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(54) Title: POLYESTER AND METHOD FOR PREPARING SUCH A POLYESTER

(57) Abstract: A polyester, comprising ethylene 2,5-furandicarboxylateunits, has an intrinsic viscosity of at least 0.45 d L/g, and has a relative content of carboxylic acid end groups, expressed as the fraction of the molar amount of carboxylic acid end groups divided by the sum of the molar amounts of hydroxyl end groups and carboxylic acid end groups in the range of 0.10to 0.70. The polyester can be prepared with a method wherein a starting mixture comprising 2,5-furandicarboxylic acid and ethylene glycol is subjected to esterification and subsequent polycondensation at reduced pressure when the molar ratio of 2,5-furandicarboxylic acid to ethylene glycol in the starting mixture is 1:1.01 to 1:1.15,wherein water,that is formed during the reaction between 2,5-furandicarboxylic acid and ethylene glycol, and some ethylene glycol are removed in a distillation system, and wherein ethylene glycol that is removed with water, is separated from water and at least partly recycled.

Polyester and method for preparing such a polyester

The present invention relates to a polyester and a method for the preparation of a polyester. More in particular, the invention relates to a polyester that comprises 2,5-furandicarboxylate moieties and ethylene glycol residues and to a method for preparing such polyesters.

2,5-Furandicarboxylic acid (FDCA) is a diacid that can be produced from natural sources such as carbohydrates. Routes for its preparation using air oxidation of 2,5-disubstituted furans such as 5-hydroxymethylfurfural or ethers thereof with catalysts comprising Co and Mn have been disclosed in e.g. WO2010/132740, WO2011/043660 and WO2011/043661.

US 2551731 describes the preparation of polyesters and polyester-amides by reacting glycols with dicarboxylic acids of which at least one contains a heterocyclic ring, such as 2,5-FDCA. Under melt polymerization conditions, using sodium- and magnesium methoxide as a catalyst, FDCA and 2.5 equivalents of ethylene glycol or FDCA dimethyl ester and 1.6 equivalents of ethylene glycol were reacted in a esterification step or transesterification step, respectively, at ambient pressure between 160 and 220 °C, after which a polycondensation was carried out between 190 and 220 °C under a few mm Hg pressure. The polycondensation process took between about 5 to over 7 hours. The product had a reported melting point of 205-210 °C and readily yielded filaments from the melt.

In US 2009/0124763 polyesters are described, having a 2,5-furandicarboxylate moiety within the polymer backbone and having a degree of polymerization of 185 or more and 600 or less. These polymers are made in a three step process involving the esterification of the 2,5-FDCA or the transesterification of the diester thereof with a diol, and a second step involving polycondensation, followed by solid state polymerization as third step.

The first step is carried out at ambient pressure at a temperature within a range of 150 to 180 °C, whereas the polycondensation step is carried out under vacuum at a temperature within a range of 180 to 230 °C. The product is then purified by dissolving the same in hexafluoroisopropanol, re-precipitation and drying, followed by the third step, a solid state polymerization at a temperature in the range of from 140 to 180 °C. For the preparation of poly(ethylene furandicarboxylate) the first two steps took over 11 hours.

In WO 2010/077133 a process for preparing furandicarboxylate-containing polyesters is described wherein the diester of FDCA is transesterified with a diol, and the ester composition thus obtained is subjected to polycondensation. The polycondensation is conducted for a period of up to 5 hours. The polycondensate may then be subjected to solid state polymerization. In an example the solid state polymerization was conducted for 60 hours. Although the molecular weight of the polyester obtained is reasonably high, the

duration of the solid state polymerization is considered too long. An improvement is described in WO 2013/062408, wherein the dimethyl ester of FDCA is transesterified with ethylene glycol, or bis(2-hydroxyethyl)-2,5-furandicarboxylate is used as starting material. The transesterification product or this starting material is then subjected to polycondensation and after a drying/crystallization step the polycondensate is subjected to solid state polymerization. The polycondensation was shown to take three hours. In an example the solid state polymerization takes two days.

KR 20140003167 describes a polyester polymer with excellent transparency which is manufactured by using a biomass originated furandicarboxylate ester compound with ethylene glycol. In comparative examples also furandicarboxylic acid has been used. The molar ratio of furandicarboxylate ester to ethylene glycol may be from 1:1.1 to 1:4. The ratio of furandicarboxylic acid to ethylene glycol varies between1:1.2 to 1:2.

US 2013/171397 describes the preparation of copolyesters formed from 2,5-furandicarboxylic acid or a lower alkyl ester thereof, at least one aliphatic or cycloaliphatic C3-C10 diol and terephthalic acid. In a comparative experiment the patent application describes the polymerization of furandicarboxylic acid and ethylene glycol in a molar ratio of 1: 1.5.

In WO 2013/120989 a continuous process for the preparation of poly(ethylene furandicarboxylate) is described wherein FDCA or a diester thereof is mixed with ethylene glycol at elevated temperature to give a paste or a homogeneous solution, the paste or solution is converted to an esterification product of FDCA and ethylene glycol, the esterification product is polycondensed under reduced pressure, wherein the polycondensation is performed in two stages. According to an example the dimethyl ester of FDCA was reacted with ethylene glycol in a molar ratio of 1:1.7. In this example the stages following the production of the esterified product took 5 hours. The polycondensation product can be subjected, if desired, to a solid stating polymerization.

It is therefore apparent that there is need for a process for the preparation of poly(ethylene furan dicarboxylate) that comprises a faster polycondensation step, but also allows a shorter solid state polymerization and still yield polyesters with a sufficiently high molecular weight.

It has now surprisingly been found that when the polyester that is subjected to solid state polymerization fulfils some characteristics as to its structure, the solid state polymerization can be shortened significantly. The characteristics relate to the end groups of the polyesters. It was further found that the preparation of such polyesters can be effected at a higher reaction rate than that of the polycondensation steps in US 2551731.

Accordingly, the present invention provides a polyester comprising ethylene 2,5-furandicarboxylate units, which polyester has an intrinsic viscosity of at least 0.45 dL/g, and which polyester has a relative content of carboxylic acid end groups, expressed as the

fraction of the molar amount of carboxylic acid end groups divided by the sum of the molar amounts of hydroxyl end groups and carboxylic acid end groups in the range of 0.10 to 0.70.

It has been found that when solid particles of the polyesters according to the invention are subjected to solid state polymerization the duration of the solid state polymerization can be shortened considerably.

It is surprising that the polyesters according to the present invention have this advantage. US 2014/0024793 discloses a process for the production of a polyester comprising an esterification reaction of ethylene glycol and 2,5-furandicarboxylic acid to form an oligomer and a condensation reaction of the oligomer obtained, wherein the esterification reaction is carried out at 200 to 250 °C. This document highlights in all formulae shown that the oligomer and polyester have hydroxyl end groups.

