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(72) Inventeurs/Inventors:
HOFACKER, STEFFEN, DE;
GERTZMANN, ROLF, DE;
FLECK, OLAF, DE;
RUTTMANN, GERHARD, DE;
BRUEMMER, HANNO, US

(73) Propriétaire/Owner:
BAYER MATERIALSCIENCE AG, DE

(74) Agent: FETHERSTONHAUGH & CO.

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(54) Title: PREPOLYMERS ON THE BASIS OF ISOPHORONE DIISOCYANATE WHICH ARE LOW IN MONOMERS AND CONTAIN NCO

(57) Abrégé/Abstract:
The invention relates to prepolymers on the basis of isophorone diisocyanate (IPDI) and polypropylene oxide glycols which are low in monomers and contain NCO and to a method for the production and use thereof.

Abstract

The invention relates to prepolymers on the basis of isophorone diisocyanate (IPDI) and polypropylene oxide glycols which are low in monomers and contain NCO and to a method for the production and use thereof.

Prepolymers on the basis of isophorone diisocyanate which are low in monomers and contain NCO

The present invention relates to low-monomer-content, NCO-containing prepolymers based on isophorone diisocyanate (IPDI) and polypropylene oxide glycols, to a process for preparing them, and to their use.

Aliphatic and cycloaliphatic diisocyanates are employed on account of their good light stability and weathering stability in high-quality polyurethane coatings, sealants, and casting compounds (cf., e.g., Wagner Sarx, Lackkunstharze, 5th edition, Carl Hanser Verlag, Munich, 1971, pages 153 to 173). In connection with the greater concern for environmental cleanliness, solvent-free systems have become particularly interesting. One possibility of preparing such systems is, for example, the use of NCO-containing prepolymers (NCO prepolymers). NCO prepolymers and binders resulting from them are known in great abundance (e.g., EP-A 0 497 131 or EP-A 1 138 707).

Prior art NCO prepolymers are prepared by reaction of relatively high molecular mass polyhydroxyl compounds such as polyether-polyols or polyester-polyols, for example, with excess amounts of diisocyanate or polyisocyanate. In this case it is of advantage for the isocyanate groups to have different reactivities. That property suppresses the unwanted monomer content as a result of this so-called selectivity. The products, moreover, have low viscosities and improved technical processing properties.

Isophorone diisocyanate (3-isocyanatomethyl-3,5,5-trimethylcyclohexylisocyanate, IPDI) possesses two such differently (selectively) reactive isocyanate groups. However, it is not readily possible to reduce the residual monomer content of a prepolymer prepared with IPDI to below 2.0% by weight (e.g., EP-A 0 497 131, example 2, or EP-A 1 138 707, comparative example). That generally necessitates an additional and technically complicated distillation step (thin-film operation) in order to separate off monomeric constituents, e.g., IPDI.

As a further possibility, DD-A 151466, in connection with the preparation of low-monomer-content prepolymers by reaction of diisocyanates or polyisocyanates or polyalcohols, describes using hydroxyl-functional organometallic catalysts. However, low-monomer-content prepolymers of this kind are only successfully prepared using solvents, some of which remains in the prepolymer. From the

standpoint of workplace hygiene, particularly in connection with subsequent use of these prepolymers in coating materials for coatings in poorly ventilated spaces, it is a disadvantage. Moreover, a low residual diisocyanate monomer content in accordance with DD-A 151466 is achieved only through the use of large amounts of hydroxyl-functional organometallic catalysts. This means, however, that critical fractions of isocyanate are consumed by reaction with the hydroxyl function of the catalyst and are not available for further synthesis of polymer. As a result of this chain terminator function on the part of the catalyst, mechanical properties as well of the coating materials to be formulated from the prepolymers are adversely affected.

The present invention provides solvent-free, NCO-containing prepolymers based on IPDI and polyhydroxyl compounds, having a residual IPDI monomer content of < 2.0% by weight, which without a distillation process to remove the monomers ought to be able to be employed directly, and do not have the stated disadvantages.

Surprisingly it has been found that the above could be achieved through the use of *Impact* polyethers, polypropylene oxide glycols prepared by the *Impact* process (e.g., US-A 3 278 459, WO 97/29 146 or EP-A 0 573 206). Without any complex distillation step, the monomer content is less than 2.0% by weight and hence is lower than when using conventional polypropylene oxide glycols prepared by the KOH process.

