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(54) Title: A POLYOL BLOCK COPOLYMER

(57) Abstract: The present invention relates to a (poly)ol block copolymer of general structure B-A-(B)n, wherein block A is a polycarbonate block or polyester block, n=t-1 and t = the number of reactive end residues on block A, wherein block B is a polyethercarbonate block and wherein > 70% of the copolymer chain ends are terminated by primary hydroxyl groups. The invention further relates to the process of producing such copolymers and products incorporating such copolymers.

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A Polyol Block Copolymer

Technical Field

The present invention relates to (poly)ol block copolymers with >70% primary hydroxyl end groups comprising polycarbonate (A) and polyether carbonate blocks (B) in a general BA(B)n structure, the process of producing such (poly)ol block copolymers from a two step process generally carried out in two separate reactions, and products and compositions incorporating such copolymers or their residues.

Background

It is generally desirable for polyols that are used in polyurethane applications to have primary hydroxyl end groups, due to the increased reactivity of these primary hydroxyl groups with isocyanates (compared to less reactive secondary hydroxyls). Polyether polyols are generally produced by either basic catalysis using sodium or potassium hydroxide or by using so-called double metal cyanide (DMC) catalysts. Advantageously, hydroxide catalysts are able to react with both ethylene oxide (EO) and propylene oxide (PO) and can be used to end-cap PO based polyols with EO, resulting in polyols with all primary hydroxyl end groups. Unfortunately, the hydroxide catalyst process includes a lengthy purification including neutralisation, filtration and drying. Furthermore, alkaline catalysts promote formation of unsaturated, non-hydroxyl end groups at higher molecular weights, resulting in reduced functionality of the polyols and poor quality polyurethanes. DMC catalysts produce polyols with very low amounts of unsaturated end groups even at higher molecular weights and do not require any purification. However, DMC catalysts are less reactive with EO than PO and do not effectively end-cap PO polyols with EO to generate polyols with 100% primary hydroxyl end groups. Instead, the EO mostly reacts into long polyethylene oxide chains leaving the PO polyol with a high molecular weight component (which results in poor quality polyurethane products) and mostly less reactive secondary hydroxyl end groups.

In order to produce polyols above ~2000 molecular weight with low unsaturation, the desired functionality and a high proportion of primary hydroxyl end groups it has been necessary to produce a primarily PO based polyol using a DMC catalyst and then end-cap this with EO using hydroxide catalysts entailing a complex purification process. This is both inefficient and expensive.

Various methods, such as those disclosed in WO2001044347 and WO2004111107, have been suggested to increase the proportion of primary hydroxyl end groups using DMC catalysts. This generally involves starting with a predominantly PO feed and increasing the ratio of EO in the feed as the reaction continues. Primary hydroxyl contents of around 40-60% have been demonstrated by this method.

It also known that DMC catalysts can be used with epoxides and carbon dioxide to produce so called ‘polyether carbonate’ polyols. Various methods include those disclosed in WO2008058913, WO2008013731 and US6762278. Typically, these processes require high pressures to enable even moderate CO_2 content within the polyols. These polyols have primarily been demonstrated with PO and hence have a very low (<5%) primary hydroxyl content.

US10174151 discloses a method for making a polyether carbonate polyol using a DMC where a polyol is first made with CO_2 and PO and then end-capped with increasing ratios of EO/PO with a DMC in a solvent (cyclic propylene or ethylene carbonate). The maximum primary hydroxyl content demonstrated by this method is 65%.

WO2015059068 and US2015/0259475 from Covestro disclose the use of a DMC catalyst for the production of polyether carbonate polyols from CO_2 and alkylene oxide in the presence of a starter compound. Many H-functional starter compounds are listed including polyether carbonate polyols, polycarbonate polyols and polycarbonates.

Polyethercarbonate polyols produced by a DMC alone generally have a structure which is rich in ether linkages in the centre of the polymer chain and richer in carbonate groups towards the hydroxyl terminal groups. This is not advantageous as the ether groups are substantially more stable to heat and basic conditions than the carbonate linkages.

WO2010062703 discloses production of block copolymers having a polycarbonate block and a hydrophilic block (e.g. a polyether). Various structures are described generally with a polyether block having polycarbonate blocks at either end. Some examples include a polycarbonate block with polyether end blocks. A two pot production is described, using in some examples a carbonate catalyst in the first reaction to produce an alternating polycarbonate block, followed by quenching of the reaction, isolation of the polyol from solvents and unreacted monomers and then a second batch reaction with a DMC catalyst (in the absence of CO_2) to incorporate the hydrophilic oligomer, such as poly(alkylene oxide). Some examples use ethylene oxide as the ether block, but no determination is made of the proportion of primary and secondary hydroxyl end groups. The polymers have use in enhanced oil recovery.

It has been advantageously found that by using polycarbonate starters and a DMC catalyst with epoxides and CO_2, (poly)ols can be produced with very high primary hydroxyl content (greater than 70%, even greater than 80% primary hydroxyl end groups). The use of the carbonate starters (either directly from a first reaction mixture or using purified starters materials) is advantageous in promoting even end-capping with a DMC catalyst in the presence of CO_2.

The (poly)ols can be made with varying CO_2 contents, low degrees of unsaturation, high primary hydroxyl content and don't require the purification processes used for hydroxide catalysts. The process is therefore advantageous over metal hydroxide catalysts, DMC catalysts (alone) and in enabling the use of CO2 to make (poly)ols with reduced carbon footprint.

Advantageously, the low molecular weight polycarbonate (poly)ol starters do not have to be isolated but can be made in one reactor and transferred directly into the second without removing any catalyst, unreacted monomer or solvents.

Summary of the Invention

According to the first aspect of the invention, there is provided a (poly)ol block copolymer of general structure B-A-(B)n wherein block A is a polycarbonate or polyester block, wherein n=t-1 and t = the number of reactive end residues on block A, wherein block B is a polyethercarbonate block and wherein > 70% of the copolymer chain ends are terminated by primary hydroxyl groups.

Preferably, > 75%, more preferably, >80% of the copolymer chain ends are terminated by primary hydroxyl groups.

Preferably, the polymer chains are evenly end-capped. By evenly end-capped is meant that on average more than 75% of the polymer chains are end capped with an EO residue, more typically, more than 85% of the polymer chains are end capped with an EO residue, most typically, at least 90% of the polymer chains are end capped with an EO residue.

The A block has typically greater than 70% carbonate linkages and the B block has typically less than 50% carbonate linkages.

The polycarbonate of block A may also be made by any suitable method in addition to the process as defined in the aspects herein from alkylene oxides and CO_2. For example, the polycarbonate diols may be prepared by reaction of phosgene and a dihydrocarbyl carbonate such as dimethyl carbonate, diethyl carbonate or diphenyl carbonate. Examples of polycarbonates are to be found e.g. in EP-A 1359177.

Typically, block A is a polyalkylenecarbonate block, more typically derived from alkylene oxides and CO_2, most typically, alkylene oxide and CO_2 provide at least 90% of the residues in the block, especially, at least 95% of the residues in the block, more especially, at least 99% of the residues in the block, most especially, about 100% of the residues in the block are residues of alkylene oxide and CO_2. Most typically, block A includes ethylene oxide and/or propylene oxide residues and optionally other alkylene oxide residues such as butylene oxide, glycidyl ethers, glycidyl esters and glycidyl carbonates. Typically, at least 50% of the alkylene oxide residues of block A are ethylene oxide or propylene oxide residues, more typically, at least 70% of the alkylene oxide residues of block A are ethylene oxide or propylene oxide residues, most typically, at least 90% of the alkylene oxide residues of block A are ethylene oxide or propylene oxide residues, especially, ethylene oxide at these levels.

Typically, the carbonate of block A is derived from CO_2 i.e. the carbonates incorporate CO_2 residues. Typically, block A has between 70-100% carbonate linkages, more typically, 80-100%, most typically, 90-100%. The polycarbonate block, A, of the (poly)ol block copolymer may have at least 76% carbonate linkages, preferably at least 80% carbonate linkages, more preferably at least 85% carbonate linkages. Block A may have less than 98% carbonate linkages, preferably less than 97% carbonate linkages, more preferably less than 95% carbonate linkages. Optionally, block A has between 75% and 99% carbonate linkages, preferably between 77% and 95% carbonate linkages, more preferably between 80% and 90% carbonate linkages.

Surprisingly, block A of the present invention has been found to facilitate the incorporation of more primary hydroxyl terminal ends in the B block. The block A connected to the respective B block is therefore surprisingly adapted to react with alkylene oxide so that the (poly)ol block copolymer has > 70% primary hydroxyl ends, typically, > 75%, more preferably, >80% primary hydroxyl ends

Typically, block B includes ethylene oxide and optionally other alkylene oxide residues. Typically, alkylene oxide residues provide at least 90% of the non-carbonate functional group residues in the block, especially, at least 95% of the non-carbonate functional group residues in the block, more especially, at least 99% of the non-carbonate functional group residues in the block, most especially, about 100% of the non-carbonate functional group residues in the block are residues of alkylene oxide. Typically, ethylene oxide residues form 5-100% of the alkylene oxide residues in block B, more typically, 10-100%, most typically 10-50% of the alkylene oxide residues. Typically, block B is a mixture of at least ethylene and propylene oxide residues. Typically, at least 50% of the alkylene oxide residues of block B are ethylene oxide or propylene oxide residues, more typically, at least 70% of the alkylene oxide residues of block B are ethylene oxide or propylene oxide residues, most typically, at least 90% of the alkylene oxide residues of block B are ethylene oxide or propylene oxide residues, especially, ethylene oxide at these levels. Generally, to form a primary hydroxyl end, at least the terminal alkylene oxide residue is an ethylene oxide residue. Typically, at least 70% of the terminal alkylene oxide residues are ethylene oxide residues, more typically, at least 75%, most typically, at least 80% of the terminal alkylene oxide residues are ethylene oxide residues. It is also possible for a small proportion of other alkylene oxides to form a primary hydroxyl end but such primary hydroxyl arrangements are unusual due to the preference for ring-opening at the unhindered methylene carbon.

Generally, where more than one alkylene oxide is used >50% of the ethylene oxide residues in block B are incorporated into the copolymer chain nearer to the copolymer terminal end than the A block terminal end, more typically, > 60% of the ethylene oxide residues, most typically, at least 70% are so incorporated.

Optionally, block B incorporates CO_2 residues in the carbonate groups. Typically, the polyethercarbonate blocks, B, of the (poly)ol block copolymer may have less than 40% carbonate linkages, preferably less than 35% carbonate linkages, more preferably less than 30% carbonate linkages. Block B may have at least 5% carbonate linkages, preferably at least 10% carbonate linkages, more preferably at least 15% carbonate linkages. Optionally, block B may have between 1% and 50% carbonate linkages, preferably between 5% and 45% carbonate linkages, more preferably between 10% and 40% carbonate linkages.

The polyethercarbonate blocks, B, of the (poly)ol block copolymer may have at least 60% ether linkages, preferably at least 65% ether linkages, more preferably at least 70% ether linkages. The polyethercarbonate blocks, B, of the (poly)ol block copolymer may have less than 95% ether linkages, preferably less than 90% ether linkages, more preferably less than 85% ether linkages. Optionally, block B may have between 50% and 99% ether linkages, preferably between 55% and 95% ether linkages, more preferably between 60% and 90% ether linkages.

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

Optionally, block A of the present invention may be a generally alternating polycarbonate (poly)ol residue.

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

Typically in the (poly)ol block copolymer of the invention ethylene oxide residues form 0-100% of the alkylene oxide residues in the (poly)ol block copolymer, typically 5-70%, more typically, 10-60% of the alkylene oxide residues in the (poly)ol block copolymer, most typically, 10-40% of the alkylene oxide residues in the (poly)ol block copolymer and/or, at least 5%, 10%, 15%, 20%, 25% or 30% of the alkylene oxide residues in the (poly)ol block copolymer are ethylene oxide residues .

The A block of the present invention with a starter may be defined as $-A'-Z'-Z-(Z'-A')_n-$

Accordingly, the polyblock structure of the copolymer may be defined as :

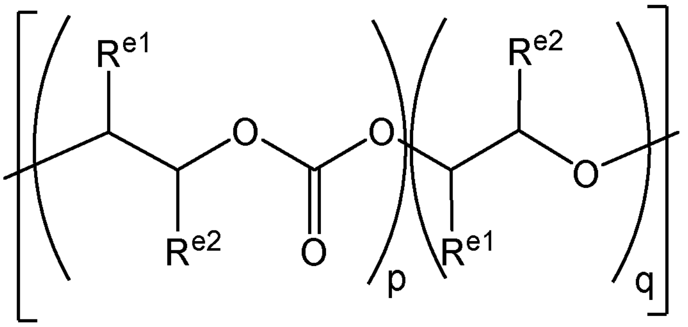
$B-A'-Z'-Z-(Z'-A'-B)_n$

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. The (poly)ol has at least 70% primary hydroxyl end groups.

For the avoidance of doubt, when t=1 then n=0 and the polyblock structure is:-

B-A'-Z'-Z, the "% of the copolymer chain ends terminated by primary hydroxyl groups" as claimed refers to the percentage of OH functional chain ends that are so terminated.

The polycarbonate block comprises -A'- which may have the following structure:

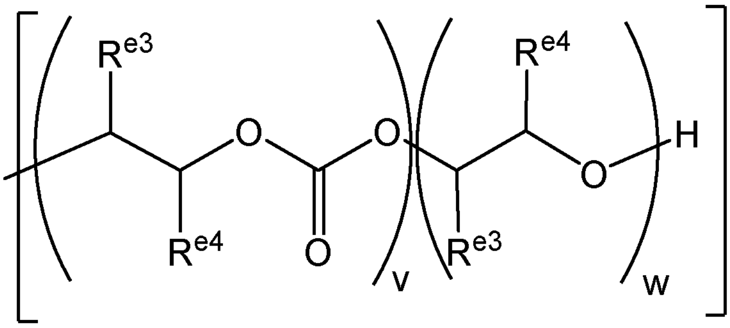


(I)

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

R^{e1} and R^{e2} depend on the nature of the alkylene oxide used to prepare block A.

