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(71) Applicant and
(72) Inventor: **KIM, Yong-Bae** [KR/KR]; 21-3 Gueu-dong, Gwangjin-gu, Seoul 143-200 (KR).

(74) Agent: **YOU ME PATENT & LAW FIRM**; Teheran Bldg., 825-33 Yoksam-dong, Kangnam-ku, Seoul 135-080 (KR).

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(54) Title: POLYMIDE RESIN FOR NON-RUBBING VERTICAL ALIGNMENT MATERIALS AND PREPARATION METHOD THEREOF

(57) **Abstract:** The present invention relates to a polyimide resin for non-rubbing vertical alignment material and a preparation method thereof, and more particularly to a method for preparing a branched diamine compound offering a uniform and high pretilt angle to be used in a polyimide orientation film, a polyimide resin for non-rubbing vertical alignment materials offering a pretilt angle of 90 ° by the non-rubbing method, and a preparation method thereof.

Description

POLYIMIDE RESIN FOR NON-RUBBING VERTICAL ALIGNMENT MATERIALS AND PREPARATION METHOD THEREOF

[1]

Technical Field

[2] The present invention relates to a polyimide resin for non-rubbing vertical alignment materials and a preparation method thereof, and more particularly to a method for preparing a branched diamine compound offering a uniform and good pretilt angle to be used in a polyimide orientation film, a polyimide resin for non-rubbing vertical alignment materials offering a pretilt angle of 90 ° by the non-rubbing method , and a preparation method thereof.

Background Art

[3] Liquid crystal displays can be classified into the twist nematic (hereinafter referred to as 'TN') mode wherein nematic liquid crystal molecules are aligned between two transparent electrode substrates on which orientation films are coated, the super twist nematic (hereinafter referred to as 'STN') mode, the in - plain switching (hereinafter referred to as 'IPS') mode, the vertical alignment (hereinafter referred to as 'VA') mode, and the thin film transistor (hereinafter referred to as 'TFT') mode. Orientation film used in the liquid crystal display orients liquid crystal molecules, offers a pretilt angle between the substrate surface and the liquid crystal molecules to improve reactivity, and stabilizes orientation of liquid crystal molecules. The pretilt angle required for each liquid crystal display mode are: 1 to 6 ° for the TN mode, 3 to 8 ° for the STN mode, 1 to 2 ° for the IPS mode, and 90 to 88 ° for the VA mode. The pretilt angle should be uniform over the entire substrate. The orientation film is very important because it determines reliability of the liquid crystal display, uniformity of display , afterimage, voltage hold ratio , etc.

[4] Especially for the TFT-mode liquid crystal display, it is known that a low voltage hold ratio reduces applied voltage, and thus reduces contrast. If residual charge is large, an afterimage appears even when the applied voltage is turned off . Therefore, the display characteristic of the liquid crystal display declines, and no image is shown in the liquid crystal display after long use. Especially for the TFT-mode liquid crystal display, the residual DC voltage cannot be eliminated.

[5] Currently, many polymer compounds are known as liquid crystal alignment

materials. Among them, the most typical polymer compounds are polyamic-acid-based polymers prepared from imidization of polyamic acid and soluble polyimide-based polymer compositions. According to the literature, a variety of polymer compositions, such as polyacryls, polyvinyls, polyamides, and polyamides wherein the hydrogen atom of the amide bond has been substituted by other functional group, are considered. However, they are not being put into practice because they have problems in orientation of liquid crystal molecules, electro-optical characteristics of liquid crystal display, coatability, heat resistance, chemical resistance, etc .

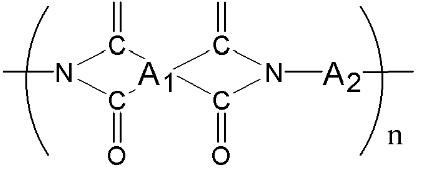
[6] Also, a polyimide liquid crystal alignment material using an aliphatic branched diamine having a linear alkoxy, alkyl ester, or fluorinated alkyl group at the side chain as a monomer is known. However , such polyimide orientation film offers a low pretilt angle of about 3 to 25 ° because the length and distribution of side chains are difficult to control.

[7] Branched polyimide compounds are used to obtain a high pretilt angle. However , just using branched polyimide compounds does not offer a uniformly high pretilt angle on the entire substrate. The pretilt angle of liquid crystal molecules is known to be largely affected by the shape of the orientation film surface and length of the side chain.

[8] Japan Patent Publication No. Hei 5-043687 discloses a liquid crystal display using a liquid crystal orientation film made from a polyimide resin having the repeating unit represented by the following Structural Formula I:

[9] [Structural Formula I]

[10]



[11] wherein A_1 is a quaternary organic group forming tetracarboxylic acid and derivatives thereof , A_2 is a secondary organic group forming diamine, and n is an integer.

[12] However, it is difficult to attain a pretilt angle of 90° with such a polyimide orientation film, and afterimage appears frequently. Moreover, a polyimide and polyamic acid do not mix well, and block copolymerization of a polyimide and polyamic acid is a very complicated process.

Disclosure of Invention

Technical Problem

[13] Thus, it is an object of the present invention to provide a method of preparing a branched diamine compound useful for preparing a polyimide resin for non-rubbing vertical alignment materials.

[14] It is another object of the present invention to provide a polyimide resin for vertical alignment materials prepared from said branched diamine compound, which offers uniform orientation by offering a pretilt angle of 90° by maximizing interaction of liquid crystal molecules and side chains of a polyimide on the glass substrate surface, and a preparation method thereof.

[15] It is still another object of the present invention to provide a liquid crystal orientation film using said polyimide resin, and a liquid crystal display comprising the same.

