phenolic compound (M), the aromatic solvent (A), and the catalyst (C) when the introductions thereof into the reactor are completed.

[0059]

In the present embodiment, the polymerization solution used more preferably contains 12 to 23 parts by mass of the phenolic compound (M), 77 to 88 parts by mass of the aromatic solvent (A), and 0.5 to 9 parts by mass of the catalyst (C), and the polymerization solution still more preferably contains 13 to 21 parts by mass of the phenolic compound (M), 79 to 87 parts by mass of the aromatic solvent (A), and 0.8 to 8 parts by mass of the

catalyst (C). Within the preferred ranges described above, the control of the polyphenylene ether polymerization tends to be further stabilized.

[0060]

The absolute pressure of the reactor gas phase is 0.098 MPa or more and 0.392 MPa or less. The case where the absolute pressure of the reactor gas phase is more than 0.392 MPa is not preferred because an excessively large equipment will be required. The case where the absolute pressure is less than 0.098 MPa is not preferred because the pressure will be in a negative pressure range instead of atmospheric pressure, and thus, equipment compatible with vacuum is required.

[0061]

<Flow-through of the oxygen-containing gas (O)>

The timing to start flow-through of the oxygen-containing gas (O) is not particularly limited, but, in preparing the polymerization solution, flow-through of the oxygen-containing gas (O) is preferably started after any of the phenolic compound (M), the aromatic solvent (A), and the catalyst (C) is introduced into the reactor.

[0062]

Examples of the oxygen-containing gas (O) that can be used include specifically, but not particularly limited to, a mixture of oxygen and an optional inert gas, air, or a mixture of air and an optional inert gas. Examples of the inert gas that can be used include

specifically, but not particularly limited to, optional inert gases having no considerable influence on the polymerization reaction. Typical examples of inert gas include nitrogen.

[0063]

Specifically, without particular limitations, the oxygen-containing gas (O) preferably has an oxygen concentration of 5 to 25% by volume, more preferably contains a nitrogen-containing gas and air and has an oxygen concentration of 6 to 20% by volume, still more preferably contains a nitrogen-containing gas and air and has an oxygen concentration of 8 to 12% by volume. With such preferable oxygen concentrations, gradual heating, the polymerization rate and the like tend to be further stabilized.

[0064]

In the case where the unreacted gas in the oxygen-containing gas (O) after flow-through has an oxygen concentration of more than 11.6%, it is preferred to control the oxygen concentration to 11.6% or less by introduction of an inert gas such as nitrogen into the reactor gas phase from the viewpoint of preventing the solvent used from exploding.

[0065]

The amount of oxygen-containing gas (O) to flow through is, without particular limitations, preferably from 0.5 NL/min to 15 NL/min, more preferably from 3

NL/min to 14 NL/min, still more preferably from 6 NL/min to 13 NL/min, based on 1 kg of the phenolic compound (M) subjected to the polymerization reaction. With an amount of 0.5 NL/min or more, the intended polyphenylene ether reaches the desired molecular weight faster, and the productivity tends to be increased. In contrast, with an amount of 15 NL/min or less, problems such as oversizing of the equipment and an increase in the amount of exhaust gas can be avoided, and superior economic performance tends to be achieved.

[0066]

(Removal of the foaming layer)

In the early stage of the oxidative polymerization in a common polyphenylene ether polymerization step, a foaming layer may occur. Continuation of the oxidative polymerization causes the phenolic compound (M) in the polymerization solution to be consumed to thereby stop the foaming. It is thus assumed that the cause of foaming of the polymerization solution in the early stage of the oxidative polymerization lies in a possible relationship between an abundance of the phenolic compound (M) in the polymerization solution and the foaming.

[0067]

In the method for producing a polyphenylene ether according to the present embodiment, the oxidative polymerization is continuously performed while occurrence

of the foaming layer in the first polymerization step is suppressed by the first pressure of the reactor gas phase. This allows the production efficiency per unit volume of the reactor to be increased. It should be noted that the occurrence of the foaming layer can be evaluated with the amount of foaming, which can be measured in accordance with the method described in the example described hereinafter.

[0068]

In the method for producing a polyphenylene ether according to the present embodiment, oxidative polymerization is performed by controlling an absolute pressure of the second polymerization step lower than the first pressure. This prevents the polymerization activity from decreasing and enables the reaction time to be reduced. It should be noted that the reaction time can be measured in accordance with the method described in the example described hereinafter.