The polyethercarbonate block B may have the following structure:



(II)

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

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

Each R^{e1}, R^{e2}, R^{e3}, or R^{e4} may be 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.

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

As set out above, the nature of R^{e1}, R^{e2}, R^{e3} and R^{e4} will depend on the alkylene oxide used in the reaction. For example, if the alkylene oxide is cyclohexene oxide (CHO), then R^{e1} and R^{e2} (or R^{e3} and R^{e4}) will together form a six membered alkyl ring (e.g. a cyclohexyl ring). If the alkylene oxide is ethylene oxide, then R^{e1} and R^{e2} (or R^{e3} and R^{e4}) will be H. If the alkylene oxide is propylene oxide, then R^{e1} (or R^{e3}) will be H and R^{e2} (or R^{e4}) will be methyl (or R^{e1} (or R^{e3}) will be methyl and R^{e2} (or R^{e4}) will be H, depending on how the alkylene oxide is added into the polymer backbone. If the alkylene oxide is butylene oxide, then R^{e1} (or R^{e3}) will be H and R^{e2} (or R^{e4}) will be ethyl (or *vice versa*). If the alkylene oxide is styrene oxide, then R^{e1} (or R^{e3}) may be hydrogen, and R^{e2} (or R^{e4}) may be phenyl (or *vice versa*). If the alkylene oxide is a glycidyl ether, then R^{e1} (or R^{e3}) will be an ether group ($-CH_2-OR_{20}$) and R^{e2} (or R^{e4}) will be H (or *vice versa*). If the alkylene oxide is a glycidyl ester, then R^{e1} (or R^{e3}) will be an ester group ($-CH_2-OC(O)R_{12}$) and R^{e2} (or R^{e4}) will be H (or *vice versa*). If the alkylene oxide is a glycidyl carbonate, then R^{e1} (or R^{e3}) will be a carbonate group (CH_2- $OC(O)OR_{18}$) and R^{e2} (or R^{e4}) will be H (or *vice versa*).

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

Thus, R^{e1} and R^{e2} (or R^{e3} and R^{e4}) may be independently selected from hydrogen, alkyl or aryl, or R^{e1} and R^{e2} (or R^{e3} and R^{e4}) may together form a cyclohexyl ring, preferably R^{e1} and R^{e2} (or R^{e3} and R^{e4}) may be independently selected from hydrogen, methyl, ethyl or phenyl, or R^{e1} and R^{e2} (or R^{e3} and R^{e4}) may together form a cyclohexyl ring.

The identity of Z and Z' will depend on the nature of the starter compound.

The starter compound may be of the formula (III):

$$Z\!\left(R^Z\right)_a \qquad \text{(III)}$$

Z can be any group which can have 1 or more, typically, 2 or more $-R^Z$ groups attached to it. Thus, Z 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. Optionally Z is alkylene, heteroalkylene, arylene, or heteroarylene.

It will be appreciated that 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.

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).

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

Z' corresponds to R^z, except that a bond replaces the labile hydrogen atom. Therefore, the identity of each Z' depends on the definition of R^Z in the starter compound. Thus, it will be appreciated that each Z' may be –O-, -NR'-, –S-, -C(O)O-, -P(O)(OR')O-, -PR'(O)(O-)$_2$ or –PR'(O)O- (wherein R' may be H, or optionally substituted alkyl, heteroalkyl, aryl, heteroaryl, cycloalkyl or heterocycloalkyl, preferably R' is H or optionally substituted alkyl), preferably Z' may be –C(O)O-, -NR'- or –O-, more preferably each Z' may be –O-, -C(O)O- or a combination thereof, more preferably each Z' may be –O-.

Preferably, the (poly)ol block copolymer has a molecular weight (Mn) in the range of from about 300 to 20,000 Da, more preferably in the range of from about 400 to 8000 Da, most preferably from about 500-6000 Da.

The polycarbonate block, A, of the (poly)ol block copolymer preferably has a molecular weight (Mn) in the range of from about 200 to 4000 Da, more preferably in the range of from about 200 to 2000 Da, most preferably from about 200 to 1000 Da, especially from about 400 to 800 Da.

The polyethercarbonate blocks, B, of the (poly)ol block copolymer preferably have a molecular weight (Mn) in the range of from about 100 to 20,000 Da, more preferably of from about 200 to 10,000 Da, most preferably from about 200 to 5000 Da.

Alternatively, the polyethercarbonate blocks B and hence also the (poly)ol block copolymer may have a high molecular weight. The polyethercarbonate blocks B may have a molecular weight (Mn) of at least about 25,000 Daltons, such as at least about

40,000 Daltons, e.g. at least about 50,000 Daltons, or at least about 100,000 Daltons. High molecular weight (poly)ol block copolymers of the present invention may have molecular weights above about 100,000 Daltons.

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

Typically, the mol/mol ratio of block A to block B is in the range 25:1 to 1:250. Typically the weight ratio of block A to block B is in the range 50:1 to 1:100.

According to the second aspect of the invention, there is also provided a composition comprising the (poly)ol block copolymer according to the first aspect of the present invention. The composition may also comprise of one or more additives from those known in the art. The additives may include, but are not limited to, catalysts, blowing agents, stabilizers, plasticisers, fillers, flame retardants, defoamers, and antioxidants.

Fillers may be selected from mineral fillers or polymer fillers, for example, styrene-acrylonitrile (SAN) dispersion fillers.

The blowing agents may be selected from chemical blowing agents or physical blowing agents. Chemical blowing agents typically react with (poly)isocyanates and liberate volatile compounds such as CO_2. Physical blowing agents typically vaporize during the formation of the foam due to their low boiling points. Suitable blowing agents will be known to those skilled in the art, and the amounts of blowing agent added can be a matter of routine experimentation. One or more physical blowing agents may be used or one or more chemical blowing agents may be used, in addition one or more physical blowing agents may be used in conjunction with one or more chemical blowing agents.

Chemical blowing agents include water and formic acid. Both react with a portion of the (poly)isocyanate producing carbon dioxide which can function as the blowing agent. Alternatively, carbon dioxide may be used directly as a blowing agent, this has the advantage of avoiding side reactions and lowering urea crosslink formation, if desired water may be used in conjunction with other blowing agents or on its own.

Typically, physical blowing agents for use in the current invention may be selected from acetone, carbon dioxide, optionally substituted hydrocarbons, and chloro/fluorocarbons. Chloro/fluorocarbons include hydrochlorofluorocarbons, chlorofluorocarbons, fluorocarbons and chlorocarbons. Fluorocarbon blowing agents are typically selected from the group consisting of: difluoromethane, trifluoromethane, fluoroethane, 1,1-difluoroethane, 1,1,1-trifluoroethane, tetrafluoroethanes difluorochloroethane, dichloromono-fluoromethane, 1,1-dichloro-1-fluoroethane, 1,1-difluoro-1,2,2-trichloroethane, chloropentafluoroethane, tetrafluoropropanes, pentafluoropropanes, hexafluoropropanes, heptafluoropropanes, pentafluorobutanes.

Olefin blowing agents may be incorporated, namely trans-1-chloro-3.3.3-trifluoropropene (LBA), trans-1,3,3,3-tetrafluoro-prop-1-ene (HFO-1234ze), 2,3,3,3-tetrafluoro-propene (HFO-1234yf), cis-1,1,1,4,4,4-hexafluoro-2-butene (HFO-1336mzz). Typically, non-halogenated hydrocarbons for use as physical blowing agents may be selected from butane, isobutane, 2,3-dimethylbutane, n- and i-pentane isomers, hexane isomers, heptane isomers and cycloalkanes including cyclopentane, cyclohexane and cycloheptane. More typically, non-halogenated hydrocarbons for use as physical blowing agents may be selected from cyclopentane, iso-pentane and n-pentane.

Typically, where one or more blowing agents are present, they are used in an amount of from about 0 to about 10 parts, more typically 2-6 parts of the total formulation. Where water is used in conjunction with another blowing agent the ratio of the two blowing agents can vary widely, e.g. from 1 to 99 parts by weight of water in total blowing agent, preferably, 25 to 99+ parts by weight water

Preferably, the blowing agent is selected from cyclopentane, iso-pentane, n-pentane. More preferably the blowing agent is n-pentane.

Typical plasticisers may be selected from succinate esters, adipate esters, phthalate esters, diisooctylphthalate (DIOP), benzoate esters and N,N-bis(2-hydroxyethyl)-2-aminoethane sulfonic acid (BES).

Typical flame retardants will be known to those skilled in the art, and may be selected from phosphonamidates, 9,10-dihydro-9-oxa-phosphaphenanthrene-10-oxide (DOPO), chlorinated phosphate esters, Tris(2-chloroisopropyl)phosphate (TCPP), Triethyl phosphate (TEP), tris(chloroethyl) phosphate, tris(2,3-dibromopropyl) phosphate, 2,2-bis(chloromethyl)-1,3-propylene bis(di(2-chloroethyl) phosphate), tris(1,3-dichloropropyl) phosphate, tetrakis(2-chloroethyl) ethylene diphosphate, tricresyl phosphate, cresyl diphenyl phosphate, diammonium phosphate, melamine, melamine pyrophosphate, urea phosphate, alumina, boric acid, various halogenated compounds, antimony oxide, chlorendic acid derivatives, phosphorus containing polyols, bromine containing polyols, nitrogen containing polyols, and chlorinated paraffins. Flame retardants may be present in amounts from 0-60 parts of the total mixture.

The compositions of the invention can also further comprise a (poly)isocyanate.

Typically, the (poly)isocyanate comprises two or more isocyanate groups per molecule. Preferably, the (poly)isocyanates are diisocyanates. However, the (poly)isocyanates may be higher (poly)isocyanates such as triisocyanates, tetraisocyanates, isocyanate polymers or oligomers, and the like. The (poly)isocyanates may be aliphatic (poly)isocyanates or derivatives or oligomers of aliphatic (poly)isocyanates or may be aromatic (poly)isocyanates or derivatives or oligomers of aromatic (poly)isocyanates. Typically, the (poly)isocyanate component has a functionality of 2 or more. In some embodiments, the (poly)isocyanate component comprises a mixture of diisocyanates and higher isocyanates formulated to achieve a particular functionality number for a given application.

In some embodiments, the (poly)isocyanate employed has a functionality greater than 2. In some embodiments, such (poly)isocyanates have a functionality between 2 to 5, more typically, 2-4, most typically, 2-3.

Suitable (poly)isocyanates which may be used include aromatic, aliphatic and cycloaliphatic polyisocyanates and combinations thereof. Such polyisocyanates may be selected from the group consisting of: 1,3-Bis(isocyanatomethyl)benzene, 1,3-Bis(isocyanatomethyl)cyclohexane (H6-XDI), 1,4-cyclohexyl diisocyanate, 1,2-cyclohexyl diisocyanate, 1,4-phenylene diisocyanate, 1,3-phenylene diisocyanate, 1,4-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, 1,6-hexamethylaminediisocyanate (HDI), isophorone diisocyanate (IPDI), 2,4-toluene diisocyanate (TDI), 2,4,4-trimethylhexamethylene diisocyanate (TMDI), 2,6-toluene diisocyanate (TDI), 4,4′ methylene-bis(cyclohexyl isocyanate) (H12MDI), naphthalene-1,5-diisocyanate, diphenylmethane-2,4′-diisocyanate (MDI), diphenylmethane-4,4′-diisocyanate (MDI), triphenylmethane-4,4′,4″triisocyanate, isocyanatomethyl-1,8-octane diisocyanate (TIN), m-tetramethylxylylene diisocyanate (TMXDI), p-tetramethylxylylene diisocyanate (TMXDI), Tris(p-isocyanatomethyl)thiosulfate, trimethylhexane diisocyanate, lysine diisocyanate, m-xylylene diisocyanate (XDI), p-xylylene diisocyanate (XDI), 1,3,5-hexamethyl mesitylene triisocyanate, 1-methoxyphenyl-2,4-diisocyanate, toluene-2,4,6-triisocyanate, 4,4’-biphenylene diisocyanate, 3,3’-dimethyl-

4,4’-diphenyl diisocyanate, 4,4’-dimethyldiphenyl methane-2,2’,5,5’-tetraisocyanate and mixtures of any two or more of these. In addition, the (poly)isocyanates may be selected from polymeric version of any of these isocyanates, these may have high or low functionality. Preferred polymeric isocyanates may be selected from MDI, TDI, and polymeric MDI.

According to the third aspect of the invention, there is also provided a polyurethane produced from the reaction of a polyol block copolymer of the first aspect of the present invention and a (poly)isocyanate. A polyurethane can also be produced from the reaction of a composition according to the second aspect of the present invention and a (poly)isocyanate. The polyurethane may be 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). The polyurethane may be formed via a process that involves extruding, moulding, injection moulding, spraying, foaming, casting and/or curing. The polyurethane may be formed via a ‘one pot’ or ‘pre-polymer’ process.

According to the fourth aspect of the present invention, there is also provided a polyurethane comprising a block copolymer residue according to the first aspect of the present invention.

The block copolymer residue of the polyurethane of the fourth aspect may include any one or more features as defined in relation to the first aspect of the invention.

According to the fifth aspect of the invention, there is also provided an isocyanate terminated polyurethane prepolymer comprising the reaction product of the polyol block copolymer according to the first aspect of the present invention or the composition of the second aspect of the present invention and an excess of (poly)isocyanate such as at least >1 mole of isocyanate groups per mole OH groups. The isocyanate terminated prepolymer may be formed into a polyurethane via reaction with one or more chain extenders (such as water, diols, triols, diamines etc) and/or further polyisocyanates and/or other additives.