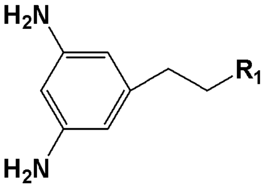
[16] To attain the objects, the present invention provides a method of preparing a branched diamine compound represented by Chemical Formula 1 below, which comprises the steps of:

[17] a) reacting a C_1 to C_{16} 2-alkylmalonic acid 1,3-di- *tert*-butyl ester derivative with 3,5-dinitrobenzoyl chloride in a solvent to prepare a C_1 to C_{16} dinitrophenyl alkene compound;

[18] b) adding BF_3Et_2O/Et_3SH to said dinitrophenyl alkene compound and dehydrating the same to prepare a dinitroalkenyl benzene compound represented by Chemical Formula 3 below; and

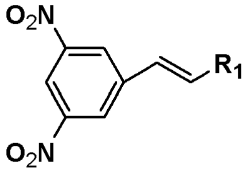
[19] c) reducing said compound represented by Chemical Formula 3 with hydrogen in the presence of Pd/C catalyst:

[20] Chemical Formula 1



Technical Problem

[21] Chemical Formula 3



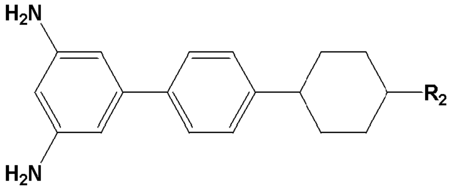
[22] wherein R_1 is a C_1 to C_{18} alkyl.

[23] The present invention also provides a method of preparing a diamine compound represented by Chemical Formula 2 below, which comprises the steps of:

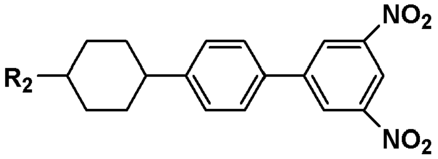
[24] a) reacting a C_1 to C_{10} 4-(alkylcyclohexyl)benzyl boronic acid compound with 1-bromo-3,5-dinitrobenzene to prepare a compound represented by Chemical Formula 4 below; and

[25] b) reducing said compound represented by Chemical Formula 4 with hydrogen in the presence of a Pd/C catalyst:

[26] Chemical Formula 2



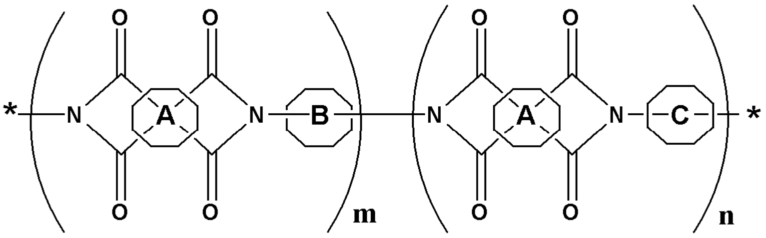
[27] Chemical Formula 4



[28] wherein R_2 is a C_1 to C_{10} alkyl or alkoxy.

[29] The present invention also provides a polyimide resin for non-rubbing vertical alignment materials represented by the following Chemical Formula 7:

[30] Chemical Formula 7



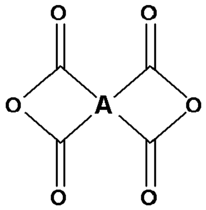
[31] wherein A is a quaternary organic group, B is a branched secondary organic group, C is a secondary organic group with no side chain, and m ? n, and when m is 1, n is an integer of 1 or larger .

[32] The present invention also provides a method of preparing said polyimide resin for non-rubbing vertical alignment materials represented by Chemical Formula 7, which comprises the steps of:

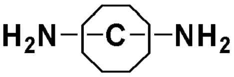
[33] a) reacting said branched diamine compound represented by Chemical Formula 1 or Chemical Formula 2 with a tetracarboxylic acid anhydride represented by Chemical Formula 5 below and a diamine compound with no side chain represented by Chemical Formula 6 below in a solvent to prepare a polyamic-acid-based block copolymer; and

[34] b) heat treating said polyamic-acid-based block copolymer to convert it to a polyimide by dehydration-cyclization:

[35] Chemical Formula 5



Chemical Formula 6



[36] wherein A is a quaternary organic group, and C is a secondary organic group with no side chain.

[37] The present invention also provides a liquid crystal orientation film prepared using said polyimide resin.

[38] The present invention also provides a liquid crystal display comprising said liquid crystal orientation film.

[39] Hereinafter, the present invention is described in more detail.

[40] The present invention is characterized by a method of preparing a branched diamine compound represented by Chemical Formula 1 or Chemical Formula 2, which can be used to prepare a liquid crystal orientation film requiring a uniform and high pretilt angle, and a dinitro compound represented by Chemical Formula 3 or Chemical Formula 4, which is an intermediate thereof.

[41] The present invention is also characterized by a polyimide resin prepared from said diamine compound represented by Chemical Formula 1 or Chemical Formula 2, which offers good liquid crystal orientation and a pretilt angle of 90 ° by the non-rubbing method in a wide range, and a preparation method thereof.

[42] The characteristics of a polyimide resin are determined by the average major-axis

length of liquid crystal molecules, length of the side chains of diamine affecting the pretilt angle, and spacing of the side chain. They are dependent on the kind and content of tetracarboxylic acid and diamine. In t he present invention, it is possible to control the characteristics of a polyimide-based copolymer by controlling such factors.

[43] In the present invention, the structure of a polyimide resin is designed as follows to obtain uniform orientation and a pretilt angle of 90° by maximizing interaction of liquid crystal molecules and side chains of polyimide on a glass substrate surface.

[44] Preferably, the length of the side chains of said branched diamine compound represented by Chemical Formula 1 or Chemical Formula 2 is determined so that the proportion of the side chain length of a polyimide to the average major-axis length of liquid crystal molecules is 0.8 to 1.5.

