CLAIMS

1. A (poly)ol block copolymer comprising a polycarbonate or polyethercarbonate block, A (-A'-Z'-Z-(Z'-A')$_n$-), (poly)ester blocks, B, and (poly)ethercarbonate or (poly)ether blocks, C, wherein the (poly)ol block copolymer has the polyblock structure:

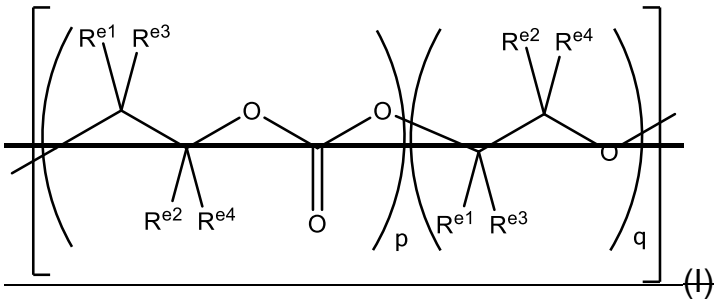
C-B-A'-Z'-Z-(Z'-A'-B-C)$_n$

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, or a polyethercarbonate chain having at least 30% ether linkages, wherein each B is a (poly)ester block formed by epoxide and cyclic anhydride reaction/copolymerisation and/or cyclic ester ring-opening reaction/polymerisation, and each C is independently a (poly)ethercarbonate or (poly)ether block having 50-100% ether linkages; and

wherein Z'-Z-(Z')$_n$ is a starter residue.

2. The (poly)ol block copolymer according to claim 1, wherein -A'- has the following structure:

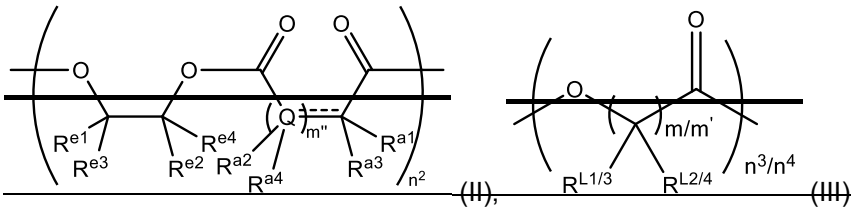


(I)

wherein in the case of the polycarbonate chain if q is not 0, the ratio of p:q is at least 7:3 and

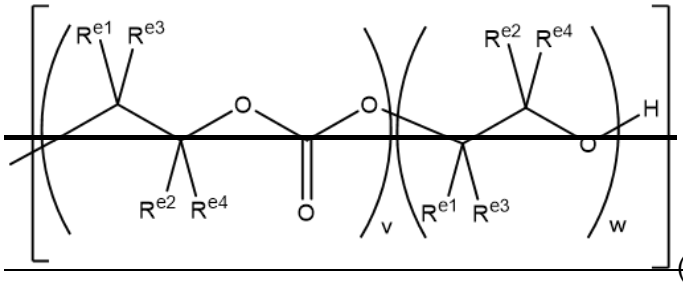
wherein in the case of the polyethercarbonate chain the ratio of p:q is at least 3:7;

block B has one of the following structures



wherein n^2 is 1 or more and n^3/n^4 is 1 or more

and block C has the following structure:



wherein w is 1 or more and v is 0 or more and if v is not 0, the ratio of w:v is at least 1:1; with the proviso that if the total of n^2 and n^3/n^4 is 1 then w is at least 2 and if w is 1 then the total of n^2 and n^3/n^4 is at least 2;

R^{e1}, R^{e2}, R^{e3} and R^{e4} independently depend on the epoxide residue in the respective block;

R^{a1}, R^{a2}, R^{a3} and R^{a4} or $R^{L1/L3}$, $R^{L2/L4}$, m, m' and m'' depend on the cyclic anhydride or ester residue in block B.

3. A (poly)ol block copolymer according to any preceding claim wherein v=0 and block C is a (poly)ether.

4. A (poly)ol block copolymer according to any of claims 1 to 3 wherein v is 1 or more and block C is a (poly)ether carbonate.

5. A (poly)ol block copolymer according to any preceding claim, wherein each R^{e1}, R^{e2}, R^{e3}, or R^{e4} is independently selected from H, halogen, hydroxyl, or optionally substituted alkyl (such as methyl, ethyl, propyl, butyl, $-CH_2Cl$, $-CH_2-OR_{20}$, $-CH_2-OC(O)R_{12}$, or $-CH_2-OC(O)OR_{18}$), alkenyl, alkynyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl, heteroalkyl or heteroalkenyl, preferably selected from H or optionally substituted alkyl.

6. A (poly)ol block copolymer according to any preceding claim, wherein R^{e1} or R^{e3} and R^{e2} or R^{e4} together form a saturated, partially unsaturated or unsaturated ring containing carbon and hydrogen atoms, and optionally one or more heteroatoms.

7. A (poly)ol block copolymer according to any preceding claim, wherein the starter residue depends on the nature of the starter compound, and wherein the starter compound has the formula (V):

$$Z(R^Z)_a \quad (V)$$

wherein Z can be any group which can have 1 or more, typically, 2 or more –RZ groups attached to it and may be selected from optionally substituted alkylene, alkenylene, alkynylene, heteroalkylene, heteroalkenylene, heteroalkynylene, cycloalkylene, cycloalkenylene, hererocycloalkylene, heterocycloalkenylene, arylene, heteroarylene, or 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 Rz is –OH, -C(O)OH or a combination thereof (e.g. each Rz 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.

8. A (poly)ol block copolymer according to claim 7, wherein a is an integer which is at least 2.

9. A (poly)ol block copolymer according to any preceding claim, 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, 3-buten-1-ol, 3-butyn-1-ol, 2-methyl-3-buten-2-ol, 2-methyl-3-butyn-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-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 propylene glycol mono-methyl ether, phenols such as linear or branched C_3-C_{20} 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, 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), 1-2-propanediol, 1,3-propanediol (propylene glycol), 1,2-butanediol, 1-3-butanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,8-octanediol, 1,10-decanediol, 1,12-dodecanediol, 1,4-cyclohexanediol, 1,2-diphenol, 1,3-diphenol, 1,4-diphenol, neopentyl glycol, catechol, cyclohexenediol, 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 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 polyalkylene glycols (PEGs or PPGs) having 5 or more –OH groups, or compounds having mixed functional groups including ethanolamine, diethanolamine, methyldiethanolamine, and phenyldiethanolamine.

10. 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 the molecular weight (Mn) of block A is in the range 200-4000 Da, wherein the molecular weight (Mn) of block B is in the range 50-5000 Da, and wherein the molecular weight (Mn) of block C 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, the molecular weight (Mn) of block B is 50-1000 Da, more typically 50-500, most typically 50-400, and/or the molecular weight (Mn)of block C is typically 200-10,000 Da, more typically 200-5000 Da.~~

~~11. A (poly)ol block copolymer according to claim 10, wherein the molecular weight (Mn) is measured by Gel Permeation Chromatography (GPC).~~

~~12. A (poly)ol block copolymer according to any preceding claim, wherein block A is a polycarbonate and typically, has at least 76%, more typically, at least 80% or most typically at least 85% carbonate linkages.~~

~~13. A (poly)ol block copolymer according to any preceding claim, wherein block A has less than 98% carbonate linkages, more typically, less than 97% carbonate linkages or most typically less than 95% carbonate linkages.~~

~~14. A (poly)ol block copolymer according to any preceding claim, wherein block A is a polycarbonate and typically, has between 75% and 99% carbonate linkages, more typically, between 77% and 95% carbonate linkages, most typically between 80 and 90% carbonate linkages.~~

~~15. A (poly)ol block copolymer according to any preceding claim, wherein block C has less than 40 % carbonate linkages, more typically, less than 30% carbonate linkages, most typically, less than 20% carbonate linkages.~~

~~16. A (poly)ol block copolymer according to any preceding claim, wherein block C has at least 5% carbonate linkages, more typically at least 10% carbonate linkages, most typically at least 15% carbonate linkages.~~

~~17. A (poly)ol block copolymer according to any preceding claim, wherein block C has between 0% and 50% carbonate linkages, more typically between 0% and 35% carbonate linkages, most typically, between 0% and 20% carbonate linkages.~~

~~18. A (poly)ol block copolymer according to any preceding claim, wherein block C has at least 60% ether linkages, more typically, at least 70% ether linkages, most typically at least 80% ether linkages.~~

19. A (poly)ol block copolymer according to any preceding claim, wherein block C has less than 95% ether linkages, more typically, less than 90% ether linkages, most typically less than 85% ether linkages.

