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(54) Title: METHOD FOR PREPARING POLYALKYLENEBIGUANIDINE SALT

(57) Abstract: A method for preparing polyalkylenebiguanidine salt, which does not require a high-viscosity reactor and a toxic solvent, and is capable of producing various polyalkylenebiguanidine salt, is disclosed. The method comprises the steps of: polymerizing alkylenediamine dihydrochloride and dicyanamide metal salt in the presence of solvent or without solvent; neutralizing the polymerization product by adding water, and alkali metal compound or alkaline earth metal compound into the polymerization product; separating a neutralized polyalkylenebiguanidine polymer layer from an aqueous layer after inducing a phase-separation by settling the neutralized polymerization product; and adding acid into the separated polyalkylenebiguanidine polymer layer. Alternatively, the polyalkylenebiguanidine salt can be prepared by the method comprising the steps of: polymerizing alkylenediamine dihydrochloride and dicyanamide metal salt in the presence of solvent; and removing solvent and byproduct from the obtained polymerization product.

Description

METHOD FOR PREPARING POLYALKYLENEBIGUANIDINE SALT

Technical Field

[1] The present invention relates to a method for preparing polyalkylenebiguanidine salt, and more specifically to a method for preparing polyalkylenebiguanidine salt, which does not require a high-viscosity reactor and a toxic solvent, and is capable of producing various polyalkylenebiguanidine salt.

Background Art

[2] The research on antibiotic ability of a substituted guanidine and guanidine derivatives has been carried out since the early 1930s. The antibacterial and antifungal ability of guanidine derivatives has been studied in the various fields of medicine, storage and preservation of farm products, germicide for industrial use, germicide for swimming pool, germicide for food factory, antibiotic fiber, antibiotic daily necessaries, eye lotion preservation, and so on. Especially, polyalkylenebiguanidine hydrochloride salt, which is reported to have a good antibiotic ability, has been studied actively. For example, U. S. pat. Nos. 3,468,898, 4,022,834, 4,567,174 and 4,670,592 disclose the antibiotic property of biguanidine salt, and U. S. pat. Nos. 2,643,232 and 3,428,576 disclose the method for preparing polyhexamethylenebiguanidine hydrochloride salt.

[3] In the method disclosed in U. S. pat. No. 2,643,232, polyhexamethylenebiguanidine salt is produced by polymerizing bisdicyandiamide and diamine or diamine salt. However, the method has a drawback in that it requires the preliminary process for preparing bisdicyanamide. More precisely, hexamethylenebisdicyanamide, one of the reactants, should be prepared by reacting hexamethylenediamine dihydrochloride with sodium dicyanamide in the presence of butanol solvent, and the product of the preliminary process must be filtered before use. Another problem of the method is that hexamethylene bisdicyandiamide and hexamethylenediamine dihydrochloride exist in solid state at room temperature, and the compounds should be pulverized in order to increase the reaction efficiency, which makes the method unsuitable for large-scale production. In order to solve these problems, U. S. pat. No. 3,428,576 provides the method for preparing polyhexamethylenebiguanidine salt which uses aqueous hydrochloride solution as a reactant and solvent. In this method, sodium dicyanamide and hexamethylenediamine reacts with aqueous hydrochloride

solution. The reaction is carried out while removing water. After completion of the reaction, the reaction product is dissolved with methanol to remove sodium chloride (NaCl) byproduct by precipitation. Then the reaction product is heated to remove methanol, and the final product, polyhexamethylenebiguanidine hydrochloride salt, is obtained. However, the method has drawbacks in that the reaction time is too long, and the reactor must be maintained in the vacuum state. Besides, in the method, sodium chloride (NaCl) byproduct, which is produced as the reaction proceeds, increases the viscosity of the reactants, which prevents the reaction mixture from being stirred in a conventional reactor. Accordingly, the reaction should be carried out in a specially designed reactor such as high-viscosity reactor. Furthermore, the reaction requires toxic solvent, such as methanol, to remove NaCl byproduct, and additional heating process to remove methanol, and the reactor should be maintained in a vacuum state in order to improve the removal efficiency of methanol. In addition, the method has other drawback in that only polyhexamethylenebiguanidine hydrochloride salt can be produced.

