A method for producing a poly(lactic acid) resin, the method comprising the steps of:
carrying out direct polycondensation using lactic acid as a main raw material to prepare a crystallized prepolymer having a weight average molecular weight of 5,000 to 25,000, an enthalpy of fusion $\Delta H_m$ of 50 to 65 [J/g] and an acid value $A$ [mol/ton] satisfying the Inequality (1) below:

$$450/(M_w/10,000-0.14)<A<950/(M_w/10,000-0.14) \quad (1)$$

(wherein $M_w$ represents the weight average molecular weight of the crystallized prepolymer); and
subjecting the crystallized prepolymer to solid-phase polymerization.
A method for producing an aliphatic polyester resin having a high molecular weight and, in a preferred embodiment, having a high melting point as well as excellent thermal stability and hue can be provided.
The present invention relates to a method for efficiently producing a polylactic acid resin having a high molecular weight and, in a preferred embodiment, having a high melting point as well as excellent thermal stability and hue.

In recent years, from the viewpoint of environmental protection, polylactic acid resins have been paid attention, and polylactic acid resins are especially have been paid attention as plant-based carbon neutral materials. Polylactic acid resins have melting points of as high as about 170°C and can be processed by melt-molding. Further, since lactic acid, which is the monomer for those resins, can now be produced inexpensively by a fermentation method using a microorganism, polylactic acid resins are expected as bioplastics which can replace the petroleum-based commodity plastics, and gradually becoming common.

Major methods for production of polylactic acid resins are the ring-opening polymerization method by polymerization of lactide, which is a lactic acid dimer, by ring-opening, and the direct polycondensation method by dehydration polycondensation using lactic acid. The direct polycondensation method is said to be capable of more inexpensively producing a polylactic acid resin compared to the ring-opening polymerization method since the step of synthesizing lactide is not necessary and lactic acid can be directly used as a polymerization raw material.


[Patent Document1] JP 8-183840 A (pp. 1 to 4)

In the techniques described in Patent Documents 1 to 3, there is a problem in that the obtained molecular weight is low and use of a solvent is necessary for obtaining a high-molecular-weight product. Further, in the method of Patent Document 3, there is the problem of coloring of the polymer.

In the technique described in Patent Document 4, the molecular weight after solid-phase polymerization is insufficient even when the molecular weight before the solid-phase polymerization was high.

In the techniques described in Patent Documents 5 to 8, since crystallization in water, crystallization for a long time, or crystallization with hot air containing moisture is carried out before solid-phase polymerization, acidic compounds increase in the polymer, so that the rate of solid-phase polymerization and the yield of the polymer decrease, which is problematic.

In the technique described in Patent Document 9, crystallization before solid-phase polymerization is insufficient,
and a sufficient rate of solid-phase polymerization cannot be obtained. In the technique described in Patent Document 10, contacting with air occurs for a long time during the process from melt polymerization to solid-phase polymerization because of pulverization and the like, leading to an increase in acidic substances and hence resulting in a decreased solid-phase polymerization efficiency.

[0009] The present invention aims to provide a method for efficiently producing a poly(lactic acid) resin having a high molecular weight and, in a preferred embodiment, having a high melting point as well as excellent thermal stability and hue.

MEANS FOR SOLVING THE PROBLEMS

[0010] As a result of a study for solving the above problems, the present inventors discovered a method for efficiently producing a poly(lactic acid) resin having a high molecular weight and, in a preferred embodiment, having a high melting point as well as excellent thermal stability and hue, thereby reaching the present invention.

[0011] That is, the above object of the present invention can be achieved by a method for producing a poly(lactic acid) resin, the method comprising the steps of:

1. carrying out direct polycondensation using lactic acid as a main raw material to prepare a crystallized prepolymer having a weight average molecular weight of 5,000 to 25,000, an enthalpy of fusion \( \Delta H_m \) of 50 to 65 [J/g] and an acid value \( A \) [mol/ton] satisfying the Inequality (1) below; and
2. subjecting the crystallized prepolymer to solid-phase polymerization.

[0012]

\[
450/(M_w/10,000-0.14) < A < 950/(M_w/10,000-0.14)
\]  

(wherein \( M_w \) represents the weight average molecular weight of the crystallized prepolymer.)

In the production method of the present invention, the lactide content \( L \) of the crystallized prepolymer is preferably 0.1 to 3.0 [wt%].

[0013] Preferably, in the production method of the present invention, the crystallized prepolymer is poly-L-lactic acid or poly-D-lactic acid, and, in the case of poly-L-lactic acid, the D-lactic acid content \( d \) is 0.2 to 2.0 [mol%), and in the case of poly-D-lactic acid, the L-lactic acid content \( 1 \) is 0.2 to 2.0 [mol%].

[0014] In the production method of the present invention, the crystallized prepolymer is preferably in the form of a pellet.

[0015] In the production method of the present invention, the enthalpy of fusion \( \Delta H_m \) of the crystallized prepolymer is preferably not less than 53 [J/g].

[0016] In the production method of the present invention, the acid value \( A \) [mol/ton] of the crystallized prepolymer preferably satisfies the Inequality (2) below:

[0017]

\[
550/(M_w/10,000-0.14) < A < 850/(M_w/10,000-0.14)
\]  

In the production method of the present invention, the temperature increasing rate in the solid-phase polymerization is preferably not more than 10°C per hour.

[0018] In the production method of the present invention, the final temperature in the solid-phase polymerization is preferably 155 to 165°C.

[0019] In the production method of the present invention, the crystallized prepolymer is preferably produced using a tin compound or sulfonic acid compound as a catalyst.

[0020] In the production method of the present invention, the weight average molecular weight is preferably 5,000 to 25,000; the enthalpy of fusion \( \Delta H_m \) is preferably 50 to 65 [J/g]; and the acid value \( A \) [mol/ton] satisfies the Inequality (1) below:

[0021]

\[
450/(M_w/10,000-0.14) < A < 950/(M_w/10,000-0.14)
\]  

(wherein \( M_w \) represents the weight average molecular weight of the crystallized prepolymer).
In the production method of the present invention, the crystallized poly(lactic acid) prepolymer is preferably prepared by carrying out direct polycondensation using lactic acid as a main raw material to obtain a prepolymer, and crystallizing the prepolymer.

EFFECT OF THE INVENTION

[0022] A poly(lactic acid) resin having a high molecular weight and, in a preferred embodiment, having a high melting point as well as excellent thermal stability and hue can be efficiently produced.

BEST MODE FOR CARRYING OUT THE INVENTION

[0023] The present invention is described in detail below.

[0024] In the present invention, the poly(lactic acid) resin is a polymer containing as a major component(s) L-lactic acid and/or D-lactic acid, and, in cases where L-lactic acid is a major component, the resin is called poly-L-lactic acid, and in cases where D-lactic acid is a major component, the resin is called poly-D-lactic acid.

[0025] In cases where the poly(lactic acid) resin is poly-L-lactic acid, the L-lactic acid unit is preferably contained in an amount of not less than 70 mol%, more preferably contained in an amount of not less than 90 mol%, still more preferably contained in an amount of not less than 95 mol%, especially preferably contained in an amount of not less than 98 mol%.

[0026] In cases where the poly(lactic acid) resin is poly-D-lactic acid, the D-lactic acid unit is preferably contained in an amount of not less than 70 mol%, more preferably contained in an amount of not less than 90 mol%, still more preferably contained in an amount of not less than 95 mol%, especially preferably contained in an amount of not less than 98 mol%.

[0027] The poly(lactic acid) resin is preferably a mixture of poly-L-lactic acid and poly-D-lactic acid, and is more preferably forming a stereocomplex.

[0028] The resin is also preferably a block copolymer constituted by a segment(s) composed of L-lactic acid units and a segment(s) composed of D-lactic acid units. The segment composed of L-lactic acid units herein means a polymer containing L-lactic acid as a major component, which polymer contains not less than 70 mol% of L-lactic acid units. The L-lactic acid units are more preferably contained in an amount of not less than 90 mol%, still more preferably contained in an amount of not less than 95 mol%, especially preferably contained in an amount of not less than 98 mol%. The segment composed of D-lactic acid units herein means a polymer containing D-lactic acid as a major component, which polymer contains not less than 70 mol% of D-lactic acid units. The D-lactic acid units are more preferably contained in an amount of not less than 90 mol%, still more preferably contained in an amount of not less than 95 mol%, especially preferably contained in an amount of not less than 98 mol%.

[0029] In the present invention, lactic acid is used as a main raw material to produce a poly(lactic acid) resin by direct polycondensation. The main raw material to be used is preferably high purity lactic acid in which, in terms of impurities in the lactic acid, the total amount of alcohols is not more than 70 ppm; the total amount of organic acids is not more than 800 ppm; the total amount of aldehydes is not more than 50 ppm; and the total amount of esters is not more than 400 ppm.

[0030] The optical purity of the lactic acid to be used is preferably not less than 95%, more preferably not less than 98%, especially preferably not less than 99%. In cases where the lactic acid is L-lactic acid, the D-lactic acid content is preferably not more than 2.5%, more preferably not more than 1.0%, especially preferably not more than 0.5%. In cases where the lactic acid is D-lactic acid, the L-lactic acid content is preferably not more than 2.5%, more preferably not more than 1.0%, especially preferably not more than 0.5%.

[0031] In the present invention, the polylactic acid may contain component units other than L-lactic acid and D-lactic acid units as long as the performance of the obtained polylactic acid is not adversely affected. Examples of the other component units include polybasic acids, polylcohols, hydroxypolycarboxylic acid and lactone. Specific examples of the units include: polycarboxylic acids such as succinic acid, adipic acid, sebacic acid, fumaric acid, terephthalic acid, isophthalic acid, 2,6-naphthalenedicarboxylic acid, 5-sulfosalicylic acid monosodium salt, cyclohexanedicarboxylic acid, 5-sulfosalicylic acid monotetradecylphosphonium salt, furandicarboxylic acid, and derivatives thereof; polyalcohols such as ethylene glycol, propylene glycol, butanediol, pentanediol, hexanediol, octanediol, isosorbide, neopentyl glycol, glycerin, trimethylolpropane, pentaerythritol, trimethylolpropane, polylcohol prepared by addition of ethylene oxide or propylene oxide to pentaerythritol, aromatic polylcohol prepared by addition reaction of bisphenol with ethylene oxide, diethylene glycol, triethylene glycol, polyethylene glycol and polypropylene glycol, and derivatives thereof; hydroxyalkylcarboxylic acids such as glycolic acid, 3-hydroxybutyric acid, 4-hydroxybutyric acid, 4-hydroxyvaleric acid and 6-hydroxycaproic acid; and lactones such as glycolide, ε-caprolactone glycolide, ε-caprolactone, β-propiolactone, δ-butyrolactone, β- or γ-butyrolactone, pivalolactone and δ-valerolactone.

[0032] The method of the present invention for producing a poly(lactic acid) resin comprises the steps of:
carrying out melt polymerization to obtain a prepolymer;
crystallizing the prepolymer to prepare a crystallized prepolymer having a weight average molecular weight of 5,000
to 25,000, an enthalpy of fusion \( \Delta H_m \) of 50 to 65 [J/g] and an acid value \( A \) [mol/ton] satisfying the Inequality (1)
below; and
subjecting the crystallized prepolymer to solid-phase polymerization.