In general there are a number of methods to determine the end groups in polyesters. Such methods include titration, infrared and nuclear magnetic resonance (NMR) methods. Often the separate methods are used to quantify the four main end groups: carboxylic acid end groups, hydroxyl end groups, alkyl ester groups, such as the methyl ester end groups (for polyesters from the dialkyl ester of a dicarboxylic acid) and the end groups that are obtained after decarboxylation. A.T Jackson and D.F. Robertson have published an ^{1}H-NMR method for end group determination in “Molecular Characterization and Analysis of Polymers” (J.M. Chalmers en R.J. Meier (eds.), Vol. 53 of “Comprehensive Analytical Chemistry”, by B. Barcelo (ed.), (2008) Elsevier, on pages 171-203. In this method the hydroxyl end group is determined in polyethylene terephthalate (PET) by using a selection of harsh solvents such as 3-chlorophenol, 1,1,1,3,3,3-hexafluoro-2-propanol, trichloroacetic acid or trifluoroacetic acid. It is preferred to use deuterated 1,1,2,2-tetrachloroethane (TCE-d2) as solvent without any derivatization of the polyester. A similar method can be carried out for polyesters that comprise furandicarboxylate moieties and ethylene glycol residues. The measurement of the end groups for the latter polyesters can be performed at room temperature without an undue risk of precipitation of the polyester from the solution. This ^{1}H-NMR method using TCE-d2 is very suitable to determine the hydroxyl end groups (HEG) and the decarboxylation end groups (DecarbEG). It can also be used to determine the content of diethylene glycol. Peak assignments are set using the TCE peak at a chemical shift of 6.04 ppm. The furan peak at a chemical shift of 7.28 ppm is integrated and the integral is set at 2.000 for the two protons on the furan ring. The HEG is determined from the two methylene protons of the hydroxyl end group at 4.0 ppm. The content of DEG is determined from the integral of the shifts at 3.82 to 3.92 ppm, representing four protons. The decarboxylated end groups are found at a shift of 7.64-7.67 ppm, representing one proton. When the polyester also comprises methyl ester end groups, the methyl signal will occur at about 3.97 ppm, representing 3 protons.

The carboxylic acid end groups are determined by using the titration method according to ASTM D7409, adapted for poly(ethylene 2,5-furandicarboxylate). A thus

modified method thereof involves the titration of a 4% w/v solution of poly(ethylene 2,5-furandicarboxylate) in ortho-cresol with 0.01M KOH in ethanol as titrant to its equivalence point, using 0.5 mg of bromocresol green (2,6-dibromo-4-[7-(3,5-dibromo-4-hydroxy-2-methyl-phenyl)-9,9-dioxo-8-oxa-9λ6-thiabicyclo[4.3.0]nona-1,3,5-trien-7-yl]-3-methyl-phenol) in 0.1 ml ethanol as indicator.

For the purpose of the present application the values for HEG and the decarboxylated end groups are obtained by ^{1}H-NMR using TCE-d2, whereas the values for CEG are determined by the titration method described above.

The content of the various end groups can be expressed as relative to other end groups. As indicated above the relative content of carboxylic acid end groups is in the range of 0.10 to 0.70 relative to the sum of hydroxyl and carboxylic acid end groups. More suitably, the relative content of carboxylic acid end groups is at least 0.11, leading to a range of 0.11 to 0.70 and is, more preferably, in the range of 0.14 to 0.65 based on the sum of the hydroxyl and carboxylic acid end groups. It is also possible to express the amount of end groups as an absolute value per weight unit of polyester. Expressed as an absolute feature, the amount of carboxylic acid end groups is advantageously in the range of 15 to 122 meq/kg. The absolute amount of carboxylic acid end groups is directly obtained from the titration.

About 10 mg of a polyester is weighed and put in an 8ml glass vial. To the vial 0.7 ml of TCE-d2 is added and the polyester is dissolved at room temperature whilst agitating the mixture in the vial. The dissolved mixture is subjected to ^{1}H-NMR, whilst the peak for TCE-d2 is set at 6.04 ppm. The furan peak is centered at 7.28 ppm, and it is integrated and the integral set to 2.000, to represent the 2 protons on the furan ring. The ^{1}H-NMR signals are integrated and the amounts of end groups are calculated as follows:

Hydroxyl end groups (HEG) = 5494 * integral at 4.0 ppm/2;

Decarboxylated end groups (DecarbEG) = 5494 * integral at 7.65 ppm.

When the polyester also comprises methyl ester end groups, the methyl signal will occur at 3.97 ppm and the content of the ester end groups is then calculated as:

Ester end groups (EEG) = 5494 * integral at 3.97 ppm/3.

The polyester according to the present invention has a certain molecular weight. This molecular weight is usually not at its maximum. The molecular weight can be increased by subjecting the polyester of the present invention to solid state polymerization. Nevertheless, the polyester according to the present invention can be used for several purposes. Such purposes include the production of fibers, including those produced in melt spinning/drawing processes and those produced in melt-blown processes, the production of films or sheets for packaging and the like, the production of injection molded items, the production of bottles, or the production oriented tapes for strapping. The molecular weight of the present polyester is higher than the ester of the diol and FDCA with one or two furandicarboxylate groups. The molecular weight is expressed in terms of intrinsic viscosity. First the relative viscosity (η_{rel}) is

determined in a 60/40 w/w mixture of phenol and tetrachloroethane at 30 °C and a concentration (c) of 0.4 g/dL. This procedure is similar to the ASTM D4603 standard for the determination of the inherent viscosity for poly(ethylene terephthalate). The intrinsic viscosity is then calculated using the Billmyer equation:

Intrinsic viscosity (IV) = $\{\eta_{rel} -1+3*\ln(\eta_{rel})\}/(4*c)$

The intrinsic viscosity is suitably greater than 0.45 dL/g and more preferably in the range of 0.45 to 1.0 dL/g. If the polyester is to undergo an additional step of solid stating then the molecular weight is preferably in the range of 0.45 to 0.75 dL/g. When the polyester is to be used without an additional step of solid stating, the molecular weight is preferably in the range that is preferred for the desired end-use application, for example in the range of 0.65 to 1.0 dL/g, which is a suitable molecular weight for the end-use application of bottles.

The polyester according to the present invention suitably consists of ethylene furandicarboxylate units for at least 90 mole%, preferably for at least 95 mole%. The balance may comprise other monomer units, such as other diols and diacids. Other suitable monomer diols include diethylene glycol and other suitable diacids, include terephthalic acid, adipic acid, phthalic acid and isophthalic acid. More preferably, the polyester consists of poly(ethylene 2,5-furandicarboxylate) that further comprises diethylene glycol residues, wherein the amount of diethylene glycol residues amounts to at most 0.045 moles of diethylene glycol residues per mole of 2,5-furandicarboxylate.

Whereas many prior art polyesters that contain furandicarboxylate groups are grey, brown or yellow colored, the polyesters according to the present invention suitably have hardly any color. The color is expressed in terms of absorbance. The polyesters are suitably clear in that they have a light absorbance of at most 0.08, preferably at most 0.05, measured as a 30 mg/mL solution in a dichloromethane:hexafluoroisopropanol 8:2 (vol/vol) mixture at 400 nm.