Disclosure of Invention

Technical Problem

[4] Therefore, it is an object of the present invention to provide the method for preparing polyalkylenebiguanidine salt, which does not require a high-viscosity reactor by preventing the viscosity of the polymerization product from increasing excessively.

[5] It is other object of the present invention to provide the method for preparing polyalkylenebiguanidine salt, which does not require toxic solvent, and by which the final product, polyalkylenebiguanidine salt, can be obtained with simple process.

[6] It is another object of the present invention to provide the method for preparing various polyalkylenebiguanidine salt.

[7] It is yet another object of the present invention to provide the method for preparing polyalkylenebiguanidine salt, which does not require additional preliminary process to produce a reactant, and has good reaction efficiency, and in which the homogeneous reaction can be carried out.

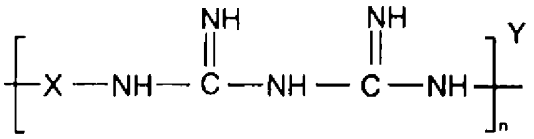
Technical Solution

[8] To accomplish these objects, the present invention provides the method for preparing polyalkylenebiguanidine salt of the following formula 1, which comprises the steps of: polymerizing alkylenediamine dihydrochloride and dicyanamide metal salt in the presence of solvent or without solvent; neutralizing the polymerization product by adding water, and alkali metal compound or alkaline earth metal compound

into the polymerization product; separating a neutralized polyalkylenebiguanidine polymer layer from an aqueous layer after inducing a phase-separation by settling the neutralized polymerization product; and adding acid into the separated polyalkylenebiguanidine polymer layer.

[9] [Formula 1]

[10]



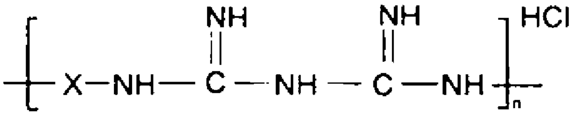
$$\left[X-NH-\overset{\overset{\displaystyle NH}{\|}}{C}-NH-\overset{\overset{\displaystyle NH}{\|}}{C}-NH \right]_n^{Y}$$

[11] In formula 1, Y is independently selected from the group consisting of hydrochloride, hydrobromide, hydroiodide, nitric acid, carbonic acid, sulfuric acid, phosphoric acid, acetic acid, benzoic acid, dehydrogenated acetic acid, propionic acid, gluconic acid, sorbic acid, fumaric acid, maleic acid and epichlorohydric acid, and n is an integer of 1 or more, preferably 2 to 100, and X represents a C3-C17 bridging group interposed between the adjacent nitrogen atoms.

[12] The present invention also provides the method for preparing polyalkylenebiguanidine salt of the following formula 2, which comprises the steps of: polymerizing alkylenediamine dihydrochloride and dicyanamide metal salt in the presence of solvent; and removing solvent and byproduct from the obtained polymerization product.

[13] [Formula 2]

[14]



$$\left[X-NH-\overset{\overset{\displaystyle NH}{\|}}{C}-NH-\overset{\overset{\displaystyle NH}{\|}}{C}-NH \right]_n^{HCl}$$

[15] In formula 2, X and n have the same meanings as defined in formula 1.

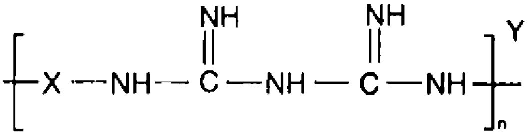
Mode for Invention

[16] A more complete appreciation of the invention, and many of the attendant advantages thereof, will be better appreciated by reference to the following detailed description.

[17] Polyalkylenebiguanidine salt prepared according to the present invention can be represented by the following formula 1.

