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(54) Thermotropic polymers based on 2,5-furandicarboxylic acid.

(57) Thermotropic polymer comprising a 2,5-furandicarboxylic acid residue; one or more residues selected from the group of dicarboxylic acid residues and hydroxycarboxylic acid residues, the residues comprising a non-cyclic $(CH_2)_m$- group where m is 3 or more and/or a non-cyclic $(CH=CH)_n$- group where n is 1 or more; one or more residues selected from the group of dihydric alcohol residues; and one or more residues selected from the group of aromatic hydroxycarboxylic acid residues; wherein the thermotropic polymer has a number average molar mass (M_n) of 10 kg/mole or more.

Dit octrooi is verleend ongeacht het bijgevoegde resultaat van het onderzoek naar de stand van de techniek en schriftelijke opinie. Het octrooischrift komt overeen met de oorspronkelijk ingediende stukken.

Thermotropic polymers based on 2,5-furandicarboxylic acid

The invention relates to a thermotropic polymer and to a process for preparing the thermotropic polymer.

Furan-2,5-dicarboxylic acid (FDCA), also known as dehydromucic acid, has become a promising renewable building block after the development of successful methods to produce FDCA from bio-based feedstock on a large scale and in an industrially feasible way. It has been identified by the US Department of Energy as one of twelve priority chemicals for establishing the green chemistry industry of the future. FDCA has in particular been suggested as an important renewable building block for terephthalate-based polymers because it can substitute terephthalic acid in such polymers, for example polyesters such as poly(ethylene terephthalate).

The potential applications of furan-based building blocks, especially FDCA, for polymer applications have been explored and reviewed extensively. Most of the prior art documents which describe polymers based on FDCA suggest a process wherein FDCA, FDCA methanol diester or ethanol diesters are transesterified with a diol in the presence of a transesterification catalyst. The formation of the FDCA-based polymer is achieved with the formation of water, methanol or ethanol, respectively, as the low molecular weight condensate, which can easily be removed by evaporation. A wide range of diols have been proposed for the preparation of FDCA-based polymers, for example ethylene glycol, 1,3-propanediol, 2,2-dimethyl-1,3-propanediol, 1,4-butanediol, 2,3-butanediol, 1,6-hexanediol, cyclohexanedimethanol and isohexides such as isosorbide and isoidide.

However, FDCA has a limited thermal stability and is likely to degrade at processing temperatures applied in conventional polymerization processes. Such degradation may entail decarboxylation of the FDCA, yielding a mono-acid that acts as a chain-stopper and so produces a polymer of an undesired composition. Since the molecular weight of produced FDCA-based polymers is generally dependent on the reaction temperature during polymerization, high temperatures are required to achieve a high molecular weight. Due to the limited thermal stability of FDCA, an undesired extent of

FDCA degradation occurs in conventional processes at the temperatures that are required to obtain a sufficiently high molar mass polymer. This problem of degradation can of course be overcome by performing the polymerization at lower temperatures, but then the molar mass of the produced polymer becomes too low for many applications.

A particular class of FDCA-based polymers is formed by those that are thermotropic. These compounds find application in *e.g.* electrical and mechanical parts; high-strength fibers, films and tapes; and in environments where chemical resistance is required. The articles of these compounds can for example be prepared by spinning or compression molding. The preparation of FDCA-based thermotropic polymers requires the incorporation of rigid, and preferably aromatic, monomers to increase the chain stiffness and induce a liquid crystal state in the melt. However, these residues are responsible for an even higher melting temperature of the polymer in comparison with the non-thermotropic polymers. This makes it even more difficult to obtain material with a high molar mass. It appears that a process wherein FDCA is successfully incorporated into thermotropic polymers with a high average molar mass (*e.g.* more than 10,000 or 20,000 g/mole) is still lacking.

In WO2013062408, a process is described for the production of poly(ethylene-2,5-furandicarboxylate). The obtained product is claimed to have a number-average molar mass M_n of 25,000 g/mole or higher and to have a good color. However, a solid state post treatment is required to obtain such molecular weight. In addition, the synthesized products are not thermotropic and the process does not allow the use of other diol monomers than ethylene glycol.

Examples where FDCA is used in thermotropic polymers are EP0294863 and WO2013092667. In both documents, an acidolytic transesterification reaction is described wherein the hydroxy groups of the monomers are present as acetoxy groups, yielding acetic acid as the condensate. In EP0294863, FDCA is used as a compound in fully aromatic thermotropic polymers as a replacement of terephthalic acid to decrease the melting and processing temperature of the final polymer. However, the melting points of these polymers lie well beyond 300 °C. It should further be noted that a solid state post treatment is performed to obtain the desired products. WO2013092667 reports the synthesis of fully aromatic thermotropic polymers using FDCA and vanillic acid having melting temperatures below 300 °C. However, these polymers still require reaction temperatures above their melting temperature to build up molecular weight, which results in a product of a lower quality due to *e.g.* degradation of FDCA and of the product.

It is therefore an object of the present invention to provide an FDCA-based thermotropic polymer having a number average molar mass (M_n) of at least 10 kg/mole or at least 20 kg/mole. It is also an object that the FDCA-based thermotropic polymer is of a higher purity and/or that its chains comprise less FDCA degradation products than known FDCA-based thermotropic polymers of the same number average molar mass. It is in particular an objective that essentially no impurities and/or FDCA degradation products are present. It is a further object that not only the FDCA, but also the other monomers used in such process are derived from biological material, *i.e.* that they are bio-based.

It is therefore also an object to provide a process for preparing an FDCA-based thermotropic polymer wherein less by-products are formed and/or less FDCA degradation products are incorporated in the chains than in known processes. It is in particular an object that essentially no degradation of FDCA takes place during the process. It is more in particular an object that the process yields the polymer directly in a high purity so that there is no necessity to perform additional purification steps. It is a further object that the polymerization can be performed in the melt, so that post treatments for attaining desired molar masses are not necessary.

One or more of these objects have been reached by using a particular monomeric composition in the preparation of the FDCA-based polymer.

