

Claims

1. A (poly)ol block copolymer of general structure B-A-(B)_n wherein block A is a polycarbonate block or polyester block, wherein $n=t-1$ and t = the number of reactive end residues on block A, wherein block B is a polyethercarbonate block and wherein > 70%
5 of the copolymer chain ends are terminated by primary hydroxyl groups.
2. A (poly)ol block copolymer according to claim 1, wherein > 75%, more preferably, >80% of the copolymer chain ends are terminated by primary hydroxyl groups.
3. A (poly)ol block copolymer according to any preceding claim, wherein the mol/mol ratio of block A to block B is in the range 25:1 to 1:250.
- 10 4. A (poly)ol block copolymer according to any preceding claim, wherein the carbonates present in block A are derived from CO₂.
5. A (poly)ol block copolymer according to any preceding claim, wherein block A is derived from alkylene oxides and CO₂.
6. A (poly)ol block copolymer according to any preceding claim, wherein block A is
15 partly derived from alkylene oxides and wherein optionally the alkylene oxides are selected from cyclohexene oxide, styrene oxide, ethylene oxide, propylene oxide, butylene oxide, substituted cyclohexene oxides (such as limonene oxide, C₁₀H₁₆O or 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, C₁₁H₂₂O), alkylene oxides (such as ethylene oxide and substituted ethylene oxides), unsubstituted or substituted oxiranes (such as
20 oxirane, epichlorohydrin, 2-(2-methoxyethoxy)methyl oxirane (MEMO), 2-(2-(2-methoxyethoxy)ethoxy)methyl oxirane (ME2MO), 2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)methyl oxirane (ME3MO), 1,2-epoxybutane, glycidyl ethers, glycidyl esters, glycidyl carbonates, vinyl-cyclohexene oxide, 3-phenyl-1,2-epoxypropane, 2,3-epoxybutane, isobutylene oxide, cyclopentene oxide, 2,3-epoxy-
25 1,2,3,4-tetrahydronaphthalene, indene oxide, and functionalized 3,5-dioxaepoxides.
7. A (poly)ol block copolymer according to any preceding claim, wherein block A is a polyalkylenecarbonate block, more typically derived from alkylene oxides and CO₂.
8. A (poly)ol block copolymer according to any preceding claim, wherein the alkylene oxides and CO₂ provide at least 90% of the residues in the block not including
30 any starter, especially, at least 95% of the residues in the block, more especially, at least 99% of the residues in the block, most especially, about 100% of the residues in the block not including any starter are residues of alkylene oxide and CO₂.

- 50 -

9. A (poly)ol block copolymer according to claim 7 or 8, wherein the block A alkylene oxide residues are ethylene oxide and/or propylene oxide residues and optionally, in addition, other alkylene oxide residues.
10. A (poly)ol block copolymer according to any preceding claim, wherein at least
5 50% of the alkylene oxide residues of block A are ethylene oxide or propylene oxide residues, more typically, at least 70% of the alkylene oxide residues of block A are ethylene oxide or propylene oxide residues, most typically, at least 90% of the alkylene oxide residues of block A are ethylene oxide or propylene oxide residues, especially, ethylene oxide at these levels.
- 10 11. A (poly)ol block copolymer according to any preceding claim, wherein block A has between 70-100% carbonate linkages, more typically, 80-100%, most typically, 90-100% and/or wherein the polycarbonate block, A, of the (poly)ol block copolymer has at least 76% carbonate linkages, preferably at least 80% carbonate linkages, more preferably at least 85% carbonate linkages and/or wherein block A has less than 98%
15 carbonate linkages, preferably less than 97% carbonate linkages, more preferably less than 95% carbonate linkages and/or optionally, block A has between 75% and 99% carbonate linkages, preferably between 77% and 95% carbonate linkages, more preferably between 80% and 90% carbonate linkages.
12. A (poly)ol block copolymer according to any preceding claim, wherein the A block
20 has a high carbonate content and the B block a low carbonate content, for example, the A block has greater than 70% carbonate linkages and/or, for example, the B block has less than 50% carbonate linkages.
13. A (poly)ol block copolymer according to any preceding claim, wherein the carbonate residues of block B are derived from CO₂.
- 25 14. A (poly)ol block copolymer according to any preceding claim, wherein block B is derived from alkylene oxides and CO₂.
15. A (poly)ol block copolymer according to any preceding claim, wherein block B is partly derived from alkylene oxides and wherein optionally the alkylene oxides are selected from cyclohexene oxide, styrene oxide, ethylene oxide, propylene oxide,
30 butylene oxide, substituted cyclohexene oxides (such as limonene oxide, C₁₀H₁₆O or 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, C₁₁H₂₂O), alkylene oxides (such as ethylene oxide and substituted ethylene oxides), unsubstituted or substituted oxiranes (such as oxirane, epichlorohydrin, 2-(2-methoxyethoxy)methyl oxirane (MEMO), 2-(2-(2-

- 51 -

methoxyethoxy)ethoxy)methyl oxirane (ME2MO), 2-(2-(2-methoxyethoxy)ethoxy)ethoxy)methyl oxirane (ME3MO), 1,2-epoxybutane, glycidyl ethers, glycidyl esters, glycidyl carbonates, vinyl-cyclohexene oxide, 3-phenyl-1,2-epoxypropane, 2,3-epoxybutane, isobutylene oxide, cyclopentene oxide, 2,3-epoxy-
 5 1,2,3,4-tetrahydronaphthalene, indene oxide, and functionalized 3,5-dioxaepoxides.