\[ 450/(M_w/10,000-0.14) < A < 950/(M_w/10,000-0.14) \]  \hspace{1cm} (1)
(IV) oxide, dibutyltin(IV) oxide, diocytlin(IV) oxide, diphenyltin(IV) oxide, tributyltin oxide, triethyltin(IV) hydroxide, triphe-
nyltin(IV) hydroxide, tributyltin hydroxide, monobutylin(IV) oxide, tetramethyltin(IV), tetraethyltin(IV), tetrabutyltin(IV), dibu-
tyldiphenyltin(IV), tetrabutyltin(IV), tributyltin(IV) acetate, triisobutyltin(IV) acetate, triphenyltin(IV) acetate, dibutyltin
acetate, dibutyltin diocytlate, dibutyltin diacetate, dibutyltin(IV) dilaurate, dibutyltin(IV) maleate, dibutyltin bis(acetylatedonate), tributyltin
(IV) chloride, dibutyltin dichloride, monobutylin trichloride, diocytlin dichloride, triphenyltin(IV) chloride, tributyltin sulfide,
tributyltin sulfite, tin(II) trifluoromethanesulfonate, ammonium hexachlorostannate(IV), dibutyltin sulfide, diphenyltin
sulfide, triethyltin sulfite and tin(II) phthalocyanine. Among these, tin compounds other than tin(II) chloride are preferred.
Specific examples of the tin compounds include titanium tetraacetate and titanium(IV) oxide. Specific examples of the lead
compounds include diisopropyllead(II), lead monochloride, lead acetate, lead(II) octoate, lead(II) isooctoate, lead(II)
ononanoate, lead(II) laurate, lead(II) oleate, lead(II) linoleate, lead naphthenate, lead(II) neodecanoate, lead oxide and lead(II) sulfate. Specific
examples of the zinc compounds include zinc oxide, methylpropoxy zinc, zinc chloride, zinc acetate, zinc(II) octoate,
zinc naphthenate, zinc carbonate, zinc(II) chloride and zinc sulfate. Specific examples of the cobalt compounds include cobalt
chloride, cobalt acetate, cobalt(II) octoate, cobalt(II) isooctoate, cobalt(II) isononanoate, cobalt(II) laurate, cobalt(II)
oleate, cobalt(II) linoleate, cobalt naphthenate, cobalt(II) neodecanoate, cobalt(II) carbonate, cobalt(II) sulfate and cobalt
(II) oxide. Specific examples of the iron compounds include iron(II) chloride, iron(II) acetate, iron(II) naphth
enate, iron(II) carbonate, iron(II) sulfate and iron(III) oxide. Specific examples of the lithium compounds include lithium
propoxide, lithium chloride, lithium acetate, lithium octoate, lithium naphthenate, lithium carbonate, lithium sulfate and lithium
oxide. Specific examples of the rare earth compounds include triisopropoxyeuropium(III), trisopropoxynedum
ydim(III), triisopropoxylanthanum, trisopropoxysamarium(III), trisopropoxyyttrium, dysprosium chloride,
europium chloride, lanthanum chloride, neodymium chloride, samarium chloride, yttrium chloride, dysprosium(III) triac-
etate, europium(III) triacetate, lanthanum acetate, neodymium triacetate, samarium acetate, yttrium triacetate, dyspro-
sium(III) carbonate, dysprosium(IV) carbonate, europium(II) carbonate, lanthanum carbonate, neodymium carbonate,
samarium(II) carbonate, samarium(III) carbonate, yttrium carbonate, dysprosium(IV) sulfate, europium(II) sulfate, lanthanum
sulfate, neodymium sulfate, samarium sulfate, yttrium sulfate, europium dioxide, lanthanum oxide, neodymium oxide,
samarium(III) oxide and yttrium oxide. Other examples of the metal catalysts include potassium compounds such as
potassium isopropoxide, potassium chloride, potassium acetate, potassium octoate, potassium naphthenate, potassium
t-butyl carbonate, potassium sulfate and potassium oxide; copper compounds such as copper(II) diisopropoxide, copper
(II) chloride, copper(II) acetate, copper octoate, copper naphthenate, copper(II) sulfate and diconper carbonate; nickel
compounds such as nickel chloride, nickel acetate, nickel octoate, nickel carbonate, nickel(II) sulfate and nickel oxide;
zirconium compounds such as tetraisopropoxycycliricon(IV), zirconium trichloride, zirconium acetate, zirconium octoate,
zirconium naphthenate, zirconium(II) carbonate, zirconium(IV) carbonate, zirconium sulfate and zirconium(II) oxide;
antimony compounds such as triisopropoxantimony, antimony(III) fluoride, antimony(V) fluoride, antimony acetate and
antimony(III) oxide; magnesium compounds such as magnesium diisopropoxide, magnesium chloride, magnesium ac-
etate, magnesium lactate, magnesium carbonate, magnesium sulfate and magnesium oxide; calcium compounds such as
diisoproxyxycalcium, calcium chloride, calcium acetate, calcium octoate, calcium naphthenate, calcium lactate and
calcium sulfate; aluminum compounds such as aluminum, aluminum isopropoxide, aluminum chloride, aluminum acetate,
aluminum octoate, aluminum sulfate and aluminum oxide; germanium compounds such as germanium, tetraisopropox
ygermane and germanium(IV) oxide; manganese compounds such as triisopropoxymanganate(III), manganese trichlo-
ride, manganese acetate, manganese(II) octoate, manganese(II) naphthenate and manganese(II) sulfate; and bismuth
compounds such as bisbuth(III) chloride, bismuth powder, bismuth(III) oxide, bismuth acetate, bismuth octoate and
bismuth neodecanoate. Still other preferred examples of the metal catalysts include compounds composed of two or
more kinds of metallic elements, such as sodium stannate, magnesium stannate, potassium stannate, calcium stannate,
manganese stannate, bismuth stannate, barium stannate, strontium stannate, sodium titanate, magnesium titanate,
aluminum titanate, potassium titanate, calcium titanate, cobalt titanate, zinc titanate, manganese titanate, zirconium
titanate, bismuth titanate, barium titanate and strontium titanate.

[0037] The acid catalyst other than sulfur-containing compounds containing sulfur having an oxidation number of not
less than +5 may be either a Bronsted acid as a proton donor or a Lewis acid as an electron-pair acceptor, and may be
either an organic acid or an inorganic acid. Examples of the acid catalyst include monocarboxylic acid compounds such as
formic acid, acetic acid, propionic acid, heptanoic acid, octanoic acid, octylic acid, nonanoic acid, isononanoic acid,
trifluoroacetic acid and trichloroacetic acid; dicarboxylic acid compounds such as oxalic acid, succinic acid, maleic acid,
tartaric acid and malonic acid; tricarboxylic acid compounds such as citric acid and tricarballylic acid; acidic amino acids
such as aspartic acid and glutamic acid; ascorbic acid; retinoic acid; phosphoric acid compounds such as phosphoric
acid, metaphosphoric acid, phosphorous acid, hypophosphorous acid, polyphosphoric acid, phosphoric acid monoesters
including monododecyl phosphate and monooctadecyl phosphate, phosphoric acid diesters including didodecyl phos-
phate and dioctadecyl phosphate, phosphoric acid monoesters and phosphoric acid diesters; boric acid; and hydro-
chloric acid.
The form of the acid catalyst other than sulfur-containing compounds containing sulfur having an oxidation number of not less than +5 is not restricted, and may be either a solid acid catalyst or a liquid acid catalyst. Examples of the solid acid catalyst include natural minerals such as acid clay, kaolinite, bentonite, montmorillonite, t alc, zirconium silicate and zeolite; oxides such as silica, alumina, titania and zirconia; oxide complexes such as silica alumina, silica magnesia, silica boria, alumina boria, silica titania and silica zirconia; chlorinated alumina; fluorinated alumina; and cation exchange resins.

In cases where polymerization of the poly(lactic acid) resin is carried out using a catalyst having stereoselective polymerizability and, as a raw material, a racemic body which is a mixture of the same amount of L-lactic acid and D-lactic acid, poly-L-lactic acid and poly-D-lactic acid can be produced at the same time.

In the present invention, in view of obtaining a poly(lactic acid) resin having a high molecular weight and a high melting point, tin compounds, titanium compounds, lead compounds, zinc compounds, cobalt compounds, iron compounds, lithium compounds, rare earth compounds, antimony compounds, bismuth compounds, and sulfur-containing compounds containing sulfur having an oxidation number of not less than +5 are preferred, and, in view of achieving high productivity, tin compounds, titanium compounds, lead compounds, zinc compounds, cobalt compounds, iron compounds, lithium compounds, rare earth compounds, sulfonic acid compounds, phosphorous compounds, and sulfur-containing compounds containing sulfur having an oxidation number of not less than +5 are more preferred. Tin compounds, titanium compounds, rare earth compounds, sulfur-containing compounds containing sulfur having an oxidation number of not less than +5, and phosphorous compounds are still more preferred. Further, in view of obtaining a poly(lactic acid) resin having also excellent thermal stability and hue, the metal catalyst is still more preferably a tin organic carboxylate having two ligands, and is especially preferably a tin(II) acetate or tin(II) octanoate. Two or more of these may also be used in combination, and, in cases where these are used in combination, it is preferred to use one or more selected from tin compounds and one or more selected from sulfur-containing compounds containing sulfur having an oxidation number of not less than +5.

In the present invention, in view of efficiently obtaining a poly(lactic acid) resin having a high molecular weight and a high melting point, the amount of the sulfur-containing compound containing sulfur having an oxidation number of not less than +5 to be added is preferably 30 to 3,000 ppm, more preferably 35 to 2,700 ppm, still more preferably 40 to 2,500 ppm, especially preferably 45 to 2,200 ppm in terms of sulfur atoms, with respect to the raw material used (L-lactic acid, D-lactic acid and/or the like).

In the present invention, the timing of the addition of the sulfur-containing compound containing sulfur having an oxidation number of not less than +5 as a catalyst is preferably at the beginning of the melt polymerization step or during the melt polymerization step in view of efficiently obtaining a poly(lactic acid) resin having a high molecular weight and a high melting point.

The amount of other catalysts to be added is not restricted, and is preferably 0.0001 to 2 parts by weight, more preferably 0.001 to 1 part by weight, still more preferably 0.005 to 0.5 part by weight, especially preferably 0.01 to 0.3 part by weight with respect to 100 parts by weight of the poly(lactic acid) resin.

In the present invention, the reaction conditions for the melt polymerization step are not restricted, and the step may be carried out under various conditions. The melt polymerization step is preferably carried out continuously under conditions containing at least the two stages described below.

Melt polymerization conditions 1: 140°C to 160°C, 13.3 to 66.6 kPa
Melt polymerization conditions 2: 160°C to 180°C, 1.3 to 6.5 kPa

In the present invention, in view of efficiently obtaining a poly(lactic acid) resin having a high molecular weight, the melt polymerization step is carried out preferably at a temperature of 140°C to 180°C, and, in view of efficiently obtaining a poly(lactic acid) resin also having a high melting point and excellent hue, the melt polymerization step is carried out preferably at a temperature of 145°C to 175°C, more preferably at a temperature of 140°C to 170°C, in terms of the substantial reaction temperature. The temperature during the melt polymerization step may be controlled either by a single stage process wherein the temperature is kept constant, or by a multistage process with two or more stages wherein the temperature is changed stepwise. In view of efficiently obtaining a poly(lactic acid) resin having a high molecular weight and a high melting point, the temperature is preferably controlled by a multistage process with two or more stages. Examples of such a process include a method wherein the reaction is first allowed to proceed at a temperature of 140°C to 160°C and then at a temperature of 160 to 180°C.

In the present invention, in view of efficiently obtaining a poly(lactic acid) resin having a high molecular weight, the melt polymerization step is carried out preferably at a pressure of 0.13 to 130 kPa, and, in view of efficiently obtaining a poly(lactic acid) resin also having excellent hue, the melt polymerization step is preferably carried out at a pressure of 1 to 100 kPa, more preferably carried out at a pressure of 10 to 90 kPa, still more preferably carried out at a pressure of 10 to 80 kPa, especially preferably carried out at a pressure of 20 to 70 kPa, in terms of the substantial reaction
pressure. The pressure during the melt polymerization step may be controlled either by a single stage process wherein the pressure is kept constant, or by a multistage process with two or more stages wherein the pressure is changed stepwise. In view of efficiently obtaining a poly(lactic acid) resin having a high molecular weight and excellent hue, the pressure is preferably controlled by a multistage process with two or more stages. Examples of such a process include a method wherein the reaction is first allowed to proceed at a pressure of 13.3 to 66.6 kPa and then at a pressure of 1.3 to 6.5 kPa. The reaction is also preferably carried out under the flow of an inert gas such as nitrogen.

In the present invention, the melt polymerization step is preferably carried out for a reaction time of 0.5 to 50 hours, and, in view of efficiently obtaining a poly(lactic acid) resin also having excellent hue, the melt polymerization step is preferably carried out for a reaction time of 1 to 45 hours, more preferably carried out for a reaction time of 2 to 40 hours, still more preferably carried out for a reaction time of 3 to 35 hours, especially preferably carried out for a reaction time of 4 to 30 hours. In cases where the temperature and the pressure during the melt polymerization step are controlled by a multistage process with two or more stages, examples of such a process include a method wherein the reaction is first allowed to proceed at a temperature of 140 to 160°C at a pressure of 13.3 to 66.6 kPa for a reaction time of 2 to 15 hours and then at temperature of 160 to 180°C at a pressure of 1.3 to 6.5 kPa for a reaction time of 2 to 15 hours. Even in the cases where the temperature and the pressure during the melt polymerization step are controlled by a multistage process with two or more stages, the total reaction time of the melt polymerization step is preferably 0.5 to 50 hours.

In the present invention, the reflux condenser is preferably connected to the upper part of the reactor, and, in view of efficiently obtaining a poly(lactic acid) resin also having excellent hue, the apparatus in which a reactor is connected to a reflux condenser is preferably used.

In the present invention, the reactor may be constituted either by a single reaction chamber or by two or more reaction chambers separated by a divider(s) and/or the like. In view of efficiently obtaining a poly(lactic acid) resin having a high molecular weight, the reactor is preferably constituted by two or more reaction chambers.

In the present invention, the reflux condenser is preferably connected to the upper part of the reactor, and, more preferably, a vacuum pump is connected to the reflux condenser. In the present invention, the reflux condenser is used for separating volatile components, and any reflux condenser may be used as long as it has a vaporization section having a function to return a part of the volatile components into the reaction system. More specifically, any reflux condenser may be used as long as it removes water among the volatile components and returns lactic acid and lactide and/or their low-molecular-weight polymers into the reactor in the melt polymerization step. Examples of the condenser constituting the condensation section herein include those of the double-pipe type, multitubular type, coil type, plate type, plate fin type, centrifugal type, spiral type and jacket type.
500/(Mw/10,000-0.14)<a<900/(Mw/10,000-0.14) (3)

550/(Mw/10,000-0.14)<a<850/(Mw/10,000-0.14) (4)

The weight average molecular weight is the value of weight average molecular weight in terms of a poly(methyl methacrylate) standard as measured by gel permeation chromatography (GPC) using hexafluoroisopropanol as a solvent, and the acid value a is the amount of carboxyl termini as measured by neutralization titration with an alkaline solution.

The crystallization step is described below.

In the present invention, for carrying out the solid-phase polymerization step, crystallization of the prepolymer is necessary. Therefore, a crystallization treatment is carried out after completion of the melt polymerization step before the beginning of the solid-phase polymerization step.

