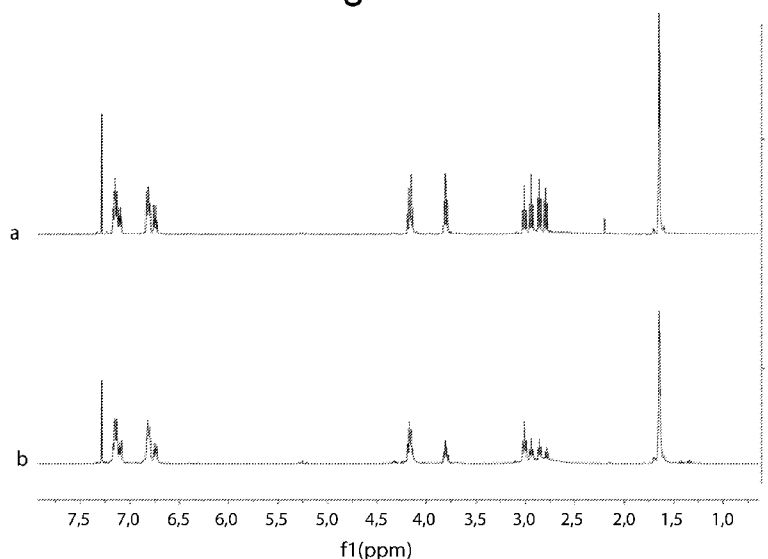




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(54) Title: PROCESS FOR PREPARING A POLYMER FROM MUSTARD CARBONATE ANALOGUES

Fig. 2



(57) Abstract: The present invention relates to a process for preparing a polymer that comprises at least a step of carrying out a mass polymerization of a reaction mixture comprising at least one mustard carbonate analogue of general formula $R_1OOCO-R_2-Z-R_3-OCOOR_4$ (I) and at least one hydroxy-substituted aromatic compound of general formula $Ar(OH)_n$ (II), wherein in said general formulas: R_1 and R_4 , equal or different, are linear or branched C_1-C_6 alkyl; R_2 and R_3 , equal or different, are a linear or branched C_2-C_4 alkylene, preferably ethylene; Z is a radical selected from: S; N-Y, wherein Y is selected from: hydrogen, linear or branched C_1-C_6 alkyl, or a radical $-R_6OCOOR_5$ where R_6 is a linear or branched C_2-C_4 alkyl and R_5 is a linear or branched C_1-C_6 alkyl; Ar is an aromatic radical selected from: benzene, naphthalene, phenanthrene, anthracene, biaryl radical or two or more



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PROCESS FOR PREPARING A POLYMER FROM MUSTARD CARBONATE ANALOGUES

The present invention relates to a process for preparing a polymer starting from mustard carbonate analogues. The present invention further relates to the polymer obtainable with the aforesaid process.

The compound bis(2-chloroethyl) sulphide ($S(CH_2CH_2Cl)_2$), also known as sulphur mustard or mustard gas, is a compound that was used as a chemical weapon during the First World War because of its vesicant action.

In addition to the aforesaid sulphur mustard, also known in the art are nitrogen mustards (e.g. bis(2-chloroethyl) amine of formula $HN(CH_2CH_2Cl)_2$) and oxygen mustards (e.g. bis(2-chloroethyl) ether of formula $O(CH_2CH_2Cl)_2$). The mustards can also exist in monochloride form (so-called asymmetrical mustards or half-mustards), for example 2-(chloroethyl) methyl sulphide of formula $CH_3SCH_2CH_2Cl$.

Today, the mustards are used mainly as electrophile reagents in organic syntheses, for example for the preparation of pharmaceutical intermediates, textile dyes, inks and solvents. The high toxicity for humans and for the environment that characterises these compounds, however, makes industrial use of the mustards very difficult, entailing adoption of stringent safety measures.

Within the context of the application of Green Chemistry principles, in the state of the art mustard carbonate analogues compounds have been described, i.e. compounds in which the chlorine atoms of the mustards

are replaced by alkyloxycarbonyloxy groups (-OC(O)OR). Thanks to the absence of chlorine, mustard carbonate analogues are substantially innocuous compounds for humans and for the environment, while having
5 electrophilic reactivity that is similar to, though lower than, that of mustards.

Mustard carbonate analogues compounds, therefore, are a highly attractive alternative to the industrial use of the mustards containing chlorine.

10 Mustard carbonate analogues can be obtained by reaction of a mustard precursor diol or triol with a dialkyl carbonate, possibly in the presence of a basic catalyst.

For example, by reacting 2-(methylthio)ethanol with
15 dimethyl carbonate (DMC) in the presence of potassium carbonate, the mustard carbonate analogue 2-(methylthio)ethyl methyl carbonate (half mustard) and methyl alcohol are obtained. For example, by reacting triethanolamine with DMC in the presence of potassium
20 carbonate, N',N'',N'''-tris[2-(methoxycarbonyloxy)ethyl]amine and methyl alcohol are obtained.

In consideration of the advantages exhibited by mustard carbonate analogues with respect to the mustards containing chlorine, in the prior art there is
25 a strong need to find new uses for mustard carbonate analogues, in particular as reagents in industrial synthesis processes in accordance with Green Chemistry principles.

From this perspective, for example, the
30 publication of F. Aricò et al., ChemPlusChem 2015, 80, 471-474, describes the use of mustard carbonate analogues for the synthesis of azacrown ethers. The

synthesis process comprises the reaction of mustard carbonate analogues with aromatic diols in the presence of potassium nitrate as templating agent. The synthesis is carried out in conditions of high dilution in
5 acetonitrile solvent.

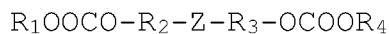
The Applicant has now found that sulphur or nitrogen mustard carbonate analogues can advantageously be used to synthesise new polymers having mechanical and hydrolysis resistance properties. Such polymers can
10 be exploited in the sectors where materials having the aforesaid properties are required.

In addition, because of the thiolic functions, they can have a variety of applications as polymer electrolytes for lithium ion batteries, adhesives and
15 sealants, chelants, resins for the absorption of heavy metals in solution, oxidation-responsive polymers for applications in the field of medicine. These polymers can be starting materials for new materials because of the reactivity of sulphur in its lowest oxidation
20 state.

In particular, the Applicant has observed that by mass polymerization, i.e. in the substantial absence of a solvent, mustard carbonate analogues with hydroxy-substituted aromatic compounds having at least two
25 hydrogen atoms (e.g. two OH groups) sufficiently acid to interact with the carbonate groups of the mustards it is possible to obtain polycondensation of the reagents with formation of a polymeric product. The polymerization reaction also produces, as by-products,
30 carbon dioxide and the alcohol corresponding to the alkyl residue that forms the starting carbonate analogues.

