

TITLE

POLYMERIZATION OF OLEFINS

FIELD OF THE INVENTION

5 Olefins such as ethylene may be polymerized using polymerization catalysts containing transition metals complexed to neutral bidentate ligands and using as cocatalysts "alkylhaloaluminoxanes". These cocatalysts often give high polymer yields, even at relatively low
10 ratios of aluminum containing cocatalyst to transition metal. Haloalkylaluminum compounds also give good yields of polyethylene at relatively low ratios of aluminum containing cocatalyst to transition metal.

TECHNICAL BACKGROUND

15 Recently it has been found that certain complexes of late transition metals, such as Ni, Pd, Fe, and others are effective catalysts for the polymerization of various olefins, such as ethylene, propylene, higher
20 α -olefins, norbornenes, cyclopentenes, and others, and copolymers thereof. In some instances olefins containing polar groups such as esters may also be copolymerized. Descriptions of many of these polymerizations will be found in World Patent
25 Application 96/23010, and U.S. Patent 5,714,556.

While some of these complexes may by themselves be able to polymerize such olefins, more commonly a cocatalyst, particularly an alkylaluminum compound, is also added to the polymerization to form an active
30 polymerization system. Typically these cocatalysts have been alkylaluminoxanes (especially methylaluminoxanes), dialkylaluminum chlorides, and trialkylaluminum compounds. Sometimes, and particularly with trialkylaluminum compounds a second
35 cocatalyst, such as another Lewis acid, is also added. While alkylaluminum compounds are effective cocatalysts, they often suffer from one or more drawbacks, such as relatively low catalyst productivity

and/or rates, poor catalyst stability, and/or the need for relatively high amounts of the alkylaluminum compound in order to obtain good polymerization rates and/or catalyst productivity. Therefore catalyst systems which are overall improved are desirable.

The use of various alkylaluminum compounds as cocatalysts for the polymerization of olefins using various early transition metal catalysts such as Ziegler-Natta-type catalysts and metallocene-type catalysts is well known. Among the alkylaluminum compounds which have been used for such cocatalysts have been alkylhaloaluminoxanes such as diethyldichloroaluminoxane.

L. A. Volkov, et al., Vysokomol. Soedin., Ser. B, vol. 15, p. 455-457 (1973) report the use of bis(ethylchloroaluminum)oxide as a cocatalyst (with other cocatalysts) for the polymerization of 1,3-butadiene using a $\text{CoCl}_2(\text{pyridine})_2$ complex. The use of bidentate ligands is not mentioned.

Netherlands Patent Application 66/04717 reports the polymerization of butadiene using cobalt tris(acetylacetonate) and bis(ethylchloroaluminum)oxide as a cocatalyst. The use of neutral ligands is not mentioned.

U.S. Patents 5,714,556 and 5,866,663 describe the use of various polymerization processes using various late transition metal complexes as catalysts, together with various alkylaluminum compounds as catalysts. The use of alkylhaloaluminoxanes is not specifically described, and the polymerization processes described herein with haloalkylaluminum compounds are also not specifically described.

SUMMARY OF THE INVENTION

This invention concerns a process for the polymerization of an olefin or olefins comprising the step of contacting, under polymerizing conditions:

(i) (a) a transition metal polymerization catalyst wherein a metal of Groups 3 through 10 (new notation) is complexed to a neutral bidentate ligand, and (b) an alkylaluminum cocatalyst; and

5 (ii) at least one olefin capable of being polymerized thereby, characterized in that the alkylaluminum cocatalyst comprises a compound of the formula $R^1_a X_b AlO_d$, wherein:
a and b are each independently about 0.50 to about 1.50, and d is 0.5 to 1.0, both provided that $a+b+d$ is 2.0-2.5;

each R^1 is independently hydrocarbyl or substituted hydrocarbyl; and

X is carboxylate, fluoride, chloride, bromide or
15 iodide.

This invention also concerns a process for the polymerization of olefins, and particularly ethylene, comprising the step of contacting, under polymerizing conditions:

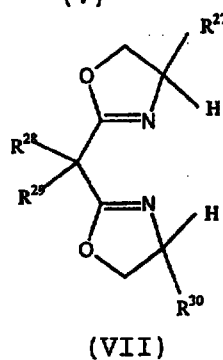
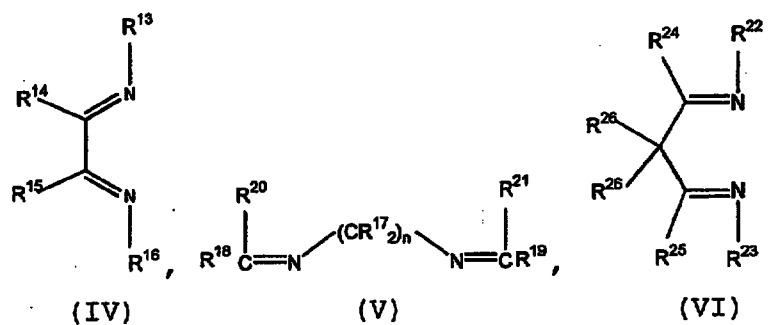
20 (i) (a) a transition metal polymerization catalyst wherein a metal of Groups 3 through 10 (new notation) is complexed to a neutral bidentate ligand, and (b) an alkylaluminum cocatalyst; and

(ii) ethylene,
25 characterized in that the alkylaluminum cocatalyst comprises a compound of the formula $R^{60}_q AlZ_t$, wherein:
q and t are each independently about 0.50 to about 2.50, provided that $q+t$ is about 3.0;

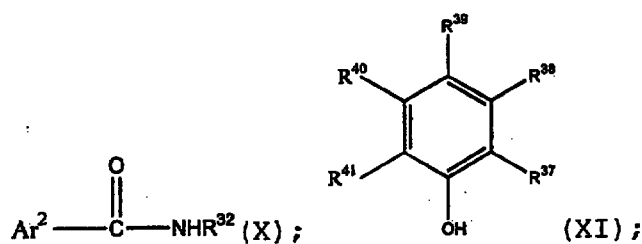
each R^{60} is independently hydrocarbyl or
30 substituted hydrocarbyl; and

Z is fluoride, chloride, bromide or iodide;
and further provided that the molar ratio of aluminum in $R^{60}_q AlZ_t$ to the transition metal in said transition metal polymerization catalyst is 75 to 500.

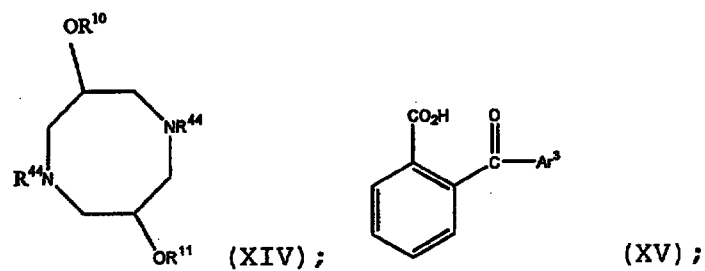
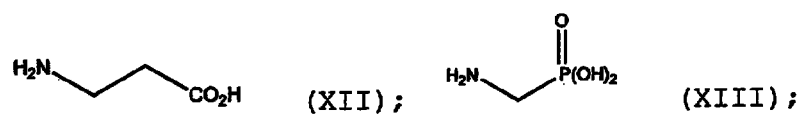
35 In the aforementioned processes, the polymerization catalyst is preferably a V, Cr, a rare earth metal, Fe, Co, Ni or Pd complex of a ligand selected from the group consisting of:

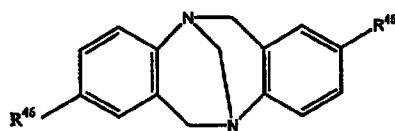


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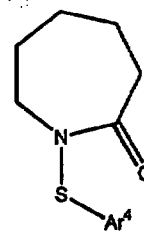


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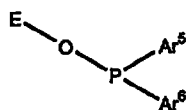




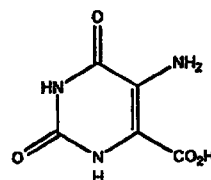
(XVI);



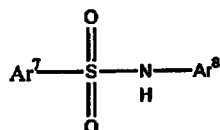
(XVII);



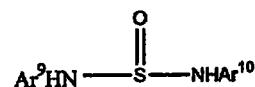
(XVIII);



(XIX);

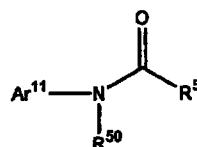


(XX);



(XXI);

5



(XXIII); and

 $R^{47}R^{48}R^{49}P$ (XXII); $R^{31}S-CR^{33}R^{34}(CR^{35}R^{36})_m-SR^{31}$ (XXIV);

wherein:

10 Ar^1 is an aromatic moiety with n free valencies,
or diphenylmethyl;

each Q is $-NR^{52}R^{53}$ or $-CR^{54}=NR^{55}$;

p is 1 or 2;

E is 2-thienyl or 2-furyl;

15 each R^{52} is independently hydrogen, benzyl,
substituted benzyl, phenyl or substituted phenyl;

each R^{54} is independently hydrogen or hydrocarbyl;

and

20 each R^{55} is independently a monovalent aromatic
moiety;

m is 1, 2 or 3;

R^{53} is hydrogen or alkyl;

each R^{33} , R^{34} , R^{35} , and R^{36} is independently
hydrogen, hydrocarbyl or substituted hydrocarbyl;

each R^{31} is independently hydrocarbyl or substituted hydrocarbyl containing 2 or more carbon atoms;

5 each R^{32} is independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

Ar^2 is an aryl moiety;

R^{38} , R^{39} , and R^{40} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or an inert functional group;

10 R^{37} and R^{41} are each independently hydrocarbyl, substituted hydrocarbyl or an inert functional group whose E_s is about -0.4 or less;

Ar^3 is an aryl moiety;

15 R^{45} and R^{46} are each independently hydrogen or hydrocarbyl;

Ar^4 is an aryl moiety;

Ar^5 and Ar^6 are each independently hydrocarbyl;

Ar^7 and Ar^8 are each independently an aryl moiety;

20 Ar^9 and Ar^{10} are each independently an aryl moiety or $-CO_2R^{56}$, wherein R^{56} is alkyl containing 1 to 20 carbon atoms;

Ar^{11} is an aryl moiety;

R^{50} is hydrogen or hydrocarbyl;

R^{51} is hydrocarbyl or $-C(O)-NR^{50}-Ar^{11}$;

25 R^{44} is aryl;

R^{47} and R^{48} are each independently phenyl groups substituted by one or more alkoxy groups, each alkoxy group containing 1 to 20 carbon atoms;

30 R^{49} is alkyl containing 1 to 20 carbon atoms, or an aryl moiety;

R^{22} and R^{23} are each independently phenyl groups substituted by one or more alkoxy groups, each alkoxy group containing 1 to 20 carbon atoms; and

35 R^{24} is alkyl containing 1 to 20 carbon atoms, or an aryl moiety;

each R^{26} is hydrogen, hydrocarbyl, or substituted hydrocarbyl, provided that both of R^{26} taken together may form a ring;

R¹⁰ and R¹¹ are each independently hydrogen or acyl containing 1 to 20 carbon atoms;

R¹³ and R¹⁶ are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom
5 bound to the imino nitrogen atom has at least two carbon atoms bound to it;

R¹⁴ and R¹⁵ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or R¹⁴ and R¹⁵ taken together are hydrocarbylene substituted
10 hydrocarbylene to form a carbocyclic ring;

R¹⁸ is hydrocarbyl or substituted hydrocarbyl, and R²⁰ is hydrogen, hydrocarbyl or substituted hydrocarbyl or R¹⁸ and R²⁰ taken together form a ring;

R¹⁹ is hydrocarbyl or substituted hydrocarbyl, and
15 R²¹ is hydrogen, substituted hydrocarbyl or hydrocarbyl, or R¹⁹ and R²¹ taken together form a ring;

each R¹⁷ is independently hydrogen, substituted hydrocarbyl or hydrocarbyl, or two of R¹⁷ taken together form a ring;

20 R²⁷ and R³⁰ are independently hydrocarbyl or substituted hydrocarbyl;

R²⁸ and R²⁹ are each independently hydrogen, hydrocarbyl or substituted hydrocarbyl; and

n is 2 or 3.

25

DETAILS OF THE PREFERRED EMBODIMENTS

In the polymerization processes and catalyst compositions described herein certain groups may be present. By hydrocarbyl is meant a univalent radical
30 containing only carbon and hydrogen. By substituted hydrocarbyl herein is meant a hydrocarbyl group which contains one or more (types of) substituents that do not interfere with the operation of the polymerization catalyst system. Suitable substituents in some
35 polymerizations may include some or all of halo, ester, keto (oxo), amino, imino, carboxyl, phosphite, phosphonite, phosphine, phosphinite, thioether, amide, nitrile, and ether. Preferred substituents are halo,

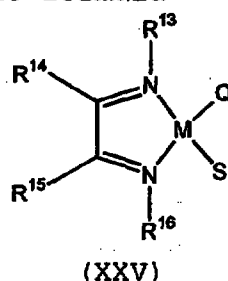
ester, amino, imino, carboxyl, phosphite, phosphonite, phosphine, phosphinite, thioether, and amide. Which substituents are useful in which polymerizations may in some cases be determined by reference to World Patent Application 96/23010 and U.S. Patent 5,714,556. By (substituted) hydrocarbylene is meant a group analogous to hydrocarbyl, except the radical is divalent. By benzyl is meant the $C_6H_5CH_2-$ radical, and substituted benzyl is a radical in which one or more of the hydrogen atoms is replaced by a substituent group (which may include hydrocarbyl). By an aryl moiety is meant a univalent group whose free valence is to a carbon atom of an aromatic ring. The aryl moiety may contain one or more aromatic ring and may be substituted by inert groups. By phenyl is meant the C_6H_5- radical, and a phenyl moiety or substituted phenyl is a radical in which one or more of the hydrogen atoms is replaced by a substituent group (which may include hydrocarbyl). Preferred substituents for substituted benzyl and phenyl include those listed above for substituted hydrocarbyl, plus hydrocarbyl. If not otherwise stated, hydrocarbyl, substituted hydrocarbyl and all other groups containing carbon atoms, such as alkyl, preferably contain 1 to 20 carbon atoms.

By an alkylaluminum compound is meant a compound which has at least one alkyl group bound to an aluminum atom.

For (IV) through (XXIV) preferred formulas and compounds (as ligands for polymerization catalysts) are found in World Patent Application 96/23010 and U.S. Patent 5,714,556, both of which are hereby included by reference, and preferred grouping and compounds in these applications are also preferred herein. However the compound numbers and group (i.e., R^x) numbers in these documents may vary from those herein, but they are readily convertible. These documents also describe synthesis of the various ligands.