20. A (poly)ol block copolymer according to any preceding claim, wherein block C has between 50% and 100% ether linkages, more typically between 65% and 100% ether linkages, most typically, between 80% and 100% ether linkages.

21. A (poly)ol block copolymer according to any preceding claim, wherein block A further comprises ether linkages.

22. A (poly)ol block copolymer according to claim 21 wherein block A has less than 24% ether linkages, more typically, less than 20% ether linkages, most typically, less than 15% ether linkages.

23. A (poly)ol block copolymer according to claims 21 or 22, wherein block A has at least 1% ether linkages, more typically, at least 3% ether linkages, most typically, at least 5% ether linkages.

24. A (poly)ol block copolymer according to any of claims 21-23, wherein block A has between 1% and 25% ether linkages, typically between 5% and 20% ether linkages, more typically, between 10% and 15% ether linkages.

25. A (poly)ol block copolymer according to any of claims 21-24 wherein the epoxide is asymmetric and the polycarbonate has between 40-100% head to tail linkages, preferably more than 50% head to tail linkages.

26. A (poly)ol block copolymer according to any of claims 21-25 wherein between 0.1 and 20% of the total epoxide in block A is an epoxide substrate containing more than one epoxide moiety, preferably a bis-epoxide.

27. A (poly)ol block copolymer according to any preceding claim, wherein block A is a generally alternating polycarbonate (poly)ol residue.

28. A (poly)ol block copolymer according to any preceding claim, wherein the mol/mol ratio of epoxide residues in block A to epoxide and, optionally, cyclic ester residues in block B and C combined is in the range 25:1 to 1:250.

29. A (poly)ol block copolymer according to any preceding claim where t is 2 or more, more typically 2-6, especially, 3-6, most typically 2 or 3.

30. A (poly)ol block copolymer according to any preceding claim, wherein block C is a polyether chain selected from the group consisting of polyoxymethylene, poly(ethylene oxide), polypropylene oxide), poly(butylene oxide), poly(glycidylether oxide), poly(chloromethylethylene oxide), poly(cyclopentene oxide), poly(cyclohexene oxide) and poly(3 -vinyl cyclohexene oxide).

31. A (poly)ol block copolymer according to any of claims 1 to 30, wherein at least 30% of the epoxide residues of block A are ethylene oxide or propylene oxide residues, typically, at least 50% of the epoxide residues of block A are ethylene oxide or propylene oxide residues, more typically, at least 75% of the epoxide residues of block A are ethylene oxide or propylene oxide residues, most typically, at least 90% of the epoxide residues of block A are ethylene oxide or propylene oxide residues.

32. A (poly)ol block copolymer according to any of claims 1 to 31, wherein at least 30% of the epoxide residues of block C , and block B if present therein, are ethylene oxide or propylene oxide residues, typically, at least 50% of the epoxide residues of block C are ethylene oxide or propylene oxide residues, more typically, at least 75% of the epoxide residues of block C are ethylene oxide or propylene oxide residues, most typically, at least 90% of the epoxide residues are ethylene oxide or propylene oxide residues.

33. A (poly)ol block copolymer according to any of claims 1-32, wherein the epoxide in block A and block C, and block B if present therein, is ethylene oxide and/or propylene oxide at a level of at least 95% of the total epoxide residues in both blocks.

34. A (poly)ol block copolymer according to any of claim 1 to 6, 8 to 28 or 30 to 33, wherein t=1 and the polyblock structure is: C-B-A'-Z'-Z

35. 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.

36. A composition according to claim 35 further comprising a (poly)isocyanate.

37. A composition according to claim 35 or 36, 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.

38. A composition according to claim 35 or 36, wherein a trimerisation catalyst is present.

39. A composition according to claim 38, 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.

40. A polyurethane produced from the reaction of a polyol block copolymer according to any of claims 1 to 34 or a composition according to claim 35 and a (poly)isocyanate.

41. A polyurethane comprising a block copolymer residue having a polycarbonate or polyethercarbonate block, A (-A'-Z'-Z-(Z'-A')$_n$-), (poly)ester blocks, B, and (poly)ethercarbonate or (poly)ether blocks, C, wherein the residue has the polyblock structure:

C-B-A'-Z'-Z-(Z'-A'-B-C)$_n$

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, or a polyethercarbonate chain having at least 30% ether linkages, each B is a (poly)ester block formed by epoxide and cyclic anhydride reaction/copolymerisation and/or cyclic ester ring-opening reaction/polymerisation, and each C is independently a (poly)ethercarbonate or (poly)ether block having 50-100% ether linkages; and wherein Z'-Z-(Z')$_n$ is a starter residue.

42. A polyurethane according to claim 41, wherein the residue includes any one or more of the features defined in claims 2-34.

43. A polyurethane according to of any of claims 40-42, 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 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).

44. A polyurethane according to claim 43, wherein the polyurethane is formed via a process that involves extruding, moulding, injection moulding, spraying, foaming, casting and/or curing.

45. A polyurethane according to claim 43 or 44, wherein the polyurethane is formed via a 'one pot' or 'pre-polymer' process.

46. An isocyanate terminated polyurethane prepolymer comprising the reaction product of a block copolymer according to any of claims 1 to 34 or a composition according to claim 35 with an excess of (poly)isocyanate.

47. An isocyanate terminated polyurethane prepolymer comprising a block copolymer residue having a polycarbonate or polyethercarbonate block, A (-A'-Z'-Z-(Z'-A')$_n$-), (poly)ester blocks, B, and (poly)ethercarbonate or (poly)ether blocks, C, wherein the residue has the polyblock structure:

C-B-A'-Z'-Z-(Z'-A'-B-C)$_n$

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, or a polyethercarbonate chain having at least 30% ether linkages, each B is a (poly)ester block formed by epoxide and cyclic anhydride reaction/copolymerisation and/or cyclic ester ring-opening reaction/polymerisation, and each C is independently a (poly)ethercarbonate or (poly)ether block having 50-100% ether linkages; and wherein Z'-Z-(Z')$_n$ is a starter residue.

48. An isocyanate terminated polyurethane prepolymer according to claim 47, wherein the residue includes any one or more of the features defined in claims 2-34.

49. A lubricant composition comprising a (poly)ol block copolymer of any of claims 1 to 34.

50. A surfactant composition comprising a (poly)ol block copolymer of any of claims 1 to 34.

51. A process for producing a (poly)ol block copolymer according to any of claims 1 to 34 comprising a first polymerisation reaction of a suitable catalyst with CO_2 and

epoxide, in the presence of a starter and/or solvent to produce a polycarbonate or polyethercarbonate (poly)ol copolymer, a second reaction of the copolymer of the first reaction with either epoxide and cyclic anhydride for reaction/copolymerisation and/or a cyclic ester for ring opening reaction/polymerisation in the presence of a suitable ester catalyst to produce a polycarbonate-ester or poly ether carbonate-ester block copolymer and a third reaction/polymerisation reaction of the block copolymer of the second reaction with an epoxide (and optionally, CO_2) in the presence of a suitable third reaction catalyst .

52. A process according to claim 51, further comprising a fourth reaction comprising the reaction of the poly block copolymer of the third reaction with a monomer or further polymer in the absence of a third reaction catalyst to produce a higher polymer.

53. A process according to claim 52, wherein the monomer or further polymer is a (poly)isocyanate and the product of the fourth reaction is a polyurethane.

54. 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, a second reaction takes place in either the first or a second reactor or both, and a third reaction takes place in the second reactor;

wherein the first reaction is the reaction of a carbonate or ethercarbonate catalyst with CO_2 and epoxide, in the presence of a starter and/or solvent to produce a polycarbonate or polyethercarbonate (poly)ol copolymer respectively, the second reaction is the reaction of the polycarbonate or polyether carbonate (poly)ol copolymer, an ester catalyst and either, an epoxide and an anhydride, or a cyclic ester to produce to produce a polycarbonate or poly ether carbonate ester block copolymer, and the third reaction is the reaction of a third reaction catalyst with the block copolymer of the second reaction and epoxide and optionally, CO_2 to produce the (poly)ol block copolymer.