Accordingly, the present invention relates to a thermotropic polymer comprising

- a 2,5-furandicarboxylic acid residue;

- one or more residues of a type B, the residues being selected from the group of dicarboxylic acid residues and hydroxycarboxylic acid residues, the residues comprising a non-cyclic -$(CH_2)_m$- group where m is 3 or more and/or a non-cyclic -$(CH=CH)_n$- group where n is 1 or more;
- one or more residues of a type C, the residues being selected from the group of dihydric alcohol residues; and
- one or more residues of a type D being selected from the group of aromatic hydroxycarboxylic acid residues;

wherein the thermotropic polymer has a number average molar mass (M_n) of 10 kg/mole or more, determined via size exclusion chromatography in hexafluoroisopropanol against poly(methyl methacrylate) standards.

By a thermotropic polymer is meant a polymer exhibiting liquid crystalline behavior above its melting temperature. This means that it is capable of forming an anisotropic melt. Anisotropy can be confirmed by standard polarized light techniques using cross-polarizers.

The temperature range where this liquid crystalline behavior is observed is preferably from the melting temperature of the polymer up to 300 °C, and more preferably up to the degradation of the polymer. In other words, a thermotropic polymer of the invention preferably does not show any isotropization of its melt prior to degradation, which gives a wide range of processing temperatures for these polymers.

An advantage of a polymer of the invention is that the liquid crystalline melt makes that the processing of the polymer is more convenient than the processing of known FDCA-based polymers. The presence of pre-oriented liquid crystalline domains result in a lower melt viscosity and allows for the formation of oriented structures such as fibers, tapes and films which have high degrees of orientation. It has also been found that the high degree of orientation of the fibers of a polymer of the invention makes that the fibers have a higher tensile strength and a higher tensile modulus than fibers spun from non thermotropic polymers. Furthermore, it is expected that the decrease or absence of the degradation products in the final polymer yields more homogeneous fibers, less defects and therefore a better mechanical performance compared to FDCA-based thermotropic polyesters synthesized at higher temperatures.

The one or more residues of type B are selected from the group of dicarboxylic acid residues and hydroxycarboxylic acid residues and comprise a non-cyclic -$(CH_2)_m$- group where *m* is 3 or more and/or a non-cyclic -$(CH{=}CH)_n$- group where *n* is 1 or more. Usually, the one or more residues of type B are non-aromatic.

The dicarboxylic acid residues of type B (if present) usually comprise a non-cyclic -$(CH_2)_m$- group, which may be directly connected to the two carboxylic acid groups. Such dicarboxylic acid residues are for example selected from the group of glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, undecanedioic acid, dodecanedioic acid and brassylic acid residues.

In dicarboxylic acid residues of type B that comprise a non-cyclic -$(CH{=}CH)_n$- group, this group may be directly connected to the two carboxylic acid groups such as in maleic acid, fumaric acid, muconic acid and conformational isomers of muconic acid. There may however also be one or more CH_2-units (methylene units) present between the two carboxylic acid groups, such as in glutaconic acid and traumatic acid.

The hydroxycarboxylic acid residues of type B (if present) may comprise a non-cyclic -$(CH_2)_m$- group, which may be directly connected to the carboxylic acid group. Such dicarboxylic acid residues are for example omega-hydroxy-carboxylic acids, such as 4-hydroxybutanoic acid, 5-hydroxypentanoic acid or 6-hydroxyhexanoic acid.

The hydroxycarboxylic acid residues of type B (if present) may comprise a non-cyclic -$(CH{=}CH)_n$- group, which is in particular directly connected to a phenyl group. Such hydroxycarboxylic acid residues are for example selected from the group of ferulic acid, *p*-coumaric acid and sinapic acid residues.

In residues of type B, *m* is 3 or more. In particular, *m* is in the range of 4–10, preferably it is 6. Usually, *n* is 1, but *n* may also be higher, *e.g.* 2, 3 or 4.

The non-cyclic -$(CH_2)_m$-group in a residue of type B forms a chain of at least three carbon atoms. Such chain may be connected to an oxygen atom. In that case, the one of the one or more residues of type B comprises an -O-(CH_2)- group.

The one or more residues of type C are selected from the group of dihydric alcohol residues. Preferably, the residues of type C comprise aromatic diol residues, in particular selected from the group of hydroquinone residues, biphenol residues and dihydroxybiphenyl ether residues. These residues may have one or more protons on the aromatic ring(s) substituted with a substitute selected from the group of methyl, ethyl, propyl, methoxy, ethoxy and propoxy groups, for example a methylhydroquinone residue.

The one or more residues of type C may comprise an -O- group. The oxygen atom is in particular an ether oxygen atom that is connected to the aromatic ring(s) or to two aliphatic moieties connected to aromatic rings. In a particular embodiment, the one or more residues of type C comprise a carbon chain that is interrupted by one or more oxygen atoms.

The residues of type D provide the thermotropic polymer of the invention with the thermotropic properties. To this end, the one or more residues of type D are selected from the group of aromatic hydroxycarboxylic acid residues. Preferably, the hydroxy group and the carboxylic acid group are directly connected to the same aromatic moiety. The residues of type D are preferably selected from the group of vanillic acid, *p*-hydroxybenzoic acid and syringic acid residues.

A thermotropic polymer of the invention may further comprise one or more residues of a type E, the residues of type E being selected from the group of amino acids, diamines such as aromatic diamines, and aminoalcohols. A residue of type E is for example selected from the group of 1,4-diaminobutane, 1,6-hexanediamine, 1,4-cyclohexanediamine, *p*-phenylene diamine, *p*-aminobenzoic acid, 4-aminophenol, isophorone diamine and 2-aminoethanol residues. The one or more residues of type E (if present) may in particular comprise a non-cyclic -$(CH_2)_m$- group where m is 3 or more and/or a non-cyclic -$(CH{=}CH)_n$- group where n is 1 or more.

The one or more residues of type E may comprise an -O-(CH_2)- group. The oxygen atom is in particular an ether oxygen atom that is connected to two aliphatic moieties. More in particular, the one or more residues of type E may comprise a carbon chain that is interrupted by one or more oxygen atoms.