There are many different ways of preparing active polymerization catalysts of Ni, Pd or other transition metal coordination compounds of compounds (IV) through (XXIV), many of which are described in World Patent Application 96/23010 and U.S. Patent 5,714,556, and those so described are applicable herein. "Pure" compounds which themselves may be active polymerization catalysts may be used, or the active polymerization catalyst may be prepared in situ by a variety of methods.

For instance, olefins, including ethylene, may be polymerized by contacting, at a temperature of about -100°C to about $+200^{\circ}\text{C}$ the cocatalyst (in formulas sometimes dubbed W herein), which is capable of abstracting either Q^- or S^- to form WQ^- or WS^- , and a second compound of the formula



and one or more olefins wherein:

M is a transition metal such as Ni or Pd;
 R^{13} and R^{16} are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

R^{14} and R^{15} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or R^{14} and R^{15} taken together are hydrocarbylene or substituted hydrocarbylene to form a ring;

Q is alkyl, hydride, perfluorocarboxylate, chloride, iodide, or bromide; and

S is alkyl, carboxylate, perfluorocarboxylate, hydride, chloride, iodide, or bromide, or other anions.

Which late transition metal containing polymerization catalysts will polymerize which olefins

will also be found in World Patent Application 96/23010 and U.S. Patent 5,714,556. Preferred monomers are monolefins and nonconjugated diolefins. Monomers useful herein include ethylene, propylene, other α -olefins of the formula $R^{67}CH=CH_2$, wherein R^{67} is n-alkyl containing 2 to about 20 carbon atoms, cyclopentene and norbornene. Preferred monomers are ethylene, propylene and cyclopentene, and ethylene is especially preferred. Olefins containing polar groups such as esters may also be used as comonomers with some of these polymerization catalysts.

Conditions for such polymerizations will also be found in World Patent Application 96/23010 and U.S. Patent 5,714,556. Briefly and generally, the temperature at which the polymerization is carried out is about $-100^{\circ}C$ to about $+200^{\circ}C$, preferably about $-20^{\circ}C$ to about $+80^{\circ}C$. The polymerization pressure which is used with a gaseous olefin is not critical, atmospheric pressure to about 275 MPa, or more, being a suitable range. With a liquid monomer the monomer may be used neat or diluted with another liquid (solvent) for the monomer. These polymerizations may be batch, semi-batch or continuous processes, and may be carried out in liquid medium or the gas phase (assuming the monomers have the requisite volatility). These details will also be found in World Patent Application 96/23010 and U.S. Patent 5,714,556. All the polymerizations may be run in the presence of a chain transfer agent, such as hydrogen or a silane, for example a silane of the formula R^{70}_3SiH wherein each R^{70} is hydrocarbyl or substituted hydrocarbyl, especially alkyl, for instance triethylsilane or trimethylsilane. Other alkylaluminum compounds may also be added, as additional cocatalysts and/or scavengers for impurities such as water.

In all these polymerization processes a preferred ligand is (IV). In all cases herein where (IV) appears, including as a ligand, it is preferred that R^{13} and R^{16} are each independently hydrocarbyl provided

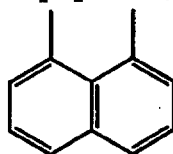
that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; and R^{14} and R^{15} are each independently hydrogen, hydrocarbyl, or R^{14} and R^{15} taken together are hydrocarbylene to form a
 5 ring. Some useful combinations and/or individual groupings for R^{13} , R^{14} , R^{15} and R^{16} are shown in Table I.

Table I

R^{13}	R^{14}	R^{15}	R^{16}
2,6-i-PrPh	Me	Me	2,6-i-PrPh
2,6-i-PrPh	H	H	2,6-i-PrPh
2,6-MePh	H	H	2,6-MePh
2,6-MePh	Me	Me	2,6-MePh
2,6-MePh	An	An	2,6-MePh
4-t-Bu-2,6-MePh	An	An	4-t-Bu-2,6-MePh
2-Cl-4,6-MePh	An	An	2-Cl-4,6-MePh
2,6-Cl-4-MeOPh	An	An	2,6-Cl-4-MeOPh
2,4,6-MePh	Me	Me	2,4,6-MePh
2-CF ₃ -6-MePh	An	An	2-CF ₃ -6-MePh
2,6-i-PrPh	An	An	2,6-i-PrPh
2,6-EtPh	Me	Me	2,6-EtPh
2,6-EtPh	An	An	2,6-EtPh
2-t-BuPh	Me	Me	2-t-BuPh
1-Np	Me	Me	1-Np
Ph ₂ CH	H	H	Ph ₂ CH
2-PhPh	Me	Me	2-PhPh
Ph	a	A	Ph
Ph	Me	Me	Ph
Ph	Ph	Ph	Ph
2,4,6-MePh	An	An	2,4,6-MePh
2,4,6-MePh	Ph	Ph	2,4,6-MePh

^a -CMe₂CH₂CMe₂-

In Table 1 and otherwise herein the following abbreviations are used: Me=methyl; Et=ethyl; Cl=chloro; Br=bromo; i-Pr=isopropyl; Ph=phenyl; t-Bu=t-butyl; and An=1,8-naphthylidene,

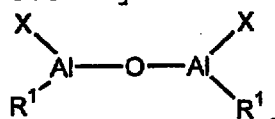


5 To indicate substitution on a phenyl ring, the nomenclature is abbreviated, the number of ring positions indicating how many of the substituents are on the ring. For instance, 4-Br-2,6-MePh indicates
10 4-bromo-2,6-dimethylphenyl.

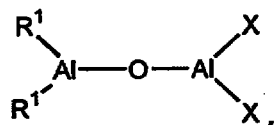
In all transition metal compounds it is preferred that the transition metal is a group 5 to group 10 element, more preferably, Co, Fe, V, Cr, Ni or Pd, especially preferably Ni or Pd, and most preferably Ni.

15 One cocatalyst herein is an alkylaluminum compound, an alkylhaloaluminoxane, of the formula $R^1_a X_b AlO_d$, wherein R^1 , X, a, b and d are as defined above. By an alkylaluminum compound is meant a
20 compound in which an aluminum atom has at least one alkyl group bound to it. In $R^1_a X_b AlO_d$, it is preferred that R^1 is alkyl containing 1 to 20 carbon atoms, more preferably contains 1 to 4 carbon atoms, and/or preferably that X is fluoride, chloride, bromide, or iodide, more preferably chloride or bromide and
25 especially preferably chloride, and/or that a and b are each independently about 0.75 to about 1.25, more preferably each about 1.0, and/or that d is about 0.5 to about 0.7, more preferably about 0.5. When X is carboxylate it is preferred that the conjugate acid of
30 X have a pKa in water of <2. The desired cocatalysts can be made by methods known in the art, see for instance M. Boleslawski, et al., Przem. Chem., vol. 65, p. 141-143 (1986); V. D. Petrova, et al., Izv. Akad. Nauk SSSR, Ser. Khim. p. 1373-1379 (1978); and
35 A. Storr, et al., J. Am. Chem. Soc., vol. 90, p. 3173-3177 (1968).

