

ALKYLENE OXIDE POLYMERIZATION USING ALUMINUM COMPOUNDS AND
CYCLIC AMIDINES

This invention relates to a process for polymerizing one or more alkylene oxides
5 or copolymerizing one or more alkylene oxides with one or more copolymerizable
monomers which is not an alkylene oxide.

Alkylene oxide polymers and copolymers are produced globally in large
quantities. Polyether polyols, for example, are an important raw material for producing
polyurethanes. Among other things, they are used to make high resiliency, molded, or
10 rigid foams. Polyether monols are used, for example, as surfactants and industrial
solvents, among other uses. Carbonate- and ester-modified alkylene oxide polymers also
find uses in these and other applications.

Polyether monols and polyols are produced by polymerizing an alkylene oxide in
the presence of a starter compound. The starter compound has one or more functional
15 groups at which the alkylene oxide can react to begin forming the polymer chains. The
main functions of the starter compound are to provide molecular weight control and to
establish the number of hydroxyl groups the polyether will have.

A catalyst is needed to obtain economical polymerization rates. The most
commonly used catalysts are alkali metal hydroxides such as potassium hydroxide and
20 the so-called double metal cyanide (DMC) catalyst complexes, of which zinc
hexacyanocobaltate catalyst complexes are the most commercially important type.

Alkali metal hydroxides provide the benefits of low catalyst costs and acceptable
polymerization rates. They are versatile in that they effectively polymerize many
alkylene oxides. The product polyether usually, but not always, has a narrow molecular
25 weight distribution. A particular advantage of these catalysts is that they can be used
to polymerize ethylene oxide onto an alcoholic starter. This ability is quite important
industrially as many polyether polyols manufactured as polyurethane raw materials are
block copolymers made by polymerizing propylene oxide and then ethylene oxide onto a
starter compound. The alkali metal hydroxide catalyst permits this to be done easily
30 and inexpensively, as both polymerizations can be performed in the same vessel using
the same catalyst system, without recovering the intermediate poly(propylene oxide)
polyol.

Nonetheless alkali metal hydroxides have well-known drawbacks. Alkali metal
hydroxide catalysts promote a side reaction that forms unsaturated monoalcohols, which

become alkoxyated to form unwanted monofunctional species. The presence of these unwanted monofunctional species can also broaden molecular weight distribution. Polyols made using these catalysts need to be neutralized and purified to remove catalyst residues, which adds significant capital and operating expense to the manufacturing process. In addition, the product polyether tends to have a broad molecular weight distribution when made in a back-mixed continuous process.

DMC catalysts provide rapid polymerization rates compared to alkali metal catalysts, even when used at very low catalyst concentrations. In addition, they have distinct and important advantages over alkali metal catalysts. The DMC catalysts rarely if at all promote the side reaction that produces monofunctional by-products, so the hydroxyl functionality of the product is close to the theoretical value (as defined by the starter). A second main advantage is that no neutralization step is needed. The catalyst residues often can be left in the product, unlike the case when alkali metal hydroxides are used as the polymerization catalyst. This can result in significantly lower production costs. A third advantage is that, unlike alkali metal hydroxide catalysts, DMC catalyst complexes produce low polydispersity polymers when the polymerization is performed in a back-mixed continuous main reactor.

Nonetheless, the DMC catalysts have disadvantages as well. They tend to perform poorly in the presence of high concentrations of hydroxyl groups, and especially in the presence of low molecular weight starter compounds like glycerin that have hydroxyl groups in the 1,2- or 1,3- positions with respect to each other. Under these conditions, the catalysts are difficult to activate, perform sluggishly and often become deactivated before the polymerization is completed. This represents a significant limitation on the widespread adoption of DMC catalysts. It is often necessary to produce the polyether in two or more discrete steps, in which the early stages of the polymerization are conducted in the presence of an alkali metal catalyst and, after cleaning up the resulting intermediate product, the remainder of the polymerization is performed using the DMC catalyst. This approach requires the intermediate to be neutralized and purified (because the DMC catalyst is deactivated by strong bases), thus re-introducing costs which the DMC-catalyzed polymerization is intended to avoid.

Another very significant disadvantage of the DMC catalysts is they cannot be used on an industrial scale to produce ethylene oxide-capped polyethers. Instead of adding onto the chain ends in a regular and controlled manner, the ethylene oxide instead tends to produce very high molecular weight poly(ethylene oxide) polymers.

Despite many attempts to resolve this problem, it has not been satisfactorily addressed, and ethylene oxide-capped polyethers are almost always made at industrial scale using an alkali metal hydroxide catalyst to perform the capping step.

Yet another problem associated with DMC catalysts is they produce a small
5 amount of very high molecular weight (40,000+ g/mol) polymers. The presence of these polymers increases polyol viscosity, broadens molecular weight distribution, and can also adversely affect the ability of the polyether polyols made with DMC catalyst complexes to produce flexible polyurethane foam.

Certain Lewis acids have been evaluated as alkylene oxide polymerization
10 catalysts. The Lewis acids require essentially no activation time, but become deactivated rapidly and therefore cannot produce high molecular weight polymers or high conversions of alkylene oxide to polymer. In addition, poly(propylene oxide) polymers produced by Lewis acid catalysis tend to have a large proportion of primary hydroxyl groups.

15 In addition, various aluminum compounds have been described for use as alkylene oxide polymerization catalysts.

In *Polym. Chem.* 2012, 3, 1189-1195 there is described a propylene oxide polymerization in the presence of a poly(propylene oxide) starter compound, triisobutylaluminum and a phosphazene base. This polymerization is conducted in
20 toluene solution at 20°C. The phosphazene base is used in large quantities, about one mole per equivalent of starter. US Published Patent Application No. 2018-0237586 describes another solution polymerization of propylene oxide in the presence of a trialkyl aluminum and a nitronium alkoxide, the latter of which is described as a starter. Again, large amounts of the nitronium alkoxide are used. High molecular weight
25 polyethers that have a broad molecular weight distribution are obtained.

Macromolecules 2008, 41, 7058-7063 describes a polymerization of epichlorohydrin using a triisobutylaluminum compound and in the presence of tetraoctylammonium bromide, at temperatures up to room temperature, and in the absence of a starter.

30 US Patent No. 6,919,486 describes polymerizing propylene oxide in the presence of a polyether triol starter and an aluminum phosphonate catalyst. Ethylene oxide capping is also described. The polymerizations are performed in the absence of solvent and at a temperature of 110°C.

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
5 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.

10 This invention 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;
15 (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 invention offers several advantages, from both process and product perspectives.

20 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
25 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.

30 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 invention 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 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 invention 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 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.

From the product standpoint, the advantages of the invention include i) low polydispersities (M_w/M_n); ii) absence of the “high molecular weight tail” that is seen in DMC catalyzed polymerizations; iii) low formation of unwanted monofunctional species due to the isomerization of alkylene oxide into unsaturated alcohols; and iv) when propylene oxide is homopolymerized, the production of polyethers that have very low proportions of primary hydroxyl groups.

The aluminum compound is an aluminum compound containing at least one trisubstituted aluminum atom. At least one, at least two or all three of the substituents of at least one trisubstituted aluminum atom are hydrocarbyl. Two or more of the substituents on a trisubstituted aluminum atom may together form a ring structure.