16. A (poly)ol block copolymer according to any preceding claim, wherein block B is a polyalkylenecarbonate block.

17. A (poly)ol block copolymer according to any preceding claim, wherein block B includes ethylene oxide residues and optionally other alkylene oxide residues, wherein
 10 typically, alkylene oxide residues provide at least 90% of the non-carbonate functional group residues in the block, especially, at least 95% of the non-carbonate functional group residues in the block, more especially, at least 99% of the non-carbonate functional group residues in the block, most especially, about 100% of the non-carbonate functional group residues in the block are residues of alkylene oxide.

18. A (poly)ol block copolymer according to any preceding claim, wherein ethylene oxide residues form 5-100% of the alkylene oxide residues in block B, more typically, 10-100%, most typically 10-50% of the alkylene oxide residues in block B, and/or, at least 5%, 10%, 15%, 20%, 25% or 30% of the alkylene oxide residues in block B are ethylene oxide residues.

19. A (poly)ol block copolymer according to any preceding claim, wherein block B comprises a mixture of alkylene oxide residues and the other non-ethylene oxide residues are selected from cyclohexene oxide, styrene oxide, propylene oxide, butylene oxide, substituted cyclohexene oxides (such as limonene oxide, C₁₀H₁₆O or 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, C₁₁H₂₂O), alkylene oxides (such as ethylene oxide and substituted ethylene oxides), unsubstituted or substituted oxiranes (such as
 25 oxirane, epichlorohydrin, 2-(2-methoxyethoxy)methyl oxirane (MEMO), 2-(2-(2-methoxyethoxy)ethoxy)methyl oxirane (ME2MO), 2-(2-(2-methoxyethoxy)ethoxy)ethoxy)methyl oxirane (ME3MO), 1,2-epoxybutane, glycidyl ethers, glycidyl esters, glycidyl carbonates, vinyl-cyclohexene oxide, 3-phenyl-1,2-epoxypropane, 2,3-epoxybutane, isobutylene oxide, cyclopentene oxide, 2,3-epoxy-
 30 1,2,3,4-tetrahydronaphthalene, indene oxide, and functionalized 3,5-dioxaepoxides.

20. A (poly)ol block copolymer according to any preceding claim, wherein at least 5% of the alkylene oxide residues of block B are ethylene or propylene oxide residues, more typically, at least 10% of the alkylene oxide residues of block B are ethylene or propylene

- 52 -

oxide residues, most typically, at least 20% of the alkylene oxide residues of block B are ethylene or propylene oxide residues, optionally, at least 50% of the alkylene oxide residues of block B are ethylene or propylene oxide residues, most especially, at least 70 or 90% of the alkylene oxide residues of block B are ethylene or propylene oxide residues.

21. A (poly)ol block copolymer according to any preceding claim, wherein at least 70% of the terminal alkylene oxide residues are ethylene oxide residues, more typically, at least 75%, most typically, at least 80% of the terminal alkylene oxide residues are ethylene oxide residues.

22. A (poly)ol block copolymer according to any preceding claim, wherein the polyethercarbonate block(s), B, of the (poly)ol block copolymer have less than 40% carbonate linkages, preferably less than 35% carbonate linkages, more preferably less than 30% carbonate linkages and/or block(s) B have at least 5% carbonate linkages, preferably at least 10% carbonate linkages, more preferably at least 15% carbonate linkages and/or blocks B have between 1% and 50% carbonate linkages, preferably between 5% and 45% carbonate linkages, more preferably between 10% and 40% carbonate linkages.

23. A (poly)ol block copolymer according to any preceding claim, wherein the polyethercarbonate block(s), B, of the (poly)ol block copolymer have at least 60% ether linkages, preferably at least 65% ether linkages, more preferably at least 70% ether linkages and/or wherein the polyethercarbonate block(s), B, of the (poly)ol block copolymer have less than 95% ether linkages, preferably less than 90% ether linkages, more preferably less than 85% ether linkages and/or wherein, block(s) B have between 50% and 99% ether linkages, preferably between 55% and 95% ether linkages, more preferably between 60% and 90% ether linkages.