The polyesters according to the present invention have a molecular weight expressed as intrinsic viscosity of at least 0.45 dL/g. The intrinsic viscosity is a measure closely linked to the weight average molecular weight Mw. The weight average molecular weight and the number average molecular weight can also be determined through the use of gel permeation chromatography (GPC). GPC measurement is suitably performed at 25 ºC. For the calculation polystyrene standards are used. As eluent suitably a solvent mixture of chloroform:2-chlorophenol 6:4 (vol/vol) can be used. In the experimental part GPC measurements were carried out under these conditions on a Merck-Hitachi LaChrom HPLC system equipped with two PLgel 5 µm MIXED-C (300x7.5 mm) columns. Calculation of the molecular weight was carried out by Cirrus™ PL DataStream software. When the weight average molecular weight Mw and number average molecular weight Mn would also be determined for the polyester according to present invention the polydispersity index (Mw/Mn) is suitably in the range of 1.9 to 2.6.

The polyester according to the present invention may be amorphous. Such an amorphous product is usually directly obtained from the polycondensation. However, the polyester according to the present invention is preferably semi crystalline. The crystallinity of a polymer tends to affect its physical properties, such as its density and melting temperature. Polymer crystallinity can be determined with Differential Scanning Calorimetry (DSC) by quantifying the heat associated with melting of the polymer. The crystallinity is often expressed as net enthalpy of melting in terms of number of Joules per gram which number is derived from the DSC technique. The polyester according to the present invention preferably has a crystallinity of at least 25 J/g, measured by DSC. A maximum enthalpy in terms of number of Joules per gram is typically 80 J/g. The polyester according to the present invention having a certain degree of crystallinity then also has a melting point. The melting point of a polymer is easily determined by DSC and measured at the top of the endothermic peak. The ISO11357-3 standard describes such a melting determination. In accordance with this determination, the polyester according to the present invention suitably has a melting point of at least 215 °C. In highly crystalline polyester the melting point may exceed 230 °C, and even be as high as 245 °C.

It is common that polyester compositions contain some moisture, especially as some moisture pick-up is common when the polyester is exposed to atmospheric air. Since the stability of the polyester according to the invention is improved when the polyester composition contains as little moisture as feasible, compositions comprising the polyester according to the present invention preferably have a moisture content of at most 100 ppmw more preferably at most 50 ppmw, determined in accordance with ISO 15512.,

When the polyester according to the present invention is subjected to solid state polymerization the polymerization rate during solid state polymerization is less dependent on the size of the polyester particles than for polyesters with lower content of carboxylic acid end groups. This being the case, it allows the skilled person to select the most feasible particle size of the polyester in order to subject it to solid state polymerization. Suitably, the particle size is selected such that there are 40 to 350 particles per gram. Typically such a particle size boils down to polyester particles with a mass of 2.8 to 25 mg. Such particles can easily be handled and still provide a good polymerization rate when they are subjected to solid state polymerization. These particle sizes are also amenable to processing via air conveyance schemes and are suitably processed in existing driers, hoppers, and extrusion screws. Particles which are too small can lead to increased hazards due to dust and difficulty in processing due to an increased tendency to stick or “hang up” on various surfaces.

It has further been found that the polyester according to the present invention can be prepared by deviating from the prior art methods for making similar polyesters. Generally speaking, many documents in the prior art with respect to furandicarboxylic acid based polyesters have prescribed to start from a diester of the diacid as the preferred starting

material. For example, the use of dimethyl furandicarboxylate has been described. It will be understood that the polyester according to the present invention is not readily made from such a starting material, as the content of carboxylic acid end groups will generally be far too low in such a preparation. If such a product is intended it may be possible to add water into the mixture of the diester and ethylene glycol. One way of achieving this may be done via the use of wet ethylene glycol. The added water may cause the saponification of some of the diesters, thereby yielding carboxylic acid groups. Another possibility is to use a mixture of FDCA and the diester thereof. Such a mixture may also be obtained by adding the FDCA diacid during the transesterification of the diester of FDCA with ethylene glycol to yield the ethylene diester of FDCA. In particular, addition of FDCA during the transesterification stage, more in particular towards the end of this stage, affords an opportunity to add acid end groups to the resulting composition. In this way a number of carboxylic end groups are obtained that is in accordance with the polyester according to the present invention. It is also possible to use a mixture of water and ethylene glycol when starting from FDCA. This may be useful, for example, to improve the initial mixing of FDCA to form a slurry, without increasing the ethylene glycol content beyond the desirable range and thereby achieve a number of carboxylic end groups in accordance with the polyester of the present invention. It is also possible to add FDCA diacid late in the esterification period or during the pre-polycondensation period in order to adjust the number of carboxylic end groups such that the resultant composition after melt polycondensation will have a number of carboxylic end groups in accordance with the polyester according to the present invention.

It has been found that when the preparation of a polyethylene furandicarboxylate starts from the dimethyl ester of the diacid, the content of the carboxylic acid end group in the resulting polymer is less than about 10 meq/kg and also less than 0.1 when expressed as a fraction of the carboxylic acid end groups to the sum of the carboxylic acid end groups plus hydroxyl end groups. It has also been found that, whereas the prior art prescribes a significant excess of diol with regard to the furandicarboxylic acid, suitable polyesters are obtained if the excess of diol is rather small. Accordingly, the present invention further provides a method for the preparation of a polyester, wherein a starting mixture comprising 2,5-furandicarboxylic acid and ethylene glycol is subjected to esterification to form an ester composition, wherein the molar ratio of 2,5-furandicarboxylic acid to ethylene glycol in the starting mixture is 1:1.01 to 1:1.15; and wherein the ester composition thus obtained is subjected to polycondensation at reduced pressure in the presence of a polycondensation catalyst to obtain a polycondensate, wherein water, that is formed during the reaction between 2,5-furandicarboxylic acid and ethylene glycol, and some ethylene glycol is removed in a distillation system, and wherein ethylene glycol that is removed with water is separated from water and at least partly recycled.

The polycondensate thus obtained comprises a higher content of carboxylic acid end groups than polycondensates that have been prepared from starting mixtures that contained a larger excess of ethylene glycol.

The esterification reaction of furan dicarboxylic acid and ethylene glycol is known in the art. Hence, the skilled person will realize that although there is no need for using an esterification catalyst, the use of such a catalyst may be contemplated. Hence in an embodiment the 2,5-furandicarboxyic acid and ethylene glycol are suitably reacted in the presence of an esterification catalyst. As esterification catalysts are advantageously acidic, and since one of the reactants is an acid, the necessity to use an esterification catalyst is lacking. However, when such a catalyst is used, it is suitably a Brønsted or Lewis acid. The Brønsted acids may be strong mineral acids such as sulphuric acid, nitric acid or hydrochloric acid. Suitable Lewis acids include compounds of metals such as the chlorides, bromides, tosylates, alkoxides and triflates of metal selected from the group consisting of, zinc, titanium, tin, calcium and mixtures thereof. It is also possible to use organic esters of the metal acids, such as the alkyl esters of titanic acid, stannic acid and the like. Hence, the esterification catalyst is preferably selected from catalysts containing one or more metals selected from the group consisting of titanium, tin, calcium and antimony. The catalysts, if used, may be added from the start of the esterification reaction. However, since the esterification proceeds easily without the use of an esterification catalyst, the esterification is preferably carried out in the absence of an esterification catalyst, which is dedicated to the esterification reaction.