[18] [Formula 1]

[19]



$$\left[X - NH - \overset{\overset{NH}{\|}}{C} - NH - \overset{\overset{NH}{\|}}{C} - NH \right]_{n}^{Y}$$

[20] In formula 1, Y is independently selected from the group consisting of hydrochloride, hydrobromide, hydroiodide, nitric acid, carbonic acid, sulfuric acid, phosphoric acid, acetic acid, benzoic acid, dehydrogenated acetic acid, propionic acid, gluconic acid, sorbic acid, fumaric acid, maleic acid and epichlorohydric acid, and n is an integer of 1 or more, preferably 2 to 100, and X represents a C3-C17 bridging group interposed between the adjacent nitrogen atoms, and optionally can be alkylene group having a heterogeneous atom such as oxygen and sulfur therebetween.

[21] In order to prepare polyalkylenebiguanidine salt of formula 1 according to the present invention, the reactants, alkylenediamine dihydrochloride and dicyanamide metal salt [$MN(CN)_2$, where in M is a metal] are injected into a reactor sequentially or simultaneously, and then the reactants are polymerized. If desired, solvent can be added into the reactor during or before the polymerization. Exemplary alkylenediamine dihydrochloride includes hexamethylenediamine dihydrochloride, decamethylenediamine dihydrochloride, bis- ω -aminopropyl ether dihydrochloride, 4,4'-diaminodicyclohexylmethane dihydrochloride, 1,4-di-(ω -aminopropoxy)benzene dihydrochloride, N,N'-di-isobutyl-aminohexa methylenediamine dihydrochloride, trimethylenediamine dihydrochloride, bis-(1-amino-3-propyl)-ether dihydrochloride, 1,3-bis-methylamino neopentane dihydrochloride and the mixtures thereof. The preferable alkylenediamine dihydrochloride includes hexamethylenediamine dihydrochloride. Exemplary metal of dicyanamide metal salt includes sodium, zinc, calcium, copper and the mixtures thereof. The preferable metal includes sodium. The alkylenediamine dihydrochloride and dicyanamide metal salt need not be used in equal amount(mole), and the amounts of the reactants can be varied in wide range. However, if one reactant is used excessively, there might exist excessive unreacted reactant, and the reaction efficiency might be deteriorated.

[22] In case of using solvent, the solvent acts as solvent and heating medium in the polymerization reaction of alkylenediamine dihydrochloride and dicyanamide metal salt. The solvent increases the stirring efficiency of alkylenediamine dihydrochloride and dicyanamide metal salt which is in the solid phase, and prevents the viscosity of the reaction mixture from increasing excessively. Preferable solvent is organic solvent such as polyhydric alcohol or its derivative, which has boiling point of 150 °C or more

and does not directly participate in the polymerization reaction of alkylenediamine dihydrochloride and dicyanamide metal salt. The specific examples of the solvent include ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol, polyethylene glycol (Mw is 1,000 or less), 1,3-propylene glycol, 1,2-propylene glycol, dipropylene glycol, tripropylene glycol, polypropylene glycol (Mw is 1,000 or less), 2-methyl-1,2-propyleneglycol, 1,2-butyleneglycol, 1,4-butyleneglycol, 1,5-penthanediol, neopentylglycol, 1,6-hexanediol, trimethylolethane, trimethylolpropane, glycerol, alpha-methyl glucoside, 2-methyl-2,4-pentane glycol, methylcellulose, ethylene carbonate, propylene carbonate, propyleneoxide modified bisphenol A, dibromoneopentyl glycol and the mixtures thereof. The preferable amount of the solvent is 1 to 200 weight parts, more preferably 5 to 100 weight parts with respect to the total 100 weight parts of alkylenediamine dihydrochloride and dicyanamide metal salt. If the amount of the solvent is less than 1 weight part with respect to the total 100 weight parts of alkylenediamine dihydrochloride and dicyanamide metal salt, the viscosity of the reaction mixture does not decreases sufficiently, which can deteriorate stirring efficiency and prevents homogeneous reaction from being carried out. If the amount of the solvent is more than 200 weight parts, the reaction time can be prolonged, and the reaction residue and the reaction cost may increase. Because the solvent decreases the viscosity of the reaction mixture, a conventional reactor as well as a high-viscosity reactor can be used for the method of the present invention. Exemplary reactor, which is suitable for the present invention, includes a stirring vessel, a kneader, an extruder, a mixer, a mill reactor, and so on. More preferable reactor includes a stirring vessel. The temperature in which the reaction mixtures and the solvent is injected into the reactor is not limited to a specific range, but considering the convenience in handling of reactants, and working conditions, the preferable temperature is room temperature. The preferable polymerization temperature is 100 ℃ to 200 ℃ , and the preferable polymerization reaction time is 2 to 24 hours. In addition, it is preferable to remove water in the reaction mixture by nitrogen purging from the top of the reactor. When the reaction temperature or time of the polymerization reaction is less than the above-mentioned range, the polymerization reaction can not be carried out adequately. On the contrary, if the reaction temperature or time of the polymerization reaction is more than the above-mentioned range, side reactions may occur to an excessive extent, which may increase the amount of the byproducts. As the polymerization reaction proceeds, the viscosity of the reaction mixture increases, and the state of the reaction mixture changes from mobile and sticky polymer to a paste-type solid. Accordingly the progress of the reaction can be estimated with the viscosity of the reaction mixture.

