Title: CARBONATE GROUP COMPRISING TERPENE-DERIVED MONOMERS AND ISOXYLANATE-FREE POLYURETHANES

Abstract: Terpene or terpenoid derivatives comprising at least two cyclic carbonate groups and isocyanate-free polyurethanes obtainable form the reaction of monomers with at least two cyclic carbonate groups with amine monomers comprising at least two amino groups.
Description

[0001] Carbonate group comprising terpene-derived monomers and isocyanate-free polyurethanes

[0002] The present invention relates terpene derived monomers with carbonate groups and to isocyanate-free polyurethanes obtainable by the reaction of monomers which are at least partially based on renewable raw materials.

[0003] Polyurethanes are an important group of polymers which are industrially produced in large amounts.

[0004] A characteristic feature of polyurethanes is the urethane group -NH-CO-O-. Dependent on the synthesis method the properties of polyurethanes span over a wide range and polyurethanes are such useful for a multiplicity of different uses.

[0005] By far the greatest amount of polyurethanes industrially produced is obtained via the reaction of polyols with polyisocyanates. Isocyanates (like toluylene diisocyanate (TDI) or diphenyl methane disocyanate (MDI), which are often used) are usually toxic and thus comprehensive safety measures have to be taken in the connection with the monomer handling.

[0006] Isocyanate-free polyurethanes are manufactured without the use of isocyanates (as already implied by their name). The synthesis of polyurethanes with dicarbonates and diamines as starting materials is known and yields polymers having a hydroxyl group in beta-position relative to the urethane group. Suitable dicarbonate monomers described in the literature and commercially available e.g. from Specific Polymers (Clapiers, France) are vinylcyclohexene dicarbonate, resorcinol bis carbonate, terephthalate bis carbonate and diglycerol carbonate. A good overview of processes for the isocyanate-free synthesis of polyurethanes can be found in the PhD thesis of Dr. Luc Ubaghs (Rheinisch Westfälische University of Aachen, Germany) having the title "Isocyanate-free synthesis of (functional) polyureas, polyurethanes and urethane-containing copolymers" published in 2005.

[0007] The monomers mentioned above, as the isocyanates, are not based on renewable raw materials.
[0008] US 7,045,577 discloses the synthesis of isocyanate-free polyurethanes based on renewable resources. Monomers comprising cyclic carbonate groups and derived from plant oils are reacted with diamines. The carbonates used, due to their origin from plant oils bear glycerol ester groups in a significant amount. In the course of the reaction with diamines to obtain the polyurethanes a more or less complete aminolysis of the glycerol ester bonds is observed, which reduces the degree of crosslinking and liberates glycerol, which acts as a plasticizer, which is undesirable.

[0009] Furthermore, the isocyanate free polyurethanes in accordance with US 7,054,577, based on plant oils, compete with the food products as well as with the biofuel manufacture, which is undesirable.


[0011] It was thus an object of the present invention to provide suitable novel monomers for the manufacture of isocyanate free polyurethanes and isocyanate free polyurethanes which can be synthesized from monomers which are at least partially based on renewable raw materials and which do not show the disadvantages mentioned above.

[0012] This object is solved in accordance with the present invention by terpene or terpenoid derivatives in accordance with claim 1 and isocyanate-free polyurethanes in accordance with claim 9. Preferred embodiments of the invention are disclosed in the dependent claims 2 to 8 for the terpene or terpenoid derivatives and in claims 10 to 14 for the isocyanate-free polyurethanes.

[0013] The terpene or terpenoid derivatives in accordance with the present invention comprise at least two cyclic carbonate groups.

[0014] Respective monomers may be characterized by general formula I

[0015] ![Diagram](image-url)
[0016] wherein R defines the terpene or terpenoid structural element, which terpene or terpenoid structural element may be bound to one or both cyclic carbonate groups through one or two carbon atoms.

[0017] Monomers with more than two cyclic carbonate groups are in principle suitable too, thereby yielding crosslinked products. Respective products are known to the skilled person and described in the literature, so that no further detailed explanation needs to be given here.