In the esterification reaction water is being formed. It has been found that it is advantageous to remove the water formed during the reaction of 2,5-furandicarboxylic acid and ethylene glycol. In this way the esterification reaction being an equilibrium reaction, may be led to completion. The removal of water from the esterification mixture may be conducted in any known manner. It is suitable to pass any water formed in a vaporous phase through a condenser and remove the condensate that includes the liquefied water. The vaporous phase may comprise also some ethylene glycol. Therefore, the vaporous phase is advantageously passed through a distillation system wherein water and ethylene glycol are separated. The ethylene glycol is suitably, at least partly, but preferably substantially completely, recycled to the esterification mixture. The water thus separated is discharged. Hence, the method according to the present invention is preferably carried out such that water is removed in a distillation system wherein the majority of ethylene glycol that is removed with water is separated from water and at least partly recycled.

It will be evident that the degree with which the ethylene glycol is entrained in the vaporous phase of water formed is dependent on the temperature and other conditions at which the esterification is carried out. The conditions that are used in the prior art include a temperature in the range of about 180 to 280 °C and about ambient pressure. These conditions were maintained for a period of about 4 hours. In the method according to the

present invention the esterification reaction between 2,5-furandicarboxylic acid and ethylene glycol is preferably carried out at a temperature of 160 to 240 °C. The pressure is suitably in the range of 0.9 to 5 bar, and the reaction is advantageously continued for a period of 0.5 to 4 hr. The reaction is conveniently carried out in an inert atmosphere, such as under nitrogen, neon, helium or argon. The starting mixture may comprise a diluent, such as water, which is suitably discharged during the reaction.

Applicants have found that diethylene glycol (DEG) is readily formed during the esterification reaction of FDCA and ethylene glycol. Compounds such as choline, tetraethylammonium hydroxide (TEAOH), tetramethylammonium hydroxide (TMAOH), tetrabutylammonium hydroxide, salts of carboxylic acids such as calcium or sodium acetate, basic salts of mineral acids, such as Na_2SO_4 and Na_2HPO_4, alkali metal hydroxides, such as sodium hydroxide, or residual calcium or sodium in the FDCA can suppress the formation rate of DEG. Suitable dosages are of 0.01 to 1 mmol/mol FDCA, preferably, 0.02 to 0.5 mmol/mol FDCA, more preferably 0.04 to 0.30 mmol per mol FDCA. Tetraethylammonium hydroxide, tetramethylammonium hydroxide and Na_2HPO_4 have been found to be particularly effective.

When the esterification is being carried out in a batch process then it is possible to monitor the reaction progress by determining the amount of water which is produced, and comparing that to the stoichiometrically determined theoretical water at 100% esterification. When at least 70 % of the theoretical amount of water has been removed, the esterification is stopped and the pressure is reduced to start a polycondensation stage. During the pressure reduction unreacted ethylene glycol is removed by vaporization from the reacting mixture. The exact timing for the end of esterification is determined by trials, and is dependent on the subsequent rate of pressure reduction and efficiency of water removal, but typically in batch processes the extent of water removal is suitably at least 70% and may be as high as virtually 100%. Preferably, the extent of water removal is in the range of 70 to 96%. The esterification stage should preferably not be continued beyond the point of 96% or the resulting product may be deficient in carboxylic acid end groups. If the esterification stage is continued for too short a period before the ethylene glycol removal has reached the lower limit, then the product will generally be too high in carboxylic acid end groups. If the esterification extent is carried out to less than 70%, i.e. less than 70% of the theoretical amount of water has been removed, for instance at 40%, so much ethylene glycol may volatize from the mixture during the pressure reduction that the resulting ester composition will be high in carboxylic end groups.

When the process is being conducted in a continuous manner then the esterification reaction progress will be controlled through the use of temperature, ethylene glycol feed ratio, and average residence time. The amount of water being removed from the system will again give an indication of the extent of the esterification reaction. Also in continuous processes the amount of water removed is controlled and the esterification reaction is prolonged until at

least 70% of the stoichiometric amount of water, based on 100% esterification of FDCA feed has been removed. Reactors, equipment, and controls for the production of poly(ethylene terephthalate) such as described in the book Modern Polyesters: Chemistry and Technology of Polyesters and Copolyesters by J. Scheirs and T.E. Long (eds.), Wiley, 2003, can also be used to advantage for the production of the poly(ethylene 2,5-furandicarboxylate) of the present invention.

By the pressure reduction the excess amount of ethylene glycol is removed. In a batch process the pressure is reduced. In practice, the pressure reduction may take some time. The process of reducing the pressure may take from 0.1 to 1.8 hours. It is advantageous to slowly reduce the pressure in order to prevent the carry-over of the relatively low molecular weight esters into the vacuum system. Therefore, the ester composition passes through a stage wherein the pressure is in the range of 20 to 700 mbar. At this pressure a prepoly-condensation takes place. The eventual polycondensation occurs at a reduced pressure in the region of 0.05 to 20 mbar.

In case of a continuous process the temperature of the ester composition is suitably raised compared to the starting temperature of the esterification. Subsequently, the further heated ester composition is subjected to a pressure reduction. By the pressure reduction the composition is depleted of ethylene glycol. After the pressure reduction the product is maintained at the reduced pressure, and optionally, further heated so that a prepoly-condensation stage takes place under evaporation of further ethylene glycol, yielding an oligomer of ethylene furandicarboxylate. This prepolycondensation may take place in a continuous stirred tank reactor or a horizontal reactor operating with perforated rotating disks. The pressure at this pre-polycondensation reaction may be 20 to 700 mbar. The temperature of the pre-polycondensation is suitably from 180 to 240 ºC. For further pressure reduction the pre-polycondensation product may be passed to a further reactor where it is lead to further polycondensation. For such polycondensation reactions disc-type or cage-type reactors may be used. The pressure in the polycondensation reaction is suitable from 0.05 to 20, suitably from 0.05 to 5 mbar.

It has been found that the esterification reaction for 2,5-furandicarboxylic acid is quite fast and as a result it is most common to “over esterify” and leave an inadequate amount of carboxylic acid end groups in the polyester. The potential extent of the esterification reaction can be somewhat controlled by using a dimensionless parameter defined herein as:

Esterification Potential (EsPo) = $(MR-1)^2 * P_{H2O}(T)$, wherein MR represents the molar ratio of ethylene glycol over 2,5-furandicarboxylic acid, MR being greater than 1;

$P_{H2O}(T)$ represents the pure component vapor pressure (in bar) of water at temperature T, which is the final reaction temperature in the esterification mixture before the pressure is reduced to enter the prepolycondensation stage. P_{H2O} is determined in

accordance with an established equation for the vapor pressure of pure water. The Antoine equation

$\log_{10} P = A - B/(C + T)$, where T is the temperature at the end of esterification, expressed in ºC, A = 5.2594, B = 1810.94, and C = 244.485 gives the required vapor pressure of pure water in bar. It has been found that the best results as to polycondensate are obtained if the esterification potential is at most 0.8, preferably from 0.05 to 0.5.