The isocyanate terminated polyurethane prepolymer of the fifth aspect may include any one or more features as defined in the first aspect of the invention unless such a feature is mutually exclusive.

Catalysts that may be added to the polyol block copolymer of the first aspect of the present invention and/or compositions of the second aspect of the present invention may be catalysts for the reaction of (poly)isocyanates and a polyol. These catalysts include suitable urethane catalysts such as tertiary amine compounds and/or organometallic compounds.

Optionally, a trimerisation catalyst may be used. An excess of (poly)isocyanate, or more preferably an excess of polymeric isocyanate relative to polyol may be present so that polyisocyanurate ring formation is possible when in the presence of a trimerisation catalyst. Any of these catalysts may be used in conjunction with one or more other trimerisation catalysts.

According to the sixth aspect of the invention, there is provided a lubricant composition comprising a (poly)ol block copolymer according to the first aspect of the present invention.

According to the seventh aspect of the invention, there is provided a surfactant composition comprising a (poly)ol block copolymer according to the first aspect of the present invention.

According to the eighth aspect of the invention, there is also provided a process for producing a (poly)ol block copolymer comprising the reaction of a DMC catalyst with a polycarbonate or polyester (poly)ol (co)polymer according to block A of the first aspect, CO_2 , ethylene oxide and optionally one or more other alkylene oxides to produce a (poly)ol block copolymer according to the first aspect or a process for producing a (poly)ol block copolymer comprising a first reaction in a first reactor and a second reaction in a second reactor; wherein the first reaction is the reaction of a carbonate catalyst with CO_2 and alkylene oxide, in the presence of a starter and optionally a solvent to produce a polycarbonate (poly)ol copolymer according to block A of the first aspect and the second reaction is the reaction of a DMC catalyst with the polycarbonate (poly)ol copolymer of the first reaction, CO_2 , ethylene oxide and optionally one or more other alkylene oxides to produce a (poly)ol block copolymer according to the first aspect of the invention.

The process may further comprise a third or further reaction comprising the reaction of the block copolymer of the first aspect of the invention with a monomer or further polymerto produce a higher polymer.

The monomer or further polymer may be a (poly)isocyanate and the product of the third or further reaction may be a polyurethane.

According to the ninth aspect of the present invention, there is also provided a process for producing a (poly)ol block copolymer in a multiple reactor system; the system comprising a first and second reactor wherein a first reaction takes place in the first reactor and a second reaction takes place in the second reactor; wherein the first reaction is the reaction of a carbonate catalyst with CO_2 and alkylene oxide, in the presence of a starter and optionally a solvent to produce a polycarbonate (poly)ol copolymer according to block A of the first aspect and the second reaction is the reaction of a DMC catalyst with the polycarbonate (poly)ol compound of the first reaction, CO_2, ethylene oxide and optionally one or more other alkylene oxides to produce a (poly)ol block copolymer according to the first aspect of the invention.

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

Additionally, not loading the total amount of each component at the start of the reaction and having the catalyst for a first reaction in a separate reactor to the catalyst for the reaction or second reaction, can provide more even catalysis, and more uniform polymer products. In addition, polymers having a narrower molecular weight distribution, desired ratio and distribution along the chain of ether to carbonate linkages, and/or improved (poly)ol stability are possible.

The DMC catalyst can be pre-activated. Such pre-activation may be achieved by mixing one or both catalysts with alkylene oxide (and optionally other components). Pre-activation of the DMC catalyst is useful as it enables safe control of the reaction (preventing uncontrolled increase of unreacted monomer content) and removes unpredictable activation periods.

It will be appreciated that the present invention relates to a reaction in which carbonate and ether linkages are added to a growing polymer chain. Having separate reactions allows the first reaction to proceed before a second stage in the reaction. Mixing alkylene oxide, carbonate catalyst, starter compound and carbon dioxide, may permit growth of a polymer having a high number of carbonate linkages. Thereafter, adding the products to the DMC catalyst permits the reaction to proceed by adding a higher incidence of ether linkages to the growing polymer chain. Ether linkages are more thermally stable than carbonate linkages and less prone to degradation by bases such as the amine catalysts used in PU formation. Therefore, applications additionally get the benefit of high carbonate linkages (such as increased strength, chemical resistance, both oil and hydrolysis resistance etc) that are introduced from the A block whilst retaining the stability of the (poly)ol through the predominant ether linkages from the B blocks at the ends of the polymer chains. This benefit is in addition to the high incidence of primary hydroxyl end groups on the (poly)ol provided by the ethylene oxide.

Additional benefits of the invention when carried out in a two-reactor system is to control the polymerisation reaction, to increase CO_2 content of the polyethercarbonate (poly)ols at low pressures (enabling more cost effective processes and plant design) and to make a product that has high CO_2 content but good stability and application performance. The processes herein may allow the product prepared by such processes to be tailored to the necessary requirements.

The (poly)ol block copolymers of the present invention may be prepared from a suitable alkylene oxide and carbon dioxide in the presence of a starter compound and a carbonate catalyst for a first reaction; and then ethylene oxide and optionally one or more other alkylene oxides and carbon dioxide in the presence of a double metal cyanide (DMC) catalyst in a second reaction.

The carbonate catalyst of the present invention may be a catalyst that produces a polycarbonate (poly)ol with greater than 76% carbonate linkages, preferably greater than 80% carbonate linkages, more preferably greater than 85% carbonate linkages, most preferably greater than 90% carbonate linkages and such linkage ranges may accordingly be present in block A.

If one of the alkylene oxides used is asymmetric (e.g. propylene oxide), the polycarbonate (poly)ols may comprise a high proportion of such alkylene oxides in head to tail linkages, such as greater than 70%, greater than 80% or greater than 90% head to tail linkages. Alternatively, the polycarbonate (poly)ols with such asymmetric alkylene oxides may have no stereoselectivity, providing (poly)ols with approximately 50% head to tail linkages on such residues.

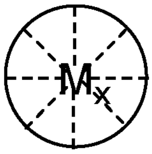
The carbonate catalyst may be heterogeneous or homogeneous.

The carbonate catalyst may be a mono-metallic, bimetallic or multi-metallic homogeneous complex.

The carbonate catalyst may comprise phenol or phenolate ligands.

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

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

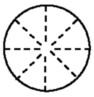


(IV)

wherein:

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

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


is a multidentate ligand or plurality of multidentate ligands;

L is a coordinating ligand, for example, L may be a neutral ligand, or an anionic ligand, preferably one that is capable of ring-opening an alkylene oxide;

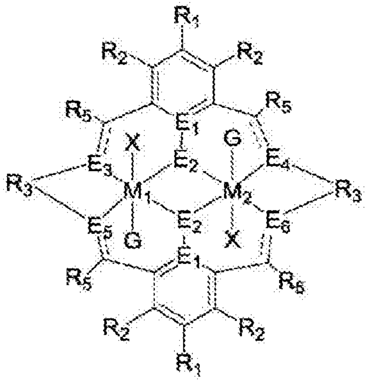
v is an integer that independently satisfies the valency of each M, and/or the preferred coordination geometry of each M or is such that the complex represented by formula (IV) above has an overall neutral charge. For example, each v may independently be 0, 1, 2 or 3, e.g. v may be 1 or 2. When v > 1,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

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

Such catalysts include those in WO2010022388 (metal salens and derivatives, metal porphyrins, corroles and derivatives, metal tetraaza annulenes and derivatives), W02010028362 (metal salens and derivatives, metal porphyrins, corroles and derivatives, metal tetraaza annulenes and derivatives), WO2008136591 (metal salens), WO2011105846 (metal salens), WO2014148825 (metal salens), WO2013012895 (metal salens), EP2258745A1 (metal porphyrins and derivatives), JP2008081518A (metal porphyrins and derivatives), CN101412809 (metal salens and derivatives), WO2019126221 (metal aminotriphenol complexes), US9018318 (metal beta-diiminate complexes), US6133402A (metal beta-diiminate complexes) and US8278239 (metal salens and derivatives), the entire contents of which, especially, insofar as they relate to suitable carbonate catalysts for the reaction of CO_2 and alkylene oxide, in the presence of a starter and optionally a solvent to produce a polycarbonate polyol copolymer according to block A are incorporated herein by reference.

Such catalysts also include those in WO2009/130470, WO2013/034750, WO2016/012786, WO2016/012785, WO2012037282 and WO2019048878A1 (all bimetallic phenolate complexes), the entire contents of which, especially, insofar as they relate to suitable carbonate catalysts for the reaction of CO_2 and alkylene oxide, in the presence of a starter and optionally a solvent to produce a polycarbonate polyol copolymer according to block A are incorporated herein by reference.

The carbonate catalyst may have the following structure:



(V)

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)-$(X)_2$, Y(III)-X, Sc(III)-X 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, 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, $\overline{\text{- - - - -}}$ is $=$, and wherein when E_3, E_4, E_5 or E_6 are NR_4, O or S, $\overline{\text{- - - - -}}$ 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, phosphonate, halide, nitrate, hydroxyl, carbonate, amino, nitro, 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.

Each of the occurrences of the groups R_1 and R_2 may be the same or different, and R_1 and R_2 can be the same or different.

DMC catalysts are complicated compounds which comprise at least two metal centres and cyanide ligands. The DMC catalyst may additionally comprise at least one of: one or more complexing agents, water, a metal salt and/or an acid (e.g. in non-stoichiometric amounts).

The first two of the at least two metal centres may be represented by M’ and M”.

M’ may be 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), M’ is optionally selected from Zn(II), Fe(II), Co(II) and Ni(II), optionally M’ is Zn(II).

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), optionally M” is selected from Co(II), Co(III), Fe(II), Fe(III), Cr(III), Ir(III) and Ni(II), optionally M” is selected from Co(II) and Co(III).

It will be appreciated that the above optional definitions for M’ and M” may be combined. For example, optionally M’ may be selected from Zn(II), Fe(II), Co(II) and Ni(II), and M” may optionally be selected from Co(II), Co(III), Fe(II), Fe(III), Cr(III), Ir(III) and Ni(II). For example, M’ may optionally be Zn(II) and M” may optionally be selected from Co(II) and Co(III).

If a further metal centre(s) is present, the further metal centre may be further selected from the definition of M’ or M”.

Examples of DMC catalysts which can be used in the process of the invention include those described in US 3,427,256, US 5,536,883, US 6,291,388, US 6,486,361, US 6,608,231, US 7,008,900, US 5,482,908, US 5,780,584, US 5,783,513, US 5,158,922, US 5,693,584, US 7,811,958, US 6,835,687, US 6,699,961, US 6,716,788, US 6,977,236, US 7,968,754, US 7,034,103, US 4,826,953, US 4,500 704, US 7,977,501, US 9,315,622, EP-A-1568414, EP-A-1529566, and WO 2015/022290, the entire contents of which, especially, insofar as they relate to DMC catalysts for the production of the block copolymer of the first aspect defined herein or reactions of the eighth or ninth aspect defined herein, are incorporated herein by reference.

It will be appreciated that the DMC catalyst may comprise:

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

wherein M’ and M” are as defined above, d, e, f and g are integers, and are chosen such that the DMC catalyst has electroneutrality. Optionally, d is 3. Optionally, e is 1. Optionally f is 6. Optionally g is 2. Optionally, M’ is selected from Zn(II), Fe(II), Co(II) and Ni(II), optionally M’ is Zn(II). Optionally M” is selected from Co(II), Co(III), Fe(II), Fe(III), Cr(III), Ir(III) and Ni(II), optionally M” is Co(II) or Co(III).

It will be appreciated that any of these optional features may be combined, for example, d is 3, e is 1, f is 6 and g is 2, M’ is Zn(II) and M” is Co(III).

Suitable DMC catalysts of the above formula may include zinc hexacyanocobaltate(III), zinc hexacyanoferrate(III), nickel hexacyanoferrate(II), and cobalt hexacyanocobaltate(III).

There has been a lot of development in the field of DMC catalysts, and the skilled person will appreciate that the DMC catalyst may comprise, in addition to the formula above, further additives to enhance the activity of the catalyst. Thus, while the above formula may form the "core" of the DMC catalyst, the DMC catalyst may additionally comprise stoichiometric or non-stoichiometric amounts of one or more additional components, such as at least one complexing agent, an acid, a metal salt, and/or water.

For example, the DMC catalyst may have the following formula:

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

wherein M', M", X"', d, e, f and g are as defined above. M"' can be M' and/or M". X" is an anion selected from halide, oxide, hydroxide, sulphate, carbonate, cyanide, oxalate, thiocyanate, isocyanate, isothiocyanate, carboxylate and nitrate, optionally X" is halide. i is an integer of 1 or more, and the charge on the anion X" multiplied by i satisfies the valency of M"'. r is an integer that corresponds to the charge on the counterion X"'. For example, when X"' is Cl^-, r will be 1. l is 0, or a number between 0.1 and 5. Optionally, l is between 0.15 and 1.5.

R^c is a complexing agent or a combination of one or more complexing agents. For example, R^c may be a (poly)ether, a polyether carbonate, a polycarbonate, a poly(tetramethylene ether diol), a ketone, an ester, an amide, an alcohol (e.g. a C_{1-8} alcohol), a urea and the like, such as 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, 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, for example, R^c may be tert-butyl alcohol, dimethoxyethane, or polypropylene glycol.

As indicated above, more than one complexing agent may be present in the DMC catalysts used in the present invention. Optionally one of the complexing agents of R_c may be a polymeric complexing agent. Optionally, R_c may be a combination of a polymeric complexing agent and a non-polymeric complexing agent.. Optionally, a combination of the complexing agents tert-butyl alcohol and polypropylene glycol may be present.