Residues of type E contain an amino group. Whereas connections between residues of type A – D are ester linkages, the connections with a residue of type E are amide linkages. So, a polymer comprising one or more residues of type E is a polyesteramide rather than a polyester. In the event that one or more residues of type E are present in a polymer of the invention, the ratio of the amount of amide linkages to the amount of ester linkages in the polymer is usually in the range of 1:99 – 50:50, in particular in the range of 5:95 – 40:80, more in particular in the range of 10:90 – 25:75.

The number average molar mass (M_n) of a thermotropic polymer is at least 10 kg/mole. It may also be at least 12 kg/mole, at least 15 kg/mole, at least 17 kg/mole, at least 20 kg/mole, at least 22 kg/mole, at least 25 kg/mole, at least 27 kg/mole, at least 30 kg/mole, at least 35 kg/mole, at least 40 kg/mole, at least 45 kg/mole, or at least 50 kg/mole.

The amount of 2,5-furandicarboxylic acid residues present in the polymer is usually from 5 to 25 mol% based on the total amount of residues, preferably 8 to 20 mole%, and more preferably 10-15 mole%.

The amount of the one or more residues of type B present in the polymer is usually 15 mol% or higher, based on the total amount of residues. Preferably, it is lower than 25 mol% based on the total amount of residues.

The amount of the one or more residues of type C is in general such that it equals the total amount of the 2,5-furandicarboxylic acid residues and the dicarboxylic acid residues of type B.

The amount of the one or more residues of type D present in the polymer is usually 20 mol% or higher, based on the total amount of residues. Preferably, the amount is lower than 60 mol% based on the total amount of residues. Usually, the amount is between 20 and 50 mole%, preferably it is in the range of 25 to 40 mol% based on the total amount of residues.

The amount of the one or more residues of type E – if present in the mixture – may be in the range of 1 to 25 mol% based on the total amount of residues.

The invention further relates to a process for preparing a thermotropic polymer according to the invention, comprising mixing

- one or more monomers of a type A' selected from the group of 2,5-furandicarboxylic acid and esters of 2,5-furandicarboxylic acid;
- one or more monomers of a type B' selected from the group of dicarboxylic acids, esters of dicarboxylic acids, hydroxycarboxylic acids and esters of hydroxycarboxylic acids, the monomers comprising a non-cyclic $-(CH_2)_m-$ group where m is 3 or more and/or a non-cyclic $-(CH=CH)_n-$ group where n is 1 or more;
- one or more monomers of a type C' selected from the group of dihydric alcohols and esters of dihydric alcohols;
- one or more monomers of a type D' selected from the group of aromatic hydroxycarboxylic acids and esters of aromatic hydroxycarboxylic acids;
- optionally one or more monomers of a type E' selected from the group of diamines, aminoalcohols and esters thereof;
- a catalyst;

followed by

- heating the resulting mixture so that polymerization of the monomers takes place, wherein the temperature is chosen such that the mixture remains in a liquid state and that it does not exceed 250 °C; then
- applying reduced pressure to the resulting mixture to remove volatiles generated during the polymerization, wherein the temperature is in the range of 200 to 300 °C, preferably in the range of 200 to 250 °C.

It is preferred that the monomers of the type A' are FDCA, but it is also possible to use the FDCA mono- or di-ester. In case one or both acid groups of monomers of the type A' are present as an ester, the ester is preferably a methyl or an ethyl ester.

In a process of the invention, the one or more monomers of the type B' comprise a non-cyclic $-(CH_2)_m-$ group where m is 3 or more and/or a non-cyclic $-(CH=CH)_n-$ group where n is 1 or more. It has been found that these flexible moieties decrease the melting point of the polymer which allows that the melt polymerization can be performed at a lower temperature. This has the advantage that the degradation of thermally instable monomers is limited. It has surprisingly been found that at such lower temperature a polymer with a high number average molar mass (M_n) is formed. This is surprising since lowering the temperature during polymerization usually yields a product with a lower M_n.

In addition, the presence of the flexible moieties makes the polymer product less prone to crystallization, which also makes it easier to keep the mixture in a liquid state, even when the reaction temperature is close to the melting temperature, or lower than the melting temperature.

In a process of the invention, the temperature during polymerization is chosen such that the mixture remains in a liquid state and that it does not exceed 250 °C, preferably does not exceed 230 °C. The decrease of the melting point of the polymer opens the possibility to apply such reaction temperatures. At a temperature in the range of 230–250 °C, less degradation of the starting materials occurs (especially of the monomer(s) of the A' type), which results in an FDCA-based thermotropic polymer of a higher purity and/or an FDCA-based thermotropic polymer wherein the chains comprise less FDCA degradation products. At a temperature of 230 °C or lower, it has been found that essentially no FDCA degradation occurs, and that the produced thermotropic polymer has an even higher quality than when it is prepared at a temperature in the range of 230–250 °C.

The one or more monomers of the type B' are selected from the group of dicarboxylic acids, esters of dicarboxylic acids, hydroxycarboxylic acids and esters of hydroxycarboxylic acids, wherein the monomers comprise a non-cyclic $-(CH_2)_m-$ group where m is 3 or more and/or a non-cyclic $-(CH=CH)_n-$ group where n is 1 or more.

In a dicarboxylic acid monomer of type B' that comprises a non-cyclic $-(CH=CH)_n-$ group, this group may be directly connected to the two carboxylic acid groups such as in maleic acid, fumaric acid, muconic acid and conformational isomers of muconic acid. There may however also be one or more CH_2-units (methylene units) present between the two carboxylic acid groups, such as in glutaconic acid and traumatic acid.

The hydroxycarboxylic acid monomers of type B' (if present) may comprise a non-cyclic $-(CH_2)_m-$ group, which may be directly connected to the carboxylic acid group. Such dicarboxylic acid residues are for example omega-hydroxy-carboxylic acids, such as 4-hydroxybutanoic acid, 5-hydroxypentanoic acid or 6-hydroxyhexanoic acid.

The hydroxycarboxylic acid monomers of type B' (if present) may comprise a non-cyclic $-(CH=CH)_n-$ group, which is in particular directly connected to a phenyl group. Such hydroxycarboxylic acid residues are for example selected from the group of ferulic acid, *p*-coumaric acid and sinapic acid residues.