The aluminum compound may contain 1, 2, 3, 4 or more aluminum atoms (such as up to 100, up to 50, up to 25, up to 12 or up to 5 aluminum atoms), of which at least one is trisubstituted.

A hydrocarbyl substituent may be aliphatic, cycloaliphatic, aromatic or any combination of two or more thereof, and is bonded to the aluminum atom via an aluminum-carbon bond. The hydrocarbyl substituent in some cases has up to 12, up to 6 or up to 4 carbon atoms. The hydrocarbyl group may be, for example, a linear or branched alkyl group such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, t-butyl and the like. A hydrocarbyl substituent(s) may be unsubstituted or inertly substituted.

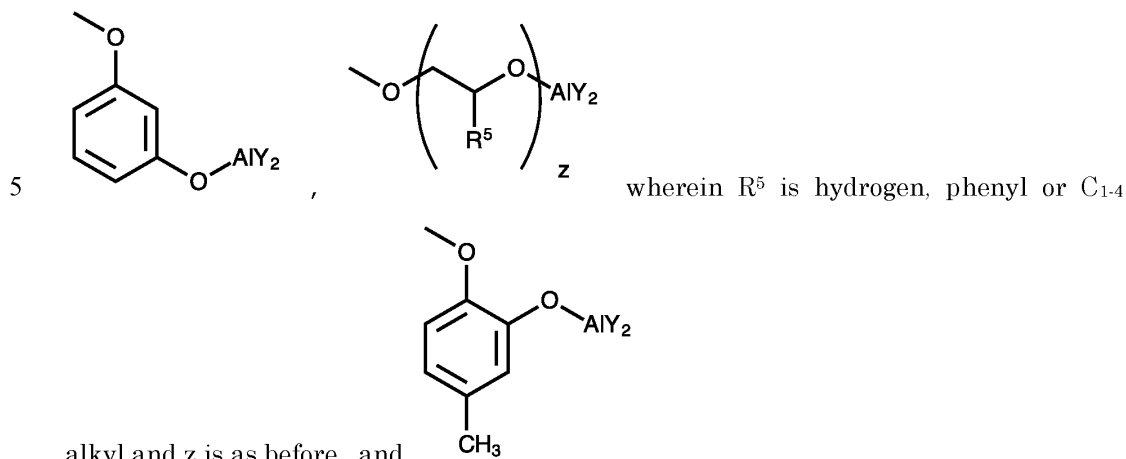
The non-hydrocarbyl substituent groups bonded to the aluminum atom(s) may be, for example, halogen, phosphonate, hydride, oxo (*i.e.*, -O-), alkoxide or phenoxide. Two or more of the substituents on a trisubstituted aluminum atom may together form a ring structure.

Non-hydrocarbyl substituent groups bonded to the aluminum atom(s) may be, for example, halogen, phosphonate, hydride, oxo (*i.e.*, -O-), alkoxide or phenoxide.

A halogen substituent may be, for example, fluorine, chlorine, bromine or iodine.

An alkoxide or phenoxide substituent may have the form $-O-R^2$ or $-O(-R^2-O)_z-R^2-O-Z$ wherein each R^2 is independently a hydrocarbyl or substituted hydrocarbyl group, z is zero or a positive number, Z is hydrocarbyl, inertly substituted hydrocarbyl, hydrogen or $-AlY_2$ where each Y is halogen, hydrocarbyl, phosphonate, hydrogen, oxo (*i.e.*, -O-) or alkoxide or phenoxide. The alkoxide or phenoxide may include a polyether chain such as a poly(oxyethylene) or poly(oxypropylene chain). Specific examples of alkoxide or

phenoxide substituents include ethoxide, n-propoxide, isopropoxide, t-butoxide, n-butoxide, isobutoxide, phenoxide, 2,6-di-t-butyl-4-methyl phenoxide, 2,6-diisopropylphenoxide, 2,6-diphenylphenoxide, 2,4,6-trimethylphenoxide, 4-fluorophenoxide, 4-chlorophenoxide, 3, 4, 5-trifluorophenoxide,



Any of these substituent groups except hydride may form all or part of a bridge between aluminum atoms. Thus, for example, an oxo (-O-) group may bond two aluminum atoms to form an aluminoxane. Similarly, a divalent hydrocarbon radical may be bonded to two aluminum atoms to form a bridge therebetween, as may an -O-R²-O- diradical or a -O-(R²-O)_z-R²-O- diradical.

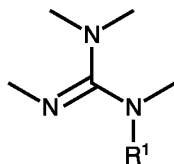
In some embodiments, at least one aluminum atom is substituted with one or two hydrocarbyl groups, and is substituted with one or two halogen, oxo, ether, hydride or phosphonate groups. If more than one aluminum atom is present in the aluminum compound, all of the aluminum atoms may be substituted in such a manner.

Specific examples of aluminum compounds include trimethyl aluminum, triethyl aluminum, triisopropyl aluminum, tri(n-propyl) aluminum, triisobutyl aluminum, tri(n-butyl)aluminum, tri(t-butyl)aluminum, tri(octadecyl)aluminum, 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 (AlBHTMe₂), 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 (DIBAL), isobutyl

aluminum dihydride, dimethyl aluminum 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, isobutyl aluminum diiodide, and a tetraalkylaluminoxane in which each alkyl group of the tetraalkylaluminoxane independently contains 1 to 6 carbon atoms.

An "inert" substituent for purposes of this invention is one that is not reactive towards hydroxyl groups, amino groups or isocyanate groups. Examples of inert substituents include, for example, hydrocarbyl substituents, ether groups, ester groups tertiary amino groups, amide groups, halogen and the like.

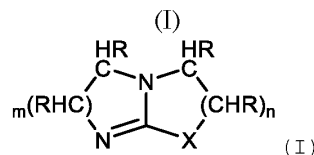
Cyclic amidines useful herein include an $-N-CH=N-$ moiety as part of the ring structure. In some embodiments, the cyclic amidine is a triaza compound having a



moiety as part of the ring structure, wherein R^1 is as defined below.

Suitable cyclic amidines include bicyclic amidines, including those represented by Structure I as follows:

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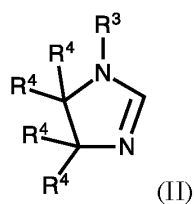
wherein X is CHR or NR^1 , wherein each R is independently hydrogen, unsubstituted or inertly substituted alkyl (including cycloalkyl), unsubstituted or inertly substituted phenyl or a non-protic nucleophilic group and each R^1 is independently hydrogen,

hydrocarbyl or inertly substituted hydrocarbyl, and m and n are each independently a positive integer. m is preferably 1 or 2 and most preferably 2. n is most preferably 1, 2 or 3.

