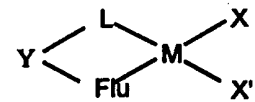




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(21) International Application Number: PCT/US98/14734 (22) International Filing Date: 13 July 1998 (13.07.98) (30) Priority Data: 60/052,414 14 July 1997 (14.07.97) US (71) Applicant (for all designated States except US): THE BOARD OF TRUSTEES OF THE LELAND STANFORD, JR. UNIVERSITY [US/US]; Suite 350, 900 Welch Road, Palo Alto, CA 94304-1850 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): WAYMOUTH, Robert, M. [US/US]; 420 Alger Drive, Palo Alto, CA 94306 (US). LECLERC, Margrete, K. [DE/US]; Apartment #3, 801 Middlefield Road, Palo Alto, CA 94301 (US). (74) Agent: DULIN, Jacques, M.; Heller Ehrman White & McAuliffe, 525 University Avenue, Palo Alto, CA 94301 (US).	(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>With amended claims.</i>	
(54) Title: CATALYSTS AND PROCESSES FOR THE SYNTHESIS OF ALTERNATING ETHYLENE/ α -OLEFIN COPOLYMERS, AND ISOTACTIC COPOLYMERS THEREOF		
(57) Abstract		
<p>Catalysts, catalyst systems and processes for production of alternating copolymers of ethylene and alpha olefins, and to novel classes of atactic and isotactic alternating copolymers of ethylene and alpha olefins, which copolymers include a wide range of crystallinity and exhibit commercially useful properties. Appropriate selection of ligand substituents permit the catalysts to be symmetric or assymmetric, resulting in atactic, or isotactic or atactic, respectively, alternating copolymers of ethylene with alpha olefins. The novel class of bridged fluorenyl metallocene catalysts of the invention is assymmetric structural form interconvert between states during polymerization of ethylene with alpha olefins to produce alternating isotactic or atactic copolymers. Exemplary metallocene components of the inventive catalyst systems comprised bridged cyclopentadienyl-fluorenyl complexes of general formula (1), in which: M is a Group 3,4 or 5 Transition metal, a Lanthanide or an Actinide; X and X' are the same or different uninegative ligands; L is a substituted or unsubstituted cyclopentadienyl (Cp) or indenyl ligand; Flu is a substituted or unsubstituted fluorenyl ligand; and Y is a bridging group. When the Cp ligand is symmetric, atactic alternating E/α-olefin copolymers are produced and when the Cp ligand is assymmetric, alternating isotactic or atactic E/α-olefin copolymers are produced.</p>	 (1)	

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**TITLE : CATALYSTS AND PROCESSES FOR THE SYNTHESIS OF
ALTERNATING ETHYLENE/ α -OLEFIN COPOLYMERS, AND
ISOTACTIC COPOLYMERS THEREOF**

DESCRIPTION

CROSS REFERENCE TO RELATED APPLICATIONS:

10 This is the Regular application of copending Provisional application Serial Number 60/052,414 filed July 14, 1997 by us for “**Alternating Ethene/Propene Copolymerization with $\text{Me}_2\text{C}(3\text{-RCp})(\text{Flu})\text{ZrMe}_2/\text{MAO}$ ”**, the benefit of the filing date of which is hereby claimed under 35 USC Section 119.

15 **TECHNICAL FIELD:**

The invention relates to catalysts, catalyst systems and processes for production of alternating copolymers of ethylene and alpha olefins, and to novel classes of atactic and isotactic alternating copolymers of ethylene and alpha olefins, which copolymers will include a wide range of crystallinity and exhibit commercially useful properties.

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BACKGROUND:

The copolymerization of ethylene with alpha olefins using transition metal catalysts is well known. Metallocene catalysts have recently proven useful for olefin copolymerization as copolymers produced with metallocene catalysts tend to have more random comonomer distributions and better compositional homogeneity than copolymers produced with heterogeneous catalysts (H. H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R. M. Waymouth, *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143). The properties of olefin copolymers depend on not only the relative amounts of the comonomers but on the sequence distribution of the comonomers along the polymer chain and, for copolymers containing alpha olefins, on the stereochemistry of the copolymers. While metallocene catalysts have proven useful for the synthesis of olefin copolymers with random distributions of comonomers along

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the chain there is a need for catalyst systems which can produce olefin copolymers with a specific non-random comonomer distribution.

Atactic alternating copolymers are known. Chien et al reported that achiral bridged bis fluorenyl metallocenes yield very low r_1r_2 values for ethylene/propylene copolymerization, although they do not report any production of alternating copolymers (Yu, Z.; Marquez, M.; Rausch, M. D.; Chien, J. C., J. Polym. Sci. Part A: Polym. Chem. **1995**, 33, p 2795-2801). Galimberti report the synthesis of elastomeric ethylene/propylene copolymers with alternating structures in the presence of achiral bridged bisfluorenyl metallocenes (Galimberti, M. Resconi, L.; Albizzati, E. Eur. Pat. Appl. EP 632,066, 04 Jan, 1995). In addition, Uozumi et al. report that achiral bis indenyl catalysts yield alternating ethylene/octene copolymers. (Uozumi, T.; Miyazawa, K.; Sano, T.; Soga, K., Macromol. Rapid. Commun. **1997**, 18, p. 883-889. Since all of these catalysts are achiral any resulting polymers would be atactic.

Crystalline alternating copolymers are known for comonomers that are not readily homopolymerized. For example, Natta reported that using a VCl_4/AlR_3 catalyst cyclopentene can be copolymerized with ethylene to give crystalline (and probably isotactic) alternating ethylene/cyclopentene copolymers (Natta, G.; Dall'Asta, G.; Mazzanti, G.; Pasquon, I.; Valvassori, A.; Zambelli, A., Makromol. Chem. **1962**, 54, p. 95-101.) Harrington reports that crystalline copolymers of ethylene/cyclic olefins can be prepared with bridged monocyclopentadienyl-amido metallocenes (Harrington, B. A. PCT WO 96/40806, 19 Dec. 1996). Harrington does not report the tacticity of the copolymers produced. Xu reports that crystalline isotactic alternating ethylene/stryrene copolymers can be prepared with certain bridged monocyclopentadienyl-amido metallocenes (Xu, G. Macromolecules, 1998, 31, 2395,2402.)

Thus there is a need for catalysts systems that are able to readily copolymerize alpha olefins and ethylene to give alternating isotactic ethylene/alpha olefin copolymers.

