

Method for Preparing Amino-Terminated Polyether

Field of the Invention

The present invention pertains to macromolecular material field, and relates to a
5 method for preparing amino-terminated polyether.

Background of the Invention

Amino-terminated polyether is a sort of polymers with flexible polyether skeleton
and terminated with amino, most of which are obtained from relevant polyether glycols
10 through chemical treatment of terminal hydroxyl. Amino-terminated polyether can be
categorized into aromatic polyether and aliphatic polyether, depending on the structure
of hydrocarbyl bonded to the terminal amino. At present, amino-terminated polyether
is mainly used as curing agent of epoxy resin, and a raw material for adhesive,
polyurethane, and spray polyurea elastomer (SPUA), and is widely applied in corrosion
15 protection, pipeline, building, ship, water conservancy, transportation, machinery,
mining industries and wearing field. Up to now, there are mainly three methods for
synthesizing amino-terminated polyether, i.e., catalytic reductive amination method,
leaving group method, and cyanogen alkylation method.

The catalytic reductive amination method deals with the terminal hydroxyl of
20 polyether glycol, and replaces the terminal hydroxyl with amino by ammonolysis. The
catalytic reductive amination method should be performed at high temperature and high
pressure, the equipment investment and operating cost is high, and the catalyst
preparation procedure is complex. A high pressure reduction amination method is
mainly used in industrial production in foreign countries.

The leaving group method mainly comprises phosgene method, sulfonyl chloride method, and halogenation method, etc. A drawback of amino-terminated polyether synthesized by leaving group method is that the raw material can not be available easily and the pollution to the environment is severe; especially, there are many by-products during reaction. In the post-treatment of the product, a large amount of alkali is required to neutralize the acid generated in the reaction, and a great deal of inorganic salts will be generated and hard to separate.

The cyanogen alkylation method deals with the active hydrogen in the terminal hydroxyl of polyether glycol, and terminates by means of the reaction between a compound containing groups of -NCO or -CN and the active hydrogen in terminal hydroxyl of polyether glycol, and then obtains amino-terminated polyether through appropriate treatment. The method has a simple process route, but there are many side reactions in the process of reaction between polyether glycol and acrylonitrile; in addition, acrylonitrile tends to self-polymerize, and thereby has stringent requirement for the reaction conditions. Therefore, cyanogen alkylation method is difficult to operate in actual application.

Hereinafter some references involving synthesis of amino-terminated polyether will be described.

CN1546550A disclosed a method for preparing polyetheramine by amination of tri-functional polyether with a molecular mass of 5,000 or bi-functional polyether with a molecular mass of 2,000 in the presence of hydrogen. The catalyst used in the method is a Raney catalyst, wherein metallic nickel accounts for 60-80 wt%, metallic aluminum accounts for 10-35 wt%, and metallic chromium accounts for 2-10 wt%.

CN101982482A disclosed a method for preparing polyetheramine by non-crystalline alloy catalyst. The non-crystalline alloy catalyst used in the method mainly comprises Ni in a content of 40-50%, Al in a content of 40-50%, and catalyst promoter element M no more than 10% by mass, wherein M is one or more selected
5 from Mo, La, Cr, and Mn.

CN101001902A disclosed a polyetheramine and a method for preparing the same. In this method, a chlorine-terminated adduct is produced by first reacting an oligomer of hydroxyl compound (with a molecular mass of no less than 92) with epichlorohydrin, and then the polyetheramine is obtained by reacting the resulted chlorine-terminated
10 adduct with oligomer of aliphatic amine.

CN101522607A disclosed a method for preparing polyetheramine with a formula of $R_2(NR_1R_3)_n$, wherein n is an integer in a range of 1-20, R_1 is an organic group having 2-600 oxy-alkylene groups, R_1 and R_3 can be identical or different, representing a hydrogen atom or an organic group having 1-400 carbon atoms. The catalyst used in
15 the method is a metallic catalyst comprising Co in a content of 80wt%, or a Raney catalyst comprising 80wt% of Co or Al and less than 5wt% of Cu.

CN101921392A disclosed a method for preparing polyetheramine, in which, polyether with different molecular mass is polymerized from ethylene oxide, propylene oxide, or mixture of them; next, polyether nitrile is obtained by reacting the polyethers
20 with acrylic nitrile; then, polyetheramine is obtained by catalytic hydrogenation.

US4618717 disclosed a method for preparing primary amine from oxyethylene glycol monoalkyl ether. The catalyst used in the method comprises 50-90wt% of Ni, 10-15wt% of Cu, and 0.5-5wt% of an oxides selected from the group consisting of

chromium oxide, iron oxide, titanium oxide, zirconium oxide, thorium oxide, magnesium oxide, manganese oxide, and zinc oxide.

US5352835 disclosed a method for preparing primary amine by reacting polyoxyalkylene alcohol or polyol having a molecular mass of 230-5,000 and ammonia
5 in the presence of hydrogen. The catalyst used in the method is a supported catalyst, comprising γ -alumina as support, and 15-30wt% of Ni, 3-20wt% of Cu and optionally 0.5~1wt% Mo supported on the support, wherein the total pore volume of the γ -alumina measured by mercury intrusion is 0.70-1.2cc/g, and the pore diameter of the γ -alumina measured by nitrogen desorption method is 70~110Å; the total active metals supported
10 on the support account for 10-40wt% of the catalyst, and the γ -alumina accounts for at least 50wt% of the catalyst.

US4766245 disclosed a method for preparing amino-terminated polyether, comprising contact hydroxyl-terminated polyether having a molecular mass of no less than 500 with hydrogen and ammonia in the presence of Raney's nickel/aluminum
15 catalyst in the condition of free of water. The catalyst comprises 60-75wt% of Ni and 40-25wt% of metallic aluminum. The reaction is performed at a temperature of 235~250°C and a pressure of 140-190kg/cm³.

US5003107 disclosed a method for preparing poly(oxytetramethylene) diamine by reducing ammoniation reaction of poly(oxytetramethylene) glycol in the presence of
20 hydrogen and ammonia. The catalyst used in the method mainly comprises Ni, Cu, Cr, and Mo contained in an oxygen-free support, wherein, the content of Ni is 70-75wt%, the content of Cu is 20-25wt%, the content of Cr is 0.5-5wt%, and the content of Mo is 1-5wt%. The reaction is performed at a temperature of 150~220°C and a pressure of 100~10,000psig the ratio between ammonia and polyether alcohol is 10-150:1, and the

ratio between hydrogen and polyether alcohol is 0.5-80:1; the resultant mixture from the reaction is separated by fractionation. Polytetrahydrofuran having a molecular mass of 1000 or 2000 is aminated in a continuous tubular reactor, the conversion can be 91-96%; however, polytetrahydrofuran having a molecular mass of 2000 is aminated in a batch
5 reactor, the conversion is only 76%.

US0139289 disclosed a method for preparing amine from alcohol, aldehyde, or ketone. The catalyst used in the method is composed of Ni, Cu, and Sn.

US3236895 disclosed a method for preparing polyetheramine by ammonolysis of polyether glycol in the presence of Raney nickel catalyst in anhydrous ethanol or
10 cyclohexane at a temperature of 235-255°C and a pressure of 140-170kg/cm³, and the conversion of polyether glycol is 40-70%.

