

SURFACE-ACTIVE AGENT

FIELD

The present invention relates to ionic surface-active agents, to processes for making them, and to certain applications.

5 BACKGROUND

Ionic surfactants are typically produced from petrochemical raw materials. Examples include ammonium and sodium lauryl and lauryl ether sulphates, methylester sulphonates, ammonium and imidazolium salts, and phospholipids, all of which can produce significant amounts of CO₂ emissions in their manufacture, or otherwise lack environmental sustainability.

- 10 Surface-active agents combining polyether and polycarbonate blocks are known in the art of oil extraction. WO2010/062703A1 and WO2015/031348A1 describe polymer compositions and supercritical CO₂ solutions of a potentially wide range of such polymers to assist with oil extraction. Such solutions form an emulsion waste product with water to assist with the oil extraction. There is no indication of any solubility in water or the use of such a water soluble polymer. The polymer compositions are designed to dissolve in liquid or supercritical CO₂ applications. WO2010/062703A1 mentions examples with a polyether block and a polycarbonate block but such is not exemplified, and the or block are not fully characterised or tested. WO2015/031348A1 describes polycarbonate block of the type Y-O-APC-O-C_xH_y wherein APC is a polycarbonate and C_xH_y is a saturated or unsaturated hydrocarbon. The terminal group Y can be H or several other groups such as a polyether chain, but the latter is not exemplified or further identified.

US2021/309801A1 discloses degradable ethylene oxide-based copolymers manufactured via boron-activated copolymerization of ethylene oxide monomers with carbon dioxide and their use as surfactants. Certain tri-block amphiphilic compounds are reported.

- 25 WO2022/096889A1, WO2020/222019A1, WO2020/222018A1, WO2021/176211A1 and WO2021/176212A1 disclose polyol block copolymer compositions and processes for producing them.

US2020/0085059A1 describes antimicrobial cationic polycarbonates and polyurethanes comprising one or more pendent guanidinium and/or isothiuronium groups.

- 30 US2011/0151566A1 describes a biodegradable cationic polymer comprising first repeat units derived from a first cyclic carbonyl monomer by ring-opening polymerizations, wherein more than 0% of the first repeat units comprise a side chain moiety comprising a quaternary amine group; a subunit derived from a monomeric diol initiator for the ring-opening polymerisation; and an optional endcap group.

- 35 WO2014/042924 describes an antimicrobial composition comprising an anionic drug and an amine polymer. The amine polymer is a primary amine-containing polycarbonate prepared by organocatalysed ring opening polymerisation.

- 40 Our co-pending application WO2023/072843A1 discloses a surface-active agent comprising a polycarbonate block polyether which may be manufactured by reacting carbon dioxide and an epoxide in the presence of a carbonate catalyst, and a monofunctional starter compound to form a polycarbonate compound and subsequently reacting the polycarbonate compound with an epoxide and an ether catalyst to produce the or each polycarbonate chain or block polyether. Our

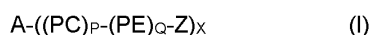
co-pending application GB2301055.6 discloses a surface-active agent comprising a polycarbonate block polyether which may be manufactured in similar fashion from a polyfunctional starter compound. These disclosures relate only to non-ionic surfactants.

- 5 It would be beneficial to replace current wholly petrochemical or otherwise environmentally undesirable ionic surfactants with more sustainable alternatives that incorporate a portion of abundant and cheaper captured CO₂ and could be made from a single epoxide feed, such as ethylene oxide, which can also be produced sustainably. The incorporation of CO₂ into these co-polymers offers new, beneficial properties to the surfactant, including the opportunity to enhance biodegradation. The incorporation of CO₂ containing chains or block can enhance the
- 10 biodegradability of such surfactants, even at longer chain lengths.

It would also be beneficial to provide ionic surfactants with a high degree of adaptability as concerns chain length, chain hydrophobicity and consequent ability to target particular end-use applications by providing a range of properties, and a greater degree of control over macromolecular symmetry than has hitherto been achievable.

15 SUMMARY

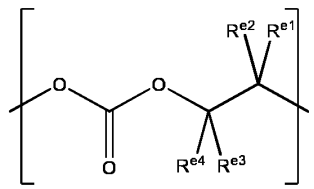
According to a first aspect of the present invention there is provided an ionic surface-active agent comprising a polycarbonate or poly(carbonate ether) of the formula I:



wherein:

- 20 A is derived from a functional starter compound;

PC represents a carbonate block with P repeat units of formula:

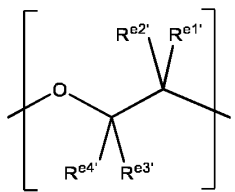


wherein:

R^{e1}, R^{e2}, R^{e3}, and R^{e4} are all H; or

- 25 one of R^{e1}, R^{e2}, R^{e3}, and R^{e4} is methyl, ethyl, propyl, butyl, or an ether, ester or carbonate group, and the remaining three of R^{e1}, R^{e2}, R^{e3}, and R^{e4} are all H;

PE represents a polyether block with Q repeat units of formula:



wherein:

$R^{e1'}$, $R^{e2'}$, $R^{e3'}$, and $R^{e4'}$ are all H; or

one of $R^{e1'}$, $R^{e2'}$, $R^{e3'}$, and $R^{e4'}$ is methyl, ethyl, propyl, butyl, or an ether, ester or carbonate group, and the remaining three of $R^{e1'}$, $R^{e2'}$, $R^{e3'}$, and $R^{e4'}$ are all H;

at least one Z is an ionic constituent;

5 wherein the value of the or each P is independently from 1 to 50;

wherein the value of the or each Q is independently from 0 to 50; and

X is 1 or more.

10 The surface-active agent may comprise a block copolymer comprising individual PC and PE blocks; or may comprise a random or statistical copolymer comprising only PC blocks which may incorporate ether (PE) linkages. For the avoidance of doubt the PC blocks of a block copolymer may (or may not) also contain ether (PE) linkages, and the PE blocks (when present) of a block copolymer may (or may not) contain carbonate (PC) linkages.

At least one Z may be anionic; in which case the surface-active agent is an anionic surfactant.

15 Examples of anionic Z include O-[ION], O-C(O)-[ION] and O-C(O)-O-[ION] wherein [ION] is selected from sulphates, sulphonates, phosphates, hydrogen and dihydrogen phosphates phosphites, hypophosphites, carboxylates, gluconates and suitable combinations of two or more thereof.

At least one Z may be cationic; in which case the surface-active agent is a cationic surfactant.

20 Examples of cationic Z include [ION], O-[ION], O-C(O)-[ION] and O-C(O)-O-[ION] wherein [ION] is selected from nitrogen-containing moieties such as secondary, tertiary or quaternary ammonium, pyridinium, pyrrolinium, pyrrolidinium, imidazolium, guanidinium, piperazinium, piperidinium, from phosphonium or sulphonium, and from suitable combinations of two or more thereof.

25 At least one Z may be zwitterionic; in which case the surface-active agent is a zwitterionic surfactant.

30 Examples of zwitterionic Z include any suitable combination of the aforesaid anionic and cationic examples. In other words, Z may include O-[ANION]-[CATION], O-C(O)-[ANION]-[CATION] and O-C(O)-O-[ANION]-[CATION], and may include [CATION]-[ANION], O-[CATION]-[ANION], O-C(O)-[CATION]-[ANION] and O-C(O)-O-[CATION]-[ANION], where [ANION] is selected from any suitable one of the examples given above for [ION] in relation to anionic surfactants, and wherein [CATION] is selected from any suitable one of the examples given above for [ION] in relation to cationic surfactants.

35 When the surface-active agent is anionic, a cationic counterion is typically provided in association with it. This may for example be selected from alkali metal or alkaline earth metal cations, or from nitrogen-containing cations such as primary, secondary, tertiary or quaternary ammonium ions, and from suitable combinations of two or more thereof.

When the surface-active agent is cationic, an anionic counterion is typically provided in association with it. This may for example be selected from halides, carboxylates, sulphates, nitrates, hydroxides, and from suitable combinations of two or more thereof. In some

circumstances other types of anion such as the fluorine-containing anions $[\text{PF}_6]^-$, $[\text{BF}_4]^-$ and the like may be used.

When the surface-active agent is zwitterionic, a counterion may not be necessary.

- 5 The value of the or each P may be independently from 1 to 50, from 1 to 45, from 1 to 40, from 1 to 35, from 1 to 30, from 1 to 25, from 1 to 20, or from 1 to 15. Preferably the value of the or each P is independently from 1 to 15.

The value of the or each Q may be independently from 0 to 50, from 0 to 45, from 0 to 40, from 0 to 35, from 0 to 30, from 0 to 25, from 0 to 20, or from 0 to 15. Preferably the value of the or each Q is independently from 0 to 15.

- 10 In the present invention the polymer chain $\text{A}-((\text{PC})_{\text{P}}-(\text{PE})_{\text{Q}})_x$ acts as a hydrophobe and Z acts as a hydrophile. However the hydrophobicity of the polymer chain can be adjusted by selection of the P:Q ratio (polycarbonate being more hydrophobic than polyether) and the hydrophobic properties of the chain may thereby be controlled for tailored suitability to the end use application.

- 15 It will be apparent that when a monofunctional starter (e.g. a mono-ol or polyalkylene glycol monoethyl ether) is selected then in that case X is 1. Selection of a difunctional starter (e.g. a diol) will cause X to be 2, and so on.

Preferably X is 1, 2 or 3.

- 20 Monofunctional starter compounds (from which A may be derived) may be selected from C_1 to C_{30} alcohols, C_1 to C_{30} carboxylic acids or monofunctional polyethers such as polyalkylene glycol monomethyl ether. In all cases, the hydrocarbon chains may be linear, branched, cyclic, aromatic, and/or contain hetero-atoms, or be substituted. Typically, when the monofunctional starter is an alcohol or carboxylic acid, it is preferably a C_1 to C_{11} , more preferably a C_2 to C_{11} , alcohol or carboxylic acid, typically a C_{2-6} or C_{2-4} alcohol or carboxylic acid. Typically when the monofunctional starter compound is a polyalkylene glycol monoethyl ether, it is preferably a PEG or PPG monomethyl ether.
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Polyfunctional starter compounds (from which A may be derived) may be selected from compounds of the formula;



- 30 Y can be any group which can have 2 or more $-\text{R}^Y$ groups attached to it. Thus, Y may be selected from optionally substituted alkylene, alkenylene, alkynylene, heteroalkylene, heteroalkenylene, heteroalkynylene, cycloalkylene, cycloalkenylene, heterocycloalkylene, heterocycloalkenylene, arylene, heteroarylene, or Y may be a combination of any of these groups, for example Y may be an alkylarylene, heteroalkylarylene, heteroalkylheteroarylene or alkylheteroarylene group. Optionally Y is alkylene, heteroalkylene, arylene, or heteroarylene.