THE INVENTION

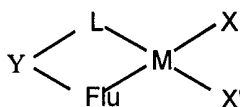
SUMMARY, OBJECTS AND ADVANTAGES:

It is among the objects and advantages of the invention to provide methods of selecting metallocene catalyst symmetries for production of two novel classes of copolymers of ethylene with alpha olefins which have alternating structures, a first class of atactic alternating

copolymers and a second class of isotactic alternating copolymers, which copolymers exhibit a wide range of crystallinity and accordingly a wide range of interesting and useful properties. It is another object and advantage of the invention to provide methods of making and use of a class of fluorenyl bridged metallocene catalysts, which by appropriate selection of ligand substituents in accord with the teachings of the invention may be symmetric or assymmetric, resulting in atactic, or isotactic or atactic, respectively, alternating copolymers of ethylene with alpha olefins which exhibit a wide range of commercially useful properties. It is still another object and advantage of the invention to provide a novel class of bridged fluorenyl metallocene catalysts which in assymmetric structural form interconvert between states during polymerization of ethylene with alpha olefins to produce alternating isotactic or atactic copolymers. Still other objects and advantages will be evident from a detailed consideration of the specification, formulas, schemes, and claims of this application, and from the inherent characteristics and properties of the polymers described herein and which are produceable from the catalysts hereof inaccord with the processes herein described.

The invention is directed to novel processes and catalysts for the production of alternating copolymers of ethylene and alpha olefins. A degree of alternation of up to 83% is easily obtained and higher degrees of alternation with these polymerization systems are indicated. Another aspect of this invention are processes for producing novel classes of isotactic or atactic alternating copolymers of ethylene and alpha olefins, the presence or not and degree of tacticity of which is controlled by the symmetry (or assymetry) of at least one of the ligands.

In a broad aspect, the invention relates to catalysts and processes for the alternating copolymerization of ethylene and alpha olefins. The catalyst systems of the present invention encompass bridged metallocene complexes in the presence of a cocatalyst. Exemplary metallocene components comprise bridged cyclopentadienyl-flourenyl complexes of the general formula:

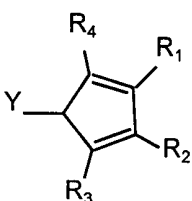


Formula 1

in which: M is a Group 3, 4 or 5 Transition metal, a Lanthanide or an Actinide; X and X' are the same or different uninegative ligands, such as but not limited to hydride, halogen, hydrocarbyl, halohydrocarbyl, amine, amide, or borohydride substituents (preferably halogen,

alkoxide, or C₁ to C₇ hydrocarbyl); L is a substituted or unsubstituted cyclopentadienyl (Cp) or indenyl ligand; Flu is a substituted or unsubstituted fluorenyl ligand; and Y is a bridging group. Exemplary preferred Transition Metals include Titanium, Hafnium, Vanadium, and, most preferably, Zirconium. An exemplary Group 3 metal is Yttrium, a Lanthanide is Samarium, and an Actinide is Thorium.

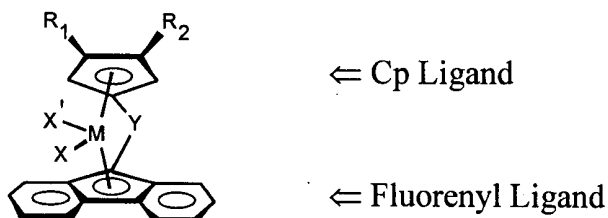
The ligand L may be any mononuclear or polynuclear hydrocarbyl or silahydrocarbyl ring, typically at least a mono-substituted cyclopentadienyl ring. Preferably L has the formula:



Formula 2

where R₁ is a substituted or unsubstituted alkyl, alkylsilyl or aryl substituent of 1 to about 30 carbon atoms, and R₂ - R₄ are the same or different hydrogen or substituted or unsubstituted alkyl, alkylsilyl or aryl substituents of 1 to about 30 carbon atoms, and any adjacent pair of R₁ - R₄ may be connected in a ring.

A particularly preferred group of bridged Cp-fluorenyl complexes have the general formula:



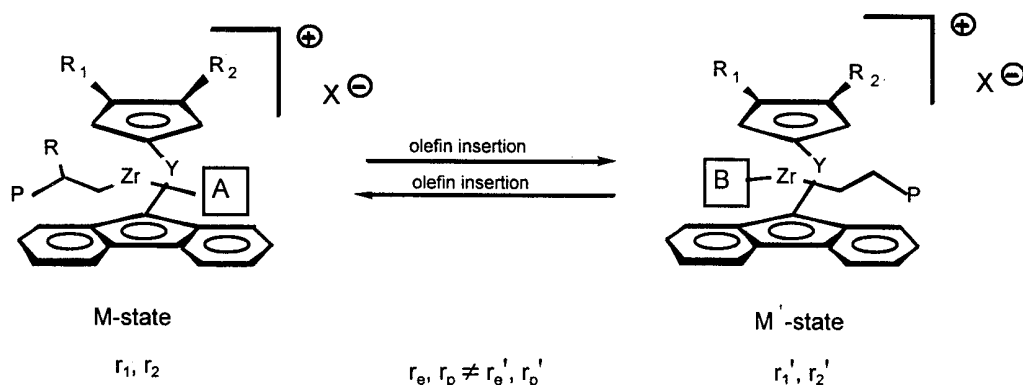
Formula 3

where M is a transition metal such as Ti, Hf, or Zr, R₁ and R₂ may be the same or different alkyl, alkylsilyl, or aryl, or substituted alkyl, alkylsilyl or aryl substituents of 1 to about 30 carbon atoms, or a ring thereof, and Y may be a bridging group preferably selected from a C₁-C₄ alkylidene radical and Ge, Si, P, B, or In radicals.

In a first aspect of the invention we have found surprisingly that when the Cp ligand is symmetric, e.g., R₁ = R₂ = a primary alkyl group such as a methyl group and Y = (CH₃)₂C or (CH₃)₂Si, that atactic alternating copolymers of ethylene and alpha olefins are formed.