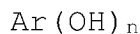
The synthesis process developed by the Applicant is a process that is simple to carry out and has low environmental impact because of reduced energy consumption and of possible recovery of reaction by-products.

In accordance with a first aspect, the present invention then relates to a process for preparing a polymer that comprises at least a step of carrying out a mass polymerization of a reaction mixture comprising at least a mustard carbonate analogue of general formula (I)



(I)

and at least one hydroxy-substituted aromatic compound of general formula (II)



(II),

wherein in said general formulas:

R_1 and R_4 , equal or different, are a linear or branched C_1 - C_6 alkyl;

R_2 and R_3 , equal or different, are a linear or branched C_2 - C_4 alkylene, preferably ethylene;

Z is a radical selected from: S; N-Y, wherein Y is selected from: hydrogen, linear or branched C_1 - C_6 alkyl; or a- R_6 OCOOR₅ radical where R_6 is a linear or branched C_2 - C_4 alkyl and R_5 is a linear or branched C_1 - C_6 alkyl;

Ar is an aromatic radical selected from: benzene, naphthalene, phenanthrene, anthracene, biaryl radical or two or more aromatic radicals bridged by a linear or branched C_1 - C_{10} alkylene group, said Ar group being

optionally substituted;

n is an integer number from 2 to 5.

In accordance with a second aspect, the present invention relates to a polymer obtainable with the
5 aforesaid process.

According to a preferred aspect, in said general formula (I):

Z is S;

R₁ and R₄, equal or different, are a linear or
10 branched C₁-C₆ alkyl;

R₂ and R₃, equal or different, are a linear or branched C₂-C₄ alkylene.

According to an additional preferred aspect, in said general formula (I):

15 Z is N-Y, wherein Y is selected from: hydrogen, linear or branched C₁-C₆ alkyl, or a radical -R₆OCOR₅ where R₆ is a linear or branched C₂-C₄ alkyl and R₅ is a linear or branched C₁-C₆ alkyl;

R₁ and R₄, equal or different, are linear or
20 branched C₁-C₆ alkyl;

R₂ and R₃, equal or different, are a linear or branched C₂-C₄ alkylene, preferably ethylene.

According to a preferred aspect, in said general formula (II) Ar is an aromatic radical selected from:
25 benzene, naphthalene, biphenyl or two or more aromatic radicals bridged by a linear or branched C₁-C₁₀ alkylene group, each of these groups being optionally substituted. More preferably, the hydroxy-substituted aromatic compound of general formula (II) is selected
30 from: hydroquinone, cathecol, resorcinol, pyrogallol, 4,4'-dihydroxydiphenyl and bisphenol-A, each of these groups being optionally substituted.

According to a preferred aspect, n is equal to 2 or 3.

The polymers according to the invention can be obtained in crosslinked form. For example, when in the
5 compound of general formula (I) Z is N-Y and Y is a -R₆OCOR₅ radical, where R₆ is a linear or branched C₂-C₄ alkylene and R₅ is a linear or branched C₁-C₆ alkyl, the resulting polymer is a crosslinked polymer.

A crosslinked polymer can also be obtained when in
10 the hydroxy-substituted aromatic compound of general formula (II) n is equal to or higher than 3.

When the aromatic radical Ar of the compound of general formula (II) is substituted with one or more substituents, said substituents are preferably selected
15 from: halogen, linear or branched C₁-C₆ alkyl, -OR, -COR or -NHCOR, where R is a linear or branched C₁-C₆ alkyl.

Preferred examples of mustard carbonate analogues of general formula (I) that can be used for the purposes
20 of the present invention are the following: bis[2-(ethoxycarbonyloxy)ethyl]sulphide and bis[2-(methoxycarbonyloxy)ethyl]sulphide, N',N'',N'''-tris[2-(methoxycarbonyloxy)ethyl]amine and N',N'-bis[2-(ethoxycarbonyloxy)ethyl]N'''-methylamine.

25 In accordance with the present invention, the synthesis reaction is a bulk polycondensation reaction, i.e. a polymerization reaction that is carried out in the substantial absence of solvents.

For the purposes of the present invention, the
30 expression "in the substantial absence of solvents" indicates that the reaction mixture may contain one or more solvents, for example to regulate its viscosity,

in a total quantity that is lower than or equal to 10% by volume, preferably lower than 1% by volume, still more preferably lower than 0.1% by volume. When present, the solvent is preferably a polar aprotic
5 solvent, such as for example N,N-dimethylformamide, dimethyl sulphoxide, N-methyl-2-pyrrolidone and dimethyl isosorbide. Preferably, no solvent is added to the reaction mixture.

For the purposes of the present invention, the
10 term "solvent" means a compound, in the liquid state at the reaction conditions, which is not substantially embedded in the structure of the final polymer.

In accordance with the aforesaid bulk reaction mode, the reaction mixture then comprises the reactants
15 of general formula (I) and (II), in addition to any optional ingredients, such as catalysts and additives, but it is substantially devoid of solvents.

The reagents of general formula (I) and (II) may be obtained through synthesis processes known to a
20 person skilled in the art or are available on the market.

The mustard carbonate analogues may be obtained, for example, by reaction of an alkanolamine (e.g. diethanolamine, triethanolamine) or a hydroxyalkyl
25 sulphide (e.g. bis(2-hydroxyethyl)sulphide) with a dialkyl carbonate (e.g. dimethyl carbonate (DMC), diethyl carbonate (DEC), dipropyl carbonate (DPC), dibutyl carbonate (DBC), etc.), possibly in the presence of a basic catalyst.

30 In accordance with the present invention, the reaction mixture may comprise one or more mustard carbonate analogues of general formula (I), that are

different from each other.

The reaction mixture may further comprise one or more hydroxy-substituted aromatic compounds of general formula (II), that are different from each other.

5 Preferably, the polycondensation reaction is carried out keeping the reaction mixture at a temperature in the range of 130°C - 350°C, preferably 150°C - 250°C.

10 Preferably, the polycondensation reaction is carried out keeping the reaction mixture at an absolute pressure in the range of 0.1 atm - 2 atm.

15 Preferably, the polycondensation reaction is carried out keeping the reaction mixture at the reaction conditions for a time interval in the range of 30 minutes - 48 hours. The duration of the reaction also varies as a function of the temperature at which the reaction is made to occur and of the degree of polymerization to be obtained; in fact these polymers are obtained through a stepwise condensation reaction and therefore the preparation of polymers with high
20 molecular weight is a relatively easy operation.

The reaction mixture can also comprise at least one basic polymerization catalyst. The catalyst can be of the organic or inorganic type.