The non-cyclic $-(CH_2)_m-$group in a monomer of type B' forms a chain of at least three carbon atoms. Such chain may be connected to an oxygen atom. In that case, the one of the one or more monomers of type B' comprises an $-O-(CH_2)-$ group.

In case one or both acid groups of monomers of the type B' are present as an ester, the ester is preferably a methyl or an ethyl ester.

In case the hydroxy group of a type B' hydroxycarboxylic acids is present as an ester, the hydroxy group is in particular acetylated.

The one or more monomers of type C' are selected from the group of dihydric alcohols and esters of dihydric alcohols. Preferably, the type C' monomer is an aromatic dihydric alcohol, in particular selected from the group of hydroquinone, biphenol and dihydroxybiphenyl ether monomers. These monomers may have one or more protons on the aromatic ring(s) substituted with a substitute selected from the group of methyl, ethyl, propyl, methoxy, ethoxy and propoxy groups, for example a methylhydroquinone residue.

In case an ester of a monomer of type C' is used, the hydroxy groups are preferably acetylated. For example, a monomers of the type C' is 1,4-diacetoxybenzene or 4,4'-diacetoxybiphenyl.

The one or more monomers of type C' may comprise an -O- group. The oxygen atom is in particular an ether oxygen atom that is connected to the aromatic ring(s) or to two aliphatic moieties connected to aromatic rings.

In a particular embodiment, the one or more monomers of type C' comprise a carbon chain that is interrupted by one or more oxygen atoms.

The one or more monomers of type D' are selected from the group of aromatic hydroxycarboxylic acids and esters of aromatic hydroxycarboxylic acids. Preferably, the hydroxy group and the carboxylic acid group of a monomer of type D' are directly connected to the same aromatic moiety. A monomer of type D' is in particular selected from the group of *p*-acetoxybenzoic acid, 4-acetoxy-(3-methoxy)benzoic acid, and 4-acetoxy-(3,5-dimethoxy)benzoic acid.

One or more monomers of a type E' may be used in a process of the invention, the monomers of type E' being selected from the group of amino acids, diamines such as aromatic diamines, and aminoalcohols. A monomer of type E' is for example selected from the group of 1,4-diaminobutane, 1,6-hexanediamine, 1,4-cyclohexanediamine, *p*-phenylene diamine, *p*-aminobenzoic acid, 4-aminophenol, isophorone diamine and 2-aminoethanol residues. The one or more monomers of type E' (if present) may in particular comprise a non-cyclic $-(CH_2)_m-$ group where m is 3 or more and/or a non-cyclic $-(CH=CH)_n-$ group where n is 1 or more.

The catalyst in a process of the invention usually comprises a metal atom, for example a transition metal. The catalyst may be selected from selected from the group of $Zn(OAc)_2$, titaniumalkoxides such as $Ti(OBu)_4$, stannous octonate, magnesium acetate and antimony trioxide. The amount of catalyst used in these polymerizations can vary up to an amount of 1 wt% with respect to the total mass of monomer used.

The amount of the one or more monomers of type A' present in the mixture is usually from 5 to 25 mol% based on the total amount of monomers, preferably 8 to 20 mole%, and more preferably 10-15 mole%.

The amount of the one or more monomers of type B' present in the mixture is usually 15 mol% or higher, based on the total amount of monomers. Preferably, it is lower than 25 mol% based on the total amount of monomers.

The amount of the one or more monomers of type C' present in the mixture is in general such that it equals the total amount of the one or more monomers of type A' and the dicarboxylic acid of type B'.

The amount of the one or more monomers of type D' present in the mixture is usually 20 mol% or higher, based on the total amount of monomers. Preferably, the amount is lower than 60 mol% based on the total amount of monomers. Usually, the amount is between 20 and 50 mole%, preferably it is in the range of 25 to 40 mol% based on the total amount of monomers.

The amount of the one or more monomers of type E' – if present in the mixture – may be in the range of 1 to 25 mol% based on the total amount of monomers.

The invention further relates to a polymer obtainable by a process of the invention.

EXAMPLES

Methods used:

Differential scanning calorimetry (DSC) analysis was performed on a TA instruments Q1000 machine at constant heating rates of 10 °C/min. Exothermic and endothermic processes occurring in the measured temperature range were recorded and the peak melting temperature (T_m) was extracted from the melting endotherm of the second heating run.

Thermogravimetric analysis (TGA) was performed on a TA instruments Q100 machine, at constant heating rates of 10 °C/min under a nitrogen rich flow. The weight loss over temperature was obtained and the onset temperature for degradation (T_{ons}) was determined from this data.

Dynamic mechanical thermal analysis (DMTA) was performed on a TA instruments Q800 machine at constant heating rates of 2 °C/min. The glass transition temperature (T_g) was extracted from this data as the peak value of the loss modulus (E").

Polarization optical microscopy experiments were conducted on a Zeiss Axioplan 2 Imaging optical microscope under crossed polarizers with or without a λ wave plate and CD achorplan objectives (32x Zoom). A THMS 600 heating stage connected to a Linkam TMS 94 control unit was mounted on the optical microscope. Samples were prepared by placing a small amount of grinded polymer in-between two glass slides and heating with 50 °C to 250 – 300 °C depending on the melting temperature of the polymer. The samples were then pressed and left to cool to 50 °C at a cooling rate of 20 °C/min. Melting temperatures and isotropization temperatures were determined during the second heating run performed with 20 °C/min °C and the sample was heated until the polymer degraded.

1,1,1,3,3,3-Hexafluoroisopropanol size exclusion chromatography (HFIP-SEC) was performed on a system equipped with a (Waters 1515 isocratic) HPLC pump, a (Waters 2414) refractive index detector (40 °C), an (waters 2707) autosampler and a PSS PFG guard column followed by 2 PFG-linear-XL (7 micrometre, 2 8 300 mm) columns in series at 40 °C. HFIP with potassium trifluoroacetate (3 g/L) was used as eluent at a flow rate of 0.8 ml/min. Molecular weights (M_n) and polydispersity (PDI) values were calculated against poly(methyl methacrylate) standards.

