

PROCESS FOR PREPARING POLYETHER POLYOLS AND POLYOLS PREPARED THEREWITH

This invention relates to a process for preparing polyether
5 polyols. This invention particularly relates to a process for
preparing polyether polyols which are useful for preparing rigid
polyurethane foams.

Polyether polyols are useful for preparing polyurethane
10 products. It is known to use polyether polyols in processes for
preparing polyurethane products such as flexible foam, rigid foam,
elastomers and sealants. Of these, rigid polyurethane foams are an
important product having both insulative and structural uses.

U.S. Patent No. 4,332,936 to Nodelman discloses preparing
15 polyether polyols which are described as being particularly suitable
for the production of rigid polyurethane foams. Therein, it is
disclosed to mix or dissolve a multifunctional hydroxy initiator, such
as sucrose, with dimethylformamide prior to reacting the initiator
20 with an alkylene oxide in the presence of an amine catalyst.

U.S. Patent No. 5,030,758 and No. 5,141,968, both to Dietrich,
et al., disclose preparing polyether polyols using amine catalysts.
These references are directed to aromatic amine initiated polyols.

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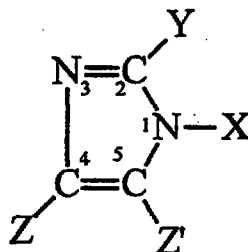
It would be desirable in the art of preparing polyether polyols
useful for preparing rigid polyurethane foams to prepare the polyols
using a process which could be used at high temperatures. It would
also be desirable in the art to prepare polyols using a process which
30 includes using a catalyst with high reactivity. Additionally, it
would be desirable in the art to prepare polyols using a process
wherein the catalyst has high reactivity at high temperatures. It
would also be desirable to prepare polyether polyols in a finished
polyether polyol diluent under conditions of imidazole catalysis which
35 is characterized by reaction of initiators and by non-reaction of
diluent with alkylene oxides.

In one aspect, the present invention is a process for preparing
a polyether polyol comprising admixing an initiator with an alkylene
40 oxide in the presence of an imidazole catalyst under high temperature
alkoxylation conditions sufficient to prepare a rigid polyether polyol

with the proviso that when an aromatic amine initiator is used, alkoxylation is done at a temperature greater than 125°C.

In another aspect, the present invention is a polyether polyol prepared by a process comprising admixing an initiator with an alkylene oxide in the presence of an imidazole catalyst under high temperature alkoxylation conditions sufficient to prepare a rigid polyether polyol with the proviso that when an aromatic amine initiator is used, alkoxylation is done at a temperature greater than 125°C.

In one embodiment, the present invention is a process for preparing rigid polyether polyols in the presence of an imidazole catalyst. For the purposes of the present invention, an imidazole catalyst is any compound having the general formula:



wherein X, Y, Z, and Z' are hydrogen, methyl groups, ethyl groups, or phenyl groups in combination to include: imidazole, N-methylimidazole, 2-methylimidazole, 4-methylimidazole, 2-ethylimidazole, 2-ethyl-4-methylimidazole, N-phenylimidazole, 2-phenylimidazole, and 4-phenylimidazole. Combinations of these compounds can be used and are also referred to herein as imidazole catalysts.

In the process of the present invention, a polyol is prepared by admixing an initiator with an alkylene oxide in the presence of an imidazole catalyst. Initiators are starting materials useful for preparing polyols characterized in that they include at least 2 active hydrogen containing groups. For the purposes of the present invention, an active hydrogen containing group is any group having a hydrogen which can react with an alkylene oxide in the presence of an imidazole catalyst. Preferably the active hydrogen containing group is an amino or hydroxy group. The active hydrogen containing group can be on an aliphatic or aromatic molecule. For example, the initiators useful with the process of the present invention can be an

aliphatic alcohol or amine having at least two active hydrogens containing groups. In the alternative, the initiators useful with the process of the present invention can be an aromatic diamine or polyamine.