25 Preferably, the basic polymerization catalyst is selected from: carbonate or hydrogencarbonate of an alkali or alkaline-earth metal; hydroxide of an alkali or alkaline-earth metal; C₁-C₄ alkoxides (e.g. sodium methoxide, potassium tert-butoxide), 1,8-diazabicyclo[5.4.0]-7-undec-5-ene (DBU); 1,5-diazabicyclo[4.3.0]-5-nonene (DBN); basic alumina,
30 hydrotalcite or mixtures thereof.

Preferably, the catalyst is present in the reaction mixture in a total quantity in the range of 0.5% - 5% by weight relative to the weight of the reaction mixture.

5 Without wishing to refer to any specific theory, it is believed that the formation of the polymer is the result of a substitution reaction between the carbonate -OCOR groups of the mustard carbonate analogue and the -OH groups of the hydroxy-substituted aromatic
10 compound, which allows condensation of the Ar radical of the reagent of general formula (II) with the segment R₂-Z-R₃ of the reagent of general formula (I), thus forming polymer chains containing segments -Ar-O-R-Z-R-O-, where Ar, R and Z have the meanings previously
15 indicated.

The aforesaid polycondensation reaction also leads to the formation of alcohol ROH as a consequence of the combination of the leaving group R of the mustard and the OH group of the aromatic compound, as well as to
20 the evolution of gaseous CO₂ caused by the decomposition of the alkylcarbonic acid.

The aforesaid reaction mechanism seems to be experimentally supported by the observation that, during the reaction, gaseous CO₂ evolves in equimolar
25 quantity with respect to the number of carbonate groups that can react with the hydroxyaromatic compound according to the specific composition of the reaction mixture.

The monitoring of the quantity of CO₂ produced
30 during the reaction can be used as a tool for the management of the synthesis process, in particular as an indicator of the degree of progress reached by the

reaction.

Since the polymerization reaction is a polycondensation reaction, the optimal ratio between the number of total moles of alkylcarbonate groups of the reagent of general formula (II) and the number of total moles of OH groups of the compound of general formula (II) present in the reaction mixture is equal to 1:1. However, for practical purposes the aforesaid molar ratio in the reaction mixture is preferably in the range of 0.8:1.3. The molecular weight of the final polymer and its terminal groups also depend on the molar ratio.

The terminal groups of the chain of the polymer obtained at the end of the process according to the present invention are ROOCO- groups, where R has the meaning of R₁ or R₄, or -OH groups, as a function of the excess reagent.

However, the terminal groups of the polymer may be possibly replaced after the reaction with other functional groups with the techniques known to the person skilled in the art.

At the end of the reaction, the reaction mixture containing the polymer is preferably subjected to washing to eliminate the excess reagents or any possible catalyst present, using a suitable solvent (e.g. methanol).

The obtained polymer product can also be subjected to concentration or purification, for example by means of techniques known in the art, e.g. by dissolution and precipitation.

The process according to the present invention can be carried out by techniques and apparatuses that are

known to the person skilled in polymer synthesis.

The following embodiment examples are provided merely to illustrate the present invention and should not be construed in a sense that would limit the scope of protection defined by the accompanying claims.

In the examples, reference shall be made to the following accompanying figures, where:

- Figure 1: (a) $^1\text{H-NMR}$ spectrum of the reagent bis[2-(ethoxycarbonyloxy)ethyl]sulphide; (b) $^1\text{H-NMR}$ spectrum of the reagent bis[2-(methoxycarbonyloxy)ethyl]sulphide;

- Figure 2: (a) $^1\text{H-NMR}$ spectrum of the polymer according to the present invention obtained in accordance with Example 5; (b) $^1\text{H-NMR}$ spectrum of the polymer according to the present invention obtained in accordance with Example 6;

- Figure 3: (a) IR spectrum of the polymer according to the present invention obtained in accordance with Example 5;

- Figure 4: (a) $^1\text{H-NMR}$ spectrum of the polymer according to the present invention obtained in accordance with Example 7; (b) $^1\text{H-NMR}$ spectrum of the polymer according to the present invention obtained in accordance with Example 7 after washing with methanol;

- Figure 5: (a) $^1\text{H-NMR}$ spectrum of the reagent $\text{N}',\text{N}'\text{-bis[2-(ethoxycarbonyloxy)ethyl]N''''-methylamine}$; (b) $^1\text{H-NMR}$ spectrum of the polymer according to the present invention obtained in accordance with Example 9.

EXAMPLES

1. Synthesis of $\text{N}',\text{N}'',\text{N}'''\text{-tris[2-(methoxycarbonyloxy)ethyl]amine}$

A reaction mixture was prepared containing 0.50 grams of triethanolamine, 0.70 grams of K_2CO_3 and 25 mL of dimethyl carbonate (DMC). The mixture was kept under stirring at the reflux temperature ($90^\circ C$).
5 Triethanolamine, initially insoluble, dissolved in the DMC as the reaction progressed.

At the end of the reaction, the mixture was cooled down to ambient temperature and then filtered. The excess DMC was evaporated, recovering 0.9 grams of
10 N',N'',N''' -tris[2-(methoxycarbonyloxy)ethyl]amine. The yield of the reaction was 85%.

2. Synthesis of bis[2-(methoxycarbonyloxy)ethyl]sulphide

A reaction mixture was prepared containing 2.00
15 grams of bis(2-hydroxyethyl)sulphide, 2.20 grams of K_2CO_3 and 50 mL of dimethyl carbonate (DMC). The mixture was kept under stirring at the reflux temperature ($90^\circ C$) for 24 hours.

At the end of the reaction, the mixture was cooled
20 down to room temperature and then filtered. The excess DMC was evaporated, recovering 3.90 grams of bis[2-(methoxycarbonyloxy)ethyl]sulphide. The yield of the reaction was 97%.

The 1H -NMR spectrum of bis[2-
25 (methoxycarbonyloxy)ethyl]sulphide obtained is shown in figure 1 (spectrum b).

3. Synthesis of bis[2-(ethoxycarbonyloxy)ethyl]sulphide

A reaction mixture was prepared containing 2.00
30 grams of bis(2-hydroxyethyl)sulphide, 2.20 grams of K_2CO_3 and 50 mL of diethyl carbonate (DEC). The mixture was kept under stirring at the reflux temperature

(120°C) for 24 hours.

At the end of the reaction, the mixture was cooled down to ambient temperature and then filtered. The excess DEC was evaporated, recovering 4.00 grams of bis[2-
5 (ethoxycarbonyloxy)ethyl]sulphide. The yield of the reaction was 91%.

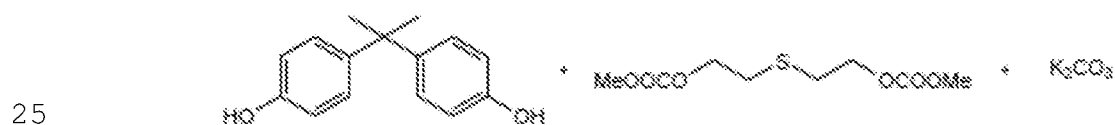
The $^1\text{H-NMR}$ spectrum of bis[2-(ethoxycarbonyloxy)ethyl]sulphide obtained is shown in figure 1 (spectrum a).