It will be appreciated that if the water, complexing agent, acid and/or metal salt are not present in the DMC catalyst, h, j, k and/or l will be zero respectively. If the water, complexing agent, acid and/or metal salt are present, then h, j, k and/or l are a positive number and may, for example, be between 0 and 20. For example, h may be between 0.1 and 4. j may be between 0.1 and 6. k may be between 0 and 20, e.g. between 0.1 and 10, such as between 0.1 and 5. l may be between 0.1 and 5, such as between 0.15 and 1.5.

The polymeric complexing agent is optionally selected from a polyether, a polycarbonate ether, and a polycarbonate. The polymeric complexing agent may be present in an amount of from about 5% to about 80% by weight of the DMC catalyst, optionally in an amount of from about 10% to about 70% by weight of the DMC catalyst, optionally in an amount of from about 20% to about 50% by weight of the DMC catalyst.

The DMC catalyst, in addition to at least two metal centres and cyanide ligands, may also comprise at least one of: one or more complexing agents, water, a metal salt and/or an acid, optionally in non-stoichiometric amounts.

An exemplary DMC catalyst is of the formula $Zn_3[Co(CN)_6]_2 \cdot hZnCl_2 \cdot kH_2O \cdot j[(CH_3)_3COH]$, wherein h, k and j are as defined above. For example, h may be from 0 to 4 (e.g. from 0.1 to 4), k may be from 0 to 20 (e.g. from 0.1 to 10), and j may be from 0 to 6 (e.g. from 0.1 to 6). As set out above, DMC catalysts are complicated structures, and thus, the above formulae including the additional components is not intended to be limiting. Instead, the skilled person will appreciate that this definition is not exhaustive of the DMC catalysts which are capable of being used in the invention.

The starter compound which may be used in the processes for forming polycarbonate polyols of the present invention comprises at least two groups selected from a hydroxyl group (-OH), a thiol (-SH), an amine having at least one N-H bond (-NHR'), a group having at least one P-OH bond (e.g. –PR'(O)OH, PR'(O)(OH)$_2$ or -P(O)(OR')(OH)), or a carboxylic acid group (-C(O)OH).

Thus, the starter compound which may be used in the processes for forming polycarbonate block polyethercarbonate polyols may be of the formula (III):

$Z \leftarrow (R^Z)_a$ (III) as defined above.

The starter compounds for the first and second reaction may be the same or different. Where there are two different starter compounds, there may be two starter compounds in the second reaction, wherein the starter compound in the first reaction is a first starter compound, and wherein the second reaction comprises adding the first crude reaction mixture to the second reactor comprising a second starter compound and double metal cyanide (DMC) catalyst and, optionally, solvent and/or alkylene oxide and/or carbon dioxide.The second reaction of the present invention may be conducted at least about 1 minutes after the first reaction, optionally at least about 5 minutes, optionally at least about 15 minutes, optionally at least about 30 minutes, optionally at least about 1 hour, optionally at least about 2 hours, optionally at least about 5 hours. It will be appreciated that in a continuous reaction these periods are the average period from addition of monomer in the first reactor to transfer of monomer residue into the second reactor.

If polymeric, the starter compound may have a molecular weight (Mn) of at least about 200 Da or of at most about 1000 Da.

For example, having a molecular weight of about 200 to 1000 Da, optionally about 300 to 700 Da, optionally about 400 Da.

The or each starter compound typically has two or more R^z groups, optionally three or more, optionally four or more, optionally five or more, optionally six or more, optionally seven or more, optionally eight or more R^z groups, particularly wherein R^z is hydroxyl. .

It will be appreciated that any of the above features may be combined. For example, a may be between 1 or 2 and 8, each R^Z may be –OH, -C(O)OH or a combination thereof, and Z may be selected from alkylene, heteroalkylene, arylene, or heteroarylene.

Exemplary starter compounds for either reaction and generally in the processes for forming polycarbonate (poly)ols of the present invention include 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), 1-3-propanediol, 1,2-butanediol, 1-3-butanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,8-octanediol, 1,10-decanediol, 1,12-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.

For example, the starter compound may be a monofunctional alcohol such as ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 1-hexanol, 1-octanol, 1-decanol, 1-dodecanol, a phenol such as nonyl-phenol or octyl phenol or a mono-functional carboxylic acid such as formic acid, acetic acid, propionic acid, butyric acid, fatty acids, such as stearic acid, palmitic acid, oleic acid, linoleic acid, linolenic acid, benzoic acid, acrylic acid.

For example, the starter compound may be a diol 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, poly(caprolactone) diol, 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. It will be appreciated that the starter compound may be 1,6-

hexanediol, 1,4-cyclohexanedimethanol, 1,12-dodecanediol, poly(caprolactone) diol, PPG 425, PPG 725, or PPG 1000. Preferably the the starter compound may be a diol such as 1,2-ethanediol (ethylene glycol), 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, poly(caprolactone) diol, 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. It will be appreciated that the starter compound may be 1,6-hexanediol, 1,4-cyclohexanedimethanol, 1,12-dodecanediol, poly(caprolactone) diol, PPG 425, PPG 725, or PPG 1000.

Further exemplary starter compounds may include diacids such as oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, undecanedioic acid, dodecanedioic acid or other compounds having mixed functional groups such as lactic acid, glycolic acid, 3-hydroxypropanoic acid, 4-hydroxybutanoic acid, 5-hydroxypentanoic acid.

The ratio of the starter compound, if present, to the carbonate catalyst may be in amounts of from about 1000:1 to about 1:1, for example, from about 750:1 to about 5:1, such as from about 500:1 to about 10:1, e.g. from about 250:1 to about 20:1, or from about 125:1 to about 30:1, or from about 50:1 to about 20:1. These ratios are molar ratios. These ratios are the ratios of the total amount of starter to the total amount of the carbonate catalyst used in the processes. These ratios may be maintained during the course of addition of materials.

The DMC catalyst for the production of a block copolymer according to a first aspect defined herein or according to the eighth and ninth aspect of the invention may be pre-activated. Optionally, the DMC catalyst may be pre-activated in reactor 2 or the reactor or separately. Optionally, the DMC catalyst may be pre-activated with a starter compound or with the polycarbonate or polyester (poly)ol (co)polymer according to block A of the first aspect or the reaction product of the first or second reaction. When the DMC catalyst is pre-activated with the reaction product of the first reaction, it may be pre-activated with some or all of the reaction product of the first reaction. The DMC catalyst may be pre-activated with the (poly)ol block copolymer of the first aspect, B-A’-Z’-Z-(Z’-

A'-B)$_n$ which may be added into the reactor, or may be the remaining product from a previous reaction, the so-called 'reaction heel'.

The (poly)ol block copolymer according to the eighth and ninth aspect may be according to one or more features of the first aspect of the invention,

The product of the first reaction may be a low molecular weight polycarbonate (poly)ol. The preferred molecular weight (Mn) of the polycarbonate (poly)ol depends on the preferred overall molecular weight of the (poly)ol block copolymer. The molecular weight (Mn) of the polycarbonate (poly)ol block A may be in the range from about 200 to about 4000 Da, from about 200 to about 2000 Da, from about 200 to about 1000 Da, or from about 400 to about 800 Da, as measured by Gel Permeation Chromatography.

Block A may be a generally alternating polycarbonate (poly)ol.

The polycarbonate or polyester (poly)ol (co)polymer according to block A of the first aspect or the product of the first reaction may be fed into the separate reactor containing a pre-activated DMC catalyst. The first product may be fed into the separate reactor as a crude reaction mixture.

The first reaction of the present invention may be carried out under CO_2 pressure of less than 20 bar, preferably less than 10 bar, more preferably less than 8 bar of CO_2 pressure. The second reaction of the present invention may be 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 of CO_2 pressure.

The CO_2 may be added continuously in the first reaction, preferably in the presence of a starter.

The two reactions may both be carried out at a pressure of between about 1 bar and about 60 bar carbon dioxide, optionally about 1 bar and about 40 bar, optionally about 1 bar and about 20 bar, optionally between about 1 bar and about 15 bar, optionally about 1 bar and about 10 bar, optionally about 1 bar and about 5 bar.

The second reaction may be carried out under CO_2, or a mixture of CO_2 and an inert gas such as N_2 or Ar.

The CO_2 may be introduced into either reactor via standard methods, such as directly into the headspace or directly into the reaction liquid via standard methods such as a inlet tube, gassing ring or a hollow shaft stirrer. The mixing may be optimised by using different configurations of stirrer, such as single agitators or agitators configured in multiple stages.

The first reaction process being carried out under these relatively low CO_2 pressures and the CO_2 added continuously can produce a (poly)ol with high CO_2 content, under low pressure.

The first reaction may be carried out in a batch, semi-batch or continuous process. In a batch process, all the carbonate catalyst, alkylene oxide, CO_2, starter and optionally solvent are present at the beginning of the reaction. In a semi-batch or continuous reaction, one or more of the carbonate catalyst, alkylene oxide, CO_2, starter and/or solvent are added into the reactor in a continuous or semi-continuous manner.

The second reaction comprising DMC may be carried out as a continuous process or a semi-batch process. In a semi-batch or continuous process one or more of the DMC catalyst, alkylene oxide, CO_2, starter and/or solvent is added into the reaction in a continuous or semi-continuous manner.

The polycarbonate or polyester (poly)ol (co)polymer may be added to the DMC catalyst continuously or semi-continuously. Preferably, the polycarbonate or polyester (poly)ol (co)polymer is added continuously. By semi-continuously it is meant that the polycarbonate or polyester (poly)ol is added in at least two portions, wherein at least one portion is added after the start of the reaction. Preferably, the polycarbonate or polyester (poly)ol is added in several portions.

Typically, at least a portion of the polycarbonate or polyester (poly)ol (co)polymer is added after the start of the reaction.

Typically, the DMC catalyst is pre-activated with a starter compound, or the polycarbonate or polyester (poly)ol (co)polymer, or with the (poly)ol block copolymer product.

Optionally, the crude reaction mixture fed into the second reactor may include an amount of unreacted alkylene oxide and/or CO_2 and or starter.

Optionally, the crude reaction mixture feed may include an amount of carbonate catalyst. Optionally, the carbonate catalyst may have been removed prior to the addition to the second reactor.

The polycarbonate product of the first reaction may be referred to as the crude product.

The polycarbonate or polyester (poly)ol (co)polymer according to block A of the first aspect or the polycarbonate product of the first reaction may be fed into the reaction or second reaction in a single portion or in a continuous or semi-continuous manner, optionally comprising unreacted alkylene oxide and/or carbonate catalyst. Preferably, the product of the first reaction is fed into the second reactor in a continuous manner. This is advantageous as the continuous addition of the product of reaction 1 as a starter for the DMC catalyst allows the DMC catalyst in reactor 2 to operate in a more controlled manner. This may prevent deactivation of the DMC catalyst in reactor 2. The polycarbonate or polyester (poly)ol (co)polymer according to block A of the first aspect or the polycarbonate of reaction 1 may be fed into the second reactor prior to DMC activation and may be used during the DMC activation. The DMC catalyst may also be pre-activated with the (poly)ol block copolymer of the first aspect, $B\text{-}A'\text{-}Z'\text{-}Z\text{-}(Z'\text{-}A'\text{-}B)_n$ which may be added into the reactor, or may be the remaining product from a previous reaction, the so-called ‘reaction heel’.

The temperature of the reaction in the first reactor may be in the range of from about 0°C to 250 °C, preferably from about 40 °C to about 160 °C, more preferably from about 50 °C to 120 °C.

The temperature of the reaction in the second reactor may be in the range from about 50 to about 160 °C, preferably in the range from about 70 to about 140 °C, more preferably from about 70 to about 110 °C.

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

The first reaction may be carried in more than one reactor that feeds the crude reaction mixture into the second reaction, and reactor, continuously. Preferably, reaction 2 is run in a continuous mode.

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

Advantageously, the two reactions can be run independently to get optimum conditions for each. If the two reactors are nested they may be effective to provide different reaction conditions to each other simultaneously.

Optionally, the polycarbonate (poly)ol may have been stabilised by an acid prior to addition to the second reactor. The acid may be an inorganic or an organic acid. Such acids include, but are not limited to, phosphoric acid derivatives, sulfonic acid derivatives (e.g. methanesulfonic acid, p-toluenesulfonic acid), carboxylic acids (e.g. acetic acid, formic acid, oxalic acid, salicylic acid), mineral acids (e.g. hydrochloric acid, hydrobromic acid, hydroiodic acid), nitric acid or carbonic acid. The acid may be part of an acidic resin, such as an ion exchange resin. Acidic ion exchange resins may be in the form of a polymeric matrix (such as polystyrene or polymethacrylic acid) featuring acidic sites such as strong acidic sites (e.g. sulfonic acid sites) or weak acid sites (e.g. carboxylic acid sites). Example ionic exchange resins include Amberlyst 15, Dowex Marathon MSC and Amberlite IRC 748.

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

The solvent may act to dissolve one or more of the materials. However, the solvent may also act as a carrier, and be used to suspend one or more of the materials in a suspension. Solvent may be required to aid addition of one or more of the materials during the steps of the processes of the present invention.

The process may employ a total amount of solvent, and wherein about 1 to 100% of the total amount of solvent may be mixed in the first reaction, with the remainder added in the second reaction; optionally with about 1 to 75% being mixed in the first reaction, optionally with about 1 to 50%, optionally with about 1 to 40%, optionally with about 1 to 30%, optionally with about 1 to 20%, optionally with about 5 to 20%.

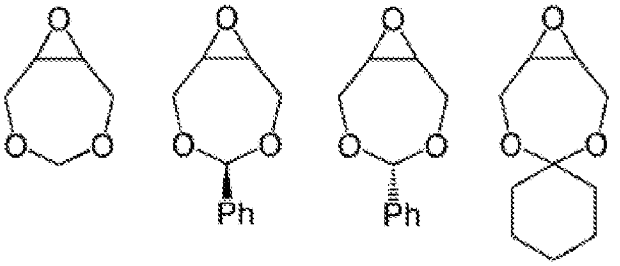
The total amount of the carbonate catalyst may be low, such that the first reaction of the invention may be carried out at low catalytic loading. For example, the catalytic loading of the carbonate catalyst may be in the range of about 1:500-100,000 [total carbonate catalyst]:[total epoxide], such as about 1:750-50,000 [total carbonate catalyst]:[total epoxide], e.g. in the region of about 1:1,000-20,000 [total carbonate catalyst]:[total epoxide], for example in the region of about 1:10,000 [total carbonate catalyst]:[total epoxide]. The ratios above are molar ratios. These ratios are the ratios of the total amount of carbonate catalyst to the total amount of epoxide used in the first reaction.

