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PRODUCTION PROCESS OF POLYPHENYLENE ETHERS

FIELD OF THE INVENTION

The present invention relates to a process for producing a polyphenylene ether, which comprises allowing an oxygen-containing gas to pass through a solution for polymerization containing a good solvent, a metal salt, an amine compound and a phenol compound, thereby carrying out oxidative polymerization of the phenol compound to obtain the polyphenylene ether, mixing the polymer solution with an aqueous solution of a chelating agent to terminate the polymerization, and adding a poor solvent for polyphenylene ethers to the polyphenylene ether solution, from which the metal salt, chelating agent and water have been removed by separation, thereby precipitating polyphenylene ether particles. More specifically, the present invention relates to a method of effectively recovering the good solvent.

BACKGROUND OF THE INVENTION

Polyphenylene ether resin compositions using a polyphenylene ether as a raw material are plastic materials widely employed for products or parts

used in the electric or electronic field, automobile field and the other industrial material fields because they can be formed into products or parts of a desired shape by the method such as melt injection or melt extrusion.

As a process for producing a polyphenylene ether, there has been known a process comprising the steps of: allowing an oxygen-containing gas to pass through a solution for polymerization comprising a good solvent, a metal salt, an amine compound and a phenol compound, thereby carrying out oxidative polymerization of the phenol compound to obtain a polyphenylene ether; terminating the polymerization by mixing the solution with an aqueous solution of a chelating agent; adding a poor solvent for polyphenylene ethers to the polyphenylene ether solution, from which the metal salt, chelating agent and water have been removed by separation, thereby precipitating polyphenylene particles; collecting the particles by filtration; and then drying the collected particles.

In the above-described production process, recovery of the good solvent and poor solvent from the mixed solution from which the polyphenylene

ether particles have been filtered out can be carried out by, for example in the case where toluene is used as the good solvent and methanol is used as the poor solvent, adding a sufficient amount of water to the mixed solution to separate it into two phases, that is, a good solvent phase containing the good solvent and an aqueous phase containing the poor solvent and water, and distilling the good solvent phase to recover the good solvent and distilling the aqueous phase to recover the poor solvent.

In the above-describe method to distill the aqueous phase to recover methanol, it is possible to suppress foaming in a distillation column and effectively recover methanol by the addition of any one of ordinarily employed alcohol series, glycerin series and silicone series antifoaming agents or a mixture of two or more thereof.

Even by the use of an antifoaming agent usually regarded effective for distillation of an aromatic organic solvent, such as a silicone series antifoaming agent, foaming in a distillation column upon distillation of the good solvent phase in the polyphenylene ether production cannot be suppressed. Under the

present situation, the good solvent must be recovered under distillation conditions taking into account the foaming problem.

The industrial filed pertain to the production of polyphenylene ethers which needs recovery of a high-purity good solvent has not yet had a technique capable of sufficiently meeting the demands for recovery efficiency and productivity.

SUMMARY OF THE INVENTION

The present invention relates to a process for producing a polyphenylene ether, which comprises the steps of allowing an oxygen-containing gas to pass through a solution for polymerization composed of a good solvent, a metal salt, an amine compound and a phenol compound, thereby carrying out oxidative polymerization of the phenol compound, mixing the solution with an aqueous solution of a chelating agent to terminate the polymerization, adding a poor solvent for polyphenylene ethers to the polyphenylene ether solution, from which the metal salt, chelating agent and water have been removed by separation, to precipitate polyphenylene ether particles, and then filtering the resulting solution. More

specifically, the present invention relates to a method for recovering the good solvent by distilling the mixed solution from which the polyphenylene ether particles have been filtered out. Further specifically, an object of the present invention is to provide a method being capable of suppressing foaming upon distillation and being free from problems in recovery efficiency, purity of the solvent recovered and productivity, so as to sufficiently meet the demands in this industrial field.

The present inventors made extensive studies with a view to attaining the above-described object. As a result, they found, in a production process of a polyphenylene ether, which comprises allowing an oxygen-containing gas to pass through a solution for polymerization having a good solvent for polyphenylene ethers, a metal salt, an amine compound and a phenol compound, thereby carrying out oxidative polymerization of the phenol compound, mixing the solution with an aqueous solution of a chelating agent to terminate the polymerization, separating and removing the metal salt, chelating agent and water from the resulting mixture, adding a poor solvent for

polyphenylene ethers to the polyphenylene ether solution to precipitate polyphenylene ether particles, and then filtering the solution, a method of effectively suppressing foaming in a distillation column, thereby efficiently recovering the good solvent for polyphenylene ethers at high purity upon recovery of the good solvent by distilling the mixed solution from which the polyphenylene ether particles have been filtered. Thus, they have completed a method of recovering a good solvent in polyphenylene ether production which method can sufficiently meet the demands in the relevant industrial field.