At this point the ester composition is subjected to a step of prepolycondensation. Thereto, the pressure is reduced and, optionally, a polycondensation catalyst is added. The prepolycondensation step is used to remove excess or unreacted ethylene glycol and to reduce the pressure to remove most of the other volatiles, while avoiding excessive foaming or carryover into the vacuum lines. The temperature is raised and the polycondensation reaction begins to occur, with liberation and removal of ethylene glycol which is generated via reaction. It is important to note that the esterification reaction also continues, generating water which is also removed from the reaction mixture. In very small batch equipment the same reactor may be used for all stages of the reaction. When the reaction is performed in larger scale batch equipment this stage may completed in the same equipment as the esterification reaction, and after this stage the reactant mixture may then be transferred to a vessel especially designed for good mass transfer to promote the polycondensation reaction. Alternatively, the reactant mixture may be moved to a different vessel prior to initiating the pressure let-down and the prepolycondensation and the polycondensation are then conducted in a single vessel. The addition of polycondensation catalyst may already have occurred at the start of the esterification reaction, so that no further addition of the catalyst to the esterification product is desired at this point.

Other compounds, such as stabilizing agents, may also be added to the esterification product. The stabilizing agents may include antioxidants. Preferable antioxidants are phosphite-containing compounds, phosphate compounds, phosphonate compounds, and hindered phenolic compounds. Antioxidants include such compounds as trialkyl phosphites, mixed alkyl/aryl phosphites, alkylated aryl phosphites, sterically hindered aryl phosphites, aliphatic spirocyclic phosphites, sterically hindered phenyl spirocyclics, sterically hindered bisphosphonites, alkyl phosphates, aryl phosphates, mixed alkyl/aryl phosphates, alkylphosphonoacetates, hydroxyphenyl propionates, hydroxy benzyls, alkyl phenols, aromatic amines, hindered amines, hydroquinones and mixtures thereof. Such other compounds may also be added in batch or any other type of operation. Hence compositions containing the polyester according to the invention may comprise such compounds.

Poly(ethylene 2,5-furandicarboxylate) is a slowly crystallizing polyester under quiescent conditions. Nucleating agents may be added to the polyester to increase the nucleation density, and thereby increase the overall crystallization rate under quiescent conditions.

For crystallization of the polyester according to the present invention, typically prior to an SSP process, crystallization may be conducted from the melt (as may be done in an underwater pelletizer with in-situ crystallization) or from the glassy state (after cooling of polymer granulates). To this end it may be desirable to add a nucleating agent to the polyester after the polycondensation, typically still in the melt phase. Typical addition levels will be from 0.05 to 2 wt%, or more preferably 0.1 to 1 wt%, based on the total polyester. The inorganic minerals may be added at higher levels, such as up to 5 or even 10 wt% if desired.

Nucleating agents may include inorganic minerals, organic salts, high melting waxes, or other polymers. Examples of inorganic minerals include talc, titanium dioxide, fused silica, boron nitride, mica, and calcium carbonate. Some examples of the organic salts sodium stearate, zinc stearate, other stearate salts, salts of other fatty acids, FDCA disodium salt, sodium salt of saccharine, salts of benzoic acid, aromatic phosphonates, sulfonic acid ester salts of isophthalic acid, and commercial materials such as bis(4-propylbenzylidene) propyl sorbitol, available as Millad®NX88 from Milliken Chemicals and 3,4-Dimethylbenzylidene sorbitol, available as Millad®3988, phosphate salts and esters, available as NA-11, methylen-bis(4,6-di-t-butylphenyl)phosphate sodium salt, or NA-21, aluminium-hydroxy-bis[2,2''-methylene-bis(4,6-di-t-butyl-phenyl)-phosphate. High melting waxes include materials such as stearamides and erucamides, or bis-amides. Polymers can include materials such as ionomers e.g. Surlyn ionomers from Du Pont, or Aculyn ionomers from Rohm and Haas, PEG2000 (polyethylene glycol), PET, PBT or others. Nucleating agents may also be used in the crystallization of polymers in different situations. Polymer crystallization can be conducted for a number of reasons, each of which would then be performed under different conditions. For example, to create a semi-crystalline part in an injection molding machine it would be required to have a rapid crystallization of the polymer during cooling from the melt. On the other hand, for crystallization of material prior to drying of reclaimed scrap, it would be desired to have the polymer crystallize rapidly from the glassy state, or on the up-heat.

In a more continuous operation the prepolycondensation reaction may be conducted in a dedicated vessel, typically with the overhead vapors being collected separately from the vapors generated during the esterification stage. During this process stage the pressure is typically reduced from approximately 1 bar or more used during esterification down to about 20 to 700 mbar, and more preferably to about 20 to 100 mbar. The duration of the prepolycondensation is suitably in the range of 0.5 to 2 hours.

At this point the ester composition is subjected to a step of polycondensation. As is known from the prior art the pressure at this step is further reduced. Pressures of less than about 5 mbar and preferably less than about 3 mbar may be applied. Lower pressures are preferred for good mass transfer and removal of ethylene glycol and water being liberated in the polycondensation and esterification reactions, respectively. Polycondensation temperatures according to the prior art include about 180 to 280°C. The polycondensation

according to the invention is preferably carried out at a temperature of 245 to 270 °C and suitably at a pressure of 0.05 to 5 mbar. Under these conditions it is ensured that the ester composition as well as the polycondensate formed is in a molten stage. The polycondensation is suitably continued for a period ranging from 1 to 3 hours. Preferably, the combined period for the prepolycondensation and the polycondensation stages is in the range of 1.5 to 4 hours.

The polycondensation may be terminated when the desired intrinsic viscosity has been reached. This can be monitored by measuring the torque of a stirrer that is provided in the reactor wherein the polycondensation is being carried out. It can also be monitored, for example, by a melt viscometer at the outlet of the reactor in a continuous process arrangement. When the viscosity is sufficiently high, the polycondensation is stopped and the product is discharged, yielding the polycondensate.

As indicated above, the polycondensation is preferably carried out in the presence of a polycondensation catalyst. Many polycondensation catalysts may be used. Such catalysts include the catalysts comprising one or more elements selected from tin, titanium, zinc, antimony, calcium, manganese, cobalt, hafnium, lead, magnesium, aluminium, cerium, zirconium and mixtures thereof. These compounds may be the acetate or carbonate salts of these metals. Alternatively, metal alkoxides, alkyl metal compounds, or other organometallic compounds are also possible. Other suitable catalysts include the oxides and halides of the elements mentioned. Preferred catalysts include titanium alkoxides, antimony acetate, antimony oxide, and antimony glycolate, i.e. the reaction product of antimony oxide and ethylene glycol. The amounts of the polycondensation catalyst are typically in the range of 0.005 mol% to 0.2 mol%, based on the number of moles of 2,5-furandicarboxylic acid in the starting mixture, preferably in the range of 0.01 to 0.10 mol%.

The polycondensation catalysts may be added to the ester composition when the ester composition has been formed. It is also possible to add the polycondensation catalyst to the starting mixture of 2,5-furan dicarboxylic acid and ethylene glycol, optionally in the presence of an esterification catalyst. The esterification catalyst, if present, is suitably present in an amount of 0.005 mol% to 0.2 mol%, based on the number of moles of 2,5-furandicarboxylic acid. When the polycondensation catalyst is added in the starting mixture or at an intermediate point of the esterification process the ester composition formed is suitably not isolated. In a batch process, after forming of the ester composition, the resulting product is preferably kept in the reaction zone where the esterification took place and the product as such is subjected to a pressure reduction in the prepolycondensation step. In a continuous process, after forming of the ester composition, the resulting product is transported to the next reaction vessel and subjected to a pressure reduction to accomplish evaporation of the ethylene glycol excess to start the prepolycondensation step.

