

WHOLLY AROMATIC POLYESTER AMIDE AND METHOD FOR PRODUCING THE SAME

TECHNICAL FIELD

The present invention relates to a wholly aromatic polyester amide and a method for producing the same.

BACKGROUND ART

A liquid crystal polymer has been used suitably and widely as high function engineering plastics because of having excellent fluidity, mechanical strength, heat resistance, chemical resistance, electrical properties and the like with good balance. As the liquid crystal polymer, a wholly aromatic polyester amide is used together with a wholly aromatic polyester. For example, Patent Document 1 discloses an aromatic polyester amide obtained by reacting p-aminophenol, 4-hydroxybenzoic acid, 4,4'-dihydroxybiphenyl, terephthalic acid and isophthalic acid. Patent Document 2 discloses an aromatic polyester amide obtained by reacting p-aminophenol, 4-hydroxybenzoic acid, 6-hydroxy-2-naphthoic acid, 4,4'-dihydroxybiphenyl and terephthalic acid.

Patent Document 1: Japanese Unexamined Patent Application, Publication No. H02-086623

Patent Document 2: Japanese Unexamined Patent Application, Publication No. H05-170902

DISCLOSURE OF THE INVENTION

Problems to be Solved by the Invention

However, the wholly aromatic polyester amide mentioned in Patent Document 1 has insufficient heat resistance, and the wholly aromatic polyester amide mentioned in Patent Document 2 does not sufficiently achieve a balance between melting point lowering and heat resistance.

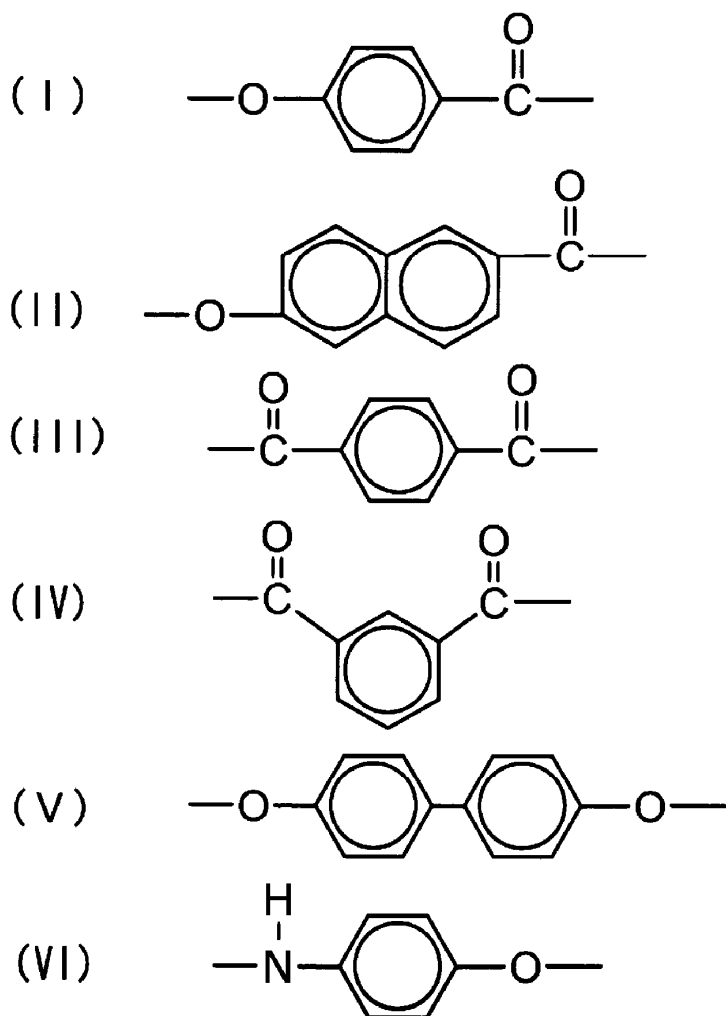
In light of the problems mentioned above, an object of the present invention is to provide a wholly aromatic polyester amide sufficiently achieving a balance between melting point lowering and heat resistance, and a method for producing the same.

Means for Solving the Problems

The present inventors have intensively studied so as to solve the problems mentioned above. As a result, they have found that the problems mentioned above can be solved by a wholly aromatic polyester amide consisting of a constituent unit derived from 4-hydroxybenzoic acid, a constituent unit derived from 6-hydroxy-2-naphthoic acid, a constituent unit derived from 1,4-phenylene dicarboxylic acid, a constituent unit derived from 1,3-phenylene dicarboxylic acid, a constituent unit derived from 4,4'-dihydroxybiphenyl and a constituent unit derived from N-acetyl-p-aminophenol, wherein a content of each constituent unit is in a specific range and a content of a total of the constituent unit derived from 6-hydroxy-2-naphthoic acid and the constituent unit derived from 1,3-phenylene dicarboxylic acid is in a specific range, and a molar ratio of the constituent unit derived from N-acetyl-p-aminophenol to a total of the constituent unit derived from

4,4'-dihydroxybiphenyl and the constituent unit derived from N-acetyl-p-aminophenol is in a specific range, and thus the present invention has been completed. More specifically, the present invention provides the following.

(1) A wholly aromatic polyester amide that exhibits optical anisotropy when melted, the wholly aromatic polyester amide consisting of the following constituent units (I) to (VI) as essential constitutional components:



wherein

a content of the constituent unit (I) is 50 to 70 mol% with respect to all of the constituent units;

a content of the constituent unit (II) is 0.5 mol% or higher and lower than 4.5 mol% with respect to all of the constituent units;

a content of the constituent unit (III) is 10.25 to 22.25 mol% with respect to all of the constituent units;

a content of the constituent unit (IV) is 0.5 mol% or higher and lower than 4.5 mol% with respect to all of the constituent units;

a content of the constituent unit (V) is 5.75 to 23.75 mol% with respect to all of the constituent units;

a content of the constituent unit (VI) is 1 to 7 mol% with respect to all of the constituent units;

a content of a total of the constituent unit (II) and the constituent unit (IV) is 1 mol% or higher and lower than 5 mol% with respect to all of the constituent units;

a content of a total of the constituent units (I) to (VI) is 100 mol% with respect to all of the constituent units; and

a molar ratio of the constituent unit (VI) to a total of the constituent unit (V) and the constituent unit (VI) is 0.04 to 0.37.

(2) The wholly aromatic polyester amide according to (1), wherein a mole number of a total of the constituent unit (III) and the constituent unit (IV) is 1 to 1.1 times a mole number of a total of the constituent unit (V) and the constituent unit (VI), or a mole number of a total of the constituent unit (V) and the constituent unit (VI) is 1 to 1.1 times a mole number of a total of the constituent unit (III) and the

constituent unit (IV).