Each R is preferably hydrogen, phenyl or lower (C₁₋₄) alkyl. When R is a non-protic nucleophilic group, it should be devoid of hydrogen atoms that are reactive towards hydroxyl groups and isocyanate groups. Such a non-protic nucleophilic group may include, for example, a tertiary phosphine or tertiary amino group. The nitrogen atom of an amino group or phosphorus atom of a phosphine group may be bonded directly to a carbon atom of the ring structure. Alternatively, the amine nitrogen or phosphine phosphorus atom may be indirectly bonded to a carbon atom of the ring structure through some bridging group which may be, for example, alkylene or other hydrocarbyl group. A non-protic nucleophilic group may take the form $-(CH_2)_yN(R^2)_2$ or $-(CH_2)_yP(R^2)_2$, wherein y is from 0 to 6, preferably 0, 1 or 2, more preferably 0, and each R² is independently an alkyl group, inertly substituted alkyl group, phenyl group, or inertly substituted phenyl group.

Specific bicyclic amidine compounds include 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), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) and 6-(dibutylamino)-1,8-diazabicyclo[5.4.0]undec-7-ene, where the butyl groups of the 6-(dibutylamino)-1,8-diazabicyclo[5.4.0]undec-7-ene are independently n-butyl, sec-butyl or t-butyl groups.

Other suitable cyclic amidine compounds include imidazole and imidazole derivatives, including those corresponding to Structure II:



wherein R³ and each R⁴ is independently hydrogen, unsubstituted hydrocarbyl or inertly substituted hydrocarbyl. R³ preferably is hydrogen, alkyl, alkenyl, phenyl, or alkyl-substituted phenyl; if alkyl or alkenyl R³ preferably has up to 12, up to 8, up to 6 or up to 4 carbon atoms. R³ may be methyl or ethyl. Any R⁴ may be hydrogen, alkyl, alkenyl, phenyl, or alkyl-substituted phenyl; if alkyl or alkenyl R⁴ preferably has up to 12, up to 8, up to 6 or up to 4 carbon atoms. R⁴ may be methyl or ethyl.

Specific examples of imidazole and imidazole derivatives include 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.

The polymerization is performed in the presence of one or more starter compounds. The starter compound has one or more functional groups capable of being alkoxylated. The starter may contain any larger number of such functional groups. The functional groups may be, for example, primary, secondary or tertiary hydroxyl, primary amino, secondary amino or thiol. A preferred starter contains 1 or more such functional groups, preferably 2 or more of such functional groups, and may contain as many as 12 or more of such functional groups.

In certain embodiments, the functional groups are all hydroxyl groups and the starter does not contain primary and/or secondary amino groups or thiol groups. In some embodiments, the starter compound will have 2 to 8, 2 to 4 or 2 to 3 hydroxyl groups.

In certain embodiments, the functional groups are all primary and/or secondary amine groups and the starter does not contain primary and/or secondary hydroxyl groups (other than residual water) or thiol groups. In some embodiments, the starter compound will have 2 to 8, 2 to 4 or 2 to 3 primary and/or secondary amine groups.

The starter compound has an equivalent weight per functional group less than that of the polyether product. It may have an equivalent weight of 9 (in the case of water) to 6000 or more. In some embodiments, the starter compound has an equivalent weight of 9 to 4000, 9 to 2500, 30 to 1750, 30 to 1400, 30 to 1000, 30 to 500, or 30 to 250.

Equivalent weight of an alcohol or polyol is conveniently determined using titration methods such as ASTM 4274-16, which yield a hydroxyl number in mg KOH/gram of polyol that can be converted to equivalent weight using the relation $\text{equivalent weight} = 56,100 \div \text{hydroxyl number}$.

Among the suitable starters are vinyl alcohol, propenyl alcohol, allyl alcohol, acrylic acid, hydroxyethyl acrylate, hydroxyethyl methacrylate, a C₁₋₅₀ alkanol, phenol, cyclohexanol, an alkylphenol, water (considered for purposes of this invention as having two hydroxyl groups), ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, 1,4-butane diol, 1,6-hexane diol, 1,8-octane diol, cyclohexane dimethanol, glycerin, trimethylolpropane, trimethylolethane,

pentaerythritol, sorbitol, sucrose, phenol, polyphenolic starters such as bisphenol A or 1,1,1-tris(hydroxyphenyl)ethane, and the like.

Other suitable starters are amine compounds such as morpholine, piperadine, piperazine, toluene diamine (any isomer or mixture of isomers), phenylene diamine (any isomer or mixture of isomers), ethylene diamine, diethylene triamine, higher polyethylene polyamines having up to 8 nitrogen atoms, 1,3-propane diamine, 1,2-propane diamine, 1,4-butane diamine, cyclohexane diamine, isophorone diamine, bis(aminomethyl)cyclohexane and bis(3-aminopropyl) methyl amine.

Still other suitable starters are hydroxyl-terminated polyethers (including alkoxylates, especially ethoxylates and/or propoxylates, of hydroxyl-containing and/or amine starters including those just described) having hydroxyl equivalent weights less than that of the product of the polymerization. Such a polyether starter may have, for example, a hydroxyl equivalent weight of at least 125 and up to 6000, up to 4000, up to 2500, up to 1750, up to 1500, up to 1000, up to 500, or up to 250 g/equivalent. In some embodiments, the polyether starter may be a homopolymer of propylene oxide and/or a random or block copolymer of propylene oxide and one or more other alkylene oxides (especially ethylene oxide), which has a hydroxyl equivalent weight as mentioned in this paragraph and in which no more than 25%, no more than 15% or no more than 10% of the hydroxyl groups are primary.

In some embodiments, the aluminum compound is soluble in the starter at the proportions present at the start of the polymerization. Solubility is evaluated by combining the aluminum compound with the starter at the appropriate proportions and stirring at up to 160°C, preferably up to 75°C, for 15 minutes. The formation of a clear fluid upon visual inspection indicates that the aluminum compound is soluble in the starter.

Similarly, in some embodiments, the cyclic amidine is soluble in the starter at the proportions present at the start of the polymerization, solubility being evaluated in the manner just described with regard to the aluminum compound. Preferably, both the aluminum compound and cyclic amidine are soluble in the starter in the proportions present at the start of the polymerization.

The alkylene oxide(s) may be, for example, ethylene oxide, 1,2-propylene oxide (generally referred to herein as "propylene oxide"), oxetane, 1,2-butene oxide, 2-methyl-1,2-butanexoxide, 2,3-butane oxide, tetrahydrofuran, epichlorohydrin, hexene oxide, octene oxide, styrene oxide, divinylbenzene dioxide, a glycidyl ether such as Bisphenol A

diglycidyl ether, epichlorohydrin or other polymerizable oxirane. In some embodiments, the alkylene oxide is 1,2-propylene oxide, ethylene oxide, or a mixture of at least 50% (preferably at least 80%) by weight propylene oxide and correspondingly up to 50% (preferably up to 20%) by weight ethylene oxide. In some embodiments, two or more
5 alkylene oxides are polymerized simultaneously (to form random copolymers), and/or the composition of the alkylene oxide is changed one or more times, or even continuously, throughout the course of the polymerization to form block and/or random/block copolymers.

