

METHOD FOR PREPARING POLYPHENYLENE ETHER

TECHNICAL FIELD

[0001] This disclosure relates to a method for preparing polyphenylene ether.

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BACKGROUND

[0002] Polyphenylene ether is excellent in electric insulation, heat resistance, hydrolysis resistance and flame retardance, and resin compositions containing the polyphenylene ether are widely used in the field of consumer electronics, office automation apparatus, automobile components, etc.

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[0003] Conventionally, various methods are disclosed as methods for preparing polyphenylene ether via oxidative polymerization of phenolic compounds. For example, JPH11-12354A (PTL 1) discloses a method for the purpose of obtaining a bimodal molecular weight distribution via continuous polymerization of a phenolic compound, where a polyphenylene ether from lines as bypass of a main polymerization line, which has a low molecular weight, is merged in a shortstop tank in a state that polymerization is shortstopped, while a specific catalyst is used. Further, PTL 1 discloses that a preferable result is obtained by applying slurry polymerization, such that the viscosity of liquid is not much increased due to partial precipitation of polyphenylene ether when the molecular weight of the polyphenylene ether is increased.

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[0004] On the other hand, in solution polymerization as a preparing method with a productivity higher than the aforementioned slurry polymerization, there is a problem that in order to perform oxidative polymerization of a phenolic compound by passing an oxygen-containing gas through a polymerization solution, foaming of a content of 10 to 30% of the content of the polymerization solution occurs in an early period of the oxidative polymerization. In order to solve such problem, for example, in the method as disclosed in JP2010-270250A (PTL 2), foaming is suppressed by adding 0.000001 to 0.0001 parts by mass of a defoamer into a polymerization solution containing 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.

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CITATION LIST

Patent Literature

[0005] PTL1: JPH11-12354A

PTL2: JP2010-270250A

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SUMMARY

[0006] However, based on the technique as disclosed in PTL 2, when adding a defoamer into the polymerization solution to perform polymerization reaction, there is a risk of deterioration in activity of oxidative polymerization, etc. In
10 this way, in conventional techniques, it has not been achieved in preparation of polyphenylene ether to sufficiently suppress foaming while maintaining the polymerization activity.

[0007] This disclosure is made based on consideration on the aforementioned problems, and aims to provide a method for preparing polyphenylene ether,
15 which is capable of sufficiently suppressing foaming in an early period of oxidative polymerization, and improving productivity per volume unit of reactor.

[0008] Having intensively studied the aforementioned purpose, we have discovered that in a reactor for preparing polyphenylene ether, it is possible to,
20 for example, complete oxidative polymerization without pasting a foaming region in an early period of polymerization reaction, by dispersing a solution which has been subjected to previous oxidative polymerization, and thereby completed this disclosure.

[0009] In other words, this disclosure is as follows.

25 The method for preparing polyphenylene ether of this disclosure has a polymerization process, in which an oxygen-containing gas is passed through a polymerization solution prepared by adding a phenolic compound, an aromatic solvent and a catalyst into a previously prepared polyphenylene ether, to thereby subject the phenolic compound to oxidative polymerization.

30 Here, the method for preparing polyphenylene ether of this disclosure further has a pre-polymerization process, in which an oxygen-containing gas is passed through a pre-polymerization solution containing a phenolic compound, an aromatic solvent and a catalyst, to thereby subject the phenolic compound to oxidative polymerization, where the previously prepared

Moreover, in the method for preparing polyphenylene ether of this disclosure, the ratio of the amount of the previously prepared polyphenylene ether relative to the amount of the phenolic compound added into the polymerization solution is preferably 10 mass% or more and 30 mass% or less.

10 **[0010]** According to this disclosure, it is possible to achieve a method for preparing polyphenylene ether, which is capable of sufficiently suppressing foaming in an early period of oxidative polymerization, and improving productivity per volume unit of reactor.

15 DETAILED DESCRIPTION

[0011] Hereinafter, an embodiment for applying this disclosure (hereinafter referred to merely as “the present embodiment”) is described in details. This disclosure is not limited to the following embodiment, but may be performed by varying within the scope of the subject thereof.

20 [0012] (Method for preparing polyphenylene ether)

The method for preparing polyphenylene ether according to the present embodiment has a polymerization process, in which in a reactor, an oxygen-containing gas is passed through a polymerization solution containing a phenolic compound, an aromatic solvent and a catalyst, to thereby subject the phenolic compound to oxidative polymerization.

According to the method for preparing polyphenylene ether of the present embodiment according to the aforementioned configuration, it is possible to complete oxidative polymerization without pasting the foaming region in an early period of polymerization reaction, and thus is capable of sufficiently suppressing foaming in an early period of oxidative polymerization, and improving productivity per volume unit of reactor.

[0013] In the present embodiment, it is possible to obtain a polyphenylene ether by adjusting a polymerization solution containing a phenolic compound, an aromatic solvent, a catalyst, and optionally other materials, containing the

same in a reactor, passing an oxygen-containing gas through the polymerization solution in the reactor, and subject the phenolic compound to oxidative polymerization.

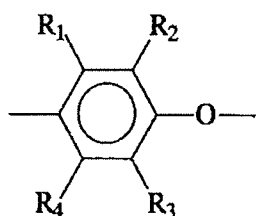
[0014] Hereinafter, resulting products obtained in the polymerization process (and the pre-polymerization process) and materials (a phenolic compound, an aromatic solvent, a catalyst and other materials) used in the polymerization process (and the pre-polymerization process) are described in details.

[0015] <Polyphenylene ether>

The polyphenylene ether prepared in the polymerization process in the method for preparing polyphenylene ether of the present embodiment is described hereinafter.

The polyphenylene ether prepared via the polymerization process is not specifically limited, and may be concretely a homopolymer or a copolymer having a repeating unit represented with the following Chem. (1).

[0016] [Chem. 1]



...(1)

[In the aforementioned Chem. (1), R₁ and R₄ each independently represent any one selected from the group consisting of hydrogen, primary or secondary lower alkyl, phenyl, amino alkyl, and hydrocarbon oxy; R₂ and R₃ each independently represent any one selected from the group consisting of hydrogen, primary or secondary lower alkyl, and phenyl.]

