Abstract:
The invention further pertains to polyester blends presenting improved maximum elongation characteristic.

Title: PROCESS FOR THE PRODUCTION OF POLY (ETHYLENE 2,5- FURANDICARBOXYLATE) FROM 2,5-FURAN - DICARBOXYLIC ACID AND USE THEREOF, POLYESTER COMPOUND AND BLENDS THEREOF

The present invention generally concerns polyester compounds derived from renewable monomer materials and manufacturing process thereof. The invention further pertains to polyester blends presenting improved maximum elongation characteristic.
PROCESS FOR THE PRODUCTION OF POLY (ETHYLENE 2,5- 
FURANDICARBOXYLATE) FROM 2,5-FURANDICARBOXYLIC ACID AND 
USE THEREOF, POLYESTER COMPOUND AND BLENDS THEREOF

The present invention generally concerns polyester compounds 
derived from renewable monomeric materials and manufacturing process 
therefor. The invention further pertains to polyester blends presenting im-
proved maximum elongation characteristic.

BACKGROUND OF THE INVENTION

Numerous efforts have been done seeking to provide renewable 
polymers to replace petroleum derivatives, such as polyethylene tereph-
thalate (PET). PET is presently widely used in numerous applications, espe-
cially packaging.

Whatever the nature of the replacement material, some require¬
ments must be complied with, such as processability by injection and blow 
molding techniques, chemical resistance, optical clarity, etc., which hinder 
developments.

In this sense, renewable source derived polymers are highly de-
sired. In the attempt to provide renewable polymers, furan dicarboxylic acid 
(FDCA) has been proposed as a potential compound to replace terephthalic 
acid, resulting in the furan based counterpart of PET by copolymerization of 
FDCA with diols. Furan polyesters obtained by reaction of FDCA or esters 
thereof with diols or polyols using esterification and polycondensation steps 
were disclosed in patent documents US2551731 and US4876327. However, 
such a basic FDCA polymer does not comply with the requirements to re-
place or be blended with PET. Such prior art references do not teach me-
chanical characteristics or % elongation of the proposed polymers.

Improvements in the cited general process have also been dis-
closed. For instance, patent documents JP2008291243, JP2008291244, 
JP2009215467, WO2007052847, WO2008057220, WO2009118377 or 
WO2010077133 teach processes including specific monomers, catalysts 
and/or reaction conditions. These methods and products thereof have a 
number of disadvantages as well. For instance, prior art does not teach any
polymer with adequate % elongation, useful to be used in oriented film applications or blends with petroleum derivatives polymers with thermal properties comparable to PET.

The parameter of maximum % elongation is important for film and packaging applications. Therefore, any improvement to the maximum % elongation of a copolymer predominantly derived from 2,5-FDCA and EG are sought.

Thus, there remains a need in the art for a renewable polymer material that can be used for partial or total replacement of PET.

**DESCRIPTION OF THE INVENTION**

In order to overcome the prior art inconveniences, an improved route to synthesize a furan dicarboxylic acid (FDCA) copolymer was developed. The copolymer according to the present invention presents properties comparable to PET in terms of transparency, stability at high temperature, good mechanical properties and molding processability. In addition, the copolymer according to the present invention possesses a Young's Modulus and Yield Stress superior to PET, and lower % elongation.

Therefore, the present invention refers to a process for the production of poly(ethylene 2,5-furandicarboxylate) (PEF) from 2,5-furandicarboxylic acid (2,5-FDCA) comprising the steps of:

1. Esterification of 2,5-FDCA with diol (particularly ethylene glycol or EG) in the presence of 3,4-furandicarboxylic acid (3,4-FDCA) and triol (particularly tris hydroxy methyl propane or THMP) in the presence of at least one catalyst, such as titanium isopropoxide, in order to obtain a compound that is subsequently submitted to

2. Polycondensation in the presence of at least one catalyst, such as titanium isopropoxide and/or antimony oxide.

2,5 Furan dicarboxylic acid is represented by the following formula:

\[
\text{HC} \quad \text{O} \\
\begin{array}{c}
\text{O} \\
\text{O} \\
\text{O} \\
\end{array}
\]

Dimethyl 3,4-furandicarboxylate is represented by the following formula:
The use of specific comonomers controls the properties of the final product, particularly allowing application in bottles. THMP introduces branching in the chain of PEF for enhanced resistance to melting and extensional viscosity improvement, which is particularly important for extrusion and in the production of foamed trays.