[0018] Cyclic carbonate groups are obtainable e.g. by the catalytic addition of carbon dioxide to epoxides in accordance with the following reaction scheme

\[
\begin{align*}
\text{O} & \quad + \quad \text{CO}_2 \\
\text{O} & \quad \xrightarrow{\text{reaction}} \quad \text{O} \quad \text{C} \quad \text{O}
\end{align*}
\]

[0019] Terpenes are a group of chemical compounds, which are naturally occurring and present as secondary ingredients in organisms. In principle they are derived from isoprene and are characterized by a great variety of carbon skeletons and a small number of functional groups. More than 8000 different terpenes and more than 30,000 closely related terpenoids are known. Most of the terpenes are natural materials, primarily from plants and sometimes of animal origin. Naturally occurring are primarily hydrocarbon-, alcohol-, glycosodic-, ether, aldehyde, ketone-, carboxylic acid or ester-terpenes, but there are also representatives of further groups of materials amongst the terpenes. The terpenes are the major ingredient of the ethereal oils produced in plants.

[0020] A common feature of the terpenes is the fact that they ultimately are derivable from isoprene, i.e. they comprise a number of carbon atoms which is a multiple of 5. According to the IUPAC nomenclature terpenes and terpenoids are differentiated; terpenes only contain carbon and hydrogen atoms, whereas terpenoids contain hetero atoms and in so far the number of carbon atoms in terpenoids is no longer a multiple of five.
necessarily. Terpenes and terpenoids are often named by trivial names derived from the scientific name of the organism from which the respective compound was isolated for the first time.

[0023] In accordance with a preferred embodiment the terpenes or terpenoids are acyclic or cyclic, in particular mono-, bi-, tri-, tetra- or pentacyclic, i.e. they may comprise one, two, three, four or five rings in the molecule. The isoprene units may be connected head-head, head-tail or tail-tail (the molecule part comprising the isopropylene unit referred to as head and the unsubstituted part referred to as tail.

[0024] In accordance with another preferred embodiment the terpene or terpenoid derivatives in accordance with the present invention are derived from hemiterpenes (C₉), monoterpenes (C₁₀), sesquiterpenes (C₁₅), diterpenes (C₂₀), sesterterpenes (C₂₅), triterpenes (C₃₀) and tetraterpenes (C₄₀). Terpenes having more than 40 carbon atoms, generally referred to as polyterpenes, are also preferred.

[0025] Citral, nerol, linalool and geraniol may be mentioned as representatives of the group of the acyclic monoterpenoids whereas myrcene and the isomeric ocimens, which occur naturally, are representatives of acyclic monoterpenes.

[0026] Terpene or terpenoid derivatives which are obtainable through catalytic addition of carbon dioxide to respective compounds comprising at least two epoxide groups represent another preferred embodiment in accordance with the present invention.

[0027] A significant number of cyclic monoterpenes and monoterpenoids comprises a skeleton based on cyclohexane rings. Compounds of this type are also preferred as they occur widely in nature and are thus available in large amounts.

[0028] 1-Methyl-4-isopropylcyclohexane (also known as p-menthane) forms the basic skeleton for the terpinenes, limonene, the phellandrenes or of terpinolene, the structures of which are represented below and which form a particularly preferred group of terpenes or terpenoid basic structures for the terpene or terpenoid derivatives comprising at least two cyclic carbonate groups in accordance with the present invention.
[0029] \( \beta \)-phellandrene

[0030] A particularly preferred monoterpane in this regard is limonene.

[0031] (R) \(-(+)\)-limonene is the major component in the ethereal oils in the shell of citric fruits, whereas (S)-(\(-\))limonene is present in noble firs and in peppermint oil. The racemic mixture of both is present in nutmegs.

[0032] (R) \(-(+)\)-limonene is obtained in large amounts in the course of the production of fruit juices, in particular of orange juice, constitutes a particularly preferred terpene from which the monomers with cyclic carbonate groups are derived.

[0033] Limonene is also commercially available in epoxidized form as limonene dioxide which is used as diluent in the manufacture of epoxy resin products.
[0034] The manufacture of the monomers with cyclic carbonate groups starting from terpenes or terpenoids shown below using limonene as an example; in principle all terpenes with at least two double bonds may be converted into the respective carbonate group containing compounds in accordance with the reaction scheme provided.

