Claims

1. A polyol block copolymer comprising a polycarbonate block, A (-A'-Z'-Z-(Z'-A')$_n$-), and polyethercarbonate blocks, B, wherein the polyol block copolymer has the polyblock structure:

$$B\text{-}A'\text{-}Z'\text{-}Z\text{-}(Z'\text{-}A'\text{-}B)_n$$

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, 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')$_n$ is a starter residue.

2. A polyol block copolymer according to claim 1, wherein the starter residue depends on the nature of the starter compound, and wherein the starter compound has the formula (III):

$$Z\text{-}(R^Z)_a \qquad \text{(III)}$$

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, 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;

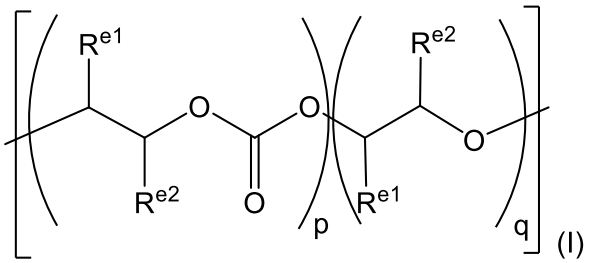
a is an integer which is at least 1, typically, at least 2, optionally a is in the range of between 1 or 2 and 8, optionally a is in the range of between 2 and 6;

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 R^z 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.

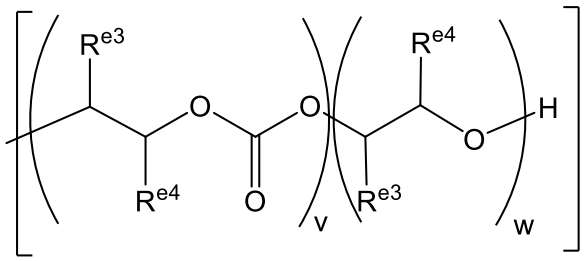
3. A polyol block copolymer according to claim 1 or 2, wherein -A'- has the following structure:



(I)

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

and block B has the following structure:



(II)

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 epoxide used to prepare blocks A and B.

4. A polyol block copolymer according to any preceding claim, wherein a is an integer which is at least 2.

5. A polyol block copolymer according to any of claims 1-4, wherein a is 1 and accordingly the copolymer is of formula B-A'-Z'-Z.

6. A polyol 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.

7. A polyol block copolymer according to any preceding claim, wherein the polyol 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, and wherein 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.

8. A polyol block copolymer according to any preceding claim, wherein block A has between 75% and 99% carbonate linkages, more typically, between 77% and 95% carbonate linkages, most typically between 80 and 90% carbonate linkages.

9. A polyol block copolymer according to any preceding claim, wherein block B has between 1% and 50% carbonate linkages, more typically between 5% and 45% carbonate linkages, most typically, between 10% and 40% carbonate linkages, and/or wherein block B has between 50%

and 99% ether linkages, more typically between 55% and 95% ether linkages, most typically, between 60% and 90% ether linkages.

10. A polyol block copolymer according to any preceding claim, wherein block A further comprises ether linkages,

preferably 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.

11. A polyol block copolymer according to claim 10, wherein the epoxide is asymmetric and the polycarbonate has between 40-100% 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.

12. A polyol block copolymer according to any preceding claim, wherein block A is a generally alternating polycarbonate polyol residue, and/or wherein the mol/mol ratio of block A to block B is in the range 25:1 to 1:250.

13. A polyol block copolymer according to any of claims 1 to 12, 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, and/or wherein at least 30% of the epoxide residues of block B are ethylene oxide or propylene oxide residues, typically, at least 50% of the epoxide residues of block B are ethylene oxide or propylene oxide residues, more typically, at least 75% of the epoxide residues of block B are ethylene oxide or propylene oxide residues, most typically, at least 90% of the epoxide residues of block B are ethylene oxide or propylene oxide residues.

14. A composition comprising the polyol block copolymer of any preceding claim and one or more additives selected from catalysts, blowing agents, stabilizers, plasticisers, fillers, flame retardants, and antioxidants, wherein the composition optionally further comprises a (poly)isocyanate.

15. A polyurethane produced from the reaction of a polyol block copolymer according to any of claims 1 to 13 or a composition according to claim 14 and a (poly)isocyanate, optionally

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).

16. An isocyanate terminated polyurethane prepolymer comprising the reaction product of a block copolymer according to any of claims 1 to 13 or a composition according to claim 14 with an excess of (poly)isocyanate.

17. A lubricant composition or a surfactant composition comprising a polyol block copolymer of any of claims 1 to 13.

18. A process for producing a polycarbonate ethercarbonate polyol 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 CO_2 and epoxide, in the presence of a starter and~~/or~~ optionally a solvent to produce a polycarbonate polyol copolymer and the second reaction is the reaction of a DMC catalyst with the polycarbonate polyol copolymer of the first reaction and CO_2 and epoxide to produce the polyol block copolymer, wherein the process optionally further comprises a third reaction comprising the reaction of the poly block copolymer of the second reaction with a monomer or further polymer in the absence of a DMC catalyst to produce a higher polymer, preferably wherein the monomer or further polymer is a (poly)isocyanate and the product of the third reaction is a polyurethane.

19. A process for producing a polyol 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 first reaction is the reaction of a carbonate catalyst with CO_2 and epoxide, in the presence of a starter and/or solvent to produce a polycarbonate polyol copolymer and the second reaction is the reaction of a DMC catalyst with the polycarbonate polyol compound of the first reaction and CO_2 and epoxide to produce the polyol block copolymer.

20. A process according to claim 18 or 19, wherein the product of the first reaction is a low molecular weight polycarbonate polyol product having a molecular weight (Mn) in the range 200 to 4000 Daltons as measured by Gel Permeation Chromatography (GPC).

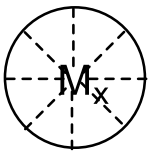
21. A process according to any of claims 18 -20, wherein the product of the first reaction is fed into the second reactor, as a crude reaction mixture, wherein said second reactor contains a pre-activated DMC catalyst.

22. A process according to any of claims 18-21, 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.

23. A process according to any of claims 18-22, 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.

24. A process according to any of claims 18-23, wherein the carbonate catalyst is a catalyst capable of producing polycarbonate chains with greater than 76% carbonate linkages, and/or wherein the carbonate catalyst is a metal catalyst comprising phenol or phenolate ligands.

25. A process according to any of claims 18-24, wherein the carbonate catalyst is a catalyst of Formula (IV):



(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;

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.

26. A process according to any of claims 18-25, wherein the DMC catalyst is based upon $Zn_3[Co(CN)_6]_2$ (zinc hexacyanocobaltate).

27. A process according to any of claims 18-26, wherein the product of the first 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 reaction comprises unreacted epoxide and/or carbonate catalyst.