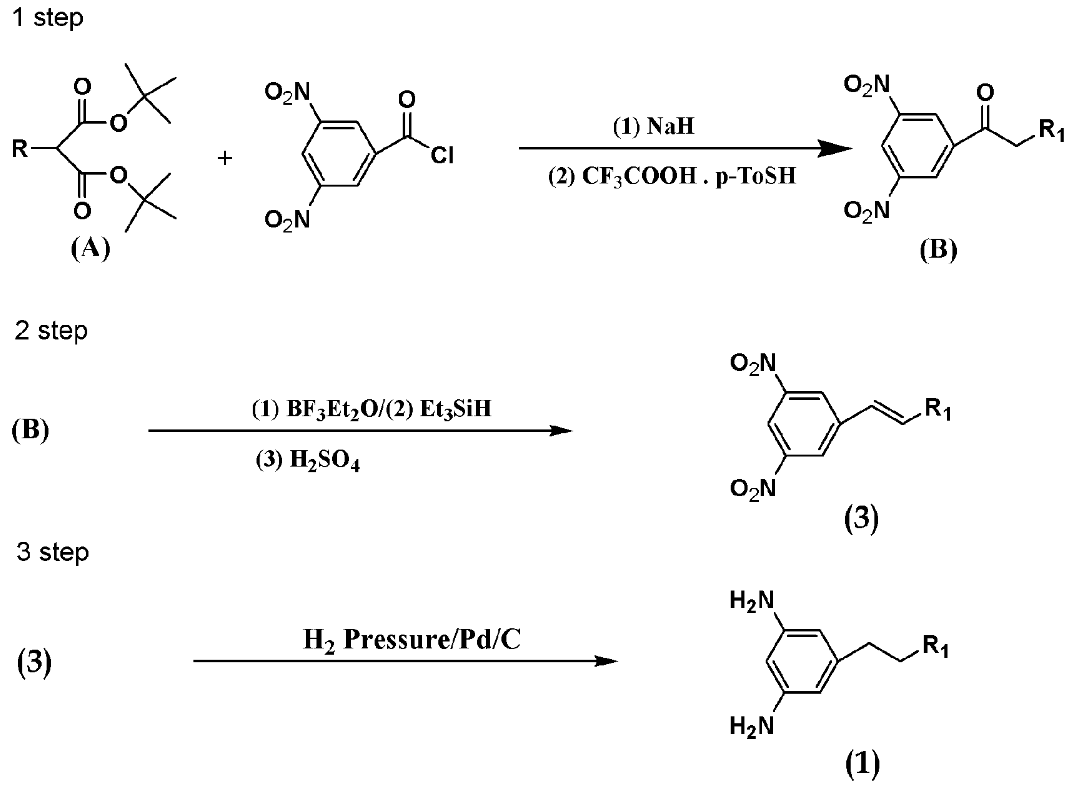
[45] Also, the spacing of side chains is an important factor that determines the density of side chains on the substrate surface. Preferably , the diamine compound with no side chains is introduced in the main chain of a polyimide, so that the spacing of the side chains of a polyimide liquid is 1.5 to 3.5 times the length of crystal molecules.

[46] By controlling the length and density of side chains of a polyimide as such, it is possible to copolymerize a polyimide resin offering uniform orientation and a high pretilt angle near 90 °, causing no afterimage, and offering a high voltage hold ratio, without rubbing.

[47] Hereinafter, the preparing method of said branched diamine compound represented by Chemical Formula 1 or Chemical Formula 2 is described in more detail.

[48] The diamine compound represented by Chemical Formula 1 is prepared by Scheme 1 below, and the dinitro compound represented by Chemical Formula 3 is an intermediate thereof:

[49] <u>Scheme 1</u>



[50] wherein R_1 is C_1 to C_{16} alkyl.

[51] Said diamine compound represented by Chemical Formula 1 is prepared by the following three steps.

[52] (Step 1)

[53] First, sodium hydride is added to a 2-alkylmalonic 1,3-di- *tert*-butyl ester derivative (A). After reacting for 12 hours at 5 °C , a reaction solution dissolving 3,5-dinitrobenzoyl chloride in an appropriate solvent is added dropwise. Then, *p* - toluenesulfonic acid as a catalyst is added to the reaction solution. After adding trifluoroacetic acid, CO_2 is removed under reduced pressure for 12 hours to obtain a dinitrophenylalkene compound (B).

[54] Here, the equivalence proportion of the compound (A) and the 3,5-dinitrobenzoyl chloride compound is 1:1. For the solvent, any solvent capable of dissolving the above compounds can be used.

[55] (Step 2)

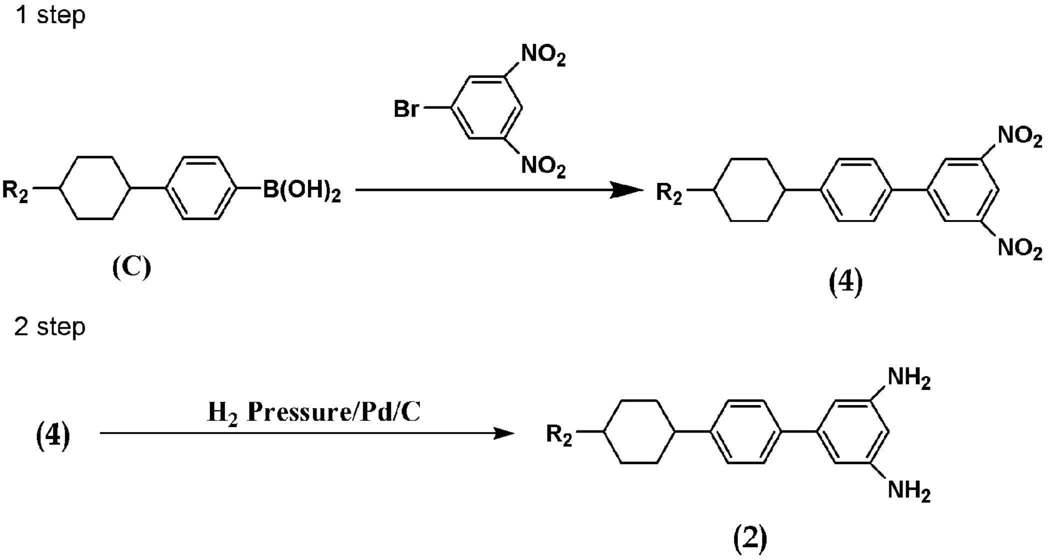
[56] Et_3SH and $BF_3 \cdot Et_2O$ are added to the reaction solution dissolving the compound (B) in an appropriate solvent. After 6 hours of reaction, the obtained dinitrophenylalkane-1-ol is dissolved in an organic solvent. After adding a 4A molecular sieve and H_2SO_4, dehydration is carried out for 4 hours to obtain a dinitroalkenylbenzene compound represented by Chemical Formula 3.