US3654370 disclosed a method for catalytic amination of polyether glycol having a molecular mass of 1,000 and polyether triol having a molecular mass of 1,500 in a continuous tubular reactor with cyclohexane as the solvent. The catalyst used in the
15 method is prepared with co-precipitation method, and comprises 75wt% of Ni, 23wt% of Cu, and 2wt% of Cr. The reaction is conducted at a temperature of 235-246°C and a pressure of 210kg/cm³.

DE1643426 disclosed a method for preparing polyoxyalkylene amine from the corresponding alcohol in the presence of Ni-Cu-Cr catalyst. The catalyst used in the
20 method comprises 60-85mol% of Ni, 14-37mol% of Cu, and 1-5mol% of Cr.

DE3608716 disclosed a method for preparing polyoxyalkylene amine from the corresponding alcohol in the presence of Ni-Al-Mo catalyst. The catalyst used in the method comprises 0.2-5wt% of Mo and 0-40wt% of Al.

DE4428004 disclosed a method for preparing amine from the corresponding alcohol. Calculated by oxide, the catalyst used in the method comprises 20-85% of Zr, 1-30% of Cu, 30-70% of Ni, 0.1-5% of Mo, and 0-10% of Al or Mn.

DE1953263 disclosed a method for preparing amine from the corresponding alcohol.
5 The catalyst used in the method comprises 70-95% of Co and Ni, 5-30% of Cu, wherein, the weight ratio of Co and Ni is from 4:1 to 1:4.

DE10211101 disclosed a method for preparing amine from alcohol or aldehyde. The catalyst used in the method is composed of Ni, Cu, and Sn; calculated by oxide, the content of Zr is 22-40%, the content of Cu is 1-30%, the content of Ni is 15-50%, and
10 the content of Co is 15-50%.

Summary of the Invention

The object of the present invention is to provide a method for preparing amino-terminated polyether by catalytic reductive amination method.

15 The present invention provides a method for preparing amino-terminated polyether by catalytic reductive amination of polyether glycol in the presence of hydrogen, at least one aminating agent, and a catalyst, the method comprises the following steps:

in the presence of a Raney catalyst, contacting polyether glycol having a number-average molecular weight of no less than 100 with at least one aminating agent
20 and hydrogen in a reactor to proceed catalytic reductive amination reaction; and
cooling down obtained reaction mixture to 25-60°C, removing unreacted gas, discharging the reaction mixture, removing water, residual aminating agent, and other low-boiling by-products from the reaction mixture by reduced pressure distillation, so as to obtain amino-terminated polyether;

wherein, the amount of the Raney nickel catalyst is 2-15% of the amount of the polyether glycol (preferably 2-10%, more preferably 2-5%) by weight; the amount of the aminating agent is 1.5-20 times of the amount of hydroxyl groups in the polyether glycol by mole, and the amount of hydrogen is 0.4-15 times of the amount of hydroxyl groups in the polyether glycol by mole; the catalytic reductive amination reaction is conducted at a temperature is 120-250°C and a pressure of 8-35MPa (preferably 8-20MPa) for a period duration of 1.5-8h;

the Raney nickel catalyst comprises Ni, Al, and metal M. based on the total weight of the catalyst and calculated by element, the content of Ni is in a range of 80-95wt%, the content of Al is in a range of 5-20wt%, and the content of metal M is in a range of 0.5-5wt%; and the metal M is one, two, or three selected from Cr, Fe, Cu, and Zn.

In order to further improve the conversion of raw material, the metal M preferably comprises Zn and one or two selected from Cr, Fe, and Cu. More preferably, based on the total weight of the metal M and calculated by element, the content of Zn is in a range of 30-70wt%, and the total content of Cr, Fe and Cu is in a range of 30-70wt%. Still more preferably, based on the total weight of the metal M and calculated by element, the content of Zn is in a range of 50-70wt%, and the total content of Cr, Fe and Cu is in a range of 30-50wt%.

Usually, the Raney nickel catalyst in the present invention may be prepared by the method comprising the following steps:

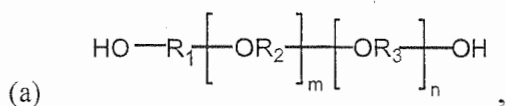
- a) adding ternary, quaternary, or quinary alloy powder comprising different components into water solution of sodium hydroxide under vigorous agitation and stirring at a temperature of 45-100°C for a period duration of 0.5-5h, to dissolve the alloy powder, then reacting at a temperature of 50-100°C for a period duration

of 0.5-5h to activate, wherein the concentration of sodium hydroxide is 10-40wt%,
the amount of sodium hydroxide is 1-3 times of the weight of the alloy powder;

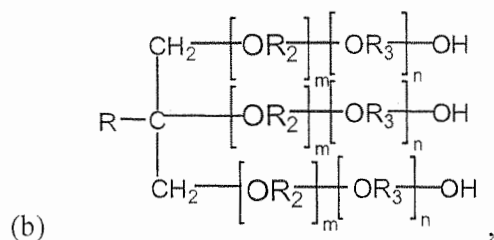
- b) standing the mixture obtained by step (1) to separate the supernatant white
flocculate, washing black precipitate with warm water for several times to
neutrality, and then washing with anhydrous ethanol for 2-5 times to obtain Raney
nickel catalyst; next, storing the Raney nickel catalyst in anhydrous ethanol.

The alloy powder comprises Ni, Al, and metal M, wherein, the metal M is one, two,
or three selected from Cr, Fe, Cu, and Zn. Preferably, the metal M comprises Zn and
one or two selected from Cr, Fe, and Cu. The composition of the alloy powder can be
determined as appropriate according to the composition of the Raney nickel catalyst as
mentioned above. A person skilled in the art can select and control the composition of
the alloy powder with the common knowledge in the art, to ensure the finally obtained
Raney nickel catalyst comply with the composition mentioned above.

In the method according to the present invention, the polyether glycol has the
following general structural formula (a) or (b):

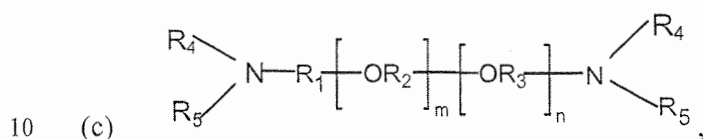


in formula (a), R₁, R₂, and R₃ are independently selected from linear or branched
divalent aliphatic groups with 2-4 carbon atoms (e.g., linear or branched alkylene
groups with 2-4 carbon atoms); m is 0-115, preferably 2-90; n is 0-115, preferably 2-90;
and the sum of m and n is 1-115, preferably 2-90;

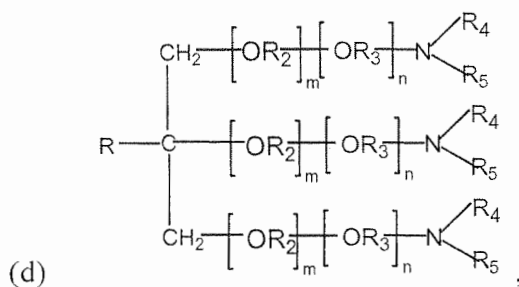


in formula (b), R is selected from hydrogen and linear or branched aliphatic groups having 1-6 carbon atoms (e.g., linear or branched alkyl groups having 1-6 carbon atoms); R₂ and R₃ are independently selected from linear or branched divalent aliphatic groups having 2-4 carbon atoms (e.g., linear or branched alkylene groups having 2-4 carbon atoms); m is 0-40, preferably 1-30; n is 0-40, preferably 1-30; and the sum of m and n is 1-115, preferably 2-90.