(3) The wholly aromatic polyester amide according to (1) or (2), wherein a melting point of the wholly aromatic polyester amide is 360°C or lower.

(4) The wholly aromatic polyester amide according to any one of (1) to (3), wherein a deflection temperature under load of the wholly aromatic polyester amide is 260°C or higher; and the deflection temperature under load is measured in a state of a polyester amide resin composition obtained by melt-kneading 60 mass% of the wholly aromatic polyester amide with 40 mass% of a milled fiber having an average fiber diameter of 11 μm and an average fiber length of 75 μm at a melting point of the wholly aromatic polyester amide + 20°C.

(5) The wholly aromatic polyester amide according to any one of (1) to (4), wherein a melt viscosity at a temperature that is 10 to 30°C higher than a melting point of the wholly aromatic polyester amide and a shear rate of 1,000/sec is 500 Pa·s or lower.

(6) A method for producing a wholly aromatic polyester amide that exhibits optical anisotropy when melted,

the method comprising acylating 4-hydroxybenzoic acid, 6-hydroxy-2-naphthoic acid, 4,4'-dihydroxybiphenyl, and N-acetyl-p-aminophenol with a fatty acid anhydride in the presence of a fatty acid metal salt and conducting transesterification with 1,4-phenylene dicarboxylic acid and 1,3-phenylene dicarboxylic acid, wherein

with respect to all of the monomers consisting of 4-

hydroxybenzoic acid, 6-hydroxy-2-naphthoic acid, 1,4-phenylene dicarboxylic acid, 1,3-phenylene dicarboxylic acid, 4,4'-dihydroxybiphenyl, and N-acetyl-p-aminophenol, an amount used of 4-hydroxybenzoic acid is 50 to 70 mol%, an amount used of 6-hydroxy-2-naphthoic acid is 0.5 mol% or higher and lower than 4.5 mol%, an amount used of 1,4-phenylene dicarboxylic acid is 10.25 to 22.25 mol%, an amount used of 1,3-phenylene dicarboxylic acid is 0.5 mol% or higher and lower than 4.5 mol%, an amount used of 4,4'-dihydroxybiphenyl is 5.75 to 23.75 mol%, an amount used of N-acetyl-p-aminophenol is 1 to 7 mol%, an amount used of a total of 6-hydroxy-2-naphthoic acid and 1,3-phenylene dicarboxylic acid is 1 mol% or higher and lower than 5 mol%, and an amount used of a total of 4-hydroxybenzoic acid, 6-hydroxy-2-naphthoic acid, 1,4-phenylene dicarboxylic acid, 1,3-phenylene dicarboxylic acid, 4,4'-dihydroxybiphenyl, and N-acetyl-p-aminophenol is 100 mol%;

a molar ratio of an amount used of N-acetyl-p-aminophenol to an amount used of a total of 4,4'-dihydroxybiphenyl and N-acetyl-p-aminophenol is 0.04 to 0.37; and

an amount used of the fatty acid anhydride is 1.02 to 1.04 times a hydroxy equivalent of a total of 4-hydroxybenzoic acid, 6-hydroxy-2-naphthoic acid, 4,4'-dihydroxybiphenyl, and N-acetyl-p-aminophenol.

(7) The method according to (6), wherein the fatty acid metal salt is an acetic acid metal salt, and the fatty acid anhydride is acetic anhydride.

(8) The method according to (6) or (7), wherein a mole

number of a total of 1,4-phenylene dicarboxylic acid and 1,3-phenylene dicarboxylic acid is 1 to 1.1 times a mole number of a total of 4,4'-dihydroxybiphenyl and N-acetyl-p-aminophenol, or a mole number of a total of 4,4'-dihydroxybiphenyl and N-acetyl-p-aminophenol is 1 to 1.1 times a mole number of a total of 1,4-phenylene dicarboxylic acid and 1,3-phenylene dicarboxylic acid.

Effects of the Invention

According to the present invention, the wholly aromatic polyester amide of the present invention, which consists of specific constituent units and exhibits optical anisotropy when melted, sufficiently achieves a balance between melting point lowering and heat resistance.

The wholly aromatic polyester amide of the present invention can undergo injection molding, extrusion molding, compression molding and the like without using a molding machine having a special structure since its molding temperature is not very high.

As mentioned above, the wholly aromatic polyester amide of the present invention is excellent in moldability and can be molded using various molding machines, thereby being capable of being easily processed into various three-dimensional molded articles, fibers, films and the like. Therefore, it is possible to easily obtain molded articles such as a connector, a CPU socket, a relay switch component, a bobbin, an actuator, a noise reduction filter case, or a heat fixing roll of OA equipment, which are suitable applications of the wholly

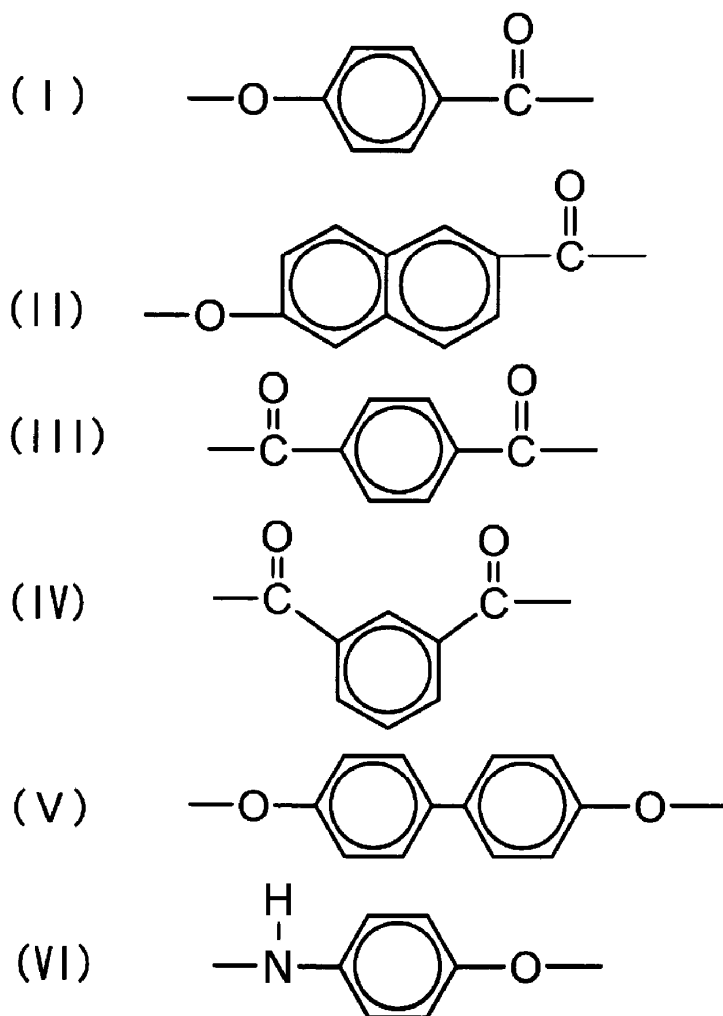
aromatic polyester amide of the present invention.

