159159

Process for the production of polyether polyols

The invention relates to an improved process for the production of polyether polyols by means of double metal cyanide (DMC) catalysis by polyaddition of alkylene oxides onto starter compounds having active hydrogen atoms.

Double metal cyanide (DMC) catalysts for the polyaddition of alkylene oxides onto starter compounds having active hydrogen atoms have long been known (c.f. for example US-A 3 404 109, US-A 3 829 505, US-A 3 941 849 and US-A 5 158 922). Using these DMC catalysts for the production of polyether polyols brings about, in particular, a reduction in the proportion of monofunctional polyethers with terminal double bonds, so-called monools, in comparison with the conventional production of polyether polyols by means of metal hydroxide catalysts. The resulting polyether polyols may be further processed to yield high-grade polyurethanes (for example elastomers, foams, coatings).

A general feature of DMC-catalysed production of polyether polyols is the occurrence of an induction period, i.e. the DMC catalyst has initially to be activated by a certain minimum quantity of alkylene oxide, before continuous alkylene oxide addition can proceed to polyether chain synthesis (c.f. for example J.F. Schuchardt, S.D. Harper, 32nd Annual Polyurethane Technical Marketing Conference, 1989, p. 360 ff.). Induction times are typically between a few minutes and several hours and are dependent on reaction parameters such as catalyst concentration, molar mass of the starter compound used, reaction temperature and alkylene oxide quantity during activation.

DE-OS 15 95 759 describes a process for the production of polyether polyols by means of DMC catalysis, in which a polyether polyol is produced by polyaddition of an epoxide in the presence of a DMC catalyst, a telogen capable of reacting with the epoxide and having an average molecular weight of at least 300 g/mol and a telogen capable of reacting with the epoxide and having an average molecular weight of at least 31 g/mol. After activation of the mixture, i.e. after the end of the induction

G00002

period, addition of the epoxide continues until the desired polyether OH number is reached. A disadvantage of this process is that the entire quantity of starter compound is initially introduced in full and a high catalyst concentration is therefore required, since catalyst activity is markedly reduced by the short-chain starter compound initially introduced. One consequence of this is high material costs, resulting from the large quantities of catalyst which have to be used. In addition, the catalyst has to be separated off after alkoxylation, making the process yet more complex and costly. Moreover, the catalyst has initially to be activated prior to alkoxylation proper. However, the occurrence of such an induction phase results, on the one hand, in a deterioration in the space-time yield and, on the other hand, in an increased potential risk from the quantity of free alkylene oxide used in the reactor for the purpose of activation.

DDR-WP 203 734 discloses a process for DMC-catalysed polyether polyol production, in which the DMC catalyst is initially introduced alone into the reactor and activated with pure propylene oxide. The reaction temperature increases during activation from room temperature to 80°C, owing to the exothermic nature of the reaction. Once activation is complete (end of the induction period), epoxide and starter compound are added simultaneously. The reaction temperature is in the range from 20°C to 140°C. In this manner, living prepolymers may be produced, which, according to DDR-WP 203 735, may then be further extended with propylene oxide in a continuous process at a temperature in the range from 40°C - 120°C. The process described in DDR-WP 203 734 exhibits several disadvantages, however. On the one hand, activation of the catalyst is performed using large amounts of pure propylene oxide. Pure propylene oxide is potentially extremely hazardous, since, in the event of cooling failure, the heat liberated by the exothermic propoxylation reaction cannot be absorbed and dissipated by an additional component, e.g. a starter compound. The considerable localised heating caused thereby may lead to explosive thermal decomposition of the polyethers formed. However, even when the heating/cooling circuit is fully functional, localised heating may occur. Due to the small quantity of contents present in the reactor, only a very small heat exchange surface is available, such that effective control of the reaction temperature is very

difficult or wholly impossible, as a result of which thermally induced ageing and deactivation of the catalyst cannot be ruled out. Furthermore, in this process very high-molecular weight chains are formed by the large quantities of propylene oxide used for catalyst activation, resulting in wide molar-mass distribution and a marked increase in the viscosity of the polyether polyol, which restricts considerably the use of such products for polyurethane applications.

