

Process for the preparation of polyether polyols

5 The invention relates to a process for the preparation of polyether polyols by means of double metal cyanide (DMC) catalysis, in which the induction phase is shortened markedly.

10 According to prior art polyether polyols are prepared by polyaddition of alkylene oxides to starter compounds having active hydrogen atoms, by means of metal hydroxide catalysis (for example KOH), see Ullmanns "Encyclopädie der technischen Chemie", Vol. 14, 1963, p. 49 et seq. The polyaddition reaction rates are very slow in this process. Depending on the reaction temperature, catalyst concentration and OH number of the polyether polyol prepared, in the prior art process monofunctional polyethers having terminal double bonds, so-called monools, form additionally and restrict the use of the product for subsequent
15 polyurethane applications. Furthermore, after the polyaddition the base which was used must be removed. This can be achieved, for example, either by the addition of acids, by the use of neutralising adsorbers, ion exchangers or by other methods. The water of neutralisation which arises in this case and the salts which have formed must likewise be separated before further processing. This brief description of the
20 process used according to the present state of the art illustrates the labour- and cost-intensive nature of polyether polyol preparation.

Double metal cyanide (DMC) catalysts for the preparation of polyether polyols have long been known (see, for example, US-A 3 404 109, US-A 3 829 505, US-A 3 941
25 849 and US-A 5 158 922). The use of these DMC catalysts for the preparation of polyether polyols in particular brings about a reduction in the proportion of monofunctional polyethers having terminal double bonds, so-called monools, by comparison with the conventional preparation of polyether polyols by means of basic catalysts. The polyether polyols thus obtained can be processed to high-grade
30 polyurethanes (for example elastomers, foams, coatings). Improved DMC catalysts

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such as are described in EP-A 700 949, EP-A 761 708, WO 97/40086, WO 98/16310, DE-A 197 45 120, DE-A 197 57 574 and DE-A 198 10 269, for example, are additionally extremely highly active and enable polyether polyols to be prepared at very low catalyst concentrations (25 ppm or less), such that it is no longer
5 necessary to separate the catalyst from the polyol.

Induction times which are sometimes protracted are a disadvantage of DMC-catalysed polyether polyol preparation. During this phase the chain is built up only very slowly, such that only a very poor space-time yield is achieved. This in turn
10 means a reduction in the economic advantage afforded over the KOH-catalysed process by the more rapid polyaddition and substantially simplified working-up of the product.

One possibility of reducing the induction times resides in elevating the alkylene oxide concentration in the reactor. However, a high concentration of free alkylene oxide constitutes a major hazard potential, because catalyst activation may result in intensified liberation of heat and consequently uncontrolled temperature increases. This would lead to greater thermal loading of the polyol, such that on the one hand, product quality might be impaired, for example owing to higher viscosities or
15 broader molecular weight distributions and, on the other hand, the catalyst activity could be reduced by accelerated ageing. In an extreme case, an uncontrolled temperature increase may even lead to adiabatic thermal decomposition of the polyether polyol.
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In the light of the difficulties described in the section above, the reactor is normally (see, for example, WO 97/23544) charged only with part of the total quantity of alkylene oxide necessary for carrying out the reaction to the polyol. Then only after waiting until a pronounced pressure drop in the reactor signals that the catalyst is completely activated, is further alkylene oxide supplied to the reactor.
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It has now surprisingly been found that the induction phase in DMC-catalysed polyether polyol preparation can be shortened markedly if small quantities of alkylene oxide are supplied to the reactor in continuous manner during the induction phase also, preferably quantities such that a constant pressure prevails in the reactor.

5 The quantity of free alkylene oxide used for activation should here be oriented on the basis of either the maximum permissible reactor temperature ($T_{\max}$) or, if this is above the decomposition temperature of the polyether polyol to be prepared, on the basis of the decomposition temperature ($T_{\max}$) thereof. The threshold concentration ($C_{\text{threshold}}$) of free alkylene oxide in the reactor can be calculated as a function of the
10 reaction temperature (T_{reaction}) and the reaction enthalpy (ΔH_R), in accordance with the following formula:

$$15 \quad C_{\text{threshold}} \leq \frac{T_{\max} - T_{\text{reaction}}}{\Delta H_R}$$

The invention therefore provides a process for the preparation of polyether polyols by DMC-catalysed polyaddition of alkylene oxides to starter compounds having active hydrogen atoms, in which alkylene oxide is supplied in continuous manner to
20 the reactor during the induction phase. The total quantity of starter compound and catalyst necessary for the preparation of the polyether polyols is preferably in the initial reactor charge on commencement of the reaction. The alkylene oxide is preferably added such that the pressure in the reactor is held constant during the induction phase.

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The DMC catalyst is activated during the induction phase generally at temperatures of from 20 to 200°C, preferably within the range 40 to 180°C, particularly preferably at temperatures of from 50 to 150°C. The reaction can in this phase be carried out at total pressures of from 0.001 to 20 bar, preferably at total pressures of from 0.5 to 10
30 bar and particularly preferably at total pressures of from 1 to 6 bar.