When the viscosity is sufficiently high, the polycondensation is stopped and the product is discharged, yielding the polycondensate. The discharging operation can take various forms, depending on the nature of the polycondensation process. For example, if the polycondensation is conducted batch-wise, then the discharge may advantageously be conducted by closing off the vacuum and pressuring the reaction vessel with nitrogen or other inert gas. It can also be discharged through the use of gear pumps, either under pressure or under vacuum. If the polycondensation is conducted in a continuous manner then the discharge is also advantageously conducted in a continuous manner, for example, through the use of gear pumps to remove the polycondensate from the reaction vessel.

The polycondensate can be further processed even in the melt form. For example, it can be directed via pumps and or extruders through a melt filtration apparatus to a spinneret assembly, where it is directly formed into melt-spun fibers and subjected to drawing operations to form a filament bundle and subjected to optional further operations to form a multifilament yarn. It could instead be passed through a die to form a sheet and cooled over a series of rollers to make sheet or film, suitable for example for use in thermoforming operations. It has been found that it is very advantageous to treat the polycondensate melt thus obtained to a pelletizing step, such that solid particles are obtained. Thereto, the melt may be passed through a die yielding strands which are cooled in water and that are then cut into small particles. Such particles are typically of uniform size and cylindrical in shape. The melt may also be subjected to a process known as “under water pelletization” or “die face cutting”, wherein the melt is passed through a die, with a multitude of holes, which is in contact on one side with a cooling medium, such as water, and a rotating hub of cutters is used to cut the emerging melt to form pellets. Such particles are typically of uniform size and nearly spherical. Other methods can also be used. As an example, solid chips of polycondensate may be ground to small particles. The particles are suitably such that the average number of particles per gram is in the range of 40 to 350 particles per gram. Typically such a particle size boils down to polyester particles with a mass of 2.8 to 25 mg per particle. It has been found that when the polycondensation step is carried out to obtain a polycondensate with an intrinsic viscosity of greater than 0.45, and more preferably greater than 0.50, e.g. greater than about 0.52 dL/g, the step of converting the polycondensate melt into particles is more efficient, with fewer process upsets due to strand breaks and with a more even distribution of particle sizes and with less dust or fines. This is desirable for further processing of the polycondensate particles.

When the polycondensate is recovered as solid material from the polycondensation step, the polycondensate is rather amorphous. In order to render the polycondensate into a more crystalline material, the polycondensate is preferably crystallized at a temperature in the range of 90 to 200 °C. Thereto, the polycondensate is subjected to a heating step, whilst still in a solid state, at the temperature indicated. In certain arrangements the heating step may

entail controlling the temperature of the pellet during pelletization such that the final pellet temperature is in a range where crystallization occurs. Prior to any step of additional heating any adhered water from the pelletizing step is removed. This procedure is suitably carried out by bringing the temperature of the polycondensate to the desired temperature in the range of 90 to 200 °C. For poly(ethylene 2,5-furandicarboxylate) it has been found that the most rapid crystallization occurs at approximately 170 °C. It has also been found that if the particles are held for approximately 1 hour at 90 to 120 °C the subsequent crystallization at 170 °C is faster. The heating step can suitably be conducted at atmospheric pressure or under vacuum. The heat can suitably be provided by a water bath. The optimal temperature program will depend on the particular arrangements used for the crystallization. Typically, the polycondensate is kept a temperature in the range of 90 to 140 ºC for a period of 0.2 to 2.5 hrs, followed by a crystallization step for 1 to 48 hours at a temperature in the range of 120 to 200ºC. It has been found that the polyester chains in the polycondensate crystallize under these conditions yielding a semi-crystalline polyester. The polyester thus obtained suitably has a crystallinity of at least 25 J/g, measured by DSC. It suitably has a melting point of at least 215 °C. The polycondensate also has a relative content of carboxylic acid end groups, expressed as the fraction of the molar amount of carboxylic acid end groups divided by the sum of the molar amounts of hydroxyl end groups and carboxylic acid end groups in the range of 0.10 to 0.70.

According to the present invention an underwater pelletizing system can be used that produces pellets of the polyester according to the invention in a hot enough condition to self-initiate the crystallization process therein and ultimately provide a sufficiently crystalline character such that the polyester pellets obtained do not require a separate heating step in order to undergo crystallization. This elevated heat condition may be accomplished by reducing the residence time of the pellets in the water slurry in order to leave enough heat in the polyester pellets during the drying stage so that the crystallization process is initiated from inside the pellets. To do this, it is desired to separate the pellets from the water as soon as possible and to significantly increase the speed of pellet flow from the exit of the underwater pelletizer and into and through a dryer. The hot pellets leaving the dryer can then be carried on a conventional vibrating conveyor or other vibrating or handling equipment for a time sufficient to achieve the desired crystallinity and avoid agglomeration. The hot pellets can also be stored in a heat retaining condition, such as in a heat insulating container, to complete the desired crystallization process. For example, coated steel or plastic containers may be acceptable or stainless steel boxes that are conventionally used for polyethylene terephthalate. This system is similar to the one described for polyethylene terephthalate in US 8366428. The present invention will be further illustrated by means of the following examples.

EXAMPLES

In the following examples the hydroxyl end groups were determined by ^{1}H-NMR using the procedure as described in the description above. In the experiments ^{1}H (Inverse Gated Decoupled) nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 500 digital NMR with Cryo Platform using the residual solvent as internal standard. The NMR analysis was made within a few hours after the sample had been prepared. The carboxylic end groups content was determined by titration.

The results of these determinations are amounts of the respective end groups expressed in meq/kg. For the relative content of carboxylic acid end groups based on the sum of the carboxylic acid end groups and hydroxyl end groups the following formula is used: CEG/(CEG + HEG).

EXAMPLE 1

A number of polymerizations were carried out to show the preparation of polyesters according to the present invention.

Ethylene glycol (MEG) and 2,5-furandicarboxylic acid (FDCA) were mixed in an MEG:FDCA molar ratio of 1.15 or 1.30, along with Sb_2O_3 as a catalyst, present at 314 ppm of antimony. The reaction mixtures in experiments 1 and 3 further contained 42 ppm TEAOH (0.04 mmol/mol FDCA) and the reaction mixture in experiment 2 contained 80 ppm (0.09 mmol/mol) of TEAOH. The mixtures were subjected to esterification without addition of an esterification catalyst for a period of time (t_e) at elevated temperature. Water that was formed was evaporated and passed into a distillation column. The condensed water was removed and any MEG that was entrained or evaporated was separated and recycled back to the reaction mixture. The reaction was continued at atmospheric pressure until 85% of the theoretical water, based on furandicarboxylic acid feed, was collected. The temperature at that time was 240 °C and the reaction time was 270 minutes. The pressure was reduced, and prepolycondensation was started, the pressure reaching 20 mbar in approximately 70 minutes. The vacuum take-off point was switched at this point so that any additional ethylene glycol could be removed without passing through the distillation column. The pressure was further reduced to below 5 mbar. The ester composition with the catalyst was subjected to a polycondensation at a temperature of 245 or 251 °C, as indicated in Table 1. The polycondensation was continued for a period t_p until the intrinsic viscosity (IV) was about 0.5 dL/g. The polycondensation rate (P rate) was calculated as the rate of IV increase (*1000) in dL/g per minute. The relative CEG was determined as CEG/(CEG + HEG). The reaction conditions and the results are shown in Table 1.