EP-A 879 259 also discloses a process in which the alkylene oxide and the starter compound are added simultaneously. The DMC catalyst is introduced previously into the reactor. In addition, a polyether polyol may optionally be introduced into the reactor. This process also exhibits the disadvantage of the occurrence of an induction phase. This is caused by the simultaneous addition of epoxide and starter compound during activation or by the starter compound initially present, since the starter compound, even in a very low concentration, is presumed initially to effect temporary deactivation of the catalyst. This phenomenon is also described in WO 98/52689, for example, in which an increase in the activity of the DMC catalyst is achieved by the removal of water residues from pre-propoxylated starter compounds. Water may also be regarded as a low-molecular weight starter compound, such that even slight traces of a low-molecular weight starter compound lead to a marked reduction in the activity of the DMC catalyst and thus to a lengthening of the induction phase. Only after complete activation of the catalyst, which is characterised by an accelerated pressure drop in the reactor, may addition of the epoxide/starter compound mixture be continued. Since addition of the epoxide/starter compound mixture proceeds as a function of the concentration ratio in the desired polyether polyol, free propylene oxide is present in the reactor during the induction phase generally in a very high concentration, such that this process entails a relatively high safety risk.

German patent application 19937114.8 discloses a process, in which a DMC catalyst is initially present in a starter compound and the alkylene oxide concentration necessary for activation of the catalyst is kept constant during the induction phase. In

this process too, the catalyst has initially to be activated, before propoxylation proper may proceed.

The object of the present invention was therefore to develop a process for DMC-catalysed production of polyether polyols, which exhibits a markedly reduced induction phase or none at all (thus entailing a markedly reduced potential risk from free alkylene oxide) and results in polyether polyols with a narrow molar mass distribution and low viscosity.

It has now been found that polyether polyols may be produced by DMC catalysis with a markedly reduced induction period or even without an induction period, if the DMC catalyst is initially present in an inert suspending agent and is activated with pure alkylene oxide, the polyether polyol then being synthesised by the addition of a starter compound/alkylene oxide mixture. Using this process, polyether polyols with a narrow molar mass distribution and low viscosity are obtained.

The present invention therefore provides a process for the production of polyether polyols by polyaddition of alkylene oxides onto starter compounds having active hydrogen atoms by means of DMC catalysis, in which the DMC catalyst is initially present in an inert suspending agent, is activated with 1-30 wt.% alkylene oxide, relative to the total quantity of suspending agent and alkylene oxide, at temperatures of between 20°C and 200°C and the polyether polyol is then synthesised by the addition of a starter compound/alkylene oxide mixture.

In the process according to the invention, a suspending agent, which does not react with the alkylene oxide, is initially introduced into the reactor. The quantity of non-activated DMC catalyst necessary for polyaddition is then introduced into the reactor. However, the order in which the constituents are added is not crucial. It is also possible for the catalyst to be suspended in the inert suspending agent first and the suspension then to be introduced into the reactor. An adequate heat exchange surface is made available in the reactor by the suspending agent, such that the liberated heat of reaction may be very effectively dissipated. Moreover, the

suspending agent provides thermal capacity in the event of cooling failure, such that the temperature may in such an instance be kept below the decomposition temperature of the reaction mixture.

Suitable suspending agents are all polar-aprotic, weakly polar-aprotic and non-polar-aprotic solvents, which, under the conditions described below, do not react with the alkylene oxides used for polyaddition. Mention should be made at this point, by way of example, of the following polar-aprotic solvents: acetone, methyl ethyl ketone, acetonitrile, nitromethane, dimethyl sulfoxide, sulfolan, dimethylformamide, dimethylacetamide and N-methylpyrrolidone. Non-polar- and weakly polar-aprotic solvents are preferably used, however. This group includes, for example, ethers, such as for example dioxane, diethyl ether, methyl tert.-butyl ether and tetrahydrofuran, esters, such as for example acetic acid ethyl ester and acetic acid butyl ester, hydrocarbons, such as for example pentane, n-hexane, benzene and alkylated benzene derivatives (toluene, xylene, ethylbenzene) and chlorinated hydrocarbons, such as for example chloroform, chlorobenzene, dichlorobenzene and carbon tetrachloride. Toluene, xylene, ethylbenzene, chlorobenzene and dichlorobenzene are particularly preferred.