The invention accordingly provides solvent-free, low-monomer-content, NCO-containing prepolymers based on 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate (IPDI) and *Impact* polyethers, having a residual IPDI monomer content of less than 2.0% by weight, an NCO content of from 2.0 to 5.0% by weight, preferably from 3.0 to 4.5% by weight, and more preferably from 3.5 to 4.2% by weight, and a viscosity of from 5 000 to 20 000 mPas, preferably from 8 000 to 15 000 mPas, and more preferably from 9 000 to 13 000 mPas at 23°C, obtainable by reacting 3-isocyanatomethyl-3,5,5-trimethylcyclohexylisocyanate and at least one *Impact* polyether having an OH functionality of from 1.80 to 2.00, preferably from 1.90 to 2.00, and more preferably from 1.98 to 2.00 and an NCO/OH ratio of from 2.2 to 1.5, preferably from 2.0 to 1.7, and more preferably from 1.98 to 1.80 in the presence of at least one catalyst at from 20 to 100°C.

The invention further provides a process for preparing solvent-free, low-monomer-content, NCO-containing prepolymers based on 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate (IPDI) and *Impact* polyethers, having a residual IPDI monomer content of less than 2.0% by weight, an NCO content of from 2.0 to 5.0% by weight, preferably from 3.0 to 4.5% by weight, and more preferably from 3.5 to 4.2% by weight, and a viscosity of from 5 000 to 20 000 mPas, preferably from 8 000 to 15 000 mPas, and more preferably from 9 000 to 13 000 mPas at 23°C, obtainable by reacting 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl-isocyanate and at least one *Impact* polyether having an OH functionality of from 1.80 to 2.00, preferably from 1.90 to 2.00, and more preferably from 1.98 to 2.00 and an NCO/OH ratio of from 2.2 to 1.5, preferably from 2.0 to 1.7, and more preferably from 1.98 to 1.80 in the presence of at least one catalyst at from 20 to 100°C.

The invention additionally provides for the use of the solvent-free, low-monomer-content, NCO-containing prepolymers of the invention as a binder and/or a binder component in polyurethane coating compositions, polyurethane sealants, polyurethane adhesives and/or polyurethane casting compounds.

The solvent-free, low-monomer-content, NCO-containing prepolymers of the invention are prepared by initially introducing IPDI together with a catalyst into a vessel and adding at least one *Impact* polyether at a temperature between 20°C and 100°C. The NCO/OH ratio is between 2.2 and 1.5, preferably between 2.0 and 1.7, and very preferably between 1.98 and 1.80. The residual IPDI monomer content of the prepolymer of the invention is less than 2.00% by weight and preferably less than 1.95% by weight.

The polypropylene oxide glycols prepared by the *Impact* process (*Impact* polyethers) are distinguished by the fact that, owing to the use of a double metal cyanide (DMC) catalyst instead of the conventional potassium hydroxide they have been prepared on the basis of propylene oxide and so have a greater OH functionality and lower monool fractions than those which have been prepared conventionally by means of potassium hydroxide as catalyst (cf., e.g., US-A 3 278 459, US-A 3 404 109, US-A 3 829 505, WO 97/29 146 or US-A 3 941 849).

To prepare the solvent-free, low-monomer-content, NCO-containing prepolymers of the invention it is preferred to employ those *Impact* polyethers whose average

OH functionality is between 1.98 and 2.00 and which have an average molecular weight (M_n) of between 500 to 5 000 g/mol.

These polyether polyols, known as *Impact* polyethers, have been prepared by polymerizing propylene oxide using a DMC catalyst such as zinc hexacyanocobaltate at 130°C, for example, by an operation which is described in WO 97/29 146 (examples 1 to 5) and involves continuous metering of starter. Examples of suitable continuous starters include water, or low molecular mass polyols having a molecular weight of less than 300 g/mol, such as glycerol, propylene glycol, dipropylene glycol, ethylene glycol, trimethylolpropane, sorbitol, etc.

Catalysts used for the reaction of IPDI and the *Impact* polyethers can be commercially customary organometallic compounds of the elements aluminum, tin, zinc, titanium, manganese, iron, bismuth or else zirconium, such as dibutyltin laurate, zinc octoate, titanium tetraisopropoxide, for example. Also suitable, however, are tertiary amines such as 1,4-diazabicyclo[2.2.2]octane, for example.

Examples

Preliminary remark:
In order to ensure comparability of the resultant characteristics, the amounts of raw materials used were adapted on the basis of the respective equivalent weights, determined beforehand.