PREFERRED MODE FOR CARRYING OUT THE INVENTION

Embodiments of the present invention will be described below. The present invention is not limited to the following embodiments.

<Wholly Aromatic Polyester Amide>

The wholly aromatic polyester amide of the present invention consists of the following constituent unit (I), the following constituent unit (II), the following constituent unit (III), the following constituent unit (IV), the following constituent unit (V) and the following constituent unit (VI).



The constituent unit (I) is derived from 4-hydroxybenzoic acid (hereinafter also referred to as "HBA"). The wholly aromatic polyester amide of the present invention includes 50 to 70 mol% of the constituent unit (I) with respect to all of the constituent units. If the content of the constituent unit (I) is lower than 50 mol% or higher than 70 mol%, at least one of melting point lowering and heat resistance easily becomes insufficient. From the viewpoint of the achievement of a balance between melting point lowering and heat resistance, the content of the constituent unit (I) is preferably 54 to 67 mol%, and more preferably 58 to 64 mol%.

The constituent unit (II) is derived from 6-hydroxy-2-naphthoic acid (hereinafter also referred to as "HNA"). The wholly aromatic polyester amide of the present invention includes 0.5 mol% or higher and lower than 4.5 mol% of the constituent unit (II) with respect to all of the constituent units. If the content of the constituent unit (II) is lower than 0.5 mol% or 4.5 mol% or higher, at least one of melting point lowering and heat resistance easily becomes insufficient. From the viewpoint of the achievement of a balance between melting point lowering and heat resistance, the content of the constituent unit (II) is preferably 0.75 to 3.75 mol%, and more preferably 1 to 3 mol%.

The constituent unit (III) is derived from 1,4-phenylene dicarboxylic acid (hereinafter also referred to as "TA"). The wholly aromatic polyester amide of the present invention includes 10.25 to 22.25 mol% of the constituent unit (III) with respect to all of the constituent units. If the content of the constituent unit (III) is lower than 10.25 mol% or higher than 22.25 mol%, at least one of melting point lowering and heat resistance easily becomes insufficient. From the viewpoint of the achievement of a balance between melting point lowering and heat resistance, the content of the constituent unit (III) is preferably 12.963 to 20.75 mol%, and more preferably 15.675 to 19.25 mol%.

The constituent unit (IV) is derived from 1,3-phenylene dicarboxylic acid (hereinafter also referred to as "IA"). The wholly aromatic polyester amide of the present invention

includes 0.5 mol% or higher and lower than 4.5 mol% of the constituent unit (IV) with respect to all of the constituent units. If the content of the constituent unit (IV) is lower than 0.5 mol%, or 4.5 mol% or higher, at least one of melting point lowering and heat resistance easily becomes insufficient. From the viewpoint of the achievement of a balance between melting point lowering and heat resistance, the content of the constituent unit (IV) is preferably 0.5 to 3.75 mol%, and more preferably 0.5 to 3 mol%.

The constituent unit (V) is derived from 4,4'-dihydroxybiphenyl (hereinafter also referred to as "BP"). The wholly aromatic polyester amide of the present invention includes 5.75 to 23.75 mol% of the constituent unit (V) with respect to all of the constituent units. If the content of the constituent unit (V) is lower than 5.75 mol% or higher than 23.75 mol%, at least one of melting point lowering and heat resistance easily becomes insufficient. From the viewpoint of the achievement of a balance between melting point lowering and heat resistance, the content of the constituent unit (V) is preferably 8.5 to 20.375 mol%, and more preferably 11.25 to 17 mol% (e.g., 11.675 to 17 mol%).

The constituent unit (VI) is derived from N-acetyl-p-aminophenol (hereinafter also referred to as "APAP"). The wholly aromatic polyester amide of the present invention includes 1 to 7 mol% of the constituent unit (VI) with respect to all of the constituent units. If the content of the constituent unit (VI) is lower than 1 mol% or higher than 7

mol%, at least one of melting point lowering and heat resistance easily becomes insufficient. From the viewpoint of the achievement of a balance between melting point lowering and heat resistance, the content of the constituent unit (VI) is preferably 1.5 to 7 mol%, and more preferably 2 to 7 mol%.

The wholly aromatic polyester amide of the present invention includes 1 mol% or higher and lower than 5 mol% of a total of the constituent unit (II) and the constituent unit (IV) with respect to all of the constituent units. In the wholly aromatic polyester amide, when the flexible constituent unit (II) having a naphthalene skeleton and the flexible constituent unit (IV) having a benzene skeleton coexist in a total amount in the above range, it is easy to sufficiently achieve a balance between melting point lowering and heat resistance. If the content of the total is lower than 1 mol%, the proportion of the flexible constituent unit excessively decreases, so that the melting point lowering easily becomes insufficient. If the content of the total is 5 mol% or higher, the proportion of the flexible constituent unit excessively increases, so that the heat resistance easily becomes insufficient. From the viewpoint of the achievement of a balance between melting point lowering and heat resistance, the content of the total is preferably 1.75 to 4.75 mol%, and more preferably 2.5 to 4.5 mol%.

In the wholly aromatic polyester amide of the present invention, a molar ratio of the constituent unit (VI) to a total of the constituent unit (V) and the constituent unit

(VI) is 0.04 to 0.37. If the molar ratio is lower than 0.04, the proportion of the constituent unit having a biphenyl skeleton increases, so that the crystallinity of the wholly aromatic polyester amide deteriorates, and thus the achievement of a balance between melting point lowering and heat resistance easily becomes insufficient. If the molar ratio is higher than 0.37, hetero bonds other than the ester bond increase, so that the crystallinity of the wholly aromatic polyester amide deteriorates, and thus the achievement of a balance between melting point lowering and heat resistance easily becomes insufficient. From the viewpoint of the achievement of a balance between melting point lowering and heat resistance, the molar ratio is preferably 0.07 to 0.36, and more preferably 0.11 to 0.35.