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Initiators useful with the present invention include water, organic dicarboxylic acids, such as succinic acid, adipic acid, phthalic acid and terephthalic acid, aliphatic and aromatic, unsubstituted or N-mono-, N,N- and N,N'-dialkyl-substituted diamines
10 having from 1 to 4 carbon atoms in the alkyl moiety, such as unsubstituted or mono- or dialkyl-substituted ethylenediamine, diethylenetriamine, triethylenetetramine, 1,3-propylenediamine, 1,3- and 1,4-butylenediamine, 1,2-, 1,3-, 1,4-, 1,5- and 1,6-hexamethylenediamine, phenylenediamines, 2,3-, 2,4- and 2,6-
15 tolylenediamine and 4,4'-, 2,4'- and 2,2'-diaminodiphenylmethane. Other suitable initiator molecules useful with the present invention include alkanolamines, for example, ethanolamine, N-methyl- and N-ethyl-ethanolamine, dialkanolamines, for example, diethanolamine, N-methyl- and N-ethyl-diethanolamine, and trialkanolamines, for example,
20 triethanolamine, and ammonia.

Preferably, initiators used with the present invention are the polyhydric alcohols, in particular dihydric and/or trihydric alcohols, such as ethanediol, nonyl phenol, bisphenol-A, bisphenol-F, novolak
25 phenolic resins, mannich base polyols derived from phenol or alkyl phenol reacted with formaldehyde and diethanol or dipropanolamine (mannich bases), propylene glycol, dipropylene glycol, 1,4-butanediol, 1,6-hexanediol, glycerol, trimethylolpropane, pentaerythritol, sorbitol, alpha methyl glucoside and sucrose. For purposes of the
30 present invention, water is a dihydric alcohol because the reaction product of water and an alkoxide is a dihydric alcohol. More preferably, the initiators used with present invention are glycerine, water, sucrose and mixtures thereof.

35 Initiators useful with the present invention can also be alkoxylation products of the above listed initiator molecules. For example, in one preferred embodiment, an initiator useful with the present invention is a propoxylated or ethoxylated ethylene glycol. Another example of a similar useful initiator is a propoxylated or
40 ethoxylated glycerin. Still another example of a similar useful initiator is a propoxylated or ethoxylated propylene glycol.

Mixtures of initiators can be used with the present invention and are also preferred. Examples of mixed initiators include mixtures such as: sucrose and water; glycerin and sorbitol; propylene glycol and sucrose; and ethylene glycol and sucrose. More preferably, the initiators used with the present invention are propoxylated mixed initiators. Most preferably, the initiator used with the present invention is a propoxylated mixture of sucrose and glycerin.

10 In the process of the present invention, a polyol is prepared by admixing an initiator with an alkylene oxide in the presence of an imidazole catalyst. The alkylene oxides which can be used with the present invention include any which are useful in preparing polyether polyols. Preferably, the alkylene oxide has from 2 to 8 carbons.
15 More preferably, the alkylene oxide has from 2 to 4 carbons. Most preferably, the alkylene oxide is ethylene oxide, propylene oxide, butylene oxide and mixtures thereof.

The polyols prepared by the process of the present invention can be used in any application where a similar conventional polyol could be used, but are particularly useful in preparing rigid polyurethane foams. Polyols useful for preparing rigid polyurethane foams typically have: an OH functionality of from 2 to 8; an OH number of from 200 to 2000; and a molecular weight of from 62 to 2000. These
25 ranges represent the typical reaction products resulting from the alkoxylation of initiators such as water which has a low OH functionality of 2 and initiators such as sucrose which has a high OH functionality of 8. The present invention also contemplates the alkoxylation of initiators having intermediate functionalities as well
30 as mixtures of initiators.

Preferably the polyols of the present invention have an average functionality of from 2 to 8, an OH number of from 200 to 800, and a molecular weight of from 150 to 2,400. More preferably, the polyols
35 of the present invention have an average functionality of from 3 to 8, an OH number of from 200 to 600, and a molecular weight of from 300 to 2,400. Most preferably, the polyols of the present invention have an average functionality of from 4 to 8, an OH number of from 300 to 600, and a molecular weight of from 350 to 1,600.