[23] After completion of the polymerization reaction, the neutralization of the polymerization product and the byproduct removal process are carried out. The neutralization process is carried out by adding water to the polymerization product, and stirring the polymerization product to dissolve the same, and subsequently by adding alkali metal compound or alkaline earth metal compound such as sodium hydroxide and potassium hydroxide to the polymerization product and stirring the polymerization product. The amount of water can be about 5 to 40 times, preferably 10 to 40 times, more preferably 15 to 30 times in mole ratio with respect to the amount of dicyanamide metal salt used in the polymerization reaction, and the amount of the alkali metal compound or alkaline earth metal compound can be about 0.2 to 2 times, preferably 0.5 to 1.5 times in mole ratio with respect to the amount of dicyanamide metal salt. The alkali metal compound or alkaline earth metal compound can be added singly or in aqueous solution state, and stirred at the temperature of 20 ℃ to 80 ℃ , preferably 30 ℃ to 60 ℃ for 30 minutes to 3 hours, preferably 1 to 2 hours. If the amount of water, alkali metal compound or alkaline earth metal compound, or the stirring time is less than the above-mentioned range, the neutralized polyalkylenebiguanidine polymer layer may not be formed adequately, and the phase separation due to the difference of the specific gravity may not occur sufficiently. On the contrary, if the amount of alkali metal compound or alkaline earth metal compound is more than the above mentioned range, unnecessary alkali metal compound or alkaline earth metal compound exist in the target compound, and it is economically unfavorable without any special advantages. In addition, even when the amount of water or the stirring time is more than the above-mentioned range, the more preferable effect may not be obtained.

[24] After neutralizing the polymerization product and stopping the stirring, the neutralized polymerization product is stayed at room temperature for 0.5 hours or more, preferably for 3 hours or more to induce a phase-separation into a neutralized polyalkylenebiguanidine polymer layer and an aqueous layer. Then the solvent and the byproducts, for example, metal salt such as sodium chloride (NaCl) produced during the polymerization reaction dissolve into the aqueous layer. Such phase-separation is due to the difference in solubility and specific gravity between the neutralized polyalkylenebiguanidine polymer layer and the aqueous layer in which metal salt dissolves. By separating the neutralized polyalkylenebiguanidine polymer layer from

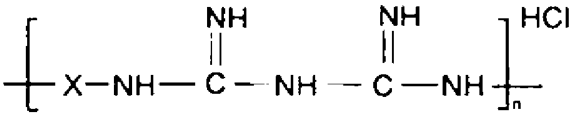
the aqueous layer with a method such as a drain method, a pure neutralized polyalkylenebiguanidine polymer layer, from which solvent and metal salt are removed, can be obtained. Then, various polyalkylenebiguanidine salt can be obtained by adding water and various acid into the separated polyalkylenebiguanidine polymer layer. Exemplary acid for preparing polyalkylenebiguanidine salt includes hydrochloride, hydrobromide, hydroiodide, nitric acid, carbonic acid, sulfuric acid, phosphoric acid, acetic acid, benzoic acid, dehydrogenated acetic acid, propionic acid, gluconic acid, sorbic acid, fumaric acid, maleic acid and epichlorohydric acid and the mixtures thereof. The amount of the acid can be about 0.2 to 2 times, preferably 0.5 to 1.5 times in mole ratio with respect to the amount of dicyanamide metal salt used in the reaction. If the amount of the acid is less than 0.2 times, the solubility and stability of the final product are deteriorated. If the amount of the acid is more than the 2 times, the pH of the final product decreases and the final product is not desirable in an economical aspect and in commercial use.