[57] (Step 3)

[58] The dinitro compound represented by Chemical Formula 3 is reduced with hydrogen in an appropriate solvent using a palladium-carbon catalyst (hereinafter referred to as ' Pd/C') to obtain a diamine compound represented by Chemical Formula 1.

[59] The diamine compound represented by Chemical Formula 2 is prepared by Scheme 2 below, and the dinitro compound represented by Chemical Formula 4 is an intermediate thereof:

[60] Scheme 2



[61] wherein R_2 is a C_1 to C_{10} alkyl.

[62] The diamine compound represented by Chemical Formula 2 is prepared by the following two steps.

[63] (Step 1)

[64] First, a reaction solution is prepared by adding *n*-BuLi dropwise under a nitrogen atmosphere to a THF solution with 1-bromo-4-(4-alkylcyclohexyl)benzene dissolved therein while maintaining the temperature equal to or below -78 ℃ . Then, triisopropyl borate is added to the reaction solution while stirring to obtain a 4-(alkylcyclohexyl)benzyl boric acid compound (C).

[65] Then, the compound (C) is reacted with 1-bromo-3,5-dinitrobenzene in an appropriate organic solvent using a tetrakis(triphenylphosphine)palladium catalyst to obtain a 3,5-dinitro-4'-(4-alkylcyclohexyl)biphenyl compound represented by Chemical Formula 4.

[66] Here, the equivalence proportion of the compound (C) and

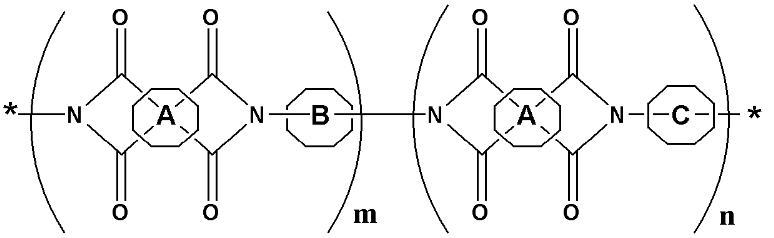
1-bromo-3,5-dinitrobenzene is 1:1.

[67] (Step 2)

[68] The dinitro compound represented by Chemical Formula 4 is contact-reduced under hydrogen pressure using a Pd/C catalyst to obtain a diamine compound represented by Chemical Formula 2.

[69] The present invention also provides a polyimide resin represented by Chemical Formula 7 below, which is prepared using the diamine compound represented by Chemical Formula 1 or Chemical Formula 2, and a preparation method thereof:

[70] Chemical Formula 7



[71] wherein A is a quaternary organic group, B is a branched secondary organic group, C is a secondary organic group with no side chain, and m ? n, and when m is 1, n is an integer of 1 or larger .

[72] In the polyimide represented by Chemical Formula 7, the branched secondary organic group (B) controls the length of side chains, and the secondary organic group with no side chain (C) controls the spacing of side chains to control the side chain distribution. In Chemical Formula 7, preferably m is 1 and n is 3 or 4.

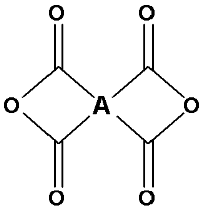
[73] The length of side chains of the branched secondary organic group is controlled so that it is 0.8 to 1.5 times the average major-axis length of liquid crystal molecules. And , the kind and number of repeating units, n, of the secondary organic group (C), are controlled so that the spacing of side chains is 1.5 to 3.5 times the major-axis length of liquid crystal molecules. The resultant polyimide resin offers a low residual DC current, a high voltage hold ratio, and a pretilt angle of 90° without afterimage. Therefore, the polyimide resin has a superior orientation characteristic.

[74] Hereinafter, the method of preparing a polyimide block copolymer according to the present invention is described more specifically.

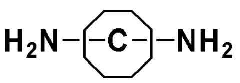
[75] In the present invention, the branched diamine compound represented by Chemical Formula 1 or Chemical Formula 2 may be reacted with the compound represented by Chemical Formula 5 or Chemical Formula 6 below to prepare a polyimide resin:

[76] Chemical Formula 5

[77]



Chemical Formula 6



[78] wherein A is a quaternary organic group, and C is a secondary organic group with no side chain.

[79] That is, the branched diamine compound represented by Chemical Formula 1 or Chemical Formula 2 and the diamine compound represented by Chemical Formula 6 are dissolved in N-methyl-2-pyrrolidone to prepare a reaction solution. Keeping the temperature at 5 ℃ , a reaction solution dissolving the tetracarboxylic acid dianhydride represented by Chemical Formula 5 is slowly added dropwise under a nitrogen atmosphere for 2 hours. Then, the resultant solution is stirred for 6 hours to obtain a polyamic-acid-based block copolymer. The viscosity of the block copolymer can be controlled using a cellosolve solvent, such as diethyleneglycol monomethyl ether, diethyleneglycol monoethyl ether, or ethyleneglycol monobutyl ether.