In specific embodiments, the starter is a poly(propylene oxide) or random
10 propylene oxide/ethylene oxide copolymer containing at least 50% or at least 70% by weight oxypropylene units and up to 50% or up to 30% ethylene oxide units, and the alkylene oxide is ethylene oxide. In such embodiments, the starter may have a hydroxyl equivalent weight of, for example, 500 to 3000, 500 to 2500 or 500 to 1750 g/equivalent. In such embodiments, the starter may be produced in the presence of an aluminum
15 compound and cyclic amidine in accordance with the invention and the ethoxylation of the starter may take place without further addition of aluminum compound and cyclic amidine, *i.e.*, in the presence of the same aluminum compound and cyclic amidine as was used to alkoxylate prior to the start of the final ethoxylation step, and/or without any step of neutralization, catalyst removal or catalyst deactivation after the starter is
20 produced and before the ethoxylation step.

The polymerization is performed by combining the starter, aluminum compound and cyclic amidine with the alkylene oxide(s) and optionally comonomer and then polymerizing the alkylene oxide(s). It is often convenient to combine at least a portion of the starter with at least part of the aluminum compound and at least part of the cyclic
25 amidine prior to contacting the aluminum catalyst and cyclic amidine with the alkylene oxide. The polymerization proceeds at a wide range of temperatures from -100°C to 250°C or more. In some embodiments, the reaction temperature is at least 80°C, at least 100°C, at least 120°C or at least 130°C. The polymerization temperature preferably does not exceed 190°C, and more preferably does not exceed 180°C. The polymerization
30 reaction usually is performed at a superatmospheric pressure, but can be performed at atmospheric pressure or even a subatmospheric pressure.

Enough of the aluminum compound is used to provide a commercially reasonable polymerization rate, but it is generally desirable to use as little of the aluminum compound as possible consistent with reasonable polymerization rates, as this both

reduces the cost for the catalyst and can eliminate the need to remove catalyst residues from the product. The amount of aluminum compound may be, for example, sufficient to provide 10 to 10,000 ppm of aluminum based on the weight of the alkylene oxide polymer or copolymer product of the polymerization. In specific embodiments, the amount of aluminum compound may be sufficient to provide at least 25 ppm, at least 50 ppm, at least 100 ppm or at least 250 ppm aluminum on the foregoing basis, and up to 5,000 ppm up to 2,500 ppm, up to 1500 ppm or up to 1000 ppm aluminum, again on the foregoing basis.

The amount of aluminum compound may be sufficient to provide, for example, at least 0.00005 moles of aluminum, at least 0.00075 moles of aluminum or at least 0.0001 moles of aluminum per equivalent of starter, and may be, for example, sufficient to provide up to 0.10 moles of aluminum, up to 0.075 moles of aluminum, up to 0.06 moles of aluminum, up to 0.05 moles of aluminum or up to 0.025 moles of aluminum per equivalent of starter.

The mole ratio of aluminum compound to cyclic amidine may be, for example, 1:10 to 10:1. A preferred ratio is at least 1:3, at least 1:2 or at least 2:3, and up to 5:1, up to 4:1, up to 3:1, up to 2.5:1, up to 2:1, up to 3:2, up to 4:3 or up to 1:1. The optimum ratio may vary among specific aluminum compound/cyclic amidine pairings. For example, when the aluminum compound is a trialkyl aluminum, the amount of cyclic amidine is preferably no greater than 0.75 mole per mole of aluminum compound.

The amount of cyclic amidine may be, for example, at least 0.00005 moles, at least 0.0001 mole or at least 0.0002 moles per equivalent of starter, and may be, for example, up to 0.10 mole, up to 0.075 moles, up to 0.06 mole, up to 0.05 mole or up to 0.025 mole per equivalent of starter.

Specific pairings of aluminum compound and cyclic amidine include:

Diethylaluminum chloride (Et_2AlCl) and DBU, Me-TBD or TBD. The mole ratio of these may be, for example, 1:2 to 4:1, especially 2:3 to 2:1;

Et_2AlCl and DBN. The mole ratio of these may be, for example, 1:2 to 4:1, especially >1:1 to 2:1;

Ethylaluminum dichloride (EtAlCl_2) and DBU or DBN. The mole ratio of these may be, for example, 1:2 to 4:1, especially >1:1 to 2:1;

EtAlCl_2 and Me-TBD or TBD. The mole ratio of these may be, for example, 1:2 to 4:1, especially 2:3 to 2:1;

DIBAL and DBU, Me-TBD or DBN. The mole ratio of these may be, for example, 1:2 to 4:1, especially 2:3 to 2:1;

DIBAL and TBD. The mole ratio of these may be, for example, 1:4 to 5:1, especially 1:2 to 4:1;

5 (iBu)₂AlCl or Al(BHT)₂Me and DBU, Me-TBD, DBN or TBD. The mole ratio of these may be, for example, 1:4 to 4:1, especially 1:2 to 4:1;

TEDA with DBU, Me-TBD or DBN. The mole ratio of these may be, for example, 1:2 to 4:1, especially 2:3 to 2:1;

10 TEDA with TBD. The mole ratio of these may be, for example, 1:6 to 4:1, especially 1:5 to 3:1;

a trialkyl aluminum compound, particularly 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 one or more of DBU, Me-TBD, DBN or TBD. The mole ratio of these may be, for
15 example, 1:2 to 4:1, especially 2:3 to 4:1 or 1:2 to 3:1.

The polymerization reaction can be performed batch-wise, semi-continuously (including with continuous addition of starter as described in US 5,777,177) or continuously.

In a batch polymerization, the aluminum compound, cyclic amidine, starter, 20 alkylene oxide(s) and optional comonomer are combined to form a reaction mixture, and the reaction mixture is heated in a reaction vessel to the polymerization temperature until the desired molecular weight is obtained. A preferred manner of performing the batch polymerization is to dissolve the aluminum compound and cyclic amidine into the starter, then combine the resulting solution with the alkylene oxide, followed by
25 subjecting the resulting mixture to polymerization conditions until the desired molecular weight is obtained and/or the alkylene oxide is consumed. The aluminum compound, the cyclic amidine, or both may be introduced in the form of a solution in an inert solvent such as a hydrocarbon like toluene or hexane.

In a semi-batch process, the aluminum compound, cyclic amidine and starter are 30 combined, preferably by dissolving the catalyst and cyclic amidine into the starter. A polyether monol or polyether polyol corresponding to the product of the polymerization, and/or a polyether of intermediate molecular weight between that of the starter and product, may be combined with the starter if desired. The contents of the vessel are heated if necessary to the polymerization temperature and a portion of the alkylene

oxide is introduced into the reaction vessel. When polymerization begins (typically as indicated by a drop of internal reactor pressure), more alkylene oxide is fed to the reactor under polymerization conditions. The alkylene oxide feed is continued until enough has been consumed to reach the target product molecular weight. Additional
5 aluminum compound and/or cyclic amidine may be added during the course of the alkylene oxide addition. In a semi-batch process, the entire amount of starter is commonly added at the start of the process. After the alkylene oxide feed is completed, the reaction mixture may be cooked down at the polymerization temperature to consume any remaining alkylene oxide.