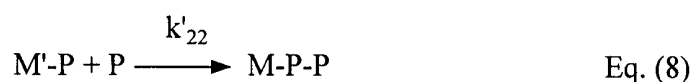
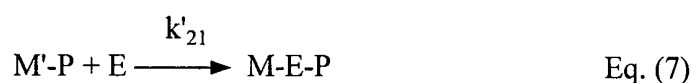
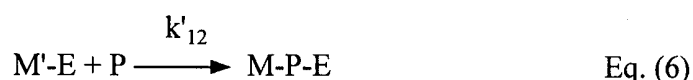
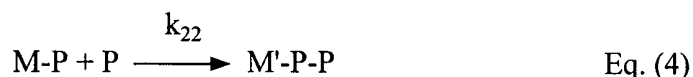
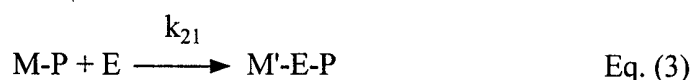
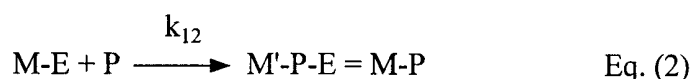
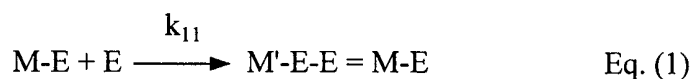
In a second aspect of the invention we have found that when the Cp ligand is assymmetric, e.g., $R_1 =$ a primary or secondary alkyl and $R_2 = H$, and $Y = (CH_3)_2C$ or $(CH_3)_2Si$, alternating, isotactic ethylene/alpha olefin copolymers are formed.

While not wishing to be bound by theory, we presently believe the alternating copolymerization of ethylene and alpha olefins with this latter class of catalysts ($R_1 \neq R_2$) proceeds by a novel mechanism whereby the catalyst interconverts between two states (state M and state M') with each monomer insertion. For catalysts where $R_1 \neq R_2$, the assymetry of the catalyst is such that the olefin inserts alternately at coordination sites A in state M and coordination site B in state M'. Since the coordination sites A and B are different, the kinetic selectivity of each site for insertion of the two comonomers can be controlled by suitable selection of R_1 and/or R_2 (that is, R_1 relative to R_2) such that in the presence of both monomers the insertion of monomer 1 at site A (state M) will predominate and the insertion of monomer 2 at site B (state M') will predominate. As the states alternate with each monomer insertion, this Cp ligand substituent selection results in control of the catalyst system to yield alternating copolymers of monomers 1 and 2 as set forth in Scheme 1 below:



Scheme 1, $R_1 \neq R_2$

Using the catalysts and process of the present invention, the copolymerization of olefins can be usefully described by a series of kinetic equations based on the well known Markov copolymerization statistics. By way of illustration, we derive these equations for ethylene/propylene copolymerization, but the approach is valid for other alpha olefins as well. For two states M and M' that interconvert with each olefin insertion, the rate of olefin insertion for two generic monomers E and P can be described by 8 equations:



where M-E and M-P are the active centers with the monomer E and P have previously inserted, respectively and k_{11} is the rate constant for insertion of monomer E at site M-E, and k_{12} is the rate constant of insertion of monomer P at site M-E, etc.. The relative reactivities at the two states are defined by the reactivity ratios with $r_1 = k_{11}/k_{12}$, $r_2 = k_{22}/k_{21}$, $r'_1 = k'_{11}/k'_{12}$, $r'_2 = k'_{22}/k'_{21}$ for the M-state and M'-state respectively.

We have found that for catalysts where R_1 = primary or secondary alkyl group and $R_2 = \text{H}$, that alternating copolymers of ethylene and alpha olefins can be obtained where the kinetic selectivities at the two states of the catalysts are different (i.e., $r_1, r_2 \neq r'_1, r'_2$). For these copolymerization systems, copolymers which show triad distributions with up to 70% EPE and PEP triads can be easily produced.

In addition, for these catalysts the stereochemistry of the alpha olefin insertion is also controlled to give isotactic alternating copolymers. This can be readily established by ^{13}C NMR spectroscopy. The ^{13}C NMR signal of the PEPEP methyl group is split into 3 peaks which can be assigned to mm, rm+mr and rr orientation of adjacent methyl groups in alt E/P (L. Zetta, G. Gatti, G. Audisio *Macromolecules* **11**, 763 (1978)). The relative intensity (estimated by multicomponent fit) of the mm-peak of polymers produced by [(3-MeCp)(Me₂C)(Flu)]ZrMe₂ (Metallocene **2**) range from 61-71% indicating an isotactic alternating copolymer. Also, [(3-iPrCp)(Me₂C)(Flu)]ZrMe₂ (Metallocene **4**) and [(Me₂Si)

(MeCp)(Flu)]ZrCl₂ (Metallocene 5) produce isotactic E/P copolymers with mm = 62 - 68% and mm = 50 - 58%.

In contrast, polymers produced by [(3,4-Me₂Cp)(Me₂C)(Flu)]ZrMe₂ (Metallocene 3) show a favored formation of the mr dyad (41-54%) of the PEPEP signal with a small preference of the isotactic over the syndiotactic dyad (mm > rr). This indicates atactic alt E/P copolymers are produced.

Thus this invention provides a process not only for producing alternating copolymers, but also for controlling the tacticity of said alternating copolymers to range from atactic to highly crystalline isotactic copolymers.

The catalyst system of the present invention consists of the transition metal component metallocene in the presence of an appropriate cocatalyst. The examples disclose methods for preparing the metallocenes in high yield. Generally, the preparation of the metallocene consists of forming the cyclopentadienyl ligand, introducing the bridging group and the fluorenyl ligand, followed by metallation with the metal tetrahalide to form the metallocene complex to which the cocatalyst is added to form the catalyst system.

Appropriate cocatalysts include alkylaluminum compounds, methylaluminoxane, or modified methylaluminoxanes (herein MAO) of the type described in the following references: U.S. Patent 4,542,199 to Kaminsky, et al.; Ewen, J. Am. Chem. Soc., 106 (1984), p. 6355; Ewen, et al., J. Am. Chem. Soc. 109 (1987) p. 6544; Ewen, et al., J. Am. Chem. Soc. 110 (1988), p. 6255; Kaminsky, et al, Angew. Chem., Int. Ed. Eng. 24 (1985), p. 507. Other cocatalysts which may be used include Lewis or protic acids, such as B(C₆F₅)₃ or [PhNMe₂H]⁺B(C₆F₅)₄⁻, which generate cationic metallocenes with compatible non-coordinating anions in the presence or absence of alkyl-aluminum compounds. Catalyst systems employing a cationic Group 4 metallocene and compatible non-coordinating anions are described in European Patent Applications 277,003 and 277,004 filed on 27.01.88 by Turner, et al.; European Patent Application 427,697-A2 filed on 09.10-90 by Ewen, et al.; Marks, et al., J. Am. Chem. Soc., 113 (1991), p. 3623; Chien, et al., J. Am. Chem. Soc., 113 (1991), p. 8570; Bochmann et al., Angew. Chem. Intl. Ed. Engl. 7 (1990), p. 780; and Teuben et al., Organometallics, 11 (1992), p. 362, and references therein.