Examples of the method of crystallization include a method wherein heat treatment is carried out in a gas phase such as nitrogen or air, or in a liquid phase such as water or ethanol, at a crystallization treatment temperature; a method wherein the prepolymer is dissolved in a solvent to prepare a solution, followed by evaporating the solvent; a method wherein the prepolymer is contacted with a solvent; and a method wherein the prepolymer in the molten state is subjected to an operation of extension or shear, followed by cooling and solidifying the prepolymer. Among the above methods, the method wherein heat treatment is carried out in the nitrogen gas phase and the method wherein the prepolymer in the molten state is subjected to an operation of extension or shear, followed by cooling and solidifying the prepolymer are preferred. A plurality of the above methods may also be used in combination.

In the method wherein the prepolymer in the molten state is subjected to an operation of extension or shear, followed by cooling and solidifying the prepolymer, the method of cooling is preferably water cooling wherein the length of time of contacting with water is preferably not more than 10 minutes, more preferably not more than 5 minutes, still more preferably not more than 3 minutes, preferably not more than 1 minute, especially preferably not more than 30 seconds. In cases where the length of time of contacting with water is within the preferred range described above, acidic compounds are unlikely to increase in the polymer. The length of time from the cooling until the solid-phase polymerization is preferably not more than 12 hours, more preferably not more than 6 hours, still more preferably not more than 3 hours, especially preferably not more than 1 hour.

The crystallization treatment temperature herein is not restricted as long as the temperature is higher than the glass-transition temperature and lower than the melting point of the prepolymer which can be obtained by the melt polymerization step. The crystallization treatment temperature is more preferably between the heating crystallization temperature and the cooling crystallization temperature as measured by differential scanning calorimetry (DSC) in advance. In cases where the poly(lactic acid) resin is a poly(lactic acid) resin, in view of efficiently obtaining a poly(lactic acid) resin having a high molecular weight and a high melting point as well as excellent hue, the crystallization treatment temperature is preferably 70 to 130°C, more preferably 75 to 130°C, most preferably 80 to 130°C.

The temperature during the crystallization step may also be controlled by a single stage process wherein the temperature is kept constant. However, the temperature is preferably controlled by a multistage process with two or more stages wherein the temperature is changed stepwise, and the temperature is more preferably increased stepwise as the reaction proceeds. Examples of such a process include a method wherein the temperature is increased in a single stage process wherein the reaction is first allowed to proceed at a temperature of 80 to 100°C and then at a temperature of 100 to 130°C. The amount of increase in the temperature at each stage is preferably not more than 30°C, more preferably not more than 25°C, still more preferably not more than 20°C.

The length of time of crystallization is preferably 1 to 7 hours, more preferably 1.5 to 5 hours, especially preferably 1.5 to 3 hours. In terms of the pressure conditions during the crystallization step, any of the conditions of reduced pressure, normal pressure and increased pressure may be employed. Among these, normal pressure is preferred. The crystallization is preferably carried out under an anhydrous atmosphere, and, in cases where the crystallization is carried out under an atmosphere containing moisture, the crystallization time is preferably as short as possible.

In cases where the temperature during the crystallization step is controlled by a multistage process with two or more stages, examples of such a process include a method wherein the first stage is carried out at a temperature of 70 to 100°C for 1 to 4 hours and the second stage is carried out at a temperature of 100 to 130°C for 1 to 4 hours. The process is more preferably carried out by a method wherein the first stage is carried out at a temperature of 70 to 90°C for 1 to 3 hours, the second stage is carried out at a temperature of 90 to 110°C for 1 to 3 hours, and the third stage is carried out at a temperature of 110 to 130°C for 1 to 3 hours. Even in cases where the temperature is controlled by a multistage process with two or more stages, the total reaction time of the crystallization step is preferably 1 to 7 hours.
[0064] Instead of increasing the temperature stepwise as described above by a multistage process wherein the temperature is kept constant at each stage, the temperature may also be increased continuously. Examples of such a process include a method wherein the temperature is first increased from 70°C to 120°C for 2 hours, that is, at a rate of 25°C per hour, and then kept constant at 160°C. In cases where the temperature is continuously increased, the temperature increasing rate is preferably not more than 30°C per hour.

[0065] In the present invention, the form of the prepolymer for the crystallization treatment is not restricted, and the prepolymer may be in the form of any of a mass, film, pellet, powder and the like. For efficient crystallization, the prepolymer is preferably in the form of a pellet or powder. The pellet means a small molded particle of a polymer having a maximum diameter of about 1 to 10 mm, especially about 1.2 to 8 mm, and about 1.5 to 6 mm in most cases, with a ball shape, prolate spheroid shape, flat ball shape, plate shape, rod shape, shape similar to these, amorphous shape or another arbitrary shape. The pellet is also called a chip. Examples of the method of pelletization include a method wherein the prepolymer in the molten state is extruded into a strand-like shape and pelletized using a pelletizer, a method wherein the prepolymer is dropped in the form of a droplet using a drip nozzle and brought into contact with a solid, gas or liquid to achieve pelletization, and a method wherein the prepolymer is extruded from a die into a gas or liquid while the extruded prepolymer is cut. The pelletization is preferably carried out under a dry atmosphere, and, in cases where the prepolymer is brought into contact with moisture, the length of time of contact is preferably as short as possible.

[0066] Examples of the method for forming the prepolymer into a powder include a method wherein the prepolymer is pulverized using a mixer, blender, ball mill or hammer pulverizer. In the case of a powder, in view of efficient crystallization, the average particle diameter is preferably 0.01 to 5 mm, more preferably 0.1 to 1 mm.

[0067] Industrially, the prepolymer is usually formed into a pellet. In the production method of the present invention, an excellent productivity and high effect can be achieved especially in cases where the crystallization treatment is carried out for a prepolymer in the form of a pellet.

[0068] The weight average molecular weight of the crystallized prepolymer is 5,000 to 25,000, preferably 10,000 to 20,000, especially preferably 12,000 to 20,000. The weight average molecular weight immediately after the melt polymerization hardly changes even through the crystallization step. In poly(lactic acid), in contrast to findings for conventional polyesters, a high weight average molecular weight leads to low reactivity in solid-phase polymerization and a low final molecular weight, while a too low weight average molecular weight leads to requirement of a low solid-phase polymerization temperature for prevention of melting during solid-phase polymerization, resulting in decreased productivity. In the present invention, by using a prepolymer having a molecular weight within the above-described range, high productivity can be achieved.

[0069] In the present invention, the enthalpy of fusion \( \Delta H_m \) of the crystallized prepolymer is 50 to 65 [J/g], more preferably 53 to 60. In conventional solid-phase polymerization, it has been suggested that a high degree of crystallinity, that is, high enthalpy of fusion, leads to low reactivity in the solid-phase polymerization, but, in the present invention, as the enthalpy of fusion increases, the reactivity in the solid-phase polymerization increases. In cases where the enthalpy of fusion \( \Delta H_m \) of the crystallized prepolymer is within the above-described preferred range, the reactivity in the solid-phase polymerization can be kept high while a high degree of crystallinity can be achieved.

[0070] The acid value \( A \) [mol/ton] of the crystallized prepolymer needs to satisfy the Inequality (1) below, preferably satisfies the Inequality (5) below, more preferably satisfies the Inequality (6) below. In cases where the acid value is too high, degradation is promoted during the solid-phase polymerization step, while in cases where the acid value is too low, the reactivity is low, so that a high molecular weight and a high melting point can be hardly achieved. The acid value is derived from terminal carboxyl groups of the polymer and oligomers such as dimers, and acidic compounds such as lactic acid, and the amount of terminal carboxyl groups of the polymer is dependent on the molecular weight. In particular, in cases where too much acidic compounds are contained, degradation occurs during the solid-phase polymerization, so that the acid value is preferably low, while in cases where the value is too low, the polymerization reactivity is low. In the present invention, it was discovered that high productivity can be obtained when the following inequalities are satisfied.

\[
\begin{align*}
450/(M_w/10,000-0.14) &< A < 950/(M_w/10,000-0.14) \quad (1) \\
500/(M_w/10,000-0.14) &< A < 900/(M_w/10,000-0.14) \quad (5) \\
550/(M_w/10,000-0.14) &< A < 850/(M_w/10,000-0.14) \quad (6)
\end{align*}
\]

(wherein \( M_w \) represents the weight average molecular weight of the crystallized prepolymer)
The lactide content $L$ is preferably 0.1 to 3.0 [wt%], more preferably 0.5 to 2.5 [wt%]. In cases where the lactide content is within the preferred range, the molecular mobility of the polymer is high, and generation of acidic compounds due to degradation can be prevented.

When the crystallized prepolymer is poly-L-lactic acid or poly-D-lactic acid, in the case of poly-L-lactic acid, the D-lactic acid content $d$ is preferably 0.2 to 2.0 [mol%], and, in the case of poly-D-lactic acid, the L-lactic acid content $1$ is preferably 0.2 to 2.0 [mol%], more preferably 0.3 to 1.5 [mol%].

The enthalpy of fusion $\Delta H_m$ means the enthalpy of the melting peak upon temperature increase as measured by differential scanning calorimetry (DSC); the acid value $A$ of the crystallized prepolymer means the amount of terminal carboxyl groups as measured by neutralization titration with an alkaline solution; the lactide content means the content in the prepolymer as measured by proton NMR; and the D-lactic acid content $d$ and the L-lactic acid content $1$ mean the contents in the total lactic acid component as measured by liquid chromatography.

The solid-phase polymerization step is described below.

The solid-phase polymerization step is preferably continuously carried out under conditions including at least the following two stages.

Solid-phase polymerization conditions 1: 130°C to 155°C
Solid-phase polymerization conditions 2: 155°C to 165°C

In the present invention, the solid-phase polymerization step is preferably carried out at a temperature of not more than the melting point of the prepolymer, and, in view of efficiently obtaining a poly(lactic acid) resin having a high molecular weight and a high melting point as well as excellent hue, the solid-phase polymerization step is preferably carried out at a temperature of 130 to 165°C, more preferably carried out at a temperature of 135 to 165°C, still more preferably carried out at a temperature of 140 to 165°C. In particular, the final temperature is preferably 155 to 165°C, more preferably 160 to 165°C.

The temperature during the solid-phase polymerization step may be controlled either by a single stage process or by a multistage process with two or more stages, and, in view of achieving a high molecular weight and excellent hue in a short time, the temperature is preferably controlled by a multistage process with two or more stages, and the temperature is more preferably increased stepwise as the reaction proceeds. Examples of such a process include a method wherein the reaction is first allowed to proceed at a temperature of 130 to 155°C and then at a temperature of 155 to 165°C. The amount of increase in the temperature at each stage is preferably not more than 15°C, more preferably not more than 10°C, still more preferably not more than 5°C.

In the present invention, in view of efficiently obtaining a poly(lactic acid) resin having a high molecular weight and a high melting point as well as excellent thermal stability and hue, the solid-phase polymerization step is preferably carried out for a reaction time of 1 to 100 hours, and, in view of efficiently obtaining a poly(lactic acid) resin also having excellent hue, the solid-phase polymerization step is preferably carried out for a reaction time of 5 to 50 hours, still more preferably carried out for a reaction time of 10 to 30 hours.

In cases where the temperature during the solid-phase polymerization step is controlled by a multistage process with two or more stages, examples of such a process include a method wherein the first stage is carried out at a temperature of 130 to 150°C for 1 to 50 hours and the second stage is carried out at a temperature of 150 to 165°C for 1 to 50 hours. In view of easily achieving a high molecular weight in a short time and obtaining excellent hue, the process is more preferably carried out by a method wherein the first stage is carried out at a temperature of 120 to 140°C for 1 to 10 hours, the second stage is carried out at a temperature of 140 to 155°C for 1 to 10 hours, and the third stage is carried out at a temperature of 155 to 165°C for 10 to 30 hours. Even in cases where the temperature is controlled by a multistage process with two or more stages, the total reaction time of the solid-phase polymerization step is preferably 1 to 100 hours.

Instead of increasing the temperature stepwise as described above by a multistage process wherein the temperature is kept constant at each stage, the temperature may also be increased continuously. Examples of such a process include a method wherein the temperature is first increased from 140°C to 160°C for 20 hours, that is, at a rate of 1°C per hour, and then kept constant at 160°C. In cases where the temperature is continuously increased, the temperature increasing rate is preferably not more than 10°C per hour.

In the present invention, the pressure conditions in the solid-phase polymerization step are not restricted, and any of the conditions of reduced pressure, normal pressure and increased pressure may be employed. In view of efficiently obtaining a poly(lactic acid) resin having a high molecular weight, the pressure conditions are preferably reduced pressure conditions or normal pressure conditions. In cases where the step is carried out under reduced pressure conditions, the step is preferably carried out at a pressure of 0.13 to 1,300 Pa. Further, the step is preferably carried out at a pressure of 1 to 1,000 Pa, more preferably carried out at a pressure of 10 to 900 Pa, still more preferably carried out at a pressure of 10 to 200 Pa.
of 100 to 800 Pa, especially preferably carried out at a pressure of 500 to 700 Pa. The pressure during the solid-phase polymerization step may be controlled either by a single stage process or by a multistage process with two or more stages, and is preferably controlled by a multistage process with two or more stages. Examples of such a process include a method wherein the reaction is first allowed to proceed at a pressure of 700 to 1,300 Pa and then at a pressure of 0.13 to 700 Pa. In cases where the reaction is carried out under normal pressure conditions, the reaction is preferably carried out under the flow of an inert gas such as dry nitrogen. The flow rate is preferably 0.01 to 200 L/min., more preferably 0.1 to 150 L/min., especially preferably 0.5 to 100 L/min. per 1 kg of the prepolymer.