The DMC catalysts suitable for the process according to the invention are known in principle and described in detail, for example, in JP-A 4 145 123, EP-A 654 302, EP-A 700 949, EP-A 743 093, EP-A 761 708, WO 97/40086, WO 98/16310, WO 99/19062, WO 99/19063, WO 99/33562, WO 99/46042 and German patent applications 198 34 572.0, 198 34 573.9, 198 42 382.9, 198 42 383.7, 199 05 611.0, 199 06 985.9, 199 13 260.7, 199 20 937.5, 199 24 672.6. The DMC catalysts described in German patent application 199 05 611.0 are a typical example, containing, in addition to a double metal cyanide compound (e.g. zinc hexacyanocobaltate(III)) and an organic complex ligand (e.g. tert.-butanol), a bile acid or the salts, esters or amides thereof.

The DMC catalyst concentration is generally in the range of from 0.0005 wt.% to 1 wt.%, preferably in the range of from 0.001 wt.% to 0.1 wt.%, particularly

preferably in the range of from 0.001 to 0.01 wt.%, relative to the quantity of polyether polyol to be produced.

The DMC catalyst suspension is brought to the temperature necessary for activation after its introduction into the reactor. Activation may be performed in the range of from 20°C - 200°C, preferably in the range of from 60°C - 180°C, particularly preferably in the range of from 120°C - 160°C.

Ethylene oxide, propylene oxide, butylene oxide, styrene oxide and mixtures thereof are used as alkylene oxides for activating the DMC catalyst. Activation is particularly preferably performed with propylene oxide or a mixture of propylene oxide and ethylene oxide.

Activation of the DMC catalyst may proceed at a reactor pressure in the range of from 0.0001 - 20 bar, preferably in the range of from 0.5 - 10 bar, particularly preferably in the range of from 1 - 6 bar.

According to the invention, the quantity of alkylene oxide for activating the DMC catalyst is 1-30 wt.%, preferably 2-25 wt.%, particularly preferably 3-15 wt.%, in each case relative to the total quantity of suspending agent and alkylene oxide.

By performing catalyst activation in this way, the induction times are markedly reduced in comparison to the prior art processes. The reaction conditions are preferably so selected that no induction period occurs. This is generally the case if the temperature during catalyst activation amounts to at least 120°C. The reactor pressure drops immediately after addition of the alkylene oxide, since, in contrast to the prior art processes, in the process according to the invention no induction phase is observed. Alkylene oxide addition does not have to interrupted at any point during the reaction and the concentration of free alkylene oxide in the reactor is very small at all times during the reaction, which constitutes a great safety advantage. The process according to the invention therefore makes it possible for addition of the starter compound for polyether polyol synthesis to be commenced immediately after

alkylene oxide addition starts. This results in an improved space-time yield at the same time as an increase in safety during the reaction.

Synthesis of the polyether polyol by polyaddition is performed according to the invention by the addition of a starter compound/alkylene oxide mixture. The starter compound/alkylene oxide molar ratio is 1:1 to 1:1000, preferably 1:2 to 1:500, particularly preferably 1:3 to 1:200.

Alkylene oxides preferably used for polyether polyol synthesis are ethylene oxide, propylene oxide, butylene oxide and mixtures thereof. Propylene oxide and mixtures of propylene oxide and ethylene oxide are particularly preferred. Synthesis of polyether chains may be performed, for example, with only one monomeric epoxide or also randomly with 2 or 3 different monomeric epoxides. Further details may be found in Ullmanns Encyclopädie der industriellen Chemie, volume A21, 1992, p. 670 ff.

Preferred starter compounds having active hydrogen atoms are compounds with molecular weights of from 18 to 2000 g/mol, preferably 62 to 1000 g/mol, and 1 to 8, preferably 2 to 6, hydroxyl groups. The following may be mentioned by way of example: butanol, ethylene glycol, diethylene glycol, triethylene glycol, 1,2-propylene glycol, 1,4-butanediol, 1,6-hexanediol, bisphenol A, trimethylolpropane, glycerol, pentaerythritol, sorbitol, cane sugar, degraded starch, water or so-called pre-extended starter compounds, which are obtained by alkoxylation from the above-mentioned compounds.

Polyaddition may be performed at a reactor pressure in the range from 0.0001 - 20 bar, preferably in the range from 0.5 - 10 bar, particularly preferably in the range from 1 - 6 bar. The reaction temperatures range from 20 - 200°C, preferably from 60 180°C, particularly preferably from 80 - 160°C.

The mixture of alkylene oxide and starter compound for polyether polyol synthesis may be introduced into the reactor via a line, in which static mixing elements may

optionally be installed in order to achieve more homogeneous mixing of alkylene oxide and starter compound, or via separate feed sections. However, it is important to ensure good mixing of the educts at all times during the reaction. An elevated degree of segregation in the reactor, i.e. in the event of poor mixing of the educts with the reactor contents, may cause complete or partial deactivation of the DMC catalyst owing to a locally increased starter compound concentration.