Comonomer 3.4-FDCA improves the characteristics of crystallization (reduced crystallinity), allowing the production of a transparent material. The degree of crystallinity, glass transition temperature (Tg), extensional viscosity are important for film manufacture, for they impact on the film transparency, thermoforming temperature, sagging of thermoformed films, chemical resistance and the extrudability of films.

In addition, according to the present invention the 2,5-FDCA used in step (1) is previously purified.

Accordingly, the FDCA monomer is fractionated. In a particular embodiment the fractionation is carried out by adding concentrated HCl (33%) to adjust the pH of the solution to between 5-6 at which precipitation is observed. The solution is then stirred followed by filtration, in order to remove the first part of the precipitate. This fraction contains a small quantity of monofunctional FDCA which would inhibit molecular weight building during polymerization. Concentrated HCl (33%) is again added into the solution until the pH of the solution reached to pH 1-2 and all FDCA is precipitated from solution. The solution is then cooled to 10°C before filtration.

The fractionation of the FDCA is important to remove monofunctional FDCA impurities which inhibit the polymerization of 2,5 FDCA.

After fractionation, the resulting product is washed. In a particular embodiment the resulting product is washed a total of 2 times with ice water and 5 times with water at room temperature in 1L aliquots.

The washing step is important to remove salt after fractionation, as salt (NaCl) inhibits the polymerization.

The use of purified 2,5-FDCA provides controlled high molecular
weight to the final polymer, i.e. in the region of 35,000 and 46,000 g mol⁻¹. This molecular weight range is comparable to commercial PET and useful in the production of bottles. By contrast, the direct polycondensation without FDCA purification does not allow the production of esters of high molecular weight.

The poly(ethylene 2,5-furandicarboxylate) according to the invention presents the following characteristics:

- from about 90 to about 99 mol% of 2,5-FDCA and from about 1 to about 10 mol% of 3,4-FDCA (diacid component), and from about 95 to about 99.8 mol% EG and from about 5 to about 0.2 mol% THPM (diol component),
- Number average molecular weight number (Mn) of about 30,000 to 80,000, particularly 30,000 to 60,000
- Weight average molecular weight (Mw) of about 60,000 to about 240,000, particularly 70,000 to about 180,000,
- Polydispersity of about 2 to about 4, particularly 2.4 to about 3.8,
- Tg between 78-92°C.

The above mentioned characteristics are comparable to PET as to transparency, stability at high temperature, good mechanical properties and molding processability. In addition, PEF according to the present invention possesses a Young’s Modulus and Yield Stress superior to PET and a lower % elongation.

The PEF of the invention may be subject to conventional processing methods in order to obtain films, bottles or pieces. In a particular embodiment the present invention also concerns the use of an additive ingredient, such as stabilizing additives that prevent the degradation and subsequent loss of qualities of the polymer during processing, such as oxidative stabilizers and hydrolysis stabilizers. These ingredients are common additives for PET.

In a particular aspect, the invention also refers to blends comprising the PEF as described above and a conventional polymer. The conventional polymer presents a melting point close to PEF, such as PET. The blends according to the present invention improve the maximum elongation of copolymers without limiting the thermal properties of the material, i.e. glass...
transition temperature and melting point.

In a particular embodiment the ratio (PEF: conventional polymer) ranges from about 99:1 (PEFPET) to about 50:50 (PEFPET). The blends provide improved mechanical characteristics and are particularly useful for application-oriented films (mono and bi-oriented). In this specific embodiment the maximum elongation (strain at break) of polyesters containing 2,5 FDCA according to the invention is substantially improved.

The polyester blends, more specifically polyester blends whose major component is a polyester derived from 2,5 FDCA and ethylene glycol, are useful for extrusion blown film, stretch blow molding and biaxially orientated film applications, and enable the production of films and sheets with improved maximum elongation values compared to the renewably sourced polyester alone.

The following examples are provided for illustration and are not intended as limitations to the scope of the present invention, other than what is described in the attached claims.