Table 1

Exp. No.	Esterification					Polycondens.		P rate	HEG, meq/kg	CEG, meq/kg	Rel. CEG
	MEG/FDCA	T, °C	t_e, min	P_{H2O}, bar	EsPo	T, °C	T_p, min				
1	1.15	241	270	33.8	0.76	245	160	5.18	121	19	0.14
2	1.15	241	270	33.8	0.76	245	170	4.88	130	16	0.11
3	1.30	244	268	35.7	3.21	251	270	2.61	120	6	0.05

Experiment Nos. 1 and 2 are according to the present invention, whereas Experiment No. 3 is used for comparison purposes.

The results show that at an MEG/FDCA ratio of 1.15 and an EsPo of 0.76 the polycondensation is much faster than when the MEG/FDCA ratio is 1.30 and the EsPo thus is 3.21 to arrive at the same intrinsic viscosity, hence at the same molecular weight. The resulting polycondensates have higher relative CEG contents.

EXAMPLE 2

The procedure of Example 1 was repeated with different MEG/FDCA ratios and different temperatures. Each reaction mixture also included 80 ppm of TEAOH (0.09 mmol/mol FDCA). The polycondensation reactions were continued until a somewhat higher IV was obtained than in Example 1. The relative CEG was determined as CEG/(CEG + HEG). The conditions and results are shown in Table 2.

Table 2

Exp No.	Esterification				Polycondens.		IV, dL/g	P rate	rel. CEG	HEG, meq/kg	CEG, meq/kg
	MEG/FDCA	T, °C	t_e, min	EsPo	T, °C	T_p, min					
4	1.18	225	157	0.82	261	147	0.41	2.77	0.10	142	16
5	1.12	216	150	0.31	262	179	0.59	3.28	0.23	62	19
6	1.11	213	140	0.24	261	140	0.61	4.35	0.54	35	35
7	1.12	214	175	0.29	261	150	0.61	4.06	0.30	59	25

Experiments Nos. 5 through 7, which are according to the present invention, yield the polyester according to the invention with a higher molecular weight and a higher relative CEG value via a higher polycondensation rate compared to Experiment No. 4, wherein the IV is too low.

EXAMPLE 3

The polycondensate from experiment 7 of Example 2 above, having an IV of 0.61 dL/g, a relative CEG ratio of 0.30, and an absolute CEG content of 25 meq/kg, was crystallized by increasing its temperature to 125 °C and holding for about 1 hour, after which the material was cooled and any agglomerates were broken up. The material was then heated to 170 °C and held for about 3 hrs, followed by a temperature ramp to 195 °C (at a rate of 12.5°C/hr) and holding for about 12 hours. The material thus obtained exhibited a

peak melting point of 204 °C and 50 J/g crystallinity as determined by DSC. The material was loaded into a rotary vacuum tumble dryer and heated under vacuum to 190-195 °C. The chips were sampled periodically, with the results shown in Table 3 below. In the Table the intrinsic viscosity (IV), the peak melting point (T peak) and the crystallinity (dHm) are shown at loading into the tumble dryer and after 13 and 50 hours in the tumble dryer, respectively.

Table 3

Time (hrs)	IV, dL/g	T peak, °C	dHm, J/g
0	0.56	204	50
13	0.67	209	58
50	0.79	217	66

The experiment shows that the heat treatment in the solid state results in an increased molecular weight, as shown by the increase in intrinsic viscosity, and in a higher crystallinity as shown by the higher value in the DSC measurement.

COMPARATIVE EXPERIMENT 1

An FDCA-based polymer was prepared starting from a starting mixture comprising the dimethylester of FDCA and ethylene glycol in a molar ratio of 1:2.0. in the presence of 120 ppm of zinc (added as acetate) as a transesterification catalyst and 300 ppm of antimony (added as glycolate) for the esterification. This experiment is according to the teachings of WO 2013/120989. During the transesterification methanol formed was removed and any evaporated ethylene glycol was recycled to the reaction mixture. The transesterification continued for 2 hours at a maximum of 210 °C. The mixture obtained after 2 hrs was subjected to a pressure reduction and prepolycondensation at 390 to 530 mbar and a temperature of 210°C for 2 hrs, and subsequently to polycondensation at a pressure of less than 2 mbar and a temperature of 240 °C for 4 hrs. After melt polymerization the material had an IV of 0.33 dL/g, a relative CEG ratio of less than 0.05, and an absolute CEG content of 9 meq/kg. The methyl ester content was 13 meq/kg. The HEG content was greater than 200 meq/kg. It appeared that the process took over 8 hours to obtain a relatively low molecular weight polyester.

The material was sieved to remove the dust and long particles, as significant dust was present. The material was then heated in a rotary vacuum drum dryer, to dry, crystallize, and solid state the chips. Table 4 below shows the progress. The material was heated to 180-195 °C, but agglomeration was significant and the material needed to be frequently discharged to break up agglomerates.

Table 4

Time (hrs)	IV, dL/g	T peak, °C	dHm, J/g
0	0.33	211	41
142	-	211	55
330	0.49	217	78
400	0.52	220	74
570	0.61	229	86
828	0.68	228	87
972	0.76	231	87

Table 4 shows that the polyesters that do not have the desired amount of carboxylic acid end groups can only be polymerized to the desired molecular weight by exposing the polyester to solid state conditions for a very long time.

EXAMPLE 4

Ethylene glycol (MEG) and 2,5-furandicarboxylic acid (FDCA) were mixed in an MEG:FDCA molar ratio of 1.12, along with Sb_2O_3 as a catalyst, present at 300 ppm of antimony. The mixture also contained 80 ppm (0.09 mmol/mol FDCA) of TEAOH. The mixture was subjected to esterification without addition of an esterification catalyst for a period of time (t_e) at elevated temperature. Water that was formed was evaporated and passed into a distillation column. The condensed water was removed and any MEG that was entrained or evaporated was recycled back to the reaction mixture. The reaction was continued at atmospheric pressure until 40% of the theoretical water, based on furandicarboxylic acid feed, was collected. The temperature at that time was 211 °C and the reaction time was 130 minutes. The vacuum take-off point was switched at this point so that any additional ethylene glycol could be removed without passing through the distillation column. The pressure was reduced, and prepolycondensation was started, the pressure reaching 20 mbar in approximately 44 minutes. The pressure was further reduced to below 5 mbar. The ester composition with the catalyst was subjected to a polycondensation at a temperature of 260 °C, for an additional 210 minutes. The intrinsic viscosity (IV) was 0.30 dL/g. The CEG content was 260 meq/kg and the HEG is estimated to be less than 30 meq/kg, giving a relative CEG ratio of more than 0.90.