In the present invention, the form of the crystallized prepolymer used for the solid-phase polymerization step is not restricted, and the crystallized prepolymer may be in the form of any of a mass, film, pellet, powder and the like. The form of a pellet or powder is preferred. The pellet means a small molded particle of a polymer having a maximum diameter of about 1 to 10 mm, especially about 1.2 to 8 mm, and about 1.5 to 6 mm in most cases, with a ball shape, prolate spheroid shape, flat ball shape, plate shape, rod shape, shape similar to these, amorphous shape or another arbitrary shape. The pellet is also called a chip. In the case of a powder, in view of efficient solid-phase polymerization, the average particle diameter is preferably 0.01 to 5 mm, more preferably 0.1 to 1 mm. Industrially, the prepolymer is usually formed into a pellet. In the production method of the present invention, an excellent productivity and high effect can be achieved especially in cases where the solid-phase polymerization is carried out for a prepolymer in the form of a pellet.

In the present invention, the solid-phase polymerization step may be either a batch method or continuous method, and examples of the reactor which may be used include stirred tank reactors, mixer-type reactors and column reactors. These reactors may be used as a combination of two or more of them. In view of the productivity, the step is preferably carried out by a continuous method.

The weight average molecular weight of the poly(lactic acid) resin obtained by the method of the present invention is not restricted, and is preferably not less than 100,000 in view of the mechanical properties. In particular, for excellent moldability and mechanical properties, the weight average molecular weight is preferably 100,000 to 1,200,000, more preferably 120,000 to 300,000, still more preferably 140,000 to 250,000. The weight average molecular weight is the value of weight average molecular weight in terms of a poly(methyl methacrylate) standard as measured by gel permeation chromatography (GPC) using hexafluoroisopropanol as a solvent.

The ratio of the weight average molecular weight with respect to the number average molecular weight is preferably 1.4 to 3 in view of uniformity of the physical properties of the polymer, and the ratio is more preferably 1.5 to 2.5. The rate of reduction in the weight after heating under nitrogen gas flow at 200°C for 20 minutes is preferably not more than 0.6% in view of excellent heat resistance, and the rate is more preferably not more than 0.4%.

The content of the sulfur-containing compound containing sulfur having an oxidation number of not less than +5 after the solid-phase polymerization is preferably 10 to 4,000 ppm, more preferably 30 to 3,000 ppm, still more preferably 40 to 2,000 ppm, especially preferably 50 to 500 ppm in terms of sulfur atoms, with respect to the produced polymer.

The residual rate of the sulfur-containing compound containing sulfur having an oxidation number of not less than +5 after the solid-phase polymerization is preferably 0 to 90%, more preferably 1 to 50%, especially preferably 5 to 30%. The residual rate (R) is an index of the difference between the concentrations, before and after the polymerization reaction, of the sulfur-containing compound containing sulfur having an oxidation number of not less than +5, and is represented by the Equations (7) to (9) below.

\[
R[\%] = \frac{C_p[ppm]}{C_b[ppm]} \times 100 \quad (7)
\]

\[
C_b[ppm] = \frac{W_b[g]}{W_p[g]} \times 10^6 \quad (8)
\]

\[
C_p[ppm] = \frac{W_a[g]}{W_p[g]} \times 10^6 \quad (9)
\]

(Cb, theoretical catalyst concentration calculated according to Equation (8), which is expected when all catalyst added is remaining in the polymer; Ca, actual concentration of the catalyst remaining in the polymer after the polymerization reaction which is calculated according to Equation (9))
In cases where a tin compound(s), titanium compound(s), lead compound(s), zinc compound(s), cobalt compound(s), iron compound(s), lithium compound(s) and/or rare earth compound(s) is/are used, the ratio of the molar amount of sulfur atoms of the sulfur-containing compound containing sulfur having an oxidation number of not less than +5 with respect to the total molar amount of the metals after the solid-phase polymerization is preferably 3.0 to 50 in view of the interaction between the metal compounds and the sulfur-containing compound containing sulfur having an oxidation number of not less than +5. The ratio is more preferably 4.0 to 40.

[0089] In the present invention, in order to obtain an aliphatic polyester having excellent thermal stability, a stabilizer is preferably added at the beginning of the melt polymerization step, during the melt polymerization step or after the solid-phase polymerization.

[0090] Examples of the stabilizer in the present invention include sulfur-containing compounds containing sulfur having an oxidation number of less than +5, phosphorous compounds, aromatic ketone compounds, hydrocarbon compounds having an aromatic ring(s), aliphatic dicarboxylic acids; aliphatic diols, alicyclic hydrocarbon compounds, hindered phenol compounds, vitamin compounds, triazole compounds and hydrazine derivative compounds. These may also be used in combination.

[0091] Specific examples of the sulfur-containing compounds containing sulfur having an oxidation number of less than +5 include diphenyl sulfone, ditolyl sulfone, dibenzyl sulfone, methyl phenyl sulfone, ethyl phenyl sulfone, propyl phenyl sulfone, methyl tolyl sulfone, ethyl tolyl sulfone, propyl phenyl sulfone, benzyl phenyl sulfone, phenyl tolyl sulfone, benzyl tolyl sulfone, bis(phenoxyphenyl)methane, bis(tolylsulfonyl)methane, bis(benzylsulfonyl)methane, sulfurous acid, sodium sulfite, potassium sulfite, sulfur, diaryl thiopropionate, diridocly thiopropionate, dimeristyli thiopropionate, distearyl thiopropionate, pentaerythritol-tetrakis(3-laurythiopropionate), pentaerythritol-tetrakis(3-dodecylthiopropionate), pentaerythritol-tetrakis(3-octadecylthiopropionate), pentaerythritol-tetrakis(3-myristylthiopropionate) and pentaerythritol-tetrakis(3-stearythiopropionate). Specific examples of trade names of the sulfur-containing compounds containing sulfur having an oxidation number of less than +5 include "Adekastab" AO-23, AO-4125 and AO-503A manufactured by ADEKA; "Irganox" PS802 manufactured by Ciba Specialty Chemicals; "Sumilizer" TPL-R, TPM, TPS and TP-D manufactured by Sumitomo Chemical Co., Ltd.; DSTP, DLTP, DLTOIB and DMTP manufactured by API Corporation; "Seenoxx" 412S manufactured by Shipjo Kasei; and "Cyanox" 1212 manufactured by Cyanamid Inc.

[0092] Among the phosphorous compounds, examples of organic phosphorous compounds include phosphite compounds and phosphate compounds. Specific examples of such phosphite compounds include tetrakis[2-t-butyl-4-thio (2'-methyl-4'-hydroxy-5'-t-butylphenyl)-5-methylphenyl]1,6-hexamethylen-bis(N-hydroxyethyl-N-methylsemicarbazide)-diphosphite, tetrakis[2-t-butyl-4-thio(2'-methyl-4'-hydroxy-5'-t-butylphenyl)-5-methylphenyl]-1,10-decymethylenedi-carboxylic acid-di-hydroxethylcarbonylhydrazide-diphosphite, tetrakis[2-t-butyl-4-thio(2'-methyl-4'-hydroxy-5'-t-butylphenyl)-5-methylphenyl]-1,10-decymethylenedi-carboxylic acid-di-salicyloylhydrazide-diphosphite, tetrakis[2-t-butyl-4-thio(2'-methyl-4'-hydroxy-5'-t-butylphenyl)-5-methylphenyl]-di(hydroxyethylcarbonyl)hydrazide-diphosphite and tetrakis[2-t-butyl-4-thio(2'-methyl-4'-hydroxy-5'-t-butylphenyl)-5-methylphenyl]-N,N'-bis(hydroxyethyl)oxamide-diphosphite. The phosphite compound preferably has at least one P=O bond linked to an aromatic group. Specific examples of such a compound include tris(2,4-di-t-butylphenyl) phosphite, tetrakis(2,4-di-t-butylphenyl)4,4'-biphenylephene-phosphonite, bis(2,4-di-t-butylphenyl) pentaerythritol-phosphite, bis(2,6-di-t-butyl-4-methylphenyl) pentaerythritol-phosphite, 2,2-methylenebis(4,6-di-t-butylphenyl)octylphosphite, 4,4'-butylidene-bis(3-methyl-6-t-butylphenyl-di-tridecyl)phosphite, 1,1,3-tris(2-methyl-4-diridoclylphosphite-5-t-butyl)phenyl)butane, tris(mixed mono- and di-nonylphenyl)phosphite, tris(nonylphenyl)phosphite and 4,4'-isopropylidenebis(phenyl-dialkylphosphite). Tris(2,4-di-t-butylphenyl) phosphite, 2,2-methylenebis(4,6-di-t-butylphenyl)octylphosphite, bis(2,6-di-t-butyl-4-methylphenyl) pentaerythritol-phosphite, tetrakis[2,4-di-t-butylphenyl]-4,4'-biphenylephene-phosphonite, 9,10-dihydro-9-oxa-10-phosphaenhantrene-10-oxide, triisodecyl phosphate and the like are preferably used. Specific examples of trade names of the phosphate compounds include "Adekastab" C, PEP-4C, PEP-8, PEP-11C, PEP-24G, PEP-36, HP-10, 2112, 260, 522A, 329A, 1178, 1500, C, 135A, 3010 and TPP manufactured by ADEKA; "Irgafos" 168 manufactured by Ciba Specialty Chemicals; "Sumilizer" P-16 manufactured by Sumitomo Chemical Co., Ltd.; "Sandostab" P-EPQ manufactured by Clariant Ltd.; "Weston" 618, 619G and 624 manufactured by GE; and SANKO-HCA manufactured by Sanko Co., Ltd.

[0093] Specific examples of the phosphate compounds include monostearoyl acid phosphate, distearyl acid phosphate, methyl acid phosphate, isopropyl acid phosphate, butyl acid phosphate, octyl acid phosphate and isodecyl acid phosphate, and, among these, monostearoyl acid phosphate and distearyl acid phosphate are preferred. Specific examples of trade names of the phosphate compounds include "Irganox" MD1024 manufactured by Ciba Specialty Chemicals; "Inhibitor" OABH manufactured by Eastman Kodak Company; and "Adekastab" CDA-1, CDA-6 and AX-71 manufactured by ADEKA Corporation.

[0094] Among the phosphorous compounds, examples of inorganic phosphorous compounds include phosphate compounds, phosphite compounds and hypophosphite compounds. Specific examples of such phosphate compounds include phosphoric acid, diphosphoric acid, triphosphoric acid, lithium phosphate, beryllium phosphate, sodium phosphate,
magnesium phosphate, aluminum phosphate, potassium phosphate and calcium phosphate; specific examples of such compounds include phosphorous acid, lithium phosphate, beryllium phosphate, sodium phosphate, magnesium phosphate, aluminum phosphate, potassium phosphate and calcium phosphate; and specific examples of such phosphorous compounds include hypophosphorous acid, lithium hypophosphite, beryllium hypophosphite, sodium hypophosphite, magnesium hypophosphite, aluminum hypophosphite, potassium hypophosphite and calcium hypophosphite.

Specific examples of the aromatic ketone compounds include 1,4-dibenzoylbenzene, benzophenone, acetophenone, propiophenone and benzoylnaphthalene.

Specific examples of the hydrocarbon compounds having an aromatic ring(s) include triphenylmethane, diphenylmethane and toluene.

Specific examples of the aliphatic dicarboxylic acids include oxalic acid, succinic acid, butanoic acid, adipic acid and pentanoic acid.

Specific examples of the aliphatic diols include ethylene glycol, propanediol, butanediol, pentanediol, hexanediol, cyclhexanediol, spiroglycol and isosorbide.

Specific examples of the aliphatic hydrocarbon compounds include 1,2-dimethylcyclohexane, methylcyclohexane, 1,2,4-trimethylcyclohexane, 1,2-diethylcyclohexane, ethylcyclohexane, 1,2,4-triethylcyclohexane, 1,2-dipropylcyclohexane, propylcyclohexane and 1,2,4-tripropylcyclohexane.

