Summary

Problem that Invention is to Solve

[0012]

It is generally known that a carbonyl compound or an acetal compound in the raw material deteriorates the color tone at the time of production of a polyester, but among the compounds having the same carbonyl group or olefin bond, the degree of effect on coloring of the produced polyester differs based on the structure of each compound. The present inventors have focused attention on the fact that this effect appears to a most prominent degree, among polyesters, in PBT and PBS, and among polyurethanes, in a thermoplastic polyurethane and a polyester polyol that is a prepolymer thereof. For example, when PBT is produced using a biomass-resource-derived 1,4BG as a raw material, the deterioration of color tone is more outstanding than in the case of using the conventional 1,4BG produced from a fossil fuel such as petroleum. The reason therefor is that a carbonyl compound by-produced at the time of production of a biomass-resource-derived 1,4BG and contained in 1,4BG has a significant effect on the deterioration of color tone of PBT, compared with a carbonyl compound by-produced at the time of producing the conventional 1,4BG from a fossil fuel such as petroleum, but the reason has not been heretofore sufficiently clarified.

[0013]

The present disclosure has been made by taking into account those problems, and an object of the present disclosure is to provide methods for producing a polyester and a polyurethane by using a dicarboxylic acid component and a biomass-resource-derived diol as raw materials, where a polyester and a polyurethane are efficiently produced with good color tone.

Means for Solving Problem

[0014]

As a result of intensive studies to attain the above-described object, the present inventors have found that at the time of producing a polyester and a polyurethane by using a raw material diol derived from biomass resources, such as biomass-resource-derived 1,4BG, the content of, among carbonyl compounds in the raw material diol, a cyclic carbonyl compound having a carbon atom number of 5 or 6 is strongly correlated with the color tone of the obtained polyester and polyurethane. Then, it has been found that the color tone of the

obtained polyester and polyurethane is improved by controlling the content of the compound above in the raw material diol to a specific range.

[0015]

That is, the gist of the present disclosure resides in the following [1] to [22].

[0016]

[1] A method for producing a polyester by using, as raw materials, a dicarboxylic acid component and a diol produced directly from a biomass-resource-derived substance by a fermentation process,

wherein a content of a cyclic carbonyl compound having a carbon atom number of 5 or 6 in the diol is 12 ppm by mass or less.

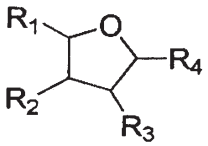
[0017]

[2] The method for producing a polyester as described in [1] above,

wherein the cyclic carbonyl compound having a carbon atom number of 5 or 6 contains a compound having a structure represented by the following formula (I):

[0018]

[Chem. 1]



Formula (I)

[0019]

(wherein in formula (I), each of R_1 to R_4 independently represents a hydrogen atom, a methyl group, a formyl group or an acetyl group, any one of R_1 to R_4 is a formyl group or an acetyl group, and the total number of carbon atoms contained in respective groups of R_1 to R_4 is 2 or less).

[0020]

[3] The method for producing a polyester as described in [1] above,

wherein the cyclic carbonyl compound having a carbon atom number of 5 or 6 contains a compound having a structure represented by the following formula (II):

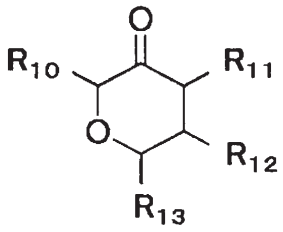
[0021]

[Chem. 2]

content of the compound having a structure represented by formula (III) in the diol is 6 ppm by mass or less:

[0051]

[Chem. 9]



Formula (III)

[0052]

(wherein in formula (III), each of R_{10} to R_{13} independently represents a methyl group or a hydrogen atom, and the total number of carbon atoms contained in respective groups of R_{10} to R_{13} is 1 or less).

[0053]

[20] The method for producing a polyurethane as described in any one of [16] to [19] above,

wherein the diol is 1,4-butanediol, and

the polyester polyol is polybutylene adipate.

[0054]

[21] The method for producing a polyurethane as described in [20] above,

wherein the 1,4-butanediol contains from 1 to 99 ppm by mass of 1-acetoxy-4-hydroxybutane.

[0055]

[22] The method for producing a polyurethane as described in any one of [16] to [21] above,

wherein a content of a nitrogen atom compound in the diol is from 0.1 to 50 ppm by mass in terms of nitrogen atom.