In one of many embodiments, these catalyst systems can be placed on a suitable support such as silica, alumina, or other metal oxides, MgCl₂ or other supports. These catalysts can be used in the solution phase, in slurry phase, in the gas phase, or in bulk monomer. Both batch

and continuous polymerizations can be carried out. Appropriate solvents for solution polymerization include liquified monomer, and aliphatic or aromatic solvents such as toluene, benzene, hexane, heptane, as well as halogenated aliphatic or aromatic solvents such as CH₂Cl₂, chlorobenzene, fluorobenzene, hexafluorobenzene or other suitable solvents. Various agents can be added to control the molecular weight, including hydrogen, silanes and metal alkyls such as diethylzinc.

The bridged fluorenyl metallocenes of the present invention, in the presence of appropriate cocatalysts, are useful for the co-polymerization of ethylene with alpha-olefins, such as propylene, 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-octene, allyl trimethyl silane and combinations thereof. The polymerization of olefins is carried out by contacting the olefin(s) with the catalyst systems comprising the transition metal component and in the presence of an appropriate cocatalyst, such as an aluminoxane, or a Lewis acid such as B(C₆F₅)₃. In ethylene-propylene monomer systems, productivities in excess of 8 kg/g catalyst for the copolymerization has been attained.

Detailed Description for Carrying out the Invention, Including the Best Mode

The following detailed description illustrates the invention by way of example, not by way of limitation of the principles of the invention. This description will clearly enable one skilled in the art to make and use the invention, and describes several embodiments, adaptations, variations, alternatives and uses of the invention, including what are presently believed to be the best modes of carrying out the inventions.

In this regard, the invention is illustrated in the several examples, and is of sufficient complexity that the many aspects, interrelationships, and sub-combinations thereof simply cannot be fully illustrated in a single example. For clarity and conciseness, several of the examples show, or report only aspects of a particular feature or principle of the invention, while omitting those that are not essential to or illustrative of that aspect. Thus, the best mode embodiment of one aspect or feature may be shown in one example or test, and the best mode of a different aspect will be called out in one or more other examples, tests, structures, formulas, or discussions.

I. Metallocene Synthesis

The following metallocenes: **1**, [(3-tBuCp)(Me₂C)(Flu)]ZrMe₂; **2**, [(3-MeCp)(Me₂C)(Flu)]ZrMe₂; and **4**, [(3-iPrCp)(Me₂C)(Flu)]ZrMe₂, were prepared according to literature procedures (J. E. Ewen, R. L. Jones, A. Razavi, J. D. Ferrara, *J. Am. Chem. Soc.* **1988**, *110*, 6255-6., J. A. Ewen, M. J. Elder, R. L. Jones, L. Haspeslagh, J. L. Atwood, S. G. Bott, K. Robinson, *Makromol. Chem., Macromol. Symp.* **1991**, *48/49*, 253-295, A. Razavi, J. L. Atwood, *J. Organomet. Chem.* **1995**, *497*, 105-11, N. Herfert, G. Fink, *Makromol. Chem., Macromol. Symp.* **1993**, *66*, 157-178., J. A. Ewen, M. J. Elder in *Ziegler Catalysts* (Eds.; G. Fink, R. Mülhaupt, H.H. Brintzinger), Springer Verlag, Berlin, Heidelberg, **1995**, pp 99-109, A. Razavi, J. L. Atwood, *J. Organomet. Chem.* **1996**, *520*, 115-120.)

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Example 1 - Synthesis of [(3,4-Me₂Cp)(Me₂C)(Flu)]ZrMe₂ (Metallocene 3).

3,4,6,6' tetramethylfulvene was prepared from 1,2-dimethylcyclopentadienyl-Li (W. Mengele, J. Diebold, C. Troll, W. Röhl, H.-H. Brintzinger, *Organometallics* **1993**, *12*, 1931-1935). and acetone/pyrrolidine in methanol (3,4-Me₂Cp)(Me₂C)(Flu) was synthesized from 3,4,6,6' tetramethylfulvene and Li-fluorene following reported procedures (J. A. Ewen, M. J. Elder, R. L. Jones, L. Haspeslagh, J. L. Atwood, S. G. Bott, K. Robinson, *Makromol. Chem., Macromol. Symp.* **1991**, *48/49*, 253-295). ¹H-NMR (400 MHz, CDCl₃): δ = 7.71 (d, 2H, arom.), 7.34-7.16 (m, 6H, arom.), 5.87 (s, 1H, CH), 4.09 (s, 1H, CH); 3.09 (s, 2H, CH₂), 2.01 (s, 3H, CH₃), 1.89 (s, 3H, CH₃), 1.01 (s, 6H, CH₃).

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[(3,4-Me₂Cp)(Me₂C)(Flu)]ZrCl₂ was synthesized from Li-salt of the ligand and ZrCl₄ in CH₂Cl₂. The resulting red crystals were treated with 2.2 mol equivalent of MeLi in ether. Extraction with pentane gave [(3,4-Me₂Cp)(Me₂C)(Flu)]ZrMe₂ which was recrystallized once from toluene/pentane. ¹H-NMR (400 MHz, C₆D₆): δ = 8.07 (d, 2H, arom.), 7.50 (d, 2H, arom.), 7.32 (m, 2H, arom.), 7.07 (m, 2H, arom.), 5.15 (s, 2H, CH), 1.89 (s, 6H, CH₃) and 1.87 (s, 6H, CH₃), -1.17 (s, 6H, CH₃). Anal. calc. for C₂₅H₂₈Zr (M=419.75): C: 71.53%, H: 6.74% found: C: 71.27 % H: 7.01%.

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Example 2 - Synthesis of Me₂Si(MeCp)(Flu)ZrCl₂ (Metallocene 5):

1.75 g (0.020 mol) methylcyclopentadienyl Lithium was dissolved in 80 mL THF and was added dropwise to a solution of 5 g (0.019 mol) fluorenyldimethylsilylchlorid in 200 mL THF at room temperature and was stirred for 4 h. The solvent was removed under vacuo. The resulting oil was dissolved in 200 mL Et₂O and treated with saturated NH₄Cl and H₂O. The

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organic phase was dried over Na₂SO₄. Evaporation yields in 5.6 g (0.018 mol) of a yellow oil. It was dissolved in a mixture of hexane and ether 10:1 and filtered over silica. Yield: 5.1 g (0.017 mol). The ¹H-NMR spectrum shows a mixture of isomers.