- 35 It will be appreciated that in this case a is an integer which is at least 2. Optionally a is in the range of from 2 to 8, or from 2 to 4.

Each R^Y may be $-\text{OH}$, $-\text{NHR}'$, $-\text{SH}$, $-\text{C}(\text{O})\text{OH}$, $-\text{P}(\text{O})(\text{OR}')(\text{OH})$, $-\text{PR}'(\text{O})(\text{OH})_2$ or $-\text{PR}'(\text{O})\text{OH}$, optionally R^Y is selected from $-\text{OH}$, $-\text{NHR}'$ or $-\text{C}(\text{O})\text{OH}$, optionally each R^Y is $-\text{OH}$, $-\text{C}(\text{O})\text{OH}$ or a combination thereof (e.g. each R^Y is $-\text{OH}$).

- 40 R' may be H, or optionally substituted alkyl, heteroalkyl, aryl, heteroaryl, cycloalkyl or heterocycloalkyl, optionally R' is H or optionally substituted alkyl.

A is typically derived from the starter compound by removal of one or more hydrogen atoms and subsequent polymerisation from the deprotonated derivative(s).

There is also provided a process for producing a surface-active agent according to the first aspect of the invention the method comprising the steps of (i) reacting carbon dioxide and an epoxide in the presence of a carbonate catalyst, and a functional starter compound to form a polycarbonate compound; (ii) reacting the polycarbonate compound of step (i) with an epoxide and an ether catalyst to form a poly(carbonate ether); and (iii) modifying at least one terminal group of the poly(carbonate ether) to produce the surface-active agent according to the first aspect of the invention.

There is also provided a process for producing a surface-active agent according to the first aspect of the invention in a multiple reactor system; the system comprising at least a first and second reactor wherein a first reaction takes place in the first reactor and a second reaction takes place in the second reactor; wherein the first reaction is the reaction of a carbonate catalyst with CO₂ and epoxide, in the presence of a functional starter compound, and optionally a solvent, to produce a polycarbonate compound and the second reaction is the semi-batch or continuous reaction of an ether catalyst with the polycarbonate compound of the first reaction and epoxide to produce the a poly(carbonate ether), the process further comprising a third reaction which may take place in a third reactor, the third reaction comprising modifying at least one terminal group of the product of the poly(carbonate ether) to produce the surface-active agent according to the first aspect of the invention.

Alternatively, certain surface-active agents (derived from monofunctional starter compounds) of the first aspect may be formed by: (i) reacting a mono-hydroxy functional polyether with a carbonate catalyst, epoxide and CO₂ to produce a poly(carbonate ether); and (iii) modifying at least one terminal group of the poly(carbonate ether) to produce the surface-active agent according to the first aspect of the invention.

The terminal group(s) of the poly(carbonate ether) is or are selected from OH, O-R, O-C(O)-R, and/or O-C(O)-O-R; wherein each R is independently an optionally substituted (including with heteroatoms) straight or branched chain or cyclic alkyl, aryl, aralkyl, alkaryl, alkenyl, alkenaryl, or aralkenyl group. Preferably the or each terminal group of the poly(carbonate ether) is OH or OMe, more preferably OH.

The step of modifying the compound in step (iii) preferably introduces at least one ionic constituent onto the terminal group(s) of the polymer compound. Preferably this step comprises removing H or R from the terminal group(s) of the poly(carbonate ether) and substituting with an ionic constituent. It is also envisaged that sequential steps to introduce the ionic constituent may be involved – for example chlorination followed by amination.

When the polycarbonate or poly(carbonate) ether to be modified contains multiple modifiable terminal groups (for example when the polycarbonate or poly(carbonate) ether is a polycarbonate or poly(carbonate) ether polyol) it is sufficient for the purposes of the invention that only one of those modifiable terminal groups is converted into an ionic substituent. However, it may be desirable for more than one, or all, of such modifiable terminal groups to be modified by conversion into an ionic constituent.

In the event that fewer than all of the modifiable terminal groups are thus modified then in the compound of the claimed invention Z comprises an ionic substituent for each such modified substituent, and any remaining Z comprises an unmodified terminal group (as aforesaid) of the polycarbonate or poly(carbonate ether).

Furthermore, regardless as to whether the surface-active agent of the invention is derived from a monofunctional starter or from a polyfunctional starter, it will be apparent that it is not necessary for ionic substituents to be provided on all available terminal ends of the poly(carbonate) ether. The condition of the invention is satisfied provided that at least some of the available terminal groups are functionalised with the introduction of an ionic constituent.

In a PC chain comprising multiple Re groups, individual Re groups may be different in different sections or blocks of the chain. In a PE chain comprising multiple Re' groups, individual Re' groups may be different in different sections or blocks of the chain.

For example, if in the aforesaid processes in accordance with the invention a mixture of propylene and ethylene oxide is used as epoxide in the first reaction then in some blocks of the PC chain each Re will be H (ethylene oxide being the reagent generating such a PC blocks); whereas in other blocks of the PC chain one of the Re groups will be methyl (propylene oxide being the reagent generating such a PC section or block). The same applies *mutatis mutandis* in relation to the PE chain.

Also provided in accordance with the invention is the use of the aforesaid surface-active agents: as agrichemical, cosmetic or pharmaceutical adjuvants, excipients or auxiliaries; for the preparation or functionalisation of low-foaming detergents/cleaners, institutional cleaning & sanitation products, industrial cleaning products, personal care products, adhesives, metal working fluids, paints & coatings, as auxiliary or other reagents or excipients in the construction, mining and oilfield industries, as preparatory or functional ingredients in microcapsules, batteries, crystal growth modifiers, bio-control agents, demulsifiers, froth flotation systems, textiles, water treatment coatings, and in the processing of foods & beverages.

DESCRIPTION OF EMBODIMENTS

Preferably the surface-active agent has greater than 5 wt% CO₂ incorporation, greater than 10wt% CO₂ incorporation, more typically, greater than 15wt% CO₂ incorporation, greater than 20wt% CO₂ incorporation, or greater than 21wt% CO₂ incorporation. Preferably the surface-active agent has 5 to 40wt% CO₂ incorporation, 10 to 40wt% CO₂ incorporation, 15 to 40wt% CO₂ incorporation, 20 to 40wt% CO₂ incorporation, typically, 10 to 35wt% CO₂ incorporation, more typically, 15 to 30wt% CO₂ incorporation.

It will be appreciated that when surface-active agent is a block copolymer (i.e. when Q is other than zero) the carbonate block of the block co-polymer is hydrophobic and the ether blocks are hydrophilic. Tailoring the relative ratios of the two blocks will change the properties of the co-polymer to result in surface-active agents that can be adapted for end use.

It will also be appreciated that regardless of whether the surface-active agent of the invention is a block copolymer, the hydrophobicity of the polymer chain may be adjusted by the incorporation of ether linkages into the PC blocks and/or by the incorporation of carbonate linkages into the PE blocks (when present).

The epoxide used in the production of both the polycarbonate and polyether sections is independently selected from ethylene oxide (EO), propylene oxide (PO), butylene oxide, pentylene oxide, hexylene oxide, glycidyl ethers, glycidyl esters or glycidyl carbonates, or a mixture of two or more thereof. Preferably in generation of the polycarbonate constituents the epoxide is ethylene oxide, propylene oxide, butylene oxide or a mixture thereof, preferably ethylene oxide or propylene oxide. Preferably in generation of the polyether constituents the epoxide is ethylene oxide or propylene oxide or a mixture thereof, preferably ethylene oxide or propylene oxide, typically ethylene oxide.

It will also be appreciated that when a mixture of epoxides is used the epoxides will typically be statistically distributed along the polymer backbone.

Thus, when a mixture of epoxides is used the polycarbonate and the polyether chains respectively may be referred to as a random copolymer or a statistical copolymer.

- 5 The identity of R^{e1} , R^{e2} , R^{e3} , R^{e4} , $R^{e1'}$, $R^{e2'}$, $R^{e3'}$, and $R^{e4'}$ will depend on the nature of the epoxide used to prepare the polycarbonate or polyether. However, when one of R^{e1} to R^{e4} or one of $R^{e1'}$ to $R^{e2'}$ is methyl, ethyl, propyl, butyl, or an ether, ester or carbonate group the remaining three groups are H. Preferably R^{e1} , R^{e2} , R^{e3} , R^{e4} , $R^{e1'}$, $R^{e2'}$, $R^{e3'}$, and $R^{e4'}$ are H.

- 10 It will also be appreciated that if a mixture of epoxides are used, then each occurrence of R^{e1} and/or R^{e2} (or R^{e3} and/or R^{e4} , $R^{e1'}$ and/or $R^{e2'}$ and $R^{e3'}$ and/or $R^{e4'}$) may not be the same, for example if a mixture of ethylene oxide and propylene oxide are used in the PC constituent, R^{e1} (or R^{e3}) may be independently hydrogen or methyl, and R^{e2} (or R^{e4}) may be independently hydrogen or methyl.

- 15 The skilled person will understand that when the epoxide is asymmetric, the adjacent epoxide monomer units in the backbone may be head-to-tail linkages, head-to-head linkages, or tail-to-tail linkages.

Preferably, the surface-active agent has a molecular weight (M_n) in the range of from about 300 to 20,000 Da, more preferably in the range of from about 400 to 12000 Da, most preferably from about 1000-8000 Da.

- 20 In a block copolymer the or each polycarbonate chain or block of the surface-active agent preferably has a molecular weight (M_n) in the range of from about 200 to 5000 Da, more preferably in the range of from about 200 to 4000 Da, most preferably from about 300 to 3000 Da, especially from about 500 to 2000 Da.

- 25 When present the or each polyether chain or block of the surface-active agent preferably has a molecular weight (M_n) in the range of from about 100 to 20,000 Da, more preferably of from about 200 to 10,000 Da, most preferably from about 200 to 6000 Da.