The induction time is characterised in that only very small quantities of alkylene oxide need be dispensed-in in order to hold the reactor pressure constant. The catalyst activity increases slowly in this phase, such that the quantity being dispensed-in can be increased gradually. Complete activation of the catalyst is
5 recognisable by the fact that the alkylene oxide dispensing rate can be increased markedly without a pressure rise being observed simultaneously in the reactor. After complete activation of the catalyst the polyaddition commences, frequently proceeding so rapidly that the dispensing rate is limited only by the heat transfer rate of the reactor or of an external heat transfer means. Fig. 1 shows that a markedly
10 more rapid activation of the catalyst can be achieved by this process as compared with discontinuous dispensing.

With a 10 wt.% free alkylene oxide content, in relation to the mass of the starter used, the induction time which can be achieved with continuous dispensing is
15 comparable to that achieved with an approx. 18 wt.% content and discontinuous dispensing. The catalyst induction time is followed by the alkoxylation phase of the DMC mixture. In this phase control of the reaction is generally no longer by way of the reactor pressure but by way of the reactor temperature. The dispensing rate is therefore frequently limited, because of the high catalyst activity, by the heat transfer
20 rate of the reactor or of a heat transmission means switched in the by-pass.

The DMC catalysts suitable for the process according to the invention are known in principle and are described in detail in the prior art indicated hereinabove. Improved, high-activity DMC catalysts described, for example, in EP-A 700 949, EP-A 761
25 708, WO 97/40086, WO 98/16310, DE-A 197 45 120, DE-A 197 57 574 and DE-A 198 10 269 are preferably used. A typical example is the DMC catalysts described in DE-A 198 10 269, which in addition to a double metal cyanide compound (for example zinc hexacyanocobaltate(III)) and an organic complexing ligand (for example tert.-butanol) also contain an ethylene oxide polyether having a
30 number-average molecular weight greater than 500 g/mol.

Alkylene oxides which are preferably used are ethylene oxide, propylene oxide, butylene oxide and mixtures thereof. The building of the polyether chains by alkoxylation can be carried out, for example, with only one epoxide monomer or alternatively in random or block manner with 2 or 3 different epoxide monomers.

5 More detailed information is contained in Ullmanns "Encyclopädie der industriellen Chemie", Vol. A21, 1992, p. 670 et seq.

The starter compounds having active hydrogen atoms, which are preferably used are compounds having molecular weights of 18 to 2,000 g/mol, preferably 200 to 2,000 g/mol, and 1 to 8, preferably 2 to 6 hydroxyl groups. The following may be

10 named as examples: butanol, ethylene glycol, diethylene glycol, triethylene glycol, 1,2-propylene glycol, 1,4-butanediol, 1,6-hexanediol, bisphenol A, trimethylolpropane, glycerol, pentaerythritol, sorbitol, sucrose, degraded starch or water.

15 Starter compounds having active hydrogen atoms, such as have been prepared, for example, by conventional alkali catalysis from the aforementioned low molecular weight starters and represent oligomer alkoxylation products having number average molecular weights of 200 to 2,000 g/mol, are more advantageously used.

20 Propoxylated oligomer starter compounds having 1 to 8 hydroxyl groups, particularly preferably 2 to 6 hydroxyl groups, and number average molecular weights of 200 to 2,000 g/mol are preferably used. These compounds can be prepared, for example, in accordance with Ullmanns "Encyclopädie der industriellen

25 Chemie", Vol. A21, 1992, p. 670 et seq.

The DMC-catalysed polyaddition of the alkylene oxide to the starter compounds generally takes place at temperatures of from 20 to 200°C, preferably within the range 40 to 180°C, particularly preferably at temperatures of from 50 to 150°C. The

30 reaction may be carried out at total pressures of from 0.001 to 20 bar. The polyaddition may be carried out with the components as such or in an inert organic

solvent such as toluene or THF. The quantity of solvent is normally from 10 to 30 wt.%, in relation to the quantity of polyether polyol to be prepared.

- 5 The DMC catalyst concentration is selected such that under the given reaction conditions good control of the polyaddition is possible. The catalyst concentration is generally within the range 0.0005 wt.% to 1 wt.%, preferably within the range 0.001 wt.% to 0.1 wt.%, particularly preferably within the range 0.001 to 0.01 wt.%, in relation to the quantity of polyether polyol to be prepared.
- 10 The molecular weights of the polyether polyols prepared by the process according to the invention are within the range 1,000 to 100,000 g/mol, preferably within the range 1,500 to 50,000 g/mol, particularly preferably within the range 2,000 to 20,000 g/mol.
- 15 High molecular weight polyether alcohols are very important as starting products for polyurethane preparation. Depending on molecular weight and functionality, they are preferably used for the preparation of elastomers, prepolymers for dispersions, soft foams and polyurethane coatings.