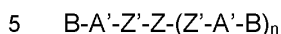
24. A (poly)ol block copolymer according to any preceding claim, wherein the polycarbonate block, A, of the (poly)ol block copolymer also comprise ether linkages.

25. A (poly)ol block copolymer according to any preceding claim, wherein the polycarbonate block, A, of the (poly)ol block copolymer has less than 24% ether linkages, preferably less than 20% ether linkages, more preferably less than 15% ether linkages such as less than 10%, for example less than 5% ether linkages. Block A may have at least 1% ether linkages, such as at least 2% ether linkages or even at least 5% ether linkages. Optionally, block A may have between 0% and 25% ether linkages, preferably

- 53 -

between 1% and 20% ether linkages, more preferably between 1% and 15% ether linkages.

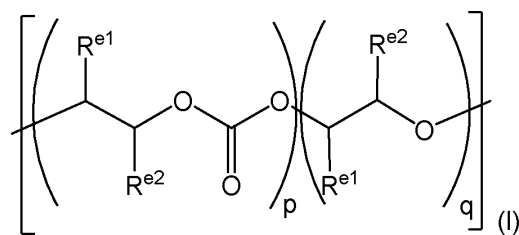
26. A (poly)ol block copolymer according to any preceding claim, wherein the (poly)block structure of the copolymer is defined as :



wherein n= t-1 and wherein t= the number of terminal OH group residues on the block A; and wherein each A' is independently a polycarbonate chain having at least 70% carbonate linkages, and wherein each B is independently a polyethercarbonate chain having 50-99% ether linkages and at least 1% carbonate linkages and wherein Z'-Z-(Z')_n

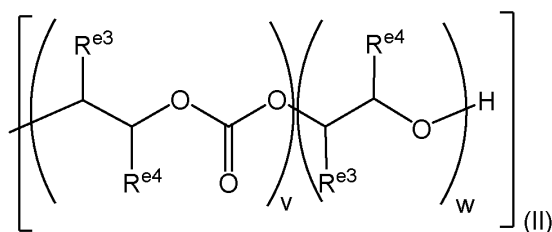
10 is a starter residue.

27. A (poly)ol block copolymer according to claim 26, wherein -A'- has the following structure:



wherein the ratio of p:q is at least 7:3;

15 and block B has the following structure:



wherein the ratio of w:v is greater or equal to 1:1; and

R^{e1}, R^{e2}, R^{e3} and R^{e4} depend on the nature of the alkylene oxide used to prepare blocks A and B.

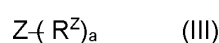
28. A (poly)ol block copolymer according to claim 27, wherein each R^{e1}, R^{e2}, R^{e3}, or
20 R^{e4} is independently selected from selected from H, halogen, hydroxyl, or optionally substituted alkyl (such as methyl, ethyl, propyl, butyl, -CH₂Cl, -CH₂-OR₂₀, -CH₂-OC(O)R₁₂, or -CH₂-OC(O)OR₁₈), alkenyl, alkynyl, cycloalkyl, heterocycloalkyl, aryl,

- 54 -

heteroaryl, heteroalkyl or heteroalkenyl, preferably selected from H or optionally substituted alkyl.

29. A (poly)ol block copolymer according to any of claims 27-28, wherein R^{e1} and R^{e2} or R^{e3} and R^{e4} together form a saturated, partially unsaturated or unsaturated ring
5 containing carbon and hydrogen atoms, and optionally one or more heteroatoms.

30. A (poly)ol block copolymer according to any of claims 26-29, wherein the starter residue depends on the nature of the starter compound, and wherein the starter compound has the formula (III):



10 wherein Z can be any group which can have 1 or more, typically, 2 or more $-R^Z$ groups attached to it and may be selected from optionally substituted alkylene, alkenylene, alkynylene, heteroalkylene, heteroalkenylene, heteroalkynylene, cycloalkylene, cycloalkenylene, heterocycloalkylene, heterocycloalkenylene, arylene, heteroarylene, or
15 Z may be a combination of any of these groups, for example Z may be an alkylarylene, heteroalkylarylene, heteroalkylheteroarylene or alkylheteroarylene group;

a is an integer which is at least 1, typically, at least 2, optionally a is in the range of between 1 or 2 and 8, optionally a is in the range of between 2 and 6;

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

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

wherein Z' corresponds to R^Z , except that a bond replaces the labile hydrogen atom.