10 are each 1 and d is 0.5 may be formally written as

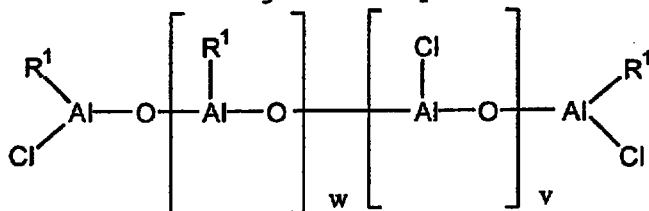


However, the molecular formula could also be written as



(XXVII)

15 which would also be a cocatalyst under the definition herein. In fact both of these species may exist in equilibrium with each other. Other more complex species, which are dimers, trimers, etc. may also be
20 present, such as an oligomeric species with the formula



In (XXVIII) w and v each independently may be 0 [if both are zero (XXVIII) is equal to (XXVI)] or an integer. When w and/or v is large, the d approaches 1. However, a and b are still each 1.0 (if w and v are equal). Other variations of the formula will be apparent. Such oligomers need not be linear.

The "molar ratio" of the alkylhaloaluminoxane
30 [moles meaning the total number of "gram-atoms" of Al
present in the alkylhaloaluminoxane] to "gram-atoms" of

transition metal present [it is understood that this refers to such metal atoms in the appropriate coordination compound(s)] is preferably about 1 or more, more preferably about 5 to about 2,000, especially preferably about 10 to about 1000, and very preferably about 25 to about 500. This ratio is often lower than is desirable than for other alkylaluminum compound cocatalysts in similar polymerizations.

Another useful cocatalyst described herein is an alkylhaloaluminum compound of the formula $R^{60}_qAlZ_t$. It is preferred that R^{60} is alkyl, more preferably alkyl containing 1 to 4 carbon atoms. Preferred specific groups for R^{60} are methyl, ethyl and isobutyl. It will be understood that, similarly to the alkylhaloaluminos above, the alkylhaloaluminum compounds may exist as mixtures of various molecules which may equilibrate with one another. In preferred formulas, q is 1.5 and t is 1.5 (the aluminum alkyl sesquihalides), or q is 2 and t is 1, or q is 1 and t is 2. Preferred groups Z are chlorine and bromine, and chlorine is especially preferred. Many of these compounds are available commercially.

Using the alkylhaloaluminum compounds, the ratio of aluminum to transition metal compound(s) is 75 to 500, preferably about 90 to about 450, more preferably about 100 to about 400, and especially preferably about 150 to about 350. At these ratios use of alkylaluminum compound is minimized, while maintaining good productivity for the catalyst.

In some instances when the alkylhaloaluminos and/or alkylhaloaluminum compounds are used as cocatalysts, polyolefins of lower molecular weight (higher melt index) are produced. This is advantageous when the lower molecular weights are desired, since chain transfer agents may not be needed or may be needed in lesser amounts. Some chain transfer agents may adversely affect the productivity of the transition

metal catalysts used, so under some conditions this may also be a productivity advantage.

In all the polymerization processes herein the alkylaluminum compounds other an alkylhaloaluminum or alkylhaloaluminum compound may also be present, as for example for use as a scavenger. These compounds do not count in the aluminum to transition metal ratio.

In these polymerizations it may also be advantageous to add another cocatalyst, which is a neutral Lewis acid, or a cation(ic) Lewis acid. Such neutral Lewis acids are described in World Patent Application 96/23010 and U.S. Patent 5,714,556. A useful Lewis acid is tris(pentafluorophenyl)boron. Cationic Lewis acids can include ionic compounds such as the tetrakis(pentafluorophenyl)borate anion salts with lithium, N,N-dimethylanilinium and triphenylcarbonium cations.

The polymerization processes herein may be run in the presence of various liquids, particularly aprotic organic liquids. The catalyst system, monomer(s), and polymer formed may be soluble or insoluble in these liquids, but obviously these liquids should not prevent the polymerization from occurring. Suitable liquids include alkanes, cycloalkanes, selected halogenated hydrocarbons, and aromatic hydrocarbons. Specific useful solvents include hexane, isooctane, cyclohexane, propane, methylene chloride, toluene and benzene.

The polymerizations herein may also initially be carried out in the solid state by, for instance, supporting the transition metal compound on a substrate such as silica, alumina, a magnesium halide, sodium chloride, or an organic polymer, activating it with the alkylaluminum compound and exposing it to monomer(s). Another method of making a supported catalyst is to start a polymerization or at least make a transition metal complex of another olefin or oligomer of an olefin such as cyclopentene on a support such as silica or alumina. These "heterogeneous" catalysts may be

used to catalyze polymerization in the gas phase or the liquid phase. By gas phase is meant that the ethylene is transported to contact with the catalyst particle while the ethylene is in the gas phase.

- 5 A preferred method of making a heterogeneous catalyst is to support the alkylhaloaluminum compound or alkylhaloaluminum compound on a solid such as silica or alumina particles. This may be done simply by exposing the particles to a solution of aluminum compound and
10 then filtering, or simply evaporating the solvent. In many instances, such as with silica and alumina, the support often contains groups on the surface which may chemically react with the aluminum compound, thereby covalently binding the aluminosilicate onto the support.
15 Aluminum compounds which are so reacted and on such surfaces are included within the meaning of those aluminum compounds in the claims herein even though they formally may not have the indicated formula since they reacted with the support. The transition metal
20 compound may then be added to the supported aluminum compound, and the combination simultaneously or later exposed to monomer(s) to begin the polymerization.

The combination of the transition metal catalyst compound mentioned above with a haloalkylaluminum compound or
25 a haloalkylaluminum compound, particularly when they are both on a solid support, is a catalyst component which is a novel composition. Where applicable the ratio of aluminum compound to transition metal, as described above, is also applicable to these catalyst
30 components. Preferred transition metal compounds and/or aluminum compounds, as described above, are also preferred in these catalyst components.

The polymers produced are useful in many applications depending on their properties. Such
35 polyolefins may be used as lubricants, molding resins, for film, for fiber, and as foam. Other uses may be found in World Patent Application 96/23010 and U.S. Patent 5,714,556.

In the Examples all pressures are gauge pressures, except for pressure less than 1 atmosphere, which are absolute pressures. Details of the calculation of methyl branches in the product polymers are found in
5 World Patent Application 96/23010. When taking melting points by DSC, a heating rate of 10°C/min was used. Melting points reported are peak melting points on the second heat. The following abbreviations are used:

Et - ethyl
10 iBu - isobutyl
DSC - Differential Scanning Calorimetry
Me - methyl
MI - melt index
MMAO-3A - modified methylaluminoxane, type 3A
15 MMAO-7 - modified methylaluminoxane, type 7
Mn - number average molecular weight
Mw - weight average molecular weight
PE - polyethylene
SMAO - silica-supported methylaluminoxane
20 Tm - melting point

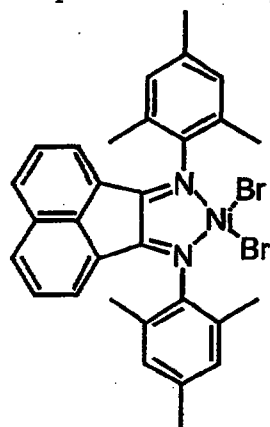
Materials

Condensed materials were handled in a nitrogen-purged glove box. Ethylene (Research Grade, 99.998%)
25 was supplied by Matheson. Nitrogen (99.998%, MG Industries) was passed through an OxiSORB® HP purification column (MG). Isooctane (HPLC grade, Aldrich Chemical Co. Milwaukee, WI, U.S.A.) was filtered through basic alumina (activity I) and stored
30 over SMAO (0.25 g/L, Albermarle, 14.2% Al). Toluene and dichloromethane (anhydrous, Aldrich) were filtered through basic alumina (activity I). 1,3-Dichloro-1,3-dimethylaluminoxane [MeAlCl]₂O (0.50 M in toluene),
1,3-dichloro-1,3-diethyldialuminoxane, [EtAlCl]₂O
35 (0.44M in toluene), and 1,3-dichloro-1,3-diisobutyldialuminoxane, [iBuAlCl]₂O (0.34M in toluene), were supplied by Aldrich. Modified methylaluminoxane-type 7, MMAO-7 (3.8 M Al in Isopar®

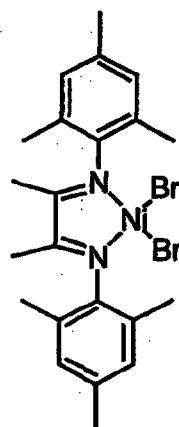
E isoparaffin solvent from Exxon, Corp., with a boiling point range of 118-137°C, and a specific gravity of 0.722), and type 3A, MMAO-3A (1.7 M Al in heptane), were supplied by Akzo Nobel.