10 A continuous polymerization includes the continuous or intermittent addition of at least alkylene oxide and starter, and continuous or intermittent removal of product during the polymerization. A continuous process is generally conducted by establishing steady-state concentrations (within the operational capabilities of the polymerization equipment) of the aluminum compound (or reaction products thereof), the cyclic
15 amidine, starter (or reaction products thereof), alkylene oxide and polymerizate under polymerization conditions in a continuous reactor such as a loop reactor, a plug flow reactor, or a continuous stirred tank reactor. The "polymerizate" is a mixture of polyethers that have molecular weights greater than that of the starter and up to that of the intended product. Additional aluminum compound, cyclic amidine, starter and
20 alkylene oxide are then continuously added to the reactor as the polymerization proceeds. These can be added as a single stream, as separate components, or in various sub-combinations, but the aluminum compound and cyclic amidine are preferably added in the form of a solution in the starter. A product stream is continuously or intermittently withdrawn from the reactor during the polymerization. The rates of the
25 additional stream(s) and product streams are selected to maintain steady-state conditions in the reactor (within the operational capabilities of the equipment), and to produce a product having a desired molecular weight.

The product stream withdrawn from the continuous reactor may be cooked down for some period of time to allow the unreacted alkylene oxide in that stream to be
30 consumed to low levels.

A continuous process is particularly suitable for producing a polyether product having a hydroxyl equivalent weight from 150 to 5000, especially from 350 to 2500 and still more preferably from 500 to 2000 g/equivalent.

In a semi-batch or continuous process as described above, the alkylene oxide(s) may be fed to the reactor on demand by continuously pressurizing the reactor with the alkylene oxide(s) to a predetermined internal reactor pressure and/or alkylene oxide partial pressure.

5 The polymerization reaction can be performed in any type of vessel that is suitable for the pressures and temperatures encountered. In a continuous or semi-continuous process, the vessel should have one or more inlets through which the alkylene oxide and additional starter compound can be introduced during the reaction. In a continuous process, the reactor vessel should contain at least one outlet through
10 which a portion of the partially polymerized reaction mixture can be withdrawn. A tubular reactor that has multiple points for injecting the starting materials, a loop reactor, and a continuous stirred tank reactor (CTSR) are all suitable types of vessels for continuous or semi-continuous operations. The reactor should be equipped with a means of providing and/or removing heat, so the temperature of the reaction mixture can be
15 maintained within the required range. Suitable means include various types of jacketing for thermal fluids, various types of internal or external heaters, and the like. A cook-down step performed on continuously withdrawn product is conveniently conducted in a reactor that prevents significant back-mixing from occurring. Plug flow operation in a pipe or tubular reactor is a preferred manner of performing such a cook-
20 down step.

The crude product obtained in any of the foregoing processes may contain up to 0.5% by weight, based on the total weight, of unreacted alkylene oxide; small quantities of the starter compound and low molecular weight alkoxylates thereof; and small quantities of other organic impurities and water. Volatile impurities (including
25 unreacted alkylene oxides) should be flashed or stripped from the product. The crude product typically contains catalyst residues and residues of the aluminum compound and/or cyclic amidine. It is typical to leave these residues in the product, but these can be removed if desired. Moisture and volatiles can be removed by stripping the polyol.

The process of the invention is useful for preparing polyether polyol products that
30 can have hydroxyl equivalent weights from as low as about 85 to as high as about 8,000 or more.

The polymerization reaction can be characterized by the "build ratio", which is defined as the ratio of the number average molecular weight of the polyether product to that of the starter compound. This build ratio may be as high as 160, but is more

commonly in the range of 2.5 to about 65 and still more commonly in the range of 2.5 to about 50. The build ratio is typically in the range of about 2.5 to about 15, or about 7 to about 11 when the polyether product has a hydroxyl equivalent weight of 85 to 400 g/equivalent.

- 5 In some embodiments the alkylene oxide is polymerized with or in the presence of one or more copolymerizable monomers that are not oxiranes. Examples of such copolymerizable monomers include carbonate precursors that copolymerize with an alkylene oxide to produce carbonate linkages in the product. Examples of such carbonate precursors include carbon dioxide, phosgene, linear carbonates and cyclic carbonates.
- 10 Other copolymerizable monomers include carboxylic acid anhydrides, which copolymerize with alkylene oxides to produce ester linkages in the product.

 In some embodiments, polyether polyols of the invention are homopolymers of propylene oxide or random copolymers containing at least 50%, at least 70% or at least 90% by weight oxypropylene units formed by polymerizing propylene oxide and

15 correspondingly up to 50%, up to 30% or up to 10% by weight oxyethylene units formed by polymerizing a mixture of propylene oxide and ethylene oxide (in each case without the presence of a copolymerizable monomer that is not an oxirane), having any one or more of the following characteristics:

- a) hydroxyl equivalent weight of at least 500, at least 750, at least 1000 or at least 1200, and up to 4000, up to 3000, up to 2500, up to 2200 or up to 2000 g/equivalent;
- 20 b) nominal hydroxyl functionality of 2 to 8;
- c) no more than 0.015, no more than 0.01, no more than 0.007 meq/g of terminal unsaturation;
- d) a polydispersity (Mw/Mn) by gel permeation chromatography of no more than
- 25 1.15, no more than 1.10, no more than 1.07 or no more than 1.05;
- e) no more than 2000 parts by million by weight (ppm), no more than 1200 ppm, no more than 1000 ppm, no more than 750 ppm, no more than 500 ppm, no more than 250 ppm, no more than 100 ppm or no more than 50 ppm, based on polyether polyol weight, of a fraction having a molecular weight by GPC of 40,000 g/mol or more; and
- 30 f) no more than 12%, no more than 10%, no more than 8%, no more than 6% or no more than 5% of the hydroxyl groups are primary hydroxyl groups as determined by ASTM D-4273 or equivalent method. The polyether product may have all of features a)-f).

In specific embodiments, the polyether polyol is a propylene oxide homopolymer or random copolymer of a mixture of at least 85% or at least 90% by weight propylene oxide and correspondingly up to 15% or up to 10% by weight ethylene oxide, based on the combined weight of all alkylene oxides, the polyether polyol in each case without the presence of a copolymerizable monomer that is not an oxirane; and the polyether polyol a) has a hydroxyl equivalent weight of 1000 to 2500 g/equivalent, b) has a nominal functionality of 2 to 8; c) has no more than 0.007 meq/g of terminal unsaturation; d) has a polydispersity (M_w/M_n) of no more than 1.07 and preferably no more than 1.05; and e) contains no more than 1200 ppm, no more than 1000 ppm, no more than 250 ppm or no more than 50 ppm of a fraction having a molecular weight by GPC of 40,000 g/mol or more. In addition, no more than 12%, no more than 10%, no more than 8%, no more than 6% or no more than 5% of the hydroxyl groups of such a polyether may be primary hydroxyl groups.

Polyether polyols produced in accordance with the invention are useful for making polyurethanes, among other things. Higher equivalent weight (500-8000 g/equivalent) polyether polyol products are useful in making elastomeric or semi-elastomeric polyurethane, including noncellular or microcellular elastomers, and flexible polyurethane foams. The flexible polyurethane foams may be made in a slabstock or molding process. Polyether polyol products having equivalent weights of about 225 to 400 are useful in making semi-flexible foams as well as the so-called viscoelastic or "memory" foams. Polyether polyols having equivalent weights of 85 to 400 are useful in making rigid polyurethane foams, such as thermal insulating foams for appliances, buildings, ship hulls and the like, as well as in various coating, adhesive, sealant and elastomer products. The polyether polyols tend to have properties quite similar to those made in conventional DMC-catalyzed polymerization process and in alkali metal hydroxide-catalyzed polymerization processes.