[0035] The reaction sequence for limonene may be shown as follows:

```
CH3
H2C  

H2C  

H2C

limonene  limonene dioxide  limonene dicarbonate
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[0036]

[0037] In the first step the double bonds are partially or fully and selectively epoxidized. Respective processes are known to the skilled person and described in the literature, so that no further detailed explanations are necessary here. It is important that at least two double bonds are epoxidized. If the starting material has more than two double bonds, more than two double bonds may be epoxidized, which leads to terpene or terpenoid derivatives with more than two cyclic carbonate groups which, when used as monomers in the course of the reaction with amines leads to a cross linking. By controlling the extent of epoxidation exceeding two double bonds the degree of cross-linking of the polymer can be controlled and adjusted. If exactly two double bonds are epoxidized and subsequently exactly two cyclic epoxide groups are obtained, the subsequent reaction of the dicarbonates obtained from such epoxides with diamines yields linear polymers; if the functionality exceeds two, cross-linking occurs, the degree of which depends on the average functionality. Several ways are thus available to the skilled person to achieve a desired
degree of cross-linking or to obtain non-cross-linked products through the use of exactly bifunctional monomers.

[0038] After epoxidation, carbon dioxide is added through catalytic addition whereby cyclic carbonates are formed, in the case of limonene dioxide as starting material limonene dicarbonate as shown before is obtained.

[0039] The reaction of oxides with carbon dioxide to yield five membered cyclic carbonates has been studied in various literature reports, e.g. Kihara et al., J. org. chem. (1993), 58, 6198.

[0040] The reaction may be preferably carried out by using a suitable catalyst system at atmospheric pressure and temperatures in the range of from 60 to 140, preferably of from 80 to 120°C, optionally in a suitable solvent.

[0041] In certain cases it may be advantageous to use carbon dioxide pressures exceeding atmospheric pressures to accelerate the reaction and to control and suppress potential side reactions. Carbon dioxide pressures of up to 3 MPa at temperatures of up to 140°C have proved to be useful.

[0042] A number of suitable homogeneous and heterogeneous catalyst systems for the respective reactions have been described in the literature. A good overview may be found in Dai et al. Catal. Lett. DOI 10.1007/s 10562-010-285-4 (published online on Feb. 9, 2010) and in the literature cited in this document. Exemplary for homogeneous catalyst systems alkali metal salts, organotin or organo antimony compounds, ionic liquids, onium salts or transition metal complexes may be mentioned. Suitable heterogeneous catalyst systems are metal oxides, zeolites, smectites and polyoxometalates. In certain cases alkali metal halide and quaternary ammonium halides have been found particularly useful. The sodium-complex catalyzed synthesis of cyclic carbonates by addition of carbon dioxide to epoxides is described in the Decortes et al., Angew. Chem. Int. Ed. 2010, 49, 9822ff. Solid phase supported quaternary ammonium halides are also suitable as catalyst systems and described for example in the above mentioned reference Dai et al. Silica gel-supported quaternary amino pyridinium halides are disclosed in Green Chem. 2009, 11, 1876 et seq.
[0043] With the catalyst systems mentioned before cyclic carbonates may be obtained with good selectivity through the reaction of epoxides with carbon dioxide.

[0044] The reaction sequence described above is principally applicable to all terpenes with at least two double bonds.

[0045] Another embodiment of the present invention is related to isocyanate-free polyurethanes obtainable by reaction of substantially glycerol-ester group free monomers comprising at the least two cyclic carbonate groups which are derived from renewable raw materials, with amine monomers comprising at least two amino groups.

[0046] The term substantially glycerol-ester group free in accordance with the present invention is to be understood to the effect that the carbonate group containing monomers either do not contain glycerol ester groups groups at all (which is particularly preferred) or, in case minor amounts of glycerol-ester groups are present, their amount is low enough to avoid the negative influence of glycerol liberated through aminolysis to detrimentally affect the properties of the polyurethanes, in particular the degree of cross-linking. This excludes plant oil based cyclic carbonates as described e.g. in US 7,045,577.