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In the process of the present invention, a reaction of an initiator and alkylene oxide is done in the presence of an imidazole

EXAMPLES

Example 1: A mixture of 300g of glycerin and 0.5g of 2-ethyl-4-methylimidazole was heated to 100°C in a 1 liter pressure vessel equipped with a stirrer. After the vessel reaches thermal equilibrium, 11.96g of propylene oxide were injected into the vessel. The initial concentration of propylene oxide was measured by gas chromatography to be 1.8 percent. After 195 minutes, the concentration of propylene oxide was 0.04 percent.

Example 2: A mixture of 10.6 pounds (4.8Kg) of VORANOL 490* and 7.1 pounds (3.2Kg) of VORANOL 370** was added to a 20 gallon (75.7L) pressure vessel. To this were added 0.1 pounds (45.4g) of 2-ethyl-4-methylimidazole and 16 pounds (7.3Kg) of sucrose. The admixture was heated and stirred under a nitrogen pad until it reaches thermal equilibrium at 120°C. Next, 43 (19.5Kg) pounds of propylene oxide were added at a rate of 0.11 pounds (49.9g) per minute and then the admixture was maintained at 120°C for five hours. The final product was analyzed for physical properties and has a viscosity of 78.7Cs at 210°F (98.8°C), a hydroxyl content of 10.73 percent, and a Gardner color of 13. * VORANOL 490 is a trade designation of The Dow Chemical Company. **VORANOL 370 is a trade designation of The Dow Chemical Company.

Example 3. A series of experiments was run where 1-methoxy-2-propanol was reacted with propylene oxide using trimethylamine and 2-ethyl-4-methylimidazole as catalysts. The reactions were run in a 1 liter, stirred stainless steel pressure vessel that was heated with electrical coil heaters to maintain temperature control. The vessel was loaded with about 300 grams of 1-methoxy-2-propanol, closed and then purged with nitrogen to remove oxygen. For the runs using trimethylamine as a catalyst, 300 ml of gaseous trimethylamine catalyst was added as a gas using a 50 ml syringe. For the runs using 2-ethyl-4-methylimidazole as a catalyst, 0.52 g of 2-ethyl-4-methylimidazole was introduced into the pressure vessel with the 1-methoxy-2-propanol. The vessel was then stirred and heated to the indicated reaction temperature and about 6 g of propylene oxide was pressured into the reaction vessel from another small pressure vessel using nitrogen gas. Samples were taken of the liquid phase using an attached dip tube for analysis of a) amine content, by titration,* and

b) unreacted propylene oxide (PO) content by gas chromatography**. The amount of PO was quantified by also including about 6 grams of methyl tertiary butyl ether as an unreactive internal standard for gas chromatography.

- 5 The rate of the reaction was followed by plotting the unreacted PO concentration versus time. A plot of the ln (natural log) of PO concentration (as wt %), if linear, gives a first order rate constant for comparison of reaction rates. For comparison between runs that may have a different amine catalyst concentration, a second order rate
- 10 constant may be derived by division of this slope by the molar base concentration. The Table below lists the rate data for these reactions. Reaction rates for propoxylation vary with amine catalyst and polyol reactant. Low equivalent weight alcohols or polyols react faster than materials already propoxylated. It can be seen that the
- 15 rate of propoxylation decreases with reaction temperature for trimethylamine and increases for imidazoles.