55. A process according to claims 51-54, wherein the catalyst used in the production of the ethercarbonate of the first reaction, the second reaction or the third reaction is selected from one or more coordinative, organic, anionic, cationic, metal alkoxide and Lewis acid/base pair catalysts.

56. A process according to claim 55, wherein the catalyst used is selected from one or more DMC, metal hydroxide (such as KOH, NaOH, CsOH), superacid (such as

~~$HSbF_6$, HPF_6, CF_3SO_3H), Lewis acidic metal salts (such as $Zn(OTf)_2$, $La(OTf)_3$, $Y(OTf)_3$), $Cu(BF_4)_2$), group 3 compounds (such as Boron or Aluminium compounds, e.g BF_3, $B(C_6F_5)_3$, $Al(CF_3SO_3)_3$), organic (such as imidazole or phosphazonium catalysts), metallosalenates and metal alkoxide (such as $Ti(OiPr)_4$) catalysts.~~

~~57. A process according to claim 55 or 56, wherein the said catalyst is a DMC catalyst.~~

~~58. A process according to claims 54-57, wherein the second reaction takes place in the first reactor.~~

~~59. A process according to any of claims 51 to 58, wherein the catalyst of the first reaction also acts as the catalyst in the second reaction.~~

~~60. A process according to any of claims 54-59, wherein the second reaction takes place in the second reactor.~~

~~61. A process according to any of claims 51 to 60, wherein the catalyst of the third reaction also acts as the catalyst for the second reaction.~~

~~62. A process according to any of claims 51-61, wherein the second reaction and/or third reaction uses residual unreacted epoxide from the first reaction.~~

~~63. A process according to any of claims 51-62, wherein the said catalyst is pre-activated, optionally in a reactor or separately, optionally wherein the said catalyst is pre-activated with a starter compound or with the reaction product of the first, second or third reaction.~~

~~64. A process according to any of claims 51-63, wherein the third reaction catalyst is pre-activated, optionally in a reactor or separately, optionally with the polycarbonate or polyethercarbonate (poly)ol copolymer according to block A or copolymer of block B-A'-Z'-Z-(Z'-A'-B)$_n$ of any of claims 1 to 34 or is pre-activated with the (poly)ol block copolymer of any of claims 1-34.~~

~~65. A process according to any of claims 51-64, wherein the product of the first reaction is a low molecular weight polycarbonate or polyethercarbonate (poly)ol product having a molecular weight (Mn) in the range 200 to 4000 Daltons as measured by Gel Permeation Chromatography (GPC).~~

~~66. A process according to any of claims 51-65, wherein the first reaction produces generally alternating polycarbonate or polyethercarbonate (poly)ol product.~~

67. A process according to any of claims 51-66, wherein the epoxide is asymmetric and wherein the reaction produces a polycarbonate having between 40-100% head to tail linkages, preferably more than 70%, more than 80% or more than 90% head to tail linkages.

68. A process according to any of claims 54-67, wherein the product of the first or second reaction is fed into the second reactor, as a crude reaction mixture, wherein said second reactor contains a pre-activated third reaction catalyst.

69. A process according to any of claims 54-68, wherein the polycarbonate or polyether carbonate (poly)ol copolymer according to block A of any of claims 1 to 34 or the block copolymer of B-A'-Z'-Z-(Z'-A'-B)$_n$ is fed into the second reactor, as a crude reaction mixture, wherein said second reactor contains a pre-activated third reaction catalyst.

70. A process according to any of claims 51-69, wherein the first reaction is carried out under CO_2 pressure of less than 20 bar, more preferably, less than 10 bar, most preferably, less than 8 bar.

71. A process according to any of claims 51-70, wherein the third reaction is carried out under CO_2 pressure of less than 60 bar, preferably less than 20 bar, more preferably less than 10 bar, most preferably, less than 5 bar.

72. A process according to any of claims 51-71, wherein the second and/or third reaction is carried out substantially in the absence of CO_2.

73. A process according to any of claims 51-72, wherein the CO_2 is added continuously in the first reaction, preferably in the presence of a starter.

74. A process according to any of claims 51-73, wherein the first reaction can be a batch, semi-batch, or continuous process.

75. A process according to any of claims 51-74, wherein the second reaction can be a continuous process or semi batch process.

76. A process according to any of claims 51-75, wherein the third reaction can be a batch, semi-batch or continuous process.

77. A process according to any of claims 68-76, wherein the crude reaction mixture fed into the second reactor includes an amount of unreacted epoxide and/or CO_2 and/or starter.

78. A process according to any of claims 68-77, wherein one or more of the catalysts of the first and/or second reaction are present in the crude reaction mixture.

79. A process according to any of claims 68-79, wherein one or more of the catalysts of the first and/or second reaction have been removed from the crude reaction mixture prior to the addition to the second reactor.

80. A process according to any of claims 54-79, wherein the temperature of reaction in the first reactor when using the carbonate catalyst 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

81. A process according to any of claims 54-80, wherein the temperature of reaction in the second reactor is in the range from about 0 to about 160°C, preferably in the range from about 50 to about 140°C, more preferably from about 70 to about 110°C.

82. A process according to any of claims 54-81, wherein the reactors are located in series.

83. A process according to any of claims 54-82, wherein the reactors are nested.

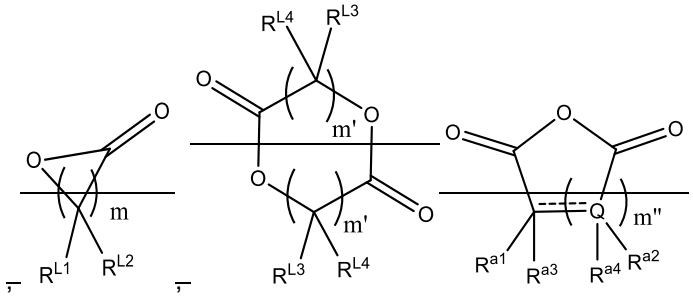
84. A process according to claim 83, wherein the first and second reactors are effective to provide different reaction conditions, such as temperature and/or pressure, to each other simultaneously.

85. A process according to any of claims 51-84, wherein the process employs a total amount of epoxide, and wherein about 1 to 100% of the total amount of epoxide is mixed in the first reaction, with any remainder added in the second and/or third 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%.

86. A product or process according to any of preceding claim, wherein the epoxides are selected from cyclohexene oxide, styrene oxide, ethylene oxide, propylene oxide, butylene oxide, substituted cyclohexene oxides (such as limonene oxide, $C_{10}H_{16}O$ or 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, $C_{11}H_{22}O$), 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-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-1,2,3,4-tetrahydronaphthalene, indene oxide, and functionalized 3,5-dioxaepoxides.

87. A product or process according to any preceding claim, wherein the cyclic anhydride or cyclic esters are selected from the groups:



wherein: m is 1 to 20, m' is 1 to 10 and m'' is 1 to 6;

R^{L1} and R^{L2} are independently selected from hydrogen, halogen, hydroxyl, nitro, alkoxy, aryloxy, heteroaryloxy, amino, alkylamino, imine, nitrile, acetylide, carboxylate or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, heteroaryl, alkylaryl or alkylheteroaryl, wherein two or more of R^{L1} and R^{L2} can optionally be taken together to form a saturated, partially saturated or unsaturated 3 to 12 membered, optionally substituted ring system, optionally containing one or more heteroatoms;