From the viewpoint of the achievement of a balance between melting point lowering and heat resistance, a mole number of a total of the constituent unit (III) and the constituent unit (IV) (hereinafter also referred to as "mole number 1A") is preferably 1 to 1.1 times a mole number of a total of the constituent unit (V) and the constituent unit (VI) (hereinafter also referred to as "mole number 2A"), or a mole number of a total of the constituent unit (V) and the constituent unit (VI) is preferably 1 to 1.1 times a mole number of a total of the constituent unit (III) and the constituent unit (IV). The mole number 1A is more preferably 1.02 to 1.06 times the mole number 2A, or the mole number 2A is more preferably 1.02 to 1.06 times the mole number 1A. The

mole number 1A is still more preferably 1.024 to 1.056 times the mole number 2A, or the mole number 2A is still more preferably 1.024 to 1.056 times the mole number 1A.

As mentioned above, the wholly aromatic polyester amide of the present invention includes each of specific constituent units (I) to (VI) and a total of the constituent unit (II) and the constituent unit (IV) in a specific amount with respect to all of the constituent units, and a molar ratio of the constituent unit (VI) to a total of the constituent unit (V) and the constituent unit (VI) is in a specific range, so that the achievement of a balance between melting point lowering and heat resistance is sufficient. The wholly aromatic polyester amide of the present invention includes 100 mol% of a total of the constituent units (I) to (VI) with respect to all of the constituent units.

Examples of an index representing the heat resistance include a deflection temperature under load (hereinafter also referred to as "DTUL"). DTUL is preferably 260°C or higher since the heat resistance tends to become higher. DTUL is a value measured in a state of a polyester amide resin composition obtained by melt-kneading 60 mass% of the wholly aromatic polyester amide with 40 mass% of a milled fiber having an average fiber diameter of 11 μm and an average fiber length of 75 μm at a melting point of the wholly aromatic polyester amide + 20°C, and can be measured in conformity with ISO 75-1,2. From the viewpoint of the achievement of a balance between melting point lowering and heat resistance, DTUL is

preferably 265°C or higher and 310°C or lower, and more preferably 267 to 300°C.

A method for producing a wholly aromatic polyester amide of the present invention will be described below. The wholly aromatic polyester amide of the present invention is polymerized using a direct polymerization method, a transesterification method or the like. In the case of polymerization, it is possible to use a melt polymerization method, a solution polymerization method, a slurry polymerization method, a solid phase polymerization method and the like, or a combination of two or more thereof. It is possible to preferably use a melt polymerization method, or a combination of a melt polymerization method and a solid phase polymerization method.

In the present invention, in the case of polymerization, it is possible to use an acylating agent for a polymerizable monomer or to use a terminal-activated monomer as an acid chloride derivative. Examples of the acylating agent include fatty acid anhydrides such as acetic anhydride.

In the case of polymerization, various catalysts can be used, and examples of typical ones include dialkyltin oxide, diaryltin oxide, titanium dioxide, alkoxytitanium silicates, titanium alcoholates, fatty acid metal salts, and Lewis acid salts such as BF_3 , and fatty acid metal salts are preferable. An amount used of the catalyst is generally about 0.001 to 1 mass%, and particularly preferably about 0.003 to 0.2 mass%, with respect to the total mass of the monomer.

When solution polymerization or slurry polymerization is performed, it is possible to use, as the solvent, liquid paraffin, high heat resistant synthetic oil, inert mineral oil and the like.

The reaction conditions are, for example, as follows: a reaction temperature of 200 to 380°C and a final ultimate pressure of 0.1 to 760 Torr (i.e., 13 to 101,080 Pa). Particularly in the melting reaction, for example, the reaction temperature is 260 to 380°C, and preferably 300 to 360°C, and the final ultimate pressure is 1 to 100 Torr (i.e., 133 to 13,300 Pa), and preferably 1 to 50 Torr (i.e., 133 to 6,670 Pa).

The reaction can be started after charging all of raw material monomers (HBA, HNA, TA, IA, BP, and APAP), an acylating agent, and a catalyst in the same reaction vessel (one-step system), and it is also possible to acylate hydroxy groups of raw material monomers HBA, HNA, BP, and APAP using an acylating agent, followed by reaction with carboxyl groups of TA and IA (two-step system).

After the temperature inside the reaction system reaches a predetermined temperature, pressure reduction is started and the pressure reaches a predetermined vacuum degree, and then the solution polymerization is performed. After torque of a stirrer reaches a predetermined value, an inert gas is introduced to turn from a depressurized state to a predetermined pressurized state via a normal pressure, and then the wholly aromatic polyester amide is discharged from

the reaction system.

It is possible to increase the molecular weight of the wholly aromatic polyester amide produced by the above polymerization method, by further subjection to solid phase polymerization where heating is preformed under normal pressure or reduced pressure in the inert gas. Preferable conditions of the solid phase polymerization reaction are as follows: a reaction temperature is 230 to 350°C, and preferably 260 to 330°C, and a final ultimate pressure is 10 to 760 Torr (i.e., 1,330 to 101,080 Pa).

The method for producing a wholly aromatic polyester amide of the present invention preferably includes acylating 4-hydroxybenzoic acid, 6-hydroxy-2-naphthoic acid, 4,4'-dihydroxybiphenyl and N-acetyl-p-aminophenol with a fatty acid anhydride in the presence of a fatty acid metal salt and conducting transesterification with 1,4-phenylene dicarboxylic acid and 1,3-phenylene dicarboxylic acid. With respect to all of the monomers consisting of 4-hydroxybenzoic acid, 6-hydroxy-2-naphthoic acid, 1,4-phenylene dicarboxylic acid, 1,3-phenylene dicarboxylic acid, 4,4'-dihydroxybiphenyl and N-acetyl-p-aminophenol, an amount used of 4-hydroxybenzoic acid is 50 to 70 mol%, preferably 54 to 67 mol%, and more preferably 58 to 64 mol%, from the viewpoint of the achievement of a balance between melting point lowering and heat resistance, an amount used of 6-hydroxy-2-naphthoic acid is 0.5 mol% or higher and lower than 4.5 mol%, preferably 0.75 to 3.75 mol%,

and more preferably 1 to 3 mol%, from the viewpoint of the achievement of a balance between melting point lowering and heat resistance,

an amount used of 1,4-phenylene dicarboxylic acid is 10.25 to 22.25 mol%, preferably 12.963 to 20.75 mol%, and more preferably 15.675 to 19.25 mol%, from the viewpoint of the achievement of a balance between melting point lowering and heat resistance,

an amount used of 1,3-phenylene dicarboxylic acid is 0.5 mol% or higher and lower than 4.5 mol%, preferably 0.5 to 3.75 mol%, and more preferably 0.5 to 3 mol%, from the viewpoint of the achievement of a balance between melting point lowering and heat resistance,