In the method according to the present invention, the obtained amino-terminated polyether has the following general structural formula (c) or (d):



in formula (c), R₁, R₂, and R₃ are independently selected from linear or branched divalent aliphatic groups with 2-4 carbon atoms (e.g., linear or branched alkylene groups with 2-4 carbon atoms); R₄ and R₅ are identical or different, and are independently selected from hydrogen and linear or branched aliphatic groups having 1-6 carbon atoms (e.g., linear or branched alkyl groups having 1-6 carbon atoms); m is 0-115, preferably 2-90; n is 0-115, preferably 2-90; and the sum of m and n is 1-115, preferably 2-90;



in formula (d), R is selected from hydrogen and linear or branched aliphatic groups having 1-6 carbon atoms (e.g., linear or branched alkyl groups having 1-6 carbon atoms); R₂ and R₃ are independently selected from linear or branched divalent aliphatic groups having 2-4 carbon atoms (e.g., linear or branched alkylene groups having 2-4 carbon atoms); R₄ and R₅ are identical or different, and are independently selected from hydrogen and linear or branched aliphatic groups having 1-6 carbon atoms (e.g., linear or branched alkyl groups having 1-6 carbon atoms); m is 0-40, preferably 1-30; n is 0-40, preferably 1-30; and the sum of m and n is 1-115, preferably 2-90.

In the method according to the present invention, the aminating agent can be any ordinary aminating agent in the art, for example, the aminating agent can be selected from ammonia (such as ammonia gas and/or ammonia liquor), aliphatic amine, and alicyclic amine. Preferably, the aminating agent is selected from ammonia gas, aliphatic amine (such as aliphatic amine having 1-10 carbon atoms) and alicyclic amine (such as alicyclic amine having 6-12 carbon atoms). More preferably, the aminating agent is selected from methylamine, dimethylamine, ethylamine, diethylamine, *n*-propylamine, *di-n*-propylamine, isopropylamine, diisopropylamine, hexylamine (such as *n*-hexylamine), and cyclohexylamine.

In the method according to the present invention, the catalytic reductive amination reaction can be conducted in presence of a solvent. The solvent can be the solvent used in the art. The catalytic reductive amination reaction can also conducted in a

condition of absent from a solvent. In view of simplicity, catalytic reductive amination reaction is preferably conducted in a condition of absent from a solvent.

In the method according to the present invention, in actual operation, the amount of hydrogen added to the reactor can be controlled by regulating the pressure of hydrogen
5 filling into the reactor. Usually, the partial pressure of hydrogen may be in the range of 1.5-8MPa.

In the method according to the present invention, the temperature for the reduced pressure distillation may be 100-120°C, and the vacuum degree may be in a range of from -0.08MPa to -0.1MPa.

10 In the method according to the present invention, the reactor can be any common reactor in the art. Preferably, the reactor is a stirred reactor.

In the method according to the present invention, the Raney nickel catalyst and the aminating agent can be recycled and reused after treatment; furthermore, the method according to the present invention achieve advantages of high product selectivity, high
15 conversion of raw material, easy post-treatment, and lower environmental pollution.

Detailed Description of the Embodiments

Hereinafter the method according to the present invention will be described in detail in combination with the examples.

20 In the following examples and comparative examples, the number-average molecular weight of the polymer is measured by an ALLIANCE 2690 gel permeation chromatograph purchased from WATERS (USA) CO. equipped with a PLgel Mixed-C gel chromatographic column procured from Agilent Co. at a temperature 25°C, wherein

tetrahydrofuran is used as the mobile phase, and narrowly distributed polystyrene is used as the standard sample.

In the following examples and comparative examples, the hydroxyl value of hydroxyl-terminated polyether is measured according to the method described in Chinese Standard GB12008.3-89, the total amine value, primary amine content, secondary amine content, and tertiary amine content in amino-terminated polyether are measured according to the method described in ASTM2074.

In the following examples and comparative examples, the composition of the prepared Raney nickel catalyst is measured with inductively coupled plasma atomic emission spectroscopy.

Preparation Example 1

A water solution of NaOH with a concentration of 40wt% is prepared by dissolving NaOH with a weight equal to 3 times of the weight of Ni-Al-Fe-Cr alloy powder in water. The water solution of NaOH is added into a stainless steel three-neck flask equipped with a thermometer, and is cool to 50°C. With vigorous agitation, Ni-Al-Fe-Cr alloy powder (based on the total weight of the alloy powder and measured by element, the content of Ni is 64wt%, the content of Al is 31wt%, the content of Fe is 2.5wt%, and the content of Cr is 2.5wt%) is added into the three-neck flask in batches (add 2-4g in each batch) within 25min. By regulating the addition rate of the alloy powder, the temperature of solution in the three-neck flask is kept at approx. 50°C. After addition, the solution in the three-neck flask is stirred at approx. 80°C for approx. 60min. After the hydrogen gas is released completely, the supernatant white flocculate is separated, and the black precipitate is transferred to a beaker, and is wash with water, till the washing liquid is neutral against litmus solution, then wash 2~3 times with

95wt% ethanol and anhydrous ethanol to obtain Raney nickel catalyst, the obtained catalyst is stored in a plugged container with anhydrous ethanol. By analyzing, it is determined that in the prepared catalyst, the content of Ni is 84.8wt%, the content of Al is 10.9wt%, the content of Fe is 2.19wt%, and the content of Cr is 2.11wt%.

5

Preparation Example 2

A water solution of NaOH with a concentration of 30wt% is prepared by dissolving NaOH with a weight equal to 3 times of the weight of Ni-Al-Cr-Cu alloy powder in water. The water solution of NaOH is added into a stainless steel three-neck flask
10 equipped with a thermometer, and is cool to 50°C. With vigorous agitation, Ni-Al-Cr-Cu alloy powder (based on the total weight of the alloy powder and measured by element, the content of Ni is 71wt%, the content of Al is 26wt%, the content of Cr is 1wt%, and the content of Cu is 2wt%) is added into the three-neck flask in batches (add 2-4g in each batch) within 25min. By regulating the addition rate of the alloy powder,
15 the temperature of solution in the three-neck flask is kept at approx. 50°C. After addition, the solution in the three-neck flask is stirred at approx. 90°C for approx. 80min. After the hydrogen gas is released completely, the supernatant white flocculate is separated, and the black precipitate is transferred to a beaker, and is wash with water, till the washing liquid is neutral against litmus solution, then wash 2~3 times with 95wt%
20 ethanol and anhydrous ethanol to obtain Raney nickel catalyst, the obtained catalyst is stored in a plugged container with anhydrous ethanol. By analyzing, it is determined that in the prepared catalyst, the content of Ni is 89.9wt%, the content of Al is 7.69wt%, the content of Cr is 0.61wt%, and the content of Cu is 1.8wt%.