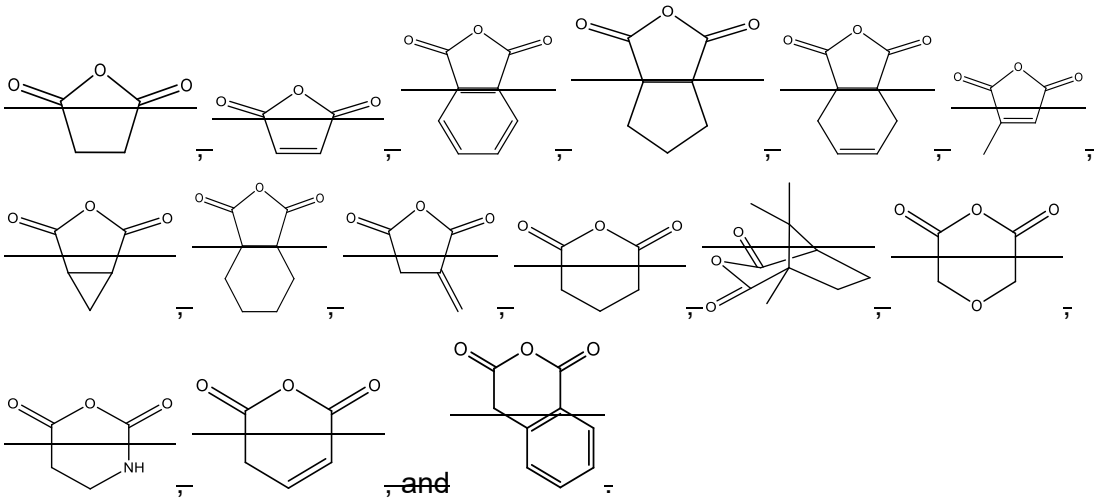
R^{L3} and R^{L4} are independently selected from hydrogen, halogen, hydroxyl, nitro, alkoxy, aryloxy, heteroaryloxy, amino, alkylamino, imine, nitrile, acetylide, carboxylate or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, heteroaryl, alkylaryl or alkylheteroaryl wherein. two or more of R^{L3} and R^{L4} can optionally be taken together to form a saturated, partially saturated or unsaturated 3 to 12 membered, optionally substituted ring system, optionally containing one or more heteroatoms; and wherein one or more R^{L3} and R^{L4} on adjacent carbon atoms can optionally be absent, thereby forming a double or triple bond;

R^{a1}, R^{a2}, R^{a3} and R^{a4} are independently selected from hydrogen, halogen, hydroxyl, nitro, alkoxy, aryloxy, heteroaryloxy, amino, alkylamino, imine, nitrile, acetylide, carboxylate or optionally substituted aliphatic, heteroaliphatic, alicyclic,

heteroalicyclic, aryl, heteroaryl, alkylaryl or alkylheteroaryl, or a polymeric species (e.g. polybis(phenol)A); wherein two or more of R^{a1}, R^{a2}, R^{a3} and R^{a4} can optionally be taken together to form a saturated, partially saturated or unsaturated 3 to 12 membered, optionally substituted ring system, optionally containing one or more heteroatoms, or can be taken together to form a double bond;

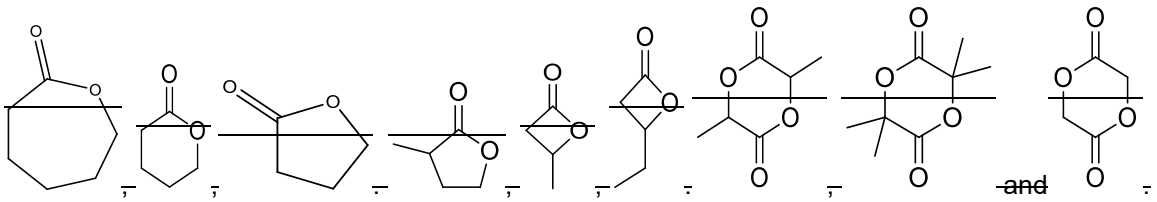
each Q is independently C, O, N or S, typically C, wherein R^{a3} and R^{a4} are either present, or absent, and ------ can either be ═══ or ———, according to the valency of Q.

88. A product or process according to any preceding claim, wherein the cyclic anhydride is selected from the group consisting of :



, and .

89. A product or process according to any preceding claim, wherein the cyclic ester is selected from the group consisting of :



and .

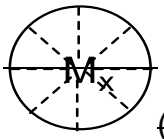
90. A process according to any of claims 51-89, wherein between 0.1 and 20% of the total epoxide in the first reaction is an epoxide substrate containing more than one epoxide moiety, preferably a bis-epoxide.

91. A process according to any of claims 51-90 wherein the carbonate catalyst is a catalyst capable of producing polycarbonate chains with greater than 76% carbonate linkages and/or wherein the ethercarbonate catalyst is capable of producing polyethercarbonate chains with greater than 30% ether linkages.

92. A process according to any of claims 51-91, wherein the carbonate catalyst is a metal catalyst comprising phenol or phenolate ligands.

93. A process according to any of claims 51-92, wherein the carbonate catalyst is a bimetallic complex comprising phenol or phenolate ligands.

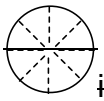
94. A process according to any of claims 51-93 wherein the carbonate catalyst is a catalyst of Formula (VI):



(VI)

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

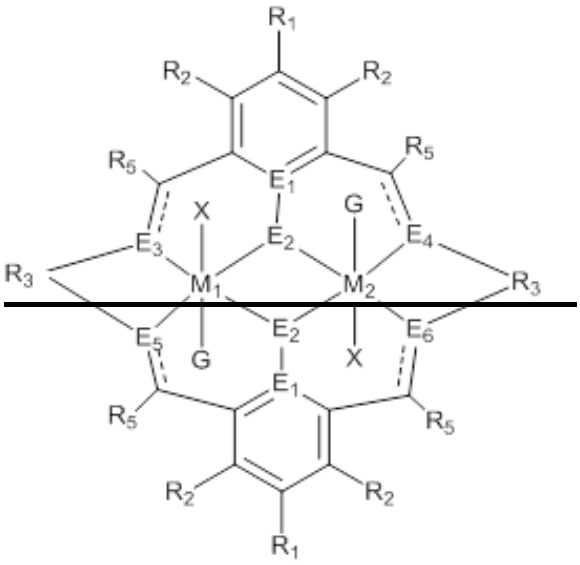
x is an integer from 1 to 4,


is a multidentate ligand or plurality of multidentate ligands;

L is a coordinating ligand;

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 (VI) above has an overall neutral charge.

95. A process according to any of claims 51-94, wherein the carbonate catalyst has the following structure:



(VII)

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)-$(X)_2$;

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;

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;

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 ———;

R_4 is independently selected from H, or optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, heteroaryl, alkylheteroaryl, -alkylC(O)OR_{19} or -alkylC≡N or alkylaryl;

X is independently selected from $OC(O)R_x$, OSO_2R_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 M_1 and M_2;

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.

96. A process according to any of claims 51-95, wherein the carbonate catalyst is selected from catalysts of formula (VI), metal salen catalysts, metal porphyrin catalysts, metal tetraaza annulene catalysts and metal beta-diiminate catalysts as defined herein.

97. A process according to any of claims 51-96, wherein the ethercarbonate catalyst for the first reaction, optionally, the catalyst for the second reaction and/or the catalyst for the third reaction is a DMC catalyst, and optionally, 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.

98. A process according to any of claims 57-97, 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), 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 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^+),

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;

the sum of the charges on the anions Y, CN and A multiplied by q, b and c respectively (e.g. Y x q + CN x b + A x 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,

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-butyn-2-ol, 3-methyl-1-pentyn-3-ol, or a combination thereof; 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'''.

99. A process according to any of claims 57-98, wherein the DMC catalyst comprises the formula:

$$M'_d[M''_e(CN)_f]_g$$

wherein M' and M'' are as defined in claim 98, and d, e, f and g are integers, and are chosen such that the DMC catalyst has electroneutrality,

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

100. A process according to any of claims 57-99, wherein the DMC catalyst comprises the formula:

$$M'_d[M''_e(CN)_f]_g \cdot hM'''X''_i \cdot jR^c \cdot kH_2O \cdot lH_rX'''$$

wherein M', M'', d, e, f and g are as defined in claim 98, 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 more, and the charge on the anion X'' multiplied by i satisfies the valency of 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''', and R^c is a complexing agent or a combination of one or more complexing agents.

101. A process according to any of claims 57-100, wherein the DMC catalyst is based upon $Zn_3[Co(CN)_6]_2$ (zinc hexacyanocobaltate).

102. A process according to any of claims 57-101, wherein the DMC catalyst is zinc hexacyanocobaltate and the one or more ligands are selected from alcohols and polyols.

103. A process according to claim 102, wherein the one or more complexing agents are selected from dimethoxyethane, tert-butyl alcohol, polyethylene glycol, polypropylene glycol, polyethercarbonate, poly(tetramethylene glycol), polycarbonate.