The process may employ a total amount of carbon dioxide, and about 1 to 99% of the total amount of carbon dioxide incorporated may be in block A. The remainder may be in block B; with optionally about 10 to 95% being incorporated into block A, optionally with about 20 to 90%, optionally with about 30 to 85% being incorporated into block A.

The process may employ a total amount of alkylene oxide, and about 1 to 95% of the total amount of alkylene oxide may be incorporated intoin block A. The remainder of alkylene oxide may be incorporated into block B; with optionally about 5 to 90% being incorporated into block A, 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% being incorporated into block A.

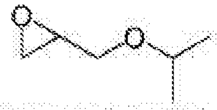
In addition to the ethylene oxide of the B block ethylene oxide may also be present in the A block and further alkylene oxides may optionally be present in either the A or B blocks. Exemplary further alkylene oxides for the A block in addition to ethylene oxide and for the B block include propylene oxide, butylene oxide, glycidyl ethers, glycidyl esters, glycidyl carbonates, and cyclohexene oxide. The alkylene oxide(s) used for the B block may be the same or different from the alkylene oxide(s) used for the A block. Accordingly, a mixture of one or more alkylene oxides may be present in one or both of the blocks. For example, the A block may comprise propylene oxide and the B block may comprise ethylene oxide, or both blocks may comprise ethylene oxide, or one or both blocks may use a mixture of alkylene oxides such as a mixture of ethylene oxide with propylene oxide. Preferably, propylene oxide is used in one or both blocks.

Examples of alkylene oxides which may be used in the present invention include, but are not limited to, 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. Examples of functionalized 3,5-dioxaepoxides include:

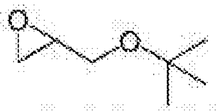


The epoxide moiety may be a glycidyl ether, glycidyl ester or glycidyl carbonate. Examples of glycidyl ethers, glycidyl esters glycidyl carbonates include:

glycidyl methyl ether

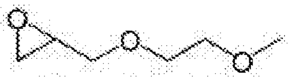


isopropyl glycidyl ether



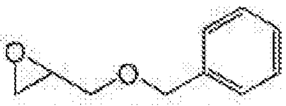
tert-butyl glycidyl ether

butyl glycidyl ether

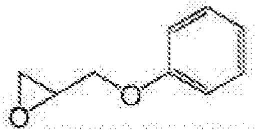


methoxyethyl glycidyl ether

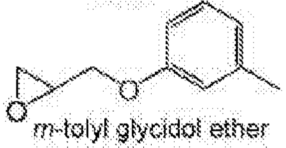
allyl glycidyl ether



phenyl glycidyl ether



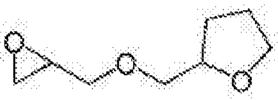
benzyl glycidyl ether



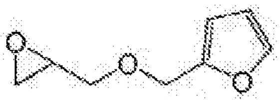
m-tolyl glycidol ether

glycidyl propargyl ether

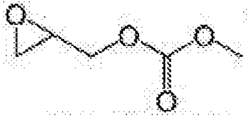
beta-chloroethyl glycidyl ether



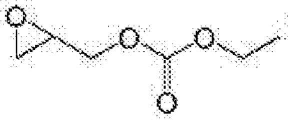
furfuryl glycidyl ether



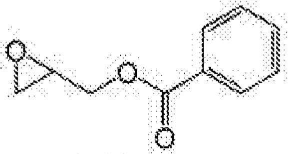
tetrahydrofurfuryl glycidyl ether



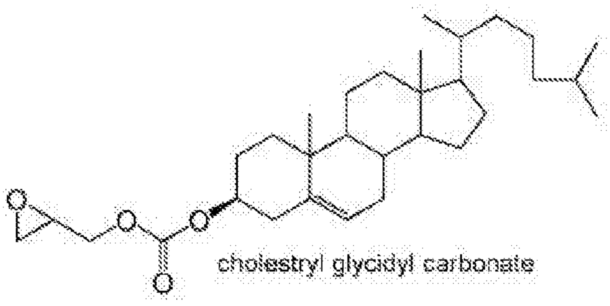
methyl glycidyl carbonate



ethyl glycidyl carbonate



glycidyl benzoate



cholestryl glycidyl carbonate

As noted above, the epoxide substrate may contain more than one epoxide moiety, i.e. it may be a bis-epoxide, a tris-epoxide, or a multi-epoxide containing moiety. Examples of compounds including more than one epoxide moiety include, bis-epoxybutane, bis-epoxyoctane, bis-epoxydecane, bisphenol A diglycidyl ether and 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexanecarboxylate. It will be understood that reactions carried out in the presence of one or more compounds having more than one epoxide moiety may lead to cross-linking in the resulting polymer.

Optionally, between 0.1 and 20% of the total alkylene oxide in the first reaction may be an alkylene oxide substrate containing more than one epoxide moiety. Preferably, the multi-epoxide substrate is a bis-epoxide.

The skilled person will appreciate that the alkylene oxide can be obtained from “green” or renewable resources. The alkylene oxide may be obtained from a (poly)unsaturated compound, such as those deriving from a fatty acid and/or terpene, obtained using standard oxidation chemistries.

The alkylene oxide moiety may contain –OH moieties, or protected –OH moieties. The –OH moieties may be protected by any suitable protecting group. Suitable protecting groups include methyl or other alkyl groups, benzyl, allyl, tert-butyl, tetrahydropyranyl (THP), methoxymethyl (MOM), acetyl (C(O)alkyl), benzolyl (C(O)Ph), dimethoxytrityl (DMT), methoxyethoxymethyl (MEM), p-methoxybenzyl (PMB), trityl, silyl (such as trimethylsilyl (TMS), *t*-butyldimethylsilyl (TBDMS), *t*-butyldiphenylsilyl (TBDPS), tri-*iso*-propylsilyloxymethyl (TOM), and triisopropylsilyl (TIPS)), (4-methoxyphenyl)diphenylmethyl (MMT), tetrahydrofuranyl (THF), and tetrahydropyranyl (THP).

The alkylene oxide optionally has a purity of at least 98%, optionally >99%.

The rate at which the materials are added may be selected such that the temperature of the (exothermic) reactions does not exceed a selected temperature (i.e. that the materials are added slowly enough to allow any excess heat to dissipate such that the temperature of the remains approximately constant). The rate at which the materials are added may be selected such that the alkylene oxide concentration does not exceed a selected alkylene oxide concentration.

The process may produce a (poly)ol with a polydispersity between 1.0 and 2.0, preferably between 1.0 and 1.8, more preferably between 1.0 and 1.5, most preferably between 1.0 and 1.3.

The process may comprise mixing double metal cyanide (DMC) catalyst, alkylene oxide, starter and optionally carbon dioxide and/or solvent to form a pre-activated mixture and adding the pre-activated mixture to the second reactor either before or after the crude reaction mixture of the first reaction, to form the second reaction mixture. However, this may take place continuously so that the pre-activated mixture is added at the same time as the crude reaction mixture. The pre-activated mixture may also be formed in the second reactor by mixing the DMC catalyst, alkylene oxide, starter and optionally carbon dioxide and/or solvent. The pre-activation may occur at a temperature of about 50 °C to 160 °C, preferably between about 70°C to 140 °C, more preferably about 90 °C to 140 °C.The pre-activated mixture may be mixed at a temperature of between about 50 to 160 °C prior to contact with the crude reaction 1 mixture, optionally between about 70 to 140 °C.

In a typical overall reaction process, the amount of said carbonate catalyst and the amount of said double metal cyanide (DMC) catalyst may be at a predetermined weight ratio of from about 300:1 to about 1:100 to one another, for example, from about 120:1 to about 1:75, such as from about 40:1 to about 1:50, e.g. from about 30:1 to about 1:30 such as from about 20:1 to about 1:1, for example from about 10:1 to about 2:1, e.g. from about 5:1 to about 1:5. The processes of the present invention can be carried out on any scale. The process may be carried out on an industrial scale. As will be understood by the skilled person, catalytic reactions are generally exothermic. The generation of heat during a small-scale reaction is unlikely to be problematic, as any increase in temperature can be controlled relatively easily by, for example, the use of an ice bath. With larger scale reactions, and particularly industrial scale reactions, the generation of heat during a reaction can be problematic and potentially dangerous. Thus, the gradual addition of materials may allow the rate of the catalytic reaction to be controlled and can minimise the build-up of excess heat. The rate of the reaction may be controlled, for example, by adjusting the flow rate of the materials during addition. Thus, the processes of the present invention have particular advantages if applied to large, industrial scale catalytic reactions.

The temperature may increase or decrease during the course of the processes of the invention.

The amount of said carbonate catalyst and the amount of said double metal cyanide (DMC) catalyst will vary depending on which carbonate catalyst and DMC catalyst is used.

Methods

Gel Permeation Chromatography

GPC measurements were carried out against narrow polydispersity poly(ethylene glycol) or polystyrene standards in THF using an Agilent 1260 Infinity machine equipped with Agilent PLgel Mixed-D columns.

Definitions

For the purpose of the present invention, an aliphatic group is a hydrocarbon moiety that may be straight chain (i.e. unbranched) branched, or cyclic and may be completely saturated, or contain one or more units of unsaturation, but which is not aromatic. The term “unsaturated” means a moiety that has one or more double and/or triple bonds. The term “aliphatic” is therefore intended to encompass alkyl, cycloalkyl, alkenyl cycloalkenyl, alkynyl or cycloalkenyl groups, and combinations thereof.

An aliphatic group is optionally a C_{1-30} aliphatic group, that is, an aliphatic group with 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29 or 30 carbon atoms. Optionally, an aliphatic group is a C_{1-15}aliphatic, optionally a C_{1-12}aliphatic, optionally a C_{1-10}aliphatic, optionally a C_{1-8}aliphatic, such as a C_{1-6}aliphatic group. Suitable aliphatic groups include linear or branched, alkyl, alkenyl and alkynyl groups, and mixtures thereof such as (cycloalkyl)alkyl groups, (cycloalkenyl)alkyl groups and (cycloalkyl)alkenyl groups.

The term "alkyl," as used herein, refers to saturated, straight- or branched-chain hydrocarbon radicals derived by removal of a single hydrogen atom from an aliphatic moiety. An alkyl group is optionally a “C_{1-20} alkyl group”, that is an alkyl group that is a straight or branched chain with 1 to 20 carbons. The alkyl group therefore has 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19 or 20 carbon atoms. Optionally, an alkyl group is a C_{1-15} alkyl, optionally a C_{1-12} alkyl, optionally a C_{1-10} alkyl, optionally a C_{1-8} alkyl, optionally a C_{1-6} alkyl group. Specifically, examples of “C_{1-20} alkyl group“ include methyl group, ethyl group, n-propyl group, iso-propyl group, n-butyl group, iso-butyl group, sec-butyl group, tert-butyl group, sec-pentyl, iso-pentyl, n-pentyl group, neopentyl, n-hexyl group, sec-hexyl, n-heptyl group, n-octyl group, n-nonyl group, n-decyl group, n-undecyl group, n-dodecyl group, n-tridecyl group, n-tetradecyl group, n-pentadecyl group, n-hexadecyl group, n-heptadecyl group, n-octadecyl group, n-nonadecyl group, n-eicosyl group, 1,1-dimethylpropyl group, 1,2-dimethylpropyl group, 2,2-dimethylpropyl group, 1-ethylpropyl group, n-hexyl group, 1-ethyl-2-methylpropyl group, 1,1,2-trimethylpropyl group, 1-ethylbutyl group, 1-methylbutyl group, 2-methylbutyl group, 1,1-dimethylbutyl group, 1,2-dimethylbutyl group, 2,2-dimethylbutyl group, 1,3-dimethylbutyl group, 2,3-dimethylbutyl group, 2-ethylbutyl group, 2-methylpentyl group, 3-methylpentyl group and the like.

The term "alkenyl," as used herein, denotes a group derived from the removal of a single hydrogen atom from a straight- or branched-chain aliphatic moiety having at least one carbon-carbon double bond. The term "alkynyl," as used herein, refers to a group derived from the removal of a single hydrogen atom from a straight- or branched-chain aliphatic moiety having at least one carbon-carbon triple bond. Alkenyl and alkynyl groups are optionally "C_{2-20}alkenyl" and "C_{2-20}alkynyl", optionally "C_{2-15} alkenyl" and "C_{2-15} alkynyl", optionally "C_{2-12} alkenyl" and "C_{2-12} alkynyl", optionally "C_{2-10} alkenyl" and "C_{2-10} alkynyl", optionally "C_{2-8} alkenyl" and "C_{2-8} alkynyl", optionally "C_{2-6} alkenyl" and "C_{2-6} alkynyl" groups, respectively. Examples of alkenyl groups include ethenyl, propenyl, allyl, 1,3-butadienyl, butenyl, 1-methyl-2-buten-1-yl, allyl, 1,3-butadienyl and allenyl. Examples of alkynyl groups include ethynyl, 2-propynyl (propargyl) and 1-propynyl.