Specific examples of the hindered phenol compounds include n-octadecyl-3-(3',5'-di-t-butyl-4'-hydroxyphenyl)-propionate, n-octadecyl-3-(3'-methyl-5'-t-butyl-4'-hydroxyphenyl)-propionate, n-tetradecyl-3-(3'-di-t-butyl-4'-hydroxyphenyl)-propionate, 1,6-hexanediol-bis-[3-(3,5-di-t-butyl-4'-hydroxyphenyl)-propionate], 1,4-butanediol-bis-[3-(3,5-di-t-butyl-4'-hydroxyphenyl)-propionate], 2,2'-methylenebis-(4'-methyl-t-butylphenol), triethylene glycol-bis-[3-(3-t-butyl-5-methyl-4'-hydroxyphenyl)-propionate], tetrakis[methylene-3-(3',5'-di-t-butyl-4'-hydroxyphenyl) propionate][methane], 3,9-bis[2-(3-t-butyl-4'-hydroxy-5-methylphenyl)propionyloxy]-1,1-diethylmethylenediamine, N,N'-tetramethylethane-bis-[3-(3'-methyl-5'-t-butyl-4'-hydroxyphenol)propionyldiamine, N,N'-bis[3-(3,5-di-t-butyl-4'-hydroxyphenol)propiony]hydrazine, N-salicyloyl-N'-salicylidenehydrazine, 3-(N-salicyloyl)amino-1,2,4-triazole, N,N'-bis[3-(3,5-di-t-butyl-4'-hydroxyphenol)propionyloxy]ethylxoyamide, pentaerythrityl-tetrakis[3-(3,5-di-t-butyl-4'-hydroxyphenol)propionate] and N,N'-hexamethylenbis-(3,5-di-t-butyl-4'-hydroxyphenol)propionate. Preferred examples of the hindered phenol compounds include triethylene glycol-bis-[3-(3,5-di-t-butyl-4'-hydroxyphenol)propionate], tetrakis[methylene-3-(3',5'-di-t-butyl-4'-hydroxyphenol)propionate][methane], 1,6-hexanediol-bis-[3-(3,5-di-t-butyl-4'-hydroxyphenol)propionate], pentaerythrityl-tetrakis[3-(3,5-di-t-butyl-4'-hydroxyphenol)propionate] and N,N'-hexamethylenbis-(3,5-di-t-butyl-4'-hydroxyhydrocinnamide). Specific examples of trade names of the hindered phenol compounds include "Adekastab" AO-20, AO-30, AO-40, AO-50, AO-60, AO-70, AO-80 and AO-330 manufactured by ADEKA Corporation; "Irganox" 245, 259, 565, 1010, 1035, 1076, 1098, 1222, 1330, 1425, 1520, 3114 and 5057 manufactured by Ciba Specialty Chemicals; "Sumilizer" BHT-R, MDP-S, BBM-S, WX-R, NW, BP-76, BP-101, GA-80, GM and GS manufactured by Sumitomo Chemical Co., Ltd.; and "Cyanox" CY-1790 manufactured by Cyanamid Inc.

Specific examples of the vitamin compounds include natural compounds such as d-α-tocopherol acetate, d-α-tocopherol succinate, d-α-tocopherol, d-β-tocopherol, d-γ-tocopherol, d-δ-tocopherol, d-γ-tocopherenil and d-δ-tocopherenil; and synthetic compounds such as dl-α-tocopherol, dl-α-tocopherol acetate, dl-α-tocopherol calcium succinate and dl-α-tocopherol nicotinate. Specific examples of trade names of the vitamin compounds include "Tocopherol" manufactured by Eisai Co., Ltd. and "Irganox" E201 manufactured by Ciba Specialty Chemicals.

Specific examples of the triazole compounds include benzotriazole and 3-(3-N-salicyloyl)amino-1,2,4-triazole.

Specific examples of the hydroxide derivative compounds include decamethylenedicarboxylic acid bis-[N-salicyloylhydrazide], isophthalic acid bis-[2-phenoxypyropionylyhydrazide], N-formyl-N-salicyloylhydrazine, 2,2-oamidobis-[ethyl-3-(3,5-di-t-butyl-4'-hydroxyphenol)propionate], oxalyl-benzyldiene-hydrazide, nickel-bis-[1-(phenyl-3-methyl-4-decanoyl-5-pyazolate), 2-ethoxy-2-ethoxylanilide, 5-t-butyl-2-ethoxy-2'-ethoxylanilide, N,N'-diethyl-N,N'-diphenyloxamide, N,N'-diethyl-N,N'-diphenyloxamide, oxalic acid-bis-[benzildenehydrazide], thiodipropionic acid-bis-[benzylidenehydrazide], bis[salicyloylhydrazine], N-salicylidene-N-salicyloylhydrazine, N,N'-bis[3-(3,5-di-t-butyl-4'-hydroxyphenol)propiony]hydrazine and N.N'-bis[2-(3,5-di-t-butyl-4'-hydroxyphenol)propionyloxy]ethylxoyamide.

Among the above examples, those having no t-butyl group are preferred. In particular, at least one selected from sulfur-containing compounds, containing sulfur having an oxidation number of less than +5, phosphorous compounds, aromatic ketone compounds, hydrocarbon compounds having an aromatic ring(s), aliphatic dicarboxylic acids, aliphatic diols and alicyclic hydrocarbon compounds is preferably contained. Preferred sulfur-containing compounds containing sulfur having an oxidation number of less than +5 are diphenylsulfone, sulfurous acid, sodium sulfite and sulfur, and "Sumilizer" TPD (pentaerythritol tetakis[(I-lauryl-thio-propionate)]) manufactured by Sumitomo Chemical Co., Ltd. Among the phosphorous compounds, more preferred inorganic phosphorous compounds are phosphoric acid compounds and phosphoric acid compounds, and more preferred organic phosphorous compounds are phosphate compounds and phosphite compounds. More preferred specific examples of the phosphorous compounds include inorganic...
phosphorous compounds such as phosphoric acid, phosphorous acid, sodium phosphate and sodium phosphate; and organic phosphorus compounds such as "Adekastab" AX-71 (dioctadecyl phosphite), PEP-8 (distearyl pentaerythritol diphosphate), PEP-36 (cyclo neopentetrayl bis(2,6-t-butyl-4-methylphenyl)phosphate), HP-10 (2,2'-methylenebis(4,6-di-t-butyl-1-phenylxyloxy)(2-ethylhexyloxy)phosphorous), PEP-24G (bis(2,4-di-t-butylphenyl)pentaerythritol diphosphate), 3010 (trisocetyl phosphite) and TPP (triphenyl phosphite) manufactured by ADEKA Corporation; "Irgafos" 168 (tris(2,4-di-t-butyphenyl)phosphate) manufactured by Ciba Specialty Chemicals; and HCA (9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide) manufactured by Sanko Co., Ltd. In particular, phosphorous compounds having a phosphorus atom(s) directly bound to a carbon atom(s) constituting an aromatic ring(s) are preferred, and HCA (9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide) manufactured by Sanko Co., Ltd. is especially preferred.

As the aromatic ketone compound, 1,4-dibenzoylbenzene and benzophenone are especially preferred; as the hydrocarbon compound having an aromatic ring(s), triphenylmethane is especially preferred; as the aliphatic dicarboxylic acid, oxalic acid is especially preferred; as the aliphatic diol, hexanediol is especially preferred; and, as the alicyclic hydrocarbon compound, 1,2-dimethylcyclohexane is especially preferred.

The amount of the stabilizer to be added is not restricted, and, in view of achieving excellent thermal stability, the amount is preferably 0.001 to 2 parts by weight, more preferably 0.01 to 1 part by weight, still more preferably 0.05 to 0.5 part by weight, most preferably 0.08 to 0.3 part by weight with respect to 100 parts by weight of the poly(lactic acid) resin. The timing of addition of the stabilizer is not restricted, and may be either before the beginning or after the completion of either the melt polymerization step or the solid-phase polymerization step. In cases where the stabilizer is added at the stage of the melt polymerization step in view of obtaining a poly(lactic acid) resin having a high melting point and a high molecular weight, the stabilizer is preferably added immediately before the completion of the above-described melt polymerization conditions 1 (140°C to 160°C, 13.3 to 66.6 kPa) or at the beginning of the above-described melt polymerization conditions 2 (160°C to 180°C, 1.3 to 6.5 kPa), more preferably added both immediately before the completion of the melt polymerization conditions 1 and at the beginning of the melt polymerization conditions 2 from the viewpoint of achieving excellent productivity. In cases where the stabilizer is added at the beginning of the melt polymerization conditions 2, the catalyst for solid-phase polymerization is preferably added after the addition of the stabilizer. In cases where the stabilizer is added at the stages of both the melt polymerization conditions 1 and the melt polymerization conditions 2, the stabilizer is preferably added in an amount of 0.001 to 1 part by weight at each stage, and, in view of achieving excellent productivity, the stabilizer is more preferably added in an amount of 0.01 to 0.5 part by weight at each stage, still more preferably added in an amount of 0.01 to 0.1 part by weight at each stage with respect to 100 parts by weight of the poly(lactic acid) resin.

In view of obtaining a poly(lactic acid) resin having excellent thermal stability, the stabilizer may also be preferably added after the completion of the solid-phase polymerization step. In this case, the method of addition of the stabilizer is not restricted, and examples of the method include a method wherein melt kneading is carried out at a temperature higher than the melting point of the poly(lactic acid) resin and a method wherein the stabilizer is dissolved in a solvent and the resulting solution is mixed, followed by removal of the solvent. In view of efficient production, the method wherein melt kneading is carried out at a temperature higher than the melting point of the poly(lactic acid) resin is preferred. The method of melt kneading may be either a batch method or continuous method, and examples of the apparatus which may be used include single screw extruders, twin screw extruders, multi-screw extruders, plastomill, kneaders and stirred tank reactors equipped with a pressure reducing device. In view of efficient uniform kneading, a single screw extruder or twin screw extruder is preferably used. The temperature at which the stabilizer is added is preferably a temperature of 180 to 250°C, and, in view of achieving excellent mechanical properties, a temperature of 190 to 230°C is more preferred. The pressure at which the stabilizer is added may be any of a reduced pressure, normal pressure and increased pressure. In view of removal of gas generated during melt kneading, the pressure is preferably a reduced pressure. In terms of the atmospheric conditions during the melt kneading, the melt kneading may be carried out either in the air or under an atmosphere of an inert gas such as nitrogen. In view of reduction in the amount of gas generated during the melt kneading, the melt kneading is preferably carried out under an atmosphere of an inert gas.

In cases where the mixing is carried out in a solvent, a solvent that dissolves the polymer and monomers is used. Examples of the solvent which may be used include chloroform, methylene chloride and acetonitrile. In cases where the solvent needs to be removed after the mixing, the method for removing the solvent is not restricted, and examples of the method which may be used include a method wherein the solvent is evaporated at room temperature and a method wherein the solvent is evaporated under reduced pressure at a temperature higher than the boiling point of the solvent.

In the present invention, in view of further improving the hydrolysis resistance, at least one selected from amine compounds, alkali metal compounds and alkaline earth metal compounds is preferably added at the beginning of the melt polymerization step or after the completion of the solid-phase polymerization step, or at any stage therebetween. By this, in cases where a polymerization catalyst, especially a catalyst having an acid, is remaining, hydrolysis of the poly(lactic acid) resin during the melt kneading and the melt molding by the remaining catalyst can be suppressed and the hydrolysis resistance can thus be increased.
Specific examples of the amine compounds include methylethylamine, triethylamine, dimethylpropylamine, ethylamine, isoamylamine, butylamine, propylamine, ethylenediamine, butanediamine, hexamethylenediamine, 1,2,3-triaminopropane, tetraethylammonium hydroxide, aniline, naphthalene, naphthalenediamine, cyclohexanediameine, benzenediamine, benzidine, diaminodiphenylether, diaminodiphenylmethane, dibenzylamine, didodecylamine, pyrimidine, 2-aminopyrimidine, 2-amino-4-methyl-6-methoxypyrimidine, pyrimidine-2,4,6-triamine, N-(2-aminoethyl)-N-pyrimidine-2-ylamine, 6-1-buty1pyrimidine-4-amino, 4,6-dimethoxy-5-phenylpyrimidine-2-amine, 2-ethoxyquinidine, 4,6-diamino, 5-phenylpyrimidine-4-amino, cis-[2-(3,5-diamo-2,4,6-triazaphenyl)ethyl]-2,4,8,10-tetraoxaspiro[5.5]undecane, ethylenediamine-tetraacetic acid, alkal metal (Li, Na, K) salts of ethylenediamine-tetraacetic acid, N,N’-disalicylidene-ethylenediamine, N,N’-disalicylidene-1,2-propylenediamine, N,N’-disalicylidene-N’-methyl-dipropylethenetriamine, 3-salicyloylaminol-1,2,4-triazole and N,N,N’-trimethylethylenediamine; hindered amine compounds such as 4-acetoxy-2,2,6,6-tetramethylpiperidine, 4-stearo1oxy-2,2,6,6-tetramethylpiperidine, 4-acrylo1oxy-2,2,6,6-tetramethylpiperidine, 4-(phenylacetoxy)-2,2,6,6-tetramethylpiperidine, 4-benzoxoxy-2,2,6,6-tetramethylpiperidine, 4-benzoyloxy-2,2,6,6-tetramethylpiperidine, 4-methoxy-2,2,6,6-tetramethylpiperidine, bis(2,2,6,6-tetramethyl-4-piperidyl)-carbonate, bis(2,2,6,6-tetramethyl-4-piperidyl)-oxalate, bis(2,2,6,6-tetramethyl-4-piperidyl)-malonate, bis(2,2,6,6-tetramethyl-4-piperidyl)-sebacate, bis(2,2,6,6-tetramethyl-4-piperidyl)-adipate, bis(2,2,6,6-tetramethyl-4-piperidyl)-terephthalate, 1,2-bis(2,2,6,6-tetramethyl-4-piperidyl)ethane, α,α’-bis(2,2,6,6-tetramethyl-4-piperidyl)-xylene, bis(2,2,6,6-tetramethyl-4-piperidyl)dicyclohexylmethane, 2,4-dicarbamate, bis(2,2,6,6-tetramethyl-4-piperidyl)-hexamethylene-1,6-dicarbamate, tris(2,2,6,6-tetramethyl-4-piperidyl)-benzene-1,3,5-tricarboxylate, tris(2,2,6,6-tetramethyl-4-piperidyl)-benzene-1,3,4,5-tricarboxylate, 1-[2-(3,5-di-t-butyl-4-hydroxyphenyl)propiony1oxy][butyl]-4-[3-(3,5-di-t-butyl-4-hydroxyphenyl)propiony1oxy]2,2,6,6-tetramethylpiperidine, condensates of 1,2,3,4-butanetetracarboxylic acid, 1,2,2,6,6-pentamethyl-4-piperidinol and β,β',β',β'-tetramethyl-3,9-[2,4,8,10-tetraoxaspiro[5.5]undecane]diethanol, and polycondensates of succinic acid dimethyl-1-(2-hydroxyethyl)-4-hydroxy-2,2,6,6-tetramethylpiperidine, and polyamines such as 3,9-bis[2-(3,5-diamino-2,4,6-triazaphenyl)ethyl]-2,4,8,10-tetraoxaspiro[5.5]undecane, ethylenediamine-tetraacetic acid, alkal metal (Li, Na, K) salts of ethylenediamine-tetraacetic acid, N,N’-disalicylidene-ethylenediamine, N,N’-disalicylidene-1,2-propylenediamine, N,N’-disalicylidene-N’-methyl-dipropylethenetriamine and 3-salicyloylaminol-1,2,4-triazole. Among these, at least one of aromatic amine compounds, alkylamine compounds having not less than 4 carbon atoms, and amine compounds having a pyrimidine skeleton is preferably contained.