[0017] The homopolymer of the polyphenylene ether is not specifically limited, and may be concretely 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,
poly(2-methyl-6-chloroethyl-1,4-phenylene)ether, etc. Among the above,
poly(2,6-dimethyl-1,4-phenylene)ether is preferable from the viewpoint of
low material cost and convenience to acquire.

5 [0018] The copolymer of the polyphenylene ether refers to a copolymer
containing a phenylene ether unit as a monomer unit. The copolymer of the
polyphenylene ether is not specifically limited, and may be concretely a
copolymer of 2,6-dimethylphenol and 2,3,6-trimethylphenol, a copolymer of
2,6-dimethylphenol and o-cresol, a copolymer of 2,6-dimethylphenol,
10 2,3,6-trimethylphenol and o-cresol, etc. Among the above, a copolymer of
2,6-dimethylphenol and 2,3,6-trimethylphenol is preferable from the
viewpoint of low material cost and convenience to acquire.

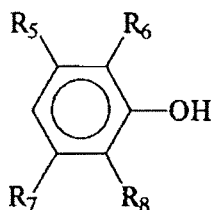
[0019] The reduced viscosity (η_{sp}/c) of the polyphenylene ether obtained via
the preparing method of the present embodiment is preferably 0.3 to 1.0 dL/g.
15 The reduced viscosity is a value measured at a temperature condition of 30°C,
using a chloroform solution of 0.5 g/dL. The reduced viscosity is preferably
within a range of 0.3 to 0.8 dL/g, and more preferably 0.3 to 0.6 dL/g. By
setting the aforementioned reduced viscosity to be 0.3 dL/g or more, there is a
tendency to obtain an original mechanical strength of the polyphenylene ether.
20 Moreover, by setting the aforementioned reduced viscosity to be 1.0 dL/g or
less, there is a tendency to obtain an effect to suppress excess increase of the
molecular weight during polymerization of the polyphenylene ether.

[0020] Regarding the method for controlling the reduced viscosity, increase
in the catalyst amount, the air passage amount and the reaction time causes a
25 tendency of increase in the reduced viscosity, and on the contrary, decrease in
the catalyst amount, the air passage amount and the reaction time causes a
tendency of decrease in the reduced viscosity.

[0021] <Phenolic compound>

The phenolic compound used in the polymerization process (and the
30 pre-polymerization process) in the method for preparing polyphenylene ether
of the present embodiment is a compound represented with the following
Chem. (2).

[Chem. 2]



...(2)

[In the aforementioned Chem. (2), R₅ and R₇ each independently represent any one selected from the group consisting of hydrogen, primary or secondary lower alkyl, phenyl, amino alkyl, and hydrocarbon oxy; R₆ and R₈ each independently represent any one selected from the group consisting of hydrogen, primary or secondary lower alkyl, and phenyl.]

[0022] The phenolic compound is not specifically limited, and may be concretely 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-fluoro phenyl)phenol, 2-methyl-6-tolylphenol, 2,6-ditolylphenol, etc. These phenolic compounds may be used singly or in a combination of two or more. Moreover, the aromatic solvent used as the polymerization solution is incorporated in the polyphenylene ether consumed in the polymerization reaction as a part of the phenolic compound, and thus has substantively no problem even if containing impurities such as phenol, o-cresol, m-cresol, p-cresol, 2,4-dimethylphenol, 2-ethylphenol and the like at a low amount.

[0023] Among the above, the phenolic compound is preferably a mixture of 2,6-dimethylphenol or 2,6-dimethylphenol and 2,3,6-trimethylphenol, and more preferably 2,6-dimethylphenol.

[0024] <Aromatic solvent>

The aromatic solvent is not specifically limited, and may be concretely one which dissolves a phenolic compound having a low molecular weight and dissolves the catalyst partially or totally.

[0025] Such aromatic solvent may be, but not limited within, for example,

aromatic hydrocarbons such as benzene, toluene, xylene, ethyl benzene and the like; halogenated aromatic hydrocarbons such as chlorobenzene, dichlorobenzene, trichlorobenzene and the like; nitro compounds such as nitrobenzene and the like, etc. Among the above, the aromatic solvent is preferably at least one selected from the group consisting of toluene, xylene and ethylbenzene, and more preferably toluene.

[0026] Optionally, the aromatic solvent may be mixed with a solvent having compatibility with water. The solvent having compatibility with water is not specifically limited, and may be concretely alcohols such as methanol, ethanol, propanol and the like; ketones such as acetone, methyl ethyl ketone and the like; esters such as ethyl acetate, ethyl formate and the like; amides such as dimethylformamide and the like; sulfoxides such as dimethyl sulfoxide and the like, etc. These solvents may be used singly or in a combination of two or more.

[0027] The aromatic solvent used in the polymerization process (and the pre-polymerization process) is preferably substantively incompatible with water. The solvent substantively incompatible with water is preferably an aromatic hydrocarbon solvent such as toluene, xylene and the like.

[0028] Moreover, the polymerization mode in the present embodiment varies depending on selection of the ratio of good solvent and poor solvent relative to the polyphenylene ether as the polymer obtained by subjecting the phenolic compound to oxidative polymerization. Specifically, the method becomes solution polymerization when the ratio of good solvent is increased, and becomes precipitation polymerization in which a polymer is precipitated in the reaction solvent as particles simultaneously with the progress of reaction, when the ratio poor solvent is increased. The polymerization mode in the present embodiment is not specifically limited, and optionally, a desired polymerization mode may be appropriately selected by adjusting the amount of poor solvent added into the aromatic solvent.

[0029] <Catalyst>

The catalyst is an effective oxidation catalyst for preparing polyphenylene ether by passing an oxygen-containing gas through a polymerization solution containing a phenolic compound, an aromatic solvent and a catalyst, and thereby subjecting the phenolic compound to efficient

oxidative polymerization.

[0030] Such catalyst is not specifically limited, and concretely, preferably contains at least one selected from the group consisting of copper compounds, bromine compounds, diamine compounds, tertiary monoamine compounds, and secondary monoamine compounds, and more preferably contains as necessary components a copper compound, a bromine compound, a diamine compound, a tertiary monoamine compound, and a secondary monoamine compound.