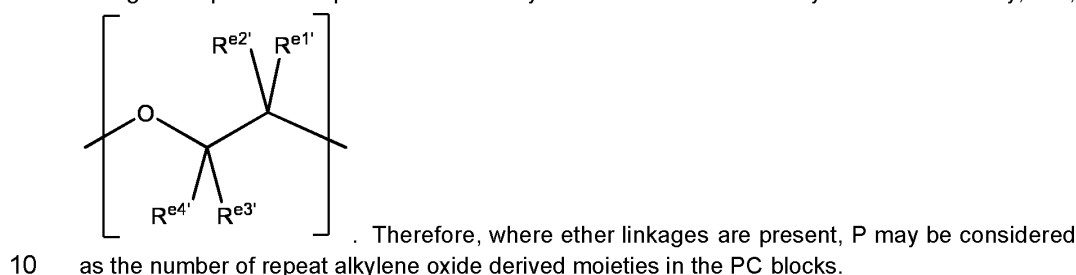
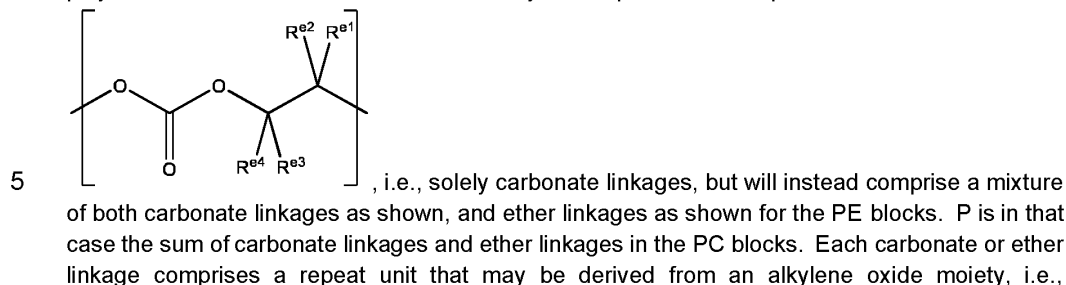
- 30 The M_n and hence the PDI of the polymers produced by the processes of the invention may be measured using Gel Permeation Chromatography (GPC). For example, the GPC may be measured using an Agilent™ 1260 Infinity GPC machine with two Agilent™ PLgel μ -m mixed-D columns in series. The samples may be measured at room temperature (293K) in THF with a flow rate of 1mL/min against narrow polystyrene standards (e.g., polystyrene low EasiVials supplied by Agilent™ Technologies with a range of M_n from 405 to 49,450 g/mol). Optionally, the samples may be measured against poly(ethylene glycol) standards, such as polyethylene glycol EasiVials supplied by Agilent™ Technologies.

- 35 The polycarbonate blocks of the surface-active agent may have at least 50% carbonate linkages, preferably at least 60% carbonate linkages, preferably at least 70% carbonate linkages, preferably at least 76% carbonate linkages, preferably at least 80% carbonate linkages, more preferably at least 85% carbonate linkages, at least 90% carbonate linkages or at least 95% carbonate linkages.

- 40 The polycarbonate blocks of the surface-active agent may also comprise ether linkages. The polycarbonate blocks may have less than 50% ether linkages, preferably less than 40% ether linkages, preferably less than 30% ether linkages, preferably less than 24% ether linkages, preferably less than 20% ether linkages, more preferably less than 15% ether linkages, less than

10% ether linkages, less than 5% ether linkages, less than 3% ether linkages or less than 1% ether linkages.

For the avoidance of doubt, where the polycarbonate blocks comprise ether linkages, the polycarbonate blocks will not solely comprise P repeat units of formula



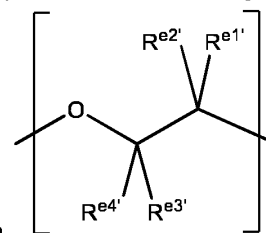
It will be apparent that when Q is zero the surface-active agent of the invention comprises an ionic polycarbonate, which may (or may not) incorporate ether linkages as random or statistical linkages in the polycarbonate chain.

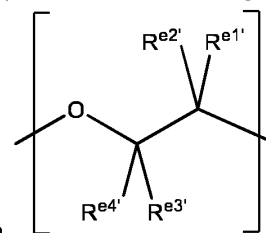
15 Optionally, the polycarbonate blocks may be generally alternating polycarbonate residues. If the epoxide is asymmetric, then the polycarbonate may have between 0-100% head to tail linkages, preferably between 40-100% head to tail linkages, more preferably between 50-100%. The polycarbonate may have a statistical distribution of head to head, tail to tail and head to tail linkages in the order 1:2:1, indicating a non-stereoselective ring opening of the epoxide, or it may preferentially make head to tail linkages in the order of more than 50%, optionally more than 60%,
20 more than 70%, more than 80%, or more than 90%.

Optionally, the polyether blocks comprises only ether linkages. Typically, the or each polyether chain or block is at least 90% derived, typically, at least 95% derived, more typically, at least 99%, most typically, 100% derived from epoxides.

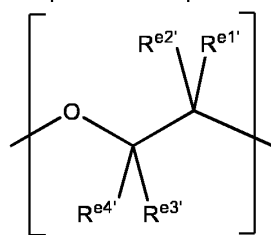
25 Typically, the polyether blocks have less than 40% carbonate linkages, typically, less than 30% carbonate linkages, typically, less than 20% carbonate linkages, more typically, less than 10% carbonate linkages, most typically less than 5%, less than 2% or less than 1% carbonate linkages. The polyether blocks may have 0% carbonate linkages. For example, the polyether blocks may have from about 0% to about 40% carbonate linkages, from about 0% to about 30% carbonate linkages, from about 0% to about 20% carbonate linkages, from about 0% to about 10% carbonate linkages,
30 linkages, from about 0% to about 5% carbonate linkages, from about 0% to about 2% carbonate linkages, or from about 0% to about 1% carbonate linkages.

For the avoidance of doubt, where the polyether blocks comprises carbonate linkages, the



polyether blocks will not solely comprise Q repeat units of formula , i.e., solely ether linkages, but will instead comprise a mixture of both ether linkages as shown, and carbonate linkages as shown for the PC blocks. Q is in that case the sum of ether linkages and carbonate linkages in the or each PE block in question. Each ether or carbonate linkage comprises a repeat unit that may be derived from an alkylene oxide moiety, i.e.,

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. Therefore, where carbonate linkages are present in the PE blocks, Q may be considered as the number of repeat alkylene oxide derived moieties in the PE block in question.

- 10 Typically, the polycarbonate blocks are derived from epoxide and CO₂. More typically, epoxide and CO₂ provide at least 70% of the residues in each chain or block, especially, at least 80% of the residues in each chain or block, more especially, at least 90% of the residues in each chain or block. Most especially, in the polycarbonate blocks at least 95% of the residues in each chain or block are residues of epoxide and CO₂. Most typically, the polycarbonate blocks include
- 15 ethylene oxide and/or propylene oxide residues and optionally butylene oxide. At least 30% of the epoxide residues of the polycarbonate blocks may be ethylene oxide or propylene oxide residues, typically, at least 50% of the epoxide residues of the polycarbonate blocks are ethylene oxide or propylene oxide residues, more typically, at least 75% of the epoxide residues of the polycarbonate blocks are ethylene oxide or propylene oxide residues, most typically, at least 90%
- 20 of the epoxide residues of the polycarbonate blocks are ethylene oxide or propylene oxide residues.

Typically, the polycarbonate blocks are derived from CO₂ i.e., the carbonates incorporate CO₂ residues. Typically, the polycarbonate blocks have between 70-100% carbonate linkages, more typically, 80-100%, most typically, 90-100%.

- 25 The value of P and the value of Q in Formula I may be adapted as appropriate for the end use, and Q may be zero in some applications.

The epoxide used in the process for manufacturing the surface-active agent of the invention may be selected from ethylene oxide, propylene oxide, butylene oxide, pentylene oxide, hexylene oxide, glycidyl ethers, glycidyl esters or glycidyl carbonates or a mixture of two or more thereof.

- 30 Typically, the epoxide is selected from ethylene oxide, propylene oxide or a mixture thereof, preferably ethylene oxide.

In the inventive process the carbonate catalyst may be heterogeneous or homogeneous.

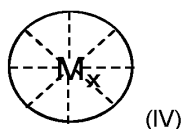
The carbonate catalyst may be a mono-metallic, bimetallic, or multi-metallic homogeneous complex or it may be a non-metallic Lewis acid-base pair (for example based upon combination

of boranes and ammonium salts, as disclosed in patents WO2016203408, WO2020121262, WO2021005470). The carbonate catalyst may be a heterogeneous catalyst, such as a metal organic framework (MOF), which may be derived from metals such as scandium or aluminium, such as those described in WO2021123761.

- 5 The carbonate catalyst may comprise phenol or phenolate ligands.

Typically, the carbonate catalyst may be a bimetallic complex comprising phenol or phenolate ligands. The two metals may be the same or different.

The carbonate catalyst may be a catalyst of formula (IV):



- 10 wherein:

M is a metal cation represented by $M-(L)_v$;

x is an integer from 1 to 4, preferably x is 1 or 2;



is a multidentate ligand or plurality of multidentate ligands;

- 15 L is a coordinating ligand, for example, L may be a neutral ligand, or an anionic ligand that is capable of ring-opening an epoxide;

v is an integer that independently satisfies the valency of each M, and/or the preferred coordination geometry of each M or is such that the complex represented by formula (IV) above has an overall neutral charge. For example, each v may independently be 0, 1, 2 or 3, e.g., v may be 1 or 2. When $v > 1$, each L may be different.

- 20 The term multidentate ligand includes bidentate, tridentate, tetradentate and higher dentate ligands. Each multidentate ligand may be a macrocyclic ligand or an open ligand.