- 5 Tris(pentafluorophenyl)boron, $B(C_6F_5)_3$, was supplied by Boulder Scientific. The following alkylaluminum chlorides were supplied by Aldrich: $MeAlCl_2$ (1.0 M in hexanes), $Me_3Al_2Cl_3$ (1.0 M in toluene), Me_2AlCl (1.0 M in hexanes), $EtAlCl_2$ (1.0 M in hexanes), $Et_3Al_2Cl_3$ (0.91
10 M in toluene), Et_2AlCl (1.0 M in hexanes), $iBuAlCl_2$ (neat). iBu_2AlCl (25 wt % in hexane) was supplied by Alfa Aesar. $iBu_3Al_2Cl_3$ (20 wt % in hexane) was supplied by Akzo Nobel.

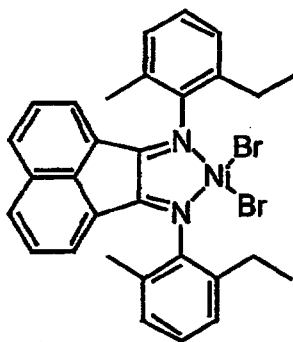
The polymerizations were carried out using various
15 nickel compounds. They were:



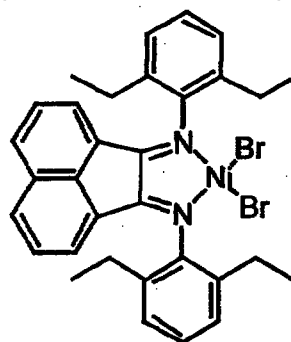
(XXIX)



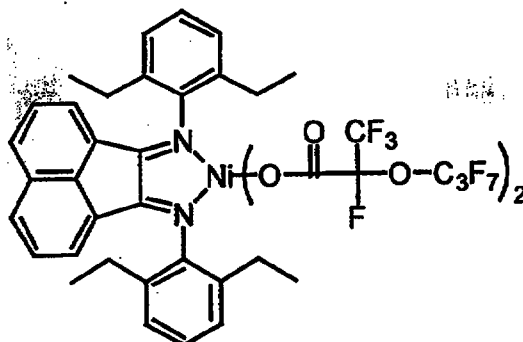
(XXX)



(XXXI)



(XXXII)



(XXXIII)

General Polymerization Procedure

A 600 mL pressure reactor equipped with a stirrer (1000 rpm) was used for the ethylene slurry polymerizations. The reactor was dried and purged at 130°C by cycling between nitrogen (1.72 MPa) and vacuum (800 Pa) two times, then by pressurizing with nitrogen (1.72 MPa) and venting to atmosphere three times. The reactor was cooled to ambient temperature under nitrogen (1.72 MPa).

Isooctane (200 mL) and catalyst or cocatalyst solutions (10 mL) were charged to addition cylinders inside the glove box, connected to the reactor, and the charging lines were back purged using the reactor nitrogen pressure. The isooctane solution was charged to the reactor using ethylene pressure, cooled to 0°C, and saturated with ethylene (410-450 kPa). The catalyst solution was charged using ethylene or nitrogen (550 kPa) depending on whether the solution contained, respectively, late transition metal compound or late transition metal compound and cocatalyst(s).

After stirring at 0°C for 5-15 min to initiate the polymerization, the reactor was heated rapidly to 60°C as the pressure was increased to 1.03 MPa ethylene. The ethylene uptake was monitored by the pressure drop from a gas reservoir. The polymerization was terminated by venting the reactor pressure. The polyethylene was collected by vacuum filtration, washed with acetone, and dried at 70°C in a nitrogen-purged vacuum oven.

Examples 1-20 and Comparative Examples A-LTypical Procedure, Method A - Example 1

This example demonstrates the *in situ* activation of (XXIX) in the polymerization reactor. [EtAlCl]₂O (0.385 mL, 0.16 mmol, 100 equivalents per Ni) was dissolved in the isooctane and charged to the reactor. (XXIX) (1.0 mg, 1.6 μmol) was dissolved in dichloromethane (10 mL) and charged to the reactor to initiate polymerization. After polymerization for 2 h at 60°C, the polyethylene was isolated to give 33.1 g (360 kg PE/g Ni). The melt index (190°C, 2160 g) was 7.2. The branch content was 30.9 CH₃/1000 CH₂ by ¹H NMR (500 MHz, Cl₂CDCDCl₂, 120°C). The peak melting temperature was 97°C (101 J/g) by DSC on the second heating cycle.

Typical Procedure, Method B - Example 2

This example demonstrates the activation of a solution of (XXIX) and the use of cyclopentene as catalyst stabilizer until the catalyst solution is charged to the reactor. [EtAlCl]₂O (0.385 mL, 0.16 mmol, 100 equivalents per Ni) was dissolved in the isooctane and charged to the reactor. (XXIX) (1.0 mg, 1.6 μmol) was dissolved in toluene (10 mL) containing cyclopentene (25 μL, 0.284 mmol, 180 equivalents per Ni). The latter solution was activated by adding B(C₆F₅)₃ (4 mg, 0.0078 mmol, 5 equivalents per Ni) and [EtAlCl]₂O (18 μL, 0.0078 mmol, 5 equivalents per Ni), then charged to the reactor to initiate the polymerization. After polymerization for 2 h at 60°C, the polyethylene was isolated to give 30.0 g (330 kg PE/g Ni). The melt index (190°C, 2160 g) was 4.8. The branch content was 29.7 CH₃/1000 CH₂ by ¹H NMR (500 MHz, Cl₂CDCDCl₂, 120°C). The peak melting temperature was 119°C (106 J/g) by DSC on the second heating cycle.

The results of the various polymerizations are shown in Tables 1-3.