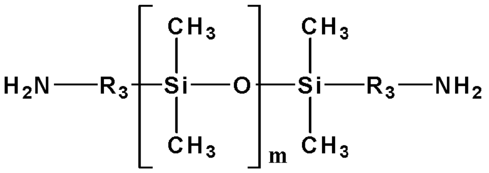
[80] Then, the polyamic-acid-based block copolymer may be heat treated in the temperature range from 100 to 230 ℃ for 30 minutes to 2 hours to convert it to a polyimide having the repeating unit of Chemical Formula 7 by dehydration-cyclization.

[81] In preparing the polyamic acid, it is preferable to use an inert solvent. For example , N-methyl-2-pyrrolidone (NMP), N,N-dimethylformamide (DMF), dimethylsulfoxide (DMSO), hexamethylphosphoamide, tetramethylenesulfone, *p* -chlorophenol, *p* -bromophenol, 2-chloro-4-hydroxytoluene, dioxane, tetrahydrofuran (THF), cyclohexanone, etc. may be used.

[82] For the tetracarboxylic acid dianhydride represented by Chemical Formula 5, any compound having a quaternary organic group can be used. For example , pyromellitic acid dianhydride (PMDA), 3,3',4,4'-benzophenonetetracarboxylic acid dianhydride (BTDA), 1,2,4,5-benzenetetracarboxylic acid dianhydride (PMDA), *cis* -1,2,3,4- cyclopentane tetracarboxylic acid dianhydride (CPDA), cyclobutane tetracarboxylic acid dianhydride (CBDA), etc. may be used.

[83] For the diamine compound represented by Chemical Formula 6, any diamine compound with no side chain substituent can be used . For example, 4,4'-diaminodiphenyl ether (ODA), 4,4'-methylenedianiline, diaminobenzophenone, 4.4'-methylenediphenyldiamine (MDA), 4.4'-hexafluoroisopropyldiphenyldiamine (6FDA), *p* -phenylenediamine, etc. may be used. Also, it is preferable to use diaminosiloxane represented by Chemical Formula 8 below to improve adhesivity to the substrate surface:

[84] Chemical Formula 8



$$H_2N-R_3-\left[\begin{matrix}CH_3\\ |\\ Si\\ |\\ CH_3\end{matrix}-O\right]_m-\begin{matrix}CH_3\\ |\\ Si\\ |\\ CH_3\end{matrix}-R_3-NH_2$$

[85] wherein R_3 is a C_3 to C_6 secondary aliphatic or aromatic hydrocarbon, and m is an integer of 1 or larger.

[86] The present invention also provides a liquid crystal orientation film prepared from said polyimide resin, which offers good liquid crystal orientation and a pretilt angle of 90° by the non-rubbing method.

[87] For this purpose, the polyimide resin for vertical alignment materials is coated on a substrate, preferably a glass substrate, on which a transparent conducting film is patterned, by the spinning method. Then, a polyimide liquid crystal orientation film having a predetermined thickness may be obtained by baking the substrate by the conventional method.

[88] Accordingly, the present invention provides a liquid crystal display comprising a liquid crystal orientation film that offers superior characteristics by the conventional method.

[89] Hereinafter, the present invention is described in more detail through Examples. However, the following Examples are only for the understanding of the present invention, and the present invention is not limited by the following Examples.

[90] **EXAMPLES**

[91] Example 1

[92] The diamine compound represented by Chemical Formula 1 was prepared according to Scheme 1.

[93] (Step 1)

[94] 177.3 g of 2-hexadecylmalonic acid di- *tert*-butyl ester (0.40 mol) was dissolved in

1 L of purified benzene under a nitrogen atmosphere , and 16 g of NaH (60% in mineral oil, 0.40 mol) was added dropwise at 5 °C . Then, the mixture was vigorously stirred for about 24 hours until no more H_2 gas was generated . After cooling to 5 °C , 92 g of 3,5-dinitrobenzoyl chloride (0.40 mol) was added, and the mixture was refluxed for 9 hours. After the reaction was completed, the solution was cooled to room temperature, filtered with celite, and extracted with hexane. After drying with anhydrous $MgSO_4$, the solution was distilled under reduced pressure to obtain 157.7 g of yellow 2-(3,5-dinitrobenzoyl)-hexadecyl-malonic acid liquid (yield: 89 %). ^1H 400 MHz NMR ($CDCl_3$): 9.2 (t, 3H), 2.2 (t, 2H), 1.4 to 1.5 (m, 18H) 1.2 to 1.3 (m, 20H), 0.8 to 0.9 (m, 3H).

[95] *p* -Toluenesulfonic acid was added to 157.7 g of the obtained 2-(3,5-dinitrobenzoyl)-hexadecyl-malonic acid as a catalyst. After adding several drops of trifluoroacetic acid, the mixture was stirred at 60 °C for 12 hours to remove CO_2. The resultant product was extracted and dried with ether. After distillation under reduced pressure, the product was recrystallized in hexane to obtain yellow 1-(3,5-dinitrophenyl)octadecan-1-one (compound B) crystal (yield: 89 %). Mass: 417 (M+), 210, 180, 149, 97, 83, 69, 55, ^1H 400 MHz NMR ($CDCl_3$): δ 9.3(t, 1H) 9.2 (q, 2H), 2.9 (t, 2H), 1.9 (m, 2H), 1.2 to 1.4 (m, 28H), 0.8 to 0.9 (m, 3H)

[96] (Step 2)