10 4. Synthesis of N',N'' -bis[2-(ethoxycarbonyloxy)ethyl] N'''' -methylamine

A reaction mixture was prepared containing 2.00 grams of bis(2-hydroxyethyl) N-methyl amine, 2.30 grams of K_2CO_3 and 50 mL of diethyl carbonate (DEC). The
15 mixture was kept under stirring at the reflux temperature (135°C) for 24 hours.

At the end of the reaction, the mixture was cooled down to ambient temperature and then filtered. The excess DEC was evaporated, recovering 4.10 grams of
20 N',N' -bis[2-(ethoxycarbonyloxy)ethyl] N'''' -methylamine. The yield of the reaction was 92%. The spectrum of the product is shown in Figure 5a.

5. Synthesis of a polymer starting from bis[2-(methoxycarbonyloxy)ethyl]sulphide and bisphenol A



In a test tube, a reaction mixture was prepared by mixing: 2.00 grams of bisphenol A, 2.05 grams of the mustard carbonate of example 2 (molar ratio 1.0:1.0)

and 0.10 mole equivalents of K_2CO_3 base.

The reaction mixture was kept under stirring at $160^\circ C$ in a sand bath. The polymerization reaction immediately started with readily evident development of
5 CO_2 and methanol.

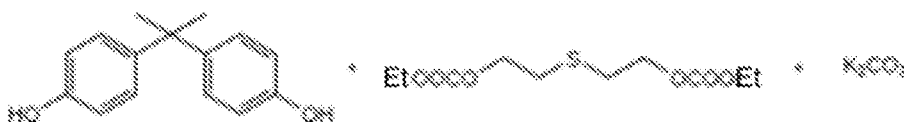
The 1H NMR spectrum of the reaction mixture after 17 hours from the start of the reaction is shown in figure 2 (spectrum A). The signals at 4.06 ppm and 3.71 ppm indicate the presence of Ar-O-CH₂-CH₂ bonds, which
10 confirm the formation of the polymer.

The quantity of polymeric material recovered is equal to 2.75 g.

Figure 3 shows the IR spectrum of the polymer that exhibits the typical signals of the vibrations CH₂-S-
15 CH₂- at 1012 cm^{-1} , 1064 cm^{-1} and in the region of $1450\text{--}1500\text{ cm}^{-1}$. In addition, the spectrum shows typical signals of the ether bond (CH₂-O-CH₂) at 1179 and 1246 cm^{-1} .

Analysis of the polymeric material by differential scanning calorimetry indicates that the polymer is
20 semicrystalline, has a melting point at $330^\circ C$ and a glass transition temperature (T_g) of $105.7^\circ C$.

6. Synthesis of a polymer starting from bis[2-(ethoxycarbonyloxy)ethyl]sulphide and bisphenol A



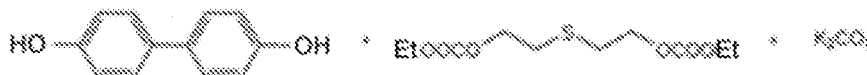
In a test tube, a reaction mixture was prepared, mixing: 0.20 grams of bisphenol A, 0.23 grams of the mustard carbonate of example 3 (molar ratio 1.0:1.0)

and 0.10 mole equivalents of K_2CO_3 base.

The reaction mixture was kept under stirring at $160^\circ C$ in a sand bath. The polymerization reaction immediately started with readily evident development of
5 CO_2 and ethanol.

The spectrum of the reaction mixture after 8 hours from the start of the reaction is shown in figure 2 (spectrum b). The signals at 4.06 ppm and 3.71 ppm indicate the presence of Ar-O- CH_2 bonds, which confirm
10 the formation of the polymer.

7. Synthesis of a polymer starting from bis[2-(ethoxycarbonyloxy)ethyl]sulphide and 4,4'-dihydroxybiphenyl



15

In a test tube, a reaction mixture was prepared, mixing: 0.20 grams of 4,4'-dihydroxybiphenyl, 0.29 grams of the mustard carbonate of example 3 (molar ratio 1.0:1.0) and 0.10 mole equivalents of K_2CO_3 base.

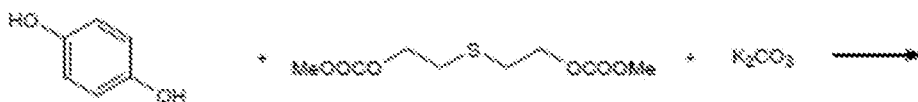
20 The mixture contained in a test tube was kept under stirring at $160^\circ C$ in a sand bath. The polymerization reaction immediately started with readily evident development of CO_2 and ethanol.

The 1H -NMR spectrum of the reaction mixture after
25 8 hours from the start of the reaction is shown in figure 4 (spectrum b). The spectrum indicates the presence of the polymer and of a certain quantity of unreacted carbonate. The mixture was then washed with methanol to remove the carbonate and the diol still
30 present in the mixture. The spectrum of the polymeric

material after washing is shown in figure 4 (spectrum a); the peak at 3.49 relates to a small quantity of residual methanol.

Analysis of the polymeric material by differential scanning calorimetry indicates that the polymer is
 5 semicrystalline and has a melting point at 203°C.

8: Synthesis of a polymer starting from bis[2-(methoxycarbonyloxy)ethyl]sulphide and hydroquinone

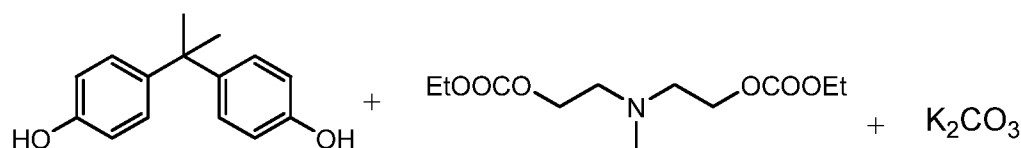


10

In a test tube, a reaction mixture was prepared, mixing 0.23 grams of hydroquinone, 0.50 grams of the mustard carbonate of example 2 (molar ratio 1.0:1.0) and 0.10 mole equivalents of K₂CO₃ base.

15 The reaction mixture was kept under stirring at 160°C in a sand bath. The polymerization reaction immediately started with readily evident development of CO₂ and methanol. The volume of carbon dioxide developed during the reaction was collected in a water
 20 column at ambient temperature, being equal to 72 mL; this value corresponds to approximately 80% of the total quantity of CO₂ that should develop in accordance with the stoichiometry of the proposed reaction.