31. A (poly)ol block copolymer according to claim 30 wherein a is an integer which is
25 at least 2

32. A (poly)ol block copolymer according to claim 30, wherein the starter compound is selected from monofunctional starter substances such as alcohols, phenols, amines, thiols and carboxylic acid, for example, alcohols such as methanol, ethanol, 1- and 2-propanol, 1- and 2-butanol, linear or branched C_3 - C_{20} -monoalcohol such as tert-butanol,
30 3-buten-1-ol, 3-buten-1-ol, 2-methyl-3-buten-2-ol, 2-methyl-3-buten-2-ol, propargyl alcohol, 2-methyl-2-propanol, 1-tert-butoxy-2-propanol, 1-pentanol, 2-pentanol, 3-pentanol, 1-hexanol, 2-hexanol, 3-hexanol, 1-heptanol, 2-heptanol, 3-heptanol, 1-

- 55 -

octanol, 2-octanol, 3-octanol, 4-octanol, 1-decanol, 1-dodecanol, phenol, 2-hydroxybiphenyl, 3-hydroxybiphenyl, 4-hydroxybiphenyl, 2-hydroxypyridine, 3-hydroxypyridine, and 4-hydroxypyridine, mono-ethers or esters of ethylene, propylene, polyethylene, polypropylene glycols such as ethylene glycol mono-methyl ether and
 5 propylene glycol mono-methyl ether, phenols such as linear or branched C₃-C₂₀ alkyl substituted phenols, for example nonyl-phenols or octyl phenols, monofunctional carboxylic acids such as formic acid, acetic acid, propionic acid and butyric acid, fatty acids, such as stearic acid, palmitic acid, oleic acid, linoleic acid, linolenic acid, benzoic acid and acrylic acid, and monofunctional thiols such as ethanethiol, propane-1-thiol,
 10 propane-2-thiol, butane-1-thiol, 3-methylbutane-1-thiol, 2-butene-1-thiol, and thiophenol, or amines such as butylamine, tert-butylamine, pentylamine, hexylamine, aniline, aziridine, pyrrolidine, piperidine, and morpholine; and/or selected from diols such as 1,2-ethanediol (ethylene glycol), 1,3-propanediol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,8-octanediol, 1,10-decanediol, 1,12-
 15 dodecanediol, 1,4-cyclohexanediol, 1,2-diphenol, 1,3-diphenol, 1,4-diphenol, neopentyl glycol, catechol, cyclohexanediol, 1,4-cyclohexanedimethanol, dipropylene glycol, diethylene glycol, tripropylene glycol, triethylene glycol, tetraethylene glycol, polypropylene glycols (PPGs) or polyethylene glycols (PEGs) having an Mn of up to about 1500g/mol, such as PPG 425, PPG 725, PPG 1000 and the like, triols such as
 20 glycerol, benzenetriol, 1,2,4-butanetriol, 1,2,6-hexanetriol, tris(methylalcohol)propane, tris(methylalcohol)ethane, tris(methylalcohol)nitropropane, trimethylol propane, polyethylene oxide triols, polypropylene oxide triols and polyester triols, tetraols such as calix[4]arene, 2,2-bis(methylalcohol)-1,3-propanediol, erythritol, pentaerythritol or polyalkylene glycols (PEGs or PPGs) having 4-OH groups, polyols, such as sorbitol or
 25 polyalkylene glycols (PEGs or PPGs) having 5 or more -OH groups, or compounds having mixed functional groups including ethanolamine, diethanolamine, methyldiethanolamine, and phenyldiethanolamine.

33. A (poly)ol block copolymer according to any preceding claim, wherein the (poly)ol molecular weight (Mn) is in the range 300-20,000 Da and optionally the molecular weight
 30 (Mn) of block A is in the range 200-4000 Da, and wherein optionally the molecular weight (Mn) of block B is in the range 100-20,000 Da, more typically, the molecular weight (Mn) of block A is 200-2000 Da, more typically 200-1000 Da, most typically 400-800 Da and/or the molecular weight (Mn) of block B is typically 200-10,000 Da, more typically 200-5000 Da.

- 56 -

34. A (poly)ol block copolymer according to claim 27, wherein the molecular weight (Mn) is measured by Gel Permeation Chromatography (GPC).
35. A (poly)ol block copolymer according to any of claims 1-34, wherein ethylene oxide residues form 0-100% of the alkylene oxide residues in the (poly)ol block copolymer, typically 5-70%, more typically, 10-60% of the alkylene oxide residues in the (poly)ol block copolymer, most typically, 10-40% of the alkylene oxide residues in the (poly)ol block copolymer and/or, at least 5%, 10%, 15%, 20%, 25% or 30% of the alkylene oxide residues in the (poly)ol block copolymer are ethylene oxide residues .
36. A (poly)ol block copolymer according to any preceding claim, wherein block A is a generally alternating polycarbonate (poly)ol residue.
37. A composition comprising the (poly)ol block copolymer of any preceding claim and one or more additives selected from catalysts, blowing agents, stabilizers, plasticisers, fillers, flame retardants, and antioxidants.
38. A composition according to claim 37 further comprising a (poly)isocyanate.
39. A polyurethane produced from the reaction of a polyol block copolymer according to any of claims 1 to 36 or a composition according to claim 37 or 38 and a (poly)isocyanate.
40. A polyurethane comprising a block copolymer residue according to any of claims 1-36.
41. An isocyanate terminated polyurethane prepolymer comprising the reaction product of a block copolymer according to any of claims 1 to 36 or a composition according to claim 36 with an excess of (poly)isocyanate.
42. An isocyanate terminated polyurethane prepolymer comprising a block copolymer residue according to any of claim 1 to 36.
43. A composition according to claim 37 or 38, wherein the catalysts for the (poly)isocyanate and the polyol block copolymer reaction include suitable urethane catalysts such as tertiary amine compounds and/or organometallic compounds.
44. A composition according to claim 37 or 38, wherein a trimerisation catalyst is present.
45. A composition according to claim 37, wherein an excess of (poly)isocyanate, more typically, an excess of polymeric isocyanate relative to polyol is present so that polyisocyanurate ring formation in the presence of the trimerisation catalyst is possible.

