*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.

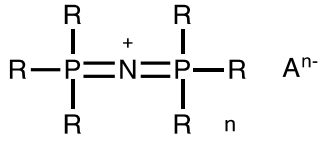
Diethylaluminum chloride is described as an alkylene oxide polymerization catalyst in a solution polymerization without a starter at temperatures up to 110°C in US 3,029,216 and in a bulk polymerization without a starter at 25°C in *J. Polym. Sci.* 1959, 34, 157-160. High molecular weight polymers are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

This disclosure provides 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, (ii) at least one starter, (iii) at least one alkylene oxide, (iv) from 0.00005 to 0.1 mole, per equivalent of starter, of at least one phosphazene-nitrogen base and optionally (v) at least one comonomer that is not an oxirane, and polymerizing the alkylene oxide(s) or copolymerizing the alkylene oxide(s) and the comonomer to form the alkylene oxide polymer or copolymer.

In one aspect, this disclosure provides 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, (ii) at least one starter, (iii) at least one alkylene oxide, (iv) from 0.00005 to 0.1 mole, per equivalent of starter, of at least one phosphorus-nitrogen base and optionally (v) at least one comonomer that is not an oxirane, and polymerizing the alkylene oxide(s) or copolymerizing the alkylene oxide(s) and the comonomer to form the alkylene oxide polymer or copolymer,

wherein the phosphorus-nitrogen base is represented by any of structures I, II, III, IIIa, IV or VI, or is a phosphine compound represented by structures (V) or (VIa), wherein:

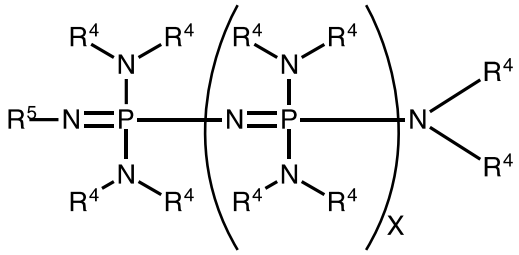
structure I is



(I)

wherein each R is hydrocarbyl, $NH_2$ or $–N=P-R_3$, A is an anion, and n is the valence of the anion A, the phosphorus-nitrogen base having a molecular mass of up to 1000 g/mol;

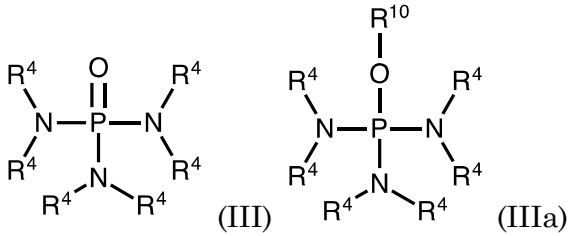
structure II is



(II)

wherein $R^5$ and each $R^4$ are independently $–P[N(R^4)_2]_3$ or hydrocarbyl, provided that any two hydrocarbyl $R^4$ groups may form a divalent hydrocarbyl group that forms a ring that includes the nitrogen atom or atoms to which such $R^4$ groups are bonded, x is a positive number and the phosphorus-nitrogen base has a molecular weight of up to 1000 g/mol;

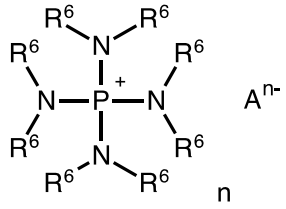
structures III and IIIa are:



(III) (IIIa)

wherein each $R^4$ are independently $–PN(R^4)_3$, hydrocarbyl (more preferably alkyl or alkylene), provided that any two $R^4$ groups may form a divalent hydrocarbyl group that forms a ring that includes the nitrogen atom or atoms to which such $R^4$ groups are bonded, $R^{10}$ is hydrocarbyl, and the phosphorus-nitrogen base has a molecular weight of up to 1000 g/mol;

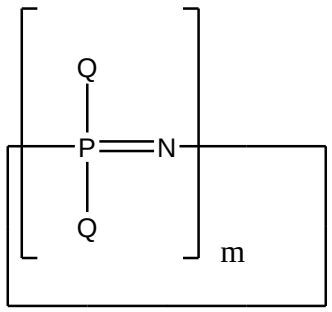
structure IV is:



(IV)

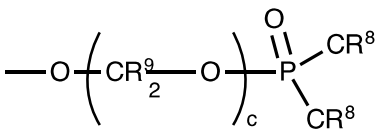
where A is an anion, and n is the valence of the anion A, and each $R^6$ is independently hydrocarbyl or -N=P-$(NR^6_2)_3$, provided further that any two $R^6$ groups may form a divalent hydrocarbyl group that forms a ring that includes the nitrogen atom or atoms to which such $R^6$ groups are bonded, and the phosphorus-nitrogen base having a molecular mass of up to 1000 g/mol;

structure VI is:



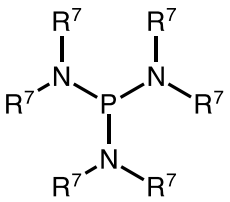
(VI)

in which m is a number from 3 to 20, each Q is independently selected from hydrocarbyl or –N=P-$R_3$, where each R is independently hydrocarbyl, aryloxy; alkoxy; and