EXAMPLES
EXAMPLE 1
PURIFICATION OF 2,5 FDCA

600 g of crude FDCA were added to 4 liters of pure water. 600 g of NaOH water solution (50: 50 wt%) were added slowly to the FDCA solution whilst stirring. When the pH of the solution reached 5.5-6.5, the solution turned clear. The clear solution was deep brown in color. About 3 heaped tea-spoons of activated charcoal were then added to the solution. The solution was heated to 50-60 °C and stirred for 30 minutes. The solution was then run through a column with sand, Hyflo Super Cel® medium and silica beads to remove the charcoal. After filtering, the solution was clear with a slight yellow coloration.

The FDCA was then fractionated by adding concentrated HCl (33%) to adjust the pH of the solution to 5-6. At this stage, the solution became slightly cloudy. The solution was then stirred overnight before filtration to remove the first part of the precipitate. This fraction contains a small quan-
tity of mono functional FDCA which would inhibit molecular weight building during polymerization.

Concentrated HCl (33%) was then added to the clear solution until the pH of the solution reached 1-2 and all FDCA precipitated from the solution. The solution was then cooled to 10 °C before filtration.

The FDCA was first washed twice with ice cold water then twice with water at room temperature. The FDCA was then washed once more with water at room temperature (total: washed with ice water 2 times and 5 times with water at room temperature).

The use of purified 2,5-FDCA provides controlled high molecular weight to the final polymer, i.e. number average molecular weights in the region of 35,000 and 46,000gmol⁻¹. This molecular weight range is comparable to commercial PET and useful in the production of bottles. By contrast, the direct polycondensation without FDCA purification does not allow the production of esters of high molecular weight.

EXAMPLE 2

MANUFACTURE OF PEF SAMPLES

ACCORDING TO THE PRESENT INVENTION

A general synthetic procedure for the direct polymerization of FDCA and ethylene glycol is given below, using titanium(IV) isopropoxide (Ti(OCH(CH3)2)4) and antimony (III) oxide (Sb2O3) as catalysts:

The reaction conditions employed for the preparation of PEF samples are comparable to conventional synthesis methods for PET and those skilled of ordinary skill in the art would be able to select alternative catalysts suitable for the task. Several procedures for the polymerization of PEF are shown below:

SAMPLE A

In the first step of esterification, FDCA (100.25 g, 0.64 mol), EG
(122.0 g, 1.97 mol), triol (THMP, 0.4353 g, 0.494 mol% of FDCA), 3,4 FDCA-methyl ester (4.8243, 0.0262 mol, 4.08 mol% compared to FDCA), and titanium(IV) isopropoxide (0.491 g) were added to the system. The mixture was heated to 170 °C for about 1 hour, 180 °C for about 1 hour, 185 °C for about 1 hour and 190 °C for 45 min. After which the reactants went clear.

In the second step of the polycondensation reaction, titanium (IV) isopropoxide (0.438 g) and Sb₂O₃ (0.313 g) were added into the system. For the final polymerization stage the reaction was heated at 240 °C for 5 hours.

**SAMPLE B**

FDCA (100.15 g, 0.64 mol), EG (134.0, 1.73 mol), triol (THMP, 0.4381 g, 0.498 mol% of FDCA), Dimethyl 3,4-furandicarboxylate (5.1018, 0.0277 mol, 4.318 mol% compared to FDCA), titanium(IV) isopropoxide (0.4796 + 0.370 g), Sb₂O₃ (0.3034 g) were used. Stabilizers IRGANOX 1010 (0.0804 g) and IRGAFOS 168 (0.3290 g) were added in the second step of reaction (polycondensation).

**SAMPLE C**

The properties of the pure poly(ethylene 3,4-furandicarboxylate) were verified. 3,4 FDCA (19.6513 g, 0.107 mol), EG (21.9182, 0.353 mol), triol (THMP, 0.0784 g, 0.536 mol% of FDCA), titanium(IV) isopropoxide (0.1065 + 0.0650 g), Sb₂O₃ (0.0676 g) were used.

