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(51) Int.Cl.⁶ C08G 63/08, C08G 63/83

(30) 1994/01/28 (08/189,015) US

(30) 1994/11/18 (08/341,808) US

(54) **POLYMERIZATION DE BETA-PROPIOLACTONES BETA-SUBSTITUEES AMORCEES PAR DES ALCOXYDES D'ALKYLE-ZINC**

(54) **POLYMERIZATION OF BETA-SUBSTITUTED-BETA-PROPIOLACTONES INITIATED BY ALKYLZINC ALKOXIDES**

(57) Cette invention se rapporte à un procédé de préparation d'un polyester qui consiste à polymériser au moins une β -propiolactone β -substituée en présence d'une quantité d'alcoxyde d'alkyle-zinc faisant office d'amorce avec ou sans l'adjonction d'un solvant, pendant une période de réaction et à une température de réaction suffisantes pour produire ledit polyester.

(57) The present invention relates to a method of preparing a polyester comprising polymerizing at least one β -substituted- β -propiolactone in the presence of an initiating amount of alkylzinc alkoxide in bulk or in solvent for a reaction time and temperature sufficient to produce said polyester.

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C08G 63/82	A1	(11) International Publication Number: WO 95/20616 (43) International Publication Date: 3 August 1995 (03.08.95)
(21) International Application Number: PCT/US95/00583 (22) International Filing Date: 13 January 1995 (13.01.95) (30) Priority Data: 08/189,015 28 January 1994 (28.01.94) US 08/341,808 18 November 1994 (18.11.94) US (71) Applicant: THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventors: SCHECHTMAN, Lee, Arnold; 2069 Edinburg Lane, Fairfield, OH 45014 (US). KEMPER, Joseph, Jay; 1066 Meadowind Court, Cincinnati, OH 45231 (US). (74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).		(81) Designated States: AM, AU, BB, BG, BR, BY, CA, CN, CZ, EE, FI, GE, HU, JP, KG, KP, KR, KZ, LK, LR, LT, LV, MD, MG, MN, MX, NO, NZ, PL, RO, RU, SI, SK, TJ, TT, UA, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ). Published <i>With international search report.</i>
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(57) Abstract The present invention relates to a method of preparing a polyester comprising polymerizing at least one β-substituted-β-propiolactone in the presence of an initiating amount of alkylzinc alkoxide in bulk or in solvent for a reaction time and temperature sufficient to produce said polyester.		

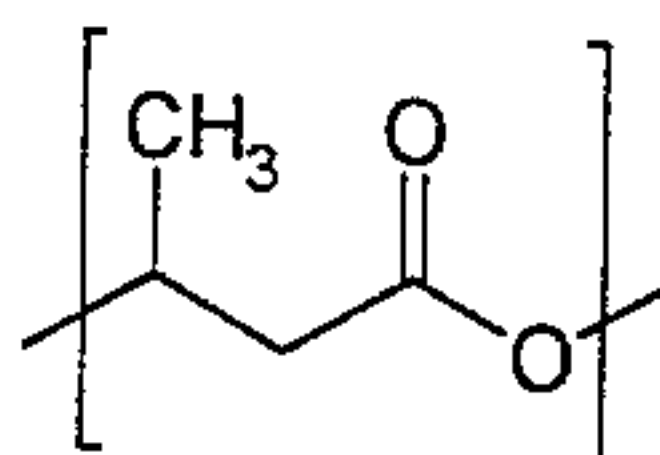
POLYMERIZATION OF BETA-SUBSTITUTED-BETA-PROPIOLACTONES
INITIATED BY ALKYLZINC ALKOXIDES

TECHNICAL FIELD

5 The present invention relates to a method of polymerizing β -lactones in the presence of an organometallic initiator. More specifically, the invention relates to a method of polymerizing at least one β -substituted- β -propiolactone in the presence of an alkylzinc alkoxide.

BACKGROUND

10 β -substituted- β -propiolactone polymers are made by a wide variety of bacteria to serve as a source of both energy and carbon supply. Perhaps the best known of these bacterially produced polyesters is poly(β -hydroxybutyrate) (PHB) characterized by a structure having a repeat unit of the formula:



The bacterially-produced form of poly(β -hydroxybutyrate) is a highly crystalline, optically active and perfectly isotactic polyester.

