Macromolecules 1974, 7, 153-160 describes low temperature polymerizations of propylene oxide in bulk, in the presence of aluminoxanes such as $(C_2H_5)_2AlOAl(C_2H_5)_2$ (TEDA). No starter is mentioned. Polyethers having molecular weights of 100,000 to 1 million are obtained. *J. Polym. Sci.* 1973, **11**, 699-712 describes using TEDA to polymerize propylene oxide in solution at 40°C, in the absence of a starter.

Diethylaluminum chloride is described as an alkylene oxide polymerization catalyst in a solution polymerization without a starter at temperatures up to 110°C in US 3,029,216 and in a bulk polymerization without a starter at 25°C in *J. Polym. Sci.* 1959, 34, 157-160. High molecular weight polymers are obtained.

This disclosure is in one aspect a method for producing an alkylene oxide polymer or copolymer, comprising combining (i) at least one aluminum compound containing at least one trisubstituted aluminum atom, wherein at least one of the substituents of at least one trisubstituted aluminum atom is hydrocarbyl; (2) at least one cyclic amidine; (3) at least one starter; (4) at least one alkylene oxide and optionally (5) at least one comonomer that is not an oxirane, and polymerizing the alkylene oxide(s) or copolymerizing the alkylene oxide(s) and optionally the comonomer to form the alkylene oxide polymer or copolymer.

The method of the disclosure offers several advantages, from both process and product perspectives.

Process advantages include rapid polymerization rates; the ability to alkoxylate starters that have a wide range of molecular weights, in particular low molecular weight starters that have hydroxyl equivalent weights of 30 to 75; the ability to use significantly lower levels of catalyst than needed with alkali metal hydroxides, thereby reducing costs and permitting at least in some cases the polyols to be used without the need to first remove catalyst residues; the ability to use higher URO (unreacted alkylene oxide) levels than can be used with the DMC catalyst without formation of unwanted higher molecular weight polymers; and the ability of the catalyst to polymerize ethylene oxide uniformly. This last advantage is of great importance industrially in view of the difficulty seen with polymerizing ethylene oxide with double metal cyanide catalysts. The ability to uniformly polymerize ethylene oxide permits the catalyst to be used to make oxyethylene-capped polyols that have high proportions of primary hydroxyl groups, and permits oxyethylene-capped poly(propylene oxide), oxyethylene-capped poly(butylene oxide), oxyethylene-capped poly(propylene oxide-co-ethylene oxide) and oxyethylene-capped poly(butylene oxide-co-ethylene oxide) polyols to be prepared using

a single catalyst for the propylene oxide, butylene oxide, propylene oxide-co-ethylene oxide and/or butylene oxide-co-ethylene oxide polymerization as well as the capping step.

The disclosure in another aspect is a polyether polyol being a homopolymer of propylene oxide or random copolymer of propylene oxide and ethylene oxide, the polyether polyol being prepared by homopolymerizing propylene oxide or a mixture of at least 70% by weight propylene oxide and correspondingly up to 30% by weight ethylene oxide, based on the weight of alkylene oxides polymerized, in the absence of any comonomer that is not an oxirane, to form the polyether polyol, characterized in that

a) the polyether has a hydroxyl equivalent weight of at least 500 up to 4000 g/equivalent;

b) the polyether has a nominal hydroxyl functionality of 2 to 8;

c) the polyether has no more than 0.01 meq/g of terminal unsaturation;

d) the polyether has a polydispersity (M_w/M_n) by gel permeation chromatography of no more than 1.10;

e) the polyether contains no more than 2000 parts by million by weight (ppm) based on polyether polyol weight, of a fraction having a number average molecular weight by GPC of 40,000 g/mol or more; and

f) no more than 12% of the hydroxyl groups of the polyether are primary hydroxyl groups as determined by ASTM D-4273 or equivalent method,

wherein at least 90% of the weight of the polyether is oxypropylene and/or oxyethylene units.