- 57 -

46. A lubricant composition comprising a (poly)ol block copolymer of any of claims 1 to 36.
47. A surfactant composition comprising a (poly)ol block copolymer of any of claims 1 to 36.
- 5 48. A process for producing a (poly)ol block copolymer comprising the reaction of a DMC catalyst with a polycarbonate or polyester (poly)ol (co)polymer according to block A of any of claims 1 to 36, CO₂, ethylene oxide and optionally one or more other alkylene oxides to produce a (poly)ol block copolymer according to any of claims 1 to 36.
- 10 49. A process for producing a (poly)ol block copolymer comprising a first reaction in a first reactor and a second reaction in a second reactor; wherein the first reaction is the reaction of a carbonate catalyst with CO₂ and alkylene oxide, in the presence of a starter and optionally a solvent to produce a polycarbonate (poly)ol copolymer according to block A of any of claims 1 to 36 and the second reaction is the reaction of a DMC catalyst with the polycarbonate (poly)ol copolymer of the first reaction, CO₂, ethylene oxide and
- 15 optionally one or more other alkylene oxides to produce a (poly)ol block copolymer according to any of claims 1 to 36.
50. A process for producing a (poly)ol block copolymer in a multiple reactor system; the system comprising 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
- 20 first reaction is the reaction of a carbonate catalyst with CO₂ and alkylene oxide, in the presence of a starter and optionally a solvent to produce a polycarbonate (poly)ol copolymer according to a starter residue terminated block A of any of claims 1 to 36 and the second reaction is the reaction of a DMC catalyst with the polycarbonate (poly)ol compound of the first reaction, CO₂, ethylene oxide and optionally one or more other
- 25 alkylene oxides to produce a (poly)ol block copolymer according to any of claims 1 to 36.
51. A process according to any of claims 48 to 50, further comprising a reaction comprising the reaction of the block copolymer of any of claims 1 to 36 with a monomer or further polymer to produce a higher polymer.
52. A process according to claim 51, wherein the monomer or further polymer is a
- 30 (poly)isocyanate and the product of the reaction is a polyurethane.
53. A process according to any of claims 48-52, wherein the DMC catalyst is pre-activated, optionally in the reactor or separately, optionally wherein the DMC is pre-activated with a starter compound or with the polycarbonate or polyester (poly)ol

- 58 -

(co)polymer according to block A of any of claims 1 to 36 or is pre-activated with the (poly)ol block copolymer of any of claims 1-36.

54. A process according to any of claims 48-53, wherein when one or more other alkylene oxides are added to the reaction of claim 48 or 51-53 or second reaction of claims 49-53 in addition to ethylene oxide, the ethylene oxide addition is increased
5 mol/mol relative to the other alkylene oxide(s) at the end part of the reaction.

55. A process according to any of claims 48-54 wherein ethylene oxide forms 5-100% mol/mol of the alkylene oxides added to the reaction of claim 48 or 51-54 or second reaction of claims 49-54, more typically, 10-100%, most typically 10-50% mol/mol of the
10 alkylene oxides added, and/or, at least 5%, 10%, 15%, 20%, 25% or 30% mol/mol of the alkylene oxides added.

56. A process according to any of claims 49-55 wherein when an asymmetric alkylene oxide is added the reaction may produce a polycarbonate having between 40-100% head to tail linkages, preferably more than 70%, more than 80% or more than 90%
15 head to tail linkages.

57. A process according to any of claims 48-56, wherein the polycarbonate or polyester (poly)ol copolymer according to block A of any of claims 1 to 36 is fed into the reactor or second reactor for the reaction with the DMC catalyst, as a crude reaction mixture, optionally, continuously or semi-continuously, wherein said reactor or second
20 reactor contains a pre-activated DMC catalyst.

58. A process according to any of claims 48-57, wherein the first reaction is carried out under CO₂ pressure of less than 20 bar, more preferably, less than 10 bar, most preferably, less than 8 bar.