Ring-opening polymerization of β -substituted- β -lactones in the presence of organometallic catalysts to produce β -substituted- β -propiolactone polymers is known. The use of alkylaluminum-water based polymerization initiators or catalysts is described by Benvenuti and Lenz in US 5,023,316 and others (for example see Agostini, D. E.; Lando, J. B.; Shelton, J. R. J. POLYM. SCI. PART A-1 **1971**, 9[A], 2775-2587 and 2789-2799; Gross, R. A.; Zhang, Y.; Konrad, G.; Lenz, R. W. MACROMOLECULES **1988**, 21, 2657-2668). Polymerization of β -butyrolactone with aluminum porphyrins is described by Aida, T.; Maekawa, S.A. and Inoue, S. in Macromolecules **1988**, 21, 1195-1202. The use of polymerization initiators derived from organotin compounds is described by Kemnitzer, J. E.; McCarthy, S. P.; Gross, R. A. in MACROMOLECULES **1993**, 26, 1221-1229 and Hori, Y.; Suzuki, M.; Takahashi, Y.; Yamaguchi, A.; Nishishita, T. in MACROMOLECULES **1993**, 26, 5533-5534. The use of organozinc-water based initiators for the polymerization of β -substituted- β -lactones is reported by Zhang, Y.; Gross, R.A.; and Lenz, R.W. in MACROMOLECULES **1990**, 23, 3206-32-12 and Tanahashi, N.; Doi, Y. in MACROMOLECULES **1991**, 24, 5732-5733. Le Borgne, A. and Spassky, N. in POLYMER **1989**, 30,

2312-2319 describe the use of a chiral alkylzinc alkoxide initiator for the polymerization of racemic β -butyrolactone. Kumagai, Y. and Doi, Y. in J. ENVIRON. POLYM. DEGRADN. 1993, 1, 81-87 describe the use of a zinc-water-polymeric alcohol initiator for the polymerization of this same monomer.

40 A disadvantage of each of the above systems mentioned for the polymerization of β -substituted- β -propiolactones to polyesters is that each system requires either long reaction times, production of low yields of polymer, limited to lower molecular weight polyester products, broad molecular weight distributions, production of mixtures of isotactic, atactic, 45 and/or syndiotactic polymer, or combinations of these deficiencies.

The alkylaluminum-water systems cited above are commonly referred to as "aluminumoxane" catalysts or initiators. The yield of polyester produced from β -substituted- β -propiolactones when these initiators are used is generally in the range of 20-60% crude yield after 7-14 days with the 50 product having a molecular weight distribution or polydispersity, weight-average molecular weight (Mw) divided by number-average molecular weight (Mn) of around 15 (see Gross, R. A.; Zhang, Y.; Konrad, G.; Lenz, R. W. MACROMOLECULES 1988, 21, 2657-2668). The use of aluminum porphyrin initiators (see Aida, T.; Maekawa, S.A. and Inoue, S. in 55 MACROMOLECULES 1988, 21, 1195-1202) will produce poly(β -butyrolactone) from β -butyrolactone with essentially quantitative yields and very narrow polydispersity (1.08-1.16), but the highest reported molecular weights of the polyester are less than 10,000 and the reaction times required are 5 to 20 days.

60 The use of distannoxane initiators (see Hori, Y.; Suzuki, M.; Takahashi, Y.; Yamaguchi, A.; Nishishita, T. in MACROMOLECULES 1993, 26, 5533-5534) is useful for the polymerization of racemic β -butyrolactone, [S]- β -butyrolactone, or [R]- β -butyrolactone to high molecular weight polymer (Mw>100,000) near quantitative yield in 4 h at 100°C. The polydispersity of 65 such produced poly(β -butyrolactone) is typically 1.7-2.7. Syndiotactic poly(β -butyrolactone) is produced when tributyltin methoxide is used to initiate the polymerization of racemic β -butyrolactone (see Kemnitzer, J. E.; McCarthy, S. P.; Gross, R. A. in MACROMOLECULES 1993, 26, 1221-1229). The yields of polyester are 24-69% after 13-18 days and the molecular 70 weights below 10,000 with the polydispersities are typically 1.04-1.12.

Polymerization of β -substituted- β -propiolactones with dialkylzinc-water initiators require 5-7 days (see Zhang, Y.; Gross, R.A.; and Lenz,

R.W. in *MACROMOLECULES* **1990**, 23, 3206-3212 and Tanahashi, N.; Doi, Y. in *MACROMOLECULES* **1991**, 24, 5732-5733). Yields of polymer are generally
75 57-84%, but can reach 100% with racemic β -butyrolactone. The polyester molecular weights are reported up to 50,000 with polydispersities typically 1.1-1.5. Unfortunately, the nature of the initiator is not well defined and the actual monomer-initiator ratio used is hard to quantitate.

The use of diethylzinc-[R]-(-)-3,3-dimethyl-1,2-butanediol to initiate
80 the polymerization of racemic β -butyrolactone in bulk leads to polyester with enhanced isotacticity (see Le Borgne, A. and Spassky, N. in *POLYMER* **1989**, 30, 2312-2319). The reaction times are short, 2.5-15 h, and the yield can be as high as 84%. However, the molecular weight of the product, especially for the higher yield reaction (<3,000), is very low.