Preparation Example 3

A water solution of NaOH with a concentration of 35wt% is prepared by dissolving NaOH with a weight equal to 2.5 times of the weight of Ni-Al-Cu-Zn alloy powder in water. The water solution of NaOH is added into a stainless steel three-neck flask equipped with a thermometer, and is cool to 50°C. With vigorous agitation, Ni-Al-Cu-Zn alloy powder (based on the total weight of the alloy powder and measured by element, the content of Ni is 69wt%, the content of Al is 27wt%, the content of Cu is 1.5wt%, and the content of Zn is 2.5wt%) is added into the three-neck flask in batches (add 2-4g in each batch) within 25min. By regulating the addition rate of the alloy powder, the temperature of solution in the three-neck flask is kept at approx. 50°C. After addition, the solution in the three-neck flask is stirred at approx. 85°C for approx. 90min. After the hydrogen gas is released completely, the supernatant white flocculate is separated, and the black precipitate is transferred to a beaker, and is wash with water, till the washing liquid is neutral against litmus solution, then wash 2-3 times with 95wt% ethanol and anhydrous ethanol to obtain Raney nickel catalyst, the obtained catalyst is stored in a plugged container with anhydrous ethanol. By analyzing, it is determined that in the prepared catalyst, the content of Ni is 86.4wt%, the content of Al is 10.2wt%, the content of Cu is 1.2wt%, and the content of Zn is 2.2wt%.

Preparation Example 4

A water solution of NaOH with a concentration of 40wt% is prepared by dissolving NaOH with a weight equal to 2 times of the weight of Ni-Al-Cu-Fe alloy powder in water. The water solution of NaOH is added into a stainless steel three-neck flask equipped with a thermometer, and is cool to 50°C. With vigorous agitation,

Ni-Al-Cu-Fe alloy powder (based on the total weight of the alloy powder and measured by element, the content of Ni is 65wt%, the content of Al is 29wt%, the content of Cu is 3wt%, and the content of Fe is 3wt%) is added into the three-neck flask in batches (add 2-4g in each batch) within 25min. By regulating the addition rate of the alloy powder, the temperature of solution in the three-neck flask is kept at approx. 50°C. After addition, the solution in the three-neck flask is stirred at approx. 90°C for approx. 60min. After the hydrogen gas is released completely, the supernatant white flocculate is separated, and the black precipitate is transferred to a beaker, and is wash with water, till the washing liquid is neutral against litmus solution, then wash 2~3 times with 95wt% ethanol and anhydrous ethanol to obtain Raney nickel catalyst, the obtained catalyst is stored in a plugged container with anhydrous ethanol. By analyzing, it is determined that in the prepared catalyst, the content of Ni is 79.5wt%, the content of Al is 15.3wt%, the content of Cu is 2.48wt%, and the content of Fe is 2.72wt%.

Preparation Example 5

A water solution of NaOH with a concentration of 25wt% is prepared by dissolving NaOH with a weight equal to 4 times of the weight of Ni-Al-Cu alloy powder in water. The water solution of NaOH is added into a stainless steel three-neck flask equipped with a thermometer, and is cool to 50°C. With vigorous agitation, Ni-Al-Cu alloy powder (based on the total weight of the alloy powder and measured by element, the content of Ni is 78wt%, the content of Al is 18.5wt%, the content of Cu is 3.5wt%) is added into the three-neck flask in batches (add 2-4g in each batch) within 25min. By regulating the addition rate of the alloy powder, the temperature of solution in the three-neck flask is kept at approx. 50°C. After addition, the solution in the three-neck

flask is stirred at approx. 90°C for approx. 120min. After the hydrogen gas is released completely, the supernatant white flocculate is separated, and the black precipitate is transferred to a beaker, and is wash with water, till the washing liquid is neutral against litmus solution, then wash 2-3 times with 95wt% ethanol and anhydrous ethanol to
5 obtain Raney nickel catalyst, the obtained catalyst is stored in a plugged container with anhydrous ethanol. By analyzing, it is determined that in the prepared catalyst, the content of Ni is 87.1wt%, the content of Al is 9.6wt%, the content of Cu is 3.3wt%.

Preparation Example 6

10 A water solution of NaOH with a concentration of 30wt% is prepared by dissolving NaOH with a weight equal to 2 times of the weight of Ni-Al-Cr alloy powder in water. The water solution of NaOH is added into a stainless steel three-neck flask equipped with a thermometer, and is cool to 50°C. With vigorous agitation, Ni-Al-Cr alloy powder (based on the total weight of the alloy powder and measured by element, the
15 content of Ni is 77wt%, the content of Al is 20.5wt%, the content of Cr is 2.5wt%) is added into the three-neck flask in batches (add 2-4g in each batch) within 25min. By regulating the addition rate of the alloy powder, the temperature of solution in the three-neck flask is kept at approx. 50°C. After addition, the solution in the three-neck flask is stirred at approx. 80°C for approx. 100min. After the hydrogen gas is released
20 completely, the supernatant white flocculate is separated, and the black precipitate is transferred to a beaker, and is wash with water, till the washing liquid is neutral against litmus solution, then wash 2-3 times with 95wt% ethanol and anhydrous ethanol to obtain Raney nickel catalyst, the obtained catalyst is stored in a plugged container with

anhydrous ethanol. By analyzing, it is determined that in the prepared catalyst, the content of Ni is 90.8wt%, the content of Al is 8.01wt%, the content of Cr is 1.19wt%.

Preparation Example 7

5 A water solution of NaOH with a concentration of 35wt% is prepared by dissolving NaOH with a weight equal to 2.5 times of the weight of Ni-Al-Fe-Zn alloy powder in water. The water solution of NaOH is added into a stainless steel three-neck flask equipped with a thermometer, and is cool to 50°C. With vigorous agitation, Ni-Al-Fe-Zn alloy powder (based on the total weight of the alloy powder and measured
10 by element, the content of Ni is 75wt%, the content of Al is 20wt%, the content of Fe is 2.5wt%, the content of Zn is 2.5wt%) is added into the three-neck flask in batches (add 2-4g in each batch) within 25min. By regulating the addition rate of the alloy powder, the temperature of solution in the three-neck flask is kept at approx. 50°C. After addition, the solution in the three-neck flask is stirred at approx. 80°C for approx.
15 100min. After the hydrogen gas is released completely, the supernatant white flocculate is separated, and the black precipitate is transferred to a beaker, and is wash with water, till the washing liquid is neutral against litmus solution, then wash 2-3 times with 95wt% ethanol and anhydrous ethanol to obtain Raney nickel catalyst, the obtained catalyst is stored in a plugged container with anhydrous ethanol. By analyzing, it is
20 determined that in the prepared catalyst, the content of Ni is 87.5wt%, the content of Al is 8.2wt%, the content of Fe is 2.1wt%, the content of Zn is 2.2wt%.

Comparative Preparation Example 1

A water solution of NaOH with a concentration of 20wt% is prepared by dissolving NaOH with a weight equal to 4 times of the weight of Ni-Al alloy powder in water. The water solution of NaOH is added into a stainless steel three-neck flask equipped with a thermometer, and is cool to 50°C. With vigorous agitation, Ni-Al alloy powder (based on the total weight of the alloy powder and measured by element, the content of Ni is 65wt%, the content of Al is 35wt%) is added into the three-neck flask in batches (add 2-4g in each batch) within 25min. By regulating the addition rate of the alloy powder, the temperature of solution in the three-neck flask is kept at approx. 50°C. After the addition, the solution in the three-neck flask is stirred at approx. 80°C for approx. 60min. After the hydrogen gas is released completely, the supernatant white flocculate is separated, and the black precipitate is transferred to a beaker, and is wash with water, till the washing liquid is neutral against litmus solution, then wash 2-3 times with 95wt% ethanol and anhydrous ethanol to obtain Raney nickel catalyst, the obtained catalyst is stored in a plugged container with anhydrous ethanol. By analyzing, it is determined that in the prepared catalyst, the content of Ni is 89.5wt%, the content of Al is 10.5wt%.