The *Impact* polyethers used in the examples below were prepared, for example, in a polymerization operation by reaction of propylene oxide using a DMC catalyst at 130°C in accordance with a process which is described in WO 97/29 146, example 3-5, and comprises continuous metering of starter.

Arcol® PPG 2000 as a polypropylene oxide glycol having a number-average molecular weight (Mn) of 2 000 g/mol is therefore preparable, for example, as follows:

30 mg of zinc hexacyanocobaltate/tert-butyl alcohol complex, preparable according to example 8-1 from EP-A 0 743 093, is suspended in 200 ml of toluene in a steel reactor vessel. 20 g of propylene oxide containing 1.9% by weight propylene glycol is introduced into the reactor and heated at 130°C for activation

of the catalyst. After the internal pressure in the reactor has fallen, 300 g of propylene oxide containing 3.8% by weight propylene glycol are metered in continuously at 130°C over 2.5 hours. The continuous starter in this case is propylene glycol. The polyether polyol obtained possesses a hydroxyl number of 56.2 mg KOH/g and a number-average molecular weight (Mn) of 2 000 g/mol.

In analogy to the exemplary preparation of Arcol® PPG 2000 it is also possible, for example, to obtain Arcol® PPG 1000 as a polypropylene oxide glycol having a number-average molecular weight (Mn) of 1 000 g/mol.

Use of *Impact* polyethers:

Example 1

222.03 g (equivalent weight = 111.44 g/eq) of 3-isocyanatomethyl-3,5,5-trimethylcyclohexylisocyanate (Desmodur® I, commercial product of Bayer AG, Leverkusen) were introduced initially under inert gas (nitrogen) with 0.10 g of benzoyl chloride into a vessel, the components were stirred together, and then 1.00 g of dibutyltin laurate was added. After heating to 45°C, 549.89 g (equivalent weight = 1003.58 g/eq) of Arcol® PPG 2000 (polypropylene oxide glycol, M_n = 2 000 g/mol, commercial product, Bayer AG, Leverkusen) were metered in. When the theoretical NCO content of 7.9% by weight had been reached, a further 249.28 g (equivalent weight = 500.45 g/eq) of Arcol® PPG 1000 (polypropylene oxide glycol, M_n = 1000 g/mol, commercial product, Bayer AG, Leverkusen) were metered in. Following complete addition, the reaction mixture was heated at 60°C until an NCO content of 3.9% by weight was reached. Thereafter it was cooled to room temperature.

The prepolymer of the invention possesses a viscosity of 10 800 mPas (23°C, plate viscometer), an NCO content of 3.9% by weight, and an IPDI monomer content of 1.80% by weight (determined by gas chromatography).

Example 2

227.82 g (equivalent weight = 111.44 g/eq) of 3-isocyanatomethyl-3,5,5-trimethylcyclohexylisocyanate (Desmodur® I, commercial product of Bayer AG, Leverkusen) were introduced initially under inert gas (nitrogen) with 0.10 g of dibutyltin laurate into a vessel and the components were stirred together. After

heating to 55°C, 538.59 g (equivalent weight = 1003.58 g/eq) of Arcol® PPG 2000 (polypropylene oxide glycol, M_n = 2 000 g/mol, commercial product, Bayer AG, Leverkusen) were metered in. When the theoretical NCO content of 8.3% by weight had been reached, a further 255.78 g (equivalent weight = 500.45 g/eq) of Arcol® PPG 1000 (polypropylene oxide glycol, M_n = 1 000 g/mol, commercial product, Bayer AG, Leverkusen) were metered in. When an NCO content of 3.9% by weight had been reached, 0.1 g of benzoyl chloride was added and the mixture was cooled to room temperature.

The prepolymer of the invention possesses a viscosity of 11 300 mPas (23°C, plate viscometer), an NCO content of 3.9% by weight, and an IPDI monomer content of 1.90% by weight (determined by gas chromatography).

Use of conventional polyethers

Comparative example 1

224.36 g (equivalent weight = 111.58 g/eq) of 3-isocyanatomethyl-3,5,5-trimethylcyclohexylisocyanate (Desmodur® I, commercial product of Bayer AG, Leverkusen) were introduced initially under inert gas (nitrogen) with 0.10 g of benzoyl chloride into a vessel, the components were stirred together, and then 1.00 g of dibutyltin laurate was added. After heating to 45°C, 546.15 g (equivalent weight = 987.68 g/eq) of Desmophen® PPG 3600Z (polypropylene oxide glycol, M_n = 2 000 g/mol, commercial product, Bayer AG, Leverkusen) were metered in. When the theoretical NCO content of 7.9% by weight had been reached, a further 250.68 g (equivalent weight = 498.67 g/eq) of Desmophen® 1600U (polypropylene oxide glycol, M_n = 1 000 g/mol, commercial product, Bayer AG, Leverkusen) were metered in. Following complete addition, the reaction mixture was heated at 60°C until an NCO content of 3.9% by weight was reached. Thereafter it was cooled to room temperature.