85 Ring-opening polymerization of lactones other than β -propiolactones with alkylzinc alkoxide initiators are known. The polymerization of ϵ -caprolactone and lactides are reported in the literature (see Barakat, I.; DuBois, Ph.; Jerome, R.; and Teyssie, Ph. in *MACROMOLECULES* **1991**, 24, 6542-6545). Specifically, the use of ethylzinc isopropoxide is reported to
90 copolymerize ϵ -caprolactone and L,L-lactide (see Bero, M.; Kasperczyk, J.; and Adamus, G. in *Makromol. Chem.* **1993**, 194, 907-912 and 913-925). Molecular weights of these copolyesters are over 100,000 with polydispersities of 1.4, and the yields range from 60-89%. These polymerizations require 2.5-21 days at temperatures between 50 and
95 100°C. Also, these investigators found that above 50°C the zinc initiators also are effective transesterification catalysts.

The use of a chiral diol-ethylzinc initiator has been disclosed for the polymerization of racemic β -butyrolactone as described above (Le Borgne, A. and Spassky, N. in *POLYMER* **1989**, 30, 2312-2319).

100 The previous attempts to polymerize β -substituted- β -propiolactones in the presence of various initiators have generally resulted in less than optimum product yields and length of reaction times.

Based on the foregoing, there is a need to provide a method of polymerizing β -substituted- β -propiolactones in the presence of an initiator
105 which results in an improved yield of the desired polymer and/or an improved reaction time.

SUMMARY

The present invention relates to a method of preparing a polyester comprising polymerizing at least one β -substituted- β -propiolactone in the

110 presence of an initiating amount of alkylzinc alkoxide in bulk or in solvent for a reaction time and temperature sufficient to produce said polyester.

DETAILED DESCRIPTION

As used herein, "alkyl" means a saturated carbon-containing chain which may be straight or branched; and substituted (mono- or poly-) or
115 unsubstituted.

As used herein, "aryl" means an aromatic; substituted (mono- or poly-) or unsubstituted, preferably unsubstituted. Preferred aryls are phenyl and naphthyl; more preferred is phenyl.

As used herein, "aralkyl" means an alkyl substituted with aryl (e.g.,
120 benzyl).

As used herein, "alkaryl" means an aryl substituted with alkyl (e.g., 4-methylphenyl).

As used herein, "alkenyl" means a carbon-containing chain which may be monounsaturated (i.e., one double bond in the chain) or
125 polyunsaturated (i.e., two or more double bonds in the chain); straight or branched; and substituted (mono- or poly-) or unsubstituted.

As used herein, "cycloalkyl" means a cyclic alkyl (e.g., cyclohexyl).

As used herein, "comprising" means that other steps and other ingredients which do not affect the end result can be added. This term
130 encompasses the terms "consisting of" and "consisting essentially of".

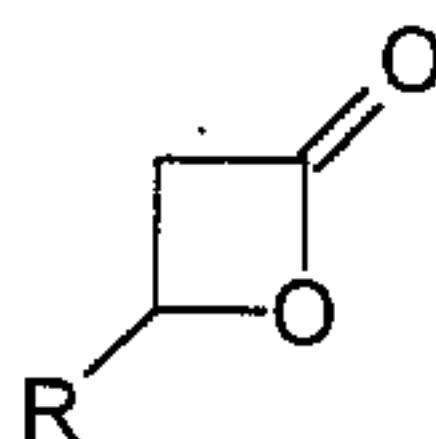
As used herein, "initiator" means an agent used to start the polymerization of a monomer.

As used herein, "an initiating amount" means a sufficient amount of an initiator to commence the chemical reaction for polymerization. In a
135 preferred embodiment, the initiating amount of initiator of the present invention for carrying out a polymerization reaction of the present invention is from about 0.005 mole% to about 1 mole%; more preferably from about 0.01 mole% to about 0.5 mole%.

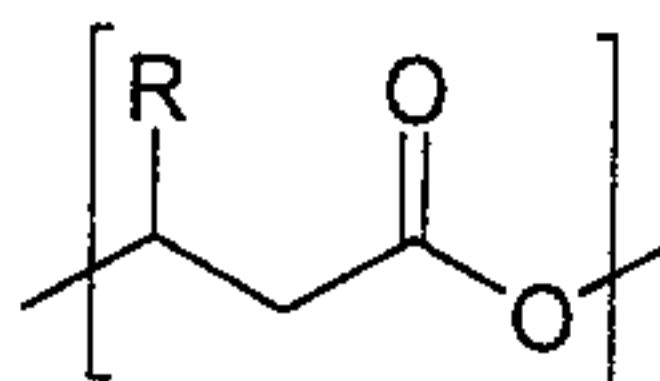
As used herein, "in bulk" refers to polymerization without added
140 solvent.