[0031] The copper compound used as a component of the catalyst is not specifically limited, and may be concretely a cuprous compound, a cupric compound or a mixture thereof. The cuprous compound is not specifically limited, and may be concretely cuprous oxide, cuprous chloride, cuprous bromide, cuprous sulfate, cuprous nitrate, etc. The cupric compound is not specifically limited, and may be concretely cupric chloride, cupric bromide, cupric sulfate, cupric nitrate, etc. Among the above compounds, as for the cuprous and cupric compounds, cuprous oxide, cuprous chloride, cupric chloride, cuprous bromide, cupric bromide are preferable. Moreover, these cuprates may be synthesized when using, from copper oxide, copper carbonate, copper hydroxide, etc. and a corresponding halogen or acid. For example, cuprous bromide is obtained by mixing cuprous oxide and (a solution of) hydrogen bromide. The copper compound is preferably a cuprous compound. These copper compounds may be used singly or in a combination of two or more.

[0032] The bromine compound used as a component of the catalyst is not specifically limited, and may be concretely hydrogen bromide, sodium bromide, potassium bromide, tetramethylammonium bromide, tetraethylammonium bromide, etc. Moreover, these bromine compounds may be used in the state of a water solution or a solution using an appropriate solvent. These bromine compounds may be used singly or in a combination of two or more.

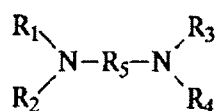
[0033] Combination of the aforementioned copper compounds and bromine compounds is preferably a water solution of cuprous oxide and hydrogen bromide. The usage of these compounds is not specifically limited, but preferably, the molar amount of bromine atoms is 2 times or more and 10

times or less to the molar amount of copper atoms. Moreover, the ratio of copper atoms per 100 mol of phenolic compound is preferably 0.02 to 0.6 mol.

[0034] The diamine compound used as a component of the catalyst is not specifically limited, and may be concretely a diamine compound, etc.

5 represented with the following Chem. (3).

[Chem. 3]



...(3)

[In the aforementioned Chem. (3), R_1 , R_2 , R_3 and R_4 are each
10 independently hydrogen or an alkyl group having a straight or branched chain with 1 to 6 carbon atoms, but may not all be hydrogen; R_5 is an alkylene group with 2 to 5 carbon atoms, having a straight chain or a methyl branch.]

[0035] Among the diamine compound represented with Chem. (3),
N,N'-di-t-butylethylenediamine is preferable.

15 [0036] These diamine compounds may be used singly or in a combination of two or more.

The usage of the diamine compound is not specifically limited, and may be 0.5 times or more to ordinarily used molar amount of copper atoms, while the upper limit thereof is not specifically limited.

20 [0037] The tertiary monoamine compound used as a component of the catalyst is not specifically limited, and may be an aliphatic tertiary amine, etc. including alicyclic tertiary amine. The tertiary monoamine compound is not specifically limited, and may be concretely trimethyl amine, triethylamine, tripropylamine, tributylamine, triisobutylamine, dimethylethylamine,
25 dimethylpropylamine, aryldiethylamine, N-butyl-dimethylamine, diethylisopropylamine, N-methylcyclohexylamine, etc.

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

The usage of the tertiary monoamine compound is not specifically

limited, but is preferably 0.1 mol to 15 mol per 100 mol of phenolic compound.

[0038] The secondary amine compound used as a component of the catalyst is not specifically limited, and may be concretely dimethylamine, diethylamine, di-n-propylamine, di-i-propylamine, di-n-butylamine, di-i-butylamine, di-t-butylamine, dipentylamine, dihexylamine, dioctylamine, didecylamine, dibenzylamine, methylethylamine, methylpropylamine, methylbutylamine, cyclohexylamine, N(substituted or non-substituted phenyl)alkanolamine, N-hydrocarbon substituted aniline, etc.

10 [0039] The N(substituted or non-substituted phenyl)alkanolamine is not specifically limited, and may be concretely N-phenylmethanolamine, N-phenylethanolamine, N-phenylpropanolamine, N-(m-methylphenyl)ethanolamine, N-(p-methylphenyl)ethanolamine, N-(2',6'-dimethylphenyl)ethanolamine, N-(p-chlorophenyl)ethanolamine, etc.

15 [0040] The N-hydrocarbon substituted aniline is not specifically limited, and may be concretely N-ethylaniline, N-butyraniline, N-methyl-2-methylaniline, N-methyl-2,6-dimethylaniline, diphenylamine, etc.

[0041] These secondary monoamine compounds may be used singly or in a combination of two or more.

20 The usage of the secondary monoamine compound is not specifically limited, but is ordinarily within a range of 0.05 mol to 15 mol per 100 mol of phenolic compound.

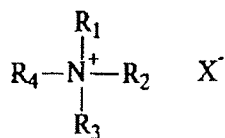
[0042] <Other materials>

25 In the method for preparing polyphenylene ether of the present embodiment, the other materials which may be contained in the polymerization solution (and the pre-polymerization solution) may be, while not limited to, for example, at least one selected from the group consisting of tetraalkyl ammonium salt compound, polyethylene-glycol-group-containing alkylamine, and polyethylene-glycol-group-containing alkyl ammonium salt
30 compound.

From the viewpoint of improvement in efficiency of the polymerization reaction, the content of the aforementioned other materials is preferably within a range of no more than 0.1 mass% per 100 mass% of polymerization solution (or pre-polymerization solution).

[0043] A specific example of the other materials is a compound represented with the following Chems. (4), (5) or (6).

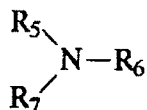
[0044] [Chem. 4]



5 ... (4)

[In the aforementioned Chem. (4), R₁, R₂, R₃ and R₄ are each independently alkyl groups with a straight or branched chain having 1 to 22 carbon atoms, and X is an anion in pair.]

[0045] [Chem. 5]



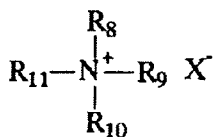
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... (5)

[In the aforementioned Chem. (5), R₅ is an alkyl group with a straight or branched chain having 1 to 22 carbon atoms; R₆ is an alkyl group with a straight or branched chain having 1 to 22 carbon atoms, a group represented as

15 -(CH₂CH₂O)_n-H [n is an integer of 1 to 40]; and R₇ is represented as -(CH₂CH₂O)_n-H [n is an integer of 1 to 40].]

