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(57) Abstract

In accordance with this invention, there is provided a living carbocationic polymerization catalyst system comprising: (1) a halide of titanium, tin, vanadium or antimony; (2) an aluminum halide selected from the group consisting of aralkyl aluminum halides and alkyl aluminum halides; and (3) an initiator selected from the group consisting of tertiary alkyl halides, tertiary aralkyl halides, tertiary polymeric halides, and water provided that if the initiator is organic, a proton scavenger is present, or, alternatively, if the initiator consists of water, a secondary or tertiary amine is present. Another aspect of the invention comprises a process for using this catalyst system for the polymerization of olefins and for producing narrow molecular weight distribution polymers in a short reaction time.

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CARBOCATIONIC CATALYST AND PROCESS FOR ITS USE

Field of the Invention

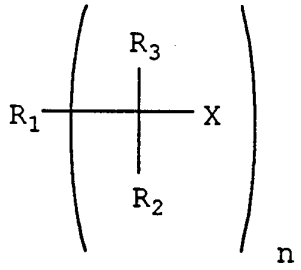
This invention relates to the living polymerization of olefins using a catalyst system comprising titanium, tin, vanadium, or antimony halides and alkyl aluminum halides.

Background of the Invention

Living and non-living catalysts have been used to polymerize olefins. In living polymerization, each catalyst molecule initiates a growing polymer chain that does not undergo chain transfer or termination reactions while monomer is present. One can determine whether or not living polymerization has occurred by comparing the number of initiator molecules with the number of polymer chains produced in the final polymer. These two numbers should be equivalent for true living polymerization. If there are a substantially greater number of polymer chains as compared to initiator molecules, then the polymerization is not living.

The basic components of known living polymerization systems include a Lewis acid, a tertiary alkyl initiator molecule containing a halogen, ester, ether acid, or alcohol group, and an electron donor molecule such as ethyl acetate.

Lewis acids of known living polymerization systems include titanium tetrachloride ($TiCl_4$), boron trichloride (BCL_3), tin tetrachloride ($SnCl_4$), iron trichloride ($FeCl_3$), aluminum trichloride ($AlCl_3$) and the like. These compounds have been described in U. S. Patents 4,910,321 and 4,929,683 and European patent application 341,012 for use in living polymerization of olefins. The exact combination of these elements, however, varies with each system. The tertiary alkyl initiators typically used in living polymerization systems are represented by the formula:



wherein R_1, R_2 and R_3 are a variety of alkyl or aromatic groups or combinations thereof, n is the number of initiator molecules, and X is the functional group upon which the Lewis acid affects a change to bring about the carbocationic initiating site. The functional group is typically a halogen, ester, ether, alcohol, or acid group depending on the Lewis acid employed.

As discussed in U.S. 5,169,914, the chosen electron pair donor component of the above systems is believed to directly relate to the ability of these catalysts to stabilize the carbocation formed and to generate living conditions. The electron donor number concept has been used to explain the activity of catalyst systems which employ ether and ester initiators. It is believed that the formation of in situ electron pair donors are responsible for the catalyst characteristics. However, the role of the

electron donor is still uncertain and has been challenged. See, M. Gyor, L, Balogh, H.C. Wang, R. Faust, Polym. Prepr. Amer. Chem. Soc., 33(1), 158 (1992).

Such living polymerization systems are useful for production of narrow molecular weight distribution polymers, however, these systems are very sensitive to certain impurities. For example, the presence of water in Lewis acid catalyzed systems has been considered detrimental because water is associated with chain transfer dominated, nonliving polymerization which results in broad molecular weight distribution polymers i.e., polymer with an Mw/Mn greater than 2.0. There is a decrease in desirable physical properties when the polymer has a broad molecular weight distribution. Recently we have found that water can be used to initiate the living polymerization of isobutylene provided that the correct Lewis acid to water ratio is used. Additionally, in co-pending U.S. application Serial No. 08/044,862 the addition of an amine to this process was found to modify the overall amount of Lewis acid required to bring about living conditions.