Examples

Preparation of high-activity DMC catalyst (synthesis according to EP-A 700 949)

- 5 A solution of 12.5 g (91.5 mmol) zinc chloride in 20 ml deionised water is added, with vigorous stirring (24,000 rpm), to a solution of 4 g (12 mmol) potassium hexacyanocobaltate in 70 ml deionised water. Immediately afterwards a mixture prepared from 50 g tert.-butanol and 50 g deionised water is added to the suspension which has formed, followed by vigorous stirring (24,000 rpm) for 10 min. A mixture
- 10 prepared from 1 g polypropylene glycol having a number average molar mass of 2,000 g/mol, 1 g tert.-butanol and 100 g deionised water is then added, and stirring (1,000 rpm) takes place for 3 min. The solid is isolated by filtration then stirred (10,000 rpm) for 10 min. with a mixture prepared from 70 g tert.-butanol, 30 g deionised water and 1 g of the above polypropylene glycol, and is filtered again.
- 15 Finally, it is stirred again (10,000 rpm) for 10 min. with a mixture prepared from 100 g tert.-butanol and 0.5 g of the above polypropylene glycol. After filtration the catalyst is dried at 50°C and standard pressure until the weight is constant.

Yield of dried, pulverulent catalyst: 6.23 g

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Example 1

Preparation of polyether polyols with continuous dispensing of propylene oxide

- 25 2696 g of a polyether of molecular weight 416 g/mol, 0.4 g DMC catalyst are placed in a 20-litre reactor and heated to 105°C. After the reactor has been rendered inert, 268 g propylene oxide (corresponding to 10% of the starter used) are added. The pressure is then 2.3 bar absolute. This pressure is held constant during the activation phase by continuous dispensing of propylene oxide. The complete activation of the
- 30 catalyst (corresponding to the end of the induction time) is recognisable by a marked increase in the dispensing rate. The temperature is held constant during the reaction.

After activation of the catalyst, the remaining quantity (10,000 g) of propylene oxide is added at a dispensing rate of 4.6 kg/h. The polyether thus prepared has a viscosity of $\eta = 384$ mPas (25°C), OH number = 55.3 mg KOH/g, double bond content = 5 mmol/kg. The induction time is 224 min.

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Example 2 (Comparison Example)

Preparation of polyether polyols with discontinuous dispensing of propylene oxide during the induction phase

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2724 g of a polyether of molar mass 416 g/mol and 0.4 g DMC catalyst are placed in a 20-litre reactor and heated to 105°C. After the reactor has been rendered inert, 545 g propylene oxide (corresponding to 20 wt.%, in relation to the mass of the starter used) are added. The pressure is then 3.4 bar absolute. Activation of the catalyst is recognisable by a more rapid fall in pressure. The temperature is held constant during the reaction. After activation of the catalyst the remaining quantity (10,234 g) of propylene oxide is added at a dispensing rate of 4.6 kg/h. The polyether thus prepared has the following properties: viscosity $\eta = 382$ mPas (25°C), OH number = 55.2 mg KOH/g, double bond content = 5 mmol/kg. The induction time is 144 min.

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Further comparison experiments with this dispensing variant demonstrate that although the activation time can be reduced by increasing the concentration of free propylene oxide in the reactor, it is at the expense of the safety of the system. The reduction of the alkylene oxide concentration to, for example, 10 wt.% fulfils no purpose in the discontinuous process variant, because in this case the induction times become so great that little or even no economic benefit remains. As is shown in Fig. 1, using the process according to the invention the concentration of free alkylene oxide for catalyst activation can be reduced without problems to 10 wt.% under the given reaction conditions, with activation times being obtained which are

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comparable with those of the discontinuous activation using approx. 18 wt.% alkylene oxide, in relation to the mass of the starter used.

**Claims**

1. Process for the preparation of polyether polyols by DMC-catalysed polyaddition of alkylene oxides to starter compounds having active hydrogen atoms, in which alkylene oxide is supplied in continuous manner to the reactor during the induction phase.
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2. Process according to Claim 1, in which the total quantity of starter compound and catalyst necessary for the preparation of the polyether polyols is in the initial reactor charge on commencement of the reaction.
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3. Process according to Claim 1 or 2, in which the pressure in the reactor is held constant during the induction phase.
- 15 4. Process according to one of Claims 1 to 3, in which starter compounds having 1 to 8 hydroxyl groups and a molecular weight of 18 to 2,000 g/mol are used.
5. Process according to Claim 4, in which propoxylated oligomer starter compounds having 1 to 8 hydroxyl groups and number average molecular weights of 200 to 2,000 g/mol are used as starter compounds having active hydrogen atoms.
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6. Process according to one of Claims 1 to 5, in which the DMC catalyst is used at concentrations of from 0.001 wt.% to 0.1 wt.%, in relation to the quantity of polyether polyol to be prepared.
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