Specific examples of the alkali metal compounds include lithium compounds such as lithium isopropoxide, lithium chloride, lithium acetate, lithium lactate, lithium octoate, lithium stearate, lithium napthenate, lithium t-buty1 carbonate, lithium sulfate and lithium oxide; sodium compounds such as sodium isopropoxide, sodium chloride, sodium acetate, sodium lactate, sodium octoate, sodium stearate, sodium napthenate, sodium t-buty1 carbonate, sodium sulfate and sodium oxide; and potassium compounds such as potassium isopropoxide, potassium chloride, potassium acetate, potassium lactate, potassium stearate, potassium napthenate, potassium t-buty1 carbonate, potassium sulfate and potassium oxide. In particular, at least one of organic carboxylic acid alkali metal compounds having not less than 4 carbon atoms is preferably contained.

Examples of the alkaline earth metal compounds include magnesium compounds such as magnesium diisopropoxide, magnesium chloride, magnesium acetate, magnesium lactate, magnesium stearate, magnesium carbonate, magnesium sulfate and magnesium oxide; calcium compounds such as calcium diisopropoxide, calcium chloride, calcium acetate, calcium octoate, calcium napthenate, calcium lactate, calcium stearate and calcium sulfate; barium compounds such as barium diisopropoxide, barium chloride, barium acetate, barium octoate, barium napthenate, barium lactate, barium stearate and barium sulfate. In particular, at least one of organic carboxylic acid alkaline earth metal compounds having not less than 4 carbon atoms is preferably contained.

The amount of the amine compound(s), alkal metal(s) and/or alkaline earth metal(s) to be added is not restricted, and, in view of achieving excellent hydrolysis resistance, the amount is preferably 0.001 to 2 parts by weight, more preferably 0.01 to 1 part by weight, still more preferably 0.05 to 0.5 part by weight, most preferably 0.08 to 0.3 part by weight with respect to 100 parts by weight of the poly(lactic acid) resin. In cases where an amine compound is used, the ratio of the molar amount of nitrogen atoms of the amine compound with respect to the molar amount of sulfur atoms of the sulfur-containing compound containing sulfur having an oxidation number of not less than +5 as a catalyst in the polymer after solid-phase polymerization is preferably 0.3 to 0.9, more preferably 0.4 to 0.8. The timing of addition of the amine compound(s), alkal metal(s) and/or alkaline earth metal(s) is not restricted, and may be either at the beginning or after the completion of either the melt polymerization step or the solid-phase polymerization step. In view of obtaining a poly(lactic acid) resin having a high melting point and a high molecular weight, the compound(s) is/are preferably added at the stage of the melt polymerization step, and, in view of achieving excellent productivity, the compound(s) is/are more preferably added immediately before the completion of the above-described melt polymerization conditions 1 ([140°C to 160°C, 13.3 to 66.6 kPa] or at the beginning of the above-described melt polymerization conditions 2 ([160°C to 180°C, 1.3 to 6.5 kPa], still more preferably added both immediately before the completion of the melt
polymerization conditions 1 and at the beginning of the melt polymerization conditions 2. Further, similarly in view of achieving excellent productivity, the compound(s) is/are preferably added after addition of the sulfur-containing compound containing sulfur having an oxidation number of not less than +5 as a catalyst. In cases where the compound(s) is/are added at the beginning of the melt polymerization conditions 2, the catalyst for solid-phase polymerization is preferably added after the addition of the amine compound(s), alkali metal(s) and/or alkaline earth metal(s). In cases where the compound(s) is/are added at the stages of both the melt polymerization conditions 1 and the melt polymerization conditions 2, the compound(s) is/are preferably added in an amount of 0.001 to 1 part by weight at each stage, and, in view of achieving excellent productivity, the compound(s) is/are more preferably added in an amount of 0.01 to 0.5 part by weight at each stage, still more preferably added in an amount of 0.01 to 0.1 part by weight at each stage with respect to 100 parts by weight of the poly(lactic acid) resin. In view of obtaining a poly(lactic acid) resin having excellent hydrolysis resistance, the compound(s) may also be preferably added after completion of the solid-phase polymerization step. The method of addition of the amine compound(s), alkali metal(s) and/or alkaline earth metal(s) is not restricted, and examples of the method include a method wherein melt kneading is carried out at a temperature higher than the melting point of the poly(lactic acid) resin and a method wherein the compound(s) is/are dissolved in a solvent and the resulting solution is mixed, followed by removal of the solvent. In view of efficient production, the method wherein melt kneading is carried out at a temperature higher than the melting point of the poly(lactic acid) resin is preferred. The method of melt kneading may be either a batch method or continuous method, and examples of the apparatus which may be used include single screw extruders, twin screw extruders, plastomill, kneaders and stirred tank reactors equipped with a pressure reducing device. In view of efficient uniform kneading, a single screw extruder or twin screw extruder is preferably used. The temperature at which the amine compound(s), alkali metal(s) and/or alkaline earth metal(s) is/are added is preferably a temperature of 180 to 250°C, and, in view of achieving excellent mechanical properties, a temperature of 190 to 230°C is more preferred. The pressure at which the amine compound(s), alkali metal(s) and/or alkaline earth metal(s) is/are added may be any of a reduced pressure, normal pressure and increased pressure. In view of removal of gas generated during melt kneading, the pressure is preferably a reduced pressure. In terms of the atmospheric conditions during the melt kneading, the melt kneading may be carried out either in the air or under an atmosphere of an inert gas such as nitrogen. In view of reduction in the amount of gas generated during the melt kneading, the melt kneading is preferably carried out under an atmosphere of an inert gas.

[0114] In cases where the mixing is carried out in a solvent, a solvent that dissolves the polymer and monomers is used. Examples of the solvent which may be used include chloroform, methylene chloride and acetonitrile. In cases where the solvent needs to be removed after the mixing, the method for removing the solvent is not restricted, and examples of the method which may be used include a method wherein the solvent is evaporated at room temperature and a method wherein the solvent is evaporated under reduced pressure at a temperature higher than the boiling point of the solvent.

[0115] The crystallized poly(lactic acid) prepolymer prepared in the present invention has a weight average molecular weight of 5,000 to 25,000, and the weight average molecular weight is preferably 10,000 to 20,000. The enthalpy of fusion $\Delta H_m$ is 50 to 65 [J/g], more preferably 53 to 60.

[0116] The acid value $A$ [mol/ton] of the crystallized prepolymer needs to satisfy the Inequality (1) below, preferably satisfies the Inequality (5) below, more preferably satisfies the Inequality (6) below.

$$450/(M_{w}/10,000-0.14)<A<950/(M_{w}/10,000-0.14) \quad (1)$$

(wherein $M_w$ represents the weight average molecular weight of the crystallized prepolymer)

$$500/(M_{w}/10,000-0.14)<A<900/(M_{w}/10,000-0.14) \quad (5)$$

$$550/(M_{w}/10,000-0.14)<A<850/(M_{w}/10,000-0.14) \quad (6)$$

[0117] The lactide content $L$ is preferably 0.1 to 3.0 [wt%], more preferably 0.5 to 2.5 [wt%].

[0118] When the crystallized prepolymer is poly-L-lactic acid or poly-D-lactic acid, in the case of poly-L-lactic acid, the D-lactic acid content $d$ is preferably 0.2 to 2.0 [mol%], more preferably 0.3 to 1.5 [mol%], and, in the case of poly-D-lactic acid, the L-lactic acid content $l$ is preferably 0.2 to 2.0 [mol%], more preferably 0.3 to 1.5 [mol%].

[0119] The ratio of the weight average molecular weight with respect to the number average molecular weight is preferably 1.2 to 3 in view of the uniformity of the physical properties of the polymer, and the ratio is more preferably 1.4
The weight average molecular weight and the number average molecular weight mean the values of weight average molecular weight and number average molecular weight in terms of a poly(methyl methacrylate) standard as measured by gel permeation chromatography (GPC) using hexafluoroisopropanol as a solvent; the enthalpy of fusion $\Delta H_m$ means the enthalpy of the melting peak upon temperature increase as measured by differential scanning calorimetry (DSC); the acid value A means the amount of terminal carboxyl groups as measured by neutralization titration with an alkaline solution; the lactide content means the content in the prepolymer as measured by proton NMR; and the D-lactic acid content and the L-lactic acid content mean the contents in the total lactic acid component as measured by liquid chromatography.

To the poly(lactic acid) resin obtained by the production method of the present invention, one or more of normal additives may be added as long as the object of the present invention is not adversely affected. Examples of such additives include fillers (glass fibers, carbon fibers, metal fibers, natural fibers, organic fibers, glass flakes, glass beads, ceramic fibers, ceramic beads, asbestos, wollastonite, talc, clay, mica, sericite, zeolite, bentonite, montmorillonite, synthetic mica, dolomite, kaolinite, silicic acid fine powder, feldspar powder, potassium titanate, shirasu balloon, calcium carbonate, magnesium carbonate, barium sulfate, calcium oxide, aluminum oxide, titanium oxide, aluminum silicate, silicon oxide, plaster, novaculite, dawsonite, white clay and the like), ultraviolet absorbers (resorcinol, salicylate, benzotriazole, benzophenone and the like), lubricants, releasing agents (montanic acid and salts thereof, esters thereof and half esters thereof, stearyl alcohol, stearamide, polyethylene wax and the like), coloring agents including dyes (nigrosine and the like) and pigments (cadmium sulfide, phthalocyanine and the like), anti-coloring agents (phosphites, hypophosphites and the like), flame retardants (red phosphorus, phosphoric acid esters, brominated polystyrene, brominated polyphenylene ether, brominated polycarbonate, magnesium hydroxide, melamine, cyanuric acid and salts thereof, and the like), electrically conducting agents or coloring agents (carbon black and the like), tribological property improving agents (graphite, fluorene resins and the like), nuclear agents (inorganic nucleating agents including talc; organic amide compounds including ethylenebislauryl amide, ethylenebis-12-dihydroxystearic acid amide and trimesic acid tricyclohexylamidine; pigment nucleating agents including copper phthalocyanine and Pigment Yellow 110; organic carboxylic acid metal salts; phenylphosphonic acid zinc; and the like) and antistatic agents.

The poly(lactic acid) resin composition obtained by the production method of the present invention may additionally contain at least one of other thermoplastic resins (polyethylene, polypropylene, acrylic resins, polyamide, polyphenylene sulfide resins, polyether ketone resins, polyester, polysulfone, polyphenylene oxide, polycetal, polyimide, polyetherimide and the like), thermostetting resins (phenol resins, melamine resins, polyester resins, silicone resins, epoxy resins and the like), soft thermoplastic resins (ethylene/glycidyl methacrylate copolymers, polyester elastomers, polyamide elastomers, ethylene/propylene terpolymers, ethylene/butene-1 copolymers and the like) and the like as long as the object of the present invention is not adversely affected.

The poly(lactic acid) resin composition obtained by the production method of the present invention, even after being once heat-melted and solidified upon processing into a molded article or the like, has a high molecular weight, and is likely to form a poly(lactic acid) resin having high heat resistance as well as excellent thermal stability and hue in a preferred embodiment.

**EXAMPLES**

The present invention will now be described more specifically by way of Examples. The number of parts in Examples herein represents parts by weight.

The measurement methods and judgment methods used in the present invention were as follows.

(1) Weight Average Molecular Weight

This is the value of weight average molecular weight in terms of a poly(methyl methacrylate) standard as measured by gel permeation chromatography (GPC) using hexafluoroisopropanol as a solvent.

(2) Acid Value

The polymer was dissolved in an o-cresol/chloroform-mixed solvent (volume ratio, 2:1), and the resulting solution was subjected to neutralization titration with a potassium hydroxide/ethanol solution at a known concentration to measure the acid value.

(3) Enthalpy of Fusion before Solid-phase Polymerization

Under nitrogen atmosphere, the temperature was increased from 30°C to 200°C at a rate of 20°C/min. to
measure the enthalpy of fusion by differential scanning calorimetry (DSC).

(4) Melting Point after Solid-phase Polymerization

[0129] Under nitrogen atmosphere, the temperature was kept at 200°C for 2 minutes and then decreased to 30°C at a rate of 20°C/min., followed by increasing the temperature at a rate of 20°C/min. to 200°C to measure the melting point by differential scanning calorimetry (DSC).