That is, the above-described object of the invention has been achieved by providing a process for producing a polyphenylene ether, which comprises the steps of:

allowing an oxygen-containing gas to pass through a solution for polymerization containing:

a good solvent for polyphenylene ethers;

a metal salt;

an amine compound; and

a phenol compound,

to carry out oxidative polymerization of the phenol compound;

mixing the polymerized solution with an aqueous solution of a chelating agent to terminate the polymerization;

separating and removing the metal salt, chelating agent and water from the resulting mixture to give a polyphenylene ether solution;

adding a poor solvent for polyphenylene ethers to the polyphenylene ether solution to precipitate polyphenylene ether particles;

filtering the resulting solution to collect the polyphenylene ether particles; and

recovering the good solvent by distilling the filtrate,

wherein said recovery of the good solvent is carried out using at least one antifoaming agent selected from fluorosilicone compound based antifoaming agents.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic view of an Oldershaw type fractionating unit used in Example 1.

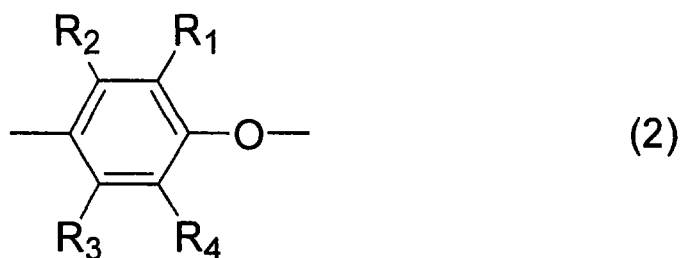
FIG. 2 is a schematic view of a distillation evaluating apparatus used in Example 2.

In the drawings, the reference symbols respectively represent the followings.

A: liquid taken out from the top plate
B: feed of good solvent phase
C: liquid taken out from the bottom plate
D: 20-plates fractionating tower
 (concentrating portion)
E: 20-plates fractionating tower
 (recovering portion)
F: oil bath
A': 2L glass cylindrical vessel
B': nitrogen inlet tube
C': ball filter
D': distillation tube
E': thermometer
F': condenser tube
G': rubber stopper
G: oil bath
H: foaming height
a: good solvent phase
b: nitrogen
c: foamed region
d: recovered toluene
e: cold water

DETAILED DESCRIPTION OF THE INVENTION

The polyphenylene ether of the invention has a main chain structure represented by Formula (2) shown below.



In the polyphenylene ether of the invention represented by the above Formula (2), R_1 and R_4 each independently represents hydrogen, primary or secondary lower alkyl, phenyl, aminoalkyl or hydrocarboxy, and R_2 and R_3 each independently represents hydrogen, primary or secondary lower alkyl or phenyl.

The "good solvent for polyphenylene ethers" is a solvent capable of favorably dissolving therein polyphenylene ethers to form a uniform polyphenylene ether solution. The good solvent preferably comprises at least one solvent selected from benzene, toluene and xylene.

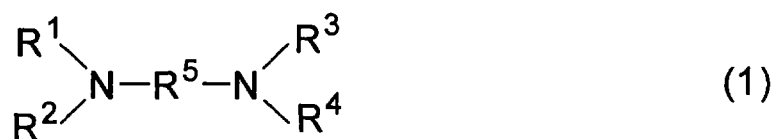
The "metal salt" is a main catalyst in oxidative polymerization of a phenol compound.

The metal salt for use in the invention preferably comprises at least one metal salt

selected from copper compounds and manganese compounds.

The "amine compound" is a compound which forms a complex with the metal salt, thereby serving as a catalyst for the oxidative polymerization of the phenol compound.

In the present invention, the amine compound preferably comprises at least one amine compound selected from diamine compounds represented by Formula (1) shown below, tertiary monoamine compounds and secondary monoamine compounds.



(wherein, R^1 , R^2 , R^3 and R^4 each independently represents a hydrogen atom or a linear or branched C_{1-6} alkyl group with the proviso that R^1 , R^2 , R^3 and R^4 do not represent a hydrogen atom at the same time, and R^5 represents a linear or methyl-branched C_{2-5} alkylene group).