The terms "cycloaliphatic", "carbocycle", or "carbocyclic" as used herein refer to a saturated or partially unsaturated cyclic aliphatic monocyclic or polycyclic (including fused, bridging and spiro-fused) ring system which has from 3 to 20 carbon atoms, that is an alicyclic group with 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19 or 20 carbon atoms. Optionally, an alicyclic group has from 3 to 15, optionally from 3 to 12, optionally from 3 to 10, optionally from 3 to 8 carbon atoms, optionally from 3 to 6 carbons atoms. The terms "cycloaliphatic", "carbocycle" or "carbocyclic" also include aliphatic rings that are fused to one or more aromatic or nonaromatic rings, such as tetrahydronaphthyl rings, where the point of attachment is on the aliphatic ring. A carbocyclic group may be polycyclic, e.g. bicyclic or tricyclic. It will be appreciated that the alicyclic group may comprise an alicyclic ring bearing one or more linking or non-linking alkyl substituents, such as –CH_2-cyclohexyl. Specifically, examples of carbocycles include cyclopropane, cyclobutane, cyclopentane, cyclohexane, bicycle[2,2,1]heptane, norborene, phenyl, cyclohexene, naphthalene, spiro[4.5]decane, cycloheptane, adamantane and cyclooctane.

A heteroaliphatic group (including heteroalkyl, heteroalkenyl and heteroalkynyl) is an aliphatic group as described above, which additionally contains one or more heteroatoms. Heteroaliphatic groups therefore optionally contain from 2 to 21 atoms, optionally from 2 to 16 atoms, optionally from 2 to 13 atoms, optionally from 2 to 11 atoms, optionally from 2 to 9 atoms, optionally from 2 to 7 atoms, wherein at least one atom is a carbon atom. Optional heteroatoms are selected from O, S, N, P and Si. When heteroaliphatic groups have two or more heteroatoms, the heteroatoms may be the same or different. Heteroaliphatic groups may be substituted or unsubstituted, branched or unbranched, cyclic or acyclic, and include saturated, unsaturated or partially unsaturated groups.

An alicyclic group is a saturated or partially unsaturated cyclic aliphatic monocyclic or polycyclic (including fused, bridging and spiro-fused) ring system which has from 3 to 20 carbon atoms, that is an alicyclic group with 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19 or 20 carbon atoms. Optionally, an alicyclic group has from 3 to 15, optionally from 3 to 12, optionally from 3 to 10, optionally from 3 to 8 carbon atoms, optionally from 3 to 6 carbons atoms. The term “alicyclic” encompasses cycloalkyl, cycloalkenyl and cycloalkynyl groups. It will be appreciated that the alicyclic group may comprise an alicyclic ring bearing one or more linking or non-linking alkyl substituents, such as $–CH_2$-cyclohexyl. Specifically, examples of the C_{3-20} cycloalkyl group include cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, adamantyl and cyclooctyl.

A heteroalicyclic group is an alicyclic group as defined above which has, in addition to carbon atoms, one or more ring heteroatoms, which are optionally selected from O, S, N, P and Si. Heteroalicyclic groups optionally contain from one to four heteroatoms, which may be the same or different. Heteroalicyclic groups optionally contain from 5 to 20 atoms, optionally from 5 to 14 atoms, optionally from 5 to 12 atoms.

An aryl group or aryl ring is a monocyclic or polycyclic ring system having from 5 to 20 carbon atoms, wherein at least one ring in the system is aromatic and wherein each ring in the system contains three to twelve ring members. The term "aryl" can be used alone or as part of a larger moiety as in "aralkyl", "aralkoxy", or "aryloxyalkyl”. An aryl group is optionally a “C_{6-12} aryl group” and is an aryl group constituted by 6, 7, 8, 9, 10, 11 or 12 carbon atoms and includes condensed ring groups such as monocyclic ring group, or bicyclic ring group and the like. Specifically, examples of “C_{6-10} aryl group” include phenyl group, biphenyl group, indenyl group, anthracyl group, naphthyl group or azulenyl group and the like. It should be noted that condensed rings such as indan, benzofuran, phthalimide, phenanthridine and tetrahydro naphthalene are also included in the aryl group.

The term "heteroaryl" used alone or as part of another term (such as "heteroaralkyl", or "heteroaralkoxy") refers to groups having 5 to 14 ring atoms, optionally 5, 6, or 9 ring atoms; having 6, 10, or 14 π electrons shared in a cyclic array; and having, in addition to carbon atoms, from one to five heteroatoms. The term "heteroatom" refers to nitrogen, oxygen, or sulfur, and includes any oxidized form of nitrogen or sulfur, and any quaternized form of nitrogen. The term "heteroaryl" also includes groups in which a heteroaryl ring is fused to one or more aryl, cycloaliphatic, or heterocyclyl rings, where the radical or point of attachment is on the heteroaromatic ring. Examples include indolyl, isoindolyl, benzothienyl, benzofuranyl, dibenzofuranyl, indazolyl, benzimidazolyl, benzthiazolyl, quinolyl, isoquinolyl, cinnolinyl, phthalazinyl, quinazolinyl, quinoxalinyl, 4H-quinolizinyl, carbazolyl, acridinyl, phenazinyl, phenothiazinyl, phenoxazinyl, tetrahydroquinolinyl, tetrahydroisoquinolinyl, and pyrido[2,3-b]-1,4-oxazin-3(4H)-one. Thus, a heteroaryl group may be mono- or polycyclic.

The term "heteroaralkyl" refers to an alkyl group substituted by a heteroaryl, wherein the alkyl and heteroaryl portions independently are optionally substituted.

As used herein, the terms "heterocycle", "heterocyclyl", "heterocyclic radical", and "heterocyclic ring" are used interchangeably and refer to a stable 5- to 7-membered monocyclic or 7-14-membered bicyclic heterocyclic moiety that is saturated, partially unsaturated, or aromatic and having, in addition to carbon atoms, one or more, optionally one to four, heteroatoms, as defined above. When used in reference to a ring atom of a heterocycle, the term "nitrogen" includes a substituted nitrogen.

Examples of alicyclic, heteroalicyclic, aryl and heteroaryl groups include but are not limited to cyclohexyl, phenyl, acridine, benzimidazole, benzofuran, benzothiophene, benzoxazole, benzothiazole, carbazole, cinnoline, dioxin, dioxane, dioxolane, dithiane, dithiazine, dithiazole, dithiolane, furan, imidazole, imidazoline, imidazolidine, indole, indoline, indolizine, indazole, isoindole, isoquinoline, isoxazole, isothiazole, morpholine, napthyridine, oxazole, oxadiazole, oxathiazole, oxathiazolidine, oxazine, oxadiazine, phenazine, phenothiazine, phenoxazine, phthalazine, piperazine, piperidine, pteridine, purine, pyran, pyrazine, pyrazole, pyrazoline, pyrazolidine, pyridazine, pyridine, pyrimidine, pyrrole, pyrrolidine, pyrroline, quinoline, quinoxaline, quinazoline, quinolizine, tetrahydrofuran, tetrazine, tetrazole, thiophene, thiadiazine, thiadiazole, thiatriazole, thiazine, thiazole, thiomorpholine, thianaphthalene, thiopyran, triazine, triazole, and trithiane.

The term “halide”, “halo” and “halogen” are used interchangeably and, as used herein mean a fluorine atom, a chlorine atom, a bromine atom, an iodine atom and the like, optionally a fluorine atom, a bromine atom or a chlorine atom, and optionally a fluorine atom.

A haloalkyl group is optionally a "C_{1-20} haloalkyl group", optionally a "C_{1-15} haloalkyl group", optionally a "C_{1-12} haloalkyl group", optionally a "C_{1-10} haloalkyl group", optionally a "C_{1-8} haloalkyl group", optionally a "C_{1-6} haloalkyl group" and is a C_{1-20} alkyl, a C_{1-15} alkyl, a C_{1-12} alkyl, a C_{1-10} alkyl, a C_{1-8} alkyl, or a C_{1-6} alkyl group, respectively, as described above substituted with at least one halogen atom, optionally 1, 2 or 3 halogen atom(s). The term "haloalkyl" encompasses fluorinated or chlorinated groups, including perfluorinated compounds. Specifically, examples of "C_{1-20} haloalkyl group" include fluoromethyl group, difluoromethyl group, trifluoromethyl group, fluoroethyl group, difluoroethyl group, trifluoroethyl group, chloromethyl group, bromomethyl group, iodomethyl group and the like.

The term "acyl" as used herein refers to a group having a formula -C(O)R where R is hydrogen or an optionally substituted aliphatic, aryl, or heterocyclic group.

An alkoxy group is optionally a "C_{1-20} alkoxy group", optionally a "C_{1-15} alkoxy group", optionally a "C_{1-12} alkoxy group", optionally a "C_{1-10} alkoxy group", optionally a "C_{1-8} alkoxy group", optionally a "C_{1-6} alkoxy group" and is an oxy group that is bonded to the previously defined C_{1-20} alkyl, C_{1-15} alkyl, C_{1-12} alkyl, C_{1-10} alkyl, C_{1-8} alkyl, or C_{1-6} alkyl group respectively. Specifically, examples of "C_{1-20} alkoxy group" include methoxy group, ethoxy group, n-propoxy group, iso-propoxy group, n-butoxy group, iso-butoxy group, sec-butoxy group, tert-butoxy group, n-pentyloxy group, iso-pentyloxy group, sec-pentyloxy group, n-hexyloxy group, iso-hexyloxy group, , n-hexyloxy group, n-heptyloxy group, n-octyloxy group, n-nonyloxy group, n-decyloxy group, n-undecyloxy group, n-dodecyloxy group, n-tridecyloxy group, n-tetradecyloxy group, n-pentadecyloxy group, n-hexadecyloxy group, n-heptadecyloxy group, n-octadecyloxy group, n-nonadecyloxy group, n-eicosyloxy group, 1,1-dimethylpropoxy group, 1,2-dimethylpropoxy group, 2,2-dimethylpropoxy group, 2-methylbutoxy group, 1-ethyl-2-methylpropoxy group, 1,1,2-trimethylpropoxy group, 1,1-dimethylbutoxy group, 1,2-dimethylbutoxy group, 2,2-dimethylbutoxy group, 2,3-dimethylbutoxy group, 1,3-dimethylbutoxy group, 2-ethylbutoxy group, 2-methylpentyloxy group, 3-methylpentyloxy group and the like.

An aryloxy group is optionally a "C_{5-20} aryloxy group", optionally a "C_{6-12} aryloxy group", optionally a "C_{6-10} aryloxy group" and is an oxy group that is bonded to the previously defined C_{5-20} aryl, C_{6-12} aryl, or C_{6-10} aryl group respectively.

An alkylthio group is optionally a "C_{1-20} alkylthio group", optionally a "C_{1-15} alkylthio group", optionally a "C_{1-12} alkylthio group", optionally a "C_{1-10} alkylthio group", optionally a "C_{1-8} alkylthio group", optionally a "C_{1-6} alkylthio group" and is a thio (-S-) group that is bonded to the previously defined C_{1-20} alkyl, C_{1-15} alkyl, C_{1-12} alkyl, C_{1-10} alkyl, C_{1-8} alkyl, or C_{1-6} alkyl group respectively.

An arylthio group is optionally a “C_{5-20} arylthio group”, optionally a “C_{6-12} arylthio group”, optionally a “C_{6-10} arylthio group” and is a thio (-S-) group that is bonded to the previously defined C_{5-20} aryl, C_{6-12} aryl, or C_{6-10} aryl group respectively.

An alkylaryl group is optionally a “C_{6-12} aryl C_{1-20} alkyl group”, optionally a a “C_{6-12} aryl C_{1-16} alkyl group”, optionally a “C_{6-12} aryl C_{1-6} alkyl group” and is an aryl group as defined above bonded at any position to an alkyl group as defined above. The point of attachment of the alkylaryl group to a molecule may be via the alkyl portion and thus, optionally, the alkylaryl group is $-CH_2-Ph$ or $-CH_2CH_2-Ph$. An alkylaryl group can also be referred to as “aralkyl”.

A silyl group is optionally $–Si(R_s)_3$, wherein each R_s can be independently an aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl group as defined above. Optionally, each R_s is independently an unsubstituted aliphatic, alicyclic or aryl. Optionally, each R_s is an alkyl group selected from methyl, ethyl or propyl.

A silyl ether group is optionally a group $OSi(R_6)_3$ wherein each R_6 can be independently an aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl group as defined above. Each R_6 can be independently an unsubstituted aliphatic, alicyclic or aryl. Optionally, each R_6 is an optionally substituted phenyl or optionally substituted alkyl group selected from methyl, ethyl, propyl or butyl (such as n-butyl (nBu) or tert-butyl (tBu)). Exemplary silyl ether groups include $OSi(Me)_3$, $OSi(Et)_3$, $OSi(Ph)_3$, $OSi(Me)_2(tBu)$, $OSi(tBu)_3$ and $OSi(Ph)_2(tBu)$.

A nitrile group (also referred to as a cyano group) is a group CN.

An imine group is a group –CRNR, optionally $–CHNR_7$ wherein R_7 is an aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl group as defined above. R_7 may be unsubstituted aliphatic, alicyclic or aryl. Optionally R_7 is an alkyl group selected from methyl, ethyl or propyl.

An acetylide group contains a triple bond $-C\equiv C-R_9$, optionally wherein R_9 can be hydrogen, an aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl group as defined above. For the purposes of the invention when R_9 is alkyl, the triple bond can be present at any position along the alkyl chain. R_9 may be unsubstituted aliphatic, alicyclic or aryl. Optionally R_9 is methyl, ethyl, propyl or phenyl.

An amino group is optionally -NH_2, -NHR_{10} or -$N(R_{10})_2$ wherein R_{10} can be an aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, a silyl group, aryl or heteroaryl group as defined above. It will be appreciated that when the amino group is $N(R_{10})_2$, each R_{10} group can be the same or different. Each R_{10} may independently an unsubstituted aliphatic, alicyclic, silyl or aryl. Optionally R_{10} is methyl, ethyl, propyl, $SiMe_3$ or phenyl.