Catalyst systems based on BCl_3 and $TiCl_4$ using a number of combinations of the previously described components have very similar process characteristics. First, the Lewis acid concentrations must exceed the concentration of initiator sites by 16 to 40 times in order to achieve 100 percent conversion in 30 minutes (based upon a degree of polymerization equal to 890) at -75 to -804°C. Much longer polymerization times are required for higher polymerization temperatures. These catalyst systems are also typically used with solvents such as methyl chloride.

For an industrially applicable process, these catalysts and polymerization conditions fall short of commercial usefulness. Improvements in these systems would include reduction in polymerization time while maintaining narrow molecular weight distribution.

Summary of the Invention

In accordance with this invention, there is provided a living carbocationic polymerization catalyst system comprising: (1) a halide selected from the group consisting of titanium, tin, vanadium and antimony; (2) an aluminum halide selected from the group consisting of aryl aluminum halides, aralkyl aluminum halides, and alkyl aluminum halides; (3) an initiator selected from the group consisting of tertiary alkyl halides, tertiary aralkyl halides, tertiary polymeric halides and water; and (4) a proton scavenger if the initiator is organic or, alternatively, a secondary or tertiary amine if the initiator is water; and (5) if the aluminum halide is a dihalide, a stabilizer. Another aspect of the invention comprises a process for using this catalyst system for the polymerization of olefins and for producing narrow molecular weight distribution polymers in a short reaction time.

Description of Preferred Embodiments

In a preferred embodiment, this invention relates to a living carbocationic polymerization catalyst system and process based upon a catalyst composition comprising:

(1) a halide selected from the group consisting of haildes of titanium, tin, vanadium, and antimony;

(2) an aluminum halide selected from the group consisting of aryl aluminum halides, aralkyl aluminum halides, and alkyl aluminum halides;

(3) an initiator selected from the group consisting of tertiary alkyl halides, tertiary aralkyl halides, tertiary polymeric halides, and water provided that if the initiator selected is organic, a proton scavenger is present, or, alternatively, if the initiator consists of water, a secondary or tertiary amine is present; and

(4) optionally, stabilizer, if the aluminum halide is a dihalide.

This catalyst system can be used, among other things, for the polymerization of olefins, including cyclic, linear, or branched olefins and diolefins. Preferred olefins include isoolefins, alpha-olefins, and styrenics.

Preferred styrenes include alkyl, alkoxy or halogenated styrenes, particularly para-methyl styrene, alpha-methyl styrene, para chlorostyrene and the like. This system has the benefit of producing polymers with narrow molecular weight distribution within a short time period.

Preferred isoolefins include any C_4 to C_{30} isoolefin, particularly isobutene, isohexene, isooctene and the like. Preferred alpha-olefins include any C_2 to C_{30} alpha-olefin, particularly ethylene, propylene, butene, pentene, hexene, heptene, octene, and the like. Preferred styrenes include styrene, para-methyl-styrene, alpha-methyl styrene, and the like. In a particulalry preferred embodiment, isobutylene and para-methyl styrene are the monomers.

Preferred halides include any halide of titanium, tin, vanadium or antimony, preferably chloride, fluoride or bromide, even more preferably chloride. Titanium (IV) halides are preferred, particularly titanium (IV) chlorides, with titanium tetrachloride being especially preferred. Particularly preferred embodiments include titanium tetrabromide, tin (IV) chloride, tin (IV) bromide, antimony hexachloride, antimony hexafluoride, vanadium tetrachloride, and vanadium tetrabromide.

Preferred aluminum halides include dialkyl aluminum halides and monoalkyl aluminum halides. Preferred alkyls may be linear, branched or cyclic and may contain up to 30 carbon atoms with 1-4 carbon atoms most preferred.

Preferred aluminum halides are represented by the formula:

$$R_nAlX_{3-n}$$

where R is a C_1 to C_{15} linear, cyclic or branched chain alkyl, aryl, aralkyl, or alicyclic group and n = 1 or 2. X is a halogen. When n is equal to 2, the two R groups can be the same or different C_1 to C_{15} groups, preferably the same linear group, most preferably ethyl, but R may also be the same or different cyclic or branched chain alkyl, aryl, aralkyl, or alicyclic group. For the purposes of this invention and any claims thereto, aralkyl is defined to mean a compound containing both aryl and aliphatic structures. X may be the same or different halogen but is preferably chloride. The preferred aluminum halides are diethylaluminum chloride, ethyl aluminum dichloride, methyl aluminum dichloride, isobutyl aluminum dichloride, and dimethyl aluminum chloride, or a

combination thereof. Brominated versions of the above are also preferred.