The present invention answers the need for an improved method of preparing β -substituted- β -propiolactone polymers. The present invention relates to a method of preparing a polyester comprising polymerizing at least one β -substituted- β -propiolactone in the presence of an initiating amount of alkylzinc alkoxide in bulk or in solvent for a reaction time and temperature sufficient to produce said polyester.

The β -propiolactone is substituted at the β position by any conventional non-interfering substituent. Suitable substituents include organic residues, halo, nitro, and the like. Suitable organic residues include hydrocarbon residues, either unsubstituted or substituted, suitable substituents for such substituted hydrocarbon residues include halo and nitro, oxygen or sulfur-containing organic residues such as ether residue or a carboalkoxy group ($-\text{COOR}'$) wherein R' is alkyl. Suitable hydrocarbon residues include alkyl, alkenyl, aryl, aralkyl, alkaryl, and cycloalkyl. Substituents containing up to 19 carbon atoms, particularly hydrocarbon substituents, are preferred. The β -substituted- β -propiolactones are represented by the structural formula:



wherein R is the non-interfering substituent. The β -substituted- β -propiolactone polyester produced by the present method has a repeat unit having the formula:



where R is the non-interfering substituent.

The polyesters formed by the method disclosed herein are useful as biodegradable and general thermoplastic materials, for example, as biocompatible materials in medical applications and in drug delivery systems for the controlled release of pharmaceuticals in the body. Biodegradable polyesters formed by the method disclosed herein preferably are predominantly of $[\text{R}]$ configuration.

The method of the present invention involves polymerizing at least one β -substituted- β -propiolactone in the presence of an initiating amount of simple alkylzinc alkoxide in bulk or a solvent for the β -substituted- β -

propiolactone(s) and for the initiator for a time and at a temperature sufficient to produce the polyester.

175 The alkylzinc alkoxide initiator useful in the present invention is known. The structure of the initiator has the formula:



where R^1 and R^2 are independently a C_1 , C_2 , C_3 , C_4 , C_5 , C_6 , C_7 , C_8 , C_9 , or C_{10} alkyl.

180 In a preferred embodiment of the present invention, the initiator is a nonchiral alkylzinc alkoxide; more preferably the initiator is ethylzinc isopropoxide, methylzinc isopropoxide, ethylzinc ethoxide, or ethylzinc methoxide; more preferably still, ethylzinc isopropoxide.

When the polymerizing is conducted in a solvent for the initiator and
185 for the β -substituted- β -propiolactone(s), the solvent is preferably an aryl hydrocarbon comprising from about 6 to about 15 carbons or alkyl hydrocarbon comprising from about 5 to about 18 carbons; more preferably toluene or xylene.

In a manner similar to that disclosed in several publications (see Le
190 Borgne, A. and Spassky, N. in POLYMER **1989**, 30, 2312-2319; Barakat, I.; DuBois, Ph.; Jerome, R.; and Teyssié, Ph. in MACROMOLECULES **1991**, 24, 6542-6545, or Herold, R.J.; Aggarwal, S.L.; and Neff, V. in CANADIAN J. CHEM. **1963**, 41, 1368-1380) the initiator, alkylzinc alkoxide is prepared by slow addition of the alcohol to a solution of dialkylzinc in aliphatic
195 hydrocarbon solvent such as hexane or aromatic hydrocarbons such as toluene. The initiator solution can then be used directly or the initiator can be isolated from solvent as a solid.

All initiator preparations disclosed herein are conducted in glassware which had been flame dried while being flushed with argon and finally
200 maintained under a positive pressure of argon. Transfers of the initiator solutions are carried out either by cannulation or with a syringe, under an argon atmosphere. Transfers of the initiator powders are carried out in a drybox under an inert atmosphere. The alcohol for the initiator preparation is typically dried by reflux over sodium metal, followed by distillation under
205 an argon atmosphere. The diethylzinc used to prepare the initiator is obtained as a solution in hydrocarbon solvent, hexane or toluene, and used in this solvent.