The prepolymer possesses a viscosity of 9200 mPas (23°C, plate viscometer), an NCO content of 3.9% by weight, and an IPDI monomer content of 2.15% by weight (determined by gas chromatography).

Comparative example 2

230.00 g (equivalent weight = 111.44 g/eq) of 3-isocyanatomethyl-3,5,5-trimethylcyclohexylisocyanate (Desmodur® I, commercial product of Bayer AG, Leverkusen) were introduced initially under inert gas (nitrogen) with 0.10 g of dibutyltin laurate into a vessel and the components were stirred together. After heating to 55°C, 535.12 g (equivalent weight = 987.68 g/eq) of Desmophen® 3600Z (polypropylene oxide glycol, M_n = 2 000 g/mol, commercial product, Bayer AG, Leverkusen) were metered in. When the theoretical NCO content of 8.4% by weight had been reached, a further 257.08 g (equivalent weight = 498.22 g/eq) of Desmophen® 1600U (polypropylene oxide glycol, M_n = 1 000 g/mol, commercial product, Bayer AG, Leverkusen) were metered in. When an NCO content of 3.9% by weight had been reached, 0.1 g of benzoyl chloride was added and the mixture was cooled to room temperature.

The prepolymer possesses a viscosity of 9 200 mPas (23°C), an NCO content of 3.9% by weight, and an IPDI monomer content of 2.07% by weight (determined by gas chromatography).

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CLAIMS:

1. A low-monomer-content, solvent-free, NCO-containing prepolymer based on 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate (IPDI) and an *Impact* polyether, having a residual IPDI monomer content of less than 2.00% by weight, obtained by reacting 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate with at least one *Impact* polyether having a functionality of 1.80-2.00, an NCO/OH ratio of from 2.2 to 1.5, and a viscosity of from 5 000 to 20 000 mPas at 23°C in the presence of at least one catalyst at from 20 to 100°C.

2. The low-monomer-content, solvent-free, NCO-containing prepolymer of claim 1, having an NCO/OH ratio of from 1.98 to 1.80.

3. The low-monomer-content, solvent-free, NCO-containing prepolymer of claim 1 or 2, having a viscosity of from 9 000 to 13 000 mPas at 23°C.

4. The low-monomer-content, solvent-free, NCO-containing prepolymer of claim 1, 2 or 3, having a residual monomer content of less than or equal to 1.95% by weight.

5. The low-monomer-content, solvent-free, NCO-containing prepolymer of claim 1, 2, 3 or 4, comprising a polypropylene oxide glycol having a number-average molecular weight (Mn) of from 500 to 5 000 g/mol and a hydroxyl functionality of from 1.80 to 2.00.

6. The low-monomer-content, solvent-free, NCO-containing prepolymer of claim 5, wherein the polypropylene oxide glycol has a hydroxyl functionality of from 1.98 to 2.00.

7. The low-monomer-content, solvent-free, NCO-containing prepolymer of claim 5, comprising a mixture of polypropylene oxide glycols having a number-average molecular weight (Mn) of 1 000 and 2 000 g/mol and a hydroxyl functionality of from 1.98 to 2.00.

8. A process for preparing a solvent-free, low-monomer-content, NCO-containing prepolymer based on 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate (IPDI) and an *Impact* polyether, having a residual

monomer content of less than 2.00% by weight, an NCO content of from 2.0 to 5.0% by weight, and a viscosity of from 5 000 to 20 000 mPas at 23°C, comprising reacting 3-isocyanatomethyl-3,5,5-trimethyl-cyclohexyl isocyanate and at least one *Impact* polyether having an OH functionality of from 1.80 to 2.00 and an NCO/OH ratio of from 2.2 to 1.5 in the presence of at least one catalyst at from 20 to 100°C.

9. Use of the low-monomer-content, solvent-free, NCO-containing prepolymer of any one of claims 1 to 7, as a binder or a binder component in a polyurethane coating composition, a polyurethane adhesive, a polyurethane sealant or a polyurethane casting compound.

FETHERSTONHAUGH & CO.
OTTAWA, CANADA

PATENT AGENTS