[0055a]

In one aspect, the present disclosure refers to a method for producing a polyester comprising: performing a reaction by using, as raw materials, a dicarboxylic acid component, and a diol produced directly from a biomass-resource-derived substance by a fermentation process, wherein a content of a cyclic carbonyl compound having a carbon atom number of 5 or 6 in the diol is from 0.01 ppm to 12 ppm by mass, and wherein said diol produced directly from a biomass-resource-derived substance by a fermentation process is selected from the group consisting of ethylene glycol, 2-methyl-1,3-propanediol, neopentyl glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,4-cyclohexanediol, 1,4-cyclohexanedimethanol, and isosorbide.

[0055b]

In another aspect, the present disclosure refers to a method for producing a polyester polyol, comprising: performing reaction by using, as raw materials, a dicarboxylic acid component and a diol produced directly from a biomass-resource-derived substance by a fermentation process, wherein a content of a cyclic carbonyl compound having a carbon atom number of 5 or 6 in the diol is from 0.01 ppm to 12 ppm by mass, and wherein said diol produced directly from a biomass-resource-derived substance by a fermentation process is selected from the group consisting of ethylene glycol, 2-methyl-1,3-propanediol, neopentyl glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,4-cyclohexanediol, 1,4-cyclohexanedimethanol, and isosorbide.

[0055c]

In another aspect, the present disclosure refers to a method for producing a polyurethane, comprising: reacting a polyester polyol produced by the production method of a polyester polyol as disclosed herein with an isocyanate compound.

[0055d]

In yet another aspect, the present disclosure refers to a method for producing a polyurethane, comprising: reacting a polyester polyol and an isocyanate compound, wherein the polyester polyol is produced by an esterification and/or transesterification reaction of a dicarboxylic acid and a diol, wherein the diol is produced directly from a biomass-resource-derived substance by a fermentation process and a content of a cyclic carbonyl compound having a carbon atom number of 5 or 6 in the diol is from 0.01 ppm to 12 ppm by mass, and wherein said diol produced directly from a biomass-resource-derived substance by a fermentation process is selected from the group consisting of ethylene glycol, 2-methyl-1,3-propanediol, neopentyl glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,4-cyclohexanediol, 1,4-cyclohexanedimethanol, and isosorbide.

Effects of Invention

[0056]

According to the present invention, a polyester and a polyurethane each having high quality and good color tone can be produced using a diol derived from biomass resources.

CLAIMS

[Claim 1]

A method for producing a polyester comprising:

performing a reaction by using, as raw materials, a dicarboxylic acid component, and a diol produced directly from a biomass-resource-derived substance by a fermentation process,

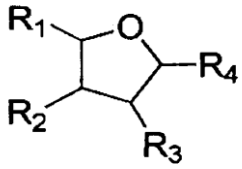
wherein a content of a cyclic carbonyl compound having a carbon atom number of 5 or 6 in the diol is from 0.01 ppm to 12 ppm by mass, and

wherein said diol produced directly from a biomass-resource-derived substance by a fermentation process is selected from the group consisting of ethylene glycol, 2-methyl-1,3-propanediol, neopentyl glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,4-cyclohexanediol, 1,4-cyclohexanedimethanol, and isosorbide.

[Claim 2]

The method for producing a polyester according to claim 1,

wherein the cyclic carbonyl compound having a carbon atom number of 5 or 6 contains a compound having a structure represented by the following formula (I):



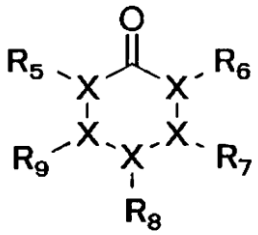
Formula (I)

wherein in formula (I), each of R_1 to R_4 independently represents a hydrogen atom, a methyl group, a formyl group or an acetyl group, with the proviso that one of R_1 to R_4 is a formyl group or an acetyl group, and the total number of carbon atoms contained in respective groups of R_1 to R_4 is 2 or less.

[Claim 3]

The method for producing a polyester according to claim 1,

wherein the cyclic carbonyl compound having a carbon atom number of 5 or 6 contains a compound having a structure represented by the following formula (II):



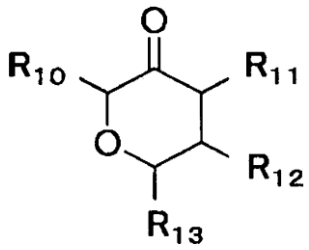
Formula (II)

wherein in formula (II), X represents a carbon atom or an oxygen atom, with the proviso that 1 X is an oxygen atom, each of R_5 to R_9 independently represents a methyl group or a hydrogen atom, and the total number of carbon atoms contained in respective groups of R_5 to R_9 is 1 or less.