9. Synthesis of a polymer starting from N',N'-bis[2-(ethoxycarbonyloxy)ethyl]N'''-methylamine and
 25 bisphenol A



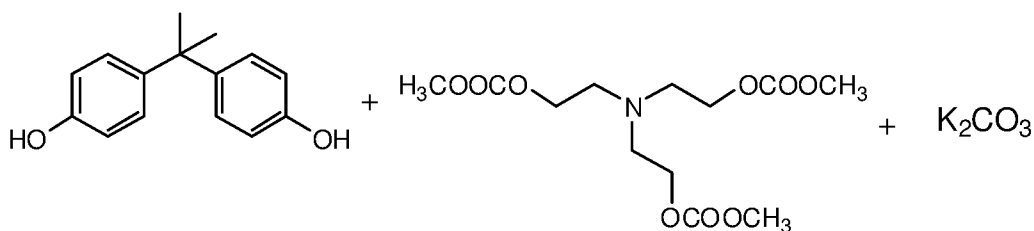
In a test tube, a reaction mixture was prepared, mixing: 0.26 grams of bisphenol A, 0.30 grams of the mustard carbonate of example 4 (molar ratio 1.0:1.0) and 0.10 mole equivalents of K_2CO_3 base.

5 The reaction mixture was kept under stirring at $160^\circ C$ in a sand bath. The polymerization reaction immediately started with readily evident development of CO_2 and ethanol.

The spectrum of the reaction mixture after 3 hours from the start of the reaction is shown in figure 5 (spectrum b). The signals at 4.09 ppm and 3.65 ppm indicate the presence of $Ar-O-CH_2-CH_2-N(CH_3)-$ bonds, which confirm the formation of the polymer.

Analysis of the polymeric material by differential scanning calorimetry indicates that the polymer is stable up to $350^\circ C$, not showing any sharp melting points.

10 10. Synthesis of a polymer starting from N',N'',N''' -tris[2-(methoxycarbonyloxy)ethyl]amine and bisphenol A



In a test tube, a reaction mixture was prepared, mixing: 0.42 grams of bisphenol A, 0.40 grams of the mustard carbonate of example 1 (molar ratio 3.0:2.0) and 0.10 mole equivalents of K_2CO_3 base (calculated with respect to bisphenol A).

30

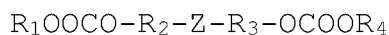
The reaction mixture was kept under stirring at $160^\circ C$ in a sand bath. The polymerization reaction

immediately started with readily evident development of CO₂ and ethanol.

After three hours the reaction was stopped. The product has the consistency of a resin that was found
5 to be insoluble in common organic solvents.

CLAIMS

1. Process for preparing a polymer that comprises at least a step of carrying out a mass polymerization of a reaction mixture comprising at least a mustard
5 carbonate analogue of general formula (I)



(I)

and at least one hydroxy-substituted aromatic compound of general formula (II)

10 $Ar(OH)_n$

(II),

wherein in said general formulas:

R_1 and R_4 , equal or different, are linear or branched C_1-C_6 alkyl;

15 R_2 and R_3 , equal or different, are linear or branched C_2-C_4 alkylene, preferably ethylene;

Z is a radical selected from: S; N-Y, wherein Y is selected from: hydrogen, linear or branched C_1-C_6 alkyl, or a radical $-R_6OCOOR_5$ where R_6 is a linear or
20 branched C_2-C_4 alkyl and R_5 is a linear or branched C_1-C_6 alkyl;

Ar is an aromatic radical selected from: benzene, naphthalene, phenanthrene, anthracene, biaryl radical or two or more aromatic radicals bridged by a linear or
25 branched C_1-C_{10} alkylene group, said Ar group being optionally substituted;

n is an integer number from 2 to 5.

2. The process according to claim 1, wherein in said general formula (II) said Ar radical is selected
30 from: benzene, naphthalene, biphenyl or two or more aromatic radicals bridged by a linear or branched C_1-C_{10}

alkylene group, each of said radicals being optionally substituted.

3. The process according to claim 1, wherein in said general formula (I):

5 Z is S;

R₁ and R₄, equal or different, are linear or branched C₁-C₆ alkyl;

R₂ and R₃, equal or different, are linear or branched C₂-C₄ alkylene.

10 4. The process according to claim 1, wherein in said general formula (I):

Z is N-Y, wherein Y is selected from: hydrogen, linear or branched C₁-C₆ alkyl, or a radical -R₆OCOOR₅ where R₆ is a linear or branched C₂-C₄ alkyl and R₅ is a
15 linear or branched C₁-C₆ alkyl;

R₁ and R₄, equal or different, are linear or branched C₁-C₆ alkyl;

R₂ and R₃, equal or different, are linear or branched C₂-C₄ alkylene, preferably ethylene.

20 5. The process according to claim 1, wherein in said at least one compound of general formula (I) is selected from: bis[2-(ethoxycarbonyloxy)ethyl]sulfide, bis[2-(methoxycarbonyloxy)ethyl]sulfide, N',N'',N'''-tris[2-(methoxycarbonyloxy)ethyl]amine e N',N'-bis[2-
25 (ethoxycarbonyloxy)ethyl]N'''-methylamine.

6. The process according to claim 1, wherein said at least one compound of general formula (II) is selected from: hydroquinone, cathecol, resorcinol, pyrogallol, 4,4'-dihydroxydiphenyl and bisphenol-A,
30 each of said compounds being optionally substituted.

7. The process according to any of the preceding claims, wherein said radical Ar is substituted with one

or more of the following substituents: halogen, linear or branched C₁-C₆ alkyl, -OR, -COR or -NHCOR, wherein R is a linear or branched C₁-C₆ alkyl.

8. The process according to claim 1, wherein said
5 reaction mixture comprises at least one basic polymerization catalyst.

9. The process according to the preceding claim, wherein said basic polymerization catalyst is selected from: carbonate or hydrogencarbonate of an alkali or
10 alkaline-earth metal; hydroxide of an alkali or alkaline-earth metal; C₁-C₄ alkoxides; 1,8-diazabicyclo[5.4.0]-7-undec-5-ene (DBU); 1,5-diazabicyclo[4.3.0]-5-nonene (DBN); basic alumina, hydrotalcite and mixtures thereof.

15 10. The process according to claim 1, wherein the molar ratio between the alkyl-carbonate ROOCO- groups of said compound of general formula (I), wherein R has the meaning of R₁ or R₄ indicated above, and the OH groups of the hydroxy-substituted aromatic compound of
20 general formula (II) in the reaction mixture is within the range 0.8:1.3.