(5) Amount of D-isomer

[0130] The polymer was hydrolyzed with a sodium hydroxide solution and neutralized with hydrochloric acid. The amount of the D-isomer was then measured with a liquid chromatography to which an optical resolution column was attached.

(6) Lactide Content

[0131] The polymer was dissolved in deuterated chloroform and subjected to measurement by proton NMR. The lactide content was calculated based on the ratio between the areas of the peaks derived from lactide and the polymer.

(7) Hue

[0132] The hue was evaluated according to the following standards based on visual observation:

5: Colorless;
4: Intermediate between 3 and 5;
3: Colored in pale yellow;
2: Intermediate between 1 and 3;
1: Colored in yellow.

[Example 1]

[0133] In a reaction vessel equipped with an agitator and a reflux condenser, 100 parts by weight of 90 wt% aqueous L-lactic acid (amount of the D-isomer, 0.4%; manufactured by Wako Pure Chemical Industries, Ltd.) solution was placed, and, as catalysts, tin(II) acetate (manufactured by Kanto Chemical Co., Inc.) was added at 120 ppm in terms of tin atoms with respect to L-lactic acid (excluding water contained together in the material) and methanesulfonic acid (manufactured by Wako Pure Chemical Industries, Ltd.) was added at 1,100 ppm in terms of sulfur atoms with respect to L-lactic acid (excluding water contained together in the material). The temperature was adjusted to 155°C and the pressure was gradually decreased to 700 Pa. The reaction was allowed to proceed for 3.5 hours while water was removed, and the polymerization reaction was then carried out at a temperature of 175°C at a pressure of 400 Pa for 7 hours, to obtain a prepolymer having a weight average molecular weight of 14,700. The obtained prepolymer was dropped onto a belt under nitrogen atmosphere without allowing contact with the ambient air, and cooled, to obtain a pellet in the shape of a ball having a diameter of 3 mm. Immediately thereafter, the pellet was treated under nitrogen atmosphere at 100°C for 1 hour and then at 120°C for 1 hour, to allow crystallization. The crystallized prepolymer had an acid value of 452 [mol/ton] and an enthalpy of fusion of 55.3 [J/g]. Immediately thereafter, at a pressure of 50 Pa, the temperature was continuously increased from 140°C to 160°C for 20 hours (temperature increasing rate, 1°C per hour), and solid-phase polymerization was then carried out at 160°C for 20 hours. In 100 parts by weight of the obtained poly(lactic acid) resin, 0.2 part by weight of stearyl acid phosphate was mixed, and the resulting mixture was subjected to melt kneading using a biaxial extruder at 190°C. Properties of the obtained poly(lactic acid) resin were as shown in Table 1.

[Examples 2 to 15, Comparative Examples 1 to 8]

[0134] The operation was carried out in the same manner as in Example 1 except that the conditions for melt polymerization, conditions for crystallization of the prepolymer and conditions for solid-phase polymerization were as shown in Tables 1 and 2. The results are shown in Tables 1 and 2. It should be noted that, in Example 9, the length of time of temperature increase in the solid-phase polymerization was increased to 25 hours. In Comparative Examples 2 to 8, the production of the pellet was carried out in the air.
<table>
<thead>
<tr>
<th></th>
<th>Example 1</th>
<th>Example 2</th>
<th>Example 3</th>
<th>Example 4</th>
<th>Example 5</th>
<th>Example 6</th>
<th>Example 7</th>
<th>Example 8</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Melt polymerization condition</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Final temperature [°C]</td>
<td>170</td>
<td>170</td>
<td>170</td>
<td>170</td>
<td>170</td>
<td>170</td>
<td>170</td>
<td>170</td>
</tr>
<tr>
<td>Final pressure [kPa]</td>
<td>1.32</td>
<td>1.32</td>
<td>1.32</td>
<td>1.32</td>
<td>1.32</td>
<td>1.32</td>
<td>1.32</td>
<td>1.32</td>
</tr>
<tr>
<td>Retention time of final temperature &amp; pressure [hr]</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>9</td>
<td>9</td>
</tr>
<tr>
<td><strong>Crystallization condition</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heat treatment step 1</td>
<td>80°C×1hr in Nitrogen gas</td>
<td>80°C×1hr in air</td>
<td>80°C×1 hr in Nitrogen gas</td>
<td>80°C×1hr in air</td>
<td>80°C×1hr in Nitrogen gas</td>
<td>80°C×1hr in Nitrogen gas</td>
<td>80°C×1hr in Nitrogen gas</td>
<td>80°C×1hr in air</td>
</tr>
<tr>
<td>Heat treatment step 2</td>
<td>100°C×1 hr in Nitrogen gas</td>
<td>100°C×1 hr in Nitrogen gas</td>
<td>100°C×1 hr in Nitrogen gas</td>
<td>100°C×1 hr in Nitrogen gas</td>
<td>100°C×1 hr in Nitrogen gas</td>
<td>100°C×1 hr in Nitrogen gas</td>
<td>100°C×1 hr in Nitrogen gas</td>
<td>100°C×1 hr in Nitrogen gas</td>
</tr>
<tr>
<td>Heat treatment step 3</td>
<td>120°C×1 hr in Nitrogen gas</td>
<td>120°C×1 hr in Nitrogen gas</td>
<td>120°C×1 hr in Nitrogen gas</td>
<td>120°C×1 hr in Nitrogen gas</td>
<td>120°C×1 hr in Nitrogen gas</td>
<td>120°C×1 hr in Nitrogen gas</td>
<td>120°C×1 hr in Nitrogen gas</td>
<td>120°C×1 hr in Nitrogen gas</td>
</tr>
</tbody>
</table>
### Crystallized prepolymer properties (before solid-phase polymerization)

<table>
<thead>
<tr>
<th></th>
<th>Example 1</th>
<th>Example 2</th>
<th>Example 3</th>
<th>Example 4</th>
<th>Example 5</th>
<th>Example 6</th>
<th>Example 7</th>
<th>Example 8</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Weight average molecular weight Mw</strong></td>
<td>14,700</td>
<td>14,600</td>
<td>14,100</td>
<td>10,800</td>
<td>10,500</td>
<td>10,100</td>
<td>19,700</td>
<td>19,300</td>
</tr>
<tr>
<td>450/ (Mw/10,000-0.14)</td>
<td>338</td>
<td>341</td>
<td>354</td>
<td>479</td>
<td>495</td>
<td>517</td>
<td>246</td>
<td>251</td>
</tr>
<tr>
<td>950/ (Mw/10,000-0.14)</td>
<td>714</td>
<td>720</td>
<td>748</td>
<td>1,011</td>
<td>1,044</td>
<td>1,092</td>
<td>519</td>
<td>531</td>
</tr>
<tr>
<td><strong>Acid value A [mol/ton]</strong></td>
<td>457</td>
<td>595</td>
<td>710</td>
<td>655</td>
<td>823</td>
<td>1,050</td>
<td>301</td>
<td>378</td>
</tr>
<tr>
<td><strong>Enthalpy of fusion ΔHm [J/g]</strong></td>
<td>55.3</td>
<td>54.6</td>
<td>53.4</td>
<td>53.8</td>
<td>52.5</td>
<td>54.5</td>
<td>56.6</td>
<td>56.2</td>
</tr>
<tr>
<td><strong>Lactide content L [wt%]</strong></td>
<td>1.59</td>
<td>1.54</td>
<td>1.45</td>
<td>1.55</td>
<td>1.54</td>
<td>1.45</td>
<td>1.62</td>
<td>1.42</td>
</tr>
<tr>
<td><strong>D-lactic acid content d [mol%]</strong></td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
<td>1.1</td>
<td>1.1</td>
</tr>
<tr>
<td><strong>Solid-phase polymerization condition</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Temperature increasing rate [°C/hr]</strong></td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td><strong>Final temperature [°C]</strong></td>
<td>160</td>
<td>160</td>
<td>160</td>
<td>160</td>
<td>160</td>
<td>160</td>
<td>160</td>
<td>160</td>
</tr>
<tr>
<td>Polymer properties</td>
<td>Example 1</td>
<td>Example 2</td>
<td>Example 3</td>
<td>Example 4</td>
<td>Example 5</td>
<td>Example 6</td>
<td>Example 7</td>
<td>Example 8</td>
</tr>
<tr>
<td>--------------------</td>
<td>-----------</td>
<td>-----------</td>
<td>-----------</td>
<td>-----------</td>
<td>-----------</td>
<td>-----------</td>
<td>-----------</td>
<td>-----------</td>
</tr>
<tr>
<td>Weight average molecular weight</td>
<td>231,000</td>
<td>184,000</td>
<td>155,000</td>
<td>223,000</td>
<td>184,000</td>
<td>149,000</td>
<td>212,000</td>
<td>165,000</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>169</td>
<td>169</td>
<td>168</td>
<td>169</td>
<td>169</td>
<td>167</td>
<td>168</td>
<td>168</td>
</tr>
<tr>
<td>Amount of D-isomer (%)</td>
<td>0.8</td>
<td>0.9</td>
<td>0.9</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.9</td>
<td>0.9</td>
</tr>
<tr>
<td>Hue</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>4</td>
<td>4</td>
</tr>
</tbody>
</table>
**Table 2**

<table>
<thead>
<tr>
<th>Melt polymerization condition</th>
<th>Example 9</th>
<th>Example 10</th>
<th>Examples 11</th>
<th>Example 12</th>
<th>Example 13</th>
<th>Example 14</th>
<th>Example 15</th>
</tr>
</thead>
<tbody>
<tr>
<td>Final temperature [°C]</td>
<td>170</td>
<td>170</td>
<td>170</td>
<td>170</td>
<td>180</td>
<td>160</td>
<td>170</td>
</tr>
<tr>
<td>Final pressure [kPa]</td>
<td>1.32</td>
<td>1.32</td>
<td>2.64</td>
<td>0.66</td>
<td>1.32</td>
<td>1.32</td>
<td>1.32</td>
</tr>
<tr>
<td>Retention time of final temperature &amp; pressure [hr]</td>
<td>9</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Crystallization condition</th>
<th>Heat treatment step 1</th>
<th>Heat treatment step 2</th>
<th>Heat treatment step 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>80°C × 1 hr in air</td>
<td>100°C × 1 hr in air</td>
<td>120°C × 1 hr in Nitrogen gas</td>
</tr>
<tr>
<td></td>
<td>80°C × 1 hr in Nitrogen gas</td>
<td>100°C × 1 hr in Nitrogen gas</td>
<td>120°C × 2 hr in Nitrogen gas</td>
</tr>
<tr>
<td></td>
<td>80°C × 1 hr in Nitrogen gas</td>
<td>100°C × 1 hr in Nitrogen gas</td>
<td>120°C × 1 hr in Nitrogen gas</td>
</tr>
<tr>
<td></td>
<td>80°C × 1 hr in Nitrogen gas</td>
<td>100°C × 1 hr in Nitrogen gas</td>
<td>120°C × 1 hr in Nitrogen gas</td>
</tr>
<tr>
<td></td>
<td>80°C × 1 hr in Nitrogen gas</td>
<td>100°C × 1 hr in Nitrogen gas</td>
<td>120°C × 1 hr in Nitrogen gas</td>
</tr>
<tr>
<td></td>
<td>80°C × 1 hr in Nitrogen gas</td>
<td>100°C × 1 hr in Nitrogen gas</td>
<td>120°C × 1 hr in Nitrogen gas</td>
</tr>
<tr>
<td></td>
<td>80°C × 1 hr in Nitrogen gas</td>
<td>100°C × 1 hr in Nitrogen gas</td>
<td>120°C × 1 hr in Nitrogen gas</td>
</tr>
<tr>
<td></td>
<td>80°C × 1 hr in Nitrogen gas</td>
<td>100°C × 1 hr in Nitrogen gas</td>
<td>120°C × 1 hr in Nitrogen gas</td>
</tr>
</tbody>
</table>
### Crystallized prepolymer properties (before solid-phase polymerization)

<table>
<thead>
<tr>
<th></th>
<th>Example 9</th>
<th>Example 10</th>
<th>Examples 11</th>
<th>Example 12</th>
<th>Example 13</th>
<th>Example 14</th>
<th>Example 15</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight average molecular weight Mw</td>
<td>19,000</td>
<td>14,500</td>
<td>13,300</td>
<td>15,600</td>
<td>24,000</td>
<td>8,400</td>
<td>14,700</td>
</tr>
<tr>
<td>(450/ (Mw/10,000-0.14))</td>
<td>256</td>
<td>344</td>
<td>378</td>
<td>317</td>
<td>199</td>
<td>643</td>
<td>338</td>
</tr>
<tr>
<td>(9501 (Mw/10,000-0.14))</td>
<td>540</td>
<td>725</td>
<td>798</td>
<td>669</td>
<td>420</td>
<td>1,357</td>
<td>714</td>
</tr>
<tr>
<td>Acid value A [mol/ton]</td>
<td>510</td>
<td>426</td>
<td>491</td>
<td>393</td>
<td>239</td>
<td>1,257</td>
<td>452</td>
</tr>
<tr>
<td>Enthalpy of fusion (\Delta H_m) [J/g]</td>
<td>56.5</td>
<td>56.9</td>
<td>52.7</td>
<td>57.9</td>
<td>59.1</td>
<td>51.1</td>
<td>55.3</td>
</tr>
<tr>
<td>Lactide content L [wt%]</td>
<td>1.45</td>
<td>1.56</td>
<td>2.60</td>
<td>0.50</td>
<td>1.61</td>
<td>1.53</td>
<td>1.59</td>
</tr>
<tr>
<td>D-lactic acid content d [mol%]</td>
<td>1.1</td>
<td>1.0</td>
<td>0.9</td>
<td>0.9</td>
<td>1.8</td>
<td>0.5</td>
<td>1.0</td>
</tr>
</tbody>
</table>