[25] Polyalkylenebiguanidine salt prepared in the forms of various salt according to the present invention, includes preferably 0 to 10 weight%, more preferably 0.01 to 5 weight% of residual solvent, and the weight average molecular weight thereof is preferably 300 to 20,000, more preferably 500 to 10,000, most preferably 700 to 5,000.

[26] Polyalkylenebiguanidine hydrochloride salt of the following formula 2 can also be prepared by polymerizing alkylenediamine dihydrochloride and dicyanamide metal salt in the presence of solvent; and by removing solvent and byproduct from the obtained polymerization product.

[27] [Formula 2]

[28]



$$\left[X-NH-\overset{NH}{\overset{\|}{C}}-NH-\overset{NH}{\overset{\|}{C}}-NH \right]_n HCl$$

[29] In formula 2, X and n have the same meanings as defined in formula 1.

[30] The solvent and the reaction conditions of the polymerization process can be the same with those of the polymerization process of polyalkylenebiguanidine salt of the formula 1. The process of removing the solvent and the byproduct is carried out by adding water to the polymerization product, and stirring the polymerization product to dissolve the same, and subsequently by settling the polymerization product at the temperature of 20 °C to 80 °C , preferably at room temperature for 0.5 hours and more,

preferably for 3 hours and more. The amount of water can be about 5 to 40 times, preferably 10 to 40 times, more preferably 15 to 30 times in mole ratio with respect to dicyanamide metal salt used in the polymerization reaction. If the amount of water or the staying time is less than those mentioned ranges, polyalkylenebiguanidine hydrochloride salt does not dissolve sufficiently or the separation due to the difference in specific gravity may not be performed sufficiently. If the amount of water is more than the mentioned range, it makes the process economically unfavorable without any special advantages. Such separation is carried out due to the difference in solubility and specific gravity between the polyalkylenebiguanidine hydrochloride layer and the aqueous layer in which metal salt and solvent dissolve. When water is added to the polymerization product, and the polymerization product is stirred, and then settled, polyalkylenebiguanidine hydrochloride salt layer and the aqueous layer are phase-separated. At this time, the solvent and the byproducts, for example, metal salt such as sodium chloride (NaCl) produced in the polymerization reaction dissolve into the aqueous layer. By separating the polyalkylenebiguanidine hydrochloride salt layer from the aqueous layer with a method such as a drain method, a pure polyalkylenebiguanidine hydrochloride salt can be obtained. The obtained polyalkylenebiguanidine hydrochloride salt includes preferably 0 to 10 weight%, more preferably 0.01 to 5 weight% of residual solvent, and the weight average molecular weight thereof is preferably 300 to 20,000, more preferably 500 to 10,000, most preferably 700 to 5,000.

[31] Hereinafter, the preferable examples are provided for better understanding of the present invention. However, the present invention is not be limited to the following examples.

[32] [Example 1] Preparation of polyhexamethylenebiguanidine hydrochloride salt

[33] 92.7g of hexamethylenediamine dihydrochloride, 189.1g of sodium dicyanamide and 28.2g of propylene glycol(PG) were added into a vessel reactor equipped with a stirrer at room temperature, and the polymerization reaction was carried out at 150 °C for 6 hours while being stirred at the rate of 100rpm. During the reaction, nitrogen purging was carried out from the top of the reactor. After completion of the polymerization reaction, 355g of water was slowly added to the polymerization product, and the polymerization product was stirred for 1 hour for complete dissolution. Then 80g of 50wt% aqueous sodium hydroxide solution was added to the polymerization product, and the polymerization product was stirred at 45 °C for 1 hour for neutralization reaction. After stopping stirring, the polymerization product was stayed at

the room temperature for 3 hours. Then, the lower aqueous layer was drained for separation from the upper pure neutralized polyhexamethylenebiguanidine polymer layer. 751g of water was added to the neutralized polyhexamethylenebiguanidine polymer layer, and the polymer layer was stirred, and then 50.6g of 36wt% aqueous hydrochloride solution was added to the stirred polymer layer to obtain polyhexamethylenebiguanidine hydrochloride salt.