- Such catalysts include those in WO2010022388 (metal salens and derivatives, metal porphyrins, corroles and derivatives, metal tetraaza annulenes and derivatives), WO2010028362 (metal salens and derivatives, metal porphyrins, corroles and derivatives, metal tetraaza annulenes and derivatives), WO2008136591 (metal salens), WO2011105846 (metal salens), WO2014148825 (metal salens), WO2013012895 (metal salens), EP2258745A1 (metal porphyrins and derivatives), JP2008081518A (metal porphyrins and derivatives), CN101412809 (metal salens and derivatives), WO2019126221 (metal aminotriphenol complexes), US9018318 (metal beta-diiminate complexes), US6133402A (metal beta-diiminate complexes) and US8278239 (metal salens and derivatives), the entire contents of which, especially, insofar as they relate to suitable carbonate catalysts for the reaction of CO_2 and epoxide, in the presence of a starter and optionally a solvent as defined herein are incorporated herein by reference.
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- Preferably the carbonate catalysts are bimetallic phenolate catalysts. Suitable bimetallic phenolate complexes are those described in WO2009/130470, WO2013/034750, WO2016/012786, WO2016/012785, WO2012037282 and WO2019048878A1, the entire contents of which, especially, insofar as they relate to suitable carbonate catalysts for the reaction
- 35

of CO₂ and epoxide, in the presence of a starter and optionally a solvent as defined herein are incorporated herein by reference.

The ether catalyst may be any catalyst suitable for polymerising epoxides to form polyethers. Suitable ether catalysts include DMC catalysts, metal alkoxides, boron-based catalysts such as BF₃ or BH₃, anionic catalysts such as KOH, cationic, acidic or superacidic catalysts (such as HSBF₆, CF₃SO₃H), PF₅, activated monomer catalysts, organic catalysts such as imidazole or phosphazene reagents and metallosalenate catalysts. Preferably the ether catalyst is a DMC catalyst. Examples of DMC catalysts which can be used in the process of the invention include those described in US 3,427,256, US 5,536,883, US 6,291,388, US 6,486,361, US 6,608,231, US 7,008,900, US 5,482,908, US 5,780,584, US 5,783,513, US 5,158,922, US 5,693,584, US 7,811,958, US 6,835,687, US 6,699,961, US 6,716,788, US 6,977,236, US 7,968,754, US 7,034,103, US 4,826,953, US 4,500 704, US 7,977,501, US 9,315,622, EP-A-1568414, EP-A-1529566, and WO 2015/022290, the entire contents of which are incorporated by reference.

The ratio of the carbonate catalyst to the ether catalyst may be in the range of from about 300:1 to about 1:100, for example, from about 120:1 to about 1:75, such as from about 40:1 to about 1:50, e.g. from about 30:1 to about 1:30 such as from about 20:1 to about 1:1, for example from about 10:1 to about 2:1, e.g. from about 5:1 to about 1:5. These ratios are mass ratios.

The process may be carried out in a one pot reactor or may be a dual reactor process (multiple reaction system) as aforesaid.

Typically, the reaction mixture from the first step contains less than 5% CO₂ by weight of the reaction mixture prior to the second step, preferably less than 2.5%, such as less than 1.0%, less than 0.5% or less than 0.1%. Typically, the second step is carried out without the independent addition of CO₂, however it can be carried out under a pressure of CO₂. The or each polyether chain or block produced in the second step may have less than 40% carbonate linkages, preferably less than 30% carbonate linkages or less than 20% carbonate linkages, more preferably less than 10%, less than 5%, less than 2% or less than 1% carbonate linkages. Preferably the or each polyether chain or block produced in the second step is substantially free from carbonate linkages.

Typically, therefore the second step is carried out substantially in the absence of CO₂.

Accordingly, by substantially in the absence of CO₂ is meant that the second step is carried out in the presence of less than 4% CO₂ by weight, preferably less than 2%, such as less than 1.0%, less than 0.5% or less than 0.1% by weight of total reactants, catalyst, and products in the second step.

Adding the components in the separate steps may be useful to increase activity of the catalysts and may lead to a more efficient process, compared with a process in which all of the materials are provided at the start of the process. Large amounts of some of the components present throughout the process may reduce efficiency of the catalysts. Reacting this material in separate steps may prevent this reduced efficiency of the catalysts and/or may optimise catalyst activity. The reaction conditions of each step can be tailored to optimise the reactions for each catalyst.

The ether catalyst may be pre-activated prior to addition in the second step. Such pre-activation may be achieved by mixing one or both catalysts with epoxide (and optionally other components). Pre-activation of the ether catalyst is useful as it enables safe control of the reaction (preventing uncontrolled increase of unreacted monomer content) and removes unpredictable activation periods.

Although typically any residual CO₂ from the first step may be removed from the crude reaction product of the first step prior to commencement of the second step such that the second step is carried out without CO₂, it will be appreciated that a small amount of CO₂ may be present in the reaction mixture in the second step as an unused reagent of the first step. Alternatively, both
5 steps may be carried out under a pressure of CO₂.

The reactions of the present invention may be carried out in the presence of a solvent; however, it will also be appreciated that the processes may also be carried out in the absence of a solvent. When a solvent is present, it may be toluene, hexane, t-butyl acetate, diethyl carbonate, dimethyl carbonate, dioxane, dichlorobenzene, methylene chloride, propylene carbonate, ethylene
10 carbonate, acetone, ethyl acetate, propyl acetate, n-butyl acetate, tetrahydrofuran (THF), etc. The solvent may be toluene, hexane, acetone, ethyl acetate and n-butyl acetate.

Adding the components in the separate reactions and reactors may be useful to increase activity of the catalysts and may lead to a more efficient process, compared with a process in which all of the materials are provided at the start of one reaction. Large amounts of some of the components present throughout the reaction may reduce efficiency of the catalysts. Reacting this material in
15 separate reactors may prevent this reduced efficiency of the catalysts and/or may optimise catalyst activity. The reaction conditions of each reactor can be tailored to optimise the reactions for each catalyst.

Additionally, not loading the total amount of each component at the start of the reaction and having the catalyst for the first reaction in a separate reactor to the catalyst for the second reaction, may lead to even catalysis, and more uniform polymer products. This in turn may lead to polymers having a narrower molecular weight distribution, desired ratio, and distribution along the chain of ether to carbonate linkages, and/or improved stability.
20

Having the reactions with the two different catalysts separate and mixing only certain components in the first reaction and adding the remainder in the second reaction may also be useful, for example by adding a pre-activated ether catalyst or adding the reaction mixture to a pre-activated ether catalyst.
25

Preferred ether catalysts and carbonate catalysts are as for the second aspect of the invention.

The first reaction may be carried out in more than one reactor that feeds the crude reaction mixture into the second reaction, and reactor, continuously. Preferably, the second reaction is run in a continuous mode.
30

The product of the first reaction may be stored for subsequent later use in the second reactor.

The two reactors may be located in a series, or the reactors may be nested. Each reactor may individually be a stirred tank reactor, a loop reactor, a tube reactor, or other standard reactor design.
35

Definitions

The term "alkyl," as used herein, unless otherwise defined refers to saturated, linear- or branched-chain hydrocarbon radicals derived by removal of a single hydrogen atom from an aliphatic moiety. An alkyl group may be a "C₁₋₂₀ alkyl group", that is an alkyl group that is a straight or
40 branched chain with 1 to 20 carbons. The alkyl group therefore has 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19 or 20 carbon atoms. Preferably, an alkyl group is a C₁₋₁₅ alkyl, preferably a C₁₋₁₂ alkyl, more preferably a C₁₋₁₀ alkyl, even more preferably a C₁₋₈ alkyl, even more preferably a C₁₋₆ alkyl group.

- Unless defined otherwise herein, an ester group is optionally $-\text{OC}(\text{O})\text{R}^1-$ or $-\text{C}(\text{O})\text{OR}^1-$ wherein R^1 can be an aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl group. R^1 may be unsubstituted aliphatic, alicyclic or aryl. Optionally R^1 is methyl, ethyl, propyl, or phenyl. The ester group may be terminated by an aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl group. It will be appreciated that if R^1 is hydrogen, then the group defined by $-\text{OC}(\text{O})\text{R}^1-$ or $-\text{C}(\text{O})\text{OR}^1-$ will be a carboxylic acid group.

- A carbonate group is optionally $-\text{OC}(\text{O})\text{OR}^2$, wherein R^2 can be hydrogen, an aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl group. R^2 may be optionally substituted aliphatic, alicyclic or aryl. Optionally R^2 is hydrogen, methyl, ethyl, propyl, butyl (for example n-butyl, isobutyl, or tert-butyl), phenyl, pentafluorophenyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, trifluoromethyl, cyclohexyl, benzyl or adamantyl. Optionally R^2 is methyl, ethyl, propyl, or phenyl. It will be appreciated that if R^2 is hydrogen, then the group defined by $-\text{OC}(\text{O})\text{OR}^2$ will be a carbonic acid group.

- A carbonate functional group is $-\text{OC}(\text{O})\text{O}-$ and may be derived from a suitable source. Generally, it is derived from CO_2 .

- An ether group is optionally $-\text{OR}^3$ wherein R^3 can be an aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl group. R^3 may be unsubstituted aliphatic, alicyclic or aryl. Optionally R^3 is methyl, ethyl, propyl, butyl (for example n-butyl, isobutyl, or tert-butyl), phenyl, pentafluorophenyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, trifluoromethyl or adamantyl. Optionally R^3 is methyl, ethyl, propyl, or phenyl.

- As used herein, the term "optionally substituted" means that one or more of the hydrogen atoms in the optionally substituted moiety is replaced by a suitable substituent. Unless otherwise indicated, an "optionally substituted" group may have a suitable substituent at each substitutable position of the group, and when more than one position in any given structure may be substituted with more than one substituent selected from a specified group, the substituent may be either the same or different at every position. Combinations of substituents envisioned by this invention are preferably those that result in the formation of stable compounds. The term "stable", as used herein, refers to compounds that are chemically feasible and can exist for long enough at room temperature i.e. (16-25°C) to allow for their detection, isolation and/or use in chemical synthesis.

- Substituents may be depicted as attached to a bond that crosses a bond in a ring of the depicted molecule. This convention indicates that one or more of the substituents may be attached to the ring at any available position (usually in place of a hydrogen atom of the structure). In cases where an atom of a ring has two substitutable positions, two groups (either the same or different) may be present on that atom.

- Preferred optional substituents for use in the present invention include, but are not limited to, halogen, hydroxy, nitro, carboxylate, carbonate, alkoxy, aryloxy, alkylthio, arylthio, heteroaryloxy, alkylaryl, amino, amido, imine, nitrile, silyl, silyl ether, ester, sulphoxide, sulphonyl, acetylide, phosphinate, sulphonate or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl groups (for example, optionally substituted by halogen, hydroxy, nitro, carbonate, alkoxy, aryloxy, alkylthio, arylthio, amino, imine, nitrile, silyl, sulphoxide, sulphonyl, phosphinate, sulphonate or acetylide).