[0047] Principally any monomer containing at least two cyclic carbonate groups is suitable if it is derived from renewable raw materials.

[0048] In accordance with what was said before for the terpene or terpenoid derivatives in accordance with the present invention, monomers with cyclic carbonate groups based on renewable raw materials are obtainable from a great variety of natural materials. Particularly suitable are natural materials with at least two double bonds in the molecule as these may be reacted in accordance with the mentioned reaction steps in a simple manner yield the desired products with at least two cyclic carbonate groups in good purity and good yields. The epoxidation of double bonds as well as the subsequent catalytic addition of carbon dioxide generally proceed quantitatively and without significant side reactions so that the desired compounds with two cyclic carbonate groups can be obtained in good purity and good yields.
[0049] A group of preferred renewable raw materials are the terpene or terpenoid derivatives in accordance with claims 1 to 8., which occur in a great variety in nature.

[0050] Accordingly, the preferred terpene or terpenoid derivatives in accordance with the present invention and discussed hereinbefore represent a particularly preferred group of monomers for manufacturing the polyurethanes in accordance with the present invention.

[0051] The monomers a) from which the polyurethanes in accordance with the present invention may be obtained, essentially are free of glycerol ester groups as usually present in plant oils. As already mentioned before, in the course of the reaction of cyclic carbonate group containing monomers with amines aminolysis is observed as a side-reaction - which competes with the reaction of the cyclic carbonate groups if the monomers contain glycerol-ester groups. This leads to a reduction of the degree of polymerization and in addition the glycerol liberated thereby functions as a plasticizer, which has undesired effects on the properties of the polymer.

[0052] The polyurethanes in accordance with the present invention may be obtained by using one or more than one monomers with at least two cyclic carbonate groups.

[0053] The polyurethanes in accordance with the present invention are preferably obtainable by reaction of the monomers with at least two carbonate groups described hereinbefore with amines, preferably with primary amines, with at least two amino groups. Secondary amines are principally usable also, however they usually have a lower reactivity and thus are not particularly preferred.

[0054] The primary amines which are preferred in accordance with the present invention are described in some more detail below; what is said for primary amines is applicable in an analogous manner also to secondary amines.

[0055] Any primary amine, regardless of the process of its manufacture, is suitable for use in the present invention. The functionality is at least two, i.e. there are at least two amino groups in the molecule. Respective products may be characterized by the general formula NH$_2$-R-NH$_2$ wherein R represents an aliphatic, cycloaliphatic, aromatic or heteroaromatic group
without a particular limitation. In some cases aliphatic amines have shown to be particularly suitable. Respective examples for the group of these amines are dialkyl diamines such as 1,4-diamino butane, 1,5-diamino pentane and 1,6-diamino hexane, to name only a few representatives which are commercially available. The three specific amines mentioned are also naturally occurring so that with the use thereof polyurethanes may be obtained which are exclusively based on natural raw materials. 1,4-diamino butane, also known as putrescine, may be obtained by enzymatic decarboxylation of the amino acid ornithine. Putrescine is also produced in the rottenning or fouling process of meat.

[0056] 1,5-diamino pentane, also known as cadaverine, may be obtained by enzymatic decarboxylation of the amino acid lysine.

[0057] 1,6-diamino hexane (also known as hexamethylene diamine) is obtained in an industrial scale through the hydration of adipodinitrile, which itself is obtained from the renewable raw material adipic acid.

[0058] Suitable amines with at least two amino groups are commercially available in a great variety and processes for their manufacture are known to the skilled person so that no detailed further explanations are necessary here.

[0059] Especially for the aliphatic diamines referred to above with 1 to 12 carbon atoms it is often possible to carry out the reaction with the cyclic carbonate group containing monomers without the use of a solvent, which is an advantage under environmental aspects.