Example 1

100g bi-functional (i.e., there are two hydroxyl group in one molecule of polyoxypropylene ether) hydroxyl-terminated polyoxypropylene ether with number-average molecular weight of 230.8 (procured from Polyether Department of Tianjin Petrochemical) and 5g Raney nickel catalyst prepared in preparation example 1 are added into a 0.5L high pressure reactor. The high pressure reactor is purged with nitrogen and hydrogen with a pressure of 0.4MPa for 2-3 times. Approx. 50L

ammonia gas (under standard condition) is added into the reactor with agitation, and hydrogen is filled into the reactor by regulating the outlet pressure of steel cylinder of hydrogen to 2.5MPa (the mole ratio of hydrogen to hydroxyl groups in hydroxyl-terminated polyoxypropylene ether is 1:2). The reactor is heated to a
5 temperature at 200°C and maintained at the temperature for 4h, and the maximum pressure in the reactor is controlled at 15.5MPa. Then, the reactor is cooled to 50°C. The reactor is exhausted slowly and the gas is absorbed with water, and then the reaction mixture is discharged.

The reaction mixture is filtered in hot state to separate the catalyst and liquid
10 mixture containing the product, the liquid mixture is transferred to a three-neck flask to conduct reduced pressure distillation at 105°C and a vacuum degree of -0.08MPa for 1h, so as to obtain the product of amino-terminated polyether. By analyzing, it is determined that the total amine value in the obtained product is 7.25mmol/g, the conversion of polyether alcohol is 85.97wt%, and the selectivity of primary amine is
15 97.97wt%.

Comparative Example 1

Amino-terminated polyether is prepared by the method same as the method described in example 1, the difference is that the Raney nickel catalyst is prepared in the
20 comparative preparation example 1. By analyzing, it is determined that the total amine value in the obtained product is 4.83mmol/g, the conversion of polyether alcohol is 58.4wt%, and the selectivity of primary amine is 98.9wt%.

Example 2

100g bi-functional hydroxyl-terminated polyoxypropylene ether with number-average molecular weight of 230.8 (procured from Polyether Department of Tianjin Petrochemical) and 5g Raney nickel catalyst prepared in preparation example 1 are added into a 0.5L high pressure reactor. The high pressure reactor is purged with nitrogen and hydrogen with a pressure of 0.4MPa for 2-3 times. Approx. 58L dimethylamine (under standard condition) is added into the reactor with agitation, and hydrogen is filled into the reactor by regulating the outlet pressure of steel cylinder of hydrogen to 4.0MPa (the mole ratio of hydrogen to hydroxyl groups in hydroxyl-terminated polyoxypropylene ether is 1:1.3). The reactor is heated to a temperature at 210°C and maintained at the temperature for 4h, and the maximum pressure in the reactor is controlled at 13.5MPa. Then, the reactor is cooled to 50°C. The reactor is exhausted slowly and the gas is absorbed with water, and then the reaction mixture is discharged.

The reaction mixture is filtered in hot state to separate the catalyst and liquid mixture containing the product, the liquid mixture is transferred to a three-neck flask to conduct reduced pressure distillation at 105°C and a vacuum degree of -0.08MPa for 2h, so as to obtain the product of amino-terminated polyether. By analyzing, it is determined that the total amine value in the obtained product is 7.58mmol/g, the conversion of polyether alcohol is 87.79wt%, and the selectivity of tertiary amine is 96.89wt%.

Comparative Example 2

Amino-terminated polyether is prepared by the method same as the method described in example 2, the difference is that the Raney nickel catalyst is prepared in the

comparative preparation example 1. By analyzing, it is determined that the total amine value in the obtained product is 6.58mmol/g, the conversion of polyether alcohol is 77.41wt%, and the selectivity of tertiary amine is 96.89wt%.

5 Example 3

100g bi-functional hydroxyl-terminated polyoxypropylene ether with number-average molecular weight of 230.8 (procured from Polyether Department of Tianjin Petrochemical) and 5g Raney nickel catalyst prepared in preparation example 2 are added into a 0.5L high pressure reactor. The high pressure reactor is purged with
10 nitrogen and hydrogen with a pressure of 0.4MPa for 2-3 times. Approx. 50L dimethylamine (under standard condition) is added into the reactor with agitation, and hydrogen is filled into the reactor by regulating the outlet pressure of steel cylinder of hydrogen to 4.0MPa (the mole ratio of hydrogen to hydroxyl groups in hydroxyl-terminated polyoxypropylene ether is 1:1.3). The reactor is heated to a
15 temperature at 220°C and maintained at the temperature for 4h, and the maximum pressure in the reactor is controlled at 12.3MPa. Then, the reactor is cooled to 50°C, the reactor is exhausted slowly and the gas is absorbed with water, and then the reaction mixture is discharged.

The reaction mixture is filtered in hot state to separate the catalyst and liquid
20 mixture containing the product, the liquid mixture is transferred to a three-neck flask to conduct reduced pressure distillation at 120°C and a vacuum degree of -0.09MPa for 1h, so as to obtain the product of amino-terminated polyether. By analyzing, it is determined that the total amine value in the obtained product is 7.32mmol/g, the

conversion of polyether alcohol is 86.12wt%, and the selectivity of tertiary amine is 96.48wt%.

Example 4

5 Amino-terminated polyether is prepared by the method same as the method described in example 3, the difference is that the Raney nickel catalyst is prepared in the comparative preparation example 3. By analyzing, it is determined that the total amine value in the obtained product is 7.41mmol/g, the conversion of polyether alcohol is 98.1wt%, and the selectivity of tertiary amine is 95.21wt%.

10

Example 5

100g bi-functional hydroxyl-terminated polyoxypropylene ether with number-average molecular weight of 983.0 (procured from Polyether Department of Tianjin Petrochemical) and 2g Raney nickel catalyst prepared in preparation example 2
15 are added into a 0.5L high pressure reactor. The high pressure reactor is purged with nitrogen and hydrogen with a pressure of 0.4MPa for 2-3 times. Approx. 30L ammonia gas (under standard condition) is added into the reactor with agitation, and hydrogen is filled into the reactor by regulating the outlet pressure of steel cylinder of hydrogen to 2.5MPa (the mole ratio of hydrogen to hydroxyl groups in
20 hydroxyl-terminated polyoxypropylene ether is 2:1). The reactor is heated to a temperature at 200°C and maintained at the temperature for 4h, and the maximum pressure in the reactor is controlled at 11.8MPa. Then, the reactor is cooled to 60°C. The reactor is exhausted slowly and the gas is absorbed with water, and then the reaction mixture is discharged.