104. A process according to any of claims 54-103, wherein the product of the first and/or second reaction is fed into the second reactor in a single portion or in a continuous or discontinuous manner, optionally wherein the product of the first and/or second reaction comprises unreacted epoxide and/or carbonate or ethercarbonate catalyst.

105. A process according to any of claims 51-104, wherein the product of the first or second reaction is used to pre-activate the catalyst in the second or third reaction, prior to addition of epoxide and optionally CO_2 and/or cyclic anhydride and/or cyclic ester.

106. A process according to any of claims 51-105, wherein the polycarbonate (poly)ol copolymer according to block A of any of claims 1 to 34, the product of the second reaction or the (poly)ol block copolymer of any of claims 1 to 34 is used to

~~pre-activate the catalyst in the second or third reaction, prior to addition of epoxide and optionally CO_2 and/or cyclic anhydride and/or cyclic ester.~~

~~107. A process according to any of claims 51-106, wherein the same or different epoxides are used in the first and/or second and/or third reactions.~~

~~108. A process according to any of claims 51-107, wherein the epoxide used in the first or second or third reaction comprises propylene oxide, ethylene oxide or a mixture of propylene oxide and ethylene oxide.~~

1. A (poly)ol block copolymer comprising a polycarbonate or polyethercarbonate block, A (-A'-Z'-Z-(Z'-A')$_n$-), (poly)ester blocks, B, and (poly)ethercarbonate or (poly)ether blocks, C, wherein the (poly)ol block copolymer has the polyblock structure:

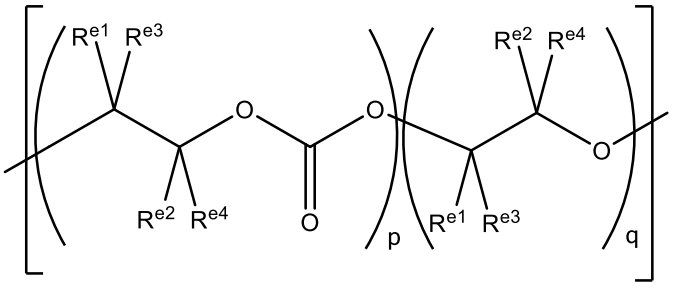
C-B-A'-Z'-Z-(Z'-A'-B-C)$_n$

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, or a polyethercarbonate chain having at least 30% ether linkages, wherein each B is a (poly)ester block formed by epoxide and cyclic anhydride reaction/copolymerisation and/or cyclic ester ring-opening reaction/polymerisation, and each C is independently a (poly)ethercarbonate or (poly)ether block having 50-100% ether linkages; and

wherein Z'-Z-(Z')$_n$ is a starter residue.

2. The (poly)ol block copolymer according to claim 1, wherein -A'- has the following structure:

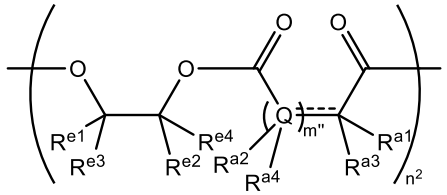


(I)

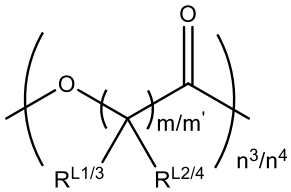
wherein in the case of the polycarbonate chain if q is not 0, the ratio of p:q is at least 7:3 and

wherein in the case of the polyethercarbonate chain the ratio of p:q is at least 3:7;

block B has one of the following structures



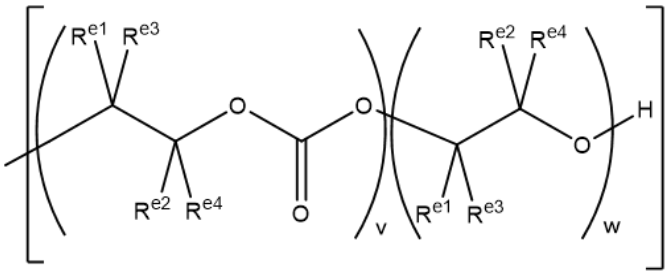
(II),



(III)

wherein n^2 is 1 or more and n^3/n^4 is 1 or more

and block C has the following structure:



(IV)

wherein w is 1 or more and v is 0 or more and if v is not 0, the ratio of w:v is at least 1:1; with the proviso that if the total of n^2 and n^3/n^4 is 1 then w is at least 2 and if w is 1 then the total of n^2 and n^3/n^4 is at least 2;

R^{e1}, R^{e2}, R^{e3} and R^{e4} independently depend on the epoxide residue in the respective block;

R^{a1}, R^{a2}, R^{a3} and R^{a4} or $R^{L1/L3}$, $R^{L2/L4}$, m, m' and m'' depend on the cyclic anhydride or ester residue in block B; and/or

wherein v=0 and block C is a (poly)ether; and/or

wherein v is 1 or more and block C is a (poly)ether carbonate; and/or

wherein each R^{e1}, R^{e2}, R^{e3}, or R^{e4} is independently selected from H, halogen, hydroxyl, or substituted alkyl, alkenyl, alkynyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl, heteroalkyl or heteroalkenyl, preferably selected from H or substituted alkyl; and/or

wherein R^{e1} or R^{e3} and R^{e2} or R^{e4} together form a saturated, partially unsaturated or unsaturated ring containing carbon and hydrogen atoms, and or one or more heteroatoms; and/or

wherein the starter residue depends on the nature of the starter compound, and wherein the starter compound has the formula (V):

$$Z-(R^Z)_a \quad (V)$$

wherein Z can be any group which can have 1 or more, or 2 or more, –RZ groups attached to it and may be selected from or substituted alkylene, alkenylene, alkynylene, heteroalkylene, heteroalkenylene, heteroalkynylene, cycloalkylene, cycloalkenylene, heterocycloalkylene, heterocycloalkenylene, arylene, heteroarylene, or 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, or at least 2, or a is in the range of between 1 or 2 and 8, or 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, or R^Z is selected from –OH, -NHR' or -C(O)OH, or each Rz is –OH, -C(O)OH or a combination thereof;

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

wherein Z' corresponds to R^z, except that a bond replaces the labile hydrogen atom; and/or

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, 3-buten-1-ol, 3-butyn-1-ol, 2-methyl-3-buten-2-ol, 2-methyl-3-butyn-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-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 propylene glycol mono-methyl ether, phenols such as linear or branched C_3-C_{20} 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, 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), 1-2-propanediol, 1,3-propanediol (propylene glycol), 1,2-butanediol, 1-3-butanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,8-octanediol, 1,10-decanediol, 1,12-dodecanediol, 1,4-cyclohexanediol, 1,2-diphenol, 1,3-diphenol, 1,4-diphenol, neopentyl glycol, catechol, cyclohexenediol, 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 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 polyalkylene glycols (PEGs or PPGs) having 5 or more –OH groups, or compounds having mixed functional groups including ethanolamine, diethanolamine, methyldiethanolamine, and phenyldiethanolamine; and/or

wherein the (poly)ol molecular weight (Mn) is in the range 300-20,000 Da and the molecular weight (Mn) of block A is in the range 200-4000 Da, wherein the molecular weight (Mn) of block B is in the range 50-5000 Da, and wherein the molecular weight (Mn) of block C is in the range 100-20,000 Da, or the molecular weight (Mn) of block A is 200-2000 Da, 200-1000 Da, or 400-800 Da, the molecular weight (Mn) of block B is 50-1000 Da, or 50-500 Da, or 50-400 Da, and/or the molecular weight (Mn) of block C is 200-10,000 Da, or 200-5000 Da, or wherein the molecular weight (Mn) is measured by Gel Permeation Chromatography (GPC); and/or

wherein block A is a polycarbonate and has at least 76%, at least 80% or at least 85% carbonate linkages; and/or

wherein block A has less than 98% carbonate linkages, less than 97% carbonate linkages or less than 95% carbonate linkages; and/or

wherein block A is a polycarbonate and has between 75% and 99% carbonate linkages, between 77% and 95% carbonate linkages, or between 80 and 90% carbonate linkages; and/or