Polyether monols produced in accordance with the invention are useful as surfactants or as industrial solvents, among other uses.

The following examples are provided to illustrate the invention but are not intended to limit the scope thereof. All parts and percentages are by weight unless otherwise indicated.

Catalyst Preparation Procedure

The starter is heated at 70°C and purged with nitrogen and/or passed through a plug of alumina before use. 20 g of starter is transferred to a 50-mL glass jar. Under nitrogen, the indicated amounts of aluminum compound and cyclic amidine (if any) are combined with the starter. The jar is capped and its contents stirred for approximately 20 minutes. If the resulting mixture appears heterogeneous, the contents of the jar are heated at 70°C for 5-10 additional minutes with continued stirring, and then cooled.

Parallel Pressure Reactor (PPR) Polymerization Procedure

Alkylen oxide polymerizations and/or propylene oxide oxide/carbon dioxide copolymerizations are performed on using a 48-well Symyx Technologies Parallel Pressure Reactor (PPR). Each of the 48 wells is equipped with an individually weighed glass insert having an internal working liquid volume of approximately 5 mL. The wells each contain an overhead paddle stirrer.

0.7 mL of the starter/catalyst/cyclic amidine mixture (containing approximately 0.72 g of the starter) is charged to each insert. Each well is pressurized with 50 psig (344.7 kPa) of nitrogen and then heated to the polymerization temperature. Upon reaching the polymerization temperature 1 mL of the epoxide is injected into each well, where it reacts with the starter in the glass insert.

The internal pressure in the headspace of each well is monitored individually throughout the polymerization. Each hour after the first injection of epoxide, the internal pressure is observed, and if the pressure in any particular well has fallen below 190 psig (1.31 MPa), another 1 mL of the alkylen oxide is injected. This is repeated up to three times throughout the entire length of the run, which is 4 hours. 4 hours after the first epoxide injection, the wells are allowed to cool to room temperature and vented. The glass inserts are allowed to stand under nitrogen at 40-50°C overnight to allow residual epoxide to volatilize, after which the inserts are weighed to determine the amount of product.

The resulting products are analyzed for molecular weight and polydispersity (M_w/M_n) by gel permeation chromatography against a polystyrene standard. Primary hydroxyl content is determined by functionalizing the product with trifluoroacetic anhydride and evaluating the resulting product by ^{19}F NMR spectroscopy, per a standard method such as ASTM D-4273.

Examples 1-6 and Comparative Sample A

In these polymerizations, the starter is a 700 molecular weight, trifunctional poly(propylene oxide) and the aluminum compound is diethylaluminum chloride (Et₂AlCl). The amount of aluminum compound in each case is 2000 parts per million based on the weight of the starter (ppm). The mole ratio of aluminum compound to the cyclic amidine initially present is as indicated in Table 1; this ratio is also the mole ratio of aluminum atoms to cyclic amidine. The polymerization temperature is 160°C. The cyclic amidine is diazabicycloundecene (DBU), methyl-triazabicyclodecene (Me-TBD), 1,8-diazabicyclo-7-undecene (DBN) or triazabicyclodecene (TBD), as indicated in Table 1, as are the amount of product produced, the % of hydroxyl groups that are primary, the number average molecular weight and the polydispersity (PDI, M_w/M_n).

Table 1—PO Polymerizations with Et₂AlCl

Sample	ppm Al compound	Cyclic amidine	Al:cyclic amidine ratio ¹	Yield, g	% 1° OH	PDI	M _n
Comp. A*	2000	None	N/A	1.50	7	1.08	1636
Ex. 1	2000	DBU	1:1	3.09	4	1.03	3865
Ex. 2	2000	Me-TBD	1:1	2.67	5	1.03	3233
Ex. 3	2000	DBN	1:1	0.99	5	1.03	1064
Ex. 4	2000	TBD	1:2	0.80	8	1.03	942
Ex. 5	2000	TBD	1:1	3.04	5	1.03	3829
Ex. 6	2000	TBD	2:1	2.39	4	1.04	2761

*Comparative. ¹Mole ratio, aluminum compound to cyclic amidine.

DBU and Me-TBD, at a mole ratio of 1:1 relative to the aluminum compound, provides a large increase in polymerization rate and product molecular weight, compared with the control which lacks any cyclic amidine compound. DBN at the same level provides no such increase at this particular ratio of Et₂AlCl:DBN; better results are expected at a higher ratio, as suggested by the results with TBD (Examples 4-6). Examples 4-6 demonstrate the effect of Al:cyclic amidine ratio with TBD. A lower ratio (*i.e.*, high relative amount of TBD), as in Ex. 4, appears to suppress catalytic activity, leading to a lower yield. Ratios of 1:1 and 2:1 lead to very large increases in both yield and product molecular weight.

Examples 7-13 and Comparative Sample B

In these polymerizations, the starter is a 700 molecular weight, trifunctional poly(propylene oxide), the alkylene oxide is propylene oxide and the aluminum compound is ethylaluminum dichloride (EtAlCl₂). The amount of aluminum compound in each case is as indicated in Table 2. The mole ratio of aluminum compound to the cyclic amidine in each case is as indicated in Table 2; this ratio is also the mole ratio of aluminum atoms to cyclic amidine in each case. The polymerization temperature is 160°C. The cyclic amidine is as indicated in Table 2, as are the amount of product produced, the % of hydroxyl groups that are primary, the number average molecular weight and the polydispersity (PDI, M_w/M_n).

Table 2—PO Polymerizations with EtAlCl₂

Sample	ppm Al compound	Cyclic amidine	Al:cyclic amidine ratio ¹	Yield, g	% 1° OH	PDI	M _n
Comp. B*	2000	None	N/A	1.41	33	1.06	1669
Ex. 7	2000	DBU	1:1	1.29	5	1.04	1570
Ex. 8	2100	DBN	1:1	0.88	4	1.03	1029
Ex. 9	2100	Me-TBD	1:1	2.98	5	1.03	3145
Ex. 10	2100	TBD	1:2	0.82	ND	ND	ND
Ex. 11	2100	TBD	1:1	2.84	5	1.03	3404
Ex. 12	2100	TBD	2:1	2.99	5	1.08	3544
Ex. 13	2100	TBD	4:1	0.73	4	1.07	871

*Comparative. ND—not done. ¹Mole ratio, aluminum atoms to cyclic amidine.

At a mole ratio of 1:1, DBU and DBN do not increase yield or product molecular weight compared to the case in which no cyclic amidine compound is present. The data using TBD (Ex. 10-13) suggest that DBU and DBN will provide benefits at higher ratios of aluminum atoms to DBU or DBN. Me-TBD provides a large increase in yield even when present at the 1:1 mole ratio. Examples 10-13 again demonstrate the sensitivity of aluminum to TBD ratio. Excellent results are seen at the 1:1 and 2:1 ratios, but only small yields and low product molecular weights are obtained at the 1:2 and 4:1 ratios.