Table 1
Polymerizations with (XXIX) (1.6 μ mol)

Example	Method	Al Cocatalyst	Al/Ni	B Cocatalyst	B/Ni	Time hr	Yield g	Yield kg/g Ni	MI dg/min	Mw	Mw/Mn	Tm, peak °C (J/g)	Branching CH ₂ /1000 CH ₂
1	A	[EtAlCl] ₂ O	200	-	-	2	33.1	360	7.2	60,200	2.68	97 (101)	30.9
2	B	[EtAlCl] ₂ O	210	B(C ₆ F ₅) ₃	5	2	30	330	4.8	87,000	3.87	119 (106)	29.7
3	A	[iBuAlCl] ₂ O	200	-	-	2	41.8	450	7.8	52,800	2.48	92 (73)	35.4
4	B	[iBuAlCl] ₂ O	210	B(C ₆ F ₅) ₃	5	2	31.9	350	4.5	72,300	2.55	94,117 (94)	26.6
5	A	[iBuAlCl] ₂ O	100	-	-	1	37.8	410	7.4	50,100	2.32	96 (68)	32.2
6	A	[MeAlCl] ₂ O	100	-	-	1	32.4	350	5.9	68,000	2.86	93 (113)	30.3
7	A	[EtAlCl] ₂ O	100	-	-	1	28.3	310	12.8	44,000	2.02	97 (116)	31.9
8	A	[iBuAlCl] ₂ O	50	-	-	1	32.2	350	9.5	51,100	2.09	97 (76)	31.6
9	A	[MeAlCl] ₂ O	50	-	-	1	22.2	240	2.8	61,300	2.27	99 (135)	25.6
A	A	[iBu ₂ Al] ₂ O	200	-	-	0.5	< 1	< 10	-	-	-	-	-
B	B	[iBu ₂ Al] ₂ O	220	B(C ₆ F ₅) ₃	5	2	28.2	310	10.2	49,400	2.4	98 (96)	31.7
C	A	Et ₂ AlOEt	100	-	-	0.25	0	0	-	-	-	-	-
D	B	Et ₂ AlOEt	110	B(C ₆ F ₅) ₃	5	2	13.1	140	6.4	51,700	2.86	91,122 (101)	33.1
E	A	iBu ₃ Al	100	-	-	0.5	1.82	20	NF	227,000	3.38	126 (135)	10
F	B	iBu ₃ Al	105	B(C ₆ F ₅) ₃	5	0.5	6.67	72	NF	166,000	5.05	125 (111)	22.4
G	A	MMAO-7	100	-	-	1	7.52	81	0.03	149,000	2.56	126 (138)	8.9
H	A	MMAO-7	1000	-	-	2	33.4	361	0.1	96,500	2.63	122 (111)	19

Table 2
Polymerizations with (XXIX) (0.3 μ mol) using Method A

Example	Al Cocatalyst	Al/Ni	Time hr	Yield g	Yield kg /g Ni	MI dg/min	Mw	Mw/Mn	Tm, peak °C (J/g)	Branching CH ₃ /1000 CH ₂
10	[iBuAlCl] ₂ O	500	1	8.24	450	8	58,500	2.15	102 (100)	27.2
11	[iBuAlCl] ₂ O	1000	2	10.5	570	5.5	65,400	2.4	98 (124)	25.4
12	[iBuAlCl] ₂ O	6000	2	11.4	610	2.2	81,400	2.99	103 (133)	21
I	MMAO-7	500	1	2.34	130	NF	177,000	4.12	126 (138)	6.8
J	MMAO-7	1000	2	9.89	530	0.08	116,000	2.99	119 (130)	15.3
K	MMAO-7	6000	2	17.3	940	0.1	101,000	2.62	119 (115)	16.2
L	MMAO-3A	1000	1	7.79	420	1.2	85,700	2.98	105 (155)	20.9

Table 3
Polymerizations with (iBuAlCl)₂O using Method A

Example	Ni Catalyst	Ni μ mol	Al/Ni	Time hr	Yield g	Yield kg/g Ni	MI dg/min	Mw	Mw/Mn	Tm, peak °C (J/g)	Branching CH ₂ /1000 CH ₂
13	(XXX)	1.6	100	1	17.7	190	5	105,000	4.66	66 (93)	48.5
14	(XXXI)	1.6	100	1	31.6	340	2.4	76,900	2.29	83 (103)	45.1
15	(XXIX)	0.79	200	1	17.5	380	11	52,200	2.32	100 (112)	27.7
16	(XXXI)	0.79	200	1	15.7	340	1.7	86,700	2.07	91 (85)	33.7
17	(XXXII)	0.79	200	1	13	280	0.53	173,000	3.25	81 (67)	42.5
18	(XXXIII)	0.79	200	1	12.2	270	0.5	173,000	2.59	75 (70)	42
19	(XXIX)	0.79	200	1	21.1	460	12	47,800	2.34	102 (130)	28.1
20	(XXIX)	0.79	100	1	19	410	11	52,100	2.31	101 (112)	29

Examples 21-23Typical Procedure, Method C - Example 21

These examples demonstrate the activation of the catalyst on a porous substrate treated with a
5 chloroaluminoxane.

Porous silica particles were treated with a solution of excess $[\text{EtAlCl}]_2\text{O}$ in toluene. The particles were filtered off, washed with toluene, and dried under vacuum. Analysis showed that the particles
10 contained 3.28 % Al. The particles were treated with a toluene solution of (XXIX) to give 0.012 mmol Ni/g (100 equiv. Al per Ni). The particles were filtered off, washed with toluene, and dried under vacuum. The supported catalyst (130 mg, 1.6 μmol Ni) was suspended
15 in toluene (10 mL) and charged to the reactor at 0°C to initiate the polymerization. After polymerization for 2 h at 60°C, the polyethylene was isolated.

Results of these 3 examples are given in Table 4.

Table 4
Polymerizations Using (XXIX) and Method C

Example	Ni μmol	Al Cocatalyst	Al/Ni	Time hr	Yield g	Yield kg	MI dg/min	Mw	Mw/Mn	Tm, peak $^{\circ}\text{C}$ (J/g)	Branching $\text{CH}_3/1000 \text{CH}_2$
21	1.6	$[\text{EtAlCl}]_2\text{O}$	100	2	14.2	150	0.16	128,000	3.25	125 (139)	12.5
22	1.6	$[\text{iBuAlCl}]_2\text{O}$	100	1	13.6	150	0.07	123,000	3.08	125 (179)	12.3
23	1.6	$[\text{MeAlCl}]_2\text{O}$	100	1	25.5	280	0.03	134,000	4.04	125 (179)	12.9

Examples 24-37 and Comparative Examples M and NExample 24 - General Polymerization Procedure

A 600 mL pressure reactor equipped with a stirrer (1000 rpm) was used for the ethylene slurry polymerizations. The reactor was dried and purged at 130°C by cycling between nitrogen (1.72 MPa) and vacuum (800 Pa absolute) two times, then by pressurizing with nitrogen (1.72 MPa) and venting to the atmosphere three times. The reactor was cooled to ambient temperature under nitrogen (1.72 MPa).

$\text{Et}_3\text{Al}_2\text{Cl}_3$ (0.0865 mL, 0.079 mmol, 100 equivalents Al per Ni) was dissolved in isooctane (200 mL). (XXIX) (1.0 mg, 1.6 μmol) was dissolved in the dichloromethane (10 mL). The solutions were charged to addition cylinders, connected to the reactor, and the charging lines were back purged using the reactor nitrogen pressure. The isooctane solution was charged to the reactor using ethylene pressure, cooled to 0°C, and saturated with ethylene (410-450 kPa). The dichloromethane solution was charged to the reactor using ethylene pressure (550 kPa).

After stirring at 0°C for 5 min to initiate the polymerization, the reactor was heated rapidly (about 3 min) to 60°C as the pressure was increased to 1.03 MPa ethylene. The ethylene uptake was monitored by the pressure drop from a gas reservoir. The polymerization was terminated after 1 h by venting the reactor pressure. The polyethylene was collected by vacuum filtration, washed with acetone, and dried at 70°C in a nitrogen-purged vacuum oven to give 35.1 g of polyethylene.