In each of the following examples the following basic procedure, unless otherwise noted, is used to prepare the polymer. The ampules to be

- 210 used for the polymerization are septum capped, and flame dried while
flushing with argon. All reactants added to the ampules are transferred with
a syringe under an argon atmosphere. All β -substituted- β -propiolactone
monomers are dried by several distillations from calcium hydride under
vacuum prior to use. Enantiomerically pure [S]- β -butyrolactone is
215 synthesized by the method of Seebach (see Müller, J.-M.; Seebach, D.
ANGEW. CHEM. INT. ED. ENGL. **1993**, 32, 477-502 ;Breitschuh, R.; Seebach,
D. CHIMIA **1990**, 44, 216-218 ;Züger, M.; Seebach, D. HELV.CHIM. **1982**, 49,
495-503 ;and Griesbeck, A.; Seebach, D. HELV.CHIM. **1982**, 70, 1320-1325).
[R]- β -butyrolactone can be obtained by several published methods (see
220 Pommier, A.; Pons, J-M. Synthesis 1993, (5), 441-459; Ohta, T.; Miyake, T.;
Takaya, H. J. Chem. Soc., Chem. Commun. 1992, 1725-26). The monomer
is purified by fractional and spinning-band distillations under vacuum prior
to the distillation from calcium hydride. The appropriate monomer is
transferred into the ampule. If solvent is used, it is added to the ampule and
225 then the initiator solution is added. Polymerization reactions in the ampules
are carried out as noted between 20 and 100°C for time periods ranging
from 3 hours to 10 days, more preferably from about 3 hours to about 4
days, for homopolymerizations and copolymerizations. The crude products
are clear, colorless viscous liquids or white solids depending on whether
230 racemic or enantiomerically enriched monomers were used. The ampules
are opened at the end of the polymerization reaction periods and bulk
reaction products are taken up into chloroform and recovered by
precipitation into ether-hexane (3:1) mixture. The polymer is dried under
vacuum.
- 235 Depending upon one's source of monomer and the desired molecular
weight of the monomer, one may wish to take steps to further purify the
monomer. For example, racemic β -butyrolactone may be further purified as
follows. Racemic β -butyrolactone is distilled several times from CaH_2 under
reduced pressure with the final distillation onto neutral alumina (activity I),
240 which is flamed under vacuum prior to the distillation, and the monomer is
stored over this alumina. Just prior to polymerization, depending on
whether the polymerization is to be a bulk or solution polymerization, either
the neat monomer or a solution of the monomer is passed through an
alumina column under dry argon directly into the polymerization vessel.
- 245 Enantiomerically enriched monomer (i.e., [R]- β -butyrolactone or [S]- β -
butyrolactone) may be further purified as follows. The monomer is distilled

from CaH_2 . It is then chromatographed on neutral alumina (activity I) with pentane as eluent. The fractions are analyzed by gas chromatography for purity and the middle cuts are combined and distilled from CaH_2 onto alumina, stored over alumina, and passed through an alumina column as described above for the racemic monomer.

For selected samples the molecular weights, and melting temperature (T_m) are given. Melting temperatures are determined by differential scanning calorimetry (DSC). Molecular weight determinations are made by gel permeation chromatography (GPC) and molecular weights are reported in terms of the number average (M_n) and weight average (M_w) molecular weights. The polydispersities or ratio of M_w to M_n are also reported. ^1H and ^{13}C NMR spectra are obtained for the various products to assist in the determination of the structures by measuring stereoregularity and tacticity effects of the polymers produced. In the case of the copolymers, the ^1H NMR spectra is useful in determining the copolymer compositions. Yields of the various products are also reported in the tables which follow after the Examples.

All molecular weight data reported in the Tables which follow are obtained by GPC using either three Phenogel or Ultrastyrigel linear $5\ \mu\text{m}$ columns (one $50 \times 7.8\ \text{mm}$ and two $300 \times 7.8\ \text{mm}$) in series. A refractive index detector is used. Samples are prepared at 0.2% in CHCl_3 , which is also the mobile phase (1.00 mL/min). Calibration is performed with narrow polystyrene standards and data analyzed using Waters Expert Ease software. NMR spectra were recorded on either a General Electric QE-300 or a Bruker AC-300 (at 300 MHz for ^1H spectra) in deuteriochloroform. Chemical shifts are reported in ppm from a TMS internal standard. ^{13}C NMR measurements are recorded at 75.4 MHz. All spectra are recorded at 25-30°C and CDCl_3 and tetramethylsilane (TMS) are used as internal references for ^{13}C and ^1H NMR spectra, respectively.

Melting temperatures (T_m) for polymer samples are determined with a Mettler T3000 system and the data processed with Mettler GraphWare TA72 software. The sample is heated at 10°C/min. The melt temperature (T_m) is reported as the peak maximum, and the glass transition temperature (T_g) is reported as the transition mid-point.

The process of the present invention may be carried out using as monomer(s) a single β -substituted- β -propiolactone to produce a homopolymer or a mixture of different β -substituted- β -propiolactones to

285 produce a copolymer. The molar ratio of zinc to monomers in the initial reaction solution will range from 0.00005 to 0.05, more preferably from 0.0005 to .01. Yield of product generally increases with higher levels of initiator in the reaction mixture. The initial monomer concentration in the solvent can vary widely. The use of approximately equal volumes of solvent and monomer is suitable, but no solvent except that introduced with the
290 initiator if any is necessary.