[0069]

The absolute pressure of the reactor gas phase is not particularly limited as long as the amount of foaming in the early stage of the oxidative polymerization is within the tolerance of the reactor. Specifically, the first pressure is preferably 0.294 MPa or more from the viewpoint of achieving a sufficient effect of preventing foaming, and is 0.392 MPa or less from the viewpoint of

preventing oversizing of the oxidative polymerization equipment.

[0070]

The method for producing a polyphenylene ether according to the present embodiment can suppress occurrence of a foaming layer in the early stage of the polymerization step to thereby make use of an extra capacity of a reactor designed for a foaming layer portion of the polymerization solution in the conventional art.

[0071]

After the polymerization step is performed as described above, the polymerization reaction is stopped when the target degree of polymerization is reached. The method for stopping polymerization reaction is not particularly limited, and the conventional known methods can be applied. Examples of the common method for stopping include a method in which an acid such as hydrochloric acid and acetic acid, ethylenediaminetetraacetic acid (EDTA) or its salt, or nitrilotriacetic acid or its salt is added to the reaction liquid to quench the catalyst, thereby stopping the polymerization. After the polymerization is stopped, the polyphenylene ether formed is separated, washed with a solvent that does not dissolve polyphenylene ethers such as methanol, and dried to thereby collect a polyphenylene ether.

[0072]

A preferred aspect of the method for producing a polyphenylene ether according to the present embodiment is to use 2,6-dimethylphenol as the phenolic compound (M), and the catalyst component (C) in the form of combination of five components: cuprous oxide as the copper compound, hydrogen bromide (used in the form of an aqueous solution) as the bromine compound, N,N'-di-t-butylethylenediamine as the diamine compound, N,N-di-n-butylamine as the secondary monoamine compound, and N,N-dimethyl-n-butylamine as the tertiary monoamine. The method for producing a polyphenylene ether according to the present embodiment is not limited to this aspect.

[0073]

As described above, the present embodiment does not require presence of an antifoaming agent, which influences the polymerization reaction, in the polymerization solution. This enables suppression of foaming of the polymerization solution and production of a polyphenylene ether without reducing the activity of the polymerization reaction.

Examples

[0074]

The present embodiment will be specifically described hereinbelow, referring to specific Examples and Comparative Examples, but the present embodiment is not

intended to be limited to the following examples. Methods for measuring physical properties and characteristics applied to Examples and Comparative Examples will be described hereinbelow.

[0075]

[Measurement of the portion of contact on the liquid level]

A scale was attached to the side of the reactor, and the distance from the bottom of the reactor, which was scored as 0 point, to the portion of contact with foam on the liquid level (the interface between the liquid phase and the foam) was measured. In each example, stirring at a constant rate of 500 rpm was started immediately after introduction of the polymerization solvent into the reactor, and measurement was performed every 10 minutes from the beginning of the oxidative polymerization. Specifically, the height of the liquid level in the stirring state in the case of stirring the polymerization solution was measured, and the maximum value in the polymerization reaction period was taken as the height of the liquid level of each example.

[0076]

[Measurement of the amount of foaming]

The amount of foaming was measured with the scale described above. The maximum value of the thickness from the liquid level measured above to the top surface of the

foaming layer in the polymerization reaction period was taken as the amount of foaming.

[0077]

[Measurements of the liquid viscosity and polymerization time]

A polymerization liquid of each example sampled as described below was adjusted to a temperature of 40°C, and its liquid viscosity (unit: cP) was determined using an oscillation liquid viscometer (VISCOMATE VM-100A) manufactured by SEKONIC Corporation. The time point at which allowing the oxygen-containing gas (O) to flow through the polymerization liquid described above was started was taken as the time point at which the oxidative polymerization was started. Additionally, the time point at which the value of the liquid viscosity described above reached 45 cP was taken as the time point at which the oxidative polymerization was stopped. Thus, the polymerization time from the beginning of the oxidative polymerization to the stopping of the oxidative polymerization was measured.

[0078]

[Example 1]

The reactor used was a cylindrical reactor having an upper limit of height for introducing a reaction liquid of 50 cm and an inner diameter of 16 cm, and being formed of SUS and equipped with a 15-liter jacket. On the bottom of the reactor, a sparger for introduction of the

oxygen-containing gas (O), a stirring turbine blade, and an exhaust valve for sampling were provided. On the side of the reactor, a baffle and a temperature adjuster were provided. On the top of the reactor, an introduction inlet for polymerization solution components and a reflux condenser including a vent gas line equipped with a decanter for separating a condensed liquid were provided. The vent gas exhaust outlet of the decanter was provided with a pressure adjusting valve and a pressure gauge.