59. A process according to any of claims 48-58, wherein the second reaction is carried out under CO₂ pressure of less than 60 bar, preferably less than 20 bar, more preferably less than 10 bar, most preferably, less than 5 bar.
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60. A process according to any of claims 48-59, wherein the CO₂ is added continuously in the first reaction, preferably in the presence of a starter.

61. A process according to any of claims 48-60, wherein the first reaction can be a batch, semi-batch, or continuous process.
30

62. A process according to any of claims 48-61, wherein the second reaction can be a continuous process or semi batch process.

- 59 -

63. A process according to any of claims 57-62, wherein the crude reaction mixture fed into the reactor or second reactor includes an amount of unreacted alkylene oxide and/or CO₂ and/or starter.
64. A process according to any of claims 57-63, wherein the carbonate catalyst is present in the crude reaction mixture.
65. A process according to any of claims 57-63, wherein the carbonate catalyst has been removed from the crude reaction mixture prior to the addition to the reactor or second reactor.
66. A process according to any of claims 48-65, wherein the temperature of reaction in the first reactor is in the range about 0°C to 250 °C, preferably from about 40 °C to about 160 °C, more preferably from about 50 °C to 120 °C.
67. A process according to any of claims 48-66, wherein the temperature of reaction in the reactor or second reactor is in the range from about 50 to about 160°C, preferably in the range from about 70 to about 140°C, more preferably from about 70 to about 110°C.
68. A process according to any of claims 48-67, wherein the reactors are located in series.
69. A process according to any of claims 48-67, wherein the reactors are nested.
70. A process according to claim 69, wherein the first and second reactors are effective to provide different reaction conditions, such as temperature and/or pressure, to each other simultaneously.
71. A process according to any of claims 57-70, wherein the crude reaction mixture is stabilised by an acid prior to addition to the reactor or second reactor.
72. A process according to any of claims 48-71, wherein the process employs a total amount of alkylene oxide, and wherein about 1 to 100% of the total amount of alkylene oxide is mixed in the first reaction, with any remainder added in the second reaction; optionally with about 5 to 90% being mixed in the first reaction, optionally with about 10 to 90%, optionally with about 20 to 90%, optionally with about 40 to 90%, optionally with about 40 to 80%, optionally with about 5 to 50%.
73. A process according to any of claims 48-72, wherein between 0.1 and 20% of the total alkylene oxide in the first reaction is an alkylene oxide substrate containing more than one epoxide moiety, preferably a bis-epoxide.

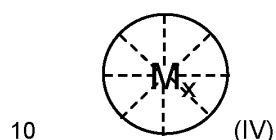
- 60 -

74. A process according to any of claims 48-73 wherein the carbonate catalyst is a catalyst capable of producing polycarbonate chains with greater than 76% carbonate linkages.

75. A process according to any of claims 48-74, wherein the carbonate catalyst is a
5 metal catalyst comprising phenol or phenolate ligands.

76. A process according to any of claims 48-75, wherein the carbonate catalyst is a bimetallic complex comprising phenol or phenolate ligands.

77. A process according to any of claims 48-76 wherein the carbonate catalyst is a catalyst of Formula (IV):



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

x is an integer from 1 to 4,



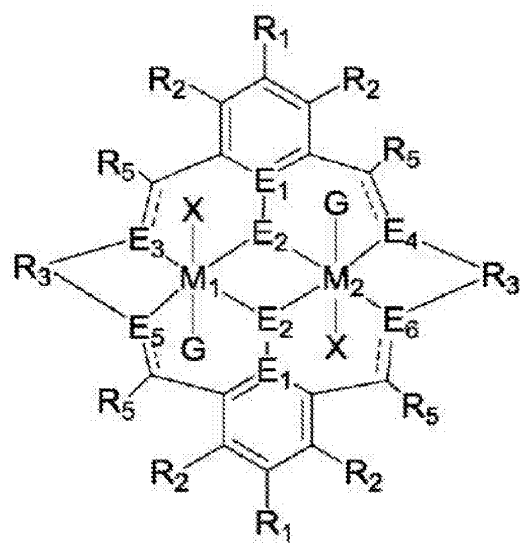
is a multidentate ligand or plurality of multidentate ligands;

L is a coordinating ligand;

15 v is an integer that satisfies the valency of M, and/or the preferred coordination geometry of M or is such that the complex represented by formula (IV) above has an overall neutral charge.