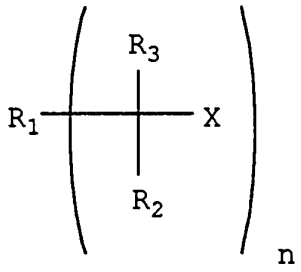
The polymerization may take place in solution or bulk phase, preferably solution. If in solution, the solvent may be polar, nonpolar or a mixture thereof but is preferably more nonpolar than polar.

The solvent medium may be a mixture of two or more solvents. Non-polar/non-polar, polar/polar and non-polar/polar mixtures and the like are all suitable for this invention. The preferred mixture is nonpolar/polar. Suitable solvents include hydrocarbons; especially hexanes, heptanes and toluene; halogenated hydrocarbons; especially chlorinated hydrocarbons, and nitro alkanes. Specific examples include, but are not limited to, methylcyclohexane, ethylcyclohexane, propylcyclohexane, methylchloride, methylenechloride, ethylchloride, propylchloride, butylchloride, chloroform, nitroethane, nitromethane, and the like.

A preferred solvent is a mixture of methylcyclohexane (MCH) and methylenechloride ($MeCl_2$) at about 30 to about 80 parts by volume MCH to 70 to 20 parts $MeCl_2$. More preferably, the solvent will contain a mixture of 40 to about 70 parts methylcyclohexane and about 60 to about 30 parts methylenechloride. A most preferred solvent medium is about 60 parts methylcyclohexane and about 40 parts methylenechloride. Mixtures of other similar polar and nonpolar solvents may be used provided the dielectric constant of the mixture approximates that of the MCH/MeCl2 mixtures described above. Preferred polar solvents include, but are not limited to, methyl chloride, ethyl chloride, methylene chloride, and 1,2-dichloroethane. Preferred nonpolar solvents include, but are not limited to,

hexane, heptane, methylcyclohexane, cyclohexane, ethylcyclohexane, and the like.

The initiator may be any one of a tertiary alkyl halide, a tertiary aralkyl halide, a tertiary polymeric halide, or water. Preferred organic initiators are represented by the formula:



where R_1, R_2 and R_3 are independently any straight or branched chain alkyl, aryl or aralkyl, preferably containing 1 to 15 carbon atoms, preferably 1-8 carbon atoms, most preferably 1 to 2 carbon atoms. X is any halogen or pseudohalogen, preferably chloride. "n" is the number of initiator sites and is a number greater than or equal to 1, preferably 1-6. Preferred aralkyls may be substituted or unsubstituted. Preferred initiators include 2-chloro-2,4,4-trimethyl pentane (TMPCl) and 1,3,5 tri (1-chloro-1-methyl ethyl) benzene (TBDCC). Other suitable initiators can be found in U.S. patent 4,946,899, which is herein incorporated by reference.

For the purposes of this invention and the claims thereto psuedohalogen is defined to be any compound that is an azide, an isocyanate, a thiocyanate, an isothiocyanate or a cyanide.

When the initiator is a tertiary polymeric halide, one of R_1, R_2 or R_3 is an olefin polymer, the remaining R groups are defined as above, and n is a number

between 1 and 1000, preferably between 1 and 500, even more preferably between 1 and 50. Preferred olefin polymers include polyisobutlyene, isobutylene-para-methylstyrene copolymers and polypropylene. The polymeric initiator may have halogenated tertiary carbon positioned at the chain end or along or within the backbone of the polymer. When the olefin polymer has multiple halogen atoms at tertiary carbons, either pendant to or within the polymer backbone, the product polymer may have a comb like structure and/or side chain branching depending on the number and placement of the halogen atoms in the olefin polymer. Likewise, the use of a chain end tertiary polymer halide initiator provides a method for producing block copolymers. Monomer added to the polymeric initiator will form a second block. Successive blocks can be formed by sequential monomer addition.