[0060] For specific uses of the polyurethanes it is desirable to adjust the degree of cross-linking of the polyurethanes in accordance with the present invention. This desired adjustment may, as already mentioned above, be achieved by the use of monomers with a functionality of more than two.

[0061] A preferred group of monomers with an amino functionality exceeding to are tri--or higher functional amidoamines which are also preferably available from renewable raw materials. Respective products are obtainable by the reaction of naturally occurring esters with more than two ester groups with diamines.

[0062] Tri--or higher functional amidoamines with terminal primary amino groups completely derived on renewable raw materials have not been described
in the literature before and they thus represent a further aspect of the present invention.

[0063] As an example the synthesis of trifunctional amidoamines of citric acid esters shall be described now.

[0064] 2-hydroxy-1,2,3-propane tricarboxylic acid (known under the trivial name citric acid) is a fruit acid occurring in various plants and is the product of metabolism in a multiplicity of organisms. Citric acid is also manufactured industrially with a transgenic variant of the fungus Aspergillus niger and is therefore obtainable in large amounts.

[0065] Through the esterification with ethanol citric acid is converted into citric acid triethyl ester quantitatively, which thereafter can be reacted with the diamines putrescine, cadaverine or hexamethylene diamine to the respective trifunctional amidoamines. Thereby products are obtained which are fully derived from renewable raw materials.

[0066] The reaction scheme in the case of citric acid is summarized below graphically:

![Chemical Reaction Diagram]

[0067]

[0068] In principle any diamine may be used in the process shown before. Through variation of the substituent R trifunctional or higher functional
amidoamines may be obtained, which are suitable as monomer b) for the manufacture of the polyurethanes in accordance with the present invention.

[0069] In the case of the preferred diamines mentioned hereinabove R represents a linear alkylene group with 4 to 6 carbon atoms, principally it is also possible to use other alkylene groups with 1 to 12 carbon atoms or other substituents R.

[0070] The reaction scheme shown above for citric acid as starting material may be transferred to other naturally occurring acids with a respective number of functional acid groups. Respective products are known to the skilled person.

[0071] In the same manner as described for the cyclic carbonate group containing monomers more than one amino group containing monomer may be used in the manufacture of the isocyanate-free polyurethanes in accordance with the present invention.

[0072] In the course of the invention isocyanate-free polyurethanes are obtained through the use of monomers which are partially or completely derived from renewable raw materials. Through the use of essentially glycerol ester group free monomers the undesired aminolysis is avoided, as well as the liberation of glycerol as undesirable byproduct.

[0073] Through the selection of suitable monomers and their functionality the degree of cross-linking can be individually adjusted and controlled. Through selection of the molar ratio of amino groups to cyclic carbonate groups the molecular weight can be adjusted as desired.

[0074] In order to achieve a quantitative or an almost quantitative conversion of the cyclic carbonate groups, the molar ratio of these groups to the amino groups should not deviate too much from an equimolar ratio, as the molecular weight of the products obtainable decreases with increasing deviation from the equimolar ratio. Molar ratios of carbonate groups to amino groups in the range of from 0.9:1 to 1.1:1, preferably of from 0.95:1 to 1.05:1 and particularly preferred of from 0.98:1 to 1.02:1 have proved to be advantageous and suitable. The skilled person is aware of the respective reactions and how to conduct the same and will select the
amino group containing monomers in a suitable manner to obtain the products with the desired properties.

[0075] Lower molecular weight polyurethane prepolymers or oligomers may be obtained by selecting molar ratios of the two monomer groups deviating to a greater extent form the equimolar ratio.

[0076] The isocyanate-free polyurethanes in accordance with the present invention are obtained without the use of toxic starting materials and accordingly there is no process risk as for example associated with the industrial synthesis of polyurethanes based on isocyanates.

[0077] The isocyanate-free polyurethanes in accordance with the present invention are in principle suitable for any application which is known for the classical polyurethanes obtained from isocyanates.