78. A process according to any of claims 48-77, wherein the carbonate catalyst has the following structure:

- 61 -



wherein M_1 and M_2 are independently selected from Zn(II), Cr(II), Co(II), Cu(II), Mn(II), Mg(II), Ni(II), Fe(II), Ti(II), V(II), Cr(III)-X, Co(III)-X, Mn(III)-X, Ni(III)-X, Fe(III)-X, Ca(II), Ge(II), Al(III)-X, Ti(III)-X, V(III)-X, Ge(IV)-(X)₂ or Ti(IV)-(X)₂;

- 5 R_1 and R_2 are independently selected from hydrogen, halide, a nitro group, a nitrile group, an imine, an amine, an ether group, a silyl group, a silyl ether group, a sulfoxide group, a sulfonyl group, a sulfinate group or an acetylide group or an optionally substituted alkyl, alkenyl, alkynyl, haloalkyl, aryl, heteroaryl, alkoxy, aryloxy, alkylthio, arylthio, alicyclic or heteroalicyclic group;
 - 10 R_3 is independently selected from optionally substituted alkylene, alkenylene, alkynylene, heteroalkylene, heteroalkenylene, heteroalkynylene, arylene, heteroarylene or cycloalkylene, wherein alkylene, alkenylene, alkynylene, heteroalkylene, heteroalkenylene and heteroalkynylene, may optionally be interrupted by aryl, heteroaryl, alicyclic or heteroalicyclic;
 - 15 R_5 is independently selected from H, or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, heteroaryl, alkylheteroaryl or alkylaryl;
- E_1 is C, E_2 is O, S or NH or E_1 is N and E_2 is O;
- E_3 , E_4 , E_5 and E_6 are selected from N, NR_4 , O and S, wherein when E_3 , E_4 , E_5 or E_6 are N, ----- is =====, and wherein when E_3 , E_4 , E_5 or E_6 are NR_4 , O or S, ----- is =====;

- 62 -

R₄ is independently selected from H, or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, heteroaryl, alkylheteroaryl, -alkylC(O)OR₁₉ or -alkylC≡N or alkylaryl;

5 X is independently selected from OC(O)R_x, OSO₂R_x, OSOR_x, OSO(R_x)₂, S(O)R_x, OR_x, phosphinate, halide, nitrate, hydroxyl, carbonate, amino, amido or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl, wherein each X may be the same or different and wherein X may form a bridge between M₁ and M₂;

10 R_x is independently hydrogen, or optionally substituted aliphatic, haloaliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, alkylaryl or heteroaryl; and

G is absent or independently selected from a neutral or anionic donor ligand which is a Lewis base.

79. A process according to any of claims 48-76 wherein the carbonate catalyst is selected from catalysts of formula (IV), metal salen catalysts, metal porphyrin catalysts, 15 metal tetraaza annulene catalysts and metal beta-diiminate catalysts as defined herein.

80. A process according to any of claims 48-79, wherein the DMC catalyst, in addition to at least two metal centres and cyanide ligands, also comprises at least one of: one or more complexing agents, water, a metal salt and/or an acid, optionally in non-stoichiometric amounts.

20 81. A process according to any of claims 48-80, wherein the DMC catalyst is prepared by treating a solution of a metal salt with a solution of a metal cyanide salt in the presence of at least one of: complexing agent, water, and/or an acid, optionally wherein the metal salt is of the formula M'(X')_p, wherein M' is selected from Zn(II), Ru(II), Ru(III), Fe(II), Ni(II), Mn(II), Co(II), Sn(II), Pb(II), Fe(III), Mo(IV), Mo(VI), Al(III), V(V), 25 V(VI), Sr(II), W(IV), W(VI), Cu(II), and Cr(III),

X' is an anion selected from halide, oxide, hydroxide, sulphate, carbonate, cyanide, oxalate, thiocyanate, isocyanate, isothiocyanate, carboxylate and nitrate,

p is an integer of 1 or more, and the charge on the anion multiplied by p satisfies the valency of M'; the metal cyanide salt is of the formula (Y)_qM''(CN)_b(A)_c, wherein M'' is 30 selected from Fe(II), Fe(III), Co(II), Co(III), Cr(II), Cr(III), Mn(II), Mn(III), Ir(III), Ni(II), Rh(III), Ru(II), V(IV), and V(V),

Y is a proton or an alkali metal ion or an alkaline earth metal ion (such as K⁺),

- 63 -

A is an anion selected from halide, oxide, hydroxide, sulphate, cyanide oxalate, thiocyanate, isocyanate, isothiocyanate, carboxylate and nitrate;

q and b are integers of 1 or more;

c may be 0 or an integer of 1 or more;

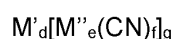
- 5 the sum of the charges on the anions Y, CN and A multiplied by q, b and c respectively (e.g. $Y \times q + CN \times b + A \times c$) satisfies the valency of M'' ;

the at least one complexing agent is selected from a (poly)ether, a polyether carbonate, a polycarbonate, a poly(tetramethylene ether diol), a ketone, an ester, an amide, an alcohol, a urea or a combination thereof,

- 10 optionally wherein the at least one complexing agent is selected from propylene glycol, polypropylene glycol, (m)ethoxy ethylene glycol, dimethoxyethane, tert-butyl alcohol, ethylene glycol monomethyl ether, diglyme, triglyme, methanol, ethanol, isopropyl alcohol, n-butyl alcohol, isobutyl alcohol and sec-butyl alcohol, 3-buten-1-ol, 2-methyl-3-buten-2-ol, 2-methyl-3-butyne-2-ol, 3-methyl-1-pentyne-3-ol, or a combination thereof;
- 15 and

wherein the acid, if present, has the formula H_rX''' , where X''' is an anion selected from halide, sulfate, phosphate, borate, chlorate, carbonate, cyanide, oxalate, thiocyanate, isocyanate, isothiocyanate, carboxylate and nitrate, and r is an integer corresponding to the charge on the counterion X''' .