1.64 g (5.4 mmol) of the ligand was dissolved in 50 mL Et₂O and 10.8 mmol of MeLi in Et₂O was added. the red solution was stirred for 1 h. 1.26 g (5.4 mmol) ZrCl₄ were added and the mixture was stirred for 45 min. The solvent was removed under vacuum. The residual red solid was dissolved in 40 mL CH₂Cl₂ and crystallized at -30 °C. Yield: 640 mg (1.38 mmol). The crude product was recrystallized once from CH₂Cl₂. ¹H-NMR: 8.17(m) 2H, 7.64-7.52 (m) 4H, 7.22-7.28 (m) 2H (fluorenyl protons); 6.29 (s) 1H, 5.71 (bs) 1H, 5.24 (s) 1H (Cp protons), 2.12 (s) 3H (methyl on Cp); 1.16 (s) 3H, 1.14 (s) 3H (Me₂Si-bridge).

II. Polymerization

Method A. Ethylene and Propylene. Copolymerizations of ethylene and propylene were carried out in a mixture of 100 mL propene and 20 ml toluene with a constant supply of ethylene at a pressure sufficient to give the desired E/P feed ratio. The reactions were started by injecting a 20 mL solution of metallocenedimethyl and MAO in toluene under Ar-pressure into an autoclave charged with 100 ml of propene and saturated with ethene at a total pressure of 82-160 psig. Low conversion and constant total pressure ensured a constant monomer feed. After 30-60 min the reaction was quenched by injection of 20 mL methanol. The copolymers were precipitated in 200 mL methanol and dried at 40 °C under reduced pressure. Quantitative ¹³C-NMR spectra of 300 mg of polymer dissolved in 4 mL of a mixture of dichlorobenzene with 10% benzene-d₆ were used for compositional analyses. The monomer feed was calculated using the fugacity equation and the experimentally estimated fugacity coefficient for ethene and propene. (R. Kravchenko, R. M. Waymouth, *Macromolecules* **1998**, 31, 1-6.)

Method B. Ethylene and Butene. 40 mL (23g) 1-butene were condensed at -78 °C in a volumetric flask and transferred into the -30 °C cooled autoclave which was purged with N₂ and 1-butene once. The autoclave was overpressurized with ethene at 30-35 psig total pressure and was equilibrated at 20 °C. 10 mL catalyst solution containing 100-105 mg MAO and 0.7-1.2 mmol zirconocenedimethyl were injected with a single ended injection tube pressurized with 100 psig Ar. The total pressure was kept constant at 33-37 psig. The reaction was quenched after 0.5 h by injecting 10 mL MeOH. The copolymer was precipitated in 200 mL

MeOH and dried at reduced pressure and 40 °C. The copolymer composition was analyzed by ¹³C-NMR according to J.C. Randall, *Macromol. Chem. Phys.*, **1989** C29, 201-317.

Method C. Ethylene and 4-methyl-1-pentene. 20 mL (13.3 g) 4-methyl-1-pentene were injected in the autoclave with 13 psig ethene pressure and equilibrated at 20 °C. 10 mL catalyst solution containing 100-105 mg MAO and 0.7-1.2 mmol zirconocenedimethyl were injected with a single ended injection tube pressurized with 100 psig Ar. The total pressure was kept constant at 17 psig. The reaction was quenched after 0.5 h by injecting 10 mL MeOH. The copolymer was precipitated in 200 mL MeOH and dried at reduced pressure and 40 °C. The copolymer composition was analyzed by ¹³C-NMR according K. Kimura, S. Yuasa, Y. Maru, *Polymer* **25**, (1984).

Examples 3 to 8 - Copolymerization of Ethylene and Propylene with Metallocenes 1, 2, and 3.

Polymerizations were carried out according to Method A and the results are presented in Table 1. The corresponding calculated triad distributions and reactivity ratios are presented in Table 2.

Table 1. Copolymerization of Ethylene and Propylene with Catalyst Systems of Metallocenes 1,2 and 3/MAO

Ex.	cat. ^{a)} /temp °C	%-E in feed	%-E in poly- mer	r ₁ ^{b)}	r ₂ ^{b)}	EEE	PEE + EEP	PEP	EPE	EPP + PPE	PPP	M _n ·10 ³ g/mol (M _w /M _n) ^{c)}
3	1/0	14.7	51	3.94	0.144	8.6	24.8	18.0	19.6	19.9	9.1	20.5 (2.4)
4	1/20	9.7	44	4.62	0.111	5.5	19.3	19.2	16.8	23.6	15.6	48.0 (1.5)
5	2/0	9.7	49	1.56	0.022	1.9	11.3	37.4	35.9	11.6	1.9	6.8 (1.8)
6	2/20	7.2	48	2.07	0.022	2.0	10.4	35.4	35.8	13.0	3.4	5.9 (2.5)
7	3/0	7.1	48	1.59	0.017	0.9	10.0	37.7	39.3	9.8	2.3	5.8 (2.3)
8	3/20	5.0	51	4.29	0.011	2.8	15.3	33.2	37.1	8.6	3.0	9.3 (1.5)

a) [Zr] = 6.4 * 10⁻⁶ - 1.76 * 10⁻⁵ M; [Al] = 1.3-1.4 * 10⁻² M.
b) based on the dyad; c) by low temp. GPC.

Note that polymers produced from metallocene 1 are random copolymers (<40% PEP and EPE triads, combined), whereas polymers produced from metallocenes 2 and 3 are highly

alternating (>70% PEP and EPE triads, combined). Moreover, the alternating copolymers from metallocene **2** are asotactic, whereas those from **3** are atactic.

Table 2: Calculated triad distribution and reactivity ratios, Metallocenes 1,2 and 3

Ex.	cat. /temp °C	Triad Distribution						fit ^[a] /10 ⁻³	Reactivity Ratios			
		EEE	PEE+ EEP	PEP	EPE	EPP+ PPE	PPP		r ₁₁	r ₂₂	r ₁₂	r ₂₁
3	1/0	8.6	24.8	17.6	20.0	19.9	9.1	3.0[b]	4.0	0.157	0.085	4.1
4	1/20	5.5	19.3	19.1	16.9	23.6	15.6	0.9[b]	5.3	0.141	0.075	4.7
									r ₁	r ₂	r' ₁	r' ₂
5	2/0	0.9	10.6	37.4	35.9	13.6	1.6	7.0[c]	1.14	0.048	1.88	0.012
6	2/20	2.3	12.7	35.4	35.8	11.9	2.0	8.9[c]	2.01	0.12	6.54	0.005
									r ₁	r ₂		
7	3/0	1.0	12.3	37.7	39.3	9.1	0.5	7.0[d]	2.1	0.009		
8	3/20	2.3	17.4	33.1	37.1	9.4	0.6	9.7[d]	4.9	0.007		

5 [a] chi-squared values; [b] calculated by Markov model 2nd order; [c] calculated by the switching model; [d] calculated by Markov model 1st order

Examples 9 and 10 - Copolymerization of Ethylene and Propylene with Metallocene 4/MAO Catalyst System, Me₂C(3-*i*PrCp)(Flu)ZrMe₂/MAO

10 Polymerizations were carried out according to Method A and are presented in Table 3. The corresponding experimental and calculated triad distributions and reactivity ratios are presented in Table 4. Note the close agreement between the experimental and calculated.