Comparative example 1:

24.6 gram p-acetoxybenzoic acid (137 mmol), 23.8 gram suberic acid (137 mmol) and 26.5 gram 1,4-diacetoxybenzene (137 mmol) were weighed in a 500 mL glass reactor together with a catalytic amount (20 mg) of $Zn(Ac)_2$.The mixture was purged with Argon/vacuum three times and the reactor was externally heated. The reaction temperature inside the reactor did not exceed 230 °C. The reaction was left to stand for 4 hours and acetic acid was distilled off. During the next step vacuum was applied to the system and the reaction temperature kept constant. After 2 hours of vacuum (< 0.5 mtorr) the reaction was stopped and the product was isolated from the melt as a low viscous slightly yellow melt. T_{ons} = 384 °C. T_m = 210 °C and T_g = 46 °C. The polymer showed a liquid crystalline melt above its melting temperature, however two separate melting and crystallization temperatures could be detected in the DSC analysis. The liquid crystalline phase was slowly lost above 300 °C, during which the isotropic and liquid crystalline phase coexisted. Molecular weight of the material was 24.8 kg/mol (M_n) and PDI = 2.46.

Example 1:

25.0 gram p-acetoxybenzoic acid (139 mmol), 10.8 gram 2,5-furandicarboxylic acid (69.5 mmol), 12.1 gram suberic acid (69.5 mmol) and 27.00 gram 1,4-diacetoxybenzene (139 mmol) were weighed in a 500 ml glass reactor together with a catalytic amount (20 mg) of $Zn(Ac)_2$.The mixture was purged with Argon/vacuum three times and the reactor was externally heated. The reaction temperature inside the reactor did not exceed 230 °C. The reaction was left to stand for 5 hours and acetic acid was distilled off. During the next step vacuum was applied to the system and the reaction temperature was increased so that temperature of the reaction mixture was 250 °C. After 15 minutes of vacuum the mixture began to solidify and the reaction was stopped. The polymer was isolated from the reactor and had a light brown color. T_{ons} = 408 °C T_m = 300 °C (according to polarization optical microscopy, no melting peak observed in DSC) and T_g = 82 °C. The polymer showed a homogenous liquid crystalline melt above its melting temperature. No isotropization of the liquid crystalline melt was observed, degradation occurred instead. Molecular weight of the material was 27.1 kg/mol (M_n) and PDI = 6.75. The FDCA content was 16.8 mole% according to ^{1}H-NMR analysis, which is in good agreement with the content added to the reactor (16.5 mole%).

The mild color, the high molecular weight and the successful incorporation of the FDCA monomers in the polymer backbone clearly show that the lowered reaction temperatures can successfully be used to synthesize this type of thermotropic polyesters. Furthermore, the addition of 2,5-FDCA compared to comparative example 1 leads to: an increase of the T_g of 36 °C, an increase of the melting temperature of 90 °C and the absence of the formation of the isotropic phase at high temperatures, indicating that the presence of 2,5-FDCA stabilizes the liquid crystalline melt.

Example 2:

24.8 gram p-acetoxybenzoic acid (138 mmol), 5.38 gram 2,5-furandicarboxylic acid (34.4 mmol), 18.0 gram suberic acid (103.3 mmol) and 26.77 gram 1,4-diacetoxybenzene (138 mmol) were weighed in a 500 ml glass reactor together with a catalytic amount (20 mg) of $Zn(Ac)_2$.The mixture was purged with Argon/vacuum three times and the reactor was externally heated. The reaction temperature inside the reactor did not exceed 230 °C. The reaction was left to stand for 5 hours and acetic acid was distilled off. During the next step vacuum was applied to the system and the reaction temperature kept constant. After 2 hours of vacuum (< 0.5 mtorr) the reaction was stopped and the product was isolated from the melt as light brown fibers. T_{onset} = 390 °C. T_m = 205 °C, T_g = 57 °C. The polymer showed a homogenous liquid crystalline melt above its melting temperature and showed no isotropization below 350 °C. Molecular weight of the material was 30.5 kg/mol (M_n) and PDI = 3.46. FDCA content was 9.0 mole% according to ^{1}H-NMR analysis, which is in reasonable agreement with the content added to the reactor (8.3 mole%).

This example shows that both the glass transition temperature and the melting temperature can be tuned by the addition of FDCA. Furthermore, this example also shows that satisfactory molecular weights can be obtained while the reaction temperature does not exceed 230 °C, and thus limiting the degradation of 2,5-FDCA.

Example 3 – 4 and comparative example 2, 3 and 4

Different polymers were synthesized according to the procedure listed in example 2. The compositions were varied and are listed in Table 1 together with the molecular weights, melting temperatures, glass transition temperature and onset temperature. The abbreviations listed in the table are: HQ = hydroquinone, BP = 4,4'-biphenol, HBA = *p*-hydroxybenzoic acid, SuA = suberic acid, FDCA = 2,5-furandicarboxylic acid, VA = vanillic acid. Molecular weight (M_n) and polydispersity (PDI) values were obtained via HFIP-SEC analysis against PMMA standards. Peak melting temperatures (T_m) were obtained via DSC analysis of the second heating run at a heating rate of 10 °C/min. The glass transition temperature (T_g) was obtained via dynamic mechanical thermal analysis at a heating rate of 2 °C and the onset temperature for degradation (T_{ons}) was obtained from TGA analysis at a constant heating rate of 10 °C/min under a nitrogen rich atmosphere.

Table 1

Ex.	Diol (mole%)	HBA (mole%)	SuA (mole%)	FDCA (mole%)	VA (mole%)	Mn (g/mol)	PDI (-)	T_m (°C)	T_g (°C)	T_{ons} (°C)
3	HQ 30	33	15	15	10	63,400	5.1	186	79	412
4	BP 30	30	15	15	10	12,000	2.3	145	82	406
C2	HQ 30	30	30	0	10	12,800	2.2	126	47	370
C3	BP 30	30	30	0	10	28,500	2.1	191	67	402
C4	BP 25	25	25	0	25	14,600	2.4	148	63	406

Examples 3-4 both contain vanillic acid, which clearly leads to a suppression of the peak melting temperature to values below 200 °C (compared to example 1 and 2, and comparative example 1). This is beneficial for the processing of the materials, since this the processing can be performed at mild temperatures and thus preventing any degradation. Furthermore, the thermal stability of both polymers is good and no degradation is observed below 350 °C. No loss of the liquid crystalline phase is observed for any of the polymers and degradation occurs instead. This results in polymers having broad processing windows.