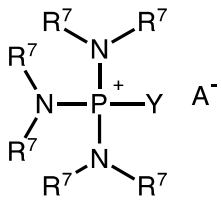


wherein c is zero or a positive number which is preferably up to 4, each $R^9$ is independently hydrocarbon, and each $R^8$ is independently hydrocarbon; and

wherein structure V and structure VIa are:



(V)



(VIa)

wherein each $R^7$ is independently hydrocarbyl, provided that any two $R^7$ groups may form a divalent hydrocarbyl group that forms a ring that includes the nitrogen

atom or atoms to which such $R^7$ groups are bonded, Y is halogen, A is a monovalent anion and the phosphorus-nitrogen base has a molecular weight of up to 1000 g/mol.

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

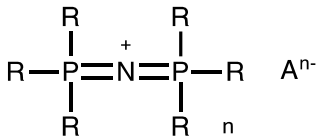
Process advantages include rapid polymerization rates; the ability to alkoxylate starters that have a wide range of molecular weights, in particular low molecular weight starters that have hydroxyl equivalent weights of 30 to 75; the ability to use significantly lower levels of catalyst than needed with 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

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, (ii) at least one starter, (iii) at least one alkylene oxide, (iv) from 0.00005 to 0.1 mole, per equivalent of starter, of at least one phosphorus-nitrogen base and optionally (v) at least one comonomer that is not an oxirane, and polymerizing the alkylene oxide(s) or copolymerizing the alkylene oxide(s) and the comonomer to form the alkylene oxide polymer or copolymer,

wherein the phosphorus-nitrogen base is represented by any of structures I, II, III, IIIa, IV or VI, or is a phosphine compound represented by structures (V) or (VIa), wherein:

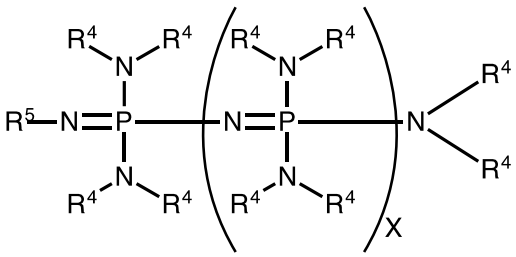
structure I is



(I)

wherein each R is hydrocarbyl, $NH_2$ or $–N=P-R_3$, A is an anion, and n is the valence of the anion A, the phosphorus-nitrogen base having a molecular mass of up to 1000 g/mol;

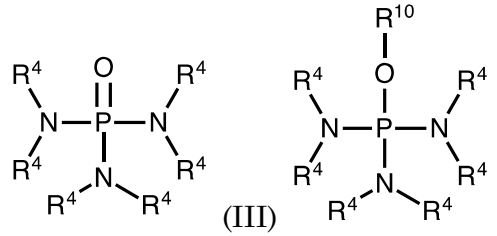
structure II is



(II)

wherein $R^5$ and each $R^4$ are independently $–P[N(R^4)_2]_3$ or hydrocarbyl, provided that any two hydrocarbyl $R^4$ groups may form a divalent hydrocarbyl group that forms a ring that includes the nitrogen atom or atoms to which such $R^4$ groups are bonded, x is a positive number and the phosphorus-nitrogen base has a molecular weight of up to 1000 g/mol;

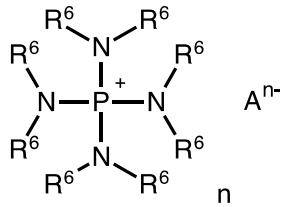
structures III and IIIa are:



(III) (IIIa)

wherein each $R^4$ are independently $–PN(R^4)_3$, hydrocarbyl (more preferably alkyl or alkylene), provided that any two $R^4$ groups may form a divalent hydrocarbyl group that forms a ring that includes the nitrogen atom or atoms to which such $R^4$ groups are bonded, $R^{10}$ is hydrocarbyl, and the phosphorus-nitrogen base has a molecular weight of up to 1000 g/mol;

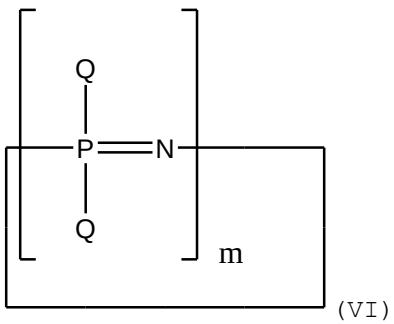
structure IV is:



(IV)

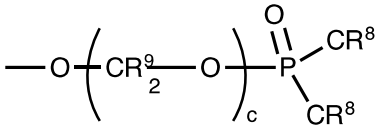
where A is an anion, and n is the valence of the anion A, and each $R^6$ is independently hydrocarbyl or $-N=P-(NR^6_2)_3$, provided further that any two $R^6$ groups may form a divalent hydrocarbyl group that forms a ring that includes the nitrogen atom or atoms to which such $R^6$ groups are bonded, and the phosphorus-nitrogen base having a molecular mass of up to 1000 g/mol;

structure VI is:



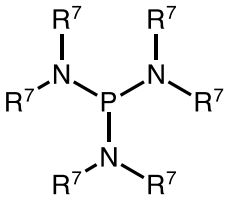
(VI)

in which m is a number from 3 to 20, each Q is independently selected from hydrocarbyl or $–N=P-R_3$, where each R is independently hydrocarbyl, aryloxy; alkoxy; and

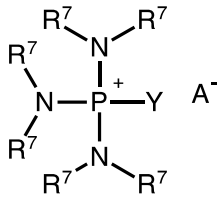


wherein c is zero or a positive number which is preferably up to 4, each $R^9$ is independently hydrocarbon, and each $R^8$ is independently hydrocarbon; and

wherein structure V and structure VIa are:



(V)



(VIa)

wherein each $R^7$ is independently hydrocarbyl, provided that any two $R^7$ groups may form a divalent hydrocarbyl group that forms a ring that includes the nitrogen atom or atoms to which such $R^7$ groups are bonded, Y is halogen, A is a monovalent anion and the phosphorus-nitrogen base has a molecular weight of up to 1000 g/mol.

2. The method of claim 1 wherein an aluminum atom of the aluminum compound is substituted with one or two hydrocarbyl groups, and is substituted with one or two halogen, oxo, ether, hydride or phosphonate 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, di methyl 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 one or more of bis(dimethylaluminum) methylphosphonate, bis(diethyl aluminum) methylphosphonate, bis(diethoxyaluminum) methylphosponate, bis(di-n-propylaluminum) methyl phosphonate, bis(diisopropyl aluminum) methylphosphonate, bis (di-n-propoxylaluminum) methyl phosphonate, bis(diisopropoxylaluminum) methylphosphonate, bis(di-t-butylaluminum) methyl phosphonate, bis(di-t-butoxyaluminum) methyl phosphonate, bis(diphenylaluminum) methyl phosphonate, bis(diphenoxyaluminum) methyl phosphonate, bis(diisobutylaluminum) methylphosphonate and a tetraalkylaluminoxane in which each alkyl group independently contains 1 to 6 carbon atoms.

6. The method of claim 1 wherein the phosphorus-nitrogen base is a fluoride, chloride, bromide, iodide, acetate, triflate, $BF4^-$ or $PF6^-$ salt of bis(triphenylphosphoranylidene)ammonium.

7. The method of claim 1 wherein the phosphorus-nitrogen base is one or more of methylimino-tris(dimethylamino)phosphorane, ethylimino-tris(dimethylamino)phosphorane, t-butylimino-tris(dimethylamino)phosphorane, tert-octylimino-tris(dimethylamino)phosphorane), phosphazene base P2, phosphazene base P2-Et, phosphazene base P2-t-Bu, phosphazene base P2-tert-octyl, ethylimino-tris(pyrrollidino)phosphorane, t-butylimino-tris(pyrrollidino)phosphorane, tert-

octylimino-tris(pyrrollidino)phosphorane, phosphazene base P4 (1-methyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)-phosphoranylidenamino]-2λ⁵,4λ⁵-catenadi(phosphazene)), 1-ethyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)-phosphoranylidenamino]-2λ⁵,4λ⁵-catenadi(phosphazene)) and 1-*tert*-Butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)-phosphoranylidenamino]-2λ⁵,4λ⁵-catenadi(phosphazene).

8. The method of claim 1 wherein the phosphorus-nitrogen base is one or more of hexamethylphosphoramide (tris(dimethylaminophosphine oxide), hexaethylphosphoramide, hexa-t-butylphosphoramide and tris (N,N-tetramethylene) phosphoramide.

9. The method of claim 1 wherein the phosphorus-nitrogen bases is one or more of 1,1,1,3,3,3-hexakis(dimethylamino)diphosphazenium fluoride, 1,1,1,3,3,3-hexakis(dimethylamino)diphosphazenium chloride, 1,1,1,3,3,3-hexakis(dimethylamino)diphosphazenium bromide, tetrakis[tris(dimethylamino)phosphoranylidenamino] phosphonium fluoride, tetrakis[tris(dimethylamino)phosphoranylidenamino]phosphonium chloride and tetrakis[tris(dimethylamino)phosphoranylidenamino] phosphonium bromide.

10. The method of claim 1 wherein the phosphorus-nitrogen base is a phosphine compound that is one or more of tris(dimethylamino)phosphine, tris(diethylamino)phosphine and tri(di-t-butylamino)phosphine.

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 proportions that provide 0.00005 to 0.05 moles of aluminum per equivalent of starter.

13. The method of any preceding claim wherein the mole ratio of the aluminum compound to the phosphorus-nitrogen base is at least 1:3, and up to 5:1.

14. 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 g/equivalent.

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

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

17. The method of any of claims 1-14 wherein the starter is a homopolymer of propylene oxide and/or a random or block copolymer of propylene oxide that has a hydroxyl equivalent weight of at least 125 and up to 4000 g/equivalent and in which no more than 25% of the hydroxyl groups are primary.