Table 3: E/P-Copolymerization catalyzed by Metallocene 4/MAO Catalyst System, [(Me₂C)(3-*i*PrCp)(Flu)]ZrMe₂/MAO

Ex.	temp. [°C]	pres. [psig]	E:P in feed	%-E ^{a)} in poly- mer	EE	EP	PP	r ₁ ^{b)}	r ₂ ^{b)}	r ₁ x r ₂	Prod. ^{c)}	M _n ·10 ³ g/mol (M _w /M _n) ^{d)}
9	20±1	162±1	0.094	49.3	10.4	78.3	11.3	2.8	0.027	0.076	7485	23.0 (1.6)
10	0±1	102±1	0.096	50.1	10.5	79.8	9.7	2.7	0.023	0.062	4960	26.6 (1.7)

a) monomer compositions were calculated from triad distribution;

- b) calculated from dyad distribution;
 c) Productivity = kg polymer/ (mol [Zr] h); d) determined by GPC.

5 **Table 4: Experimental and Calculated triad distributions and reactivity ratios for Metallocene 4/MAO**

Example		EEE	PEE + EEP	Triad Distribution				fit E ⁻³	Monomer Reactivity Ratios			
				PEP	EPE	PPE + EPP	PP P		r ₁	r ₂	r' ₁	r' ₂
9	exp.	3.3	15.2	30.8	32.9	14.1	3.7					
	calc.	3.3	15.2	32.2	32.9	13.8	2.6	10.3	2.09	0.12	6.19	0.010
10	exp.	3.2	15.1	31.8	35.4	11.9	2.6					
	calc.	3.6	17.0	32.2	35.4	10.5	2.3	12.4	2.17	0.058	7.0	0.007

Examples 11 and 12 - Copolymerization of Ethylene and α -Olefins with Metallocene 2/MAO Catalyst System, [(Me₂C)(3-MeCp)(Flu)]ZrMe₂/MAO.

- 10 Polymerizations were carried out according to Method B and C and are presented in Table 5. Example 11 is with butene and Example 12 is ethylene with 4-methyl-1-pentene

Table 5: E/ α -olefin-Copolymerization catalyzed by [(Me₂C)(3-MeCp)(Flu)]ZrMe₂/MAO

Example	Method	Temp °C	E:O in feed	%-E ^{a)} in polymer	EE	EO	OO	r ₁ ^{b)}	r ₂ ^{b)}	r ₁ x r ₂
11	B	20±1	0.018	45.5	4.3	82.1	13.6	11.6	0.006	0.07
12	C	20±1	0.03	49.3	12.9	74.4	12.7	11.5	0.01	0.12

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Example	Productivity ^{c)}	M _n •10 ³ g/mol (M _w /M _n) ^{d)}
11	4030	17.5 (1.8)
12	9800	31.2 (1.6)

- a) calculated from triads;
 b) calculated from diads;
 c) in kg polymer/(mol [Zr] hr);
 d) determined by GPC.

Example 13 and 14 - Copolymerization of Ethylene and Propylene with Metallocene 5/MAO Catalyst System, [(Me₂Si)(2-MeCp)(Flu)]ZrMe₂/MAO

Polymerizations were carried out according to Method A and are presented in Table 6.

5 The corresponding experimental and calculated triad distributions and reactivity ratios are presented in Table 7. Note the close agreement between the experimental and calculated.

Table 6: E/P-Copolymerization catalyzed by Metallocene 5/MAO Catalyst System, Me₂Si(2-MeCp)(Flu)ZrMe₂/MAO

Ex.	Temp. [°C]	pres. [psig]	E:P in feed	%-E ^{a)} in polymer	EE	EP	PP	r ₁ ^{b)}	r ₂ ^{b)}	r ₁ x r ₂	Prod. ^{c)}	M _n *10 ³ g/mol (M _w /M _n) ^{d)}
13	20±1	140±1	0.051	51.2	10.1	79.2	10.7	5.0	0.014	0.07	84000	84(1.7)
14	0±1	92±1	0.068	52.3	6.4	83.6	10.0	2.2	0.016	0.036	3000	92.5(1.8)

a) monitor compositions were calculated from triad distribution;

b) calculated from dyad distribution;

c) kg polymer/(mol [Zr] h);

d) by low temp. GPC.

Table 7: Experimental and Calculated triad distributions and reactivity ratios for Metallocene 5/MAO

Ex		Triad distribution							monomer reactivity ratios [b]			
		EEE	PEE+EEP	PEP	EPE	PPE+EPP	PPP	fit[a] E ⁻³	r ₁	r ₂	r' ₁	r' ₂
13	exp.	3.9	13.6	33.0	35.7	10.7	3.1					
	calc.	3.1	16.2	33.0	35.7	10.8	1.3	9.2	3.6	0.025	12.1	0.004
14	exp.	6.7	17.8	27.8	37.1	7.9	2.6					
	calc.	6.7	21.3	29.2	37.1	5.4	0.3	25.5	4.2	0.025	16.3	0.002

[a] chi-squared values; [b] calculated by the switching model.

The alternating polymers of this invention range from tacky amorphous gum elastomers to tough rubbery materials to semicrystalline thermoplastics.

INDUSTRIAL APPLICABILITY:

It is evident that the polymers, and the catalyst systems and processes for their production have wide industrial applicability, in that it is now possible to create an alternating isotactic or atactic structure of ethylene/alpha olefin polymers by selection of the nature and relative symmetry of the ligand substituents, and by the selection of bridge constituents of

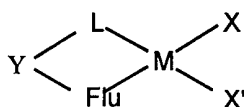
catalyst systems employing bridged metallocene components. The resulting polymers have very evident industrially useful properties, ranging from amorphous or isotactic gum elastomers to highly crystalline isotactic rigid polymers, including intermediate properties such as thermoplastic elastomers to flexible thermoplastics. Such products are recognized in industry to be useful for adhesives, films, fibers and castable and machinable products.

It should be understood that various modifications within the scope of this invention can be made by one of ordinary skill in the art without departing from the spirit thereof. We therefore wish this invention to be defined by the scope of the appended claims as broadly as the prior art will permit, and in view of the specification if need be.