[0046] [Chem. 6]



... (6)

[In the aforementioned Chem. (6), R_8 and R_9 represent alkyl groups with a straight or branched chain having 1 to 22 carbon atoms; R_{10} represents an alkyl group with a straight or branched chain having 1 to 22 carbon atoms, a group represented as $-(CH_2CH_2O)_n-H$ [n is an integer of 1 to 40]; R_{11} represents a group represented as $-(CH_2CH_2O)_n-H$ [n is an integer of 1 to 40]; and X is an anion in pair.]

[0047] In the aforementioned Chems. (4) and (6), X is preferably an anion selected from the group consisting of Cl^- and Br^- .

[0048] In the method for preparing polyphenylene ether of the present embodiment, specifically, as for the aforementioned other materials, preferably used is trioctylmethylammonium chloride, which is known as the trade names such as Aliquat336 (made by Henkel Co., Ltd.), Capriquat (made by Dojindo Molecular Technologies, Inc.) and the like.

[0049] ((Polymerization process))

Adjustment of the polymerization solution in the polymerization process may be performed by respectively introducing previously prepared polyphenylene ether, phenolic compound, aromatic solvent and components of catalyst into the reactor, or by introducing previously prepared polyphenylene ether, phenolic compound and catalyst into the reactor after previously dissolving each in the aromatic solvent, while it is preferable to introduce into the reactor the catalyst previously dissolved in a part of the aromatic solvent, and then introduce into the reactor the phenolic compound dissolved in the rest aromatic solvent.

[0050] From the viewpoint of progress of reaction and activity of catalyst, the temperature of the polymerization solution in the oxidative polymerization of the polyphenylene ether is preferably adjusted to 0 to 80°C, more preferably adjusted to 10 to 60°C, and further more preferably adjusted to 20 to 50°C. It is preferable to set the temperature as a lower value during an early part of the polymerization process, and to set the temperature as a higher value during a later part of the polymerization process. Thereby, there is a tendency that the progress of the polymerization reaction is accelerated.

[0051] The polymerization solution of the polymerization process is preferably prepared at a compounding ratio of 10 to 25 parts by mass of the phenolic compound, 75 to 90 parts by mass of the aromatic solvent and 0.1 to

10 parts by mass of the catalyst, per 100 parts by mass of the phenolic compound and the aromatic solvent in total.

By using such a compounding ratio, there is a tendency that the polymerization reaction of the polyphenylene ether can be stably controlled.

5 Further, the amount of the phenolic compound, the aromatic solvent and the catalyst in the polymerization solution is based on the mass on completion of introduction of the phenolic compound, the aromatic solvent and the catalyst into the reactor.

[0052] In the present embodiment, it is more preferable to use a
10 polymerization solution containing 12 to 23 parts by mass of the phenolic compound, 77 to 88 parts by mass of the aromatic solvent and 0.5 to 9 parts by mass of the catalyst, per 100 parts by mass of the phenolic compound and the aromatic solvent, and further more preferable to use a polymerization solution containing 13 to 21 parts by mass of the phenolic compound, 79 to 87
15 parts by mass of the aromatic solvent, and 0.8 to 8 parts by mass of the catalyst, per 100 parts by mass of the phenolic compound and the aromatic solvent. By using the aforementioned preferable compounding ratio, there is a tendency that the polymerization reaction of the polyphenylene ether can be stably controlled.

20 [0053] The absolute pressure of the reactor gas phase in the polymerization process is 0.098 MPa or more and 0.392 MPa or less. When the absolute pressure of the reactor gas phase exceeds 0.392 MPa, oversized apparatus is necessary, which is unpreferable. When less than 0.098 MPa, a region of negative pressure relative to atmospheric pressure is generated, and apparatus
25 compatible with vacuum is necessary, which is unpreferable.

[0054] (((Passage of oxygen-containing gas)))

The initiating period of passage of the oxygen-containing gas is not specifically limited, but in adjustment of the polymerization solution, it is preferable to initiate passage of the oxygen-containing gas after introducing
30 into the reactor any one of previously prepared polyphenylene ether, phenolic compound, aromatic solvent and catalyst.

[0055] The oxygen-containing gas is not specifically limited, and may be concretely a mixture of oxygen and any inert gas, air, or a mixture of air and any inert gas. The inert gas is not specifically limited, and may be

concretely anything as long as having a low effect with respect to the polymerization reaction. A representative inert gas is nitrogen.

[0056] The oxygen concentration of the oxygen-containing gas is not specifically limited, but concretely is preferably 5 to 25 volume% per 100

5 volume% of the oxygen-containing gas; in particular, in the case that a nitrogen-containing gas and air is contained, the oxygen concentration is more preferably 6 to 20 volume%, and further more preferably 8 to 12 volume%. By using such preferable oxygen concentration, there is a tendency that gradual heating and polymerization rate are further stabilized.

10 [0057] Moreover, when the oxygen concentration (the concentration of non-reacted oxygen) after gas passage in the oxygen-containing gas exceeds 11.6%, from the viewpoint of preventing explosion of the used solvent, it is preferable to control the oxygen concentration to be 11.6% or less by introducing an inert gas such as nitrogen and the like into the reactor gas

15 phase.

[0058] The passage amount of the oxygen-containing gas is not specifically limited, but is preferably 0.5 to 15 NL/min, more preferably 3 to 14 NL/min, further more preferably 6 to 13 NL/min, per 1kg of the phenolic compound provided for polymerization reaction. If being 0.5 NL/min or more, there is

20 a tendency that the target polyphenylene ether reaches the desired molecular weight in an early period, and that the productivity is improved. On the other hand, if being 15 NL/min or less, there is a tendency that the problem of oversize of the apparatus and increase in gas exhaust is avoided, which is economically excellent.

25 [0059] The absolute pressure of the reactor gas phase is not specifically limited as long as within the acceptable range of the reactor used for the oxidative polymerization, but concretely, is preferably 0.294 MPa or more from the viewpoint of obtaining an effect in foaming suppression, and is more preferably 0.392 MPa or less from the viewpoint of preventing oversize of the

30 apparatus for oxidative polymerization.