[0078] The easy adjustability of the degree of cross-linking and molecular weight may be particularly advantageous for the use of the polyurethanes in accordance with the present invention in various applications. Especially in those applications in which the user has or may have physical contact with the products (e.g. in casting resins), the polyurethanes in accordance with the present invention are particularly advantageous as there is no toxic hazard or risk in this case and no toxic or hazardous materials may be liberated when using the polyurethanes in accordance with the present invention.

[0079] The following example shows the preparation and purification of limonene dicarbonate starting from limonene dioxide and the use of limonene dicarbonate thus obtained for the manufacture of isocyanate free polyurethanes.

[0080] Example 1 - Preparation of limonene dicarbonate
[0081] Preparation of precursor product
[0082] Carbonation of limonene dioxide (obtained from Rheinmetall Nitrochemie) was performed at 100°C, 120°C and 140°C. The CO₂ pressure was varied between atmospheric pressure, 1 MPa (10 bar) and 3 MPa (30 bar). Conventional tetrabutylammonium bromide and silica-supported 4-pyrrolidinopyridinium iodide (SiO₂-(I)) were used as catalysts. SiO₂-(I) was prepared by a silane-coupling reaction of 3-
iodopropyltrimethoxysilane with silica (Aerosil® 200, Evonik) followed by quaternization of 4-pyrrolidinopyridine with SiO₂-supported propyl iodide. The halide concentration for both catalysts was 3 mole-% with respect to epoxy groups.

[0083] The formation of the cyclic carbonate groups was monitored quantitatively via IR spectroscopy. A distinct band at 1803 cm⁻¹ is assigned to the cyclic carbonate carbonyl.

[0084] With tetrabutyl ammonium bromide as catalyst, quantitative conversion of the epoxide groups could be obtained at 120 °C at carbon dioxide pressures of 1 MPa and 3 MPa after 55 h and after appr. 40 h at a temperature of 140 °C and a pressure of 3 MPa. Increasing the carbon dioxide pressure increased the speed of the conversion.

[0085] With SiO₂-I no quantitative conversion was observed after 120 h at 140°C and 3 MPa carbon dioxide pressure, i.e. tetrabutyl ammonium bromide is a more efficient catalyst for this reaction.

[0086] The product obtained was liquid at room temperature and had a decomposition temperature of approx. 200 °C. The angle of rotation was -10.9°. The NMR spectrum showed various impurities and by-products.

[0087] Example 2 - Purification of product of example 1.

[0088] The product obtained from Example 1 was dissolved in ethanol and thereafter precipitated in diethyl ether. The solid was filtered and dried. The product thus obtained had a melting point of 112 °C and a decomposition temperature of 336 °C. The NMR spectrum showed no impurities, the signals could be quantitatively assigned limonene dicarbonate. The angle of rotation was +41.0°.

[0089] Example 3 - Manufacture of isocyanate free polyurethanes

[0090] The product as obtained in example 1 was placed in a 500 ml aluminum can and degassed in vacuum at 70°C, followed by the addition of the amine. The reaction mixture was thoroughly stirred for five minutes and thereafter the viscous reaction mixture was poured into a mold and thereafter heated at 70 °C for ten hours, followed by three hours at 100 °C. In case of use of the less reactive isophorone diamine as hardener, an
additional heating for further 12 hours at 70 °C was applied. The following table shows the results obtained with various diamines.

<table>
<thead>
<tr>
<th>Molar Ratio</th>
<th>( T_g^a )</th>
<th>( T_m^b )</th>
<th>( M_n )</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>CL/Amine [mol : mol] [°C] [g/mol]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1:1</td>
<td>33</td>
<td>80-90</td>
<td>1100(^c)</td>
<td>1.3(^c)</td>
</tr>
<tr>
<td>BDA</td>
<td>2:1</td>
<td>-</td>
<td>40-60</td>
<td>600(^d)</td>
</tr>
<tr>
<td></td>
<td>1:2</td>
<td>-</td>
<td>60-80</td>
<td>430(^d)</td>
</tr>
<tr>
<td></td>
<td>1:1</td>
<td>38</td>
<td>80-90</td>
<td>1200(^c)</td>
</tr>
<tr>
<td>HMDA</td>
<td>2:1</td>
<td>-</td>
<td>40-60</td>
<td>630(^d)</td>
</tr>
<tr>
<td></td>
<td>1:2</td>
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<td>60-80</td>
<td>490(^d)</td>
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<tr>
<td></td>
<td>1:1</td>
<td>70</td>
<td>90-100</td>
<td>960(^c)</td>
</tr>
<tr>
<td>IPDA</td>
<td>2:1</td>
<td>-</td>
<td>60-80</td>
<td>680(^d)</td>
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<tr>
<td></td>
<td>1:2</td>
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<td>60-80</td>
<td>600(^d)</td>
</tr>
<tr>
<td>OCDA</td>
<td>1:1</td>
<td>62</td>
<td>90-100</td>
<td>1840(^c)</td>
</tr>
</tbody>
</table>