**EXAMPLE 3**

**COPOLYMER PROPERTIES**

The determination of the number and weight average molecular weights and the molecular weight distribution (MWD) of the samples was performed using gel permeation chromatography. The instrument was calibrated with poly(methylmethacrylate) standards (PMMA). All molecular weights provided for the samples are PMMA equivalent molecular weights. The following conditions were employed:

- **Eluent:** HFIP / 0.05M KTFAc
- **Columns:** PSS-PFG, 7μm, 100A, ID 8.0 mm x 300 mm
- PSS-PFG, 7pm, 1000A, ID 8.0 mm x 300 mm
- **Pump:** Agilent 1200 HPLC-pump
Flow rate: 1.0 ml/min
Injector: Agilent 1200 Autosampler with 50 µl injection volume
Concentration: about 3.0 g/l
Temperature: 23 °C
Detectors: Agilent 1200 Differential Refractometer

Table below show the measured properties:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mn (gmol⁻¹)</th>
<th>Mw (gmol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>46,000</td>
<td>178,200</td>
</tr>
<tr>
<td>B</td>
<td>45,500</td>
<td>160,800</td>
</tr>
<tr>
<td>C</td>
<td>29,200</td>
<td>77,850</td>
</tr>
</tbody>
</table>

Control: conventional PET presents Mn 27,500 and Mw 66,440.

EXAMPLE 4
MECHANICAL PROPERTIES OF PEF SAMPLES

(COMPRESSION MOULDED ONLY)

Sample B was compression molded, thus excluding the extrusion process and therefore minimizing the potential for thermal, thermo-oxidative and hydrolytic degradation.

Tensile tests were conducted on dog-bone shaped specimens, cut from a 110-130 µm polymeric film.

Polymeric films were obtained by compression molding at 250°C followed by quenching in cold water in order to suppress crystallinity.

Tensile tests were conducted at room temperature with an Instron 5566 equipped with a 1 kN load cell, pneumatic grips with rubber contact surface (35 psi closing pressure) and "Blue Hill" Software.

The tensile test results are shown below:

<table>
<thead>
<tr>
<th>Wt% Inclusion</th>
<th>Young’s Modulus E (MPa)</th>
<th>Yield Stress (MPa)</th>
<th>Yield Strain (%)</th>
<th>Strain at break, εMax (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample B (PEF)</td>
<td>3437.9</td>
<td>62.5</td>
<td>2.0</td>
<td>2.8</td>
</tr>
<tr>
<td>PET</td>
<td>1840.0</td>
<td>46.3</td>
<td>3.6</td>
<td>216.1</td>
</tr>
</tbody>
</table>

From the test above one can observe that:
- PEF possesses a higher young’s modulus and yield stress than commercial PET;
- PEF undergoes brittle fracture at -3% strain and therefore pos-
sesses similarities to polystyrene.

EXAMPLE 5

BLENDS

POLYESTER COMPOSITIONS

<table>
<thead>
<tr>
<th>Composition</th>
<th>Diacid component</th>
<th>Diol Component</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample A</td>
<td>96 mol% 2,5 FDCA, 4 mol% 3,4 FDCA</td>
<td>99.5 mol% ethylene glycol (EG), 0.5 mol% Tris hydroxy methyl propane (THMP)</td>
</tr>
<tr>
<td>Sample B</td>
<td>100 mol% terephthalic acid (TA)</td>
<td>95 mol% ethylene glycol (EG), 5 mol% cyclohexane dimethanol (CHDM)</td>
</tr>
</tbody>
</table>

THERMAL PROPERTIES

Samples were analysed using a Perkin Elmer Pyris 1 DSC instrument.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Tg (°C)</th>
<th>Tm (°C)</th>
<th>Tc (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample A</td>
<td>88</td>
<td>198</td>
<td>155</td>
</tr>
<tr>
<td>Sample B</td>
<td>78</td>
<td>242</td>
<td>155</td>
</tr>
</tbody>
</table>

From the test above one can observe that:

- Sample A possesses a higher Tg and, therefore, higher thermal stability than sample B.
- Sample A possesses a lower melting point than sample B and therefore a lower processing temperature, which will result in reduced processing costs and lower energy consumption than sample B.

POLYESTER BLENDS

Four polyester formulations were prepared by blending, using a twin-screw extruder at 250°C, various proportions of Sample A and Sample B.

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Polyester A (weight %)</th>
<th>Polyester B (weight %)</th>
<th>Transparent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>0</td>
<td>Yes</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>50</td>
<td>Yes</td>
</tr>
<tr>
<td>3</td>
<td>60</td>
<td>40</td>
<td>Yes</td>
</tr>
<tr>
<td>4</td>
<td>75</td>
<td>25</td>
<td>Yes</td>
</tr>
</tbody>
</table>
MONOAXIAL ORIENTATION OF POLYESTER BLENDS

Three of the polyester formulations were subsequently monoa-
axially orientated by drawing at 100°C.