[0060] During the oxidative polymerization of the phenolic compound, foam is generated in the reaction solution simultaneously with the progress of the reaction. Since that the foam is decreased when the phenolic compound in the polymerization solution is consumed along with the progress of the

oxidative polymerization, it is assumed that foaming of the polymerization solution during the early period of the oxidative polymerization is related to the existence of the phenolic compound in a large amount in the polymerization solution.

5 During the early part (the early period) of the oxidative polymerization reaction, the height of the foam is increased and then rapidly decreased along with the progress of the reaction, and during the later part (the later period) of the oxidative polymerization, the foam disappears. Here, the timing to proceed to the later part (the later period) of the oxidative
10 polymerization reaction from the early part (the early period) of the oxidative polymerization reaction may be determined on the point of time to turn into decrease of the foam height, and is preferably 10 minutes before and after the foam completely disappears. Further, actually, the foam completely disappears in about 10 minutes from the beginning of decrease of the foam
15 height.

[0061] As mentioned above, in an early period of oxidative polymerization in an ordinary polyphenylene ether polymerization process, there is a probability that a foaming layer is generated. Further, with respect to the generation of the foaming layer, it is possible to evaluate the foaming amount, where the
20 foaming amount may be measured by using the method as described in Examples below.

[0062] In the method for preparing polyphenylene ether of the present embodiment, it is possible to suppress foaming of the polymerization solution, by adding a previously prepared polyphenylene ether into a phenolic
25 compound before oxidative polymerization in the polymerization process.

[0063] In the method for preparing polyphenylene ether of the present embodiment, in order to suppress generation of the foaming layer in the early period on the polymerization process, it is possible to make use of the reactor volume designed extra for the foaming layer part of the polymerization
30 solution in the prior art.

[0064] In the present embodiment, the ratio of the amount of the previously prepared polyphenylene ether relative to the amount of the phenolic compound added into the polymerization solution is not specifically limited as long as capable of ensuring the desired effects in the present embodiment, but

from the viewpoint of capability of improving the polymerization activity and reducing the reaction time (polymerization time), is preferably 10 mass% or more, more preferably 15 mass% or more, and from the viewpoint of productivity of the polyphenylene ether, is preferably 30 mass% or less, more preferably 25% or less, and further more preferably 20% or less.

Further, the reaction time (polymerization time) may be measured by using the method as described in Examples below.

[0065] On the other hand, in the present embodiment, from the viewpoint in consideration of productivity of the polyphenylene ether, the ratio of the phenolic compound in the polymerization solution of the polymerization process is preferably 25 mass% or less, more preferably 22% or less, and further more preferably 20% or less.

[0066] (((Termination of oxidative polymerization)))

After performing the polymerization process as mentioned above, the polymerization reaction is terminated at a point of time on reaching the target degree of polymerization.

The method for terminating the polymerization reaction is not specifically limited, and a conventionally well known method may be applied. An example as an ordinary terminating method is a method for deactivating the catalyst by adding into the reaction solution as a catalyst deactivator an acid such as hydrochloric acid, acetic acid and the like, ethylenediaminetetraacetic acid (EDTA) and salts thereof, nitrolotriacetic acid and salts thereof, etc.

After termination of the polymerization, the generated polyphenylene ether is separated, washed with a solvent incapable of dissolving the polyphenylene ether such as methanol and the like, dried, and then the polyphenylene ether is collected.

[0067] Here, the previously prepared polyphenylene ether used in the polymerization process of the method for preparing polyphenylene ether of the present embodiment is not specifically limited, and may be the same as the polyphenylene ether obtained in the aforementioned polymerization process of the method for preparing polyphenylene ether of the present embodiment.

[0068] Here, the previously prepared polyphenylene ether used in the polymerization process of the method for preparing polyphenylene ether of

the present embodiment is preferably a polyphenylene ether prepared via a pre-polymerization process which is the same as the aforementioned polymerization process, if without any reason for not using the previously prepared polyphenylene ether from the viewpoint of production efficiency and
5 production cost.

In this case, the method for preparing polyphenylene ether of the present embodiment further includes before the aforementioned polymerization process a pre-polymerization process (mentioned below), in which an oxygen-containing gas is passed through a pre-polymerization
10 solution containing a phenolic compound, an aromatic solvent and a catalyst, to thereby subject the phenolic compound to oxidative polymerization.

[0069] ((Pre-polymerization process))

If without any reason for not using a previously prepared polyphenylene ether, the pre-polymerization process may be the same as the
15 aforementioned polymerization process, and adjustment of the polymerization solution, passage of the oxygen-containing gas, termination of the oxidative polymerization, etc. in the aforementioned polymerization process may be the same as those in the polymerization process.

[0070] In the present embodiment, when proceeding to the polymerization
20 process from the pre-polymerization process, it is important to continuously use at least a part of an organic phase obtained via liquid separation of the pre-polymerization solution in the pre-polymerization process in the reactor by using an organic phase an aqueous phase, to thereby recycle in the polymerization process the phenolic compound and the aromatic solvent of the
25 pre-polymerization process.

Via such liquid separation, it is possible to remove a catalyst deactivator and water, which may be contained in the pre-polymerization solution, by dissolving the same in an aqueous phase, and simultaneously keep the polyphenylene ether generated in the pre-polymerization process, the
30 non-reacted phenolic compound, the aromatic solvent, etc. in an organic phase.

[0071] The aforementioned liquid separation for the purpose of continuously using the pre-polymerization solution after the oxidative polymerization may be performed intactly if the pre-polymerization solution contains an organic

solvent and water and generates an organic phase and an aqueous phase after termination of the polymerization reaction, and may be performed while adding an appropriate organic solvent and/or water if not.