- Particularly preferred optional substituents for use in the present invention are selected from nitro, C_{1-12} alkoxy (e.g., OMe, OEt, OⁱPr, OⁱBu, O^tBu), C_{6-18} aryl, C_{2-14} heteroaryl, C_{2-14} heteroalicyclic, C_{1-6} alkyl, C_{1-6} haloalkyl, F, Cl, Br, I and OH, wherein in each of said C_{1-12} alkoxy, C_{6-18} aryl, C_{2-14}

heteroaryl, C₂₋₁₄ heteroalicyclic, C₁₋₆ alkyl and C₁₋₆ haloalkyl group may be optionally substituted by an optional substituent as defined herein.

The term “continuous” used herein can be defined as the mode of addition of materials or may refer to the nature of the reaction method as a whole.

- 5 In terms of continuous mode of addition, the relevant materials are continually or constantly added during the course of a reaction. This may be achieved by, for example, adding a stream of material with either a constant flow rate or with a variable flow rate. In other words, the one or more materials are added in an essentially non-stop fashion. It is noted, however, that non-stop addition of the materials may need to be briefly interrupted for practical considerations, for example to refill
10 or replace a container of the materials from which these materials are being added.

- In terms of a whole reaction being continuous, the reaction may be conducted over a long period of time, such as a number of days, weeks, months, etc. In such a continuous reaction, reaction materials may be continually topped-up and/or products of the reaction may be tapped-off. It will be appreciated that although catalysts may not be consumed during a reaction, catalysts may in
15 any case require topping-up, since tapping-off may deplete the amount of catalyst present.

A continuous reaction may employ continuous addition of materials.

A continuous reaction may employ a discontinuous (i.e., batch-wise or semi batch-wise) addition of materials

- 20 The term series used herein refers to when two or more reactors are connected so that the crude reaction mixture can flow from the first reactor to the second reactor.

The term nested used herein refers to when two or more reactors are configured so that one is located within the other. For example, in the present invention, when the second reactor is located inside the first reactor, allowing the conditions of both reactors to influence the other.

Examples

25

Example 1

Non-ionic precursors of compounds in accordance with the invention were prepared from monofunctional starter compounds as follows:

- 30 Mono-ol starter was added to a 100mL Parr™ high pressure reactor system. The vessel was dried by heating to 100 °C under vacuum for 60 mins before cooling and filling with low pressure CO₂. Catalyst (1), prepared according to Example 2 of WO2017/037441, was added.

To the mixture was added epoxide (propylene oxide [PO], or ethylene oxide [EO]). The mixture was stirred and pressurized to approximately half target-pressure. The mixture was then heated to target temperature and pressure held at constant temperature and target pressure.

- 35 At the end of the desired reaction time, the mixture was cooled to <10 °C and vented through an acid scrubber system.

Table 1; Example 1; experimental conditions/results

Entry	Cat 1 / g	Starter	Starter mass / g	Epoxide / mL	Temp / °C	Pressure / barg	Mn (GPC)	PDI (GPC)	<i>p</i>
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1	0.28	EtOH	1.1	EO: 30	75	20	1000	1.09	13
2	0.5	EtOH	7	EO: 100	71	20	500	1.07	6
3	0.18	EtOH	2.6	PO: 40	50	20	600	1.03	7

Example 2

Reaction 1:

- 5 Non-ionic precursors of compounds in accordance with the invention were prepared from monofunctional starter compounds as follows:

Mono-ol starter was added to a 100 mL Parr™ high pressure reactor system. The vessel was dried by heating to 100 °C under vacuum for 60 mins before cooling and filling with low pressure CO₂. Catalyst (1) prepared according to Example 2 of WO2017/037441 was added.

- 10 To the mixture was added epoxide (propylene oxide [PO] or ethylene oxide [EO]). The mixture was stirred and pressurized to approximately half target-pressure. The mixture was then heated to target temperature and pressure held at constant temperature and target pressure.

At the end of the desired reaction time, the mixture was cooled to <10 °C and vented through an acid scrubber system.

Reaction 2:

- 15 Pre-dried mono-ol starter and a DMC composed of zinc hexacyanocobaltate and tert-butyl alcohol were added to a 100 mL Parr™ high pressure reactor system. The vessel was held under vacuum for approximately 2 mins before filling with low pressure N₂ and then anhydrous ethyl acetate (15 mL).

- 20 This vessel was then heated with 130 °C with stirring and the DMC activated with 2 portions of approximately 0.3 g epoxide (EO or PO). After activation (as evidenced by pressure drops) the external heater was removed, optionally the reactor could be pressurized with CO₂, then the mixture was cooled to the target addition temperature.

- 25 Upon reaching the target temperature, the mixture from Reaction 1 and epoxide (EO or PO) was added onto the active DMC system over approximately 60-90 mins. Once addition of the mixture was complete, the mixture was left to “cook-out” for several hours before cooling, venting and taking samples for analysis by NMR and GPC.

Table 2; Example 2; Reaction 1; experimental conditions/results

Entry	Cat 1 / g	Starter	Starter mass / g	Epoxide / mL	Temp / °C	Pressure / barg	Mn (GPC)	PDI (GPC)
1	0.28	EtOH	1.1	EO: 30	75	20	1400	1.09
2	1.3	EtOH	16	PO: 300	71	20	600	1.07

Table 3; Example 2; Reaction 2; experimental conditions

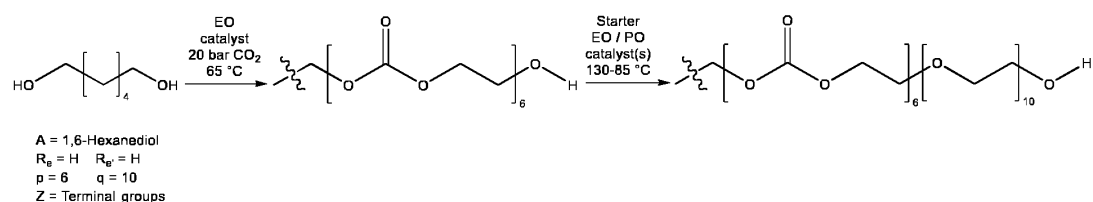
Entry	DMC / mg	Starter	Starter mass / g	Epoxide	Feed temperature / °C	Reactor gas	Reactor Pressure / barg
1	15	1-Dodecanol	0.85	EO	85	N ₂	N/A
2	50	PEG-550	0.7	PO	85	N ₂	N/A

Table 4; Example 2; Reaction 2; results

Entry	Mn (GPC)	PDI (GPC)	CO ₂ wt%	<i>p</i>	<i>q</i>
1	1800	1.23	29	13	9
2	1300	1.1	27	8	8

5 Example 3

Non-ionic precursors of compounds in accordance with the invention were prepared by a sequential reaction scheme as follows:



Reaction 1:

- 10 Diol starter was charged to the cold, dry base of a 100 mL Parr™ high pressure reactor system. The charged vessel was dried by heating to 100 °C under vacuum (approx. 1 mbar) and held for 60 mins before cooling and filling with low pressure CO₂.

- Catalyst (1) (prepared according to Example 2 of WO2017/037441) was added to the reactor. This was vacuum-purged for <5 mins at room temperature before back-filling with low pressure CO₂.

- To the mixture was added EO. The mixture was stirred and pressurized to approximately half target-pressure. The mixture was then heated to target temperature and pressure held at constant temperature and target pressure using a mass-flow controller.

- 20 At the end of the desired reaction time, the mixture was cooled to <10 °C and vented through an acid scrubber system. EO and anhydrous ethyl acetate were added to the cold stirring mixture before transferring into an intermediate holding vessel.

Reaction 2:

Pre-dried mono-ol starter and a DMC composed of zinc hexacyanocobaltate and tert-butyl alcohol was added to the cold, base of a 100 mL Parr™ high pressure reactor system. The starter+base

were held under vacuum (approx. 1 mbar) for approximately 2 mins before filling with low pressure N₂ and then anhydrous ethyl acetate (15 mL) via syringe.

This DMC/starter/ethyl acetate mixture was then heated with 130 °C with stirring and the DMC activated with 2 slugs of approximately 0.3 g PO (1 mL/min set-point). After activation (as evidenced by pressure drops) the external heater was removed, optionally the reactor could be pressurized with CO₂, then the mixture was cooled to the target addition temperature whilst continually slowly adding PO (set 0.1 mL/min) [approximately 1.2 g PO total].

Upon reaching the target temperature, the mixture from Reaction 1 was added onto the active DMC system over approximately 60-90 mins (semi-batch fashion). Once addition of the mixture was complete, the mixture was left to “cook-out” for several hours before cooling, venting and taking samples for analysis by NMR and GPC.

The results are displayed in Tables 5 to 7 below.