[Claim 4]

The method for producing a polyester according to claim 1,

wherein the cyclic carbonyl compound having a carbon atom number of 5 or 6 contains a compound having a structure represented by the following formula (III) and a content of the compound having a structure represented by formula (III) in the diol is 6 ppm by mass or less:



Formula (III)

wherein in formula (III), each of R_{10} to R_{13} independently represents a methyl group or a hydrogen atom, and the total number of carbon atoms contained in respective groups of R_{10} to R_{13} is 1 or less.

[Claim 5]

The method for producing a polyester according to claim 1,

wherein the diol is 1,4-butanediol,

the dicarboxylic acid component is at least one of a terephthalic acid and a terephthalic acid alkylate, and

the polyester is polybutylene terephthalate.

[Claim 6]

The method for producing a polyester according to claim 5,

wherein the 1,4-butanediol contains from 1 to 99 ppm by mass of 1-acetoxy-4-hydroxybutane.

[Claim 7]

The method for producing a polyester according to claim 1,

wherein a content of a nitrogen atom compound in the diol is from 0.1 to 50 ppm by mass in terms of nitrogen atom.

[Claim 8]

The method for producing a polyester according to claim 1, further comprising, prior to said performing a reaction, subjecting a biomass resource to a fermentation process wherein said fermentation process comprises pretreating said biomass resource and further subjecting the biomass resource to saccharification.

[Claim 9]

A method for producing a polyester polyol, comprising:

performing reaction by using, as raw materials, a dicarboxylic acid component and a diol produced directly from a biomass-resource-derived substance by a fermentation process,

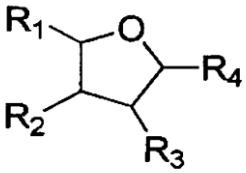
wherein a content of a cyclic carbonyl compound having a carbon atom number of 5 or 6 in the diol is from 0.01 ppm to 12 ppm by mass, and

wherein said diol produced directly from a biomass-resource-derived substance by a fermentation process is selected from the group consisting of ethylene glycol, 2-methyl-1,3-propanediol, neopentyl glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,4-cyclohexanediol, 1,4-cyclohexanedimethanol, and isosorbide.

[Claim 10]

The method for producing a polyester polyol according to claim 9,

wherein the cyclic carbonyl compound having a carbon atom number of 5 or 6 contains a compound having a structure represented by the following formula (I):



Formula (I)

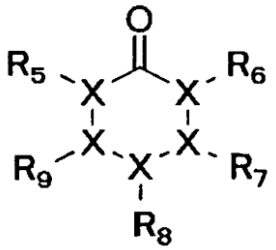
wherein in formula (I), each of R_1 to R_4 independently represents a hydrogen atom, a methyl group, a formyl group or an acetyl group, with the proviso that one of R_1 to R_4 is a formyl group or an acetyl group, and the total number of carbon atoms contained in respective

groups of R_1 to R_4 is 2 or less.

[Claim 11]

The method for producing a polyester polyol according to claim 9,

wherein the cyclic carbonyl compound having a carbon atom number of 5 or 6 contains a compound having a structure represented by the following formula (II):



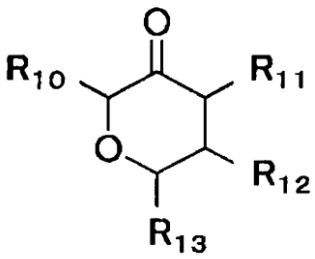
Formula (II)

wherein in formula (II), X represents a carbon atom or an oxygen atom, with the proviso that 1 X is an oxygen atom, each of R_5 to R_9 independently represents a methyl group or a hydrogen atom, and the total number of carbon atoms contained in respective groups of R_5 to R_9 is 1 or less.

[Claim 12]

The method for producing a polyester polyol according to claim 9,

wherein the cyclic carbonyl compound having a carbon atom number of 5 or 6 contains a compound having a structure represented by the following formula (III):



Formula (III)

wherein in formula (III), each of R_{10} to R_{13} independently represents a methyl group or a hydrogen atom, and the total number of carbon atoms contained in respective groups of R_{10} to R_{13} is 1 or less.

[Claim 13]

The method for producing a polyester polyol according to claim 10,

wherein the diol is 1,4-butanediol,

the dicarboxylic acid component is adipic acid, and

the polyester polyol is polybutylene adipate.