Furthermore, preparation of the polymerization solution containing an
5 organic phase obtained via this liquid separation is not specifically limited, but is, from the viewpoint of easiness to be performed industrially, preferably performed by taking the organic phase of the pre-polymerization solution out from a reactor for pre-polymerization process and move the same into another reactor for polymerization process, and then performing the
10 preparation in this reactor for polymerization process. Moreover, the preparation of the polymerization solution may be performed in a reactor for pre-polymerization process, and in this case, it is important to remove an aqueous phase which may contain a catalyst deactivator and water, and keep a part of an organic phase containing polyphenylene ether, non-reacted phenolic
15 compound, aromatic solvent, etc. in the reactor for polymerization process.
[0072] As mentioned above, since a foaming layer is probably generated in an early period of oxidative polymerization in an ordinary polyphenylene ether polymerization process, in the method for preparing polyphenylene ether according to a preferable embodiment of this disclosure, at least a part of an
20 organic phase obtained via liquid separation of the polymerization solution in the pre-polymerization process by using an organic phase and an aqueous phase is continuously used in the polymerization process, and oxidative polymerization is continuously performed without pasting a foaming region in an early part of polymerization. Thereby, it is possible to achieve
25 improvement in production efficiency per volume unit of the reactor during the polymerization process.

[0073] In this way, it is possible to add the polyphenylene ether generated in the pre-polymerization process, the non-reacted phenolic compound, the aromatic solvent, etc. into the phenolic compound before the oxidative
30 polymerization in the polymerization process, and to thereby suppress foaming of the polymerization solution.

Moreover, by using at least a part of the organic phase obtained via liquid separation of the polymerization solution in the pre-polymerization process by using an organic phase and an aqueous phase, the polymerization

activity of the polymerization process is improved in comparison with the pre-polymerization process. By using this preparing method, it becomes possible to suppress foaming in the early period of polymerization, and to thereby sufficiently use the volume of the reactor.

5 [0074] A preferable example for the method for preparing polyphenylene ether of the present embodiment is a mode which uses 2,6-dimethylphenol as the phenolic compound, and as for the catalyst components, uses cuprous oxide as the copper compound, hydrogen bromide (used in water solution) as the bromine compound, N,N'-di-t-butylethylenediamine as the diamine
10 compound, N,N-di-n-butylamine as the secondary monoamine compound, N,N-dimethyl-n-butylamine as the tertiary monoamine, while the method for preparing polyphenylene ether of the present embodiment is not limited to this mode.

[0075] As mentioned above, in the present embodiment, existence of a
15 defoamer which affects the polymerization reaction in the polymerization solution is not necessary. Therefore, the polymerization reactivity would not be deteriorated, and it is possible to prepare polyphenylene ether while suppressing foaming of the polymerization solution.

20 EXAMPLES

[0076] Hereinafter, the present embodiment is specifically described with specific examples and comparative examples thereof, while the present embodiment is not limited to the following examples. Methods for measuring the physical properties and characteristics, which are applicable to
25 the Examples and Comparative Example, are as follows.

[0077] (1) Measurement of reduced viscosity (η_{sp}/c)

A reduced viscosity (η_{sp}/c) (dL/g) at 30°C was determined with an Ubbelohde viscometer, by adjusting a chloroform solution of 0.5 g/dL of polyphenylene ether.

30 [0078] (2) Measurement of liquid surface height

The distance (cm) from a lower portion of the reactor (used as a zero point) to the contacting part of the liquid surface and a side surface of the reactor (the interface between the liquid phase and the foam) was measured as a liquid surface height of the reaction solution, by pasting a scale on the side

surface of the reactor. In other words, in each example, the liquid surface height in a stirring state when stirring the polymerization solution was measured, and maximum values during the polymerization reaction were used as the liquid surface height (cm) of each example, by initiating stirring at a constant stirring rate of 500 rpm immediately after introducing the polymerization solvent into the reactor, and performing measurement of the aforementioned distance every 10 minutes from the initiation of oxidative polymerization.

[0079] (3) Measurement of foaming amount

Under the same conditions as the aforementioned “measurement of liquid surface height”, the distance (cm) from the aforementioned surface of the liquid phase and the foam to a contacting part between an upper surface of the foaming layer above the liquid surface and the side surface of the reactor was measured as a value to exhibit the foaming volume. In each example, maximum values during the polymerization reaction were used as values (cm) to exhibit the foaming amount of each example.

[0080] (4) Measurement of foaming termination time

The time of the termination of foaming in the polymerization solution was judged via visual observation, and the time from the initiation of the oxidative polymerization to the termination of foaming was measured as a foaming termination time (min).

[0081] (5) Measurement of liquid viscosity and measurement of polymerization time

The liquid viscosity (cP) of the solution was determined by adjusting to 40°C the temperature of the polymerization solution of each example sampled as follows, by using a vibration type liquid viscometer (made by SEKONIC Corporation, VISCOMATE VM-100A). The polymerization time (min) from the initiation of the oxidative polymerization to the termination of the oxidative polymerization was measured, by using the point of time of initiating the passage of the oxygen-containing gas into the aforementioned polymerization solution as the point of time of the initiation of the oxidative polymerization, and using the point of time when the value of the aforementioned liquid viscosity becomes 250 cP as the point of time of the termination of the oxidative polymerization.

[0082] [Example 1]

The reactor is a cylindrical reactor with an upper limit of height to contain the reaction solution of 50 cm and an inner diameter of 16 cm, and used was a 15-liter jacketed reactor made by SUS, which has a sparger for
5 introduction of the oxygen-containing gas, has a stirring turbine blade and an outlet valve for sampling disposed on a bottom of the reactor, has a baffle and a temperature adjustment apparatus disposed on a side portion of the reactor, and has an inlet for polymerization solution and a reflux condenser having a decanter for condensate separation to a vent gas line attached thereto disposed
10 on an upper portion of the reactor. A pressure adjustment valve and a pressure measurement apparatus was disposed on a vent gas outlet of the decanter.

A liquid-liquid separator for separation operation is a cylindrical liquid-liquid separator with an upper limit of height to contain the
15 polymerization solution of 50 cm and an inner diameter of 16 cm, and used was a 15-liter jacketed liquid-liquid separator made by SUS, which has stirring turbine blade and an outlet valve for sampling disposed on a bottom of the separator, has a baffle and a temperature adjustment apparatus disposed on a side portion of the separator, and has a reflux condenser having an inlet for
20 polymerization solution and a decanter for condensate separation to the vent gas line attached thereto disposed on an upper portion of the separator.