an amount used of 4,4'-dihydroxybiphenyl is 5.75 to 23.75 mol%, preferably 8.5 to 20.375 mol%, and more preferably 11.25 to 17 mol% (e.g., 11.675 to 17 mol%), from the viewpoint of the achievement of a balance between melting point lowering and heat resistance,

an amount used of N-acetyl-p-aminophenol is 1 to 7 mol%, preferably 1.5 to 7 mol%, and more preferably 2 to 7 mol%, from the viewpoint of the achievement of a balance between melting point lowering and heat resistance,

an amount used of a total of 6-hydroxy-2-naphthoic acid and 1,3-phenylene dicarboxylic acid is 1 mol% or higher and lower than 5 mol%, preferably 1.75 to 4.75 mol%, and more preferably 2.5 to 4.5 mol%, from the viewpoint of the achievement of a balance between melting point lowering and heat resistance,

an amount used of a total of 4-hydroxybenzoic acid, 6-hydroxy-2-naphthoic acid, 1,4-phenylene dicarboxylic acid, 1,3-phenylene dicarboxylic acid, 4,4'-dihydroxybiphenyl and N-acetyl-p-aminophenol is preferably 100 mol%,

a molar ratio of an amount used of N-acetyl-p-aminophenol to an amount used of a total of 4,4'-dihydroxybiphenyl and N-acetyl-p-aminophenol is 0.04 to 0.37, preferably 0.07 to 0.36, and more preferably 0.11 to 0.35, from the viewpoint of the achievement of a balance between melting point lowering and heat resistance, and

an amount used of the fatty acid anhydride is preferably 1.02 to 1.04 times a hydroxy equivalent of a total of 4-hydroxybenzoic acid, 6-hydroxy-2-naphthoic acid, 4,4'-dihydroxybiphenyl and N-acetyl-p-aminophenol. The fatty acid metal salt is more preferably an acetic acid metal salt, and the fatty acid anhydride is more preferably acetic anhydride. A mole number of a total of 1,4-phenylene dicarboxylic acid and 1,3-phenylene dicarboxylic acid (hereinafter also referred to as "mole number 1B") is more preferably 1 to 1.1 times a mole number of a total of 4,4'-dihydroxybiphenyl and N-acetyl-p-aminophenol (hereinafter also referred to as "mole number 2B"), or a mole number of a total of 4,4'-dihydroxybiphenyl and N-acetyl-p-aminophenol is more preferably 1 to 1.1 times the a mole number of a total of 1,4-phenylene dicarboxylic acid and 1,3-phenylene dicarboxylic acid. The mole number 1B is further more preferably 1.02 to 1.06 times the mole number 2B, or the mole number 2B is further more preferably 1.02 to

1.06 times the mole number 1B. The mole number 1B is particularly preferably 1.024 to 1.056 times the mole number 2B, or the mole number 2B is particularly preferably 1.024 to 1.056 times the mole number 1B.

Properties of the wholly aromatic polyester amide will be described below. The wholly aromatic polyester amide of the present invention exhibits optical anisotropy when melted. Exhibiting optical anisotropy when melted means that the wholly aromatic polyester amide of the present invention is a liquid crystal polymer.

In the present invention, the fact that the wholly aromatic polyester amide is a liquid crystal polymer is an indispensable element for the wholly aromatic polyester amide to have both thermal stability and easy processability. Although some wholly aromatic polyester amides constituted of the structural units (I) to (VI) do not form an anisotropic melt phase depending on the constitutional component and the sequence distribution in the polymer, the polymer of the present invention is limited to a wholly aromatic polyester amide that exhibits optical anisotropy when melted.

Properties of melt anisotropy can be confirmed by a conventional polarization inspection method using an orthogonal polarizer. More specifically, confirmation of melt anisotropy can be carried out by melting a sample placed on a hot stage manufactured by Linkam Scientific Instruments Ltd. using a polarizing microscope manufactured by Olympus Corporation, and observing at a magnification of 150 times in

a nitrogen atmosphere. The liquid crystal polymer is optically anisotropic and transmits light when inserted between orthogonal polarizers. When the sample is optically anisotropic, polarized light is transmitted even in the state of, for example, a molten stationary liquid state.

A nematic liquid crystal polymer causes significant decrease in viscosity at the melting point or higher, so that it generally becomes an index of processability that liquid crystallinity is exhibited at a temperature of the melting point or higher. The melting point is preferably as high as possible from the viewpoint of the heat resistance. Taking thermal deterioration during melt processing of the polymer and heating capability of a molding machine into consideration, the melting point of 360°C or lower is a preferable rough indication. The melting point is more preferably 300 to 360°C, and still more preferably 340 to 358°C.

The melt viscosity of the wholly aromatic polyester amide as measured at a temperature that is 10 to 30°C higher than the melting point of the wholly aromatic polyester amide of the present invention and a shear rate of 1,000/sec is preferably 500 Pa·s or lower, more preferably 0.5 to 300 Pa·s, and still more preferably 1 to 100 Pa·s. If the melt viscosity is in the above range, the wholly aromatic polyester amide itself or a composition containing the wholly aromatic polyester amide easily secures fluidity during molding and the filling pressure hardly becomes excessive. As used herein, the

melt viscosity refers to a melt viscosity measured in conformity with ISO 11443.

As the index representing the heat resistance, a difference between the melting point and DTUL is also exemplified. The difference is preferably 90°C or lower since the heat resistance tends to become high. From the viewpoint of the achievement of a balance between melting point lowering and heat resistance, the difference is preferably higher than 0°C and 85°C or lower (e.g., 50°C or higher and 85°C or lower), and more preferably 55 to 79°C.

<Polyester Amide Resin Composition>

The wholly aromatic polyester amide of the present invention can be mixed with various fibrous, particulate and plate-like inorganic and organic fillers according to the intended use.

Examples of the inorganic filler mixed in the polyester amide resin composition of the present invention include fibrous, particulate and plate-like inorganic fillers.

Examples of the fibrous inorganic filler include a glass fiber, an asbestos fiber, a silica fiber, a silica-alumina fiber, an alumina fiber, a zirconia fiber, a boron nitride fiber, a silicon nitride fiber, a boron fiber, a potassium titanate fiber, a fiber of silicate such as wollastonite, a magnesium sulfate fiber, an aluminum borate fiber, and an inorganic fibrous material such as a fibrous material of a metal such as stainless steel, aluminum, titanium, copper or brass. A particularly typical fibrous filler is a glass fiber.