### Solid-phase polymerization condition

<table>
<thead>
<tr>
<th></th>
<th>Example 9</th>
<th>Example 10</th>
<th>Examples 11</th>
<th>Example 12</th>
<th>Example 13</th>
<th>Example 14</th>
<th>Example 15</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature increasing rate [^\circ C/hr]</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Final temperature [^\circ C]</td>
<td>160</td>
<td>160</td>
<td>160</td>
<td>160</td>
<td>160</td>
<td>160</td>
<td>165</td>
</tr>
</tbody>
</table>
**Polymer properties**

<table>
<thead>
<tr>
<th>Example 9</th>
<th>Example 10</th>
<th>Example 11</th>
<th>Example 12</th>
<th>Example 13</th>
<th>Example 14</th>
<th>Example 15</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight average molecular weight</td>
<td>141,000</td>
<td>191,000</td>
<td>182,000</td>
<td>192,000</td>
<td>174,000</td>
<td>191,000</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>166</td>
<td>167</td>
<td>167</td>
<td>166</td>
<td>167</td>
<td>169</td>
</tr>
<tr>
<td>Amount of D-isomer (%)</td>
<td>0.9</td>
<td>0.8</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>Hue</td>
<td>4</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Comparative Example 1</td>
<td>Comparative Example 2</td>
<td>Comparative Example 3</td>
<td>Comparative Example 4</td>
<td>Comparative Example 5</td>
<td>Comparative Example 6</td>
</tr>
<tr>
<td>------------------------</td>
<td>------------------------</td>
<td>------------------------</td>
<td>------------------------</td>
<td>------------------------</td>
<td>------------------------</td>
<td>------------------------</td>
</tr>
<tr>
<td><strong>Melt polymerization condition</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Final temperature [°C]</td>
<td>160</td>
<td>160</td>
<td>180</td>
<td>180</td>
<td>170</td>
<td>170</td>
</tr>
<tr>
<td>Final pressure [kPa]</td>
<td>1.32</td>
<td>1.32</td>
<td>0.5</td>
<td>0.5</td>
<td>1.32</td>
<td>1.32</td>
</tr>
<tr>
<td>Retention time of final temperature &amp; pressure [hr]</td>
<td>10</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>9</td>
</tr>
<tr>
<td><strong>Crystallization condition</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heat treatment step 1</td>
<td>80°C × 1hr in Nitrogen gas</td>
<td>50°C × 1 hr in water</td>
<td>120°C × 2hr in air</td>
<td>70°C × 1hr in air</td>
<td>120°C × 2hr in air</td>
<td>120°C × 1hr in air</td>
</tr>
<tr>
<td>Heat treatment step 2</td>
<td>absence</td>
<td>absence</td>
<td>absence</td>
<td>absence</td>
<td>absence</td>
<td>absence</td>
</tr>
<tr>
<td>Heat treatment step 3</td>
<td>absence</td>
<td>absence</td>
<td>absence</td>
<td>absence</td>
<td>absence</td>
<td>absence</td>
</tr>
</tbody>
</table>
### Comparative Example 1
- Weight average molecular weight Mw: 10,000
- 450/ (Mw/10,000-0.14): 523
- 950/ (Mw/10,000-0.14): 1,105
- Acid value A [mol/ton]: 405
- Enthalpy of fusion ΔHm [J/g]: 42.1
- Lactide content L [wt%]: 3.62
- D-lactic acid content d [mol%]: 1.1
- Temperature increasing rate [°C/hr]: 1.0
- Final temperature [°C]: 160

### Comparative Example 2
- Weight average molecular weight Mw: 8,200
- 450/ (Mw/10,000-0.14): 662
- 950/ (Mw/10,000-0.14): 1,397
- Acid value A [mol/ton]: 1,551
- Enthalpy of fusion ΔHm [J/g]: 50.5
- Lactide content L [wt%]: 0.05
- D-lactic acid content d [mol%]: 1.1
- Temperature increasing rate [°C/hr]: 1.0
- Final temperature [°C]: 160

### Comparative Example 3
- Weight average molecular weight Mw: 35,000
- 450/ (Mw/10,000-0.14): 134
- 950/ (Mw/10,000-0.14): 283
- Acid value A [mol/ton]: 417
- Enthalpy of fusion ΔHm [J/g]: 59.7
- Lactide content L [wt%]: 1.39
- D-lactic acid content d [mol%]: 2.3
- Temperature increasing rate [°C/hr]: 1.0
- Final temperature [°C]: 160

### Comparative Example 4
- Weight average molecular weight Mw: 35,000
- 450/ (Mw/10,000-0.14): 134
- 950/ (Mw/10,000-0.14): 283
- Acid value A [mol/ton]: 329
- Enthalpy of fusion ΔHm [J/g]: 58.1
- Lactide content L [wt%]: 1.47
- D-lactic acid content d [mol%]: 2.5
- Temperature increasing rate [°C/hr]: 1.0
- Final temperature [°C]: 160

### Comparative Example 5
- Weight average molecular weight Mw: 14,100
- 450/ (Mw/10,000-0.14): 354
- 950/ (Mw/10,000-0.14): 748
- Acid value A [mol/ton]: 934
- Enthalpy of fusion ΔHm [J/g]: 52.1
- Lactide content L [wt%]: 1.36
- D-lactic acid content d [mol%]: 1.36
- Temperature increasing rate [°C/hr]: 1.0
- Final temperature [°C]: 160

### Comparative Example 6
- Weight average molecular weight Mw: 19,000
- 450/ (Mw/10,000-0.14): 256
- 950/ (Mw/10,000-0.14): 540
- Acid value A [mol/ton]: 675
- Enthalpy of fusion ΔHm [J/g]: 52.0
- Lactide content L [wt%]: 1.36
- D-lactic acid content d [mol%]: 1.36
- Temperature increasing rate [°C/hr]: 1.0
- Final temperature [°C]: 160

### Comparative Example 7
- Weight average molecular weight Mw: 24,500
- 450/ (Mw/10,000-0.14): 195
- 950/ (Mw/10,000-0.14): 411
- Acid value A [mol/ton]: 455
- Enthalpy of fusion ΔHm [J/g]: 49.8
- Lactide content L [wt%]: 1.25
- D-lactic acid content d [mol%]: 1.6
- Temperature increasing rate [°C/hr]: 1.0
- Final temperature [°C]: 160

### Comparative Example 8
- Weight average molecular weight Mw: 24,800
- 450/ (Mw/10,000-0.14): 192
- 950/ (Mw/10,000-0.14): 406
- Acid value A [mol/ton]: 185
- Enthalpy of fusion ΔHm [J/g]: 57.4
- Lactide content L [wt%]: 0.05
- D-lactic acid content d [mol%]: 1.5
- Temperature increasing rate [°C/hr]: 1.0
- Final temperature [°C]: 160
<table>
<thead>
<tr>
<th>Comparative Example</th>
<th>Weight average molecular weight</th>
<th>Melting point (°C)</th>
<th>Amount of D-isomer (%)</th>
<th>Hue</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example 1</td>
<td>83,000</td>
<td>158</td>
<td>0.9</td>
<td>4</td>
</tr>
<tr>
<td>Example 2</td>
<td>81,000</td>
<td>158</td>
<td>1.0</td>
<td>5</td>
</tr>
<tr>
<td>Example 3</td>
<td>53,000</td>
<td>155</td>
<td>1.7</td>
<td>4</td>
</tr>
<tr>
<td>Example 4</td>
<td>44,000</td>
<td>155</td>
<td>0.8</td>
<td>5</td>
</tr>
<tr>
<td>Example 5</td>
<td>71,000</td>
<td>157</td>
<td>0.9</td>
<td>4</td>
</tr>
<tr>
<td>Example 6</td>
<td>68,000</td>
<td>157</td>
<td>0.9</td>
<td>5</td>
</tr>
<tr>
<td>Example 7</td>
<td>89,000</td>
<td>162</td>
<td>1.5</td>
<td>4</td>
</tr>
<tr>
<td>Example 8</td>
<td>115,000</td>
<td>166</td>
<td>1.4</td>
<td>5</td>
</tr>
</tbody>
</table>

Polymer properties
INDUSTRIAL APPLICABILITY

[0138] The poly(lactic acid) resin composition obtained by the production method of the present invention can be widely used as a molded article. Examples of the molded article include films, sheets, fibers/cloths, non-woven fabrics, injection-molded articles, extrusion-molded articles, vacuum/pressure-molded articles, blow-molded articles and complexes with other materials. These molded articles are useful for agricultural materials, garden materials, fishery materials, civil engineering and construction materials, stationery, medical supplies, automobile parts, electrical/electronic components and other uses.

Claims

1. A method for producing a poly(lactic acid) resin, said method comprising the steps of:

   carrying out direct polycondensation using lactic acid as a main raw material to prepare a crystallized prepolymer having a weight average molecular weight of 5,000 to 25,000, an enthalpy of fusion $\Delta H_m$ of 50 to 65 [J/g] and an acid value $A$ [mol/ton] satisfying the Inequality (1) below:

   \[
   \frac{450}{(M_w/10,000-0.14)} < A < \frac{950}{(M_w/10,000-0.14)}
   \]  

   (wherein $M_w$ represents the weight average molecular weight of said crystallized prepolymer); and

   subjecting said crystallized prepolymer to solid-phase polymerization.

2. The method for producing a poly(lactic acid) resin according to claim 1, wherein the lactide content $L$ of said crystallized prepolymer is 0.1 to 3.0 [wt%].

3. The method for producing a poly(lactic acid) resin according to claim 1 or 2, wherein said crystallized prepolymer is poly-L-lactic acid or poly-D-lactic acid, and, in the case of poly-L-lactic acid, the D-lactic acid content $d$ is 0.2 to 2.0 [mol%], and in the case of poly-D-lactic acid, the L-lactic acid content $l$ is 0.2 to 2.0 [mol%].

4. The method for producing a poly(lactic acid) resin according to any one of claims 1 to 3, wherein said crystallized prepolymer is in the form of a pellet.

5. The method for producing a poly(lactic acid) resin according to any one of claims 1 to 4, wherein the enthalpy of fusion $\Delta H_m$ of said crystallized prepolymer is not less than 53 [J/g].

6. The method for producing a poly(lactic acid) resin according to any one of claims 1 to 5, wherein the acid value $A$ [mol/ton] of said crystallized prepolymer satisfies the Inequality (2) below:

   \[
   \frac{550}{(M_w/10,000-0.14)} < A < \frac{850}{(M_w/10,000-0.14)}
   \]  

7. The method for producing a poly(lactic acid) resin according to any one of claims 1 to 6, wherein the temperature increasing rate in said solid-phase polymerization is not more than 10°C per hour.

8. The method for producing a poly(lactic acid) resin according to any one of claims 1 to 7, wherein the final temperature in said solid-phase polymerization is 155 to 165°C.

9. The method for producing a poly(lactic acid) resin according to any one of claims 1 to 8, wherein said crystallized prepolymer is produced using a tin compound or sulfonic acid compound as a catalyst.

10. A crystallized poly(lactic acid) prepolymer having a weight average molecular weight of 5,000 to 25,000, an enthalpy of fusion $\Delta H_m$ of 50 to 65 [J/g] and an acid value $A$ [mol/ton] satisfying the Inequality (1) below:

   \[
   \frac{450}{(M_w/10,000-0.14)} < A < \frac{950}{(M_w/10,000-0.14)}
   \]  


11. The crystallized poly(lactic acid) prepolymer according to claim 10, wherein said crystallized poly(lactic acid) prepolymer is prepared by carrying out direct polycondensation using lactic acid as a main raw material to obtain a prepolymer, and crystallizing said prepolymer.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
   C08G63/80(2006.01)i, C08G63/06(2006.01)i

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
   C08G63/80, C08G63/06

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>JP 8-231688 A (Shimadzu Corp.), 10 September 1996 (10.09.1996), claims; paragraph [0015]; examples (Family: none)</td>
<td>1-11</td>
</tr>
<tr>
<td>A</td>
<td>JP 8-193124 A (Kanebo, Ltd.), 30 July 1996 (30.07.1996), claims; paragraph [0011]; examples (Family: none)</td>
<td>1-11</td>
</tr>
</tbody>
</table>

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

* Special categories of cited documents:
  "A" document defining the general state of the art which is not considered to be of particular relevance
  "E" earlier application or patent but published on or after the international filing date
  "L" later publication of same content
  "O" document published prior to the international filing date but not later than the priority date claimed
  "Q" inter document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
  "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
  "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
  "&" document member of the same patent family

Date of the actual completion of the international search
   19 July, 2011 (19.07.11)

Date of mailing of the international search report
   02 August, 2011 (02.08.11)

Name and mailing address of the ISA/
   Japanese Patent Office

Facsimile No.

Authorized officer

Telephone No.
REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader’s convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- JP 8183840 A [0004]
- JP 2000297145 A [0004]
- JP 2000297143 A [0004]
- JP 11106499 A [0004]
- JP 2000302852 A [0004]
- JP 2001192444 A [0004]
- JP 2001064375 A [0004]
- JP 2009144132 A [0004]
- JP 2000273165 A [0004]
- WO 2009142196 A [0004]