[34] [Example 2] Preparation of polyhexamethylenebiguanidine phosphoric acid salt

[35] Except for adding 57.6g of 85wt% aqueous phosphoric acid solution instead of aqueous hydrochloride solution after the neutralization and the separating process, polyhexamethylenebiguanidine phosphoric acid salt was prepared in the same manner as described in Example 1.

[36] [Example 3] Preparation of polyhexamethylenebiguanidine gluconic acid salt

[37] Except for adding 196.2g of 50wt% aqueous gluconic acid solution instead of aqueous hydrochloride solution after the neutralization and the separating process, polyhexamethylenebiguanidine gluconic acid salt was prepared in the same manner as described in Example 1.

[38] [Example 4] Preparation of polyhexamethylenebiguanidine acetic acid salt

[39] Except for adding 30g of acetic acid instead of aqueous hydrochloride solution after the neutralization and the separating process, polyhexamethylenebiguanidine acetic acid salt was prepared in the same manner as described in Example 1.

[40] [Example 5] Preparation of polyhexamethylenebiguanidine hydrochloride salt

[41] Except for not using propylene glycol solvent and using a high-viscosity reactor, polyhexamethylenebiguanidine hydrochloride salt was prepared in the same manner as described in Example 1.

[42] [Example 6] Preparation of polyhexamethylenebiguanidine hydrochloride salt

[43] 92.7g of hexamethylenediamine dihydrochloride, 189.1g of sodium dicyanamide and 14.1g of ethylene glycol(EG) as solvent were added into a vessel reactor equipped with a stirrer at room temperature, and the polymerization reaction was carried out at 150 °C for 6 hours while being stirred at the rate of 100rpm. During the reaction, nitrogen purging was carried out from the top of the reactor. After completion of the polymerization reaction, 355g of water were slowly added to the polymerization product, and the polymerization product was stirred for 1 hour for complete dissolution. After stopping stirring, the polymerization product was settled at the room temperature for 3 hours. Then, the lower polyhexamethylenebiguanidine dihydrochloride layer was drained for separation from the upper aqueous layer.

[44] [Example 7] Preparation of polyhexamethylenebiguanidine hydrochloride salt

[45] Except for using 21.1g of ethylene glycol(EG) as solvent, polyhexamethylenebiguanidine hydrochloride salt was prepared in the same manner as described in Example 6.

[46] [Example 8] Preparation of polyhexamethylenebiguanidine hydrochloride salt

[47] Except for using 28.2g of ethylene glycol(EG) as solvent, polyhexamethylenebiguanidine hydrochloride salt was prepared in the same manner as described in Example 6.

[48] [Example 9] Preparation of polyhexamethylenebiguanidine hydrochloride salt

[49] Except for using 28.2g of propylene glycol(PG) as solvent, polyhexamethylenebiguanidine hydrochloride salt was prepared in the same manner as described in Example 6.

[50] [Example 10] Preparation of polyhexamethylenebiguanidine hydrochloride salt

[51] Except for using 42.3g of propylene glycol(PG) as solvent, polyhexamethylenebiguanidine hydrochloride salt was prepared in the same manner as described in Example 6.

[52] [Example 11] Preparation of polyhexamethylenebiguanidine hydrochloride salt

[53] Except for using 56.4g of propylene glycol(PG) as solvent, polyhexamethylenebiguanidine hydrochloride salt was prepared in the same manner as described in Example 6.