In yet another aspect, the disclosure is a polyether polyol being a propylene oxide homopolymer or random copolymer of propylene oxide and ethylene oxide, the polyether polyol being prepared by homopolymerizing propylene oxide or a mixture of at least 90% by weight propylene oxide and correspondingly up to 10% by weight ethylene oxide, based on the weight of alkylene oxides polymerized, in the absence of any comonomer that is not an oxirane, to form the polyether polyol, the polyether polyol being further characterized in a) having a hydroxyl equivalent weight of 1000 to 2500 g/equivalent, b) having a nominal functionality of 2 to 8; c) having no more than 0.007 meq/g of terminal unsaturation; d) having a polydispersity (M_w/M_n) of no more than 1.07; and e) containing no more than 1200 ppm, of a fraction having a number average molecular weight by GPC (gel permeation chromatography) of 40,000 g/mol or more, wherein at least 90% of the weight of the polyether is oxypropylene and/or oxyethylene units.

WHAT IS CLAIMED IS:

1. A method for producing an alkylene oxide polymer or copolymer, comprising combining (i) at least one aluminum compound containing at least one trisubstituted aluminum atom, wherein at least one of the substituents of at least one trisubstituted aluminum atom is hydrocarbyl; (2) at least one cyclic amidine; (3) at least one starter; (4) at least one alkylene oxide and optionally (5) at least one comonomer that is not an oxirane, and polymerizing the alkylene oxide(s) or copolymerizing the alkylene oxide(s) and optionally the comonomer to form the alkylene oxide polymer or copolymer.

2. The method of claim 1 wherein at least one aluminum atom of the aluminum compound is substituted with one or two hydrocarbyl groups, and is substituted with one or two halogen, oxo, ether or hydride groups.

3. The method of claim 1 wherein the aluminum compound includes one or more of trimethyl aluminum, triethyl aluminum, triisopropyl aluminum, tri-n-propyl aluminum, triisobutyl aluminum, tri-n-butyl aluminum, tri-t-butylaluminum and trioctadecylaluminum.

4. The method of claim 1 wherein the aluminum compound includes one or more of dimethyl aluminum chloride, methyl aluminum dichloride, diethyl aluminum chloride, ethyl aluminum dichloride, diisobutyl aluminum chloride, isobutyl aluminum dichloride, methyl aluminum di[(2,6-di-t-butyl-4-methyl)phenoxide] ($Al(BHT)_2Me$), dimethyl 2,6-di-t-butyl-4-methylphenoxide ($AlBHTMe_2$) methyl aluminum di(2,6-diisopropyl)phenoxide, dimethyl aluminum (2,6-diisopropyl)phenoxide methyl aluminum di [(2,6-diphenyl) phenoxide], dimethyl aluminum (2,6-diphenyl) phenoxide, methyl aluminum di[(2,4,6-trimethyl)phenoxide], dimethyl aluminum (2,4,6-trimethyl)phenoxide, tetraethylaluminane, tetramethylaluminane, diisobutyl aluminum hydride, isobutyl aluminum dihydride, dimethyl alumimum hydride, methyl aluminum dihydride, diethyl aluminum hydride, ethyl aluminum dihydride, diisopropyl aluminum hydride, isopropyl aluminum dihydride, diethyl aluminum ethoxide, ethyl aluminum diethoxide, dimethyl aluminum ethoxide, methyl aluminum diethoxide, dimethyl aluminum fluoride, methyl aluminum difluoride, diethyl aluminum fluoride, ethyl

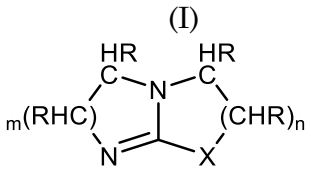
aluminum difluoride, diisobutyl aluminum fluoride, isobutyl aluminum difluoride, dimethyl aluminum bromide, methyl aluminum dibromide, diethyl aluminum bromide, ethyl aluminum dibromide, diisobutyl aluminum bromide, isobutyl aluminum dibromide, dimethyl aluminum iodide, methyl aluminum diiodide, diethyl aluminum iodide, ethyl aluminum diiodide, diisobutyl aluminum iodide and isobutyl aluminum iodide.