We claim:

1) In a method of producing copolymers of ethylene with at least one alpha olefin monomer by reaction in the presence of a catalyst system comprising a metallocene component with a cocatalyst, the improvement which comprises:

- 5 a) carrying out said reaction in the presence of said catalyst system wherein said metallocene is a bridged cyclopentadienyl-fluorenyl complex of the general formula:

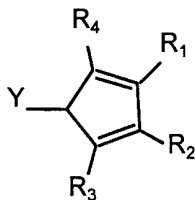


in which:

- 10 I) M is a Group 3, 4 or 5 Transition metal, a Lanthanide or an Actinide;
 ii) X and X' are the same or different uninegative ligand;
 iii) L is a substituted or unsubstituted cyclopentadienyl (Cp) or indenyl ligand;
 iv) Flu is a substituted or unsubstituted fluorenyl ligand; and
 v) Y is a bridging group; and
 b) said reaction carried out for a time sufficient to produce copolymers having
 15 alternating ethylene/alpha olefin structure.

2. An improved polymerization method as in claim 1 wherein said ligand L is a mononuclear or polynuclear hydrocarbyl or silahydrocarbyl ring.

- 20 3. An improved polymerization method as in claim 2 wherein said ligand L is at least a mono-substituted cyclopentadienyl (Cp) ring of the formula:



wherein:

- 25 a) R₁ is a substituted or unsubstituted alkyl, alkylsilyl or aryl substituent of 1 to about 30 carbon atoms, R₂-R₄ are the same or different hydrogen or substituted or unsubstituted

alkyl, alkylsilyl or aryl substituents from 1 to about 30 carbon atoms; and any adjacent pair of $R_1 - R_4$ may be connected in a ring; and

b) Y is selected from C_1-C_4 alkylidene radical, and Ge, Si, P, B or In radicals.

5 4) An improved polymerization method as in claim 3 wherein R_3 and R_4 are hydrogen.

5) An improved polymerization method as in claim 4 wherein M is selected from Ti, Hf or Zr.

10 6) An improved polymerization method as in claim 3 wherein the cyclopentadienyl ligand is symmetric, and said reaction produces atactic alternating copolymers of ethylene and alpha olefins.

15 7) An improved polymerization method as in claim 6 where Y is selected from $(CH_3)_2C$ and $(CH_3)_2Si$.

8) An improved polymerization method as in claim 3 wherein said cyclopentadienyl ligand is asymmetric, and said reaction produces alternating isotactic or atactic ethylene/alpha olefin copolymers.

20 9) An improved polymerization method as in claim 8 wherein Y is selected from $(CH_3)_2C$ and $(CH_3)_2Si$.

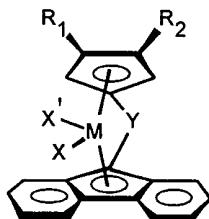
10) An improved polymerization method as in claim 1 wherein:

25 a) said alpha olefin is selected from propylene, 1-butane, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-octene, allyl trimethyl silane and mixtures thereof; and

b) the substituents on L are selected to control the symmetry of the ligand L to selectively produce alternating atactic, isotactic or atactic and isotactic copolymers.

30 11) An improved polymerization method as in claim 3 wherein said metallocene is selected from $[(3-MeCp)(Me_2C)(Flu)]ZrMe_2$, $[(3-iPrCp)(Me_2C)(Flu)]ZrMe_2$, $[(Me_2Si)(MeCp)(Flu)]ZrCl_2$ and $[(3,4-Me_2Cp)(Me_2C)(Flu)]ZrMe_2$.

12) A metallocene component for a polymerization catalyst system for polymerizing olefin monomers to produce polymers and copolymers comprising a symmetric bridged Cp fluorenyl metallocene complex of the formula:



5

wherein:

- a) $R_1=R_2$ selected from substituted alkyl, alkylsilyl or aryl substituents of 1 to about 30 carbon atoms and may be connected in a ring;
- b) M is a Group 3, 4 or 5 Transition metal, a Lanthanide or an Actinide;
- c) X and X1 are the same or different uninegative ligand; and
- d) Y is a bridging group.

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13) A metallocene polymerization catalyst component as in claim 12 wherein Y is a $C_1=C_4$ alkylidene radical and Ge, Si, P, B, or In radical.

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14) A metallocene polymerization catalyst component as in claim 13 wherein said metallocene is [(3,4- R_1 , R_2 Cp)(Y)(Flu)]Zr X, X¹.

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15) A metallocene polymerization catalyst component as in claim 14 wherein said metallocene is [(3,4- Me_2 Cp) (Me_2 C) (Flu)] Zr Me_2 .

16) An ethylene/alpha olefin copolymer having an ethylene content between about 35 and 85% by mole, wherein:

- a) the product of the reactivity ratios $r_1 \cdot r_2$, where r_1 is the reactivity ratio for ethylene and r_2 is the reactivity ratio for propylene, is less than about 0.1, and
- b) the configuration of E-AO-E sequences are predominantly isotactic, where E is an ethylene unit and AO is an alpha olefin unit.

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17) An ethylene/alpha olefin copolymer of claim 16 having an ethylene content between about 40 and 60% by mole wherein the distribution of E/AO sequences are predominantly alternating and the configuration of E-AO-E sequences are predominantly isotactic.

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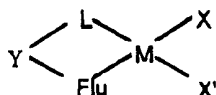
AMENDED CLAIMS

[received by the International Bureau on 21 December 1998 (21.12.98);
original claims 1, 3, 11, 12 and 14 amended;
remaining claims unchanged (3 pages)]

We claim:

1) In a method of producing copolymers of ethylene with at least one alpha olefin monomer by reaction in the presence of a catalyst system comprising a metallocene component with a cocatalyst, the improvement which comprises:

- 5 a) carrying out said reaction in the presence of said catalyst system wherein said metallocene is a bridged cyclopentadienyl-fluorenyl complex of the general formula:

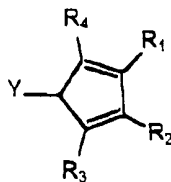


in which:

- 10 i) M is a Group 3, 4 or 5 Transition metal, a Lanthanide or an Actinide;
ii) X and X' are the same or different uninegative ligand;
iii) L is a substituted cyclopentadienyl (Cp) or indenyl ligand;
iv) Flu is a substituted or unsubstituted fluorenyl ligand; and
v) Y is a bridging group; and
- 15 b) said reaction carried out for a time sufficient to produce copolymers having alternating ethylene/alpha olefin structure.