The experiment was repeated using the same initial reaction mixture but with esterification continued until 81% of theoretical water was collected, at a time of 197 minutes and temperature of 230 C. As in the comparative experiment above, the vacuum take-off point was switched at this point so that any additional ethylene glycol was removed without passing through the distillation column. The pressure was reduced, and prepolycondensation was started, the pressure reaching 20 mbar in approximately 45 minutes. The pressure was

further reduced to below 5 mbar. The ester composition with the catalyst was subjected to a polycondensation at a temperature of 260 °C, for an additional 140 minutes. The intrinsic viscosity (IV) was 0.63 dL/g. The CEG content was 32 meq/kg and the HEG is calculated to be 64 meq/kg, giving a relative CEG ratio of 0.33.

EXAMPLE 5

In a first series of experiments, a polyester was used that was prepared from the dimethyl ester of FDCA with a large excess of ethylene glycol compared to the diester of FDCA, to prepare a purified bis(2-hydroxyethyl)-2,5-furandicarboxylate. This was subjected to polycondensation in the presence of 300 ppm of antimony as a polycondensation catalyst, yielding a poly(ethylene-2,5-furan dicarboxylate) with a number average molecular weight (Mn) of about 15,000, corresponding with an IV of 0.42 dl/g. The amount of carboxylic acid end groups (CEG) the polyester was assessed to be less than 10 meq/kg and the amount of hydroxyl end groups (HEG) was assessed at > 160 meq/kg. The relative content, expressed as CEG/(CEG+HEG) was less than 0.06. The polyester was divided in two fractions of different particle size ranges. The fractions were subjected to solid state polymerization at a temperature of about 200 °C for a period of up to 8 hours. For each fraction the Mn was determined during the polymerization and an equivalent IV was determined using the equation IV (dL/g) = $1.62*10^{-4}*Mn^{0.820}$. The results are shown in Table 5.1.

In a second series of experiments a poly(ethylene-2,5-furandicarboxylate) prepared from MEG and FDCA having an Mn of about 17,000, corresponding with an IV of about 0.49 dL/g, was subjected to solid state polymerization under the same conditions as applied in the first series of experiments, including a solid state polymerization temperature of 200°C. Also in this case fractions of different particle sizes were used. The polyester had an amount of CEG of 66 meq/kg and an assessed amount of HEG of 87 meq/kg. The relative content, expressed as CEG/(CEG+HEG) was about 0.43. The results are also shown in Table 5.2.

Table 5.1

Fractions, mm → Time, hr ↓	0.5-1.4		0.3-0.4	
	Mn	IV	Mn	IV
0	14,700	0.423	14,700	0.423
2	16,500	0.465	21,500	0.578
8	18,500	0.511	25,200	0.659

Table 5.2

Fractions, mm → Time, hr ↓	0.5-1.4		0.3-0.4	
	Mn	IV	Mn	IV
0	17,500	0.488	17,500	0.488
2	19,800	0.540	22,400	0.598
8	30,500	0.770	30,700	0.774

From a comparison between the results of Tables 5.1 and 5.2 it is apparent that the solid state polymerization rate of the polyester with CEG /(CEG+HEG) ratio of 0.43 and CEG of 66 meq/kg is much faster than the solid state polymerization rate of the comparative polyester having a CEG/(CEG+HEG) ratio of about 0.06. That is especially the case for the larger particles.

C L A I M S

1. Polyester comprising ethylene 2,5-furandicarboxylate units, which polyester has an intrinsic viscosity of at least 0.45 dL/g, and which polyester has a relative content of carboxylic acid end groups, expressed as the fraction of the molar amount of carboxylic acid end groups divided by the sum of the molar amounts of hydroxyl end groups and carboxylic acid end groups, in the range of 0.10 to 0.70.

2. Polyester according to claim 1, which has an intrinsic viscosity of at most 1.0 dl/g, preferably in the range of 0.45 to 0.75 dL/g.

3. Polyester according to claim 1 or 2, wherein the relative content of carboxylic acid end groups is in the range of 0.14 to 0.65.

4. Polyester according to any one of claims 1 to 3, wherein the amount of carboxylic acid end groups is in the range of 15 to 122 meq/kg.

5. Polyester according to any one of claims 1 to 4, which has a light absorbance of at most 0.08, measured as a 30 mg/mL solution in a dichloromethane:hexafluoroisopropanol 8:2 (vol/vol) mixture at 400 nm.

6. Polyester according to any one of claims 1 to 5, which has a polydispersity index in the range of 1.9 to 2.6.

7. Polyester according to any one of claims 1 to 6, which has a crystallinity of at least 25 J/g, measured by Differential Scanning Calorimetry (DSC).

8. Polyester according to claim 7, which has a melting point of at least 215 °C.

9. Composition comprising the polyester according to any one of claims 1 to 8, which has a moisture content of at most 100 ppmw.

10. Method for the preparation of a polyester, wherein a starting mixture comprising 2,5-furandicarboxylic acid and ethylene glycol is subjected to esterification to form an ester composition, wherein the molar ratio of 2,5-furandicarboxylic acid to ethylene glycol in the starting mixture is 1:1.01 to 1:1.15; and
wherein the ester composition thus obtained is subjected to polycondensation at reduced pressure in the presence of a polycondensation catalyst to obtain a polycondensate, wherein

water, that is formed during the reaction between 2,5-furandicarboxylic acid and ethylene glycol, and some ethylene glycol are removed in a distillation system, and wherein ethylene glycol that is removed with water is separated from water and at least partly recycled.

11. Method according to claim 10, wherein the esterification reaction between 2,5-furandicarboxylic acid and ethylene glycol is carried out at a temperature of 160 to 240 °C and a pressure of 0.9 to 5 bar for a period of 0.5 to 4 hr.

12. Method according to claim 10 or 11, wherein the polycondensation comprises a pre-polycondensation reaction conducted at a pressure of 20 to 700 mbar and a polycondensation reaction conducted at a pressure of 0.05 to 20 mbar.

13. Method according to claim 12, wherein the combined period for the pre-polycondensation and the polycondensation reactions is in the range of 1.5 to 4 hours.

14. Method according to any one of claims 10 to 13, wherein during the polycondensation step ethylene glycol that is formed is removed from the ester composition that is subjected to polycondensation.

15. Method according to any one of claims 10 to 14, wherein the polycondensation step is carried out in the presence of a polycondensation catalyst.

16. Method according to claim 15, wherein the polycondensation catalyst is selected from the catalysts comprising one or more elements selected from tin, zinc, titanium, antimony.

17. Method according to any one of claims 10 to 16, wherein the polycondensation is carried out at a temperature of 245 to 270 °C and a pressure of 0.05 to 5 mbar.

18. Method according to any one of claims 10 to 17, wherein the polycondensate is crystallized at a temperature in the range of 90 to 200 °C.

INTERNATIONAL SEARCH REPORT

International application No
PCT/NL2015/050154

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08G63/181
ADD.

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)
C08G

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)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2013/120989 A2 (UHDE INVENTA FISCHER GMBH [DE]) 22 August 2013 (2013-08-22) cited in the application abstract; claims; example page 5, line 6 - line 11	1-18
X	KR 2014 0003167 A (LOTTE CHEMICAL CORP [KR]) 9 January 2014 (2014-01-09) claims; examples; table 1	1-18
A	US 2013/171397 A1 (GHOSH TAMAL [US] ET AL) 4 July 2013 (2013-07-04) abstract; claims; example 2B	1-18

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"T" later 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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
8 June 2015	15/06/2015

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/NL2015/050154

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		EP 2800771 A1	12-11-2014
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