[0079]

(Polymerization step)

A polymerization solution composed of 0.85 kg of 2,6-dimethylphenol, 5.59 kg of toluene, and 63.2 g of a catalyst (C) (1.1 g of cuprous oxide, 8.2 g of a 47% hydrogen bromide aqueous solution, 2.6 g of di-t-butylethylenediamine, 12.7 g of di-n-butylamine, and 38.6 g of butyldimethylamine) was prepared and introduced into the reactor described above. After the liquid temperature was adjusted to 40°C and the absolute pressure (first polymerization pressure) of the reactor gas phase to 0.301 MPa, an oxygen-containing gas (O) having an absolute pressure of 0.301 MPa and an oxygen concentration of 9% was allowed to flow through the solution from the sparger as the oxygen-containing gas (O) for flow-through to start oxidative polymerization of 2,6-dimethylphenol (the oxygen-containing gas (O) had an oxygen partial pressure of $0.301 \text{ MPa} \times 0.09 = 0.02709$

MPa). After the oxidative polymerization described above was started, occurrence of foam was observed. Complete elimination of the foam was noticed 90 minutes after the oxidative polymerization was started, and thus, the absolute pressure (the second polymerization pressure) of the reactor gas phase was changed to 0.201 MPa to continue the oxidative polymerization. A small portion was sampled every five minutes after 60 minutes of the oxidative polymerization was elapsed, and the time required for the liquid viscosity to achieve a specific value (the polymerization time from the beginning of the polymerization to a time point at which the liquid viscosity reached 45 cP) was taken as the polymerization time. The oxidative polymerization was stopped by addition of 0.65 kg of a 10% aqueous solution of ethylenediaminetetraacetic acid tetrasodium salt (a reagent of DOJINDO LABORATORIES) 139 minutes after the oxidative polymerization was started. After washing with 7.65 kg of methanol, drying treatment was performed under a temperature condition of 140°C for 120 minutes to provide a polyphenylene ether of Example 1. Additionally, the amount of foaming of the polymerization solution and the height of the liquid level at the portion of contact during the oxidative polymerization were determined. The results are shown in Table 1.

[0080]

[Example 2]

The operation was performed in the same manner as in Example 1 to obtain the polyphenylene ether of Example 2 except that the first polymerization pressure was set to 0.351 MPa, and the second polymerization pressure was set to 0.251 MPa 79 minutes after the oxidative polymerization was started. That is, it was observed that the foam was completely eliminated 79 minutes after the oxidative polymerization was started in this example. Additionally, the amount of foaming of the polymerization solution and the height of the liquid level at the portion of contact during the oxidative polymerization were determined. The results are shown in Table 1.

[0081]

[Example 3]

The operation was performed in the same manner as in Example 1 to obtain the polyphenylene ether of Example 3 except that the first polymerization pressure was set to 0.351 MPa, and the second polymerization pressure was set to 0.301 MPa 80 minutes after the oxidative polymerization was started. That is, it was observed that the foam was completely eliminated 80 minutes after the oxidative polymerization was started in this example. Additionally, the amount of foaming of the polymerization solution and the height of the liquid level at the portion of contact during the oxidative polymerization were determined. The results are shown in Table 1.

[0082]

[Example 4]

The operation was performed in the same manner as in Example 2 to obtain the polyphenylene ether of Example 4 except that xylene was used as the aromatic solvent (A) instead of toluene, the first polymerization pressure was set to 0.351 MPa, and the second polymerization pressure was set to 0.251 MPa 84 minutes after the oxidative polymerization was started. That is, it was observed that the foam was completely eliminated 84 minutes after the oxidative polymerization was started in this example. Additionally, the amount of foaming of the polymerization solution and the height of the liquid level at the portion of contact during the oxidative polymerization were determined. The results are shown in Table 1.

[0083]

[Example 5]

The operation was performed in the same manner as in Example 2 to obtain the polyphenylene ether of Example 5 except that ethylbenzene was used as the aromatic solvent (A) instead of toluene, the first polymerization pressure was set to 0.351 MPa, and the second polymerization pressure was set to 0.251 MPa 83 minutes after the oxidative polymerization was started. That is, it was observed that the foam was completely eliminated 83 minutes after the oxidative polymerization was started in this example. Additionally, the amount of foaming of the polymerization solution and the height of the liquid

level at the portion of contact during the oxidative polymerization were determined. The results are shown in Table 1.