Table 5; Example 3; Reaction 1; experimental conditions/results

Entry	Econic Cat / g	Starter	Starter mass / g	EO / mL	Temp / °C	Pressure / barg	Time / h
1	0.18	1,6-Hexanediol	2.8	30	75	20	16
2	0.18	1,6-Hexanediol	3.0	30	75	20	16
3	0.22	1,6-Hexanediol	2.7	30	75	20	16

Table 6; Example 3; Reaction 2; experimental conditions

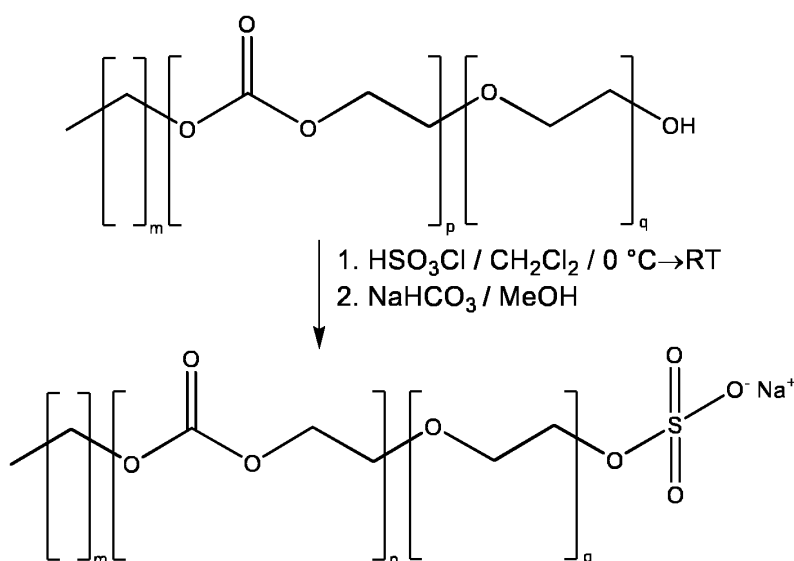
Entry	DMC / mg	Starter	Starter mass / g	Feed temperature / °C	Reactor gas	Reactor Pressure / barg
1	9	PPG400	0.4	85	N ₂	N/A
2	9	PPG400	0.4	85	N ₂	N/A
3	9	PPG400	0.4	85	N ₂	N/A

Table 7: Example 3; Reaction 2; results

Entry	Conversion / %	Mn	PDI (GPC)	CO ₂ wt%	<i>p</i>	<i>q</i>
1	100	980	1.04	17	4	12
2	100	1100	1.08	20	6	15
3	100	1050	1.08	24	6	10

Example 4

Anionic surface-active agents in accordance with the invention are prepared from the non-ionic precursor compounds prepared above in Examples 1-3 in accordance with the following scheme:



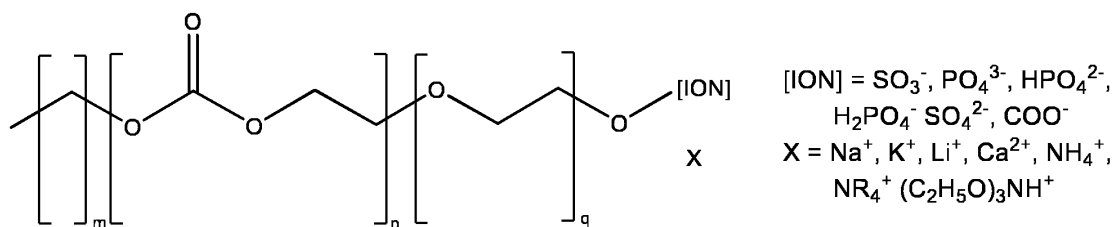
Note (for each of Examples 4 to 10):

- m is representative of the chain length of the starter compound
- in the exemplified schemes only one polymer chain extending from the starter compound is shown. It will be apparent that one or more further polymer chains may be present, depending on the functionality of the starter.
- in other embodiments of the invention, q may be zero.

To poly(carbonate ether) polymer in anhydrous CH_2Cl_2 (0.5 g/mL) at $0\text{ }^\circ\text{C}$ is added dropwise chlorosulphonic acid (1 equiv.). The reaction mixture is warmed to RT and stirred overnight. The solvent concentrated to dryness. To the resultant polymer mixture is added 10% NaOH in EtOH (0.5 g/mL), which is stirred for 1 h. The resultant solid is filtered and washed with MeOH before being dried under vacuum to yield the sodium salt of the sulphonated polymer.

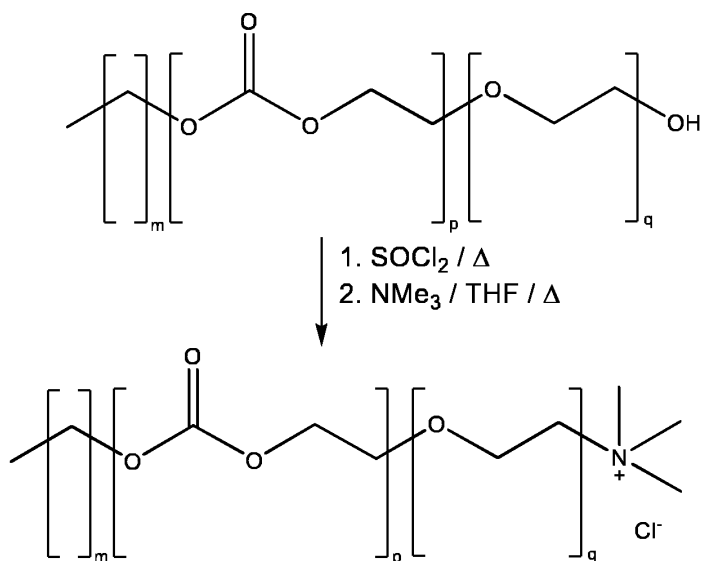
Sulphation of the polymer may also be performed using a SO_3 as the sulphating agent by one skilled in the art. Typically the alcohol terminated polymer is reacted with SO_3 in air at temperature, followed by neutralisation with a base, like NaOH or ammonia, in a continuous process.

Phosphorylation of the polymer may also be performed using techniques known by those skilled in the art. Typically, the alcohol terminated polymer is reacted with polyphosphoric acid/phosphorous pentoxide under cooling conditions, followed by a period of heating. The phosphate salt can be obtained by basic treatment with, for example, NaOH or ammonia.



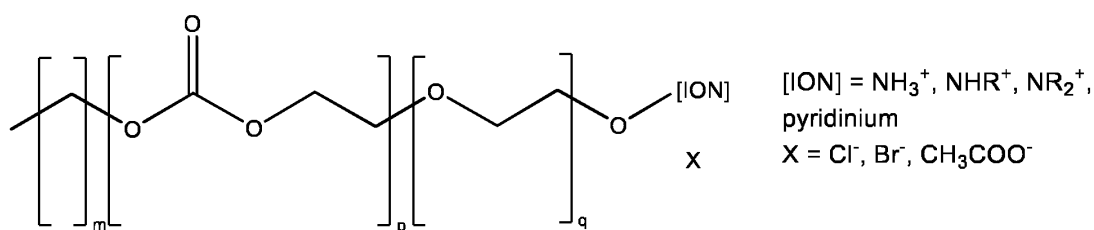
Example 5

Cationic surface-active agents in accordance with the invention are prepared from the non-ionic precursor compounds prepared above in Examples 1-3 in accordance with the following scheme:



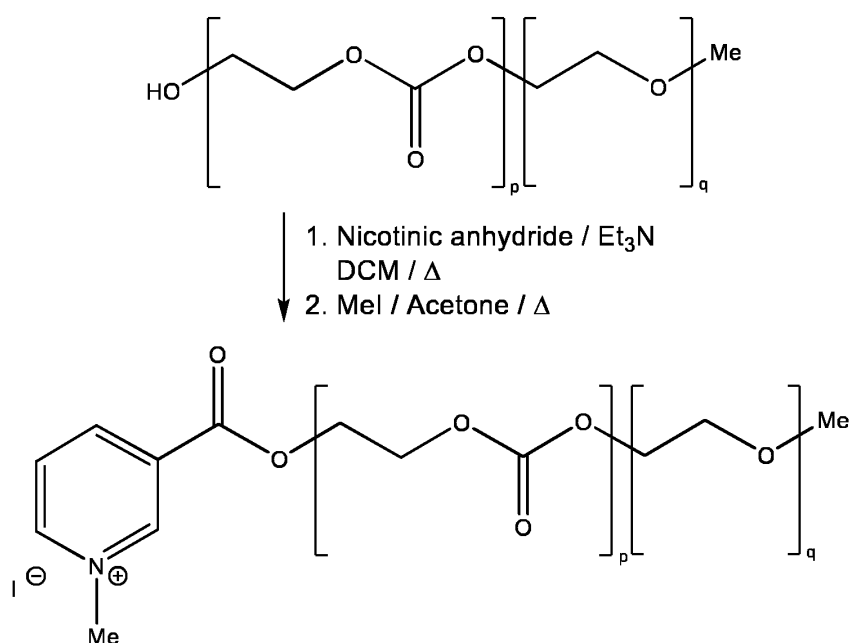
5 Note: q may be zero.

To poly(carbonate ether) polymer is added SOCl_2 (0.5 g/mL) and the reaction heated to reflux for 2 h, after which the mixture is concentrated to dryness and washed with toluene. The resultant polymer is dissolved in THF (0.5 g/mL) and trimethylamine (1 equiv.) and stirred at reflux overnight. The resultant solid is filtered and washed with EtOH before being dried under vacuum to yield the chloride salt of the cationic polymer.



Example 6

15 Cationic surface-active agents in accordance with the invention are prepared from the non-ionic precursor compounds prepared above in Examples 1-3 in accordance with the following scheme:

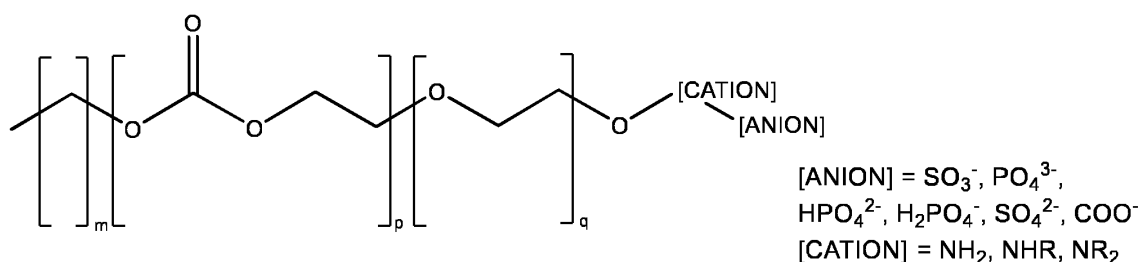


- The mono-ol product of Example 1 is dissolved in dichloromethane containing triethylamine (1.3 eq.) and nicotinic anhydride (1.05 eq.) and reacted at reflux for 16 h. The end-capped mono-ol is washed with water and brine, dried over sodium sulphate, and concentrated to dryness in vacuo to afford the desired precursor product. Ethylene carbonate by-product is removed using a Kugelrohr or short path evaporator (SPE). The precursor mono-ol is dissolved in acetone (0.05 g/mL) with methyl iodide (3 eq) and stirred at reflux for 1 h. After cooling to RT, the resultant salt is collected by filtration and washed with cold acetone to yield the cationic mono-ol.