The phenol compound for use in the invention preferably comprises at least one phenol compound selected from 2,6-dimethylphenol, 2,3,6-trimethylphenol, 2-methyl-6-butylphenol, 2-methyl-

6-ethylphenol, 2-methyl-6-phenylphenol and 2,6-dichlorophenol.

As the phenol compound of the invention, 2,6-dimethylphenol is most preferred.

The "oxygen-containing gas" is a gas containing oxygen such as oxygen.

The oxygen-containing gas of the invention is preferably a gas containing at least 5 vol.% of oxygen.

The polyphenylene ether in the invention is preferably obtained by allowing the oxygen-containing gas to flow through a solution for polymerization having, as essential ingredients, at least one good solvent for polyphenylene ethers selected from benzene, toluene and xylene, the metal salt, the amine compound and the phenol compound, thereby carrying out oxidative polymerization of the phenol compound.

In the invention, the polyphenylene ether has a reduced viscosity, as measured at 30°C by using a chloroform solution of 0.5 g/dl, of preferably 0.15 to 1.5 dl/g, more preferably from 0.30 to 1.0 dl/g.

In the present invention, the polymerization is terminated by adding an aqueous solution of a

chelating agent to the polymer solution, at the time when the polyphenylene ether reaches a desired reduced viscosity by the oxidative polymerization.

The "chelating agent" for use in the invention is a water-soluble chelating agent which forms a chelate with the above-described metal salt and permits efficient removal of the metal salt from the polymer solution.

As the aqueous chelating agent solution, an aqueous solution of ethylenediaminetetraacetate salt is preferably employed in the invention.

More preferred are those comprising at least one selected from an aqueous solution of tetrasodium ethylenediaminetetraacetate, an aqueous solution of trisodium ethylenediaminetetraacetate, an aqueous solution of tetrapotassium ethylenediaminetetraacetate and an aqueous solution of tripotassium ethylenediaminetetraacetate.

The polyphenylene ether solution of the invention is obtained by substantially removing the metal salt, chelating agent and water from the polymer solution.

The polyphenylene ether solution of the invention has preferably a polyphenylene ether content of from 10 to 30 wt.%, based on the polyphenylene ether solution.

The production process of a polyphenylene ether according to the invention comprises adding a poor solvent for polyphenylene ethers, preferably at least one selected from methanol, ethanol, isopropanol, n-butanol, acetone and methyl ethyl ketone, to the polyphenylene ether solution to precipitate polyphenylene ether particles and then filtering the resulting solution, wherein at least one antifoaming agent selected from fluorosilicone compound type antifoaming agents is used upon distilling the mixed solution from which the polyphenylene ether particles have been filtered out, thereby recovering the good solvent .

In the production process of a polyphenylene ether according to the invention, at least one antifoaming agent selected from fluorosilicone compound type antifoaming agents is added upon recovery of the good solvent, preferably in an amount of from 0.01 to 10 ppm, more preferably from 0.03 to 7 ppm, especially preferably from

0.05 to 5 ppm based on 1 part by weight of the good solvent.

The fluorosilicone compound type antifoaming agents for use in the invention preferably include fluorosilicone compounds obtained by substituting some or all of the methyl groups of polydimethylsiloxane with the corresponding number of fluoroalkyl groups or perfluoroalkyl groups or mixtures of a fluorosilicone compound with a silicon compound. Specific examples of the fluorosilicone compounds or mixtures of a fluorosilicone compound and a silicone compound preferred in the invention include an antifoaming agent "FA630" (trade name; product of Shin-Etsu Chemical) and an antifoaming agent "FQF501" (trade name; product of Toshiba Silicones).

If the mixed solution of the invention is directly distilled, foaming occurs in a distillation column, which disturbs efficient recovery of the good solvent. Direct distillation causes problems in purity and productivity.

According to an extremely preferred embodiment of the invention, after the polymerization is terminated by contacting with the aqueous solution of a chelating agent, the

mixed solution is kept at 40 to 120°C until a polymerization by-product, diphenoquinone disappears, followed by separation of a catalyst formed from the metal salt and the amine compound.

According to a particular preferred embodiment of the invention, the recovery of the good solvent and the poor solvent is carried out by mixing the filtrate (i.e., mixed solution from which polyphenylene ether particles have been filtered out) with water to separate into a good solvent phase containing said good solvent and an aqueous phase containing said poor solvent and water, fractionating these phases, and distilling the good solvent phase to recover the good solvent and distilling the aqueous phase to recover the poor solvent.