2. An improved polymerization method as in claim 1 wherein said ligand L is a mononuclear or polynuclear hydrocarbyl or silahydrocarbyl ring.

- 20 3. An improved polymerization method as in claim 2 wherein said ligand L is at least a mono-substituted cyclopentadienyl (Cp) ring of the formula:



wherein:

- 25 a) R₁ is a substituted or unsubstituted, primary or secondary alkyl, alkylsilyl or aryl substituent of 1 to about 30 carbon atoms, R₂-R₄ are the same or different hydrogen or

substituted or unsubstituted, primary or secondary alkyl, alkylsilyl or aryl substituents from 1 to about 30 carbon atoms; and any adjacent pair of $R_1 - R_4$ may be connected in a ring; and

b) Y is selected from C_1-C_4 alkylidene radical, and Ge, Si, P, B or In radicals.

5 4) An improved polymerization method as in claim 3 wherein R_3 and R_4 are hydrogen.

5) An improved polymerization method as in claim 4 wherein M is selected from Ti, Hf or Zr.

10 6) An improved polymerization method as in claim 3 wherein the cyclopentadienyl ligand is symmetric, and said reaction produces atactic alternating copolymers of ethylene and alpha olefins.

7) An improved polymerization method as in claim 6 where Y is selected from $(CH_3)_2C$ and $(CH_3)_2Si$.

8) An improved polymerization method as in claim 3 wherein said cyclopentadienyl ligand is asymmetric, and said reaction produces alternating isotactic or atactic ethylene/alpha olefin copolymers.

9) An improved polymerization method as in claim 8 wherein Y is selected from $(CH_3)_2C$ and $(CH_3)_2Si$.

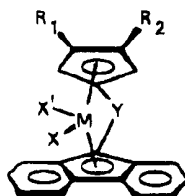
10) An improved polymerization method as in claim 1 wherein:

25 a) said alpha olefin is selected from propylene, 1-butane, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-octene, allyl trimethyl silane and mixtures thereof; and

b) the substituents on L are selected to control the symmetry of the ligand L to selectively produce alternating atactic, isotactic or atactic and isotactic copolymers.

30 11) An improved polymerization method as in claim 3 wherein said metallocene is selected from $[(3-MeCp) (Me_2C) (Flu)] ZrMe_2$, $[(3-iPrCp) (Me_2C) (Flu)] ZrMe_2$, $[(Me_2Si) (3-MeCp) (Flu)] ZrCl_2$ and $[(3,4-Me_2Cp) (Me_2C) (Flu)] ZrMe_2$.

12) A metallocene component for a polymerization catalyst system for polymerizing olefin monomers to produce polymers and copolymers comprising a symmetric bridged Cp fluorenyl metallocene complex of the formula:



5

wherein:

- a) $R_1=R_2$ selected from substituted or unsubstituted, primary or secondary alkyl, alkylsilyl or aryl substituents of 1 to about 30 carbon atoms and may be connected in a ring;
- b) M is a Group 3, 4 or 5 Transition metal, a Lanthanide or an Actinide;
- c) X and X' are the same or different uninegative ligand; and
- d) Y is a bridging group.

10

13) A metallocene polymerization catalyst component as in claim 12 wherein Y is a $C_1=C_4$ alkylidene radical and Ge, Si, P, B, or In radical.

15

14) A metallocene polymerization catalyst component as in claim 13 wherein said metallocene is $[(3,4-R_1, R_2 Cp)(Y)(Flu)]Zr X, X'$, where $R_1=R_2 = \text{Methyl}$.

20

15) A metallocene polymerization catalyst component as in claim 14 wherein said metallocene is $[(3,4-Me_2Cp)(Me_2C)(Flu)]ZrMe_2$.

16) An ethylene/alpha olefin copolymer having an ethylene content between about 35 and 85% by mole, wherein:

- a) the product of the reactivity ratios $r_1 \cdot r_2$, where r_1 is the reactivity ratio for ethylene and r_2 is the reactivity ratio for propylene, is less than about 0.1, and
- b) the configuration of E-AO-E sequences are predominantly isotactic, where E is an ethylene unit and AO is an alpha olefin unit.

25

STATEMENT UNDER ARTICLE 19

Claim 11 (page 17), line 3 (line 32 on page 17) "(MeCp) is corrected to read --(3-MeCp)--;

Claim 12 (page 18, part a), after "substituted" the phrase --or unsubstituted, primary or secondary-- has been inserted;

Claim 12 (page 18), in part c (line 10 of Claim 12), the typo "X1" has been corrected to read -- X'--;

Claim 14 (page 18), line 1 "atalyst" has been corrected to read --catalyst--; and

Claim 14 (page 18), line 2 the phrase --,where R₁= R₂ = Methyl-- has been inserted.

STATEMENT

The invention has been clarified and more precisely claimed by amendments to claims 1, 3 and 12. In claim 1, part iii) the cyclopentadienyl is limited to a substituted Cp or indenyl ligand, and in claim 3, the R₁ and R₂-R₄ substituents are defined as primary or secondary. Likewise in claim 12, R₁ and R₂ are defined as primary or secondary. Claim 14 has been clarified to define R₁ and R₂ as methyl, for the symmetric Catalyst 3 where Y is a bridging group.

Although the cited prior art discloses that certain bridged metallocene catalysts having Cp and fluorenyl groups can copolymerize olefins, the results are random copolymers. The instant application discloses that primary, secondary and aryl substituents of the class claimed produce alternating isotactic or atactic copolymers. In contrast, as shown by Examples 3 and 4 of the application, a tertiary substituent on the Cp ligand produces random copolymers.

There is no teaching in the references that selection of substituents would control properties of the resulting polymers in the manner of the claimed inventive process or catalysts. As shown in Examples 3 and 4 on pages 11 and 12 the tertiary Cp substituent (Catalyst 1) produces random polymers, while other Cp substituents produce random copolymers.

The invention as claimed clearly distinguishes over the cited references.

The RO/US is authorized to charge any fees that may be due, or credit any overpayment, to Deposit Account No. 08-1641.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/14734

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C08F 2/04, 2/18, 2/34, 10/02
US CL :526/170, 352

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)

U.S. : 526/170, 352

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 practicable, search terms used)

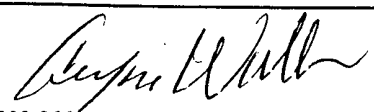
C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CA 2,017,190 A1 (SPALECK et al) 20 November 1990 (20-11-90), see page 4.	1-17
X	EP 0,612,769 A1 (TOSOH CORPORATION) 31 August 1994 (31-08-94), see page 2.	1-15

Further documents are listed in the continuation of Box C. See patent family annex.

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