Examples 14-20 and Comparative Sample C

Polymerizations are performed in the same general manner as in the previous examples, using various cyclic amidines as indicated in Table 3. The aluminum compound is diisobutyl aluminum hydride (DIBAL). The mole ratio of DIBAL to the

cyclic amidine is as indicated in Table 3, as are the amount of DIBAL and the results. The mole ratio of DIBAL to the cyclic amidine is also the mole ratio of aluminum atoms to cyclic amidine in each case.

5

Table 3—PO Polymerizations with DIBAL

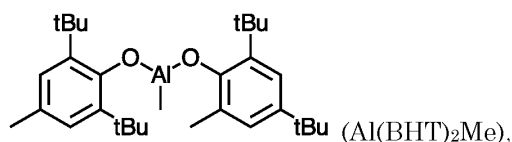
Sample	Al compound	ppm Al compound	Cyclic amidine	Al:cyclic amidine ratio ¹	Yield, g	% 1° OH	PDI	M _n
Comp. C*	DIBAL	2000	None	N/A	1.19	31	1.06	1392
Ex. 14	DIBAL	2350	DBN	1:1	1.91	5	1.03	2214
Ex. 15	DIBAL	2350	Me-TBD	1:1	2.02	5	1.03	2332
Ex. 16	DIBAL	2350	DBU	1:1	2.66	5	1.02	3016
Ex. 17	DIBAL	2100	TBD	1:2	1.60	5	1.08	1860
Ex. 18	DIBAL	2100	TBD	1:1	2.85	5	1.07	3431
Ex. 19	DIBAL	2100	TBD	2:1	2.52	7	1.08	2894
Ex. 20	DIBAL	2100	TBD	4:1	1.78	10	1.08	2011

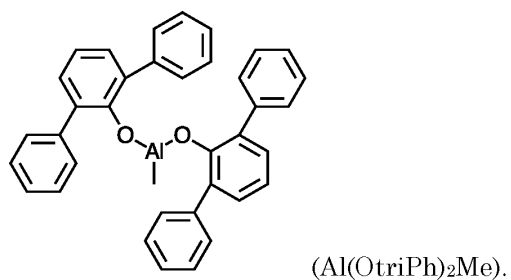
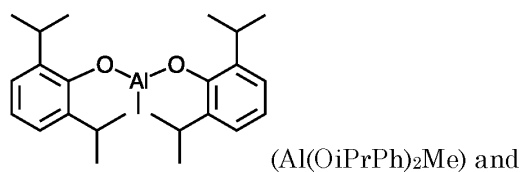
*Comparative. ¹Mole ratio, aluminum compound to cyclic amidine.

All of the cyclic amidines provide increases in yield and product molecular weight when used with DIBAL. The data with TBD indicates that DIBAL:cyclic amidine combinations are less sensitive to DIBAL:cyclic amidine ratio than are some other aluminum compounds, although best results are still seen at the 1:1 and 2:1 ratios.

Examples 21-24 and Comparative Samples D-F

Polymerizations are performed in the same general manner as in the previous examples, using various aluminum compounds as indicated in Table 4, in combination with TBD. The aluminum compounds are di(isobutyl)aluminum chloride (iBu₂AlCl),





The mole ratio of aluminum compound to the cyclic amidine is as indicated in Table 4, as are the amount of aluminum compound and the results. The mole ratio of aluminum compound to the cyclic amidine is also the mole ratio of aluminum atoms to cyclic amidine in each case.

Table 4—PO Polymerizations Using Various Al Compounds and TBD

Sample	Al compound	ppm Al Compound	Cyclic amidine	Al:cyclic amidine ratio ¹	Yield, g	% 1° OH	PDI	M _n
Comp. D*	(iBu) ₂ AlCl	2950	None	N/A	1.68	16	1.05	1846
Ex. 21	(iBu) ₂ AlCl	2950	TBD	1:1	2.75	4	1.03	3281
Comp. E*	Al(BHT) ₂ Me	2000	None	N/A	0.83	ND	1.04	1045
Ex. 22	Al(BHT) ₂ Me	2000	TBD	1:1	1.27	6	1.03	1568
Ex. 23	Al(OiPrPh) ₂ Me	6600	TBD	1:1	2.00	ND	1.03	2361
Comp. F*	Al(OtriPh) ₂ Me	8850	None	N/A	1.41	ND	1.06	1592
Ex. 24	Al(OtriPh) ₂ Me	8850	TBD	1:1	2.75	ND	1.03	3352

*Comparative. ND—not done. ¹Mole ratio, aluminum compound to cyclic amidine.

In each case, the addition of TBD leads to a large increase in yield and product molecular weight.

Examples 25-32 and Comparative Sample G

5 Polymerizations are performed in the same general manner as in the previous examples, using tetraethyldialuminoxane (TEDA) in combination with various cyclic amidines as indicated in Table 5. The mole ratio of TEDA to the cyclic amidine is as indicated in Table 5, as are the amount of TEDA and the results. Because TEDA contains two aluminum atoms, the mole ratio of aluminum atoms to cyclic amidine in
 10 each case is double the mole ratio of TEDA to the cyclic amidine reported in Table 5.

Table 5—PO Polymerizations Using TEDA

Sample	Al compound	ppm Al compound	Cyclic amidine	Al:cyclic amidine ratio ¹	Yield, g	% 1° OH	PDI	M _n
Comp. G*	TEDA	3100	None	N/A	1.47	36	1.06	1657
Ex. 25	TEDA	1550	DBN	1:1	3.04	5	1.03	3361
Ex. 26	TEDA	1550	Me-TBD	1:1	0.80	4	1.03	971
Ex. 27	TEDA	1550	DBU	1:1	2.79	5	1.03	3206
Ex. 28	TEDA	1550	TBD	1:8	0.84	ND	ND	ND
Ex. 29	TEDA	1550	TBD	1:4	2.06	ND	1.03	2556
Ex. 30	TEDA	1550	TBD	1:2	2.91	5	1.03	3579
Ex. 31	TEDA	1550	TBD	1:1	2.79	6	1.03	3357
Ex. 32	TEDA	1550	TBD	2:1	2.45	9	1.04	2831

*Comparative. ND—not done. ¹Mole ratio, aluminum compound to cyclic amidine.

The combination of TEDA with DBN, DBU and TBD provides a large increase in yield and molecular weight, compared to the case of TEDA by itself. Me-TBD does not
 15 lead to such increases at the 1:1 ratio evaluated, but is expected to provide yield and molecular weight increases at different ratios of TEDA to Me-TBD. At very low TEDA-TBD ratios, as in Example 28, the TBD has little effect on yield or molecular weight, but otherwise the TEDA/TBD combination exhibits a large positive effect over a range of TEDA:TBD ratios.

20

Examples 33-42

Various combinations of aluminum compound and cyclic amidine are evaluated in propoxylations of small molecule starters. The starters are glycerin, sorbitol, ortho-toluene diamine (oTDA), and bis(3-aminopropyl) methyl amine (BAPMA). The cyclic amidine is TBD in all cases. The mole ratio of aluminum compound to TBD is 1:1 in all cases; the mole ratio of aluminum atoms to cyclic amidine is also 1:1. Polymerizations are performed in the same general manner as in the previous examples. The aluminum compound is as indicated in Table 6, as are the results of the polymerizations.