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Draw Temperature (°C)</th>
<th>Linear Draw Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>5</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>16</td>
</tr>
</tbody>
</table>

MECHANICAL AND THERMAL PROPERTIES OF UNORIENTATED AND ORIENTATED POLYESTER FILMS

Tensile tests were conducted at room temperature with an Instron 5566 equipped with a 1kN load cell, pneumatic grips with rubber contact surface (35 psi closing pressure) and "Blue Hill" software.

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Draw Ratio</th>
<th>Young's Modulus E (MPa)</th>
<th>Yield Stress (MPa)</th>
<th>Yield Strain εYield (%)</th>
<th>Strain at break, εMax (%)</th>
<th>Tg (°C)</th>
<th>Tm (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>3438</td>
<td>63</td>
<td>2.0</td>
<td>2.8</td>
<td>88</td>
<td>198</td>
</tr>
<tr>
<td>1</td>
<td>5</td>
<td>4800</td>
<td>120</td>
<td>3.2</td>
<td>6</td>
<td>88</td>
<td>198</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>2554</td>
<td>70</td>
<td>3.6</td>
<td>3.6</td>
<td>81</td>
<td>230</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>5700</td>
<td>140</td>
<td>3.6</td>
<td>21</td>
<td>81</td>
<td>230</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>2761</td>
<td>67</td>
<td>2.9</td>
<td>2.9</td>
<td>80</td>
<td>232</td>
</tr>
<tr>
<td>4</td>
<td>16</td>
<td>2760</td>
<td>58</td>
<td>3.0</td>
<td>100</td>
<td>80</td>
<td>232</td>
</tr>
</tbody>
</table>

The results above show that the blends according to the inven-
tion present:

- good mechanical properties (high Young's modulus and yield stress)

- acceptable strain at break after biaxial orientation (when blend-
ed with a copolyester and oriented using solid state drawing)

- Good thermal properties (High Tg and High Tm values)

Comparing the formulations one observes that:

Formulation 1 with a draw ratio of 0 possesses a low strain at
break about 2.8%

Formulation 2 with a draw ratio of 5 possesses an acceptable strain at break about 20%

Formulation 4 with a draw ratio of 16 possesses a good strain at break about 100%.

Polyester blends for extrusion blown film, stretch blow molding and biaxially orientated film applications, more specifically polyester blends whose major component is a polyester derived from renewable sources and to which co-blending of this renewable polyester with a second polyester, followed by solid state drawing, enables the production of films and sheets with improved maximum elongations.

The information contained in the foregoing, as well as in the examples, allows a person skilled in the art to perform alternative embodiments not expressly described, but which perform the functions taught herein with the results revealed herein. Such equivalent embodiments are encompassed by the scope of the invention and are therefore covered by the claims presented further on.
CLAIMS

1. Process for the production of poly(ethylene 2,5-furandicarboxylate) from 2,5-furandicarboxylic acid comprising the steps of:
   (1) esterification of 2,5-furandicarboxylic acid with ethylene glycol in the presence of 3,4-furandicarboxylic acid and triol in the presence of at least one catalyst in order to obtain a compound that is subsequently submitted to
   (2) polycondensation in the presence of at least one catalyst.

2. Process, according to claim 1, wherein the triol used in the step (1) is tris hydroxy methyl propane.

3. Process, according to claim 1, wherein the catalyst used in steps (1) or (2) is titanium isopropoxide and/or antimony.

4. Process, according to claim 1, wherein the 2,5-furandicarboxylic acid used in the step (1) is previously purified by fractionation and washing steps.

5. Process, according to claim 4, wherein the fractionation is carried out by adjusting the pH to 5-6 and filtered to remove the first part of the precipitate.

6. Process, according to claim 5, comprising a second step wherein the solution is adjusted to pH 1-2 to obtain total precipitation, before cooling to 10°C and filtering to obtain purified 2,5 furandicarboxylic acid.