wherein block C has less than 40 % carbonate linkages, less than 30% carbonate linkages or less than 20% carbonate linkages; and/or

wherein block C has at least 5% carbonate linkages, at least 10% carbonate linkages or at least 15% carbonate linkages; and/or

wherein block C has between 0% and 50% carbonate linkages, between 0% and 35% carbonate linkages, or between 0% and 20% carbonate linkages; and/or

wherein block C has at least 60% ether linkages, at least 70% ether linkages, or at least 80% ether linkages; and/or

wherein block C has less than 95% ether linkages, less than 90% ether linkages, or less than 85% ether linkages; and/or

wherein block C has between 50% and 100% ether linkages, between 65% and 100% ether linkages, or between 80% and 100% ether linkages; and/or

wherein block A further comprises ether linkages, or wherein:

block A has less than 24% ether linkages, less than 20% ether linkages, or less than 15% ether linkages, and/or wherein block A has at least 1% ether linkages, at least 3% ether linkages, or at least 5% ether linkages, and/or wherein block A has between 1% and 25% ether linkages, between 5% and 20% ether linkages, or between 10% and 15% ether linkages, and/or wherein the epoxide is asymmetric and the polycarbonate has between 40-100% head to tail linkages, preferably more than 50% head to tail linkages, and/or wherein between 0.1 and 20% of the total epoxide in block A is an epoxide substrate containing more than one epoxide moiety, preferably a bis-epoxide; and/or

wherein block A is a generally alternating polycarbonate (poly)ol residue; and/or

wherein the mol/mol ratio of epoxide residues in block A to epoxide and, or, cyclic ester residues in block B and C combined is in the range 25:1 to 1:250; and/or

where t is 2 or more, or 2-6, 3-6, or 2 or 3; and/or

wherein block C is a polyether chain selected from the group consisting of polyoxymethylene, poly(ethylene oxide), poly(propylene oxide), poly(butylene oxide), poly(glycidylether oxide), poly(chloromethylethylene oxide), poly(cyclopentene oxide), poly(cyclohexene oxide) and poly(3 -vinyl cyclohexene oxide); and/or

wherein at least 30% of the epoxide residues of block A are ethylene oxide or propylene oxide residues, at least 50% of the epoxide residues of block A are ethylene oxide or propylene oxide residues, at least 75% of the epoxide residues of block A are ethylene oxide or propylene oxide residues, or at least 90% of the epoxide residues of block A are ethylene oxide or propylene oxide residues; and/or

wherein at least 30% of the epoxide residues of block C, and block B if present therein, are ethylene oxide or propylene oxide residues, at least 50% of the epoxide residues of block C are ethylene oxide or propylene oxide residues, at least 75% of the epoxide residues of block C are ethylene oxide or propylene oxide residues, or at least 90% of the epoxide residues are ethylene oxide or propylene oxide residues; and/or

wherein the epoxide in block A and block C, and block B if present therein, is ethylene oxide and/or propylene oxide at a level of at least 95% of the total epoxide residues in both blocks.

3. A (poly)ol block copolymer according to claim 1 or claim 2, wherein t=1 and the polyblock structure is: C-B-A'-Z'-Z.

4. 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.

5. A composition according to claim 4 further comprising a (poly)isocyanate; and/or

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; or

wherein a trimerisation catalyst is present, or wherein an excess of (poly)isocyanate, or an excess of polymeric isocyanate relative to polyol, is present so that polyisocyanurate ring formation in the presence of the trimerisation catalyst is possible.

6. A polyurethane:

(i) produced from the reaction of a polyol block copolymer according to any of claims 1 to 3 or a composition according to claim 4 and a (poly)isocyanate; or

(ii) comprising a block copolymer residue having a polycarbonate or polyethercarbonate block, A (-A'-Z'-Z-(Z'-A')$_n$-), (poly)ester blocks, B, and (poly)ethercarbonate or (poly)ether blocks, C, wherein the residue has the polyblock structure:

C-B-A'-Z'-Z-(Z'-A'-B-C)$_n$

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, or a polyethercarbonate chain having at least 30% ether linkages, each B is a (poly)ester block formed by epoxide and cyclic anhydride reaction/copolymerisation and/or cyclic ester ring-opening reaction/polymerisation, and each C is independently a (poly)ethercarbonate or (poly)ether block having 50-100% ether linkages; and wherein Z'-Z-(Z')$_n$ is a starter residue.

7. A polyurethane:

(i) according to claim 6 (ii) wherein the residue includes any one or more of the features defined in claim 2 or claim 3; and/or

(i) according to claim 6 (i) or 6 (ii) 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 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), or wherein the polyurethane is formed via a process that involves extruding, moulding, injection moulding, spraying, foaming, casting and/or curing, and/or wherein the polyurethane is formed via a 'one pot' or 'pre-polymer' process.

8. An isocyanate terminated polyurethane prepolymer comprising:

(i) the reaction product of a block copolymer according to any of claims 1 to 3 or a composition according to claim 4 with an excess of (poly)isocyanate; or

(ii) a block copolymer residue having a polycarbonate or polyethercarbonate block, A (A'-Z'-Z-(Z'-A')n-), (poly)ester blocks, B, and (poly)ethercarbonate or (poly)ether blocks, C, wherein the residue has the polyblock structure:

C-B-A'-Z'-Z-(Z'-A'-B-C)n

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, or a polyethercarbonate chain having at least 30% ether linkages, each B is a (poly)ester block formed by epoxide and cyclic anhydride reaction/copolymerisation and/or cyclic ester ring-opening reaction/polymerisation, and each C is independently a (poly)ethercarbonate or (poly)ether block having 50-100% ether linkages; and wherein Z'-Z-(Z')n is a starter residue, or wherein the residue includes any one or more of the features defined in claims 2-3.

9. A lubricant composition or surfactant composition comprising a (poly)ol block copolymer of any of claims 1 to 3.

10. A process for producing a (poly)ol block copolymer:

(i) according to any of claims 1 to 3 comprising a first polymerisation reaction of a suitable catalyst with CO_2 and epoxide, in the presence of a starter and/or solvent to produce a polycarbonate or polyethercarbonate (poly)ol copolymer, a second reaction

of the copolymer of the first reaction with either epoxide and cyclic anhydride for reaction/copolymerisation and/or a cyclic ester for ring opening reaction/polymerisation in the presence of a suitable ester catalyst to produce a polycarbonate-ester or poly ether carbonate-ester block copolymer and a third reaction/polymerisation reaction of the block copolymer of the second reaction with an epoxide (and or, CO_2) in the presence of a suitable third reaction catalyst, or further comprising a fourth reaction comprising the reaction of the poly block copolymer of the third reaction with a monomer or further polymer in the absence of a third reaction catalyst to produce a higher polymer, further or wherein the monomer or further polymer is a (poly)isocyanate and the product of the fourth reaction is a polyurethane; or

(ii) in a multiple reactor system; the system comprising a first and second reactor wherein a first reaction takes place in the first reactor, a second reaction takes place in either the first or a second reactor or both, and a third reaction takes place in the second reactor;

wherein the first reaction is the reaction of a carbonate or ethercarbonate catalyst with CO_2 and epoxide, in the presence of a starter and/or solvent to produce a polycarbonate or polyethercarbonate (poly)ol copolymer respectively, the second reaction is the reaction of the polycarbonate or polyether carbonate (poly)ol copolymer, an ester catalyst and either, an epoxide and an anhydride, or a cyclic ester to produce to produce a polycarbonate or poly ether carbonate ester block copolymer, and the third reaction is the reaction of a third reaction catalyst with the block copolymer of the second reaction and epoxide and or, CO_2 to produce the (poly)ol block copolymer.