An amido group is optionally –$NR_{11}C(O)$- or –$C(O)$-NR_{11}- wherein R_{11} can be hydrogen, an aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl group as defined above. R_{11} may be unsubstituted aliphatic, alicyclic or aryl. Optionally R_{11} is hydrogen, methyl, ethyl, propyl or phenyl. The amido group may be terminated by hydrogen, an aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl group.

An ester group unless otherwise defined herein is optionally –$OC(O)R_{12}$ or –$C(O)OR_{12}$ wherein R_{12} can be an aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl group as defined above. R_{12} may be unsubstituted aliphatic, alicyclic or aryl. Optionally R_{12} is methyl, ethyl, propyl or phenyl. The ester group may be terminated by an aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl group. It will be appreciated that if R_{12} is hydrogen, then the group defined by –$OC(O)R_{12}$- or –$C(O)OR_{12}$- will be a carboxylic acid group.

A sulfoxide is optionally –$S(O)R_{13}$ and a sulfonyl group is optionally –$S(O)_2R_{13}$ wherein R_{13} can be an aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl group as defined above. R_{13} may be unsubstituted aliphatic, alicyclic or aryl. Optionally R_{13} is methyl, ethyl, propyl or phenyl.

A carboxylate group is optionally -$OC(O)R_{14}$, wherein R_{14} can be hydrogen, an aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl group as defined above. R_{14} may be unsubstituted aliphatic, alicyclic or aryl. Optionally R_{14} is hydrogen, methyl, ethyl, propyl, butyl (for example n-butyl, isobutyl or tert-butyl), phenyl, pentafluorophenyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, trifluoromethyl or adamantyl.

An acetamide is optionally $MeC(O)N(R_{15})_2$ wherein R_{15} can be hydrogen, an aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl group as defined above. R_{15} may be unsubstituted aliphatic, alicyclic or aryl. Optionally R_{15} is hydrogen, methyl, ethyl, propyl or phenyl.

A phosphinate group is optionally–OP(O)(R_{16})$_2$ or –P(O)(OR_{16})(R_{16}) wherein each R_{16} is independently selected from hydrogen, or an aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl group as defined above. R_{16} may be aliphatic, alicyclic or aryl, which are optionally substituted by aliphatic, alicyclic, aryl or C_{1-6}alkoxy. Optionally R_{16} is optionally substituted aryl or C_{1-20} alkyl, optionally phenyl optionally substituted by C_{1-6}alkoxy (optionally methoxy) or unsubstituted C_{1-20}alkyl (such as hexyl, octyl, decyl, dodecyl, tetradecyl, hexadecyl, stearyl). A phosphonate group is optionally –P(O)(OR_{16})$_2$ wherein R_{16} is as defined above. It will be appreciated that when either or both of R_{16} is hydrogen for the group –P(O)(OR_{16})$_2$, then the group defined by –P(O)(OR_{16})$_2$ will be a phosphonic acid group.

A sulfinate group is optionally –S(O)OR_{17} or –OS(O)R_{17} wherein R_{17} can be hydrogen, an aliphatic, heteroaliphatic, haloaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl group as defined above. R_{17} may be unsubstituted aliphatic, alicyclic or aryl. Optionally R_{17} is hydrogen, methyl, ethyl, propyl or phenyl. It will be appreciated that if R_{17} is hydrogen, then the group defined by –S(O)OR_{17} will be a sulfonic acid group.

A carbonate group is optionally -OC(O)OR_{18}, wherein R_{18} can be hydrogen, an aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl group as defined above. R_{18} may be optionally substituted aliphatic, alicyclic or aryl. Optionally R_{18} is hydrogen, methyl, ethyl, propyl, butyl (for example n-butyl, isobutyl or tert-butyl), phenyl, pentafluorophenyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, trifluoromethyl, cyclohexyl, benzyl or adamantyl. It will be appreciated that if R_{17} is hydrogen, then the group defined by -OC(O)OR_{18} will be a carbonic acid group.

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

In an –alkylC(O)OR_{19} or –alkylC(O)R_{19} group, R_{19} can be hydrogen, an aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl group as defined above. R_{19} may be unsubstituted aliphatic, alicyclic or aryl. Optionally R_{19} is hydrogen, methyl, ethyl, propyl, butyl (for example n-butyl, isobutyl or tert-butyl), phenyl, pentafluorophenyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, trifluoromethyl or adamantyl.

An ether group is optionally -OR_{20} wherein R_{20} can be an aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl group as defined above. R_{20} may be unsubstituted aliphatic, alicyclic or aryl. Optionally R_{20} is methyl, ethyl, propyl, butyl (for example n-butyl, isobutyl or tert-butyl), phenyl, pentafluorophenyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, trifluoromethyl or adamantyl.

It will be appreciated that where any of the above groups are present in a Lewis base G, one or more additional R groups may be present, as appropriate, to complete the valency. For example, in the context of an amino group, an additional R group may be present to give $RNHR_{10}$., wherein R is hydrogen, an optionally substituted aliphatic, heteroaliphatic, alicyclic, heteroalicyclic, aryl or heteroaryl group as defined above. Optionally, R is hydrogen or aliphatic, alicyclic or aryl.

When the suffix "ene" is used in conjunction with a chemical group, e.g. "alkylene", this is intended to mean the group as defined herein having two points of attachment to other groups. As used herein, the term " alkylene", by itself or as part of another substituent, refers to alkyl groups that are divalent, i.e., with two points of attachment to two other groups.

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

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

It will be appreciated that although in formula (V), the groups X and G are illustrated as being associated with a single M_1 or M_2 metal centre, one or more X and G groups may form a bridge between the M_1 and M_2 metal centres.

For the purposes of the present invention, the epoxide substrate is not limited. The term alkylene oxide therefore relates to any compound comprising an epoxide moiety (i.e. a substituted or unsubstituted oxirane compound). Substituted oxiranes include monosubstituted oxiranes, disubstituted oxiranes, trisubstituted oxiranes, and tetrasubstituted oxiranes. Alkylene oxides may comprise a single oxirane moiety. Alkylene oxides may comprise two or more oxirane moieties.

It will be understood that the term “an alkylene oxide” is intended to encompass one or more alkylene oxides. In other words, the term “an alkylene oxide” refers to a single alkylene oxide, or a mixture of two or more different alkylene oxides. For example, the alkylene oxide substrate may be a mixture of ethylene oxide and propylene oxide, a mixture of cyclohexene oxide and propylene oxide, a mixture of ethylene oxide and cyclohexene oxide, or a mixture of ethylene oxide, propylene oxide and cyclohexene oxide.

The term polycarbonate block polyethercarbonate (poly)ol generally refers to polymers which are substantially terminated at one or each end with -OH, -SH, and/or -NHR’ groups (encompassing C-OH, P-OH, -C(O)OH, etc. moieties). R’ may be H, or optionally substituted alkyl, heteroalkyl, aryl, heteroaryl, cycloalkyl or heterocycloalkyl, optionally R’ is H or optionally substituted alkyl.

By way of example, at least about 90%, at least about 95%, at least about 98% or at least about 99% of polymers may be terminated at each end with -OH groups. The skilled person will appreciate that if the polymer is linear, then it may be capped at both ends with -OH groups. If the polymer is branched, each of the branches may be capped with -OH groups. Such polymers are generally useful in preparing higher polymers such as polyurethanes. The chains may comprise a mixture of functional groups (e.g. -OH and -SH) groups, or may contain the same functional group (e.g. all-OH groups).

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

In terms of continuous mode of addition, the relevant materials are continually or constantly added during the course of a reaction. This may be achieved by, for example, adding a stream of material with either a constant flow rate or with a variable flow rate.

In other words, the one or more materials are added in an essentially non-stop fashion. It is noted, however, that non-stop addition of the materials may need to be briefly interrupted for practical considerations, for example to refill or replace a container of the materials from which these materials are being added.

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

A continuous reaction may employ continuous addition of materials.

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

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

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

By “end part of the reaction” is meant the total reaction time after 50% of the total monomers to be incorporated into the polymer chain are so incorporated into the growing polymer chain, preferably, after 75% of the total are so incorporated into the growing polymer chain, more preferably, after 90% of the total monomers are so incorporated into the growing polymer chain, most preferably, after 95% of the total monomers are so incorporated into the growing polymer chain.

By “after the start of the reaction” is meant any time after the reaction has begun.

The term “(co)polymer” is used with reference to the polycarbonate or polyester (poly)ol. The parentheses are used to indicate that if the compound is a polycarbonate (poly)ol it may be a copolymer due to the presence of both carbon dioxide and epoxide residues, whereas if the compound is a polyester (poly)ol it may be a homopolymer if only one monomer was used (for example via ring-opening polymerisation).

The term “(poly)ol” used herein means polyol or mono-ol and therefore refers to an organic compound which comprises one or more hydroxyl groups and typically no other functional groups, such as a mono-ol, diol or triol.

Examples

Experimental

Example 1: Comparative example of with PO only in second vessel (98% secondary)

Hexanediol (2.9 g), catalyst (1) (0.2 g) and EO (30 mL) were added into a 100mL reactor. The vessel was heated to 75 °C and pressurised to 20 bar with CO_2 and stirred for 16 hours, after which it was cooled and vented. This resulted in a ca. 1100 g/mol polyethylene carbonate polyol. The contents of the reactor were transferred into a Schlenk tube, along with the addition of PO (6 mL) and EtOAc (20 mL).

In a separate 100 mL reactor, 9.2 mg of DMC catalyst and PPG400 (0.4 mL) were added. Ethyl acetate (15 mL) was injected into the vessel. The vessel was heated to 130 °C. 2 x 0.5 g of PO were added to confirm activity of the DMC catalyst.

The reactor was cooled to 85 °C at 4.5 bar with CO_2 . The first reaction mixture was then added via a HPLC pump. Addition occurred over 1 hour. The reaction was continued for 3 hours before the addition of PO (14 g) over 0.5 hours. A reaction was run for a further 16 hours before the reactor was cooled to below 10°C and the pressure was released. NMR and GPC were measured immediately.

Example 2: Comparative example with polyether starter

PPG400 (15 mL) and DMC (9 mg) were added to a 100 mL reactor and heated to 130 °C under vacuum. Four 6 g slugs of PO were added over several hours, each time waiting for the active DMC to be observed. EO was added (3 x 9mL) under a pressure of CO_2, with intervals of 2 hours, ensuring DMC remained active before each addition.

Example 3:

Example 3 was carried out as per example 1 except, hexanediol (2.75 g) was used to make polyethylene carbonate-polyol of 1200 g/mol, and PO (10 mL) and EtOAc (15 mL) were added to the Schlenk. Instead of the final PO addition in reactor 2, EO (9 mL) was added to end-cap the polyol.

Example 4:

Example 4 was carried out as per example 1 except, hexanediol (2.75 g) was used to make polyethylene carbonate-polyol of 1200 g/mol, and EtOAc (15 mL) added to the Schlenk. Instead of the final PO addition in reactor 2, EO (9 mL) was added to end-cap the polyol.

Example	Conversion %	Overall CO_2 wt %	EO:PO	M_n g/mol	PDI	Primary end groups % (**M1**)$^{\$}$	Primary end groups % (**M2**)*
1 – Comp.	100	20.0	1.00	2050	1.29	0	12
2 – Comp.	100	0	~1	1640	1.36	56	67
3 – Invention	100	21.3	3.53	1980	1.21	79	78
4 – Invention	100	18.0	5.50	1740	1.28	81	83

$^{\$}$ **Method 1** – Ref: Journal of Cellular Plastics, January/February, 1974, Page 43. *T. Groom, J. S. Babiec, Jr. and B. G. Van Leuwen*

* **Method 2** – Hofmann et al., United States Patent, 2019*, US 10,174,151 B2*

Two different literature methods were used to determine the primary hydroxyl content of the polyols.

Comparative example 1 demonstrates the very low percentage of primary end-groups produced when propylene oxide is used as the sole epoxide in the second reaction. Method 1 did not determine any primary hydroxyl groups, whilst method 2 determined 12% primary hydroxyl groups. The DMC catalyst is generally known to produce ~3% primary end groups when reacted with PO alone, so method 1 appears more reliable. Comparative example 2 was conducted with an ethylene oxide end cap but a polyether was used as the starter instead of a polycarbonate. Method 1 determined only 56% primary hydroxyl end groups, whilst method 2 was slightly higher at 67%.

Examples 3 and 4 (of the invention) used a polycarbonate starter produced by reaction of a carbonate catalyst, starter, CO_2 and ethylene oxide. They differ in that example 3 used a mixture of PO and EO in the second reactor, whilst example 4 used only EO in the second reactor (apart from the 1g PO used to activate the DMC catalyst). Examples 3 and 4 showed approximately 80% primary hydroxyl end groups, even though PO was used to activate the DMC catalyst. This demonstrates the introduction of a polycarbonate starter substantially increases the primary hydroxyl content under identical conditions.

Claims

1. A (poly)ol block copolymer of general structure B-A-(B)n wherein block A is a polycarbonate block or polyester block, wherein n=t-1 and t = the number of reactive end residues on block A, wherein block B is a polyethercarbonate block and wherein > 70% of the copolymer chain ends are terminated by primary hydroxyl groups.

2. A (poly)ol block copolymer according to claim 1, wherein > 75%, more preferably, >80% of the copolymer chain ends are terminated by primary hydroxyl groups.

3. A (poly)ol block copolymer according to any preceding claim, wherein the mol/mol ratio of block A to block B is in the range 25:1 to 1:250.

4. A (poly)ol block copolymer according to any preceding claim, wherein the carbonates present in block A are derived from CO_2.

5. A (poly)ol block copolymer according to any preceding claim, wherein block A is derived from alkylene oxides and CO_2.

6. A (poly)ol block copolymer according to any preceding claim, wherein block A is partly derived from alkylene oxides and wherein optionally the alkylene oxides are selected from cyclohexene oxide, styrene oxide, ethylene oxide, propylene oxide, butylene oxide, substituted cyclohexene oxides (such as limonene oxide, $C_{10}H_{16}O$ 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.