The initiator, whether organic or H_2O, may be present at a concentration of about 1 x 10^{-6} moles per liter to about 3 moles per liter, preferably about 1 x 10^{-1} moles per liter to about 1 x 10^{-5} moles per liter, even more preferably about 1 x 10^{-2} moles per liter to about 1 x 10^{-4} moles per liter.

When an organic initiator is used, a proton scavenger is preferably used to, *inter alia*, minimize the water initiation. Where the initiator is water, a secondary or tertiary amine may be used to modify the concentration of H_2O and thereby affect molecular weight and molecular weight distribution of the product polymer.

For the purposes of this invention and the claims thereto, a proton scavenger is defined to be a composition capable of reacting with free protons without producing a new species of catalyst, or, if it

does produce a new species of catalyst, that catalyst is substantially inactive when compared to the catalyst system of this invention. Preferred proton scavengers are 2,6-di-tert-butyl-pyridine (DTBP), 4 methyl-2,6-di-tert-butyl-pyridine, tert-octyl-tert-butylamine and 1,8-bis(di-methylamino)-napthalene used alone or in combination.

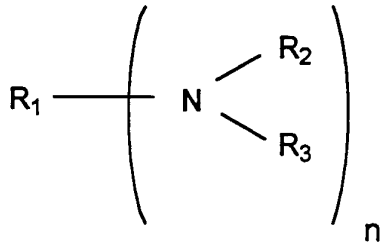
When only organic initiation is desired, the amount of proton scavenger used should be equal to or greater than the concentration of water in the polymerization system.

In addition, stabilizer may be added to the above system to aid in control of narrow molecular weight distribution. For purposes of this invention, stabilizers are defined as molecules capable of coordinating to the aluminum halide forming a 1:1 complex. These molecules usually contain heteroatoms and heteroatomic functional groups including amides, esters, ethers, sulfoxides and the like. While not wishing to be bound by any particular theory, it is believed that this control is achieved through stabilization of the inorganic intermediate formed when the titanium, tin, vanadium or antimony halide reacts with the aluminum halide. The stabilizer is optional, but preferred, if the aluminum halide is a monohalide; when the aluminum halide is a dihalide, a stabilizer is highly preferred. A number of different compounds may serve as the stabilizer including esters, amines, amides, and linear, branched or cyclic allyl, alkyl, phenyl, and benzyl compounds. Preferred stabilizers include allyl butylrate, ethyl acetate, triethylamine, trimethylamine, benzyl acetate, and the like.

The water present as an initiator in the polymerization or catalyst system as described above is

typically residual water found in solvents and the like, in spite of drying procedures used in the art. As a general rule, a proton scavenger is used with organic initiator and any secondary or tertiary amine is used with the water, even though all currently known proton scavengers are amines, but not all amines are proton scavengers.

When water serves as the initiator, an optional third component of the catalyst system is a secondary or tertiary amine. The amine can be any secondary or tertiary amine but is preferably represented by the following formula:



wherein R_1, R_2, and R_3 are each independently hydrogen or a straight, cyclic, or branched chain alkyl, aryl or aralkyl, preferably containing 1 to 15 carbon atoms, more preferably 1 to 8 carbon atoms, most preferably 1 to 4 carbon atoms, provided that only one of R_1, R_2 or R_3 should be H at any one time and that R_2 and R_3 may be joined in a cyclic structure. The aralkyls can be substituted or unsubstituted.

Preferred examples of amines include, diisopropylamine, triethylamine, tributylamine, diiosbutylamine, diethylamine, 2,6-di-tert-butylpyridine and the like. The amine is typically present at a concentration that is less than the total water concentration in the system. The titanium, tin, vanadium or antimony halide molar concentration to

water molar concentration ratio when water is used as an initiator should be at least about 125 without an optional amine present, preferably about 150 to about 300 or more, or if an optional amine is present then the ratio of aluminum halide molar concentration to water molar concentration is preferably at least about 50, even more preferably about 65 to about 300.