Table 5
Ethylene Polymerizations with (XXIX)

Example	Ni μmol	Al Cocatalyst	Al/Ni	Yield g	Yield kg/g Ni	MI dg/min	Mw	Mw/Mn	Tm °C (J/g)	Branching CH ₃ /1000 CH ₂
24	1.6	Et ₃ Al ₂ Cl ₃	100	35.1	380	17.6	50,700	2.43	91 (93)	38
25	1.6	EtAlCl ₂	100	31.9	345	5	53,100	2.32	96 (112)	37.2
26	1.6	Et ₂ AlCl	100	14	151	8	64,500	2.95	100 (121)	27.6
M ^b	1.6	MMAO-7	1000	33.4 ^a	361	0.1	96,453	2.63	122 (111)	19
N ^c	1.6	MMAO-7	100	7.52	81	0.03	148,600	2.56	126 (138)	8.9
27	0.79	Et ₃ Al ₂ Cl ₃	200	20.5	443	11.3	47,100	2.79	100 (131)	29.3
28	0.79	Et ₃ Al ₂ Cl ₃	100	11.9	257	10.8	50,600	1.88	101 (116)	28.1
29	0.79	EtAlCl ₂	200	18.9	408	24	46,400	1.83	98 (102)	31.6
30	0.79	Me ₃ Al ₂ Cl ₃	200	22.8	493	15.9	44,600	2.04	98 (114)	30.2
31	0.79	Me ₃ Al ₂ Cl ₃	100	16.8	363	11.7	47,400	2.04	100 (105)	28.8
32	0.79	MeAlCl ₂	200	19.9	431	14	50,300	1.95	98 (108)	30.3
33	0.79	Me ₂ AlCl	200	4.14	90	1.8	84,600	6.1	123 (160)	17.6
34	0.79	iBu ₃ Al ₂ Cl ₃	200	21.7	469	7.6	66,100	2.49	99 (102)	29.3
35	0.79	iBuAlCl ₂	200	14.4	312	11.5	60,100	2.46	98 (81)	32.1
36	0.79	iBu ₂ AlCl	200	20.9	452	3.6	63,200	2.66	97 (81)	27.7
37	0.79	iBu ₂ AlCl	100	6.97	151	7.1	70,200	2.39	98 (101)	25.1

^a 2 h polymerization.

^b Same as Comparative Example H.

^c Same as Comparative Example G.

CLAIMS

1. A process for the polymerization of an olefin
or olefins comprising the step of contacting, under
5 polymerizing conditions:

(i) (a) a transition metal polymerization catalyst
wherein a metal of Groups 3 through 10 (new notation)
is complexed to a neutral bidentate ligand, and (b) an
alkylaluminum cocatalyst; and

10 (ii) at least one olefin capable of being
polymerized thereby,
characterized in that the alkylaluminum cocatalyst
comprises a compound of the formula $R^1_a X_b AlO_d$, wherein:
a and b are each independently about 0.50 to about
15 1.50, and d is 0.5 to 1.0, both provided that $a+b+d$ is
2.0-2.5;

each R^1 is independently hydrocarbyl or
substituted hydrocarbyl; and

20 X is carboxylate, fluoride, chloride, bromide or
iodide.

2. A process for the polymerization of ethylene
comprising the step of contacting, under polymerizing
conditions:

25 (i) (a) a transition metal polymerization catalyst
wherein a metal of Groups 3 through 10 (new notation)
is complexed to a neutral bidentate ligand, and (b) an
alkylaluminum cocatalyst; and

(ii) ethylene,
30 characterized in that the alkylaluminum cocatalyst
comprises a compound of the formula $R^{60}_q AlZ_t$, wherein:
q and t are each independently about 0.50 to about
2.50, provided that $q+t$ is about 3.0;

each R^{60} is independently hydrocarbyl or
35 substituted hydrocarbyl; and

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Z is fluoride, chloride, bromide or iodide;
and further provided that the molar ratio of aluminum
in $R^{60}_qAlZ_t$ to the transition metal in said transition
metal polymerization catalyst is 75 to 500.

5

3. The process as recited in claim 1 characterized
in that said olefin is ethylene.

4. The process as recited in claim 1 characterized
10 in that said olefin is cyclopentene.

5. The process as recited in claim 1 characterized
in that R is alkyl containing 1 to 4 carbon atoms and X
is chlorine.

15

6. The process as recited in claim 5 characterized
in that the ratio of aluminum to transition metal is
about 25 to about 500.

20 7. The process as recited in claim 2 characterized
in that R^{60} is alkyl containing 1 to 4 carbon atoms,
and X is chlorine.

8. The process as recited in claim 2 characterized
25 in that q is 1.5 and t is 1.5, or q is 2 and t is 1, or
q is 1 and t is 2.

9. The process as recited in claim 1 characterized
in that one or both of said polymerization catalyst and
30 said alkylaluminum cocatalyst are on a solid support.

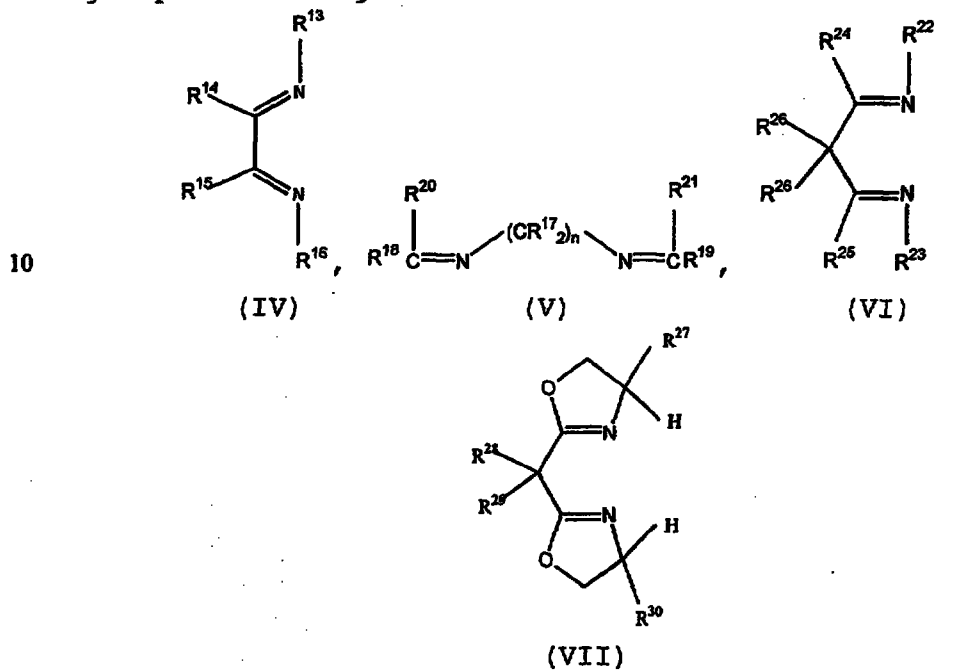
10. The process as recited in claim 2
characterized in that one or both of said
polymerization catalyst and said alkylaluminum
35 cocatalyst are on a solid support.