10 Example 7

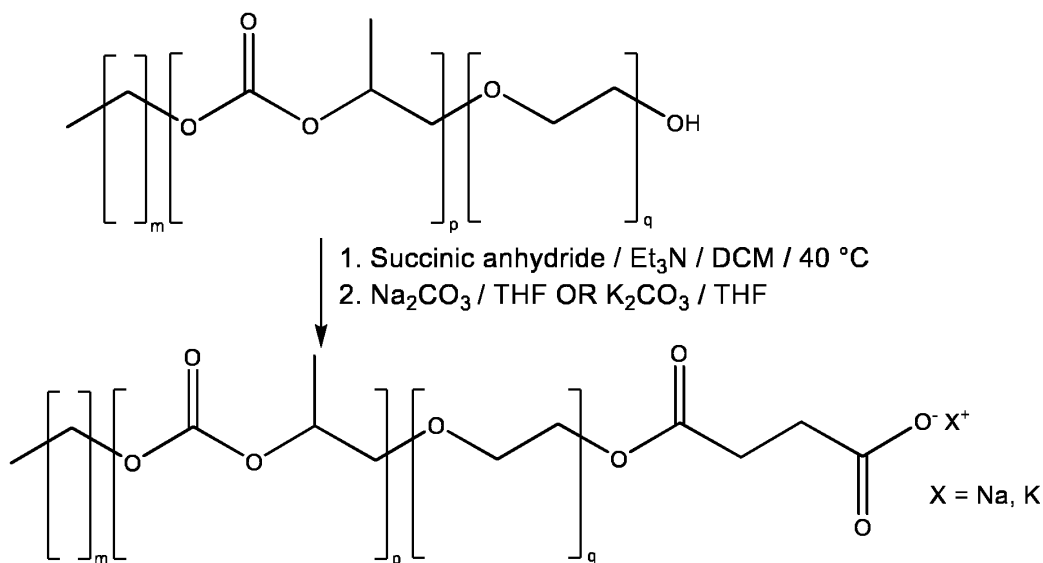
Zwitterionic surface-active agents in accordance with the invention are prepared from the non-ionic precursor compounds prepared above in Examples 1-3 in accordance with the following scheme:

- 15 The above Example 5 procedure is repeated with the incorporation of β-alanine (in place of trimethylamine) to generate a zwitterionic polymer.



20 Example 8

Anionic surface-active agents in accordance with the invention were prepared from the non-ionic precursor compounds prepared above in Examples 1-3 in accordance with the following scheme:



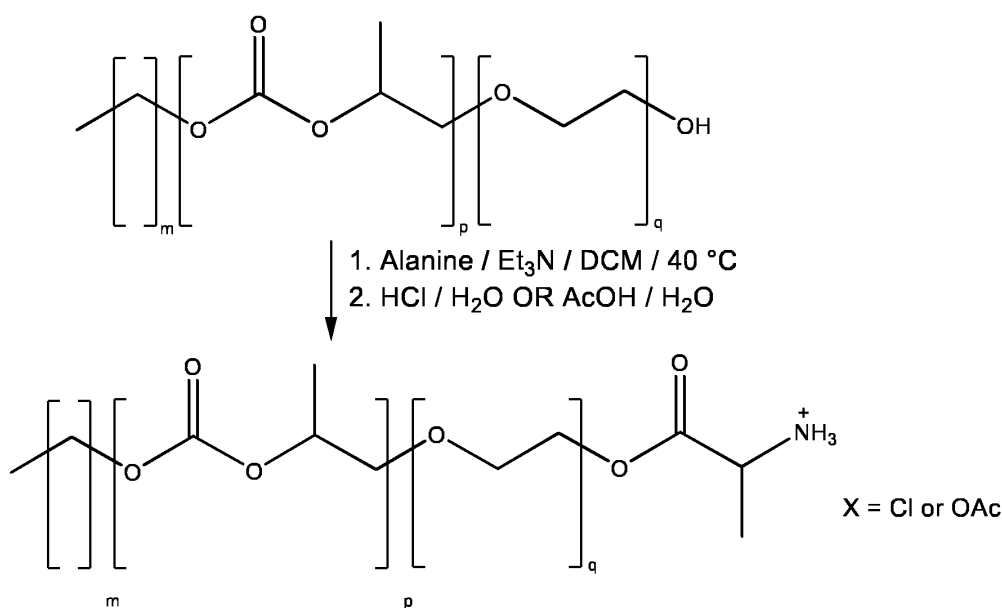
- 5 To polycarbonate polymer in DCM (0.5 g/mL) was added succinic anhydride (1.1 equiv.) and Et₃N (1.1 equiv.). The mixture was stirred at 40 °C overnight. The mixture was allowed to cool to room temperature and washed with deionised water (2 x 50 mL) and brine (2 x 50 mL). The organic solution was dried (MgSO₄) and concentrated by rotary evaporation. To this product was added either Na₂CO₃ or K₂CO₃ and the mixture stirred in THF (0.5 g/mL) at RT overnight. The sodium or potassium salts were isolated by concentrating the reaction mixture by rotary evaporation.
- 10

Table 8: Example 8; results

Entry	Counterion	Mn	CO ₂ wt%	<i>m</i>	<i>p</i>	<i>q</i>	Water soluble?
1	Na ⁺	940	33	2	7	0	Y
2	K ⁺	1000	31	2	7	0	Y
3	Na ⁺	1450	24	2	8	8	Y

Example 9

- 15 Cationic surface-active agents in accordance with the invention were prepared from the non-ionic precursor compounds prepared above in Examples 1-3 in accordance with the following scheme:



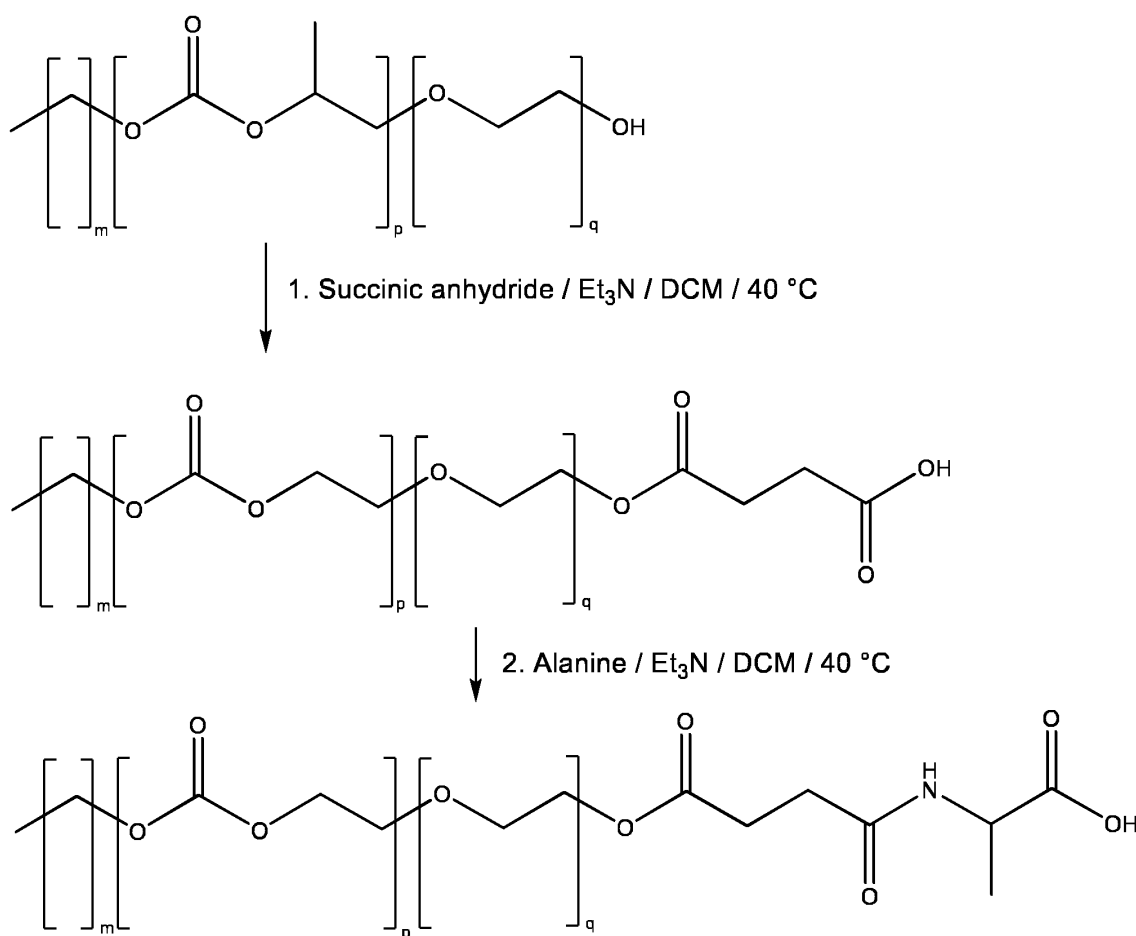
To polycarbonate polymer in DCM (0.5 g/mL) was added alanine (1.1 equiv.) and Et₃N (0.65 equiv.). The mixture was stirred at 40 °C overnight. The mixture was allowed to cool to room temperature and washed with deionised water (2 x 50 mL) and brine (2 x 50 mL). The organic solution was dried (MgSO₄) and concentrated by rotary evaporation. To this product was added HCl and the mixture stirred in H₂O (0.5 g/mL) at RT. The chloride salts were isolated by concentrating the reaction mixture by rotary evaporation.

Table 9: Example 9; results

Entry	Counterion	Mn	CO ₂ wt%	<i>m</i>	<i>p</i>	<i>q</i>	Water soluble?
1	Cl ⁻	830	37	2	7	0	Y
2	OAc ⁻	850	36	2	7	0	Y

Example 10

Zwitterionic surface-active agents in accordance with the invention are prepared from the non-ionic precursor compounds prepared above in Examples 1-3 in accordance with the following scheme:



5 To polycarbonate polymer in DCM (0.5 g/mL) was added succinic anhydride (1.1 equiv.) and Et₃N (1.1 equiv.). The mixture was stirred at 40 °C overnight. The mixture was allowed to cool to room temperature and washed with deionised water (2 x 50 mL) and brine (2 x 50 mL). The organic solution was dried (MgSO₄) and concentrated by rotary evaporation.

10 To the intermediate product in DCM (0.5 g/mL) was added alanine (1.1 equiv.) and Et₃N (0.65 equiv.). The mixture was stirred at 40 °C overnight. The mixture was allowed to cool to room temperature and washed with deionised water (2 x 50 mL) and brine (2 x 50 mL). The organic solution was dried (MgSO₄) and concentrated by rotary evaporation.