5. The method of claim 1 wherein the aluminum compound includes a tetraalkylaluminoxane in which each alkyl group independently contains 1 to 6 carbon atoms.

6. The method of any preceding claim wherein the cyclic amidine is a bicyclic amidine.

7. The method of claim 6 wherein the bicyclic amidine is those represented by the structure:

(I)

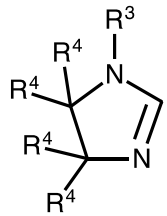


(I)

wherein X is CHR or NR^1, wherein each R is independently hydrogen, unsubstituted or inertly substituted alkyl (including cycloalkyl), unsubstituted or inertly substituted phenyl or a non-protic nucleophilic group and each R^1 is independently hydrogen, hydrocarbyl or inertly substituted hydrocarbyl, and m and n are each independently a positive integer.

8. The method of claim 6 wherein the bicyclic amidine is one or more of 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), 5-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (Me-TBD) 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) and 6-(dibutylamino)-1,8-diazabicyclo[5.4.0]undec-7-ene, where the butyl groups are independently n-butyl, sec-butyl or t-butyl groups.

9. The method of any of claims 1-5 wherein the cyclic amidine is imidazole or an imidazole derivative corresponding to the structure:



wherein R^3 and each R^4 is independently hydrogen, unsubstituted hydrocarbyl or inertly substituted hydrocarbyl.

10. The method of claim 9 wherein the cyclic amidine is one or more of imidazole, N-methyl imidazole, N-ethyl imidazole, N-phenyl imidazole, 1,2-dimethyl imidazole, 1,2-diethyl imidazole, 1,2-diphenyl imidazole, 4,5-dimethyl imidazole, 4,5-diethylimidazole, 4,5-diphenyl imidazole, 1,4,5-trimethyl imidazole, 1,4,5-triethyl imidazole, 1,4,5-triphenyl imidazole and the like.

11. The method of any preceding claim wherein the aluminum compound is present in an amount sufficient to provide 100 to 2,500 parts by weight of aluminum per million parts by weight of the alkylene oxide polymer or copolymer.

12. The method of any preceding claim wherein the aluminum compound and starter are combined at a mole ratio of 0.00005 to 0.05 moles of aluminum provided by the aluminum compound per mole of starter.

13. The method of any preceding claim wherein the aluminum compound and cyclic amidine are combined at a mole ratio of 1:3 to 5:1.

14. The method of any preceding claim wherein the aluminum compound and cyclic amidine are combined at a mole ratio of 1:2 to 4:1.

15. The method of any claim 1 wherein:

the aluminum compound is diethylaluminum chloride and the cyclic amidine is DBU, Me-TBD or TBD, and the mole ratio of the aluminum compound to the cyclic amidine is 2:3 to 2:1;

the aluminum compound is diethylaluminum chloride and the cyclic amidine is 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), and the mole ratio of the aluminum compound to the cyclic amidine is >1:1 to 2:1;

the aluminum compound is ethylaluminum dichloride and the cyclic amidine is DBU or DBN, and the mole ratio of the aluminum compound to the cyclic amidine is >1:1 to 2:1;

the aluminum compound is ethylaluminum dichloride and the cyclic amidine is Me-TBD or TBD, and the mole ratio of the aluminum compound to the cyclic amidine is 2:3 to 2:1;

the aluminum compound is DIBAL and the cyclic amidine is DBU, Me-TBD or DBN, and the mole ratio of the aluminum compound to the cyclic amidine is 2:3 to 2:1;

the aluminum compound is DIBAL and the cyclic amidine is TBD, and the mole ratio of the aluminum compound to the cyclic amidine is 1:2 to 4:1;