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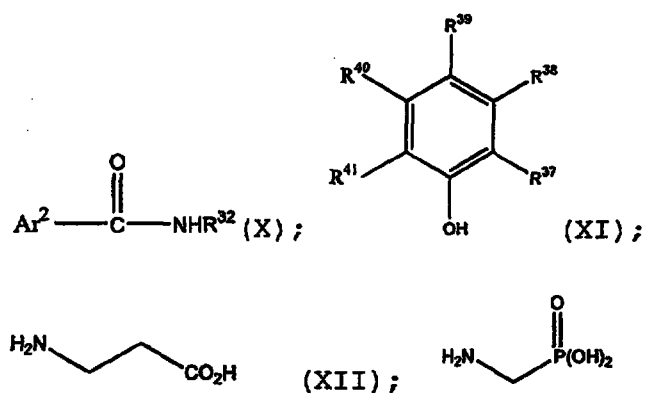


11. The process as recited in any one of claims 1-10, characterized in that the transition metal is a metal of Groups 5 to 10 (new notation).

12. The process according to any one of claims 1-10, characterized in that the transition metal polymerization catalyst is a V, Cr, a rare earth metal, Fe, Co, Ni or Pd complex of a ligand selected from the group consisting of:



15 Ar^1O_p (VIII); $\text{R}^{31}\text{R}^{32}\text{N}-\text{CR}^{33}\text{R}^{34}(\text{CR}^{35}\text{R}^{36})_m-\text{NR}^{31}\text{R}^{32}$ (IX);



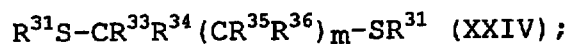
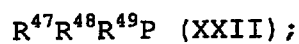
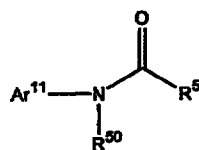
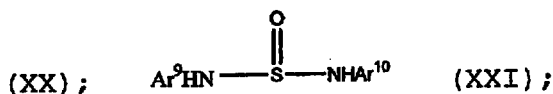
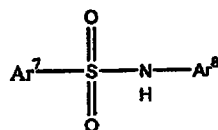
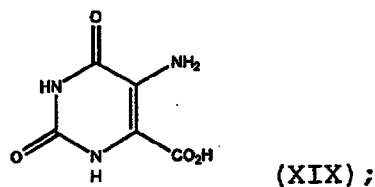
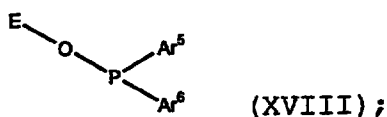
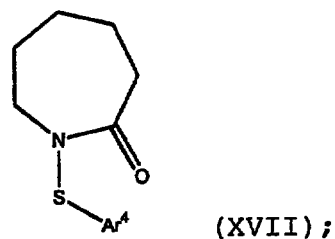
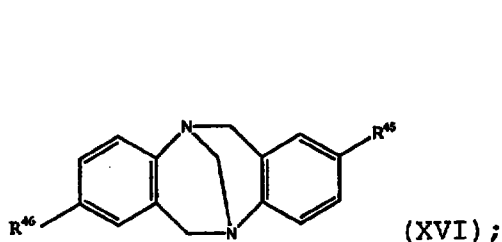
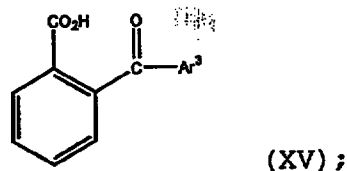
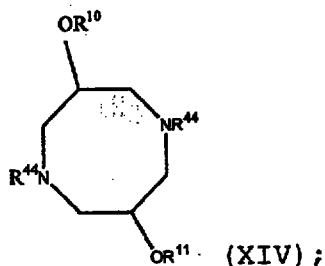
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wherein:

Ar¹ is an aromatic moiety with n free valencies,
or diphenylmethyl;

each Q is -NR⁵²R⁵³ or -CR⁵⁴=NR⁵⁵;

p is 1 or 2;

E is 2-thienyl or 2-furyl;

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- each R^{52} is independently hydrogen, benzyl;
substituted benzyl, phenyl or substituted phenyl;
each R^{54} is independently hydrogen or hydrocarbyl;
and
- 5 each R^{55} is independently a monovalent aromatic moiety;
m is 1, 2 or 3;
 R^{53} is hydrogen or alkyl;
each R^{33} , R^{34} , R^{35} , and R^{36} is independently
- 10 hydrogen, hydrocarbyl or substituted hydrocarbyl;
each R^{31} is independently hydrocarbyl or substituted hydrocarbyl containing 2 or more carbon atoms;
each R^{32} is independently hydrogen, hydrocarbyl or
- 15 substituted hydrocarbyl;
 Ar^2 is an aryl moiety;
 R^{38} , R^{39} , and R^{40} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or an inert functional group;
- 20 R^{37} and R^{41} are each independently hydrocarbyl, substituted hydrocarbyl or an inert functional group whose E_s is about -0.4 or less;
 Ar^3 is an aryl moiety;
 R^{45} and R^{46} are each independently hydrogen or
- 25 hydrocarbyl;
 Ar^4 is an aryl moiety;
 Ar^5 and Ar^6 are each independently hydrocarbyl;
 Ar^7 and Ar^8 are each independently an aryl moiety;
 Ar^9 and Ar^{10} are each independently an aryl moiety
- 30 or $-CO_2R^{56}$, wherein R^{56} is alkyl containing 1 to 20 carbon atoms;
 Ar^{11} is an aryl moiety;
 R^{50} is hydrogen or hydrocarbyl;
 R^{51} is hydrocarbyl or $-C(O)-NR^{50}-Ar^{11}$;
- 35 R^{44} is aryl;



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R^{47} and R^{48} are each independently phenyl groups substituted by one or more alkoxy groups, each alkoxy group containing 1 to 20 carbon atoms;

R^{49} is alkyl containing 1 to 20 carbon atoms, or
5 an aryl moiety;

R^{22} and R^{23} are each independently phenyl groups substituted by one or more alkoxy groups, each alkoxy group containing 1 to 20 carbon atoms; and

R^{24} is alkyl containing 1 to 20 carbon atoms, or
10 an aryl moiety;

each R^{26} is hydrogen, hydrocarbyl, or substituted hydrocarbyl, provided that both of R^{26} taken together may form a ring;

R^{10} and R^{11} are each independently hydrogen or acyl
15 containing 1 to 20 carbon atoms;

R^{13} and R^{16} are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

R^{14} and R^{15} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or R^{14} and R^{15} taken together are hydrocarbylene substituted hydrocarbylene to form a carbocyclic ring;

R^{18} is hydrocarbyl or substituted hydrocarbyl, and
25 R^{20} is hydrogen, hydrocarbyl or substituted hydrocarbyl or R^{18} and R^{20} taken together form a ring;

R^{19} is hydrocarbyl or substituted hydrocarbyl, and R^{21} is hydrogen, substituted hydrocarbyl or hydrocarbyl, or R^{19} and R^{21} taken together form a ring;

30 each R^{17} is independently hydrogen, substituted hydrocarbyl or hydrocarbyl, or two of R^{17} taken together form a ring;

R^{27} and R^{30} are independently hydrocarbyl or substituted hydrocarbyl;

35 R^{28} and R^{29} are each independently hydrogen, hydrocarbyl or substituted hydrocarbyl; and

n is 2 or 3.



13. The process as recited in claim 12
characterized in that said ligand is (IV).

14. The process as recited in claim 13
5 characterized in that said transition metal is nickel;
R¹³ and R¹⁶ are each independently hydrocarbyl provided
that the carbon atom bound to the imino nitrogen atom
has at least two carbon atoms bound to it; and R¹⁴ and
R¹⁵ are each independently hydrogen or hydrocarbyl, or
10 R¹⁴ and R¹⁵ taken together are hydrocarbylene to form a
ring.

This Sheet Has Been Replaced



* C L M S *