[97] Et_3SH (74.41 g, 0.64 mol) and BF_3Et_2O (90.2 g, 0.64 mol) were added to a solution with the 1-(3,5-dinitrophenyl)octadecan-1-one (compound B) (200.3 g, 0.32 mol) prepared in Step 1 dissolved in methyl chloride under a nitrogen atmosphere. After 6 hours of reflux, the solution was washed with an aqueous Na_2CO_3 solution, and extracted with ether. After drying with anhydrous $MgSO_4$, the concentrated solution obtained from distillation under reduced pressure was recrystallized with hexane to obtain yellow 1-(3,5-dinitrophenyl)octadecan-1-ol (compound B) crystal (yield: 87 %). 122.0 g of 1-(3,5-dinitrophenyl)octadecan-1-ol (0.29 mol) was dissolved in benzene (1.5 L), and a dried 4A molecular sieve and H_2SO_4 were added. After 4 hours of reflux, the reaction solution was filtered with celite, washed with an aqueous Na_2CO_3 solution, and extracted with ether. After drying with anhydrous $MgSO_4$, the concentrate solution obtained from distillation under reduced pressure was re-crystallized with ethanol to obtain yellow 1-(3,5-dinitro-5-octadecylenyl)benzene (compound C) crystal (yield: 83 %). Mass: 401 (M+), 383, 207, 161, 115, 69, 57, ^1H 400 MHz NMR ($CDCl_3$): δ 8.85 (p, 1H), 8.45 (p, 2H), 6.5 (m, 2H), 2.3 (m, 2H), 1.2 to 1.6 (m, 28H), 0.9 (t, 3H)

[98] (Step 3)

[99] 113.0 g of 1-(3,5-dinitro-5-octadecylenyl)benzene obtained in Step 2 was dissolved in a mixture solvent comprising 300 mL of benzene and 1 L of ethanol. After adding 11.3 g of Pd/C (10 wt%) as a catalyst, the reaction solution was stirred at room temperature for 6 hours under 4 atm of hydrogen pressure until the hydrogenation came to an end. After filtering the catalyst, the solution was dried with anhydrous $MgSO_4$. The concentrate obtained from distillation under reduced pressure was recrystallized with ethanol to obtain white 5-octadecyl benzene-1,3-diamine (compound D) crystal, which is the diamine compound of the present invention (Chemical Formula 1) (yield: 88.9 %). Mass: 360 (M+), 164, 149, 135, 122, 109, 77, 57, ^1H 400MHz NMR ($CDCl_3$): δ 5.9 (s, 3H), 2.4 (m, 2H), 1.2 to 1.6 (m, 32H), 0.9 (t, 3H).

[100] <u>Example 2</u>

[101] The diamine compound represented by Chemical Formula 2 was prepared according to Scheme 2.

[102] (Step 1)

[103] A tetrakis(triphenylphosphine)palladium catalyst and 700 mL of aqueous 2M Na_2CO_3 solution were added to a solution dissolving 123.5 g of 1-bromo-3,5-dinitrobenzene (0.5 mol: compound E) in 700 mL of benzene under a nitrogen atmosphere to prepare R eaction Solution 1. A solution dissolving 137 g of 4-(pentylcyclohexyl)benzyl boric acid in 150 mL of ethanol was slowly added dropwise, and refluxed at 95 °C for 24 hours. The product was extracted with ethyl acetate and dried. The concentrate obtained under reduced pressure was recrystallized in a mixture solution comprising ethanol and ethyl acetate to obtain yellow 3,5-dinitro-4'-(4-pentylcyclohexyl)biphenyl (compound F) crystal (yield: 68 %). Mass: 396 (M+), 270, 257, 165, 131, 55, ^1H 400 MHz NMR ($CDCl_3$): δ 9.1 (1H), 8.9 (2H), 7.4 (2H), 7.2 (2H), 2.8 (1H), 1.6 (4H), 1.5 (1H), 1.3 to 0.9 (15H)

[104] (Step 2)

[105] 196 g of 3,5-dinitro-4'-(4-pentylcyclohexyl)biphenyl (0.54 mol) prepared in Step 1 was dissolved in a mixture solution comprising benzene and ethanol. After adding 21 g of Pd/C (10 wt%) as a catalyst, the solution was stirred at room temperature for 6 hours under 4 atm of hydrogen pressure until the hydrogenation came to an end . After the reaction was completed, the catalyst was filtered, and the solution was dried with anhydrous $MgSO_4$. The concentrate obtained from distillation under reduced pressure was recrystallized in ethanol to obtain white 4'-(4-pentylcyclohexyl)biphenyl-3,5-diamine (compound G) crystal (yield: 66.7 %).

Mass: 336(M+), 270, 211, 115, 71, 55, ^{1}H NMR ($CDCl_3$): δ 7.4 (2H), 7.2 (2H), 6.0 (2H), 5.6 (1H), 1.6 (4H), 1.5 (1H), 1.3 to 0.9 (15H).

[106] Example 3

[107] 1) Preparation of polyimide orientation film

[108] 21.0 g of 4'-(4-pentylcyclohexyl)biphenyl-3,5-diamine (0.062 mol) prepared in Example 2 and 24.4 g of 4,4'-diaminodiphenyl ether were dissolved in 140.9 g of N-methyl-2-pyrrolidone under a nitrogen atmosphere. A solution with 38.9 g of 1,2,3,4-cyclopentanetetracarboxylic acid dianhydride dissolved in 120.9 g of N-methyl-2-pyrrolidone was slowly added dropwise to the resultant reaction solution for 2 hours while maintaining the temperature at 5 ℃ . After 4 hours of reaction, the reaction solution was poured into excess ultrapure water, and the precipitate was filtered. The filtrate was purified with methyl alcohol, and dried at 40 ℃ under reduced pressure to obtain polyamic acid. The obtained solid polyamic acid was dissolved in a 3:1 mixture solvent of NMP and 2-butoxyethanol to a 4 wt% solution. The solution was filtered with a 0.1 μ m filter to obtain a polyimide liquid crystal alignment material.