the aluminum compound is $(iBu)_2AlCl$ or $Al(BHT)_2Me$ and the cyclic amidine is DBU, Me-TBD, DBN or TBD, and the mole ratio of the aluminum compound to the cyclic amidine is 1:2 to 4:1;

the aluminum compound is tetraethyldialuminoxane (TEDA) and the cyclic amidine is DBU, Me-TBD or DBN, and the mole ratio of the aluminum compound to the cyclic amidine is 2:3 to 2:1;

the aluminum compound is TEDA and the cyclic amidine is TBD, and the mole ratio of the aluminum compound to the cyclic amidine is 1:5 to 3:1 or

the aluminum compound is one or more of trimethyl aluminum, triethyl aluminum, triisopropyl aluminum, tri(n-propyl) aluminum, triisobutyl aluminum, tri(n-butyl)aluminum, tri(t-butyl)aluminum, tri(octadecyl)aluminum, and the cyclic amidine is one or more of DBU, Me-TBD, DBN or TBD and the mole ratio of the aluminum compound to the cyclic amidine is 2:3 to 4:1.

16. The method of any preceding claim wherein the starter contains one or more hydroxyl groups and has a hydroxyl equivalent weight of 30 to 6000.

17. The method of any preceding claim wherein the starter contains 2 to 8 hydroxyl groups and has an equivalent weight of 30 to 250.

18. The method of any preceding claim wherein the alkylene oxide is propylene oxide, ethylene oxide or a mixture of propylene oxide and ethylene oxide.

19. The method of any of claims 1-17 wherein the starter is a homopolymer of propylene oxide and/or a random or block copolymer of propylene oxide in which no more than 25% of the hydroxyl groups are primary, which starter has a hydroxyl equivalent weight of at least 125 up to 1000 g/equivalent, and the alkylene oxide is ethylene oxide.

20. A polyether polyol being a homopolymer of propylene oxide or random copolymer of propylene oxide and ethylene oxide, the polyether polyol being prepared by homopolymerizing propylene oxide or a mixture of at least 70% by weight propylene oxide and correspondingly up to 30% by weight ethylene oxide, based on the weight of alkylene oxides polymerized, in the absence of any comonomer that is not an oxirane, to form the polyether polyol, characterized in that

a) the polyether has a hydroxyl equivalent weight of at least 500 up to 4000 g/equivalent;

b) the polyether has a nominal hydroxyl functionality of 2 to 8;

c) the polyether has no more than 0.01 meq/g of terminal unsaturation;

d) the polyether has a polydispersity (M_w/M_n) by gel permeation chromatography of no more than 1.10;

e) the polyether contains no more than 2000 parts by million by weight (ppm) based on polyether polyol weight, of a fraction having a number average molecular weight by GPC of 40,000 g/mol or more; and

f) no more than 12% of the hydroxyl groups of the polyether are primary hydroxyl groups as determined by ASTM D-4273 or equivalent method,

wherein at least 90% of the weight of the polyether is oxypropylene and/or oxyethylene units.

21. A polyether polyol being a propylene oxide homopolymer or random copolymer of propylene oxide and ethylene oxide, the polyether polyol being prepared by homopolymerizing propylene oxide or a mixture of at least 90% by weight propylene oxide and correspondingly up to 10% by weight ethylene oxide, based on the weight of alkylene oxides polymerized, in the absence of any comonomer that is not an oxirane, to form the polyether polyol, the polyether polyol being further characterized in a) having a

hydroxyl equivalent weight of 1000 to 2500 g/equivalent, b) having a nominal functionality of 2 to 8; c) having no more than 0.007 meq/g of terminal unsaturation; d) having a polydispersity (M_w/M_n) of no more than 1.07; and e) containing no more than 1200 ppm, of a fraction having a number average molecular weight by GPC of 40,000 g/mol or more, wherein at least 90% of the weight of the polyether is oxypropylene and/or oxyethylene units.

22. The polyether polyol of claim 21 wherein no more than 8% of the hydroxyl groups are primary hydroxyl groups.