The reaction temperature will preferably be in the range of 20°C to 80°C, more preferably from about 40°C to about 80°C, more preferably from about 45°C to about 60°C. If a faster reaction time is desired, the temperature is preferably from about 70°C to about 80°C, more preferably
295 about 75°C. The reaction time will typically range from 17 to 48 hours for both homopolymerization and copolymerization reactions. However, the time may be as short as 3 hours and as long as 10 days or more.

In each of Examples 1-6 and 10, the monomer used is racemic [R,S]- β -butyrolactone (BL) and the initiator is ethylzinc isopropoxide used in an
300 amount as indicated. In Examples 7 and 8 [S]- β -butyrolactone is used. Example 9 is a copolymerization of [S]- β -butyrolactone and [S]- β -pentyl- β -propiolactone. In Example 11 [R]- β -butyrolactone is used. Example 12 is a copolymerization of [R]- β -butyrolactone and [R]- β -pentadecyl- β -propiolactone. The reaction is carried out in bulk with no solvent except for
305 the small amount added with the initiator, or carried out in solution.

Example 1

An oven-dried and then flamed, dry argon flushed, pyrex tube (16 x 150 mm) capped with a septum was charged via syringe with 9.77 g (114 mmol) racemic β -butyrolactone. Ethylzinc isopropoxide in toluene (205 μ L
310 of 1.1 M solution, 0.225 mmol) was added via syringe. The reaction was allowed to proceed at 50°C for 40 h. The product, a gum, was cooled and dissolved in CHCl_3 and recovered by precipitation into a rapidly stirred ether-hexane mixture (3:1 v/v). The resulting gum was isolated by filtration or simple decantation of the liquid after clarification, and dried under
315 vacuum at room temperature.

Example 2

The basic procedure described in Example 1 was followed with 5.72 g (66.5 mmol) racemic β -butyrolactone and ethylzinc isopropoxide in toluene (180 μ L of 1.1 M solution, 0.198 mmol). Polymerization was carried
320 out at 50°C for 17 h.

Example 3

The basic procedure described in Example 1 was followed with 10.67 g (124.1 mmol) racemic β -butyrolactone and ethylzinc isopropoxide in toluene (335 μ L of 1.1 M solution, 0.369 mmol). Polymerization was carried out at 20°C for 46 h.

Example 4

The basic procedure described in Example 1 was followed with 7.76g (90.2 mmol) racemic β -butyrolactone and ethylzinc isopropoxide in toluene (406 μ L of 1.1 M solution, 0.447 mmol). Polymerization was carried out at 50°C for 17 h.

Example 5

The basic procedure described in Example 1 was followed with 10.25 g (119 mmol) racemic β -butyrolactone and ethylzinc isopropoxide in toluene (536 μ L of 1.1 M solution, 0.590 mmol). Polymerization was carried out at 20°C for 46 h.

Example 6

The basic procedure described in Example 1 was followed with 4.84 g (56.3 mmol) racemic β -butyrolactone and ethylzinc isopropoxide in toluene (501 μ L of 1.1 M solution, 0.551 mmol). Polymerization was carried out at 50°C for 17 h.

Example 7

An oven-dried and then flamed, dry argon flushed, pyrex tube (16 x 150 mm) capped with a septum was charged via syringe with 2.39 g (27.8 mmol) [S]- β -butyrolactone. Ethylzinc isopropoxide in toluene (51 μ L of 1.1 M solution, 0.056 mmol) was added via syringe. The reaction was allowed to proceed at 50°C for 21 h. During this time the liquid in the tube had solidified to a white mass. This solid was dissolved in CHCl_3 and recovered by precipitation into a rapidly stirred ether-hexane mixture (3:1 v/v). The resulting solid was isolated by filtration and dried under vacuum at room temperature (2.02 g).

Example 8

The basic procedure described in Example 7 was followed with 2.09 g (24.3 mmol) [S]- β -butyrolactone and ethylzinc isopropoxide in toluene (109 μ L of 1.1 M solution, 0.12 mmol). Polymerization was carried out at 20°C for 48 h.

Example 9

The copolymer derived from [S]- β -butyrolactone and [S]- β -pentyl- β -propiolactone was prepared as described for the homopolymer using 2.07 g (24.0 mmol) β -butyrolactone and 0.187 g (1.32 mmol) β -pentyl- β -propiolactone with ethylzinc isopropoxide (114 μ L, 1.1 M solution, 0.13 mmol) at 20°C for 93 h.