[0083] (Pre-polymerization process)

A polymerization solution containing 1.08 kg of 2,6-dimethylphenol, 4.84 kg of toluene, and 76.4 g of a catalyst (2.5 g of cuprous oxide, 15.2 g of a
25 47% water solution of hydrogen bromide, 6.1 g of N,N'-di-t-butylethylenediamine, 41.2 g of N-butyl-dimethylamine, 11.4 g of di-n-butylamine) was prepared and introduced into the aforementioned reactor, the temperature of the polymerization solution was adjusted to 40°C, and the absolute pressure of the reactor gas phase was adjusted to 0.301 MPa. Then,
30 as for the oxygen-containing gas for passage, an oxygen-containing gas with an absolute pressure of 0.301 MPa and an oxygen concentration of 9 volume% was introduced from the sparger, to initiate the oxidative polymerization of 2,6-dimethylphenol (a partial pressure of oxygen in this oxygen-containing gas was $0.301(\text{MPa}) \times 0.09 = 0.02709(\text{MPa})$).

During the polymerization reaction, the height of liquid surface was measured according to the aforementioned method (2), and the foaming amount was measured according to the aforementioned method (3). Although generation of foam was observed after initiation of the
5 aforementioned oxidative polymerization, it was regarded that the foam completely disappeared within 90 minutes after the initiation of the oxidative polymerization. Moreover, the foaming termination time was measured according to the aforementioned method (4). Further, the polymerization time was measured by sampling by small amounts every 5 minutes from the
10 point of time after 60 minutes of oxidative polymerization and measuring the liquid viscosity according to the aforementioned method (5).

After 151 minutes from the initiation of the oxidative polymerization, the oxidative polymerization was terminated by adding 0.60 kg of a 10% water solution of ethylenediaminetetraacetic acid tetrasodium salt (made by
15 Dojindo Molecular Technologies, Inc.), and the polymerization solution was stirred at 70°C for 150 minutes. Then, the polymerization solution was totally taken out from the reactor, and introduced into the liquid-liquid separator. Then, the solution was left standing for 60 minutes, and was separated into an organic phase and an aqueous phase via liquid-liquid
20 separation.

[0084] (Polymerization process)

A polymerization solution containing 1.20 kg of the organic phase obtained in the pre-polymerization process (20 mass%), 1.08 kg of 2,6-dimethylphenol, 4.84 kg of toluene and 76.4 g of a catalyst (2.5 g of
25 cuprous oxide, 15.2 g of a 47% water solution of hydrogen bromide, 6.1 g of N,N'-di-t-butylethylenediamine, 41.2 g of N-butyl-dimethylamine and 11.4 g of di-n-butylamine) was prepared and introduced into the aforementioned reactor, the temperature of the polymerization solution was adjusted to 40°C, and the absolute pressure of the reactor gas phase was adjusted to 0.301 MPa.
30 Then, as for the oxygen-containing gas for passage, an oxygen-containing gas with an absolute pressure of 0.301 MPa and an oxygen concentration of 9 volume% was introduced from the sparger, to initiate the oxidative polymerization of 2,6-dimethylphenol (a partial pressure of oxygen in this oxygen-containing gas was $0.301(\text{MPa}) \times 0.09 = 0.02709(\text{MPa})$).

During the polymerization reaction, the height of liquid surface was measured according to the aforementioned method (2), and the foaming amount was measured according to the aforementioned method (3). Although generation of foam was observed after initiation of the
5 aforementioned oxidative polymerization, it was regarded that the foam completely disappeared within 90 minutes after the initiation of the oxidative polymerization. Moreover, the foaming termination time was measured according to the aforementioned method (4). Further, the polymerization time was measured by sampling by small amounts every 5 minutes from the
10 point of time after 60 minutes of oxidative polymerization and measuring the liquid viscosity according to the aforementioned method (5).

After 146 minutes from the initiation of the oxidative polymerization, the oxidative polymerization was terminated by adding 0.60 kg of a 10% water solution of ethylenediaminetetraacetic acid tetrasodium salt (made by
15 Dojindo Molecular Technologies, Inc.), and the polymerization solution was stirred at 70°C for 150 minutes. Then, the polymerization solution was totally taken out from the reactor, and introduced into the liquid-liquid separator. Then, the solution was left standing for 60 minutes, and was separated into an organic phase and an aqueous phase via liquid-liquid
20 separation.

A wet polyphenylene ether was obtained by precipitating, washing and then filtering the obtained organic phase with 6.50 kg of methanol. A polyphenylene ether of Example 1 was obtained by subjecting the obtained wet polyphenylene ether to drying treatment at a temperature condition of
25 150°C for 120 minutes.

[0085] The details and results of Example 1 are as shown in Table 1.

[0086] [Example 2]

A polyphenylene ether of Example 2 was obtained via the same operation as Example 1, except that the organic phase obtained in the
30 pre-polymerization process was used by 0.60 kg (10 mass%) in the polymerization process. The details and results of Example 2 are as shown in Table 1.

[0087] [Example 3]

A polyphenylene ether of Example 3 was obtained via the same

operation as Example 1, except that the organic phase obtained in the pre-polymerization process was used by 1.80 kg (30 mass%) in the polymerization process. The details and results of Example 3 are as shown in Table 1.

5 **[0088]** [Example 4]

A polyphenylene ether of Example 4 was obtained via the same operation as Example 1, except that the organic phase obtained in the pre-polymerization process was used by 0.30 kg (5 mass%) in the polymerization process. The details and results of Example 4 are as shown
10 in Table 1.

[0089] [Example 5]

A polyphenylene ether of Example 5 was obtained via the same operation as Example 1, except that the organic phase obtained in the pre-polymerization process was used by 2.10 kg (35 mass%) in the
15 polymerization process. The details and results of Example 5 are as shown in Table 1.

[0090] [Example 6]

A polyphenylene ether of Example 6 was obtained via the same operation as Example 1, except that used was a polymerization solution
20 containing 1.20kg (20 mass%) of the organic phase obtained in the pre-polymerization process, 1.44 kg of 2,6-dimethylphenol, 6.46 kg of toluene and 101.9 g of a catalyst (3.4 g of cuprous oxide, 20.3 g of a 47% water solution of hydrogen bromide, 8.1 g of di-t-butylethylenediamine, 15.2 g of di-n-butylamine and 54.9 g of butyldimethylamine). The details and results
25 of Example 6 are as shown in Table 1.