The reaction mixture is filtered in hot state to separate the catalyst and liquid mixture containing the product, the liquid mixture is transferred to a three-neck flask to conduct reduced pressure distillation at 105°C and a vacuum degree of -0.08MPa for 2h, so as to obtain the product of amino-terminated polyether. By analyzing, it is
5 determined that the total amine value in the obtained product is 1.89mmol/g, the conversion of polyether alcohol is 96.2wt%, and the selectivity of primary amine is 98.6wt%.

Comparative Example 3

10 Amino-terminated polyether is prepared by the method same as the method described in example 5, the difference is that the Raney nickel catalyst is prepared in the comparative preparation example 1. By analyzing, it is determined that the total amine value in the obtained product is 1.52mmol/g, the conversion of polyether alcohol is 78.52wt%, and the selectivity of primary amine is 96.4wt%.

Example 6

100g bi-functional hydroxyl-terminated polyoxypropylene ether with number-average molecular weight of 983.0 (procured from Polyether Department of Tianjin Petrochemical) and 2g Raney nickel catalyst prepared in preparation example 3
20 are added into a 0.5L high pressure reactor. The high pressure reactor is purged with nitrogen and hydrogen with a pressure of 0.4MPa for 2-3 times. Approx. 31L dimethylamine (under standard condition) is added into the reactor with agitation, and hydrogen is filled into the reactor by regulating the outlet pressure of steel cylinder of hydrogen to 4.5MPa (the mole ratio of hydrogen to hydroxyl groups in

hydroxyl-terminated polyoxypropylene ether is 3.5:1). The reactor is heated to a temperature at 200°C and maintained at the temperature for 2h, and the maximum pressure in the reactor is controlled at 9.2MPa. Then, the reactor is cooled to 60°C. The reactor is exhausted slowly and the gas is absorbed with water, and then the
5 reaction mixture is discharged.

The reaction mixture is filtered in hot state to separate the catalyst and liquid mixture containing the product, the liquid mixture is transferred to a three-neck flask to conduct reduced pressure distillation at 105°C and a vacuum degree of -0.08MPa for 1h, so as to obtain the product of amino-terminated polyether. By analyzing, it is
10 determined that the total amine value in the obtained product is 1.91mmol/g, the conversion of polyether alcohol is 97.42wt%, and the selectivity of tertiary amine is 97.3wt%.

Example 7

15 100g bi-functional hydroxyl-terminated polyoxypropylene ether with number-average molecular weight of 983.0 (procured from Polyether Department of Tianjin Petrochemical) and 2g Raney nickel catalyst prepared in preparation example 1 are added into a 0.5L high pressure reactor. The high pressure reactor is purged with nitrogen and hydrogen with a pressure of 0.4MPa for 2-3 times. Approx. 35g
20 ethylamine in form of liquid is added into the reactor with agitation, and hydrogen is filled into the reactor by regulating the outlet pressure of steel cylinder of hydrogen to 2.5MPa (the mole ratio of hydrogen to hydroxyl groups in hydroxyl-terminated polyoxypropylene ether is 2:1). The reactor is heated to a temperature at 200°C and maintained at the temperature for 4h, and the maximum pressure in the reactor is

controlled at 10.3MPa. Then, the reactor is cooled to 60°C. The reactor is exhausted slowly and the gas is absorbed with water, and then the reaction mixture is discharged.

The reaction mixture is filtered in hot state to separate the catalyst and liquid mixture containing the product, the liquid mixture is transferred to a three-neck flask to
5 conduct reduced pressure distillation at 105°C and a vacuum degree of -0.08MPa for 1h, so as to obtain the product of amino-terminated polyether. By analyzing, it is determined that the total amine value in the obtained product is 1.71mmol/g, the conversion of polyether alcohol is 86.3wt%, and the selectivity of secondary amine is 98.21wt%.

10

Example 8

Amino-terminated polyether is prepared by the method same as the method described in example 7, the difference is that the Raney nickel catalyst is prepared in the preparation example 2. By analyzing, it is determined that the total amine value in the
15 obtained product is 1.83mmol/g, the conversion of polyether alcohol is 92.1wt%, and the selectivity of secondary amine is 97.68wt%.

Example 9

Amino-terminated polyether is prepared by the method same as the method
20 described in example 7, the difference is that the Raney nickel catalyst is prepared in the preparation example 3. By analyzing, it is determined that the total amine value in the obtained product is 1.98mmol/g, the conversion of polyether alcohol is 100wt%, and the selectivity of secondary amine is 97.24wt%.

Example 10

Amino-terminated polyether is prepared by the method same as the method described in example 7, the difference is that the Raney nickel catalyst is prepared in the preparation example 4. By analyzing, it is determined that the total amine value in the
5 obtained product is 1.91mmol/g, the conversion of polyether alcohol is 95.06wt%, and the selectivity of secondary amine is 96.89wt%.

Example 11

Amino-terminated polyether is prepared by the method same as the method
10 described in example 7, the difference is that the Raney nickel catalyst is prepared in the preparation example 5. By analyzing, it is determined that the total amine value in the obtained product is 1.76mmol/g, the conversion of polyether alcohol is 87.63wt%, and the selectivity of secondary amine is 95.98wt%.

Example 12

Amino-terminated polyether is prepared by the method same as the method described in example 7, the difference is that the Raney nickel catalyst is prepared in the preparation example 6. By analyzing, it is determined that the total amine value in the
15 obtained product is 1.82mmol/g, the conversion of polyether alcohol is 89.24wt%, and
20 the selectivity of secondary amine is 93.28wt%.

Example 13

Amino-terminated polyether is prepared by the method same as the method described in example 7, the difference is that the Raney nickel catalyst is prepared in the

preparation example 7. By analyzing, it is determined that the total amine value in the obtained product is 1.93mmol/g, the conversion of polyether alcohol is 98.6wt%, and the selectivity of secondary amine is 96.65wt%.

5 **Comparative Example 4**

Amino-terminated polyether is prepared by the method same as the method described in example 7, the difference is that the Raney nickel catalyst is prepared in the comparative preparation example 1. By analyzing, it is determined that the total amine value in the obtained product is 1.71mmol/g, the conversion of polyether alcohol
10 is 86.3wt%, and the selectivity of secondary amine is 98.21wt%.

Example 14

100g bi-functional hydroxyl-terminated polyoxypropylene ether with number-average molecular weight of 2000.0 (procured from Polyether Department of
15 Tianjin Petrochemical) and 3.5g Raney nickel catalyst prepared in preparation example 4 are added into a 0.5L high pressure reactor. The high pressure reactor is purged with nitrogen and hydrogen with a pressure of 0.4MPa for 2-3 times. Approx. 20L ammonia gas (under standard condition) is added into the reactor with agitation, and hydrogen is filled into the reactor by regulating the outlet pressure of steel cylinder of
20 hydrogen to 3.0MPa (the mole ratio of hydrogen to hydroxyl groups in hydroxyl-terminated polyoxypropylene ether is 5:1). The reactor is heated to a temperature at 200°C and maintained at the temperature for 3h, and the maximum pressure in the reactor is controlled at 9.5MPa. Then, the reactor is cooled to 60°C.

The reactor is exhausted slowly and the gas is absorbed with water, and then the reaction mixture is discharged.

The reaction mixture is filtered in hot state to separate the catalyst and liquid mixture containing the product, the liquid mixture is transferred to a three-neck flask to
5 conduct reduced pressure distillation at 105°C and a vacuum degree of -0.09MPa for 2h, so as to obtain the product of amino-terminated polyether. By analyzing, it is determined that the total amine value in the obtained product is 0.97mmol/g, the conversion of polyether alcohol is 96.1wt%, and the selectivity of primary amine is 96.32wt%.