Example 10

A homopolymer derived from racemic β -butyrolactone was prepared as follows. Racemic β -butyrolactone (12.9 g distilled from CaH_2 and stored over neutral alumina) was mixed with toluene (79.0 g distilled from sodium metal) in a dry, septum capped flask. This mixture was transferred via cannula onto a flamed, argon-flushed column of alumina and then directly into the reaction flask via a syringe needle tip on the column after discarding the first several milliliters of solution eluting from the column. The monomer solution (79.5 g solution, 11.2 g monomer, 0.13 mol) was initiated with ethylzinc isopropoxide in toluene (24 μ L of 1.1 M solution, 0.026 mmol). The reaction was allowed to proceed at 75°C for 64 h. The solution was then diluted with CHCl_3 , and the product recovered and dried as described in Example 1.

Example 11

A homopolymer derived from [R]- β -butyrolactone was prepared as follows. An oven-dried and then flamed, dry argon flushed, pyrex tube (16 x 150 mm) capped with a septum was charged by passage through an alumina column (neutral, Activity I) with 5.21 g (60.5 mmol) [R]- β -butyrolactone. Ethylzinc isopropoxide in toluene (33 μ L of 1.1 M solution, 0.036 mmol) was added via syringe. The reaction was allowed to proceed at 75°C for 24 h. The product was purified and isolated as described in Example 7.

Example 12

A copolymer derived from [R]- β -butyrolactone and [R]- β -pentadecyl- β -propiolactone was prepared as described for the atactic homopolymer in Example 10 using a monomer mixture which was charged as a toluene solution through an alumina column so that 8.72 g (0.101 mol) [R]- β -butyrolactone, 1.47 g (0.0052 mol) [R]- β -pentadecyl- β -propiolactone, and 65.5 g toluene was added. The polymerization was initiated with ethylzinc isopropoxide (48 μ L, 1.1 M solution, 0.053 mmol) and the reaction was carried out at 75°C for 42 h.

The polymerization conditions and yields for Examples 1-6 and 10 are shown in Table I and for Examples 7-9 and 11-12 in Table II. The molecular weights (M_n and M_w) from Examples 1-6 and 10 are reported in Table III, and for Examples 6-9 and 11-12 in Table IV. Also reported in Tables III and IV are peak melting temperature (T_m °C) for isotactic polymers made with [S]- β -substituted- β -propiolactones and with [R]- β -substituted- β -propiolactones.

TABLE I
Polymerization Conditions for Homopolymerization of Racemic β -Butyrolactone

Example	Temperature °C	Time h	Zn/monomer mol%	Yield %
1	50	40	0.2	94
2	50	17	0.3	90
3	20	46	0.3	87
4	50	17	0.5	100
5	20	46	0.5	94
6	50	17	1.0	90
10	75	64	0.02	95

TABLE II
Polymerization Conditions for Homopolymerization and Copolymerizations of [S]- β -Butyrolactone or [R]- β -Butyrolactone

Example	Temperature °C	Time h	Zn/monomer mol%	Yield %
7	50	21	0.2	85
8	20	48	0.5	54
9	20	93	0.5	75
11	75	24	0.06	84
12	75	42	0.05	97

TABLE III

Product Characterization for Examples in Table I

Example	Molecular Weight		
	Mn	Mw	Mw/Mn
1	45,900	49,100	1.07
2	29,800	32,900	1.06
3	31,400	34,800	1.11
4	23,700	25,200	1.10
5	22,200	23,400	1.06
6	12,700	14,300	1.13
10	218,000	345,000	1.58

TABLE IV

Product Characterization for Examples in Table II

Example	Molecular Weight			Tm °C
	Mn	Mw	Mw/Mn	
7	36,600	49,900	1.36	179
8	3,470	5,240	1.51	160
9	5,150	5,150	1.62	140
11	116,000	226,000	1.94	-
12	146,000	210,000	1.43	145

The copolymer composition of the product of Example 9 is the same as that of the monomer feed (95:5, β -butyrolactone: β -pentyl- β -propiolactone) by ^1H NMR. Inspection of the carbonyl carbon region of the ^{13}C NMR spectra show that when racemic monomer is used atactic polymer is obtained, whereas when monomer of high enantiomeric purity is used, polymer of very high to complete isotacticity is produced.

The advantages of this invention are the good control of molecular weight and high yields with relatively short reaction times compared to the existing art cited previously. Also, the tacticity of the polyester produced with alkylzinc isopropoxide initiators can be controlled by the optical purity of the monomers used.

All publications mentioned hereinabove are hereby incorporated in their entirety by reference.

It is understood that the examples and embodiments described herein are for illustrative purposes only and that various modifications or changes in light thereof will be suggested to one skilled in the art and are to

be included in the spirit and purview of this application and scope of the appended claims.