By employing the polyphenylene ether production process of the invention, a recovery efficiency of the good solvent for polyphenylene ethers shows a drastic improvement and moreover, the good solvent thus recovered has a higher purity compared with those recovered by the conventional processes. This therefore brings about a great improvement in the equipment and energy required for the recovery of the solvents.

The present invention will be illustrated in greater detail with reference to the following Examples, but the invention should not be construed as being limited thereto.

Referential Example

(A-1): In accordance with the process described in Example 3 of JP-B-59-23332 (The term "JP-B" as used herein means an "examined Japanese patent publication"), a 22 wt.% toluene solution of 2,6-dimethylphenol was added over 35 minutes in the presence of each catalyst and di-n-butylamine while feeding the mixture with oxygen. After 100 minutes, feeding of oxygen was terminated. An aqueous solution of trisodium ethylenediaminetetraacetate was added to the polymerization mixture and the resulting mixture was kept at 70°C for 2 hours. The mixture was fed to a centrifugal separator manufactured by Sharples Corp., where an aqueous solution phase containing each catalyst and trisodium ethylenediaminetetraacetate was separated. Thus, a polyphenylene ether solution (A-1) having a

polyphenylene content of 22.5% and a specific gravity of 0.894 was obtained.

In a jacket-equipped precipitation tank having an inner diameter of 133 mm, and further equipped with an exhaust port of a port size of 25 mm, at a position corresponding to a liquid level of 95 mm from the tank bottom, and with a single-stage four-inclined-paddle impeller (inclination: 45 degree, impeller size: 33 mm) as an agitator, 370 g of toluene, 420 g of methanol and 10 g of water were charged, followed by stirring at 600 rpm. After the temperature in the tank was increased to 50°C by causing warm water to flow in the jacket, the polyphenylene ether solution (A-1) was added at a rate of 190 g/min from a position diagonal to the exhaust port and a mixture of 97.5 wt.% of methanol and 2.5 wt.% of water was added at a rate of 100 g/min from the same position.

The mixture overflowing from the exhaust port was collected.

The resulting mixture was filtered through a glass filter and the mixture from which the polyphenylene ether particles had been filtered out was obtained.

The polyphenylene ether in (A-1) was found to have a reduced viscosity, as measured in 0.5 g/dl of chloroform, of 0.51 dl/g.

To 100L of the mixture was added 9.2L of water, whereby a mixture separated into a good solvent phase containing a good solvent and an aqueous phase containing a poor solvent and water was obtained.

From the resulting mixture, the aqueous phase was fractionated through a centrifugal separator of Sharples Corp., whereby a good solvent phase to be used later in Examples was obtained.

Example 1

The good solvent phase (60 kg) added, prior to distillation, with 150 mg of a fluorosilicone antifoaming agent "FA603" (trade name; product of Shin-Etsu Chemical) was distilled in a glass-made Oldershaw fractionating unit having 40 concentration plates and a diameter of 45 mm.

In the liquid reservoir at the bottom plate of the Oldershaw fractionating unit was charged 5 kg of toluene and the liquid reservoir was heated in an oil bath set at 160°C.

After the distillation of toluene started from the top of the fractionating unit, it was cooled and returned to the top plate.

When it was confirmed that the temperature of the gas phase on the top plate became stable at 110°C, the good solvent phase added with the above-described antifoaming agent was fed to the 20-th plate from the upper portion of the fractionating unit at a rate of 2700 g/hour, and then 10% of the liquid obtained by cooling the gas phase on the top plate was taken out, while 90% was returned to the top plate.

The gas phase on the bottom plate was cooled and then, taken out.

Five hours after the feeding was started, the temperatures of the gas phase on the top plate and bottom plate of the fractionating unit became stable, specifically, 66°C and 111°C, respectively.

Distillation was continued for 20 hours, but no substantial change was observed.

The amount of liquid taken out per hour was 146 g/hour from the top plate and 2554 g/hour from the bottom plate.

The liquid taken out from the top plate in the 18th hour was composed of 37% methanol, 2% water,

60% toluene and 1% the other substances, while the liquid taken out from the bottom plate was composed of 98% toluene, 0% methanol, 0% water and 1% an oligomer of polyphenylene ether and 1% the other substances.

The liquid taken out from the bottom plate was subjected to single distillation to separate the oligomer of polyphenylene ether, whereby a toluene composition containing 99% of toluene and about 1% of amine usable as a polymerization catalyst was recovered.