Examples of the particulate inorganic filler include carbon black, graphite, silica, quartz powder, glass beads, milled glass fiber, glass balloon, glass powder, a silicate such as calcium silicate, aluminum silicate, kaolin, clay, diatomaceous earth, or wollastonite, an oxide of a metal such as iron oxide, titanium oxide, zinc oxide, antimony trioxide, or alumina, a carbonate of a metal such as calcium carbonate or magnesium carbonate, a sulfate of a metal such as calcium sulfate or barium sulfate, ferrite, silicon carbide, silicon nitride, boron nitride, various metal powders and the like.

Examples of the plate-like inorganic filler include mica, glass flake, talc, various metal foils and the like.

Examples of the organic filler include a heat resistant high strength synthetic fiber such as an aromatic polyester fiber, a liquid crystal polymer fiber, an aromatic polyamide or a polyimide fiber.

These inorganic and organic fillers can be used alone, or two or more thereof can be used in combination. The combination of the fibrous inorganic filler and the particulate or plate-like inorganic filler is a combination that is preferable for achieving mechanical strength simultaneously with dimensional accuracy, electrical properties and the like. The fibrous filler is particularly preferably a glass fiber and the plate-like filler is particularly preferably mica and talc, and an amount mixed thereof is 120 parts by mass or lower, and preferably 20 to 80 parts by mass, with respect to 100 parts by mass of the wholly

aromatic polyester amide. Use of the glass fiber in combination with mica or talc enables particularly significant improvement in thermal deformation temperature, mechanical properties and the like of the polyester amide resin composition.

When these fillers are used, a sizing agent or a surface treating agent can be optionally used.

As mentioned above, the polyester amide resin composition of the present invention includes, as essential components, the wholly aromatic polyester amide of the present invention and an inorganic or organic filler. As long the effects of the present invention are not impaired, other components may be included. Other components may be any component and examples thereof include another resin, and an additive such as an antioxidant, a stabilizer, a pigment or a crystal nucleating agent.

A method for producing a polyester amide resin composition of the present invention is not particularly limited, and the polyester amide resin composition can be prepared by a conventionally known method.

<Polyester Amide Molded Article>

The polyester amide molded article of the present invention is obtained by molding the wholly aromatic polyester amide or polyester amide resin composition of the present invention. The molding method is not particularly limited and a general molding method can be employed. Examples of general molding methods include methods such as injection molding,

extrusion molding, compression molding, blow molding, vacuum molding, foam molding, rotational molding and gas injection molding methods.

The polyester amide molded article obtained by molding the wholly aromatic polyester amide of the present invention is excellent in heat resistance and toughness. The polyester amide molded article obtained by molding the polyester amide resin composition of the present invention is excellent in heat resistance and toughness and includes an inorganic or organic filler, so that the mechanical strength or the like is further improved.

The wholly aromatic polyester amide and the polyester amide resin composition of the present invention are excellent in moldability, so that a polyester amide molded article having a desired shape can be easily obtained.

Examples of preferable applications of the polyester amide molded article of the present invention having the above-mentioned properties include a connector, a CPU socket, a relay switch component, a bobbin, an actuator, a noise reduction filter case, and a heat fixing roll of OA equipment.

EXAMPLES

The present invention will be described by way of Examples, but the present invention is not limited to the following Examples.

<Example 1>

The following raw material monomers, fatty acid metal salt

catalyst, and acylating agent were charged in a polymerization vessel equipped with a stirrer, a reflux column, a monomer charge port, a nitrogen introducing port, and a depressurization/fluxion line, and nitrogen purging was started.

(I) 4-Hydroxybenzoic acid: 9.7 mol (58 mol%) (HBA)

(II) 6-Hydroxy-2-naphthoic acid: 0.17 mol (1 mol%) (HNA)

(III) Terephthalic acid: 3.2 mol (19.25 mol%) (TA)

(IV) Isophthalic acid: 0.25 mol (1.5 mol%) (IA)

(V) 4,4'-Dihydroxybiphenyl: 2.5 mol (15.25 mol%) (BP)

(VI) N-acetyl-p-aminophenol: 0.83 mol (5 mol%) (APAP)

Potassium acetate catalyst: 110 mg

Acetic anhydride: 1,734 g (an amount that is 1.03 times a hydroxy equivalent of a total of the HBA, HNA, BP and APAP)

After charging raw materials, the temperature of the reaction system was raised to 140°C, followed by a reaction at 140°C for 1 hour. Then, the temperature was further raised to 360°C over 5.5 hours and the pressure was reduced to 10 Torr (i.e., 1,330 Pa) over 20 minutes and, while distilling out acetic acid, excess acetic anhydride and other low boiling point components, melt polymerization was performed. After stirring torque reached a predetermined value, nitrogen was introduced to turn from a depressurized state to a pressurized state via a normal pressure, and then the polymer was discharged from the bottom of the polymerization vessel.

<Evaluation>

With respect to the wholly aromatic polyester amide of

Example 1, the evaluation of melting point, DTUL and melt viscosity was performed by the following methods. The evaluation results are shown in Tables 1 to 3.

[Melting Point]

After observing an endothermic peak temperature (T_{m1}) observed when a polymer is measured from room temperature under temperature rise conditions of 20°C/min using DSC (manufactured by TA Instruments), the polymer was held at a temperature of $(T_{m1} + 40)^{\circ}\text{C}$ for 2 minutes and cooled to room temperature under temperature drop conditions of 20°C/min, and then the endothermic peak temperature observed when measured again under the temperature rise conditions of 20°C/min was measured.

[DTUL]

Using a twin-screw extruder (Model TEX30 α , manufactured by The Japan Steel Works, Ltd.), 60 mass% of a polymer and 40 mass% of a glass fiber (EFH75-01, manufactured by Central Glass Co., Ltd., milled fiber, average fiber diameter of 11 μm , average fiber length of 75 μm) were melt-kneaded at a cylinder temperature of the melting point of the polymer + 20°C to obtain polyester amide resin composition pellets. Using a molding machine ("SE100DU", manufactured by Sumitomo Heavy Industries, Ltd.), the polyester amide resin composition pellets were molded under the following molding conditions to obtain a test piece for measurement (4 mm $\times$ 10 mm $\times$ 80 mm). Using the test piece, deflection temperature under load was measured by the method in conformity with ISO 75-1,2. Bending

stress used was 1.8 MPa. The results are shown in Tables 1 to 3.