[Claim 14]

The method for producing a polyester polyol according to claim 13,

wherein the 1,4-butanediol contains from 1 to 99 ppm by mass of 1-acetoxy-4-hydroxybutane.

[Claim 15]

The method for producing a polyester polyol according to claim 9,

wherein a content of a nitrogen atom compound in the diol is from 0.1 to 50 ppm by mass in terms of nitrogen atom.

[Claim 16]

The method for producing a polyester polyol according to claim 9, further comprising prior to said performing reaction subjecting a biomass resource to a fermentation process wherein said fermentation process comprises pretreating said biomass resource and further subjecting the biomass resource to saccharification.

[Claim 17]

A method for producing a polyurethane, comprising:

reacting a polyester polyol produced by the production method of a polyester polyol according to claim 9 with an isocyanate compound.

[Claim 18]

A method for producing a polyurethane, comprising:

reacting a polyester polyol and an isocyanate compound,

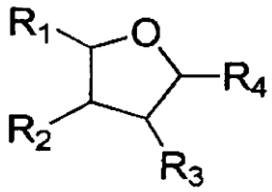
wherein the polyester polyol is produced by an esterification and/or transesterification reaction of a dicarboxylic acid and a diol, wherein the diol is produced directly from a biomass-resource-derived substance by a fermentation process and a content of a cyclic carbonyl compound having a carbon atom number of 5 or 6 in the diol is from 0.01 ppm to 12 ppm by mass, and

wherein said diol produced directly from a biomass-resource-derived substance by a fermentation process is selected from the group consisting of ethylene glycol, 2-methyl-1,3-propanediol, neopentyl glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,4-cyclohexanediol, 1,4-cyclohexanedimethanol, and isosorbide.

[Claim 19]

The method for producing a polyurethane according to claim 18,

wherein the cyclic carbonyl compound having a carbon atom number of 5 or 6 contains a compound having a structure represented by the following formula (I):



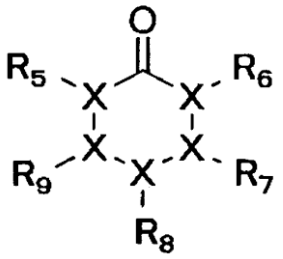
Formula (I)

wherein in formula (I), each of R_1 to R_4 independently represents a hydrogen atom, a methyl group, a formyl group or an acetyl group, with the proviso that one of R_1 to R_4 is a formyl group or an acetyl group, and the total number of carbon atoms contained in respective groups of R_1 to R_4 is 2 or less.

[Claim 20]

The method for producing a polyurethane according to claim 18,

wherein the cyclic carbonyl compound having a carbon atom number of 5 or 6 contains a compound having a structure represented by the following formula (II):



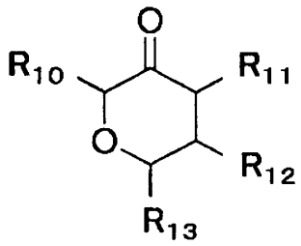
Formula (II)

wherein in formula (II), X represents a carbon atom or an oxygen atom, with the proviso that 1 X is an oxygen atom, each of R_5 to R_9 independently represents a methyl group or a hydrogen atom, and the total number of carbon atoms contained in respective groups of R_5 to R_9 is 1 or less.

[Claim 21]

The method for producing a polyurethane according to claim 18,

wherein the cyclic carbonyl compound having a carbon atom number of 5 or 6 contains a compound having a structure represented by the following formula (III) and a content of the compound having a structure represented by formula (III) in the diol is 6 ppm by mass or less:



Formula (III)

wherein in formula (III), each of R_{10} to R_{13} independently represents a methyl group or a hydrogen atom, and the total number of carbon atoms contained in respective groups of R_{10} to R_{13} is 1 or less.

[Claim 22]

The method for producing a polyurethane according to claim 18,

wherein the diol is 1,4-butanediol, and

the polyester polyol is polybutylene adipate.

[Claim 23]

The method for producing a polyurethane according to claim 22,

wherein the 1,4-butanediol contains from 1 to 99 ppm by mass of 1-acetoxy-4-hydroxybutane.

[Claim 24]

The method for producing a polyurethane according to claim 18,

wherein a content of a nitrogen atom compound in the diol is from 0.1 to 50 ppm by mass in terms of nitrogen atom.

[Claim 25]

The method for producing a polyurethane according to claim 18, further comprising prior to said reacting a polyester polyol and an isocyanate compound, subjecting a biomass resource to a fermentation process wherein said fermentation process comprises pretreating said biomass resource and further subjecting the biomass resource to saccharification to produce said diol.