[0084]

[Example 6]

The operation was performed in the same manner as in Example 2 to obtain the polyphenylene ether of Example 6 except that a polymerization solution composed of 1.04 kg of 2,6-dimethylphenol, 6.82 kg of toluene, and 77.9 g of the catalyst (C) (1.3 g of cuprous oxide, 10.1 g of a 47% aqueous solution of hydrogen bromide, and 3.2 g of di-t-butylethylenediamine, 15.7 g of di-n-butylamine, and 47.6 g of butyldimethylamine) was used, the first polymerization pressure was set to 0.351 MPa, and the second polymerization pressure was set to 0.251 MPa 78 minutes after the oxidative polymerization was started. That is, it was observed that the foam was completely eliminated 78 minutes after the oxidative polymerization was started in this example. Additionally, the amount of foaming of the polymerization solution and the height of the liquid level at the portion of contact during the oxidative polymerization were determined. The results are shown in Table 1.

[0085]

[Example 7]

The operation was performed in the same manner as in Example 1 to obtain the polyphenylene ether of Example 7

except that a polymerization solution composed of 0.85 kg of 2,6-dimethylphenol, 5.48 kg of toluene, and 175.8 g of the catalyst (C) (4.9 g of cuprous oxide, 36.8 g of a 47% aqueous solution of hydrogen bromide, and 134.1 g of di-n-butylamine) was used, the first polymerization pressure was set to 0.301 MPa, and the second polymerization pressure was set to 0.201 MPa 92 minutes after the oxidative polymerization was started. That is, it was observed that the foam was completely eliminated 92 minutes after the oxidative polymerization was started in this example. Additionally, the amount of foaming of the polymerization solution and the height of the liquid level at the portion of contact during the oxidative polymerization were determined. The results are shown in Table 1.

[0086]

[Comparative Example 1]

The operation was performed in the same manner as in Example 1 to obtain the polyphenylene ether of Comparative Example 1 except that the absolute pressure of the reactor gas phase during the entire period of polymerization reaction was set to 0.251 MPa without change. The polyphenylene ether obtained was weighed to determine the reduced viscosity. Additionally, the amount of foaming of the polymerization solution and the height of the liquid level at the portion of contact

during the oxidative polymerization were determined. The results are shown in Table 1.

[0087]

[Comparative Example 2]

The operation was performed in the same manner as in Comparative Example 1 to obtain the polyphenylene ether of Comparative Example 2 except that the absolute pressure of the reactor gas phase during the entire period of polymerization reaction was set to 0.351 MPa without change. Additionally, the amount of foaming of the polymerization solution and the height of the liquid level at the portion of contact during the oxidative polymerization were determined. The results are shown in Table 1.

[0088]

[Comparative Example 3]

The operation was performed in the same manner as in Comparative Example 1 to obtain the polyphenylene ether of Comparative Example 3 except that xylene was used as the aromatic solvent (A) instead of toluene. Additionally, the amount of foaming of the polymerization solution and the height of the liquid level at the portion of contact during the oxidative polymerization were determined. The results are shown in Table 1.

[0089]

[Comparative Example 4]

The operation was performed in the same manner as in Comparative Example 1 to obtain the polyphenylene ether of Comparative Example 4 except that ethylbenzene was used as the aromatic solvent (A) instead of toluene. Additionally, the amount of foaming of the polymerization solution and the height of the liquid level at the portion of contact during the oxidative polymerization were determined. The results are shown in Table 1.

[0090]

[Table 1]