11. A process according to:

(i) claim 10 wherein the catalyst used in the production of the ethercarbonate of the first reaction, the second reaction or the third reaction is selected from one or more coordinative, organic, anionic, cationic, metal alkoxide and Lewis acid/base pair catalysts, or wherein the catalyst used is selected from one or more DMC, metal hydroxide (such as KOH, NaOH, CsOH), superacid (such as HSbF6, HPF6, CF3SO3H), Lewis acidic metal salts

(such as Zn(OTf)2, La(OTf)3, Y(OTf)3), Cu(BF4)2), group 3 compounds (such as Boron or Aluminium compounds, e.g BF3, B(C6F5)3, Al(CF3SO3)3), organic (such as imidazole or phosphazonium catalysts), metallosalenates and metal alkoxide (such as Ti(OiPr)4) catalysts, further or wherein the said catalyst is a DMC catalyst; and/or

wherein the catalyst of the first reaction also acts as the catalyst in the second reaction; and/or

wherein the catalyst of the third reaction also acts as the catalyst for the second reaction; and/or

wherein the second reaction and/or third reaction uses residual unreacted epoxide from the first reaction; and/or

wherein the said catalyst is pre-activated, or in a reactor or separately, or wherein the said catalyst is pre-activated with a starter compound or with the reaction product of the first, second or third reaction; and/or

wherein the third reaction catalyst is pre-activated, or in a reactor or separately, or with the polycarbonate or polyethercarbonate (poly)ol copolymer according to block A or copolymer of block B-A'-Z'-Z-(Z'-A'-B)$_n$ of any of claims 1 to 3 or is pre-activated with the (poly)ol block copolymer of any of claims 1-3; and/or

wherein the product of the first reaction is a low molecular weight polycarbonate or polyethercarbonate (poly)ol product having a molecular weight (Mn) in the range 200 to 4000 Daltons as measured by Gel Permeation Chromatography (GPC); and/or

wherein the first reaction produces generally alternating polycarbonate or polyethercarbonate (poly)ol product; and/or

wherein the epoxide is asymmetric and wherein the reaction produces a polycarbonate having between 40-100% head to tail linkages, preferably more than 70%, more than 80% or more than 90% head to tail linkages; and/or

wherein the first reaction is carried out under CO_2 pressure of less than 20 bar, more preferably, less than 10 bar, most preferably, less than 8 bar; and/or

wherein the third reaction is carried out under CO_2 pressure of less than 60 bar, preferably less than 20 bar, more preferably less than 10 bar, most preferably, less than 5 bar; and/or

wherein the second and/or third reaction is carried out substantially in the absence of CO_2; and/or

wherein the CO_2 is added continuously in the first reaction, preferably in the presence of a starter; and/or

wherein the first reaction can be a batch, semi-batch, or continuous process; and/or

wherein the second reaction can be a continuous process or semi batch process; and/or

wherein the third reaction can be a batch, semi-batch or continuous process; and/or

(ii) claim 10 (ii) or claim 11 (i) wherein the second reaction takes place in the first reactor; and/or

wherein the second reaction takes place in the second reactor; and/or

wherein the product of the first or second reaction is fed into the second reactor, as a crude reaction mixture, wherein said second reactor contains a pre-activated third reaction catalyst, or wherein the crude reaction mixture fed into the second reactor may include an amount of unreacted epoxide and/or CO_2 and/or starter, and/or one or more of the catalysts of the first and/or second reaction may be present in the crude reaction mixture, and/or one or more of the catalysts of the first and/or second reaction may be removed from the crude reaction mixture prior to the addition to the second reactor; and/or

wherein the polycarbonate or polyether carbonate (poly)ol copolymer according to block A of any of claims 1 to 3 or the block copolymer of B-A'-Z'-Z-$(Z'-A'-B)_n$ is fed into the second reactor, as a crude reaction mixture, wherein said second reactor contains a pre-activated third reaction catalyst; and/or

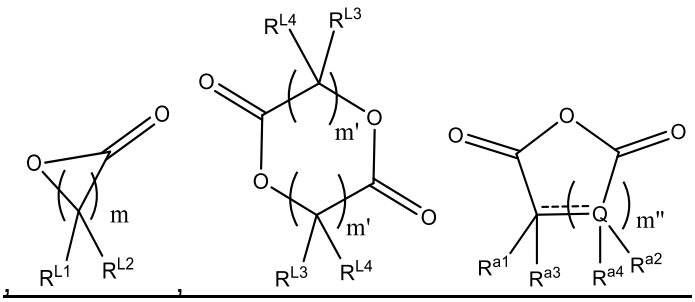
wherein the temperature of reaction in the first reactor when using the carbonate catalyst is in the range about 0°C to 250 °C, preferably from about 40 °C to about 160 °C, more preferably from about 50 °C to 120 °C; and/or

wherein the temperature of reaction in the second reactor is in the range from about 0 to about 160°C, preferably in the range from about 50 to about 140°C, more preferably from about 70 to about 110°C; and/or
wherein the reactors are located in series; and/or
wherein the reactors are nested, or wherein the first and second reactors are effective to provide different reaction conditions, such as temperature and/or pressure, to each other simultaneously

(iii) claim 10, claim 11 (i) or claim 11 (ii) wherein the process employs a total amount of epoxide, and wherein about 1 to 100% of the total amount of epoxide is mixed in the first reaction, with any remainder added in the second and/or third reaction; or with about 5 to 90% being mixed in the first reaction, or with about 10 to 90%, or with about 20 to 90%, or with about 40 to 90%, or with about 40 to 80%, or with about 5 to 50%.

12. A product or process according to any of preceding claim, wherein the epoxides are selected from cyclohexene oxide, styrene oxide, ethylene oxide, propylene oxide, butylene oxide, substituted cyclohexene oxides (such as limonene oxide, $C_{10}H_{16}O$ or 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, $C_{11}H_{22}O$), 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-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-1,2,3,4-tetrahydronaphthalene, indene oxide, and functionalized 3,5-dioxaepoxides; and/or

wherein the cyclic anhydride or cyclic esters are selected from the groups:



wherein: m is 1 to 20, m' is 1 to 10 and m'' is 1 to 6;

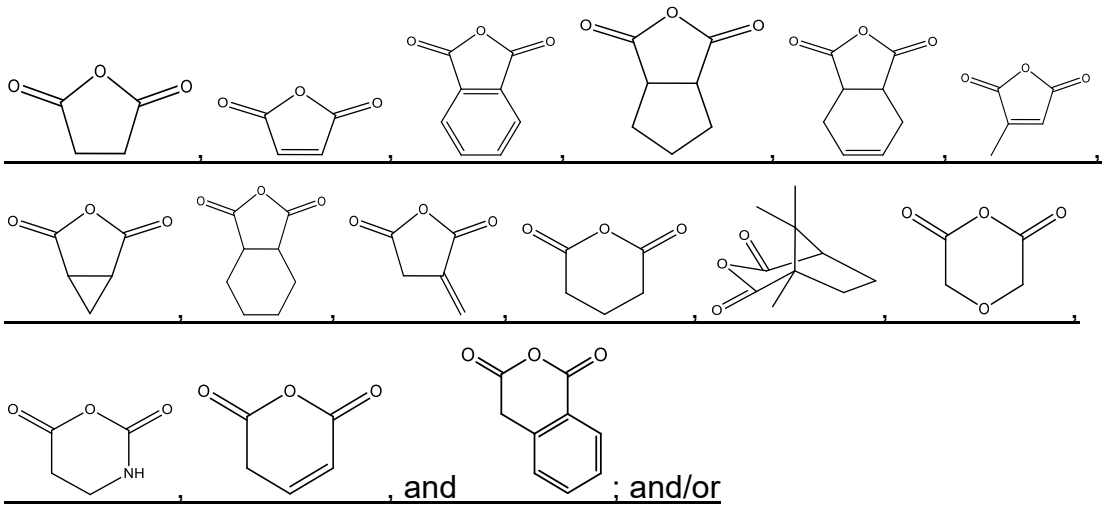
R^{L1} and R^{L2} are independently selected from hydrogen, halogen, hydroxyl, nitro, alkoxy, aryloxy, heteroaryloxy, amino, alkylamino, imine, nitrile, acetylide, carboxylate or substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, heteroaryl, alkylaryl or alkylheteroaryl, wherein two or more of R^{L1} and R^{L2} can or be taken together to form a saturated, partially saturated or unsaturated 3 to 12 membered, or substituted ring system, or containing one or more heteroatoms;

R^{L3} and R^{L4} are independently selected from hydrogen, halogen, hydroxyl, nitro, alkoxy, aryloxy, heteroaryloxy, amino, alkylamino, imine, nitrile, acetylide, carboxylate or substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, heteroaryl, alkylaryl or alkylheteroaryl wherein. two or more of R^{L3} and R^{L4} can or be taken together to form a saturated, partially saturated or unsaturated 3 to 12 membered, or substituted ring system, or containing one or more heteroatoms; and wherein one or more R^{L3} and R^{L4} on adjacent carbon atoms can or be absent, thereby forming a double or triple bond;