[54] [Example 12] Preparation of polyhexamethylenebiguanidine hydrochloride salt

[55] Except for using 28.2g of diethylene glycol(DEG) as solvent, polyhexamethylenebiguanidine hydrochloride salt was prepared in the same manner as described in Example 6.

[56] [Example 13] Preparation of polyhexamethylenebiguanidine hydrochloride salt

[57] Except for using 42.3g of diethylene glycol(DEG) as solvent, polyhexamethylenebiguanidine hydrochloride salt was prepared in the same manner as described in Example 6.

[58] [Example 14] Preparation of polyhexamethylenebiguanidine hydrochloride salt

[59] Except for using 28.2g of dipropylene glycol(DPG) as solvent, polyhexamethylenebiguanidine hydrochloride salt was prepared in the same manner as described in Example 6.

[60] [Comparative Example] Preparation of polyhexamethylenebiguanidine hydrochloride salt

[61] Except for not using solvent, polyhexamethylenebiguanidine hydrochloride salt

was prepared in the same manner as described in Example 6.

[62] The molecular weight and the polydispersity index (PDI) of polyhexamethylenebiguanidine hydrochloride salt prepared in Examples 6-14 and Comparative Example were measured, and the results were represented in Table 1. The molecular weight was measured by gel permeation chromatography(GPC). In Table 1, the 'stirring rate' is the lowest rate thereof during the polymerization reaction, and ' stirring availability' was determined by whether the stirring rate is lowered to 10rpm from the initial stirring rate of 100rpm.

[63] [Table 1]

[64]

No.	stirring rate(rpm)	stirring availability	Molecular weight(Mw)	polydispersity index (PDI=Mw/Mn)
Example 6	30	possible	758	1,923
Example 7	44	possible	789	1,938
Example 8	63	possible	803	2,319
Example 9	38	possible	866	2,687
Example 10	55	possible	750	2,204
Example 11	72	possible	814	2,119
Example 12	44	possible	772	1,900
Example 13	64	possible	786	1,913
Example 14	35	possible	844	2,176
Comparative Example	0	impossible	283	1,479

[65] As shown in Table 1, in the method of Comparative Example, the stirring of the polymerization product was impossible after 1.5 hours' polymerization at 150 ℃ . On the contrary, the stirrings were possible for all Examples, and polyhexamethylenebiguanidine hydrochloride salt prepared in Examples shows desirable molecular weight distribution and polydispersity.

[66] As described above, the present invention prevents the viscosity of the polymerization product from increasing excessively, and therefore does not require high-viscosity reactor, and obviates the major disadvantage of the conventional melt

process. In addition, the toxic solvent is not required for the present invention, and the various target salt can be easily obtained.

Claims

[1] A method for preparing polyalkylenebiguanidine salt of the following formula 1, comprising the steps of:

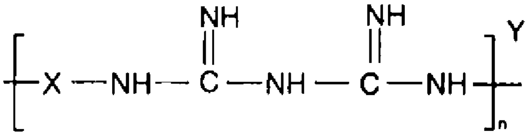
polymerizing alkylenediamine dihydrochloride and dicyanamide metal salt in the presence of solvent or without solvent;

neutralizing the polymerization product by adding water, and alkali metal compound or alkaline earth metal compound into the polymerization product;

separating a neutralized polyalkylenebiguanidine polymer layer from an aqueous layer after inducing a phase-separation by settling the neutralized polymerization product; and

adding acid into the separated polyalkylenebiguanidine polymer layer,

[Formula 1]



$$\left[X - NH - \overset{\overset{NH}{\|}}{C} - NH - \overset{\overset{NH}{\|}}{C} - NH \right]_n Y$$

wherein, Y is independently selected from the group consisting of hydrochloride, hydrobromide, hydroiodide, nitric acid, carbonic acid, sulfuric acid, phosphoric acid, acetic acid, benzoic acid, dehydrogenated acetic acid, propionic acid, gluconic acid, sorbic acid, fumaric acid, maleic acid and epichlorohydric acid, and n is an integer of 1 or more, and X represents a C3-C17 bridging group interposed between the adjacent nitrogen atoms.