The molecular weights of the polyether polyols produced using the process according to the invention are in the range from 400 to 100 000 g/mol, preferably in the range from 700 to 50 000 g/mol, particularly preferably in the range from 1000 to 20 000 g/mol.

The synthesis of polyether polyols by polyaddition may be performed wholly by the addition of a starter compound/alkylene oxide mixture. It is also possible, however, initially to synthesise only some of the polyether polyol to be produced by the addition of a starter compound/alkylene oxide mixture and then to extend further the intermediate product obtained with pure alkylene oxide, preferably propylene oxide, or an alkylene oxide mixture, preferably a mixture of propylene oxide and ethylene oxide. It is also possible to form several of these blocks from alkylene oxide or alkylene oxide mixture, e.g. synthesis of the final polyether polyol may be achieved by the initial addition of a mixture of propylene oxide and ethylene oxide to an intermediate product, which has been produced by the addition of a starter compound/propylene oxide mixture, followed by the addition of pure propylene oxide. In this way, polyether polyols may be synthesised which have several defined blocks (so-called multiblock copolymers).

Using the process according to the invention, it is possible to produce polyether polyols with very low double bond contents (≤ 6 mMol/kg) even at reaction temperatures of 145°C and higher, which is not possible with any of the DMC-catalysed polyaddition processes known hitherto. The polyether polyols produced by the process according to the invention have narrow molar mass distributions and low viscosities.

Examples

Example 1

59 g of xylene and 0.036 g of a double metal cyanide (DMC) catalyst (produced in accordance with German patent application 199 05 611, Example A) were initially introduced into a steel reactor with a volume of 2 litres. Once the reaction temperature of 150°C was reached, 4.78 g of propylene oxide (7.5 wt.%, relative to the total quantity of xylene and propylene oxide) were added. As soon as this addition was discontinued, the pressure fell from 1.75 bar to 1.4 bar (Fig. 1). 1.2 kg of a mixture of propylene oxide and propylene glycol in a weight ratio of 96/4 (molar ratio 33/1) was then added to the active catalyst suspension over a period of 2.5 hours. The suspending agent and readily volatile fractions were then removed by distillation at 120°C/10 mbar.

A polyether polyol with an OH number of 56 mg KOH/g, a viscosity (25°C) of 359 mPas and a double bond content of 5 mMol/kg was obtained. The gel-permeation chromatogram shows a very narrow molecular weight distribution without a high-molecular weight fraction (Fig. 2). All GPC measurements were performed at 25°C with THF as the mobile solvent. Polystyrenes with molecular masses of 162 g/mol, 580 g/mol, 7002 g/mol, 10856 g/mol and 319894 g/mol were used as standard.

Example 2

59 g of toluene and 0.036 g of the double metal cyanide (DMC) catalyst from Example 1 were initially introduced into a steel reactor with a volume of 2 litres. Once the reaction temperature of 150°C was reached, 4.78 g of propylene oxide (7.5 wt.%, relative to the total quantity of toluene and propylene oxide) were added over a period of approximately 30 seconds. Without interrupting the addition of propylene oxide, the addition of propylene glycol (propylene oxide/propylene glycol weight ratio = 96/4) was commenced at this point. After 2.5 hours, 1.2 kg of the

mixture of propylene oxide and propylene glycol in a weight ratio of 96/4 (molar ratio 33/1) had been added in full. The suspending agent and readily volatile fractions were then removed by distillation at 120°C/10 mbar.

A polyether polyol with an OH number of 56 mg KOH/g, a viscosity (25°C) of 352 mPas and a double bond content of 5 mMol/kg was obtained. The gel-permeation chromatogram shows a very narrow molecular weight distribution without a high-molecular weight fraction (Fig. 3).

Example 3 (Comparative Example as EP-A 879 259

59 g of a polyoxypropylene diol with an average molecular weight of 2000 g/mol (OH number 56 mg KOH/g), produced by DMC catalysis, and 0.036 g of the double metal cyanide (DMC) catalyst from Example 1 were initially introduced into a steel reactor with a volume of 2 litres. To activate the catalyst, 4.8 g of a mixture of propylene oxide and propylene glycol in a weight ratio of 96:4 (molar ratio 33/1) were added at 150°C. After 27 minutes, the pressure drop at the end of the induction phase typical of catalyst activation could be observed (Fig. 4). 1.2 kg of a mixture of propylene glycol and propylene oxide in the ratio 96:4 were then added over a period of 2.5 hours. The readily volatile fractions were then removed by distillation at 120°C/10 mbar.