Comparative Example 1

In an Oldershaw fractionating unit similar to that employed in Example 1, the good solvent phase not added with an antifoaming agent was distilled. After operation of the same procedure as in Example 1 and confirmation that the temperature of the gas phase on the top plate became stable at 110°C, the good solvent phase not added with an antifoaming agent was fed at a rate of 2700 g/hour from the upper portion to the 20-th plate of the fractionating unit.

Foaming was observed on the top plate and this foaming did not disappear even 10 hours after the feeding was started.

The liquid taken out from the top plate in the tenth hour after the feeding was started was composed of 95% toluene, 2.9% methanol, 0.1% water, 1% the oligomer of polyphenylene ether and 1% the other substances, while the liquid taken out from the bottom plate was composed of 96% toluene, 2.3% methanol, 0.1% water, 1% an oligomer of polyphenylene ether and 0.6% the other substances.

Even by single distillation of the liquid taken out from the bottom plate, methanol and water still remained with toluene.

Comparative Example 2

In an Oldershaw fractionating unit similar to that employed in Example 1, the good solvent phase not added with an antifoaming agent was distilled. After operation of the same procedure as in Example 1 and confirmation that the temperature of the gas phase in the top plate became stable at 110°C, the good solvent phase not added with an antifoaming agent was fed at a rate of 450 g/hour

from the upper portion to the 20-th plate of the fractionating unit.

From the liquid obtained by cooling the gas phase in the top plate, 10% was taken out and 90% was returned to the top plate.

The gas phase in the bottom plate was cooled and then taken out.

The liquid amount taken out per hour was 25g/hour from the top plate and 425 g/hour from the bottom plate.

The liquid taken out from the bottom plate in the 18-th hour after the feeding was started was composed of 98% toluene, 0% methanol, 1% the oligomer of a polyphenylene ether and 1% the other substances.

By single distillation of the liquid taken out from the bottom plate to separate the oligomer of a polyphenylene ether, a toluene composition containing 99% toluene and about 1% amine usable as a polymerization catalyst was recovered. The processed amount of the good solvent was however markedly smaller in Comparative Example 2 than that in Example 1.

Example 2

As in Example 1, 150 mg of a fluorosilicone antifoaming agent ("FA603", trade name; product of Shin-Etsu Chemical) was added to 60 kg of the good solvent phase and foaming of it was evaluated using a distillation evaluating unit as shown in FIG. 2.

300 ml of the above-described good solvent phase added with the antifoaming agent was charged in a 2L glass cylinder equipped with a nitrogen inlet tube having a ball filter at the tip thereof, and equipped with a distillation tube, a condenser and a thermometer at the top of the cylinder as illustrated in FIG. 2 and this cylinder was installed in an oil bath set at 100°C.

From the nitrogen inlet tube, a nitrogen gas was blown in at 20 L/min.

For 30 minutes just after blowing of a nitrogen gas was started, the foaming height of the liquid was observed.

During this period, the maximum foaming height was 8 mm.

Example 3

In a similar manner to Example 2, 30 mg of a fluorosilicone antifoaming agent ("FA603", trade

name; product of Shin-Etsu Chemical) was added to 60 kg of the good solvent phase and the foaming of the resulting mixture was evaluated using a distillation evaluating unit as shown in FIG. 2.

For 30 minutes just after blowing of a nitrogen gas was started, the foaming height of the liquid was observed.

During this period, the maximum foaming height was 15 mm.

Comparative Example 3

In a similar manner to Example 2, foaming of the good solvent phase not added with an antifoaming agent was evaluated using a distillation evaluating unit as illustrated in FIG. 2.

For 30 minutes just after blowing of a nitrogen gas was started, the foaming height of the liquid was observed.

During this period, the maximum foaming height was 64 mm.

Example 4

In a similar manner and by using a similar unit to Example 2, 150 mg of a fluorosilicone

antifoaming agent ("FQF501", trade name; product of GE Toshiba Silicones) was added to 60 kg of the good solvent phase and the foaming of the resulting mixture was evaluated.

For 30 minutes just after blowing of the nitrogen gas was started, the foaming height of the liquid was observed.

During this period, the maximum foaming height was 7 mm.

Example 5

In a similar manner and by using a similar unit to Example 2, 6 mg of a fluorosilicone antifoaming agent ("FQF501", trade name; product of GE Toshiba Silicones) was added to 60 kg of the good solvent phase and foaming of the resulting mixture was evaluated.