10

Comparative Example 5

Amino-terminated polyether is prepared by the method same as the method described in example 14, the difference is that the Raney nickel catalyst is prepared in the comparative preparation example 1. By analyzing, it is determined that the total
15 amine value in the obtained product is 0.72mmol/g, the conversion of polyether alcohol is 73.59wt%, and the selectivity of primary amine is 98.39wt%.

Example 15

100g bi-functional hydroxyl-terminated polyoxypropylene ether with
20 number-average molecular weight of 2000.0 (procured from Polyether Department of Tianjin Petrochemical) and 3.5g Raney nickel catalyst prepared in preparation example 3 are added into a 0.5L high pressure reactor. The high pressure reactor is purged with nitrogen and hydrogen with a pressure of 0.4MPa for 2-3 times. Approx. 20g diethylamine in the form of liquid is added into the reactor with agitation, and hydrogen

is filled into the reactor by regulating the outlet pressure of steel cylinder of hydrogen to 4.5MPa (the mole ratio of hydrogen to hydroxyl groups in hydroxyl-terminated polyoxypropylene ether is 6.7:1). The reactor is heated to a temperature at 200°C and maintained at the temperature for 3h, and the maximum pressure in the reactor is controlled at 11.4MPa. Then, the reactor is cooled to 60°C. The reactor is exhausted slowly and the gas is absorbed with water, and then the reaction mixture is discharged.

The reaction mixture is filtered in hot state to separate the catalyst and liquid mixture containing the product, the liquid mixture is transferred to a three-neck flask to conduct reduced pressure distillation at 105°C and a vacuum degree of -0.09MPa for 2h, so as to obtain the product of amino-terminated polyether. By analyzing, it is determined that the total amine value in the obtained product is 0.989mmol/g, the conversion of polyether alcohol is 100wt%, and the selectivity of tertiary amine is 96.21wt%.

15 **Comparative Example 6**

Amino-terminated polyether is prepared by the method same as the method described in example 15, the difference is that the Raney nickel catalyst is prepared in the comparative preparation example 1. By analyzing, it is determined that the total amine value in the obtained product is 0.9mmol/g, the conversion of polyether alcohol is 90.8wt%, and the selectivity of tertiary amine is 96.23wt%.

Example 16

100g bi-functional hydroxyl-terminated polyoxypropylene ether with number-average molecular weight of 2000.0 (procured from Polyether Department of

Tianjin Petrochemical) and 3.5g Raney nickel catalyst prepared in preparation example 2 are added into a 0.5L high pressure reactor. The high pressure reactor is purged with nitrogen and hydrogen with a pressure of 0.4MPa for 2-3 times. Approx. 28L dimethylamine (under standard condition) is added into the reactor with agitation, and hydrogen is filled into the reactor by regulating the outlet pressure of steel cylinder of hydrogen to 4.5MPa (the mole ratio of hydrogen to hydroxyl groups in hydroxyl-terminated polyoxypropylene ether is 6.7:1). The reactor is heated to a temperature at 200°C and maintained at the temperature for 3h, and the maximum pressure in the reactor is controlled at 11.4MPa. After completion, the reactor is cooled to 60°C, the reactor is exhausted slowly and the gas is absorbed with water, and then the reaction mixture is discharged.

The reaction mixture is filtered in hot state to separate the catalyst and liquid mixture containing the product, the liquid mixture is transferred to a three-neck flask to conduct reduced pressure distillation at 105°C and a vacuum degree of -0.09MPa for 2h, so as to obtain the product of amino-terminated polyether. By analyzing, it is determined that the total amine value in the obtained product is 0.96mmol/g, the conversion of polyether alcohol is 95.2wt%, and the selectivity of tertiary amine is 97.23wt%.

20 **Example 17**

100g tri-functional (i.e., there are three hydroxyl group in one molecule of polyoxypropylene ether) hydroxyl-terminated polyoxypropylene ether with number-average molecular weight of 5000.0 (procured from Polyether Department of Tianjin Petrochemical) and 5g Raney nickel catalyst prepared in preparation example 3

are added into a 0.5L high pressure reactor. The high pressure reactor is purged with nitrogen and hydrogen with a pressure of 0.4MPa for 2-3 times. Approx. 10.2L ammonia gas (under standard condition) is added into the reactor with agitation, and hydrogen is filled into the reactor by regulating the outlet pressure of steel cylinder of hydrogen to 3.0MPa (the mole ratio of hydrogen to hydroxyl groups in hydroxyl-terminated polyoxypropylene ether is 10:1). The reactor is heated to a temperature at 200°C and maintained at the temperature for 3h, and the maximum pressure in the reactor is controlled at 8.5MPa. Then, the reactor is cooled to 60°C. The reactor is exhausted slowly and the gas is absorbed with water, and then the reaction mixture is discharged.

The reaction mixture is filtered in hot state to separate the catalyst and liquid mixture containing the product, the liquid mixture is transferred to a three-neck flask to conduct reduced pressure distillation at 105°C and a vacuum degree of -0.08MPa for 2h, so as to obtain the product of amino-terminated polyether. By analyzing, it is determined that the total amine value in the obtained product is 0.58mmol/g, the conversion of polyether alcohol is 98.5wt%, and the selectivity of primary amine is 96.5wt%.

Example 18

100g tri-functional hydroxyl-terminated polyoxypropylene ether with number-average molecular weight of 5000.0 (procured from Polyether Department of Tianjin Petrochemical) and 5g Raney nickel catalyst prepared in preparation example 3 are added into a 0.5L high pressure reactor. The high pressure reactor is purged with nitrogen and hydrogen with a pressure of 0.4MPa for 2-3 times. Approx. 18L

dimethylamine (under standard condition) is added into the reactor with agitation, and hydrogen is filled into the reactor by regulating the outlet pressure of steel cylinder of hydrogen to 3.0MPa (the mole ratio of hydrogen to hydroxyl groups in hydroxyl-terminated polyoxypropylene ether is 10:1). The reactor is heated to a
5 temperature at 200°C and maintained at the temperature for 3h, and the maximum pressure in the reactor is controlled at 8.5MPa. Then, the reactor is cooled to 60°C. The reactor is exhausted slowly and the gas is absorbed with water, and then the reaction mixture is discharged.

The reaction mixture is filtered in hot state to separate the catalyst and liquid
10 mixture containing the product, the liquid mixture is transferred to a three-neck flask to conduct reduced pressure distillation at 105°C and a vacuum degree of -0.08MPa for 2h, so as to obtain the product of amino-terminated polyether. By analyzing, it is determined that the total amine value in the obtained product is 0.61mmol/g, the conversion of polyether alcohol is 100wt%, and the selectivity of tertiary amine is
15 95.85wt%.

Example 19

Amino-terminated polyether is prepared by the method same as the method described in example 18, the difference is that the Raney nickel catalyst is prepared in
20 the preparation example 2. By analyzing, it is determined that the total amine value in the obtained product is 0.54mmol/g, the conversion of polyether alcohol is 88.4wt%, and the selectivity of tertiary amine is 97.13wt%.