TABLE

Reactant	Temp	Catalyst	Basicity	slope	rate
2MP	80°C	TMA	0.034	0.0041	0.121
2MP	90°C	TMA	0.032	0.0037	0.116
2MP	100°C	TMA	0.031	0.0032	0.103
2MP	110°C	TMA	0.036	0.0018	0.050
2MP	100°C	EMI	0.035	0.0043	0.123
2MP	120°C	EMI	0.010	0.0026	0.260
Glycerine	100°C	EMI	0.026	0.012	0.462
Glycerine	100°C	TMA	0.029	0.011	0.379
Suc-Glyc	100°C	EMI	0.035	0.0044	0.126
Suc-Glyc	130°C	NMI	0.0127	0.0756	5.953

•2MP = 1-methoxy-2-propanol

- 20 •EMI = 2-ethyl-4-methylimidazole

•NMI = N-methylimidazole

•Suc-glyc is a polyether polyol based on 60/40 weight ratio of sucrose/glycerine propoxylated to an OH number of 370

•basicity as milliequivalents/gram by titration

- 25 •slope = slope of plot ln PO vs. time (minutes)

•rate = slope divided by base concentration as grams/equiv.-minute.

*The titration analysis of the catalyst was done by adding about 5 g of sample to 50 ml methanol. This was titrated using a Mettler DL40

catalyst. Preferably, from 0.0001 parts to 0.01 parts of imidazole catalyst are used. Most preferably 0.001 parts of an imidazole catalyst are used. Parts of catalyst are calculated by dividing the weight of imidazole catalyst used by the total weight of product made and diluent present in the reactor.

The reaction of an initiator and an alkylene oxide are done in the process of the present invention under high temperature alkoxylation conditions sufficient to prepare a polyether polyol. The art of preparing conventional polyether polyols by conventional processes is well known to those of ordinary skill in the art of preparing polyols. The high temperature alkoxylation conditions of the present invention substantially the same except the temperatures at which the alkoxylation are done is at from 100°C to near but not at the decomposition or discoloration point of the polyol. These conditions include a pressure of from 10 psig (69 kPa) to 100 psig (690 kPa) and a temperature of from 100°C to 150°C. More preferably the high temperature alkoxylation conditions are a pressure of from 30 psig (206 kPa) to 80 psig (551 kPa). Even more preferably, the temperature of the high temperature alkoxylation conditions is from 120°C to 150°C. Most preferably, the temperature of the high temperature alkoxylation conditions is from 130°C to 145°C. When the process of the present invention is used to prepare polyols from formulations including aromatic amine initiators, the alkoxylation is done at a temperature of greater than 125°C.

An advantage of the imidazole catalysts used with the process of the present invention when they are compared with other conventional amine catalysts such as triethylamine, trimethylamine and methyldiethylamine is that the imidazole catalysts have both a high level of reactivity at conventional alkoxylation temperatures and the reactivity of imidazole catalysts increases with temperature up to the decomposition point for most polyols and initiators. For example, trialkylamine catalysts begin to lose catalytic activity as alkoxylation temperature is increased starting at about 110°C while the imidazole catalysts continue to increase in catalytic activity until the reaction temperature reaches at least 150°C. The ability to use the process of the present invention at elevated temperatures results in increased reaction rates and decreased residence time and energy consumption for production of polyether polyols.

Another advantage of the amine catalysts generally and the imidazole catalysts in particular is that processes utilizing such catalysts can be employed to alkoxyrate initiators in polyol diluents without also alkoxyrating the diluents. Suitable diluents include any polyether or polyester polyol which was prepared such that at least two and preferably three alkylene oxides were added to each active hydrogen of the initiator. Since the amine catalysts only catalyze the addition of from one to three alkylene oxides per active hydrogen group on an initiator, polyols wherein more than 2 alkylene oxide groups have been added can be used as diluents without the polyol reacting further with alkylene oxides. This can be an advantage, particularly when alkoxyrating solid initiators such as sucrose and sorbitol. This is particularly an advantage when it is desired to prepare a substantially homogenous polyol prepared from solid initiators because a polyol which is substantially similar to the desired product polyol can be used as a solvent for the initiator.

Polyols are often prepared by both continuous and batch processes. In a batch process, a polyol is made by charging the components of a formulation in one or more steps, but essentially all of any given component is charged at one time. For example, all of the initiator for the polyol is placed into a reactor at the start of the reaction. That "batch" of raw materials is then taken through the steps of making the polyol to produce a single "batch" of polyols. In contrast, in a continuous process, the raw materials are fed into a production unit continuously, so that the polyol is at different stages of production at different points in the production unit. The imidazole catalysts of the present invention can be used with either batch or continuous processes.