11. Polymer obtainable by the process according to claim 1.

Fig. 1

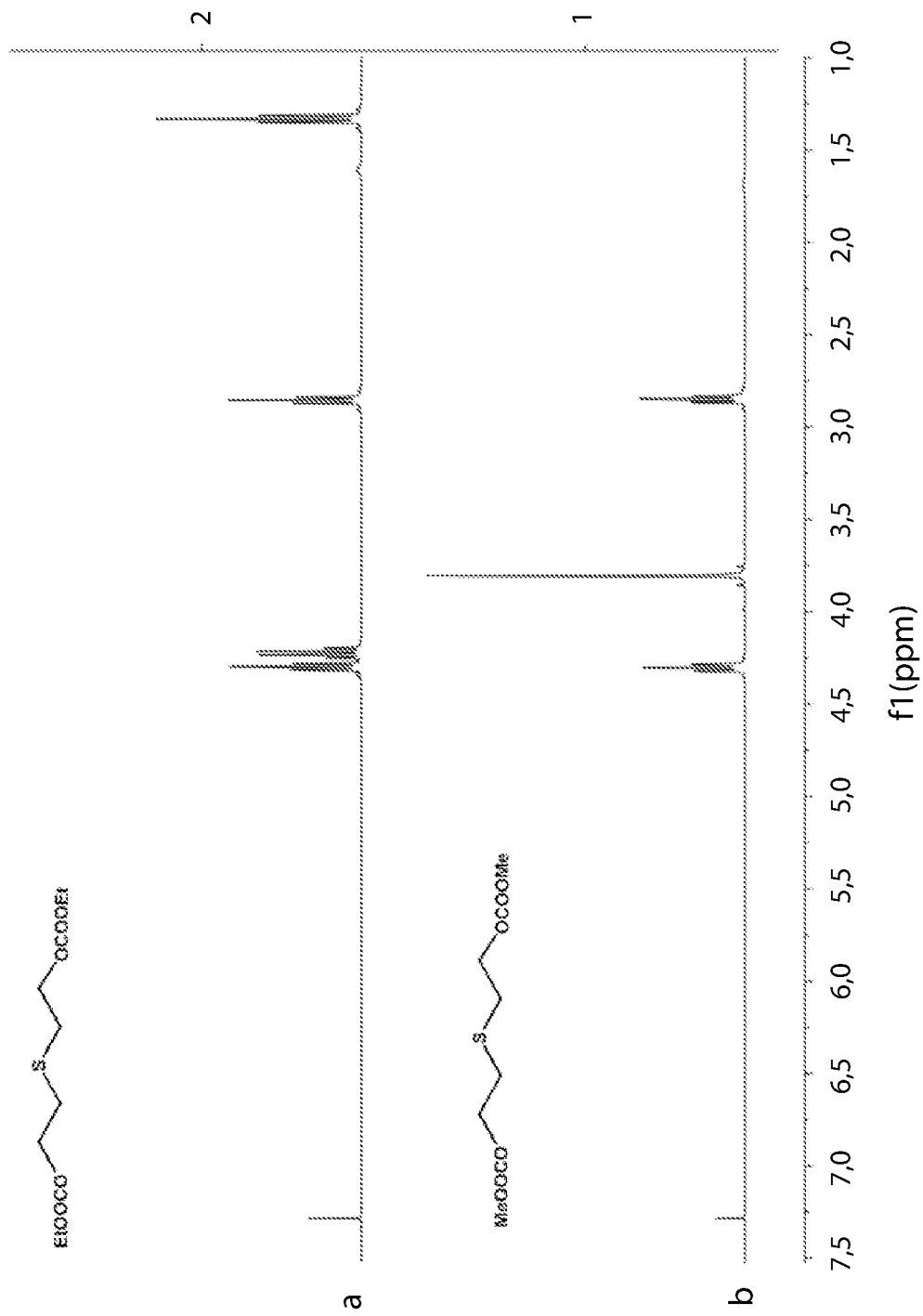