When examples 3 and 4 are compared to the comparative examples C2, C3 and C4 it is observed that the glass transition temperature is increased, without increasing the melting temperature of the material to values above 200 °C. The increase in glass transition temperature is beneficial for usage of shaped articles at higher temperatures, while the low melting temperature enables processing at temperatures below 200 °C. Furthermore, the presence of the aromatic 2,5-FDCA moiety increases the rigid character of the polymer which is expected to lead to a higher stiffness of the material.

Combining the results from examples 1 to 4, it can be seen that the low reaction temperature successfully allows for the build-up of a sufficiently high molecular weight polymer, without the degradation of 2,5-FDCA. Furthermore, the presence of 2,5-FDCA increases the glass transition temperature and enhances the stability of the liquid crystalline melt. By varying the amount of 2,5-FDCA and the amount of vanillic acid incorporated in the polymer, polymers with specific glass transitions and melting temperatures can be synthesized. Furthermore, these polymers show broad temperature ranges of their liquid crystalline melts, whereas the absence of 2,5-FDCA and vanillic acid leads to a decrease of the stability of the liquid crystalline phase.

Conclusies

1. Thermotroop polymeer omvattende
    - een 2,5-furaandicarbonzuurresidu;
    - één of meer residuen van een type B, waarin de residuen gekozen zijn uit de groep van dicarbonzuurresiduen en hydroxycarbonzuurresiduen, waarin de residuen een niet-cyclische -$(CH_2)_m$- groep omvatten waar m 3 of meer is en/of een niet-cyclische -$(CH{=}CH)_n$- groep waar n 1 of meer is;
    - één of meer residuen van een type C, waarin de residuen gekozen zijn uit de groep van dihydrische alcoholresiduen; en
    - één of meer residuen van een type D gekozen uit de groep van aromatische hydroxycarbonzuurresiduen;

    waarin het thermotrope polymeer een aantalgemiddelde molaire massa (M_n) heeft van 10 kg/mol of meer, bepaald via grootte-uitsluitings-chromatografie in hexafluorisopropanol tegen poly(methylmethacrylaat) standaarden.
2. Thermotroop polymeer volgens conclusie 1, waarin ten minste één van de één of meer residuen van type B een niet-cyclische -$(CH_2)_m$- groep omvat waar m in het bereik van 4–10 is.
3. Thermotroop polymeer volgens conclusie 1 of 2, waarin de één of meer residuen van type B dicarbonzuurresiduen omvatten gekozen uit de groep van glutaarzuur-, adipinezuur-, pimelinezuur-, suberinezuur-, azelaïnezuur-, sebacinezuur-, undecaandizuur-, dodecaandizuur-, brassylzuur-, cyclohexaandicarbonzuur- en cyclobutaandicarbonzuurresiduen.
4. Thermotroop polymeer volgens een der conclusies 1–3, waarin de één of meer residuen van type B hydroxycarbonzuurresiduen omvatten gekozen uit de groep van ferulazuur-, *p*-coumarinezuur- en sinapinezuurresiduen
5. Thermotroop polymeer volgens een der conclusies 1–4, waarin de residuen van type C aromatische diolresiduen omvatten, in het bijzonder gekozen uit de groep van hydrochinonresiduen, bifenolresiduen en dihydroxybifenyletherresiduen.
6. Thermotroop polymeer volgens een der conclusies 1–5, waarin de residuen van type D gekozen zijn uit de groep van vanillinezuur-, *p*-hydroxybenzoëzuur- en syringinezuurresiduen.

7. Thermotroop polymeer volgens een der conclusies 1–6, waarin de hydroxylgroep en de carbonzuurgroep van de één of meer residuen van type D direct verbonden zijn aan dezelfde aromatische groep.
8. Thermotroop polymeer volgens een der conclusies 1–7, verder omvattende één of meer residuen van een type E, waarin de residuen gekozen zijn uit de groep van aminozuren, diamines en aminoalcoholen.
9. Thermotroop polymeer volgens conclusie 8, waarin de residuen van type E een niet-cyclische -$(CH_2)_m$- groep omvatten waar m 3 of meer is en/of een niet-cyclische -$(CH{=}CH)_n$- groep waar n 1 of meer is.
10. Thermotroop polymeer volgens conclusie 8 of 9, waarin de ratio van de hoeveelheid amidebindingen tot de hoeveelheid esterbindingen in het bereik is van 10:90 – 25:75.
11. Werkwijze voor het bereiden van een thermotroop polymeer volgens een der conclusies 1–10, omvattende het mengen van
    - één of meer monomeren van een type A' gekozen uit de groep van 2,5-furaandicarbonzuur en esters van 2,5-furaandicarbonzuur;
    - één of meer monomeren van een type B' gekozen uit de groep van dicarbonzuren, esters van dicarbonzuren, hydroxycarbonzuren en esters van hydroxycarbonzuren, waarin de monomeren een niet-cyclische -$(CH_2)_m$- groep omvatten waar m 3 of meer is en/of een niet-cyclische -$(CH{=}CH)_n$- groep waar n 1 of meer is;
    - één of meer monomeren van een type C' gekozen uit de groep van dihydrische alcoholen en esters van dihydrische alcoholen;
    - één of meer monomeren van een type D' gekozen uit de groep van aromatische hydroxycarbonzuren en esters van aromatische hydroxycarbonzuren;
    - optioneel één of meer monomeren van een type E' gekozen uit de groep van diamines, aminoalcoholen, en esters daarvan;
    - een katalysator;

    gevolgd door
    - het verwarmen van het resulterende mengsel zodat de polymerisatie van de monomeren plaatsvindt, waarin de temperatuur zo gekozen is dat het mengsel in een vloeibare toestand blijft en dat het niet 250 °C overschrijdt; daarna

- het uitoefenen van verlaagde druk op het resulterende mengsel om vluchtige componenten die gegenereerd zijn gedurende de polymerisatie te verwijderen, waarbij de temperatuur in het bereik van 200 tot en met 300 °C is, bij voorkeur in het bereik van 200 tot en met 250 °C.