Generally, water, whether added or not, will be present in the system. The concentration of the water in the system producing polymer with a M_w/M_n of 1.5 is calculated by solving for I in the following equation [M]/[I] = DP, where M equals monomer, I equals initiator and DP equals the degree of polymerization for a water initiated polymerization, degree of polymerization is calculated by dividing the number average molecular weight of the polymer by the weight average molecular weight of the monomer(s). (For example, 0.268 mol/l of $TiCl_4$ and 2.8 mol/l of isobutylene in a 60/40 mix of methylcyclohexane/methylene chloride at -75 degrees C for 21 minutes yielding 89% polymer with a Mn of 69,100 and an Mw/Mn of 1.32 means DP = 1232 and the water concentration = 2.8/DP; therefore [I] = 2.3×10^{-3} mol/l). This value is calculated for a batch of dried solvent or solvent mixture and then the value is used when that solvent is the reaction media. For purposes of this invention, it is assumed that the concentration of water in a given system of the same solvent batch does not vary in a statistically significant manner. Even though the exact concentration may vary, the concentration is usually between 10^{-3} a to 10^{-4} M. For purposes of this invention, it is assumed that the water is free or available to act with the aluminum halide.

The halide of Ti, Sn, V, or Sb may be at a concentration of from about 10^{-1} mole/l to about 10^{-6}

mole/l, preferably from about 10^{-2} mole/l to about 10^{-5} mole/l, and more preferably from about 10^{-2} mole/l to about 10^{-4} mole/l. The concentration of Ti, Sn, V, or Sb halide is typically determined from the initiator concentration where the molar ratio of Ti, Sn, V or Sb to initiator molar concentration is one or greater, preferably from about 1 to about 64, more preferably from about 4 to about 32, most preferably from about 4 to about 8.

When organic initiators are used, the halide may be present at a ratio of the Ti, Sn, or Sb halide molar concentration to the initiator molar concentration of about 4 or greater, preferably about 4 to about 32, even more preferably about 4 to about 8. Likewise, the molar ratio of Ti, Sn, or Sb halide to aluminum halide acid may be about 1 or greater, preferably about 1 to about 30, even more preferably about 3 to about 6.

The concentration of aluminum halide is preferably less than the Ti, Sn, V, or Sb halide concentration. In preferred embodiments, the mole ratio of Ti, Sn, V, or Sb to aluminum halide may be one or greater, preferably from about 1 to about 30, more preferably from about 3 to about 6. In the practice of this invention, it is highly preferred to start the polymerization by separately adding the aluminum halide after the halide of Ti, Sn, V, or Sb is introduced. For example, the titanium, tin, vanadium or antimony halide is added to the solvent, monomer and proton scavengers, and amines. Then the aluminum halide or aluminum halide/stabilizer complex is added. The aluminum halide complex may or may not be prepared before addition to the vessel, but prior preparation of the aluminum halide/stabilizer complex is preferred.

The polymerizations of this invention are conducted under conditions known to those of ordinary skill in the art. Polymerization is typically performed in a solution phase reactor by methods known in art. Preferred conditions include polymerization reactions run at or below about -5°C, preferably at or below about -30°C, more preferably at or below about -70°C in a reactor suitable to maintain temperature conditions. Monomers which may be polymerized by this system include one more of olefins, alpha-olefins, disubstitued olefins and/or isolefins. Preferably, the monomer contains 1 to 20 carbon atoms, more preferably 1 to 8, even more preferably 2 to 6 carbon atoms. Examples of preferred olefins include isobutylene, 2-methylbutene, 2-methylpentene and the like.

The polymerization is typically complete in about ten minutes, however the polymerization may run from less than one minute to about an hour. However, longer times are still within the scope of this invention. The polymerization may also take place in any reaction vessel, including glass, pressure reactors, solution reactors, and the like.

The polymers produced by this invention have a narrow molecular weight distribution (Mw/Mn) of less than about 2.5, preferably less than about 2.0, even more preferably less than about 1.5. Polyisobutylene and other isobutylene based polymers having a narrow molecular weight distribution are the preferred polymer products produced by this catalyst system.

Examples

For the examples of this invention, the method described above was used to calculate the concentration of water in the solvents.

Molecular weights (Mw and Mn) were measured by gel permeation chromatography using a Waters 150 gel permeation chromatograph equipped with a differential refractive index (DRI) detector. The numerical analyses were performed using a commercially available standard of gel permeation chromatography software package.