[109] The liquid crystal alignment material was coated on a glass substrate on which a transparent conducting film had been patterned by the spinning method. Then , the substrate was pre-baked at 100 ℃ for 30 minutes, and then baked at 250 ℃ for 1 hour to obtain a substrate on which a 700 Å thick polyimide orientation film was formed.

[110] (2) Preparation of liquid crystal display

[111] Two sheets of such prepared substrates on which liquid crystal orientation films had been formed were set up opposing each other with a predetermined space (cell gap) therebetween without rubbing. Edges of the two substrates were sealed, and liquid crystal was injected into the cell gap. Then, the injection hole was sealed to obtain a liquid crystal cell. Two polarizing films were joined to the outer surface of the liquid crystal, that is, each surface of the two substrates comprising the liquid crystal cell, to make the polarizing axes normal to each other, to obtain a liquid crystal display. For the sealant, a thermosetting epoxy resin comprising aluminum oxide as a spacer was used. ① Degree of imidization, ② logarithmic viscosity, ③ surface tension, ④ pretilt angle, ⑤ orientation, ⑥ voltage hold ratio, and ⑦ residual DC voltage of the liquid crystal alignment material prepared from the polyimide resin of the present invention were evaluated. The results are shown in Table 1.

[112] ① Degree of imidization

[113] FT-IR analysis was performed. From the peak area ratio of absorption near 1381

cm^{-1} (C-N-C vibration = absorption by the imide bond) and absorption near 1503 cm^{-1} (absorption by the amic acid), the degree of imidization was calculated by the following Equation 1.

[114] (Equation 1)

$$T(\%) = \frac{(A_{1380}/A_{1500})_T}{(A_{1380}/A_{1500})_{260}} \times 100$$

[115] ② Logarithmic viscosity

[116] It is preferable that the polymer comprising a liquid crystal alignment material has a logarithmic viscosity (η , ln) ranging from 0.05 to 10 dl/g. The logarithmic viscosity (η , ln) value can be calculated by Equation 2 below from the viscosity measurement at 30 ℃ using N-methyl-2-pyrrolidone as a solvent.

[117] (Equation 2)

$$\eta, \ln = \frac{\ln\,(Solution\ flow\ time\,/\,Solvent\ flow\ time)}{(wt\%\ concentration\ of\ polymer)}$$

[118] ③ Surface tension

[119] According to the method disclosed in the literature (D. K. Owens. *J. Appl., Pol., Sci.* vol 13. 1741-1747 (1969)), the surface tension can be obtained from the measurement of contact angle of pure water on the liquid crystal orientation film and that of iodomethylene. The contact angle was measured using OCA20 (Dataphysics , Germany). Water and iodomethylene were dropped on the film, and the contact angle was measured after 5 seconds.

[120] ④ Pretilt angle

[121] The pretilt angle was measured using a He-Ne laser according to the crystal rotation method disclosed in the literature (T.J. Schffer, et. al., *J., Appl., Phys.* ,vol.19, 2013 (1980)).

[122] ⑤ Orientation

[123] Presence of abnormal domain in the liquid crystal cell was observed with a microscope while applying a voltage to the liquid crystal display. If there was no abnormal domain, it was evaluated as 'good'.

[124] ⑥ Voltage hold ratio

[125] A voltage of 5 V was applied to the liquid crystal display for 60 μs . The voltage hold ratio was measured 16.67 ms after stopping voltage application .

[126] ⑦ Residual DC voltage

[127] The liquid crystal display was put in a 60 ℃ hot bath for 10 minutes. After applying a DC voltage of 10 V for 1 hour, the liquid crystal display was discharged for one second. The residual DC voltage was measured 10 minutes later.

[128] Example 4

[129] A polyimide orientation film was prepared in the same manner as in Example 3 except that 4,4'-methylenedianiline was used instead of 4,4'-diaminodiphenyl ether. Characteristics of such prepared liquid crystal alignment material were evaluated. The results are shown in Table 1.

[130] Example 5

[131] A polyimide orientation film was prepared in the same manner as in Example 3 except that 4.4'-hexafluoroisopropyldiphenyldiamine (6FDA) was used instead of 4,4'-diaminodiphenyl ether. Characteristics of such prepared liquid crystal alignment material were evaluated. The results are shown in Table 1.

[132] Table 1

Classification	Drying temperature (℃)	Degree of imidization (%)	Logarithmic viscosity (dl/g)	Surface tension (dyn/cm)	Pretilt angle (°)	VHR (%)	Residual DC voltage (mV)	Orientation
Example 3	200	93	0.30	22.8	90	98	451	Good
Example 4	200	99	0.17	24.0	90	89	796	Good
Example 5	200	97	0.16	27.2	90	93	796	Good

[133] As seen in Table 1, the present invention (Examples 3 to 5) offers a good degree of imidization, logarithmic viscosity, surface tension, VHR, residual DC voltage, and orientation. In particular, a pretilt angle of 90° can be obtained by the non-rubbing method.

[134] As described above, the method of preparing a branched diamine compound represented by Chemical Formula 1 or 2 of the present invention offers a new diamine compound useful for preparing a polyimide resin for non-rubbing vertical alignment materials. And , a polyimide resin having a new repeating unit represented by Chemical Formula 7, which is prepared from the above diamine compound, offers

good liquid crystal orientation and a pretilt angle of 90° by the non-rubbing method, so that it can be used in a liquid crystal orientation film. In addition , the polyimide resin of the present invention has a superior filming property, transparency, and adhesivity, a high voltage hold ratio, and a low residual DC voltage, so that it is useful as a alignment material of a liquid crystal display.