12. Werkwijze volgens conclusie 11, waarin het type C' monomeer een aromatisch dihydrisch alcohol is.
13. Werkwijze volgens conclusie 11, waarin
    - het monomeer van type A' 2,5-furaandicarbonzuur is;
    - de één of meer monomeren van type B' gekozen zijn uit de groep van glutaarzuur, adipinezuur, pimelinezuur, suberinezuur, sebacinezuur, cyclohexaandicarbonzuur, cyclobutaandicarbonzuur, *p*-hydroxybenzoëzuur, ferulazuur-, *p*-coumarinezuur, sinapinezuur, vanillinezuur, syringinezuur, 3-hydroxypropionzuur, 4-hydroxyboterzuur, 5-hydroxypentaanzuur, 3-hydroxybenzoëzuur, 4-hydroxy-(3,5-dimethoxy)benzoëzuur en esters daarvan;
    - de één of meer monomeren van type C' gekozen zijn uit de groep van bifenol, dihydroxybifenylether, diacetoxybifenylether, 1,4-dihydroxybenzeen en 1,4-diacetoxybenzeen;
    - de één of meer monomeren van type D' gekozen zijn uit de groep van vanillinezuur, *p*-hydroxybenzoëzuur, syringinezuur en esters daarvan;
    - de één of meer optionele monomeren van type E' gekozen zijn uit de groep van 1,4-diaminobutaan, 1,6-hexaandiamine, 1,4-cyclohexaandiamine, *p*-fenyleendiamine, *p*-aminobenzoëzuur, 4-aminofenol, isoforondiamine en 2-aminoethanol;
    - de katalysator een verbinding is die een metaalion omvat.
14. Werkwijze volgens een der conclusies 10–13, waarin de hoeveelheid van de één of meer monomeren van type A' aanwezig in het mengsel van 5 tot en met 25 mol% is, gebaseerd op het totale aantal monomeren.
15. Werkwijze volgens een der conclusies 10–14, waarin de hoeveelheid van de één of meer monomeren van type B' aanwezig in het mengsel 15 mol% of meer is, gebaseerd op het totale aantal monomeren.

SAMENWERKINGSVERDRAG (PCT)

RAPPORT BETREFFENDE NIEUWHEIDSONDERZOEK VAN INTERNATIONAAL TYPE

IDENTIFICATIE VAN DE NATIONALE AANVRAGE	**KENMERK VAN DE AANVRAGER OF VAN DE GEMACHTIGDE**
Nederlands aanvraag nr. **1040533**	Indieningsdatum **09-12-2013**
	Ingeroepen voorrangsdatum
Aanvrager (Naam) **Stichting Dutch Polymer Institute, et al**	
Datum van het verzoek voor een onderzoek van internationaal type **29-03-2014**	Door de Instantie voor Internationaal Onderzoek aan het verzoek voor een onderzoek van internationaal type toegekend nr. **SN61737**

I. CLASSIFICATIE VAN HET ONDERWERP (bij toepassing van verschillende classificaties, alle classificatiesymbolen opgeven)

Volgens de internationale classificatie (IPC)

C08G63/66

II. ONDERZOCHTE GEBIEDEN VAN DE TECHNIEK

Onderzochte minimumdocumentatie

Classificatiesysteem	Classificatiesymbolen
IPC	**C08G**

Onderzochte andere documentatie dan de minimum documentatie, voor zover dergelijke documenten in de onderzochte gebieden zijn opgenomen

III.	☐	**GEEN ONDERZOEK MOGELIJK VOOR BEPAALDE CONCLUSIES**	(opmerkingen op aanvullingsblad)
IV.	☐	**GEBREK AAN EENHEID VAN UITVINDING**	(opmerkingen op aanvullingsblad)

Form PCT/ISA 201 A (11/2000)

ONDERZOEKSRAPPORT BETREFFENDE HET RESULTAAT VAN HET ONDERZOEK NAAR DE STAND VAN DE TECHNIEK VAN HET INTERNATIONALE TYPE

Nummer van het verzoek om een onderzoek naar de stand van de techniek
NL 1040533

A. CLASSIFICATIE VAN HET ONDERWERP
INV. C08G63/66
ADD.

Volgens de Internationale Classificatie van octrooien (IPC) of zowel volgens de nationale classificatie als volgens de IPC.

B. ONDERZOCHTE GEBIEDEN VAN DE TECHNIEK

Onderzochte miminum documentatie (classificatie gevolgd door classificatiesymbolen)
C08G

Onderzochte andere documentatie dan de mimimum documentatie, voor dergelijke documenten, voor zover dergelijke documenten in de onderzochte gebieden zijn opgenomen

Tijdens het onderzoek geraadpleegde elektronische gegevensbestanden (naam van de gegevensbestanden en, waar uitvoerbaar, gebruikte trefwoorden)

EPO-Internal, WPI Data

C. VAN BELANG GEACHTE DOCUMENTEN

Categorie °	Geciteerde documenten, eventueel met aanduiding van speciaal van belang zijnde passages	Van belang voor conclusie nr.
A,D	WO 2013/092667 A1 (TEIJIN ARAMID BV [NL]) 27 juni 2013 (2013-06-27) in de aanvraag genoemd * bladzijde 3, regel 5 - bladzijde 6, regel 22; conclusies 1-8; voorbeeld 1 * -----	1-15
A,D	EP 0 294 863 A1 (STAMICARBON [NL]) 14 december 1988 (1988-12-14) in de aanvraag genoemd * bladzijde 2, regel 17 - bladzijde 5, regel 31; conclusies; voorbeelden * -----	1-15
A	WO 2010/077133 A1 (FURANIX TECHNOLOGIES BV [NL]; SIPOS LASZLO [NL]) 8 juli 2010 (2010-07-08) * bladzijde 8, regel 31 - bladzijde 9, regel 37; conclusie 1 * -----	1-15

☐ Verdere documenten worden vermeld in het vervolg van vak C.