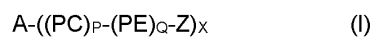
To this product was added either Na₂CO₃, K₂CO₃, HCl or acetic acid and the mixture stirred in THF (0.5 g/mL) at RT overnight. The respective anionic sodium and potassium, and cationic chloride and acetic salts, respectively, were isolated by concentrating the reaction mixture by rotary evaporation.

15 Table 10: Example 10; results

Entry	Counterion	Mn	CO ₂ wt%	<i>m</i>	<i>p</i>	<i>q</i>	Water soluble?
1	Na ⁺	910	34	2	7	0	Y
2	K ⁺	930	33	2	7	0	Y
3	Cl ⁻	930	33	2	7	0	Y
4	OAc ⁻	950	32	2	7	0	Y

CLAIMS

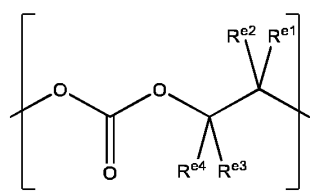
1. An ionic surface-active agent comprising a polycarbonate or poly(carbonate ether) of the formula I:



wherein:

A is derived from a functional starter compound;

PC represents a carbonate block with P repeat units of formula:

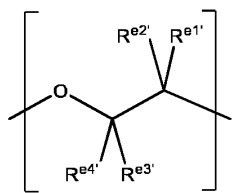


wherein:

R^{e1} , R^{e2} , R^{e3} , and R^{e4} are all H; or

one of R^{e1} , R^{e2} , R^{e3} , and R^{e4} is methyl, ethyl, propyl, butyl, or an ether, ester or carbonate group, and the remaining three of R^{e1} , R^{e2} , R^{e3} , and R^{e4} are all H;

PE represents a polyether block with Q repeat units of formula:



wherein:

$R^{e1'}$, $R^{e2'}$, $R^{e3'}$, and $R^{e4'}$ are all H; or

one of $R^{e1'}$, $R^{e2'}$, $R^{e3'}$, and $R^{e4'}$ is methyl, ethyl, propyl, butyl, or an ether, ester or carbonate group, and the remaining three of $R^{e1'}$, $R^{e2'}$, $R^{e3'}$, and $R^{e4'}$ are all H;

at least one Z is an ionic constituent;

wherein the value of the or each P is independently from 1 to 50;

wherein the value of the or each Q is independently from 0 to 50; and

X is 1 or more.

2. An ionic surface-active agent according to claim 1 wherein the polymeric chain(s) of the surface-active agent comprise a block copolymer comprising individual PC and PE blocks.
3. An ionic surface-active agent according to claim 2 wherein the PC blocks of a block copolymer may contain ether (PE) linkages, and the PE blocks (when present) of a block copolymer may contain carbonate (PC) linkages.
4. An ionic surface-active agent according to claim 2 or claim 3 wherein the polymeric chain(s) of the surface-active agent comprise a random copolymer comprising only PC blocks which incorporate ether (PE) linkages.
5. An ionic surface-active agent according to any one of claims 1 to 4 wherein at least one Z is anionic.
6. An ionic surface-active agent according to claim 5 wherein the at least one Z is selected from O-[ION], O-C(O)-[ION] and O-C(O)-O-[ION] wherein [ION] is selected from sulphates, sulphonates, phosphates, hydrogen and dihydrogen phosphates phosphites, hypophosphites, carboxylates, gluconates, and suitable combinations of two or more thereof.
7. An ionic surface-active agent according to any one of claims 1 to 4 wherein at least one Z is cationic.
8. An cationic surface-active agent according to claim 7 wherein the at least one Z is selected from [ION], O-[ION], O-C(O)-[ION] and O-C(O)-O-[ION] wherein [ION] is selected from nitrogen-containing moieties such as primary, secondary, tertiary or quaternary ammonium ions, pyridinium, pyrrolinium, pyrrolidinium, imidazolium, guanidinium, piperazinium, piperidinium, from phosphonium or sulphonium, or from any suitable combination of two or more thereof.
9. An ionic surface-active agent according to any one of claims 1 to 4 wherein at least one Z is zwitterionic.
10. An ionic surface-active agent according to claim 9 wherein the at least one Z is selected from O-[ANION]-[CATION], O-C(O)-[ANION]-[CATION]; O-C(O)-O-[ANION]-[CATION], [CATION]-[ANION], O-[CATION]-[ANION], O-C(O)-[CATION]-[ANION] and O-C(O)-O-[CATION]-[ANION], where [ANION] is selected from any suitable [ION] of claim 6, and wherein [CATION] is selected from any suitable [ION] of claim 8.
11. An ionic surface-active agent according to claim 5 or claim 6 provided in association with at least one cationic counterion.
12. An ionic surface-active agent according to claim 11 wherein the at least one cationic counterion is selected from alkali metal or alkaline earth metal cations, or from primary, secondary, tertiary or quaternary ammonium ions.
13. A cationic surface-active agent according to claim 7 or claim 8 provided in association with a least one anionic counterion.
14. A cationic surface-active agent according to claim 13 wherein the at least one anionic counterion is selected from halides, carboxylates.
15. An ionic surface-active agent according to any one of claim 1 to 14 wherein the value of the or each P is independently from 1 to 45, from 1 to 40, from 1 to 35, from 1 to 30, from 1 to 25, from 1 to 20, or from 1 to 15.

16. An ionic surface-active agent according to any one of claims 1 to 15 wherein the value of the or each Q is independently from 0 to 45, from 0 to 40, from 0 to 35, from 0 to 30, from 0 to 25, from 0 to 20, or from 0 to 15.
17. An ionic surface-active agent according to any one of claims 1 to 16 wherein A is derived from a monofunctional starter compound selected from C₁ to C₁₁ alcohols, a C₁ to C₁₁ carboxylic acids or monofunctional polyethers such as polyalkylene glycol monomethyl ethers.
18. An ionic surface-active agent according to any one of claims 1 to 16 wherein A is derived from a polyfunctional starter compounds selected from compounds of the formula;



wherein:

Y is selected from any group which can have 2 or more $-R^Y$ groups attached to it;

each R^Y is independently selected from $-OH$, $-NHR'$, $-SH$, $-C(O)OH$, $-P(O)(OR')(OH)$, $-PR'(O)(OH)_2$ or $-PR'(O)OH$, optionally R^Y is selected from $-OH$, $-NHR'$ or $-C(O)OH$, optionally each R^Y is $-OH$, $-C(O)OH$ or a combination thereof (e.g. each R^Y is $-OH$);

wherein R' may be H, or optionally substituted alkyl, heteroalkyl, aryl, heteroaryl, cycloalkyl or heterocycloalkyl, optionally wherein R' is H or optionally substituted alkyl; and

a is an integer which is at least 2.

19. An ionic surface-active agent according to claim 18 wherein Y is selected from optionally substituted alkylene, alkenylene, alkynylene, heteroalkylene, heteroalkenylene, heteroalkynylene, cycloalkylene, cycloalkenylene, heterocycloalkylene, heterocycloalkenylene, arylene, heteroarylene, or Y may be a combination of any of these groups, for example Y may be an alkylarylene, heteroalkylarylene, heteroalkylheteroarylene or alkylheteroarylene group, optionally wherein Y is alkylene, heteroalkylene, arylene, or heteroarylene.
20. An ionic surface-active agent according to claim 18 or claim 19 wherein a is in the range of from 2 to 8, or from 2 to 6.
21. A process for producing a surface-active agent according to any one of claims 1 to 20 comprising the steps of: (i) reacting a mono-hydroxy functional polyether with a carbonate catalyst, epoxide and CO₂ to produce a poly(carbonate ether); and (iii) modifying at least one terminal group of the poly(carbonate ether) to produce the surface-active agent according to the first aspect of the invention
22. A process for producing a surface-active agent according to any one of claims 1 to 20 comprising the steps of (i) reacting carbon dioxide and an epoxide in the presence of a carbonate catalyst, and a functional starter compound to form a polycarbonate compound; (ii) reacting the polycarbonate compound of step (i) with an epoxide and an ether catalyst to form a poly(carbonate ether); and (iii) modifying at least one terminal group of the poly(carbonate ether) to produce the surface-active agent.
23. A process for producing a surface-active agent according to any one of claims 1 to 20 in a multiple reactor system; the system comprising at least a first and second reactor wherein a first reaction takes place in the first reactor and a second reaction takes place in the second reactor; wherein the first reaction is the reaction of a carbonate catalyst with CO₂ and epoxide, in the presence of a functional starter compound, and optionally a solvent, to produce a polycarbonate compound and the second reaction is the semi-batch or continuous reaction of an ether catalyst with the polycarbonate compound of the first reaction and epoxide to produce the a poly(carbonate ether), the process further comprising a third reaction which may take

place in a third reactor, the third reaction comprising modifying at least one terminal group of the product of the poly(carbonate ether) to produce the surface-active agent.

24. A process according to any one of claims 21 to claim 23 wherein the terminal group(s) of the poly(carbonate ether) is or are selected from OH, O-R, O-C(O)-R, and/or O-C(O)-O-R; wherein each R is independently an optionally substituted (including with heteroatoms) straight or branched chain or cyclic alkyl, aryl, aralkyl, alkaryl, alkenyl, alkenaryl, or aralkenyl group, optionally wherein the or each terminal group of the poly(carbonate ether) is OH or OMe, preferably OH.
25. A process according to any one of claims 21 to 24 wherein the step of modifying the at least one terminal group of the poly(carbonate ether) introduces at least one ionic constituent onto the terminal group(s) of the polymer compound.
26. A process according to claim 25 wherein the modifying step comprises removing H or R from the terminal group(s) of the poly(carbonate ether) and substituting with an ionic constituent.
27. Use of the surface-active agent of any one of claims 1 to 20 as: agrichemical, cosmetic or pharmaceutical adjuvants, excipients or auxiliaries; for the preparation or functionalisation of low-foaming detergents/cleaners, institutional cleaning & sanitation products, industrial cleaning products, personal care products, adhesives, metal working fluids, paints & coatings, as auxiliary or other reagents or excipients in the construction, mining and oilfield industries, as preparatory or functional ingredients in microcapsules, batteries, crystal growth modifiers, bio-control agents, demulsifiers, froth flotation systems, textiles and water treatment coatings, and in the processing of foods & beverages.