What is Claimed is:

1. A method of preparing a polyester comprising polymerizing at least one β -substituted- β -propiolactone in the presence of an initiating amount of alkylzinc alkoxide for a reaction time and temperature sufficient to produce the polyester, wherein the alkylzinc alkoxide has the structure R^1ZnOR^2 wherein R^1 and R^2 are independently a C_1 , C_2 , C_3 , C_4 , C_5 , C_6 , C_7 , C_8 , C_9 , or C_{10} alkyl.
2. The method of Claim 1, wherein the alkylzinc alkoxide is nonchiral.
3. The method of Claim 2, wherein the polymerizing is conducted in bulk.
4. The method of Claim 2, wherein the polymerizing is conducted in a solvent for the nonchiral alkylzinc alkoxide and for the β -substituted- β -propiolactone.
5. The method of Claim 4, wherein the solvent is an aryl hydrocarbon comprising from about 6 to about 15 carbons or alkyl hydrocarbon comprising from about 5 to about 18 carbons.
6. The method of Claim 5, wherein the solvent is toluene or xylene.
7. The method of Claim 2, wherein the method comprises copolymerizing two different β -substituted- β -propiolactones to produce a copolyester.
8. The method of Claim 7, wherein the dissimilar β -substituted- β -propiolactones comprise [S]- β -butyrolactone and [S]- β -alkyl- β -propiolactone wherein the [S]- β -alkyl- β -propiolactone comprises an alkyl group having two or more carbons.
9. The method of Claim 7, wherein the dissimilar β -substituted- β -propiolactones comprise [R]- β -butyrolactone and [R]- β -alkyl- β -propiolactone wherein the [R]- β -alkyl- β -propiolactone comprises an alkyl group having two or more carbons.

10. The method of Claim 7, wherein the dissimilar β -substituted- β -propiolactones comprise [S]- β -butyrolactone and [R]- β -alkyl- β -propiolactone wherein the [R]- β -alkyl- β -propiolactone comprises an alkyl group having two or more carbons.
11. The method of Claim 7, wherein the dissimilar β -substituted- β -propiolactones comprise [R]- β -butyrolactone and [S]- β -alkyl- β -propiolactone wherein the [S]- β -alkyl- β -propiolactone comprises an alkyl group having two or more carbons.
12. The method of Claim 2, wherein said β -substituted- β -propiolactone comprises racemic β -butyrolactone.
13. The method of Claim 2, wherein the nonchiral alkylzinc alkoxide is ethylzinc isopropoxide, methylzinc isopropoxide, ethylzinc ethoxide, or ethylzinc methoxide.
14. The method of Claim 13, wherein the nonchiral alkylzinc alkoxide is ethylzinc isopropoxide.
15. The method of Claim 1, wherein the reaction time is about 3 to 100 hours.
16. The method of Claim 7 wherein the reaction time is about 3 to 100 hours.
17. The method of Claim 1, wherein the temperature is from about 20°C to about 80°C.
18. The method of Claim 17, wherein the temperature is from about 45°C to about 60°C.
19. The method of Claim 7, wherein the temperature is from about 40°C to about 80°C.
20. The method of Claim 19, wherein the temperature is from about 45°C to about 60°C.

21. The method of Claim 1, wherein the temperature is from about 70°C to about 80°C.
22. The method of Claim 7, wherein the temperature is from about 70°C to about 80°C.
23. The method of Claim 1, wherein the alkylzinc alkoxide is present in an amount to give a mole percent range of Zn to β -substituted- β -propiolactone monomers from about 0.005 to about 1.
24. The method of Claim 7, wherein the nonchiral alkylzinc alkoxide is present in an amount to give a mole percent range of Zn to β -substituted- β -propiolactone monomers from about 0.005 to about 1.
25. A polyester made by the method of Claim 1, wherein the β -substituted- β -propiolactone is substituted with an alkyl comprising from about 1 to about 19 carbons, alkenyl comprising from about 2 to about 19 carbons, aryl comprising from about 6 to about 19 carbons, aralkyl comprising from about 7 to about 19 carbons, alkaryl comprising from about 7 to about 19 carbons, or cycloalkyl comprising from about 3 to about 19 carbons.
26. A copolyester made by the method of Claim 7, wherein the two different β -substituted- β -propiolactones are independently substituted with an alkyl comprising from about 1 to about 19 carbons, alkenyl comprising from about 2 to about 19 carbons, aryl comprising from about 6 to about 19 carbons, aralkyl comprising from about 7 to about 19 carbons, alkaryl comprising from about 7 to about 19 carbons, or cycloalkyl comprising from about 3 to about 19 carbons.

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