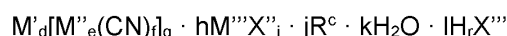
- 20 82. A process according to any of claims 48-81, wherein the DMC catalyst comprises the formula:



wherein M' and M'' are as defined in claim 79, and d, e, f and g are integers, and are chosen such that the DMC catalyst has electroneutrality,

- 25 optionally, d is 3, e is 1, f is 6 and g is 2.

83. A process according to any of claims 48-80, wherein the DMC catalyst comprises the formula:



- wherein M' , M'' , d, e, f and g are as defined in claim 79, M''' is M' and/or M'' , X''' is an anion selected from halide, oxide, hydroxide, sulphate, carbonate, cyanide, oxalate, thiocyanate, isocyanate, isothiocyanate, carboxylate and nitrate, i is an integer of 1 or
- 30

- 64 -

more, and the charge on the anion X^{r-} multiplied by i satisfies the valency of M^{m+} , h, j, k and l are each independently zero or a positive number, r is an integer that corresponds to the charge on the counterion X^{r-} , and R^c is a complexing agent or a combination of one or more complexing agents.

5 84. A process according to any of claims 48-83, wherein the DMC catalyst is based upon $Zn_3[Co(CN)_6]_2$ (zinc hexacyanocobaltate).

85. A process according to any of claims 48-84, wherein the DMC catalyst is zinc hexacyanocobaltate and the one or more ligands are selected from alcohols and polyols.

86. A process according to claim 83, wherein the one or more complexing agents are
10 selected from dimethoxyethane, tert-butyl alcohol, polyethylene glycol, polypropylene glycol, polyethercarbonate, poly(tetramethylene glycol), polycarbonate.

87. A process according to any of claims 48-86, wherein the polycarbonate or polyester (poly)ol copolymer according to block A of any of claims 1 to 36 is fed into the reactor or second reactor in a single portion or in a continuous or semi-continuous
15 manner, optionally wherein the product of the first reaction comprises unreacted alkylene oxide and/or carbonate catalyst.

88. A process according to any of claims 48-87, wherein the polycarbonate or polyester (poly)ol copolymer according to block A of any of claims 1 to 36 or the (poly)ol block copolymer of any of claims 1 to 36 is used to pre-activate the DMC catalyst in the
20 reactor or second reactor, prior to addition of alkylene oxide and CO_2 .

89. A process according to any of claims 48-88, wherein the same or different alkylene oxides are used in the first or second reactions.

90. A process according to any of claims 48-89, wherein the alkylene oxide used in the first or second reaction comprises propylene oxide, ethylene oxide or a mixture of
25 propylene oxide and ethylene oxide.

91. A process according to any of claims 48 to 90, wherein the polycarbonate or polyester (poly)ol (co)polymer is added to a DMC, CO_2 , ethylene oxide and optionally other alkylene oxides reaction mixture.

92. A process according to any of claims 48 to 91, wherein the polycarbonate or polyester (poly)ol (co)polymer is added to the DMC catalyst continuously or semi-continuously, preferably the polycarbonate or polyester (poly)ol (co)polymer is added
30 continuously.

- 65 -

93. A process according to any of claims 48 to 92, wherein at least a separate portion of the polycarbonate or polyester (poly)ol (co)polymer is added after the start of the reaction.

94. A (poly)ol block copolymer according to any of claims 1 to 36 obtainable or
5 obtained by a process according to any of claims 48 to 93.

95. A polyurethane according to any of claims 39-40, wherein the polyurethane is in the form of a soft foam, a flexible foam, an integral skin foam, a high resilience foam, a viscoelastic or memory foam, a semi-rigid foam, a rigid foam (such as a polyurethane (PUR) foam, a polyisocyanurate (PIR) foam and/or a spray foam), an elastomer (such
10 as a cast elastomer, a thermoplastic elastomer (TPU) or a microcellular elastomer), an adhesive (such as a hot melt adhesive, pressure sensitive or a reactive adhesive), a sealant or a coating (such as a waterborne or solvent dispersion (PUD), a two-component coating, a one component coating, a solvent free coating).

96. A polyurethane according to claim 95, wherein the polyurethane is formed via a
15 process that involves extruding, moulding, injection moulding, spraying, foaming, casting and/or curing.

97. A polyurethane according to claim 95 or 96, wherein the polyurethane is formed via a 'one pot' or 'pre-polymer' process.