The polyols prepared by the process of the present invention can be used in the same way as are similar conventional polyols prepared using conventional processes. For example, the polyols of the present invention can be used as prepared or admixed with additives. Where desirable, the polyols of the present invention can be admixed with other types of polyols.

The following examples are provided to illustrate the present invention. The examples are not intended to limit the scope of the present invention and should not be so interpreted. Amounts are in weight parts or weight percentages unless otherwise indicated.

autotitrator (Mettler DL40 is a trade designation of the Mettler Company). The total basicity was taken as the sum of all endpoints in the titration.

**The gas chromatography analysis was done using a 10 meter, 50 micron internal diameter glass capillary column coated with a polydimethylsiloxane stationary phase. The reaction vessel was also charged with 6 grams of methyl tertiary butyl ether (MTBE) which is used as an internal standard. By comparing peak areas of MTBE and propylene oxide and knowing their relative response factors, it is possible to calculate the concentration of unreacted propylene oxide in the liquid phase.

Example 4. A polyol based on a 60/40, by weight, mixture of sucrose/glycerine, propoxylated to an equivalent hydroxyl weight of about 150 (specification range 10.8-11.6% OH, viscosity 0.89 - 1.17 poise ($0.089 - 0.117 \text{ Ns/m}^2$)) was used as a reaction solvent. 468 grams of this polyol was admixed with 419 grams of sucrose and 1.82 grams of N-methylimidazole. This admixture was stirred in a 4 liter pressure vessel which was heated to 130°C and maintained at $130 \pm 0.5^\circ\text{C}$ for the course of the reaction. 1113 grams of propylene oxide was added using a positive displacement pump over 4.1 hours. The amount of residual propylene oxide was measured by monitoring the reactor pressure over the final 2 hr period. A rate constant was obtained by plotting the natural log of pressure against time until the pressure remains constant. The slope of this plot gives a linear first order plot with a slope of -0.0756 per minute. Division of this value by the catalyst concentration at the end of reaction (measured as 1040 ppm or 0.0127 milliequivalents/g) gives a second order rate constant of 5.95 g/meq.-min. The resulting product had 12.16% OH and a viscosity of 1.05 poise (0.105 Ns/m^2) at 210°F (98.9°C).

WHAT IS CLAIMED IS:

1. A process for preparing a polyether polyol comprising admixing an initiator with an alkylene oxide in the presence of imidazole catalyst under high temperature alkoxylation conditions
5 sufficient to prepare a polyether polyol with the proviso that when an aromatic amine initiator is used, alkoxylation is done at a temperature greater than 125°C.
2. The process of Claim 1 wherein the polyether polyol is
10 one useful for preparing rigid polyurethane foams.
3. The process of Claim 2 wherein the initiator is a mixture of aliphatic alcohols.
- 15 4. The process of Claim 4 wherein the initiator is a mixture of glycerine and sucrose.
5. The process of Claim 2 wherein the imidazole catalyst is selected from the group consisting of imidazole, N-methylimidazole,
20 2-methylimidazole, 4-methylimidazole, 2-ethylimidazole, 2-ethyl-4-methylimidazole, N-phenylimidazole, 2-phenylimidazole, 4-phenylimidazole, and mixtures thereof.
6. The process of Claim 5 wherein the imidazole catalyst
25 is 2-ethyl-4-methylimidazole.
7. The process of Claim 2 wherein the alkylene oxide is selected from the group consisting of ethylene oxide, propylene oxide, butylene oxide, and mixtures thereof.
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8. The process of Claim 11 wherein the alkylene oxide is propylene oxide.
9. The process of Claim 2 wherein the high temperature
35 alkoxylation conditions include a temperature of from 120°C to 150°C.
10. The process of Claim 2 wherein the polyether polyol has an average functionality of from 4 to 8.
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