The double bond content was 5 mMol/kg at an OH number of 56.4 mg KOH/g. The viscosity was 381 mPas at 25°C.

Example 4 (Comparative Example) Activation with more than 30 wt.% propylene oxide, relative to the total quantity of toluene and propylene oxide

42 g of toluene and 0.036 g of the double metal cyanide (DMC) catalyst from Example 1 were initially introduced into a steel reactor with a volume of 2 litres. To activate the catalyst, 36 g of propylene oxide (46 wt.% relative to the total quantity of toluene and propylene oxide) were added at 105°C. After approximately 5

minutes, the pressure drop typical of DMC catalyst activation could be observed in the reactor. 1.2 kg of a mixture of propylene oxide and propylene glycol in a weight ratio of 96/4 (molar ratio 33/1) were then added over a period of 4 hours. The suspending agent and readily volatile fractions were then removed by distillation at 120°C/10 mbar.

A polyether polyol with an OH number of 53.3 mg KOH/g, a viscosity (25°C) of 852 mPas and a double bond content of 5 mMol/kg was obtained. GPC analysis shows that high-molecular weight chains having a molecular weight in the range of $> 10^4$ g/mol have formed, which are responsible for this marked increase in viscosity (Fig. 5).

Example 5

59 g of toluene and 0.036 g of the double metal cyanide (DMC) catalyst from Example 1 were initially introduced into a steel reactor with a volume of 2 litres. Once the reaction temperature of 150°C was reached, 9.6 g of propylene oxide (15 wt.%, relative to the total quantity of toluene and propylene oxide) were added. As soon as this addition was discontinued, a pressure drop could be observed, indicating activation of the catalyst. 1.2 kg of a mixture of propylene oxide and propylene glycol in a weight ratio of 96/4 (molar ratio 33/1) was then added to the active catalyst suspension over a period of 2.5 hours. The suspending agent and readily volatile fractions were then removed by distillation at 120°C/10 mbar.

A polyether polyol with an OH number of 56 mg KOH/g, a viscosity (25°C) of 362 mPas and a double bond content of 5 mMol/kg was obtained. The gel-permeation chromatogram shows a very narrow molecular weight distribution without a high-molecular weight fraction (Fig. 6).

Claims

1. A process for the production of a polyether polyol by polyaddition of alkylene oxides onto starter compounds having active hydrogen atoms by means of double metal cyanide (DMC) catalysis, characterised in that the DMC catalyst is initially present in an inert suspending agent and is activated with 1-30 wt.% alkylene oxide, relative to the total quantity of suspending agent and alkylene oxide, at temperatures of between 20°C and 200°C and the polyether polyol is then synthesised by the addition of a starter compound/alkylene oxide mixture.

2. A process according to claim 1, in which a polar-aprotic, weakly polar-aprotic or non-polar-aprotic solvent is used as the suspending agent.

3. A process according to claim 2, in which alkylated or chlorinated aromatic compounds are used as the suspending agent.

4. A process according to any one of claims 1 to 3, in which propylene oxide or a mixture of propylene oxide and ethylene oxide is used as the alkylene oxide for activating the DMC catalyst.

5. A process according to any one of claims 1 to 4, in which the DMC catalyst is activated at temperatures of between 120°C and 160°C.

6. A process according to any one of claims 1 to 5, in which the DMC catalyst contains a bile acid or the salts, esters or amides thereof.

7. A process according to any one of claims 1 to 6, in which ethylene glycol, diethylene glycol, triethylene glycol, 1,2-propylene glycol, 1,4-butanediol, 1,6-hexanediol, bisphenol A, trimethylolpropane, glycerol, pentaerythritol, sorbitol, cane sugar, water or a pre-extended starter compound obtained by

alkoxylation from the above-mentioned compounds is used as the starter compound compound having active hydrogen atoms.

8. A polyether polyol, produced according to any one of claims 1 to 7.

5

9. A polyether polyol having a double bond content of 6 mMol/kg or less, produced by DMC-catalysed polyaddition of alkylene oxides onto starter compounds having active hydrogen atoms at a reaction temperature of at least 145°C.