Procedure

Except where noted, polymerization conditions were generally the same as those disclosed in USSN 4,910,321 (Kennedy et al.), incorporated herein. As a representative example; in a nitrogen box with a water content of approximately 5 parts per million, a resin kettle was charged with 11 microliters of 2-chloro-2,4,4-trimethyl pentane (TMPCl), 13.2 ml anhydrous methylene chloride, 19.8 ml of anhydrous methylcyclohexane and 80 microliters of 2,6-di-tert-butylpyridine (DTBP). The solution was cooled to -75°C, whereupon 5 ml of isobutylene was added. Once the solution stabilized at this temperature, 0.16 ml of a 2.5 M solution of titanium tetrachloride was added to begin the polymerization. After 1 minute, 0.125 ml of a 2.5 M solution of diethylaluminum chloride was added to the reaction. The reaction was stopped after 5 minutes with the addition of 3 ml of chilled methanol. Polymer was isolated by pouring the reaction mixture into methanol with stirring.

When water is used as the initiator, the same procedure is followed as above, except that the organic initiator is excluded and that an amine or proton trap may or may not be added before the addition of the aluminum halides to the reaction.

EXAMPLES

Table 1

Isobutylene polymerizations in Table 1 were initiated from tertiary alkyl halides and coinitiated with titanium tetrachloride and alkyl aluminum chloride in 60/40 v/v methylcyclohexane/methylene chloride at -75°C. The initiator for the reactions shown in Table 1, except where noted, was 5-tert-butyl-1,3-bis(1-chloro-1-methylehtyl) benzene. Reactions 1, 2, 15, 16, and 19 were run in the presence of alkyl butyrate ([AB] $9.0x10^{-3}$ mole/l). In reactions 5 and 6, monomer was added 4 minutes after both acids had been added. Reactions 11 and 12 were run in the presence of ethyl acetate ([EtOAC]=$9.0x10^{-3}$ mole/l). Reactions 13 and 14 were run in the presence of tri-isobutyl amine ([TAB]=$9.0x10^{-3}$ mole/l).

Reaction 8 shows that ethyl aluminum dichloride (EADC)coinitiation alone is incapable of delivering narrow MWD polymers even though yield is high. Reactions 3 and 4 show that, diethylaluminum chloride (DEAC) together with $TiCl_4$ results in greatly accelerated polymerization. In five minutes or less, complete conversion is accomplished with only a slight increase in MWD.

Table 1

Rxn.	[I] mol/l	[$TiCl_4$] mol/l	[RxAlCl] mol/l	Time min	Yield %	Mn	Mw/Mn
1	.0019	.045	.00947, x = 1	30	80	60,400	1.23
2	.0019	.045	.00947, x = 2	30	53	47,500	1.26
3	.0019	.045	.00947, x = 2	30	100	63,900	1.32
4	.0019	.045	.00947, x = 2	5	100	59,800	1.36
5	.0019	.045	.00947, x = 2	30	25	95,800	2.17
6	.0019	.045	.00947, x = 1	30	95	148,700	2.52
7	.0019	.045	.0189, x = 2	20	100	59,000	1.63
8	.0019	--	.0036, x = 1	30	86	15,000	5.31
9	.0019	--	.011, x = 2	30	0	---	---
10	.0019	.045	---	30	100	62,200	1.10
11	.0019	.045	.00947, x = 1	5	85	58,800	1.35
12	.0019	.045	.00947, x = 2	5	26	18,600	1.34
13	.0019	.045	.00947, x = 1	5	31	16,900	1.65
14	.0019	.045	.00947, x = 2	5	24	21,700	2.0
15	--	.045	.00947, x = 1	5	0	---	---
16	--	.045	.00947, x = 2	5	0	---	---
17	--	.045	.00947, x = 1	5	40	ND	ND
18	--	.045	.00947, x = 2	5	0	---	---
19	.013	.045	.00947, x = 1	5	32	1580	1.37

For all examples in Table 1, isobutylene concentration was 1.9 mol/liter, polymerization temperature was -75°C and proton trap concnetration was 2.8 $x10^{-2}$ mol/liter.