(Molding Conditions)

Cylinder temperature: melting point of polymer + 15°C

Mold temperature: 80°C

Back pressure: 2 MPa

Injection speed: 33 mm/sec

[Melt Viscosity]

Using Capilograph manufactured by TOYO SEIKI SEISAKU-SHO, LTD., a melt viscosity of a liquid crystal polymer was measured at a temperature that is 10 to 30°C higher than the melting point of the liquid crystal polymer and a shear rate of 1,000/sec in conformity with ISO 11443, using an orifice having an inner diameter of 1 mm and a length of 20 mm. The measurement temperature was as shown in Tables 1 to 3.

<Examples 2 to 18, Comparative Examples 1 to 11>

In the same manner as in Example 1, except that types and charge ratios (mol%) of raw material monomers were changed as shown in Tables 1 to 3, polymers were obtained. In the same manner as in Example 1, evaluation was performed. The evaluation results are shown in Tables 1 to 3.

[Table 1]

	Example								
	1	2	3	4	5	6	7	8	9
HBA (mol%)	58	62	58	62	58	58	60	62	58
HNA (mol%)	1	1	1	1	2	1	1.5	1.5	3
TA (mol%)	19.25	17.25	17.75	15.75	18.75	17.75	17.25	16.25	18.25
IA (mol%)	1.5	1.5	3	3	1.5	3	2.25	2.25	1.5
BP (mol%)	15.25	13.25	15.25	13.25	12.75	13.25	13	12	14.25
APAP (mol%)	5	5	5	5	7	7	6	6	5
Total (mol%)	100	100	100	100	100	100	100	100	100
HNA+IA (mol%)	2.5	2.5	4	4	3.5	4	3.75	3.75	4.5
APAP/(BP+APAP)	0.25	0.27	0.25	0.27	0.35	0.35	0.32	0.33	0.26
Melting point (°C)	355	356	343	343	353	350	347	351	345
Temperature at which melt viscosity was measured (°C)	370	370	360	360	370	370	360	370	360
Melt viscosity (Pa·s)	17.9	20.8	22.6	23.7	18.0	22.2	24.0	20.3	17.8
DTUL (°C)	300	293	278	267	274	272	275	281	269
(Melting point)-DTUL	55	63	65	76	79	78	72	70	76

[Table 2]

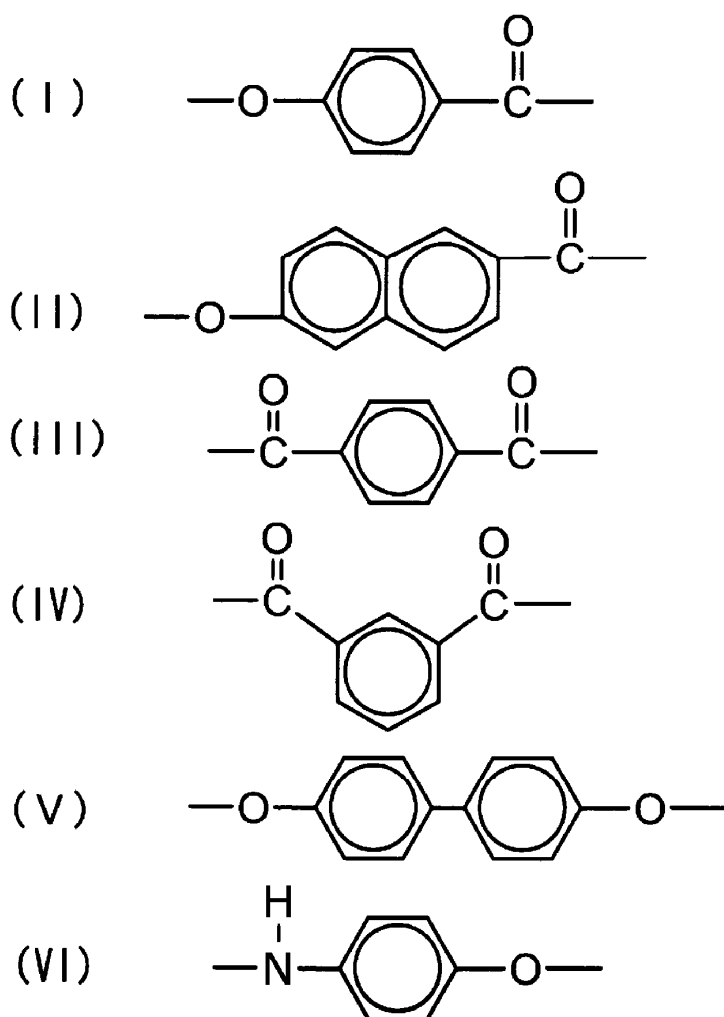
	Example								
	10	11	12	13	14	15	16	17	18
HBA (mol%)	64	60	58	60	62	60	60	60	60
HNA (mol%)	2.15	2.5	2	2	2	2.8	3	1.5	2.8
TA (mol%)	15.675	18	18.75	17.75	16.75	18.15	18.25	17.5	18.4
IA (mol%)	1.5	1	1.5	1.5	1.5	0.7	0.5	2	0.7
BP (mol%)	11.675	13.5	14.75	13.75	12.75	13.35	13.25	17	13.1
APAP (mol%)	5	5	5	5	5	5	5	2	5
Total (mol%)	100	100	100	100	100	100	100	100	100
HNA+IA (mol%)	3.65	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5
APAP/(BP+APAP)	0.30	0.27	0.25	0.27	0.28	0.27	0.27	0.11	0.28
Melting point (°C)	346	342	348	347	346	342	343	351	343
Temperature at which melt viscosity was measured (°C)	360	360	360	360	360	360	360	370	360
Melt viscosity (Pa·s)	23.7	20.1	23.6	24.6	19.4	21.7	21.3	15.6	19.1
DTUL (°C)	277	270	275	276	276	273	269	282	274
(Melting point)-DTUL	69	72	73	71	70	69	74	69	69

[Table 3]

	Comparative Example										
	1	2	3	4	5	6	7	8	9	10	11
HBA (mol%)	62	58	67	70	64	50	60	48	60	62	62
HNA (mol%)	2	2	2	2	0	2.5	5	3	2	0	1
TA (mol%)	15.25	17.25	11.25	8.75	11.45	23.75	17.5	21	16.75	15.75	15.75
IA (mol%)	3	3	4.5	5.5	6.8	0	0	3.5	2.5	3.5	3
BP (mol%)	10.75	14.75	15.25	13.75	15.75	18.75	12.5	24.5	18.75	17.75	11.25
APAP (mol%)	7	5	0	0	2	5	5	0	0	1	7
Total (mol%)	100	100	100	100	100	100	100	100	100	100	100
HNA+IA (mol%)	5	5	6.5	7.5	6.8	2.5	5	6.5	4.5	3.5	4
APAP/(BP+APAP)	0.39	0.25	0	0	0.11	0.21	0.29	0	0	0.05	0.38
Melting point (°C)	352	333	332	330	327	365	336	355	367	362	357
Temperature at which melt viscosity was measured (°C)	370	350	350	350	350	380	360	380	380	380	370
Melt viscosity (Pa·s)	20.1	25.4	30.8	37.3	20.1	61.0	20.5	29.0	23.8	21.4	26.3
DTUL (°C)	254	252	237	215	258	280	258	245	236	295	261
(Melting point)-DTUL	98	81	95	115	69	85	78	110	131	67	96