7. A (poly)ol block copolymer according to any preceding claim, wherein block A is a polyalkylenecarbonate block, more typically derived from alkylene oxides and CO_2.

8. A (poly)ol block copolymer according to any preceding claim, wherein the alkylene oxides and CO_2 provide at least 90% of the residues in the block not including any starter, especially, at least 95% of the residues in the block, more especially, at least 99% of the residues in the block, most especially, about 100% of the residues in the block not including any starter are residues of alkylene oxide and CO_2.

9. A (poly)ol block copolymer according to claim 7 or 8, wherein the block A alkylene oxide residues are ethylene oxide and/or propylene oxide residues and optionally, in addition, other alkylene oxide residues.

10. A (poly)ol block copolymer according to any preceding claim, wherein at least 50% of the alkylene oxide residues of block A are ethylene oxide or propylene oxide residues, more typically, at least 70% of the alkylene oxide residues of block A are ethylene oxide or propylene oxide residues, most typically, at least 90% of the alkylene oxide residues of block A are ethylene oxide or propylene oxide residues, especially, ethylene oxide at these levels.

11. A (poly)ol block copolymer according to any preceding claim, wherein block A has between 70-100% carbonate linkages, more typically, 80-100%, most typically, 90-100% and/or wherein the polycarbonate block, A, of the (poly)ol block copolymer has at least 76% carbonate linkages, preferably at least 80% carbonate linkages, more preferably at least 85% carbonate linkages and/or wherein block A has less than 98% carbonate linkages, preferably less than 97% carbonate linkages, more preferably less than 95% carbonate linkages and/or optionally, block A has between 75% and 99% carbonate linkages, preferably between 77% and 95% carbonate linkages, more preferably between 80% and 90% carbonate linkages.

12. A (poly)ol block copolymer according to any preceding claim, wherein the A block has a high carbonate content and the B block a low carbonate content, for example, the A block has greater than 70% carbonate linkages and/or, for example, the B block has less than 50% carbonate linkages.

13. A (poly)ol block copolymer according to any preceding claim, wherein the carbonate residues of block B are derived from CO_2.

14. A (poly)ol block copolymer according to any preceding claim, wherein block B is derived from alkylene oxides and CO_2.

15. A (poly)ol block copolymer according to any preceding claim, wherein block B is partly derived from alkylene oxides and wherein optionally the alkylene oxides are selected from cyclohexene oxide, styrene oxide, ethylene oxide, propylene oxide, 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.

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

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

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

19. A (poly)ol block copolymer according to any preceding claim, wherein block B comprises a mixture of alkylene oxide residues and the other non-ethylene oxide residues are selected from cyclohexene oxide, styrene oxide, propylene oxide, butylene oxide, substituted cyclohexene oxides (such as limonene oxide, $C_{10}H_{16}O$ 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.

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

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

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

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

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

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

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

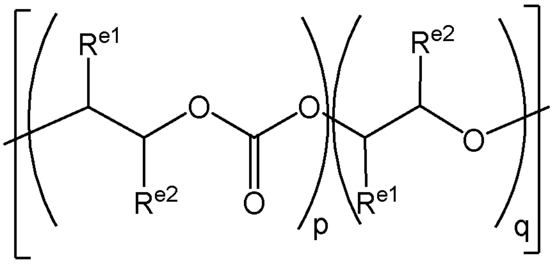
between 1% and 20% ether linkages, more preferably between 1% and 15% ether linkages.

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

B-A'-Z'-Z-(Z'-A'-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.

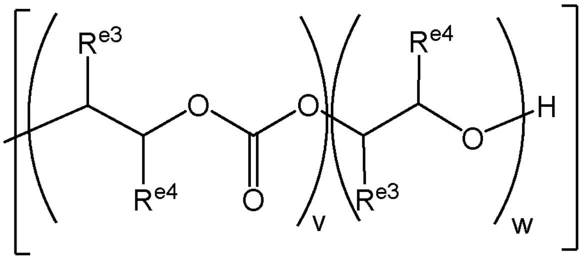
27. A (poly)ol block copolymer according to claim 26, wherein -A'- has the following structure:



(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 alkylene oxide used to prepare blocks A and B.

28. A (poly)ol block copolymer according to claim 27, wherein each R^{e1}, R^{e2}, R^{e3}, or R^{e4} is independently selected from selected from H, halogen, hydroxyl, or optionally substituted alkyl (such as methyl, ethyl, propyl, butyl, -CH$_2$Cl, -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.

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

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

$$Z\!\left(R^Z\right)_a \qquad \text{(III)}$$

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.

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

32. A (poly)ol block copolymer according to claim 30, wherein the starter compound is selected from monofunctional starter substances such as alcohols, phenols, amines, thiols and carboxylic acid, for example, alcohols such as methanol, ethanol, 1- and 2-propanol, 1- and 2-butanol, linear or branched C_3-C_{20}-monoalcohol such as tert-butanol, 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), 1-3-propanediol, 1,2-butanediol, 1-3-butanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,8-octanediol, 1,10-decanediol, 1,12-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.

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

34. A (poly)ol block copolymer according to claim 27, wherein the molecular weight (Mn) is measured by Gel Permeation Chromatography (GPC).

35. A (poly)ol block copolymer according to any of claims 1-34, wherein ethylene oxide residues form 0-100% of the alkylene oxide residues in the (poly)ol block copolymer, typically 5-70%, more typically, 10-60% of the alkylene oxide residues in the (poly)ol block copolymer, most typically, 10-40% of the alkylene oxide residues in the (poly)ol block copolymer and/or, at least 5%, 10%, 15%, 20%, 25% or 30% of the alkylene oxide residues in the (poly)ol block copolymer are ethylene oxide residues .

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

37. A composition comprising the (poly)ol block copolymer of any preceding claim and one or more additives selected from catalysts, blowing agents, stabilizers, plasticisers, fillers, flame retardants, and antioxidants.

38. A composition according to claim 37 further comprising a (poly)isocyanate.

39. A polyurethane produced from the reaction of a polyol block copolymer according to any of claims 1 to 36 or a composition according to claim 37 or 38 and a (poly)isocyanate.

40. A polyurethane comprising a block copolymer residue according to any of claims 1-36.

41. An isocyanate terminated polyurethane prepolymer comprising the reaction product of a block copolymer according to any of claims 1 to 36 or a composition according to claim 36 with an excess of (poly)isocyanate.

42. An isocyanate terminated polyurethane prepolymer comprising a block copolymer residue according to any of claim 1 to 36.

43. A composition according to claim 37 or 38, wherein the catalysts for the (poly)isocyanate and the polyol block copolymer reaction include suitable urethane catalysts such as tertiary amine compounds and/or organometallic compounds.

44. A composition according to claim 37 or 38, wherein a trimerisation catalyst is present.

45. A composition according to claim 37, wherein an excess of (poly)isocyanate, more typically, an excess of polymeric isocyanate relative to polyol is present so that polyisocyanurate ring formation in the presence of the trimerisation catalyst is possible.

46. A lubricant composition comprising a (poly)ol block copolymer of any of claims 1 to 36.

47. A surfactant composition comprising a (poly)ol block copolymer of any of claims 1 to 36.

48. A process for producing a (poly)ol block copolymer comprising the reaction of a DMC catalyst with a polycarbonate or polyester (poly)ol (co)polymer according to block A of any of claims 1 to 36, CO_2 , ethylene oxide and optionally one or more other alkylene oxides to produce a (poly)ol block copolymer according to any of claims 1 to 36.

49. A process for producing a (poly)ol block copolymer comprising a first reaction in a first reactor and a second reaction in a second reactor; wherein the first reaction is the reaction of a carbonate catalyst with CO_2 and alkylene oxide, in the presence of a starter and optionally a solvent to produce a polycarbonate (poly)ol copolymer according to block A of any of claims 1 to 36 and the second reaction is the reaction of a DMC catalyst with the polycarbonate (poly)ol copolymer of the first reaction, CO_2 , ethylene oxide and optionally one or more other alkylene oxides to produce a (poly)ol block copolymer according to any of claims 1 to 36.

50. A process for producing a (poly)ol block copolymer in a multiple reactor system; the system comprising a first and second reactor wherein a first reaction takes place in the first reactor and a second reaction takes place in the second reactor; wherein the first reaction is the reaction of a carbonate catalyst with CO_2 and alkylene oxide, in the presence of a starter and optionally a solvent to produce a polycarbonate (poly)ol copolymer according to a starter residue terminated block A of any of claims 1 to 36 and the second reaction is the reaction of a DMC catalyst with the polycarbonate (poly)ol compound of the first reaction, CO_2, ethylene oxide and optionally one or more other alkylene oxides to produce a (poly)ol block copolymer according to any of claims 1 to 36.

51. A process according to any of claims 48 to 50, further comprising a reaction comprising the reaction of the block copolymer of any of claims 1 to 36 with a monomer or further polymer to produce a higher polymer.

52. A process according to claim 51, wherein the monomer or further polymer is a (poly)isocyanate and the product of the reaction is a polyurethane.

53. A process according to any of claims 48-52, wherein the DMC catalyst is pre-activated, optionally in the reactor or separately, optionally wherein the DMC is pre-activated with a starter compound or with the polycarbonate or polyester (poly)ol

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

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

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

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

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

58. A process according to any of claims 48-57, wherein the first reaction is carried out under CO_2 pressure of less than 20 bar, more preferably, less than 10 bar, most preferably, less than 8 bar.

59. A process according to any of claims 48-58, wherein the second reaction is carried out under 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.

60. A process according to any of claims 48-59, wherein the CO_2 is added continuously in the first reaction, preferably in the presence of a starter.

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

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

63. A process according to any of claims 57-62, wherein the crude reaction mixture fed into the reactor or second reactor includes an amount of unreacted alkylene oxide and/or CO_2 and/or starter.

64. A process according to any of claims 57-63, wherein the carbonate catalyst is present in the crude reaction mixture.

65. A process according to any of claims 57-63, wherein the carbonate catalyst has been removed from the crude reaction mixture prior to the addition to the reactor or second reactor.

66. A process according to any of claims 48-65, wherein the temperature of reaction in the first reactor is in the range about 0°C to 250 °C, preferably from about 40 °C to about 160 °C, more preferably from about 50 °C to 120 °C.

67. A process according to any of claims 48-66, wherein the temperature of reaction in the reactor or second reactor is in the range from about 50 to about 160°C, preferably in the range from about 70 to about 140°C, more preferably from about 70 to about 110°C.

68. A process according to any of claims 48-67, wherein the reactors are located in series.

69. A process according to any of claims 48-67, wherein the reactors are nested.

70. A process according to claim 69, wherein the first and second reactors are effective to provide different reaction conditions, such as temperature and/or pressure, to each other simultaneously.

71. A process according to any of claims 57-70, wherein the crude reaction mixture is stabilised by an acid prior to addition to the reactor or second reactor.

72. A process according to any of claims 48-71, wherein the process employs a total amount of alkylene oxide, and wherein about 1 to 100% of the total amount of alkylene oxide is mixed in the first reaction, with any remainder added in the second reaction; optionally with about 5 to 90% being mixed in the first reaction, optionally with about 10 to 90%, optionally with about 20 to 90%, optionally with about 40 to 90%, optionally with about 40 to 80%, optionally with about 5 to 50%.

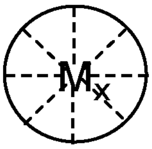
73. A process according to any of claims 48-72, wherein between 0.1 and 20% of the total alkylene oxide in the first reaction is an alkylene oxide substrate containing more than one epoxide moiety, preferably a bis-epoxide.

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

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

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

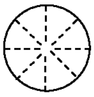
77. A process according to any of claims 48-76 wherein the carbonate catalyst is a catalyst of Formula (IV):



(IV)

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

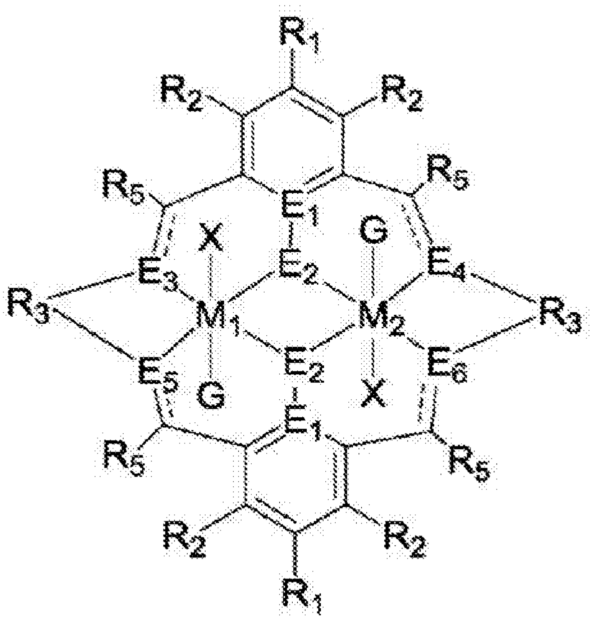
x is an integer from 1 to 4,

 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.

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



(V)

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$_2$R$_x$, 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.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2021/050525

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08G65/26 C08G18/42 C08G18/44 C08G18/48 C08G64/18
C08G64/34 C08G64/42

ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 2 258 745 A1 (ASAHI GLASS CO LTD [JP]) 8 December 2010 (2010-12-08) cited in the application examples 1-3 -----	1-97
Y	WO 2011/075343 A1 (DOW GLOBAL TECHNOLOGIES INC [US]; SHUTOV PAVEL [NL] ET AL.) 23 June 2011 (2011-06-23) paragraph [0002] -----	1-97

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 17 May 2021	Date of mailing of the international search report 26/05/2021
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Hoffmann, Michael

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/GB2021/050525

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 2258745 A1	08-12-2010	CN 101977965 A	16-02-2011
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