Example 20

Amino-terminated polyether is prepared by the method same as the method described in example 18, the difference is that the Raney nickel catalyst is prepared in the preparation example 4. By analyzing, it is determined that the total amine value in the obtained product is 0.55mmol/g, the conversion of polyether alcohol is 92.24wt%,
5 and the selectivity of tertiary amine is 94.36wt%.

Example 21

Amino-terminated polyether is prepared by the method same as the method described in example 17, the difference is that the ammonia gas is replaced with
10 ammoniacal liquor. By analyzing, it is determined that the total amine value in the obtained product is 0.62mmol/g, the conversion of polyether alcohol is 100wt%, and the selectivity of primary amine is 97.45wt%.

Above the preferred Examples of the present invention are described in details, but
15 the present invention is not limited to the details of the foregoing Examples. Within the technical conception of the present invention, the technical solution of the present invention may have various modifications within the protective scope of the present invention.

It should be noted that the concrete technical characteristics described in the
20 foregoing examples can be combined in any appropriate way under the condition of no conflict. In order to avoid unnecessary repetition, the present invention does not describe the possible combinations.

Further, the examples of the present invention may be combined freely as long as the combinations do not disobey the thought of the present invention. They shall also be deemed as the content disclosed by the present invention.

Claims

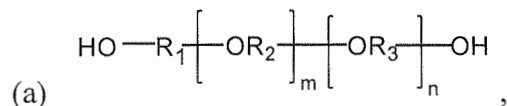
1. A method for preparing amino-terminated polyether by catalytic reductive amination of polyether glycol in the presence of hydrogen, at least one aminating agent, and a catalyst, the method comprises the following steps:

5 in the presence of a Raney catalyst, contacting polyether glycol having a number-average molecular weight of no less than 100 with at least one aminating agent and hydrogen in a reactor to proceed catalytic reductive amination reaction; and
cooling down obtained reaction mixture to 25-60°C, removing unreacted gas, discharging the reaction mixture, and removing water, residual aminating agent and
10 other low-boiling by-products from the reaction mixture by reduced pressure distillation, so as to obtain amino-terminated polyether;

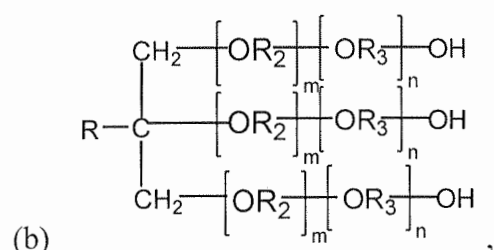
wherein the amount of the Raney nickel catalyst is 2-15% of the amount of the polyether glycol by weight; the amount of the aminating agent is 1.5-20 times of the amount of hydroxyl groups in the polyether glycol by mole, and the amount of
15 hydrogen is 0.4-15 times of the amount of hydroxyl groups in the polyether glycol by mole; the catalytic reductive amination reaction is conducted at a temperature of 120-250°C and a pressure of 8-35MPa for a period duration of 1.5-8h;

the Raney nickel catalyst consists of Ni, Al, and metal M, based on the total weight of the Raney nickel catalyst and calculated by element, the content of Ni is in a range of
20 80-95wt%, the content of Al is in a range of 5-20wt%, and the content of metal M is in a range of 0.5-5wt%; and the metal M is one, two, or three selected from Cr, Fe, Cu, and Zn.

2. The method according to claim 1, wherein the polyether glycol has the following general structural formula (a) or (b):

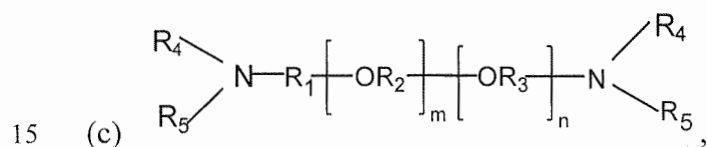


in formula (a), R_1 , R_2 , and R_3 are independently selected from linear or branched
5 divalent aliphatic groups with 2-4 carbon atoms; m is 0-115; n is 0-115; and the sum of
 m and n is 1-115;



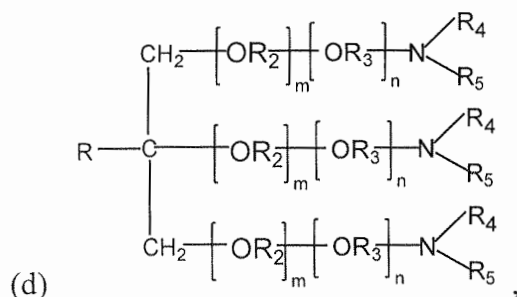
in formula (b), R is selected from hydrogen and linear or branched aliphatic groups
having 1-6 carbon atoms; R_2 and R_3 are independently selected from linear or branched
10 divalent aliphatic groups having 2-4 carbon atoms; m is 0-40; n is 0-40; and the sum of
 m and n is 1-115.

3. The method according to claim 1, wherein the amino-terminated polyether has
the following general structural formula (c) or (d):



in formula (c), R_1 , R_2 , and R_3 are independently selected from linear or branched
divalent aliphatic groups with 2-4 carbon atoms; R_4 and R_5 are identical or different,

and are independently selected from hydrogen and linear or branched aliphatic groups having 1-6 carbon atoms; m is 0-115; n is 0-115; and the sum of m and n is 1-115;



in formula (d), R is selected from hydrogen and linear or branched aliphatic groups having 1-6 carbon atoms; R₂ and R₃ are independently selected from linear or branched divalent aliphatic groups having 2-4 carbon atoms; R₄ and R₅ are identical or different, and are independently selected from hydrogen and linear or branched aliphatic groups having 1-6 carbon atoms; m is 0-40; n is 0-40; and the sum of m and n is 1-115.

4. The method according to claim 1, wherein the Raney nickel catalyst is prepared by the method comprising the following steps:

a) adding ternary, quaternary, or quinary alloy powder into water solution of sodium hydroxide under vigorous agitation and stirring at a temperature of 45-100° C for a period duration of 0.5-5h, to dissolve the alloy powder, then reacting at a temperature of 50-100° C for a period duration of 0.5-5h to activate, wherein the concentration of sodium hydroxide is 10-40wt%, the amount of sodium hydroxide is 1-3 times of the weight of the alloy powder;

b) standing the mixture obtained by step (1) to separate the supernatant white flocculate, washing black precipitate with warm water for several times to neutrality,

and then washing with anhydrous ethanol for 2-5 times to obtain Raney nickel catalyst;
next, storing the Raney nickel catalyst in anhydrous ethanol;

wherein, the alloy powder consists of Ni, Al, and metal M, wherein, the metal M is one, two, or three selected from Cr, Fe, Cu, and Zn.

5

5. The method according to claim 1, wherein the aminating agent is selected from methylamine, dimethylamine, ethylamine, diethylamine, *n*-propylamine, *di-n*-propylamine, isopropylamine, diisopropylamine, hexylamine, and cyclohexylamine.

10

6. The method according to claim 1, wherein the amount of hydrogen is controlled by regulating the pressure of hydrogen filling into the reactor in the range of 1.5-8MPa.

7. The method according to claim 1, wherein the reduced pressure distillation is conducted at a temperature of 100-120°C and a vacuum degree of from -0.08MPa to -

15

0.1MPa.

8. The method according to claim 1, wherein the reactor is a stirred reactor.