Fig. 2

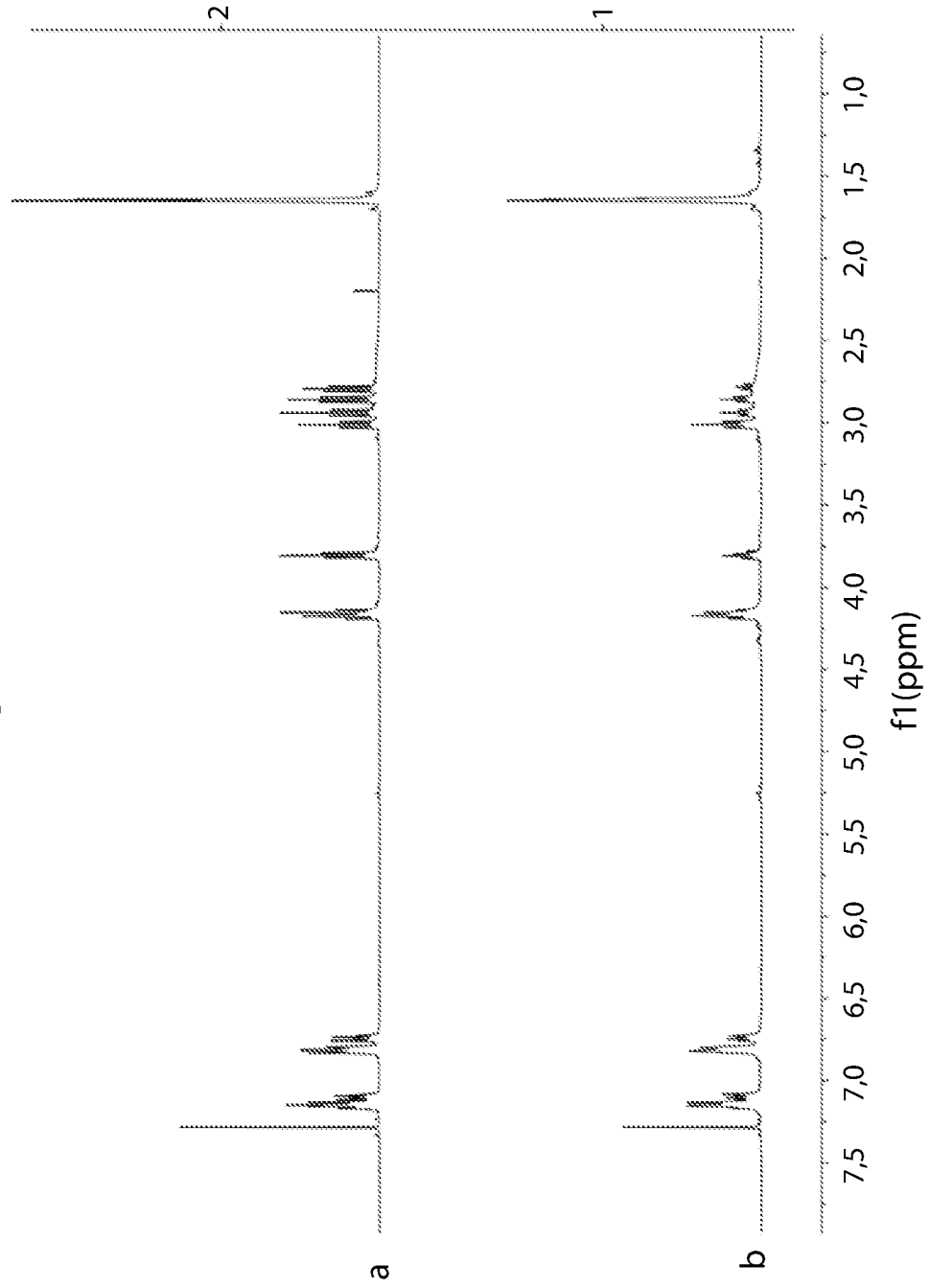
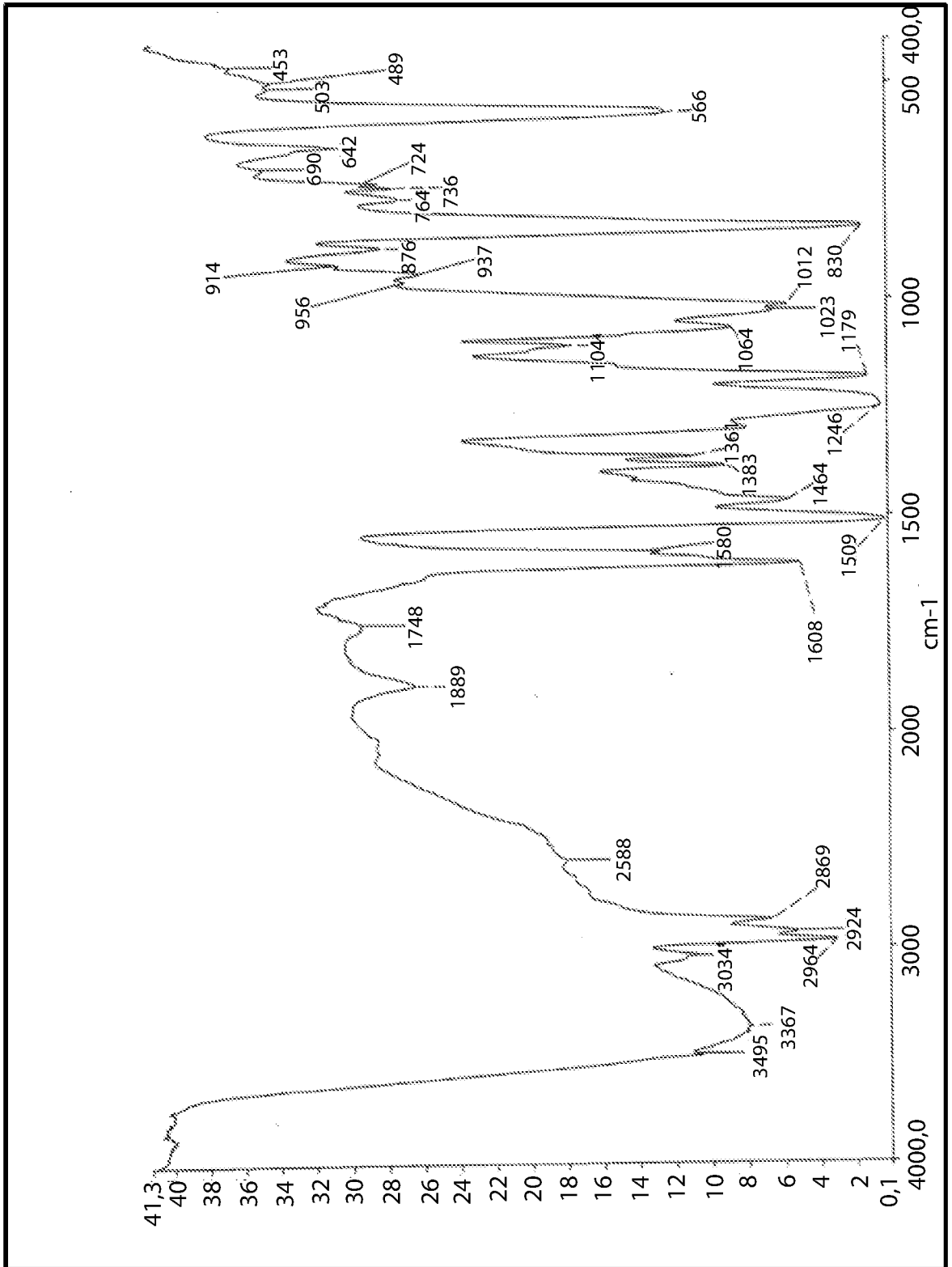