R^{a1}, R^{a2}, R^{a3} and R^{a4} are independently selected from hydrogen, halogen, hydroxyl, nitro, alkoxy, aryloxy, heteroaryloxy, amino, alkylamino, imine, nitrile, acetylide, carboxylate or substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, heteroaryl, alkylaryl or alkylheteroaryl, or a polymeric species (e.g. polybis(phenol)A); wherein two or more of R^{a1}, R^{a2}, R^{a3} and R^{a4} can or be taken together to form a saturated, partially saturated or unsaturated 3 to 12 membered, or substituted ring system, or containing one or more heteroatoms, or can be taken together to form a double bond;

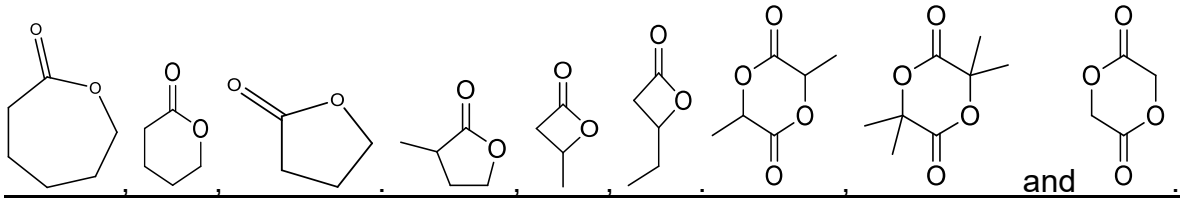
each Q is independently C, O, N or S, wherein R^{a3} and R^{a4} are either present, or absent, and ------ can either be ═══ or ———, according to the valency of Q; and/or

wherein the cyclic anhydride is selected from the group consisting of :



; and/or

wherein the cyclic ester is selected from the group consisting of :



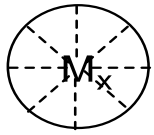
13. A process according to any of claims 10 to 12, wherein between 0.1 and 20% of the total epoxide in the first reaction is an epoxide substrate containing more than one epoxide moiety, preferably a bis-epoxide; and/or

wherein the carbonate catalyst is a catalyst capable of producing polycarbonate chains with greater than 76% carbonate linkages and/or wherein the ethercarbonate catalyst is capable of producing polyethercarbonate chains with greater than 30% ether linkages; and/or

wherein the carbonate catalyst is a metal catalyst comprising phenol or phenolate ligands; and/or

wherein the carbonate catalyst is a bimetallic complex comprising phenol or phenolate ligands; and/or

wherein the carbonate catalyst is a catalyst of Formula (VI):



(VI)

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

x is an integer from 1 to 4,

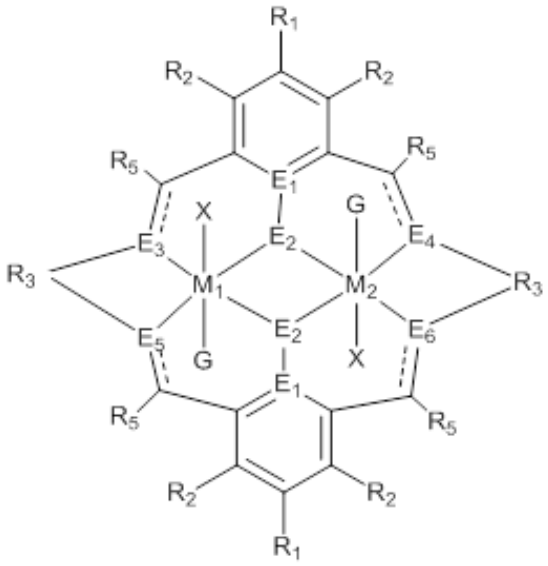


is a multidentate ligand or plurality of multidentate ligands;

L is a coordinating ligand;

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 (VI) above has an overall neutral charge; and/or

wherein the carbonate catalyst has the following structure:



(VII)

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)-$(X)_2$;

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 or substituted alkyl, alkenyl, alkynyl, haloalkyl, aryl, heteroaryl, alkoxy, aryloxy, alkylthio, arylthio, alicyclic or heteroalicyclic group;

R_3 is independently selected from or substituted alkylene, alkenylene, alkynylene, heteroalkylene, heteroalkenylene, heteroalkynylene, arylene, heteroarylene or cycloalkylene, wherein alkylene, alkenylene, alkynylene, heteroalkylene, heteroalkenylene and heteroalkynylene, may or be interrupted by aryl, heteroaryl, alicyclic or heteroalicyclic;

R_5 is independently selected from H, or 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 ———;

R_4 is independently selected from H, or substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl, heteroaryl, alkylheteroaryl, -alkylC(O)OR_{19} or -alkylC≡N or alkylaryl;

X is independently selected from $OC(O)R_x$, OSO_2R_x, $OSOR_x$, $OSO(R_x)_2$, $S(O)R_x$, OR_x, phosphinate, halide, nitrate, hydroxyl, carbonate, amino, amido or 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 M_1 and M_2;

R_x is independently hydrogen, or 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; and/or

wherein the carbonate catalyst is selected from catalysts of formula (VI), metal salen catalysts, metal porphyrin catalysts, metal tetraaza annulene catalysts and metal beta-diiminate catalysts as defined herein; and/or

wherein the ethercarbonate catalyst for the first reaction, or, the catalyst for the second reaction and/or the catalyst for the third reaction is a DMC catalyst, and or, 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, or in non-stoichiometric amounts.

14. A process according to any of claims 11 to 13 wherein the catalyst is a DMC catalyst and 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, or 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), 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 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^+),

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;

the sum of the charges on the anions Y, CN and A multiplied by q, b and c respectively (e.g. Y x q + CN x b + A x 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,

or 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-butyn-2-ol, 3-methyl-1-pentyn-3-ol, or a combination thereof; 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'''; and/or

wherein the DMC catalyst comprises the formula:

$$M'_d[M''_e(CN)_f]_g$$

wherein M' and M'' are as defined in claim 14, and d, e, f and g are integers, and are chosen such that the DMC catalyst has electroneutrality,

or, d is 3, e is 1, f is 6 and g is 2; and/or

wherein the DMC catalyst comprises the formula:

$$M'_d[M''_e(CN)_f]_g \cdot hM'''X''_i \cdot jR^c \cdot kH_2O \cdot lH_rX'''$$

wherein M', M'', d, e, f and g are as defined in claim 14, 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 more, and the charge on the anion X'' multiplied by i satisfies the valency of 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''', and R^c is a complexing agent or a combination of one or more complexing agents; and/or

wherein the DMC catalyst is based upon $Zn_3[Co(CN)_6]_2$ (zinc hexacyanocobaltate); and/or

wherein the DMC catalyst is zinc hexacyanocobaltate and the one or more ligands are selected from alcohols and polyols, or wherein the one or more complexing agents are selected from dimethoxyethane, tert-butyl alcohol, polyethylene glycol, polypropylene glycol, polyethercarbonate, poly(tetramethylene glycol), polycarbonate.

15. A process according to any of claims 10 (ii) to 14, wherein the product of the first and/or second reaction is fed into the second reactor in a single portion or in a continuous or discontinuous manner, or wherein the product of the first and/or second reaction comprises unreacted epoxide and/or carbonate or ethercarbonate catalyst.

16. A process according to any of claims 10 to 15, wherein the product of the first or second reaction is used to pre-activate the catalyst in the second or third reaction, prior to addition of epoxide and or CO_2 and/or cyclic anhydride and/or cyclic ester; and/or

wherein the polycarbonate (poly)ol copolymer according to block A of any of claims 1 to 3, the product of the second reaction or the (poly)ol block copolymer of any of claims 1 to 3 is used to pre-activate the catalyst in the second or third reaction, prior to addition of epoxide and or CO_2 and/or cyclic anhydride and/or cyclic ester; and/or

wherein the same or different epoxides are used in the first and/or second and/or third reactions; and/or

wherein the epoxide used in the first or second or third reaction comprises propylene oxide, ethylene oxide or a mixture of propylene oxide and ethylene oxide.