CLAIMS

1. A wholly aromatic polyester amide that exhibits optical anisotropy when melted, the wholly aromatic polyester amide consisting of the following constituent units (I) to (VI) as essential constitutional components:



wherein

a content of the constituent unit (I) is 50 to 70 mol% with respect to all of the constituent units;

a content of the constituent unit (II) is 0.5 mol% or higher and lower than 4.5 mol% with respect to all of the

constituent units;

a content of the constituent unit (III) is 10.25 to 22.25 mol% with respect to all of the constituent units;

a content of the constituent unit (IV) is 0.5 mol% or higher and lower than 4.5 mol% with respect to all of the constituent units;

a content of the constituent unit (V) is 5.75 to 23.75 mol% with respect to all of the constituent units;

a content of the constituent unit (VI) is 1 to 7 mol% with respect to all of the constituent units;

a content of a total of the constituent unit (II) and the constituent unit (IV) is 1 mol% or higher and lower than 5 mol% with respect to all of the constituent units;

a content of a total of the constituent units (I) to (VI) is 100 mol% with respect to all of the constituent units; and

a molar ratio of the constituent unit (VI) to a total of the constituent unit (V) and the constituent unit (VI) is 0.04 to 0.37.

2. The wholly aromatic polyester amide according to claim 1, wherein the content of the constituent unit (I) is 54 to 67 mol% with respect to all of the constituent units.

3. The wholly aromatic polyester amide according to claim 1 or 2, wherein a mole number of a total of the constituent unit (III) and the constituent unit (IV) is 1 to 1.1 times a mole number of a total of the constituent unit (V) and the constituent unit (VI), or a mole number of a total of the constituent unit (V) and the constituent unit (VI) is 1 to 1.1 times a mole number of a total of the constituent unit (III) and the constituent unit (IV).

4. The wholly aromatic polyester amide according to any one of claims 1 to 3, wherein a melting point of the wholly aromatic polyester amide is 360°C or lower.

5. The wholly aromatic polyester amide according to any one of claims 1 to 4, wherein a deflection temperature under load of the wholly aromatic polyester amide is 260°C or higher; and

the deflection temperature under load is measured in a state of a polyester amide resin composition obtained by melt-kneading 60 mass% of the wholly aromatic polyester amide with 40 mass% of a milled fiber having an average fiber diameter of 11 μm and an average fiber length of 75 μm at a melting point of the wholly aromatic polyester amide + 20°C.

6. The wholly aromatic polyester amide according to any one of claims 1 to 5, wherein a melt viscosity at a temperature that is 10 to 30°C higher than a melting point of the wholly aromatic polyester amide and a shear rate of 1,000/sec is 500 Pa·s or lower.

7. A method for producing a wholly aromatic polyester amide that exhibits optical anisotropy when melted,

the method comprising acylating 4-hydroxybenzoic acid, 6-hydroxy-2-naphthoic acid, 4,4'-dihydroxybiphenyl, and N-acetyl-p-aminophenol with a fatty acid anhydride in the presence of a fatty acid metal salt and conducting

transesterification with 1,4-phenylene dicarboxylic acid and 1,3-phenylene dicarboxylic acid, wherein

with respect to all of the monomers consisting of 4-hydroxybenzoic acid, 6-hydroxy-2-naphthoic acid, 1,4-phenylene dicarboxylic acid, 1,3-phenylene dicarboxylic acid, 4,4'-dihydroxybiphenyl, and N-acetyl-p-aminophenol, an amount used of 4-hydroxybenzoic acid is 50 to 70 mol%, an amount used of 6-hydroxy-2-naphthoic acid is 0.5 mol% or higher and lower than 4.5 mol%, an amount used of 1,4-phenylene dicarboxylic acid is 10.25 to 22.25 mol%, an amount used of 1,3-phenylene dicarboxylic acid is 0.5 mol% or higher and lower than 4.5 mol%, an amount used of 4,4'-dihydroxybiphenyl is 5.75 to 23.75 mol%, an amount used of N-acetyl-p-aminophenol is 1 to 7 mol%, an amount used of a total of 6-hydroxy-2-naphthoic acid and 1,3-phenylene dicarboxylic acid is 1 mol% or higher and lower than 5 mol%, and an amount used of a total of 4-hydroxybenzoic acid, 6-hydroxy-2-naphthoic acid, 1,4-phenylene dicarboxylic acid, 1,3-phenylene dicarboxylic acid, 4,4'-dihydroxybiphenyl, and N-acetyl-p-aminophenol is 100 mol%;

a molar ratio of an amount used of N-acetyl-p-aminophenol to an amount used of a total of 4,4'-dihydroxybiphenyl and N-acetyl-p-aminophenol is 0.04 to 0.37; and

an amount used of the fatty acid anhydride is 1.02 to 1.04 times a hydroxy equivalent of a total of 4-hydroxybenzoic acid, 6-hydroxy-2-naphthoic acid, 4,4'-dihydroxybiphenyl, and N-acetyl-p-aminophenol.

8. The method according to claim 7, wherein with respect to all of the monomers consisting of 4-hydroxybenzoic acid, 6-hydroxy-2-naphthoic acid, 1,4-phenylene dicarboxylic acid, 1,3-phenylene dicarboxylic acid, 4,4'-dihydroxybiphenyl, and N-acetyl-p-aminophenol, the amount used of 4-hydroxybenzoic acid is 54 to 67 mol%.

9. The method according to claim 7 or 8, wherein the fatty acid metal salt is an acetic acid metal salt, and the fatty acid anhydride is acetic anhydride.

10. The method according to any one of claims 7 to 9, wherein a mole number of a total of 1,4-phenylene dicarboxylic acid and 1,3-phenylene dicarboxylic acid is 1 to 1.1 times a mole number of a total of 4,4'-dihydroxybiphenyl and N-acetyl-p-aminophenol, or a mole number of a total of 4,4'-dihydroxybiphenyl and N-acetyl-p-aminophenol is 1 to 1.1 times a mole number of a total of 1,4-phenylene dicarboxylic acid and 1,3-phenylene dicarboxylic acid.