For 30 minutes just after blowing of the nitrogen gas was started, the foaming height of the liquid was observed.

During this period, the maximum foaming height was 23 mm.

Comparative Example 4

In a similar manner and by using a similar unit to Example 2, 150 mg of a silicone antifoaming agent ("KS69", trade name; product of Shi-Etsu Silicones) was added to 60 kg of the good solvent phase and foaming of the resulting mixture was evaluated.

For 30 minutes just after blowing of a nitrogen gas was started, the foaming height of the liquid was observed.

During this period, the maximum foaming height was 140 mm.

Comparative Example 5

In a similar manner and a similar unit to Example 2, 150 mg of a silicone antifoaming agent ("KS603", trade name; product of Shin-Etsu Silicones) was added to 60 kg of the good solvent phase and foaming of the resulting mixture was evaluated.

For 30 minutes just after blowing of a nitrogen gas was started, the foaming height of the liquid was observed.

During this period, the maximum foaming height was 50 mm.

Comparative Example 6

In a similar manner and by using a similar unit to Example 2, 150 mg of a mineral-oil-containing antifoaming agent ("Bronal C-448", trade name; product of Toho Chemical Industry) was added to 60 kg of the good solvent phase and foaming of the resulting mixture was evaluated.

For 30 minutes just after blowing of a nitrogen gas was started, the foaming height of the liquid was observed.

During this term, the maximum foaming height was 70 mm.

Since the production process for polyphenylene ethers according to the invention causes markedly less foaming upon distillation of the good solvent for polyphenylene ethers, recovery efficiency of the good solvent shows a drastic improvement, and the good solvent thus recovered has a high purity compared with the conventional process. It therefore brings about a great improvement in the equipment and energy required for the recovery of the solvent, thus being capable of satisfying the request of this industry.

While the present invention has been described in detail and with reference to specific examples thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

WHAT IS CLAIMED IS:

1. A process for producing a polyphenylene ether, which comprises the steps of:

allowing an oxygen-containing gas to pass through a solution for polymerization containing:

a good solvent for polyphenylene ethers;

a metal salt;

an amine compound; and

a phenol compound,

to carry out oxidative polymerization of the phenol compound;

mixing the polymerized solution with an aqueous solution of a chelating agent to terminate the polymerization;

separating and removing the metal salt, chelating agent and water from the resulting mixture to give a polyphenylene ether solution;

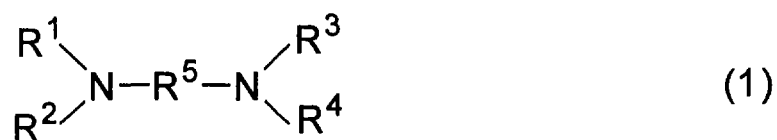
adding a poor solvent for polyphenylene ethers to the polyphenylene ether solution to precipitate polyphenylene ether particles;

filtering the resulting solution to collect the polyphenylene ether particles; and

recovering the good solvent by distilling the filtrate,

wherein said recovery of the good solvent is carried out using at least one antifoaming agent selected from fluorosilicone compound based antifoaming agents.

2. The production process of Claim 1, wherein said good solvent comprises at least one solvent selected from benzene, toluene and xylene; said poor solvent comprises at least one solvent selected from methanol, ethanol, isopropanol, n-butanol, acetone and methyl ethyl ketone; said metal salt comprises at least one metal salt selected from copper compounds and manganese compounds; and said amine compound comprises at least one amine compound selected from diamine compounds represented by the following Formula (1):



(wherein R^1 , R^2 , R^3 and R^4 each independently represents a hydrogen atom or a linear or branched C_{1-6} alkyl group, with the proviso that R^1 , R^2 , R^3 and R^4 do not represent a hydrogen atom at the same time, and R^5 represents a linear or methyl-branched

C₂₋₅ alkylene group), tertiary monoamine compounds and secondary monoamine compounds.

3. The production process of Claim 1 or 2, wherein after the polymerization is terminated by mixing with the aqueous solution of a chelating agent, said mixture is kept at 40 to 120°C until a polymerization by-product, diphenoquinone disappears, followed by separation of a catalyst formed from the metal salt and the amine compound.

4. The production process of any one of Claims 1 to 3, wherein said recovery of the good solvent is carried out by mixing said filtrate with water to separate into a good solvent phase containing said good solvent and an aqueous phase containing said poor solvent and water, fractionating these phases, and distilling said good solvent phase.