[0092] a) The glass transition temperature \( T_g \) was determined by DSC,
[0093] b) the melting point \( T_m \) was determined via a Brucker melting point analyzer
[0094] c) determined via GPC
[0095] d) calculated from the starting materials
[0096] In the table the following abbreviations are used:
[0097] BDA : 1,4-diaminobutane
[0098] CL : Product obtained in example 1
[0099] HMDA: 1,6-diaminohexane
[0100] IPDA isophorone diamine
[0101] OCDA 1,8 diaminooctane

[0102] As can be seen isophorone based products have the highest glass transition temperature and lowest molecular weight. The prepolymers obtained in accordance with this example represent attractive intermediates and additives e.g. useful in the amine cure of epoxy resins and also for the polymerization of other cyclic carbonate resins.
Claims
1. Terpene or terpenoid derivatives comprising at least two cyclic carbonate groups.
2. Terpene or terpenoid derivatives in accordance with claim 1 wherein the terpene is derived from monoterpenes, sesquiterpenes, diterpenes, sesterterpenes, triterpenes and tetraterpenes or polyterpenes.
3. Terpene or terpenoid derivatives in accordance with claim 1 wherein the terpene is derived from acyclic terpenes or from terpenes comprising one, two, three, four or five rings in the molecular structure.
4. Terpene or terpenoid derivatives in accordance with any of the preceding claims, obtainable by catalytic addition of carbon dioxide to terpene or terpenoid derivatives comprising at least two epoxide groups.
5. Terpene or terpenoid derivatives in accordance with any of the preceding claims selected from the group consisting of at least two cyclic carbonate group containing terpinene derivatives, limonene derivatives, terpinolene derivatives and phellandrene derivatives and mixtures thereof.
6. Terpene or terpenoid derivatives in accordance with any of the preceding claims derived from limonene.
7. Terpene or terpenoid derivatives in accordance with claim 5 comprising two cyclic carbonate groups.
8. Limonene dicarbonate.
9. Isocyanate-free polyurethanes obtainable by reacting
   a) at least one monomer with at least two cyclic carbonate groups and substantially free of glycerol-ester groups, based on renewable raw materials, and
   b) at least one amine monomer comprising at least two amino groups.
10. Isocyanate-free polyurethanes in accordance with claim 9, wherein the monomer with at least two cyclic carbonate groups is derived from terpenes.
11. Isocyanate-free polyurethanes in accordance with any of claims 9 or 10 wherein the at least two cyclic carbonate groups containing monomer comprises a terpene dicarbonate.
12. Polyurethane in accordance with claim 3 wherein the terpene dicarbonate is selected from the group consisting of terpinene dicarbonates, limonene
dicarbonate, terpinolene dicarbonate and phellandrene dicarbonates or mixtures thereof.

13. Isocyanate-free polyurethanes in accordance with any of claims 9 to 12 wherein the amine b) is derived from renewable raw materials.

14. Polyurethane in accordance with any of claims 9 to 13 wherein the amine is an amidoamine with a functionality of more than 2.

15. Use of the polyurethanes in accordance with any of claims 9 to 14 in casting resin systems.
## INTERNATIONAL SEARCH REPORT

**International application No**
PCT/EP2012/002549

### A. CLASSIFICATION OF SUBJECT MATTER
- **INV. C07D317/46**
- **C08G71/04**

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)
- **C07D 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, CHEM ABS Data**

### C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
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<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<tr>
<td>X</td>
<td>CA 851 734 A (AIR REDUCTION) 15 September 1970 (1970-09-15) page 10</td>
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</tr>
</tbody>
</table>

**X** Further documents are listed in the continuation of Box C.  
**X** 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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  - **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
  
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**Date of the actual completion of the international search**
- **5 September 2012**

**Date of mailing of the international search report**
- **04/10/2012**

**Name and mailing address of the ISA/**

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**Authorized officer**

Duval, Eric

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<td>SCHARF, HANS D. ET AL: &quot;Photosensitized cycloaddition of dichlorovinylene carbonate to benzene&quot;, CHEMISCHE BERICHTE, vol. 105, no. 2, 1972, pages 575-587, XP008155561, ISSN: 0009-2940, page 582; compounds 3a, 3b, 3c</td>
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