Table 6—PO Polymerizations from Small Molecules Using TBD

Sample	Al compound	ppm Al compound	Starter	Starter molecular weight	Yield, g	PDI	M _n
Ex. 33	Et ₂ AlCl	2000	glycerin	92	1.73	1.06	304
Ex. 34	EtAlCl ₂	2000	glycerin	92	1.75	1.07	302
Ex. 35	Al(BHT) ₂ Me	8000	glycerin	92	1.74	1.06	308
Ex. 36	Et ₂ AlCl	2000	sorbitol	182	1.37	1.05	462
Ex. 37	EtAlCl ₂	2000	sorbitol	182	1.28	1.05	462
Ex. 38	Al(BHT) ₂ Me	8000	sorbitol	182	1.48	1.05	439
Ex. 39	Et ₂ AlCl	2000	oTDA	122	2.47	1.01	377
Ex. 40	EtAlCl ₂	2000	oTDA	122	2.57	1.01	374
Ex. 41	Et ₂ AlCl	2000	BAPMA	142	2.19	1.07	337
Ex. 42	EtAlCl ₂	2000	BAPMA	142	2.19	1.06	330

As demonstrated by the data in Table 4, the combination of various aluminum compounds with TBD results in the effective propoxylation of various low molecular weight hydroxyl-containing and amine-containing starters. As before, polydispersity remains low.

Examples 43-45 and Comparative Samples H-J

Various combinations of aluminum compound and TBD are evaluated in ethoxylations of the 700 molecular weight triol starter described in previous examples. The ethoxylations are performed with and without TBD. The mole ratio of aluminum compound to TBD is 1:1 in all cases in which TBD is present; the mole ratio of aluminum atoms to cyclic amidine is also 1:1 in those cases. Polymerizations are performed in the same general manner as in the previous examples. The aluminum compound is as indicated in Table 7, as are the results of the polymerizations.

Table 7—EO Polymerizations Using TBD

Sample	Catalyst	ppm catalyst	Cyclic amidine	Yield, g	% 1° OH	PDI	M _n
Comp. H*	Et ₂ AlCl	2000	None	1.11	60	1.11	1293
Ex. 43	Et ₂ AlCl	2000	TBD	2.69	4	1.07	3641
Comp. I*	EtAlCl ₂	2000	None	1.03	ND	1.07	1400
Ex. 44	EtAlCl ₂	2000	TBD	2.59	5	1.07	3508
Comp. J*	Al(BHT) ₂ Me	8000	None	1.02	35	1.07	1360
Ex. 45	Al(BHT) ₂ Me	8000	TBD	2.37	ND	1.06	3253

5 *Comparative. ND is not determined.

The data in Table 7 shows that ethylene oxide is successfully polymerized onto a 700 molecular weight triol starter using an aluminum catalyst/cyclic amidine system.

Comparative Samples K-Q

10 PO polymerizations are performed in the same general manner as in the previous examples, using AlCl₃ or tris(diisopropoxylaluminum) phosphate (TDIPAP) as the aluminum compound in combination with TBD. The mole ratio of aluminum compound to TBD is as indicated in Table 8, as are the amount of aluminum compound and the results.

15 **Table 8—PO polymerizations Using AlCl₃ or Tri(diisopropylaluminum) phosphate**

Sample	Al compound	ppm Al compound	Al compound:TBD ratio ¹	Yield, g
Comp. K*	AlCl ₃	2000	N/A	0.79
Comp. L*	AlCl ₃	2000	2:1	0.75
Comp. M*	AlCl ₃	2000	1:1	0.76
Comp. N*	AlCl ₃	2000	1:2	0.74
Comp. O*	TDIPAP	2950	N/A	1.02
Comp. P*	TDIPAP	2950	1:1	1.05
Comp. Q*	TDIPAP	2950	1:3	0.86

*Comparative. ¹Mole ratio, aluminum compound to TBD.

Low yields are obtained in each case despite the presence of TBD, which is shown above to provide enhanced polymerization rates when used in conjunction with other aluminum catalysts.

5 Examples 46-57 and Comparative Samples R and S

Larger-scale propoxylations of the 700 molecular weight triol starter are performed in a semi-batch reactor using various aluminum compounds and TBD as the cyclic amidine. The cyclic amidine is omitted in Comp. Sample R. The aluminum compound:cyclic amidine molar ratio in each of Examples 46-53 and 55-57 is 1:1; this ratio is 2:1 for Example 54.

The amount of PO fed, the run time and yield are indicated in Table 9, together with the % primary hydroxyl groups, polydispersity and M_n of the product. Less PO is fed in Comparative Samples R and S and in Example 47 due to slow rates of polymerization.

Table 9

Sample	Al compound	ppm Al Compound	Cyclic amidine	PO partial pressure (psi)	PO fed (mL)	Run Time (hr)	Yield (g)	%I OH	PDI	M _n
R*	TEDA	1555	None	30	34	19.6	56	ND	1.04	1356
46	TEDA	1555	TBD	30	164	11.3	157	ND	1.03	3633
47	Al(BHT) ₂ Me	8000	TBD	8	98	62.2	109	ND	1.04	2477
48	Al(BHT) ₂ Me	8000	TBD	20	164	13.5	165	6	ND	ND
50	Al(BHT) ₂ Me	8000	TBD	30	164	12.8	161	ND	1.04	3647
51	Et ₂ AlCl	2000	TBD	20	164	19.5	163	5	1.03	3612
52	EtAlCl ₂	2000	TBD	20	164	24.5	158	ND	1.04	3512
53	AlMe ₃	1200	TBD	30	164	15.2	157	ND	1.03	3544
54	AlMe ₃	1200	TBD**	30	164	11.5	158	ND	1.03	3594
S*	AlEt ₃	1900	None	30	100	22.4	106	22	1.12	2035
55	AlEt ₃	1900	TBD	30	164	26.6	153	7	1.03	3463
56	AlEt ₃	1900	DBU	30	164	12.8	161	4	1.03	3707
57	AlEt ₃	1900	MTBD	30	164	8.4	160	4	1.03	3749

*Comparative. **Aluminum catalyst:TBD mole ratio is 2:1 in this example; the mole ratio of Al compound to cyclic amidine is 1:1 for all other examples.

Large increases in yield and molecular weight are again seen in these semi-batch polymerizations when the cyclic amidine is present. Polydispersity and the proportion of primary hydroxyl groups each are quite low. The results with AlMe_3 and AlEt_3 are particularly surprising in that low proportions of primary hydroxyl groups are obtained.

5 Trialkyl aluminum catalysts by themselves are known to be poorly stereospecific, promoting both the head-to-tail and head-to-head polymerizations of propylene oxide. This phenomenon is illustrated by Comparative Sample S, in which 22% of the hydroxyl groups are primary. Including the cyclic amidine not only increases yield and molecular weight but also promotes greater stereospecificity, yielding a product having a low

10 proportion of primary hydroxyl groups.