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Compara tive Example 1	Compara tive Example 2	Compara tive Example 3	Compara tive Example 4
Phenolic compound (M)	2,6- Dimethyl phenol 0.85 kg	2,6- Dimethyl phenol 0.85 kg	2,6- Dimethyl phenol 0.85 kg	2,6- Dimethyl phenol 0.85 kg	2,6- Dimethyl phenol 0.85 kg	2,6- Dimethyl phenol 1.04 kg	2,6- Dimethyl phenol 0.85 kg	2,6- Dimethyl phenol 0.85 kg	2,6- Dimethyl phenol 0.85 kg	2,6- Dimethyl phenol 0.85 kg	2,6- Dimethyl phenol 0.85 kg
Aromatic solvent (A)	Toluene 5.59 kg	Toluene 5.59 kg	Toluene 5.59 kg	Xylene 5.59 kg	Ethylben zene 5.59 kg	Toluene 6.82 kg	Toluene 5.48 kg	Toluene 5.59 kg	Toluene 5.59 kg	Xylene 5.59 kg	Ethylben zene 5.59 kg
Catalyst (C)	63.2 g	63.2 g	63.2 g	63.2 g	63.2 g	77.9 g	175.8 g	63.2 g	63.2 g	63.2 g	63.2 g
Control of the reactor pressure	0.301→ 0.201 MPa	0.351→ 0.251 MPa	0.351→ 0.301 MPa	0.351→ 0.251 MPa	0.351→ 0.251 MPa	0.351→ 0.251 MPa	0.301→ 0.201 MPa	0.251 MPa	0.351 MPa	0.251 MPa	0.251 MPa
Time elapsed when the reactor pressure was changed	90 min	79 min	80 min	84 min	83 min	78 min	92 min	-	-	-	-
Amount of foaming of the polymerization solution	8.2 cm	7.5 cm	7.6 cm	7.5 cm	7.7 cm	9 cm	8.5 cm	9.5 cm	7.8 cm	9.5 cm	9 cm
Liquid level of the polymerization solvent	28 cm	28 cm	28.5 cm	28.5 cm	28.5 cm	34 cm	28.5 cm	28.5 cm	28.5 cm	28.5 cm	28 cm
Polyphenylene ether yield	0.83 kg	0.83 kg	0.83 kg	0.83 kg	0.83 kg	1.03 kg	0.83 kg	0.83 kg	0.83 kg	0.83 kg	0.83 kg
Polymerization time	139 min	137 min	143 min	140 min	143 min	135 min	141 min	147 min	158 min	151 min	148 min

Industrial Applicability

[0091] The method for producing a polyphenylene ether according to the present invention has industrial applicability as technology for producing materials used in, for example, automobile parts, heat-resistant parts, parts for electronic apparatuses, and industrial parts.

Claims

1. A method for producing a polyphenylene ether, comprising:

a polymerization step of oxidatively polymerizing a phenolic compound (M) by allowing an oxygen-containing gas (O) to flow through a polymerization solution comprising the phenolic compound (M), an aromatic solvent (A), and a catalyst (C) in a reactor,

wherein the polymerization step comprises:

a first polymerization step of performing polymerization by controlling an absolute pressure of a gas phase in the reactor to a first pressure of more than 0.098 MPa and 0.392 MPa or less; and

a second polymerization step of performing polymerization by controlling the absolute pressure to a second pressure lower than the first pressure and of 0.098 MPa or more and less than 0.392 MPa after the first polymerization step.

2. The method for producing the polyphenylene ether according to claim 1, wherein the second pressure is less than 90% of the first pressure.

3. The method for producing the polyphenylene ether according to claim 1 or 2, wherein the polymerization solution comprises 10 to 25 parts by mass of the phenolic

compound (M), 75 to 90 parts by mass of the aromatic solvent (A), and 0.1 to 10 parts by mass of the catalyst (C), based on 100 parts by mass of a sum of the phenolic compound (M) and the aromatic solvent (A).

4. The method for producing the polyphenylene ether according to any one of claims 1 to 3, wherein the phenolic compound (M) comprises 2,6-dimethylphenol or a mixture of 2,6-dimethylphenol and 2,3,6-trimethylphenol.

5. The method for producing the polyphenylene ether according to any one of claims 1 to 4, wherein the aromatic solvent (A) comprises at least one selected from the group consisting of toluene, xylene, and ethylbenzene.

6. The method for producing the polyphenylene ether according to any one of claims 1 to 5, wherein the catalyst (C) comprises a copper compound, a bromine compound, and one or more selected from the group consisting of a diamine compound, a tertiary monoamine compound and a secondary monoamine compound.

7. The method for producing the polyphenylene ether according to any one of claims 1 to 6, wherein the oxygen-containing gas (O) has an oxygen concentration of 5 to 25% by volume.

8. The method for producing the polyphenylene ether according to any one of claims 1 to 7, wherein the oxygen-containing gas (O) comprises oxygen and nitrogen, and the oxygen-containing gas (O) has an oxygen concentration of 8 to 12% by volume.

9. The method for producing the polyphenylene ether according to any one of claims 1 to 8, wherein the oxygen-containing gas (O) has an oxygen partial pressure of 0.0147 MPa or more and 0.0883 MPa or less.