Claims

What is claimed is:

1. A catalyst system comprising:

(a) a halide selected from the group consisting of halides of titanium, tin, vanadium, and antimony;

(b) an aluminum halide selected from the group consisting of aryl aluminum halides, aralkyl aluminum halides, and alkyl aluminum halides;

(c) an initiator selected from the group consisting of tertiary alkyl halides, tertiary aralkyl halides, tertiary polymeric halides, and water,

provided that if the initiator is organic, a proton scavenger is present or, alternatively, if the initiator consists of water, a secondary or tertiary amine is present, and further provided that if the aluminum halide is a dihalide, a stabilizer is present.

2. The catalyst system of claim 1 wherein the aluminum halide is represented by the formula:

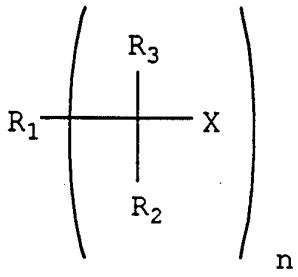
$$R_nAlX_{3-n}$$

wherein n is equal to 1 or 2, each R is, independently, a linear, branched or cyclic alkyl, aryl or aralkyl and each X is, independently, a halogen.

3. The catalyst system of claim 1 or 2 wherein the aluminum halide is a ethyl aluminum dichloride or diethyl aluminum chloride, or a mixture thereof.

4. The catalyst system of claim 1, 2 or 3 wherein the aluminum halide is a dihalide and the stabilizer is selected from the group consisting of a linear, branched or cyclic ester, amine, amide, ketone, allyl, alkyl, phenyl, and benzyl compound.

5. The catalyst system of claim 1, 2, 3 or 4 wherein the initiator is represented by the formula:



where R_1, R_2 and R_3 are independently C_1 to C_{15} linear, branched or cyclic alkyl, aralkyl or substituted aralkyl groups, X is a halogen and n is the number of initiator sites; a number from 1 to 6.

6. The catalyst system of claim 12 wherein the halogen is chlorine.

7. The catalyst system of claim 1 wherein the ratio of the halide of titanium, tin, vanadium or antimony molar concentration to the initiator molar concentration is about 4 or greater.

8. The catalyst system of claim 1 wherein the ratio of the halide of titanium, tin, vanadium, or antimony molar concentration to the aluminum halide molar concentration is about 1 or greater.

9. A process comprising contacting, under polymerization conditions, an olefin with a catalyst system comprising:

(a) a halide selected from the group consisting of halides of titanium, tin, vanadium, and antimony;

(b) an aluminum halide selected from the group consisting of aralkyl aluminum halides, aryl aluminum halides, and alkyl aluminum halides, provided that when the aluminum halide is a dihalide, a stabilizer is also present;

(c) an initiator selected from the group consisting of tertiary alkyl halides, tertiary polymeric halides and water, provided that when the initiator is organic, a proton scavenger is present, or alternatively, when the initiator consists of water, a secondary or tertiary amine is present and further provided that if the aluminum halide is a dihalide, a stabilizer is present.

10. The process of claim 9 wherein the titanium, tin, vanadium or antimony halide is allowed to contact the olefins prior to contacting the olefins with the aluminum halide.

11. The process of claim 9 conducted for about 1 minute to about 10 minutes at a temperature of -50°C or below.

12. The use of any of the catalysts of claims 1-8 to polymerize olefins.

INTERNATIONAL SEARCH REPORT

Inten ıal Application No
PCT/US 94/10523

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08F10/00 C08F2/38 C08F4/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 542 726 (BP CHEMICALS LTD.) 19 May 1993 see claims 1-10	1
A	EP,A,0 224 759 (BAYER AG) 10 June 1987 see claims 1-7	1
A	EP,A,0 397 081 (NIPPON ZEON CO., LTD.) 14 November 1990 see claims 1-9	1
A	US,A,5 247 021 (HIROSHI FUJISAWA) 21 September 1993 see claims 1-4	1
A	EP,A,0 348 963 (CESKOSLOVENSKA AKADEMIE VED) 3 January 1990 see claims 1-17	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
10 January 1995	24.01.95

Name and mailing address of the ISA	Authorized officer
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Inten al Application No
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