[0091] [Example 7]

A polyphenylene ether of Example 7 was obtained via the same operation as Example 6, except that the organic phase obtained in the pre-polymerization process was used by 1.80 kg (30 mass%) in the
30 polymerization process. The details and results of Example 7 are as shown in Table 1.

[0092] [Example 8]

A polyphenylene ether of Example 8 was obtained via the same operation as Example 1, except that in the pre-polymerization process, the

pre-polymerization process was performed by using a polymerization solution containing 1.50 kg of 2,6-dimethylphenol, 4.39 kg of toluene and 106.1 g of a catalyst (3.5 g of cuprous oxide, 21.0 g of a 47% water solution of hydrogen bromide, 8.5 g of di-t-butylethylenediamine, 15.9 g of di-n-butylamine and 57.2 g of butyldimethylamine), and in the polymerization process, used was a polymerization solution containing 1.80 kg (30 mass%) of the organic phase obtained in the pre-polymerization process, 1.50 kg of 2,6-dimethylphenol, 4.39 kg of toluene and 106.1 g of a catalyst (3.5 g of cuprous oxide, 21.0 g of a 47% water solution of hydrogen bromide, 8.5 g of di-t-butylethylenediamine, 15.9 g of di-n-butylamine and 57.2 g of butyldimethylamine). The details and results of Example 8 are as shown in Table 1.

[0093] [Example 9]

A polyphenylene ether of Example 9 was obtained via the same operation as Example 1, except that used was a polymerization solution containing 0.22 kg of polyphenylene ether (made by Asahi Kasei Chemicals Corporation, S201A), 0.86 kg of 2,6-dimethylphenol, 4.84 kg of toluene and 60.9 g of a catalyst (2.0 g of cuprous oxide, 12.1 g of a 47% water solution of hydrogen bromide, 4.9 g of di-t-butylethylenediamine, 9.1 g of di-n-butylamine and 32.8 g of butyldimethylamine), and the polymerization process was performed only for 1 time. Further, in Example 9, although generation of foam was observed after initiation of the aforementioned oxidative polymerization, it was regarded that the foam completely disappeared within 90 minutes after the initiation of the oxidative polymerization. The details and results of Example 9 are as shown in Table 1.

[0094] [Comparative Example 1]

A polyphenylene ether of Comparative Example 1 was obtained via the same operation as Example 1, except that used was a polymerization solution containing 1.26 kg of 2,6-dimethylphenol, 5.65 kg of toluene and 89.2 g of a catalyst (3.0 g of cuprous oxide, 17.8 g of a 47% water solution of hydrogen bromide, 7.1 g of di-t-butylethylenediamine, 13.3 g of di-n-butylamine and 48.0 g of butyldimethylamine), and the polymerization process was performed only for 1 time. Further, in Comparative Example 1, although generation of foam was observed after initiation of the

aforementioned oxidative polymerization, it was regarded that the foam completely disappeared within 88 minutes after the initiation of the oxidative polymerization. The details and results of Comparative Example 1 are as shown in Table 1.

5 [0095] [Comparative Example 2]

The oxidative polymerization was initiated via the same operation as Example 1, except that used was a polymerization solution containing 1.44 kg of 2,6-dimethylphenol, 6.46 kg of toluene and 101.9 g of a catalyst (3.4 g of cuprous oxide, 20.3 g of a 47% water solution of hydrogen bromide, 8.1 g of
10 di-t-butylethylenediamine, 15.2 g of di-n-butylamine and 54.9 g of butyldimethylamine), and the polymerization process was performed only for 1 time. The oxidative polymerization was stopped since that the foaming amount was about to exceed the upper limit of the reactor at the point of time 80 minutes after the initiation of the oxidative polymerization. No
15 polyphenylene ether was obtained in Comparative Example 2. The details and results of Comparative Example 2 are as shown in Table 1.

[0096] [Comparative Example 3]

The polymerization solution obtained in the pre-polymerization process was taken out by 4.80 kg, remaining 1.20 kg of organic phase
20 (inclusive of aqueous phase) in the reactor in the pre-polymerization process. The oxidative polymerization was initiated via the same operation as Example 1, except that the polymerization process was performed in the reactor in the pre-polymerization process by using this 1.20 kg of polymerization solution. The oxidative polymerization was stopped since that the predetermined liquid
25 viscosity was not reached at the point of time 150 minutes after the initiation of the oxidative polymerization. No polyphenylene ether was obtained in Comparative Example 3. The details and results of Comparative Example 3 are as shown in Table 1.

INDUSTRIAL APPLICABILITY

- [0098] According to this disclosure, it is possible to achieve a method for preparing polyphenylene ether, which is capable of sufficiently suppressing foaming in an early period of oxidative polymerization, and improving
- 5 productivity per volume unit of reactor. The method for preparing polyphenylene ether of this disclosure has industrial applicability as a technique for producing materials for automobile components, heat resistant components, electronic device components, industrial components, etc..

CLAIMS

1. A method for preparing polyphenylene ether, comprising a polymerization process, wherein an oxygen-containing gas is passed through a
5 polymerization solution prepared by adding a phenolic compound, an aromatic solvent and a catalyst into a previously prepared polyphenylene ether having a reduced viscosity of 0.3 to 1.0 dL/g, to thereby subject the phenolic compound to oxidative polymerization.

10

2. The method for preparing polyphenylene ether according to claim 1, further comprising a pre-polymerization process, wherein an oxygen-containing gas is passed through a pre-polymerization solution comprising a phenolic compound, an aromatic solvent and a catalyst, to
15 thereby subject the phenolic compound to oxidative polymerization, wherein the previously prepared polyphenylene ether is a polyphenylene ether contained in at least a part of an organic phase obtained via liquid separation of the pre-polymerization solution after the pre-oxidative polymerization by using an organic phase and an aqueous phase.

20

3. The method for preparing polyphenylene ether according to claim 1 or 2, wherein a ratio of an amount of the previously prepared polyphenylene ether to an amount of the phenolic compound added into the
25 polymerization solution is 10 mass% or more and 30 mass% or less.