7. Process, according to one of claims 5 or 6, wherein the pH is controlled by adding concentrated HCl.

8. Process, according to claim 4, wherein the washing is carried out twice with ice water and five times with room temperature water.

9. Poly(ethylene 2,5-furandicarboxylate) obtained by the process according to one of claims 1 to 8.

10. Poly(ethylene 2,5-furandicarboxylate) according to claim 9 comprising a number average molecular weight (Mn) in the region of 35,000 and 46,000gmol⁻¹.

11. Poly(ethylene 2,5-furandicarboxylate), according to claim 9, comprising at least one of the following characteristics:
- from 90 to 99mol% of 2,5- furandicarboxylic acid and from 1 to
10mol% of 3,4- furandicarboxylic acid (diacid component), and from 95 to
99.8mol% ethylene glycol and from 5 to 0.2 mol% tris hydroxy methyl pro¬
pane (diol component),

- Number average molecular weight number (Mn) of 30,000 to
80,000, particularly 30,000 to 60,000
- Weight average molecular weight (Mw) of 60,000 to 240,000, particularly 70,000 to 180,000,
- Polydispersity of 2 to 4, particularly 2.4 to 3.8,
- Tg between 78-92°C.

12. Polyester blends comprising the polymer according to one of
claims 9 to 11 and at least one second polymer presenting melting point be-
tween 130 to 300°C.

13. Polyester blends, according to claim 12, wherein at least one
second polymer presenting melting point between 180 to 260°C.

14. Polyester blends comprising the polymer according to one of
claims 9 to 11 and polyethylene terephthalate.

15. Polyester blends, according to one of claims 12, 13 or 14,
wherein the ratio between the polymer according to one of claims 9 to 11 and
the second polymer ranges from about 99:1 by weight (poly(ethylene 2,5-
furandicarboxylate:second polymer) to 50:50 by weight (poly(ethylene 2,5-
furandicarboxylate:second polymer).

16. Polyester blends comprising:
   a) A renewable polyester, wherein said polyester is a copolymer
containing a diacid component and a diol component for which at least 90
weight percent of the diacid component is derived from 2,5-furandicarboxylic
acid obtainable from biorenewable feedstocks and at least 80% by weight of the
diol component is ethylene glycol obtainable from biorenewable feedstocks.
   b) One or more blending polyesters comprising:
   i) Diacid residues comprising the residues of one or more substi-
tuted or unsubstituted aliphatic, cycloaliphatic or aromatic carboxylic acids
containing 5 to 20 carbon atoms.
ii) Diol residues comprising the residues of one or more substituted or unsubstituted linear or branched diols, selected from the group consisting of aliphatic, cycloaliphatic or aromatic diols containing 2 to 20 carbon atoms.

17. The use of purified poly(ethylene 2,5-furandicarboxylate) produced by the process as described in claims 1 to 8 in the production of films, bottles or pieces.

18. The use of polyester blends according to claims 12 to 16 in the production of films, bottles or pieces.
**INTERNATIONAL SEARCH REPORT**

**A. CLASSIFICATION OF SUBJECT MATTER**

According to International Patent Classification (IPC) and 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

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
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<tbody>
<tr>
<td>X</td>
<td>JP 2008 291244 A (MITSUBISHI CHEM CORP) 4 December 2008 (2008-12-04) tabl e 1</td>
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<td>A</td>
<td>JP 2010 280767 A (CANON KK) 16 December 2010 (2010-12-16)</td>
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<td>JP 2009 227717 A (NEC CORP) 8 October 2009 (2009-10-08)</td>
<td>1-18</td>
</tr>
</tbody>
</table>

Further documents are listed in the continuation of Box C. 

See patent family annex.

Notes:

- * Special categories of cited documents:
  - "A" document defining the general state of the art which is not considered to be of particular relevance
  - "E" earlier application or patent but published on or after the international filing date
  - "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
  - "O" document referring to an oral disclosure, use, exhibition or other means
  - "P" document published prior to the international filing date but later than the priority date claimed

- "I" 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

- "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

- "A" document member of the same patent family

Date of the actual completion of the international search: 4 March 2013

Date of mailing of the international search report: 11/03/2013

Name and mailing address of the ISA:
European Patent Office, P.B. 5818 Patentlaan 2
NL-2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer:
Lohner, Pierre

Form PCT/ISA/210 (second sheet) (April 2005)
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