[135] While the present invention has been described in detail with reference to the preferred embodiments, those skilled in the art will appreciate that various modifications and substitutions can be made thereto without departing from the spirit and scope of the present invention as set forth in the appended claims.

Technical Solution

[136]

Claims

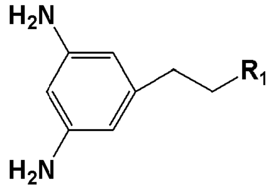
[1] 1. A method of preparing a branched diamine compound represented by Chemical Formula 1 below, which comprises the steps of:

a) reacting a C_1 to C_{16} 2-alkylmalonic acid 1,3-di- *tert*-butyl ester derivative with 3,5-dinitrobenzoyl chloride in a solvent to prepare a C_1 to C_{16} dinitrophenyl alkene compound;

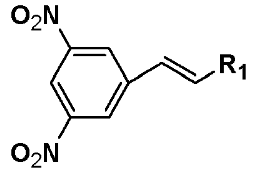
b) adding BF_3Et_2O/Et_3SH to said dinitrophenyl alkene compound and dehydrating it to prepare a dinitroalkenyl benzene compound represented by Chemical Formula 3 below; and

c) reducing said compound represented by Chemical Formula 3 with hydrogen in the presence of a Pd/C catalyst:

Chemical Formula 1



[2] Chemical Formula 3



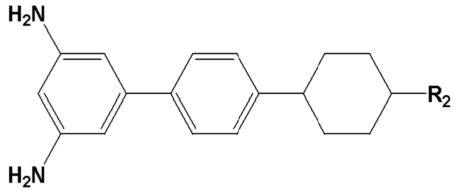
wherein R_1 is a C_1 to C_{18} alkyl.

2. A method of preparing a branched diamine compound represented by Chemical Formula 2 below, which comprises the steps of:

a) reacting a C_1 to C_{10} 4-(alkylcyclohexyl)benzyl boronic acid compound with 1-bromo-3,5-dinitrobenzene to prepare a compound represented by Chemical Formula 4 below; and

b) reducing said compound represented by Chemical Formula 4 with hydrogen in the presence of a Pd/C catalyst:

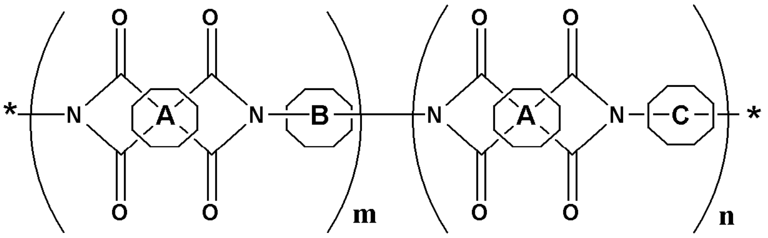
Chemical Formula 2



wherein R_2 is a C_1 to C_{10} alkyl or alkoxy.

3. A polyimide resin for non-rubbing vertical alignment materials represented by the following Chemical Formula 7:

Chemical Formula 7



wherein A is a quaternary organic group, B is a branched secondary organic group, C is a secondary organic group with no side chain, and m ? n, and when m is 1, n is an integer of 1 or larger .

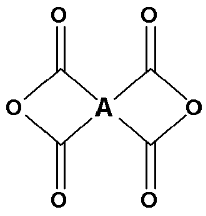
4. The polyimide resin according to Claim 3, wherein the length of side chains of said polyimide is 0.8 to 1.5 times the major-axis length of liquid crystal molecules, and the spacing of side chains is 1.5 to 3.5 times the major-axis length of liquid crystal molecules.

5. A method of preparing a polyimide resin for non-rubbing vertical alignment materials represented by Chemical Formula 7 below, which comprises the steps of:

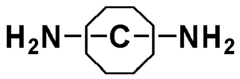
a) reacting said branched diamine compound of Claim 1 or 2 respectively represented by Chemical Formula 1 or 2 with a tetracarboxylic acid anhydride represented by Chemical Formula 5 below and a diamine compound with no side chain represented by Chemical Formula 6 below in a solvent to prepare a polyamic-acid-based block copolymer; and

b) heat treating said polyamic-acid-based block copolymer to convert it to a polyimide by dehydration-cyclization:

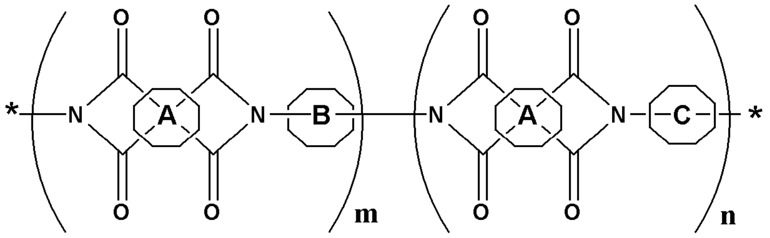
Chemical Formula 5



Chemical Formula 6



Chemical Formula 7



wherein A is a quaternary organic group, B is a branched secondary organic group, C is a secondary organic group with no side chain, and m ? n, and when m is 1, n is an integer of 1 or larger .

6. The method of preparing a polyimide resin according to Claim 5, wherein said solvent is one or more inert solvents selected from the group consisting of N-methyl-2-pyrrolidone (NMP), N,N-dimethylformamide (DMF), dimethylsulfoxide (DMSO), hexamethylphosphoamide, tetramethylenesulfone, *p* -chlorophenol, *p* -bromophenol, 2-chloro-4-hydroxytoluene, dioxane, tetrahydrofuran (THF), and cyclohexanone.

7. A liquid crystal orientation film prepared using the polyimide resin of Claim 3.

8. A liquid crystal display comprising the liquid crystal orientation film of Claim 7.