[2] The method for preparing polyalkylenebiguanidine salt of claim 1, wherein X is alkylene group having a heterogeneous atom therebetween.

[3] The method for preparing polyalkylenebiguanidine salt of claim 1, wherein the alkylenediamine dihydrochloride is selected from the group consisting of hexamethylenediamine dihydrochloride, decamethylenediamine dihydrochloride, bis- ω -aminopropyl ether dihydrochloride, 4,4'-diaminodicyclohexylmethane dihydrochloride, 1,4-di-(ω -aminopropoxy) benzene dihydrochloride, N,N'-di-isobutyl-aminohexa methylenediamine dihydrochloride, trimethylenediamine dihydrochloride, bis-(1-amino-3-propyl)-ether dihydrochloride, 1,3-bis-methylaminoneopentane dihydrochloride and the mixtures thereof.

[4] The method for preparing polyalkylenebiguanidine salt of claim 1, wherein a metal of the dicyanamide metal salt is selected from the group consisting of

sodium, zinc, calcium, copper and the mixtures thereof.

[5] The method for preparing polyalkylenebiguanidine salt of claim 1, wherein the solvent is polyhydric alcohol or its derivative.

[6] The method for preparing polyalkylenebiguanidine salt of claim 1, wherein the solvent is selected from the group consisting of ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol, 1,3-propylene glycol, 1,2-propylene glycol, dipropylene glycol, tripropylene glycol, polypropylene glycol, 2-methyl-1,2-propyleneglycol, 1,2-butyleneglycol, 1,4-butyleneglycol, 1,5-penthanediol, neopentylglycol, 1,6-hexanediol, trimethylolethane, trimethylolpropane, glycerol, alpha-methyl glucoside, 2-methyl-2,4-pentane glycol, methylcellulose, ethylene carbonate, propylene carbonate, propyleneoxide modified bisphenol A, dibromoneopentyl glycol and the mixtures thereof.

[7] The method for preparing polyalkylenebiguanidine salt of claim 1, wherein the amount of the solvent is 1 to 200 weight parts with respect to the total 100 weight parts of alkylenediamine dihydrochloride and dicyanamide metal salt.

[8] The method for preparing polyalkylenebiguanidine salt of claim 1, wherein the amount of water is about 5 to 40 times in mole ratio with respect to the amount of dicyanamide metal salt.

[9] The method for preparing polyalkylenebiguanidine salt of claim 1, wherein the amount of the acid is about 0.2 to 2 times in mole ratio with respect to the amount of dicyanamide metal salt.

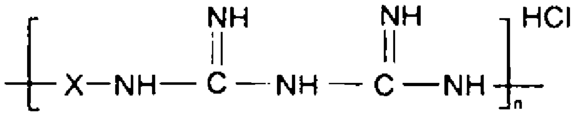
[10] The method for preparing polyalkylenebiguanidine salt of claim 1, wherein the polyalkylenebiguanidine salt includes 0 to 10 weight% of residual solvent, and the weight average molecular weight thereof is 300 to 20,000.

[11] A method for preparing polyalkylenebiguanidine salt of the following formula 2, comprising the steps of:

polymerizing alkylenediamine dihydrochloride and dicyanamide metal salt in the presence of solvent; and

removing solvent and byproduct from the obtained polymerization product,

[Formula 2]



$$\left[X-NH-\overset{NH}{\overset{\|}{C}}-NH-\overset{NH}{\overset{\|}{C}}-NH \right]_n HCl$$

wherein, X and n have the same meanings as defined in formula 1.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2004/002048

A. CLASSIFICATION OF SUBJECT MATTER

IPC7 C08G 73/02, C07C 279/16, C07C 279/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC7 C08G 73/02, C07C 279/16, C07C 279/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean Patents and applications for inventions since 1975

Electronic data base consulted during the intertnational search (name of data base and, where practicable, search terms used)
CA-on CD, PAJ, KIPASS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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A	JP2000-272236 A (NICCA CHEMICAL CO LTD) 03 October 2000 see the whole documents	1-11

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
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"P" document published prior to the international filing date but later than the priority date claimed
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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents,such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/KR2004/002048

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