☒ Leden van dezelfde octrooifamilie zijn vermeld in een bijlage

° Speciale categorieën van aangehaalde documenten

"A" niet tot de categorie X of Y behorende literatuur die de stand van de techniek beschrijft

"D" in de octrooiaanvrage vermeld

"E" eerdere octrooi(aanvrage), gepubliceerd op of na de indieningsdatum, waarin dezelfde uitvinding wordt beschreven

"L" om andere redenen vermelde literatuur

"O" niet-schriftelijke stand van de techniek

"P" tussen de voorrangsdatum en de indieningsdatum gepubliceerde literatuur

"T" na de indieningsdatum of de voorrangsdatum gepubliceerde literatuur die niet bezwarend is voor de octrooiaanvrage, maar wordt vermeld ter verheldering van de theorie of het principe dat ten grondslag ligt aan de uitvinding

"X" de conclusie wordt als niet nieuw of niet inventief beschouwd ten opzichte van deze literatuur

"Y" de conclusie wordt als niet inventief beschouwd ten opzichte van de combinatie van deze literatuur met andere geciteerde literatuur van dezelfde categorie, waarbij de combinatie voor de vakman voor de hand liggend wordt geacht

"&" lid van dezelfde octrooifamilie of overeenkomstige octrooipublicatie

Datum waarop het onderzoek naar de stand van de techniek van internationaal type werd voltooid 7 augustus 2014	Verzenddatum van het rapport van het onderzoek naar de stand van de techniek van internationaal type
Naam en adres van de instantie European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	De bevoegde ambtenaar Bourgonje, Andreas

1

ONDERZOEKSRAPPORT BETREFFENDE HET RESULTAAT VAN HET ONDERZOEK NAAR DE STAND VAN DE TECHNIEK VAN HET INTERNATIONALE TYPE

Informatie over leden van dezelfde octrooifamilie

Nummer van het verzoek om een onderzoek naar de stand van de techniek
NL 1040533

In het rapport genoemd octrooigeschrift	Datum van publicatie	Overeenkomend(e) geschrift(en)	Datum van publicatie
WO 2013092667 A1	27-06-2013	GEEN	
EP 0294863 A1	14-12-1988	EP 0294863 A1	14-12-1988
		JP S6456727 A	03-03-1989
		US 4876327 A	24-10-1989
WO 2010077133 A1	08-07-2010	EP 2370496 A1	05-10-2011
		US 2011282020 A1	17-11-2011
		WO 2010077133 A1	08-07-2010

WRITTEN OPINION

File No. SN61737	Filing date *(day/month/year)* 09.12.2013	Priority date *(day/month/year)*	Application No. NL1040533

International Patent Classification (IPC)
INV. C08G63/66

Applicant
Stichting Dutch Polymer Institute, et al

This opinion contains indications relating to the following items:

- ☒ Box No. I Basis of the opinion
- ☐ Box No. II Priority
- ☐ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- ☐ Box No. IV Lack of unity of invention
- ☒ Box No. V Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- ☐ Box No. VI Certain documents cited
- ☐ Box No. VII Certain defects in the application
- ☐ Box No. VIII Certain observations on the application

Examiner
Bourgonje, Andreas

Application number
NL1040533

WRITTEN OPINION

Box No. I Basis of this opinion

1. This opinion has been established on the basis of the latest set of claims filed before the start of the search.
2. With regard to any **nucleotide and/or amino acid sequence** disclosed in the application and necessary to the claimed invention, this opinion has been established on the basis of:

   a. type of material:

   ☐ a sequence listing

   ☐ table(s) related to the sequence listing

   b. format of material:

   ☐ on paper

   ☐ in electronic form

   c. time of filing/furnishing:

   ☐ contained in the application as filed.

   ☐ filed together with the application in electronic form.

   ☐ furnished subsequently for the purposes of search.

3. ☐ In addition, in the case that more than one version or copy of a sequence listing and/or table relating thereto has been filed or furnished, the required statements that the information in the subsequent or additional copies is identical to that in the application as filed or does not go beyond the application as filed, as appropriate, were furnished.
4. Additional comments:

Box No. V Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty	Yes:	Claims	1-15
	No:	Claims	
Inventive step	Yes:	Claims	1-15
	No:	Claims	
Industrial applicability	Yes:	Claims	1-15
	No:	Claims	

2. Citations and explanations

   see separate sheet

Re Item V.

1 The following documents are referred to in this communication:

D1	WO 2013/092667 A1 (TEIJIN ARAMID BV [NL]) 27 June 2013 (2013-06-27) cited in the application
D2	EP 0 294 863 A1 (STAMICARBON [NL]) 14 December 1988 (1988-12-14) cited in the application

2 Novelty

2.1 None of the prior art documents discloses a thermotropic polymer comprising the compounds listed in claim 1 where the thermotropic polymer has a number average molar mass of 10 Kg/mol or more. Therefore the subject matter of claims 1-15 appears to be novel.

3 Inventive Step

3.1 The closest prior art is considered to be D1 which discloses aromatic polyester synthesis using furandicarboxylic acid, Bisphenol-A , vanillic acid and hydroxy benzoic acid. It is not clear from D1 what the molar mass of the resulting polyesters would be. The difference with the subject matter of the present application is therefore the use of dicarboxylic compounds and hydroxy carboxylic acid compounds having non-cyclic -$(CH_2)_m$- where m is 3 or more and/or a non-cyclic -$(C{=}C)_n$- compound where n is 1 or more (compound B) in the present application and the molar mass that is missing in D1.

As the present application does not contain any suitable comparative examples that could establish the effect of these differences in technical features the problem to be solved starting from D1 would be to find alternative thermotropic polymers.

The skilled person, confronted with this problem, would not introduce the compounds (B) to arrive at an alternative for the D1 polymers because he would not want to introduce aliphatic moieties into an aromatic polymer. Inventive step can therefore be acknowledged for the subject matter of claims 1-15.