Fig. 3



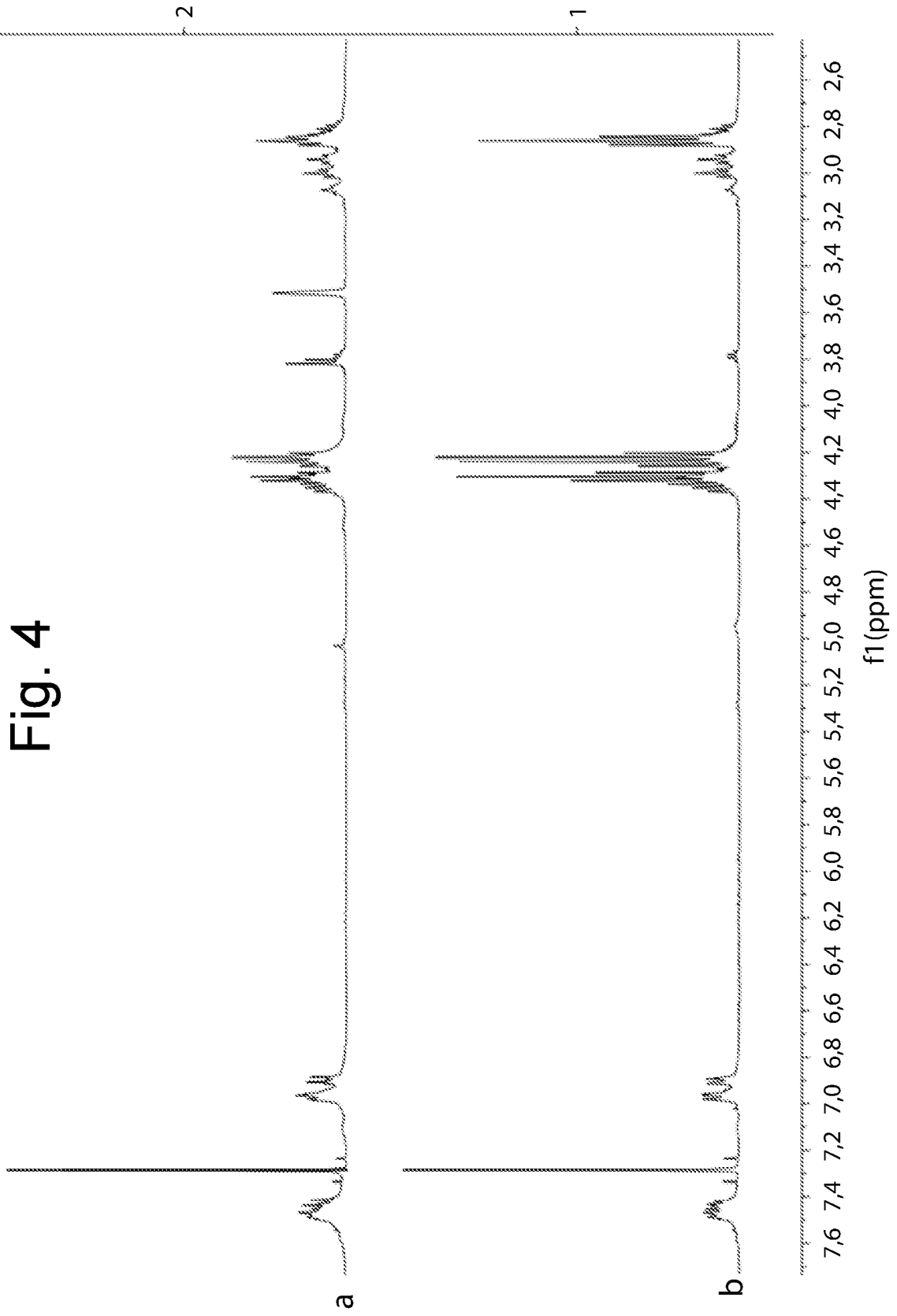
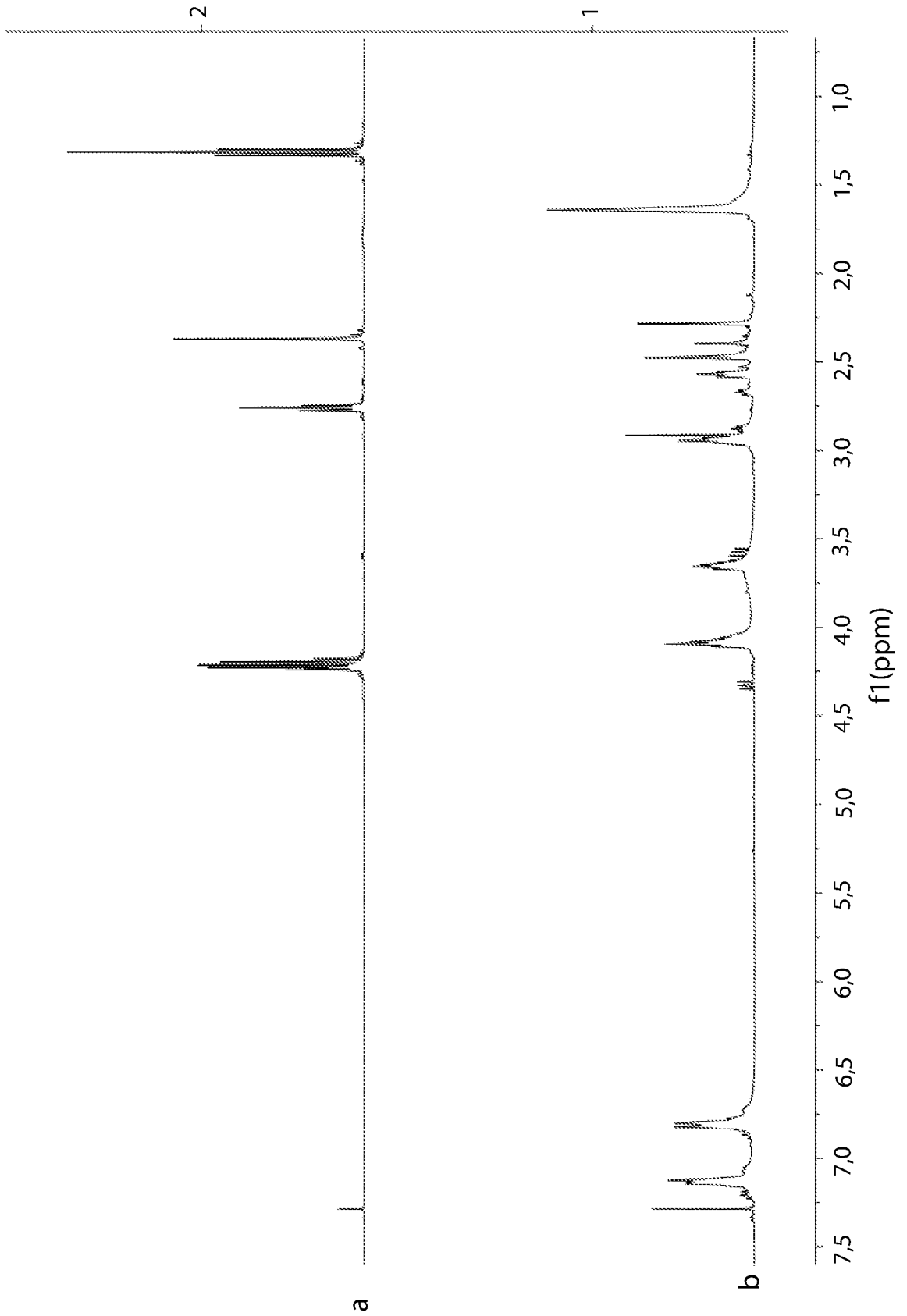


Fig. 5



INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2018/054621

A. CLASSIFICATION OF SUBJECT MATTER INV. C08G65/00 C08G65/40 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, CHEM ABS Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FABIO ARICÒ ET AL: "Abstract", PURE & APPLIED CHEMISTRY, vol. 88, no. 1-2, 1 January 2016 (2016-01-01), XP055441224, GB	1-7, 10, 11
A	ISSN: 0033-4545, DOI: 10.1515/pac-2015-0604 *Reaction schemes 6 and 7*; page 13 - page 14 ----- -/--	8,9
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents :		
"A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" 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		"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 "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family
Date of the actual completion of the international search <p align="center">16 August 2018</p>		Date of mailing of the international search report <p align="center">28/08/2018</p>
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 <p align="center">O'Sullivan, Timothy</p>

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2018/054621

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	ARICO F.ET AL: "Azacrown Ethers from Mustard Carbonate Analogues", CHEMPLUSCHEM, vol. 80, 16 October 2014 (2014-10-16), pages 471-474, XP002777386, cited in the application	1-7,10, 11
A	*Scheme 2*; page 472 *Scheme 3*; page 473 -----	8,9