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CA 2029077 C 2003/08/19

(11)(21) **2 029 077**

(12) **BREVET CANADIEN
CANADIAN PATENT**

(13) **C**

(22) Date de dépôt/Filing Date: 1990/10/31

(41) Mise à la disp. pub./Open to Public Insp.: 1992/05/01

(45) Date de délivrance/Issue Date: 2003/08/19

(51) Cl.Int.⁵/Int.Cl.⁵ C08F 2/00, C08F 210/00

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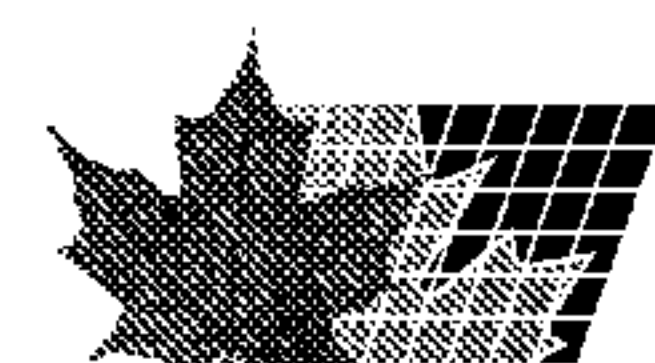
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(54) Titre : COPOLYMERES SYNDIOTACTIQUES DE PROPYLENE ET D'OLEFINES

(54) Title: SYNDIOTACTIC COPOLYMERS OF PROPYLENE AND OLEFINS

(57) **Abrégé/Abstract:**

Copolymers of propylene and olefins having from 2 to 10 carbon atoms in which the microstructure of the side chain is highly syndiotactic, more particularly random copolymers. Also disclosed is a process for preparing said copolymers by metallocene catalysts using an asymmetric bridged dicyclopentadienyl derivative of a metal of groups 4b, 5b, or 6b.



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ABSTRACT

Syndiotactic copolymers of propylene and olefins

Copolymers of propylene and olefins having from 2 to 10 carbon atoms in which the microstructure of the side chain is highly syndiotactic, more particularly random copolymers. Also disclosed is a process for preparing said copolymers by metallocene catalysts using an asymmetric bridged dicyclopentadienyl derivative of a metal of groups 4b, 5b, or 6b.

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SPECIFICATIONS

BACKGROUND INVENTION

SYNDIOTACTIC COPOLYMERS OF PROPYLENE AND OLEFINS

5 FIELD OF INVENTION: The present invention relates to copolymers
of propylene and olefins having from 2 to 10 carbon atoms having
a novel stereoregular microstructure and more particularly random
copolymers of propylene and olefins having from 2 to 10 carbon
atoms in which the microstructure of the side chains is highly
0 syndiotactic except for polyethylene units. More particularly the
present invention relates to syndiotactic random copolymers of
propylene and olefins having from 4 to 8 carbon atoms, wherein the
polypropylene units and the polyolefin units have each syndiotactic
microstructure in the random copolymer.

5 DESCRIPTION OF PRIOR ART: As is well know, olefins polymers or
copolymers such as polypropylene, polybutene, polypentene... etc.
are generally produced by techniques such as radical
polymerization, anionic polymerization, cationic polymerization and
polymerization using a Ziegler-type catalyst, as well as copolymers
0 of propylene with other olefins. These polymers are divided into
three groups, isotactic, syndiotactic and atactic polymers,
depending on the steric configuration of side chains thereof. It
has heretofore been known that usual radical, anionic and cationic
polymerization methods provide olefin polymers having mainly an

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atactic structure, and that the polymerization methods using a Ziegler-type catalyst provide olefin polymers having mainly an isotactic or atactic structure.

The isotactic structure is typically described as having the alkyl groups attached to the tertiary carbon atoms of successive monomeric units on the same side of a hypothetical plane through the main chain of the polymer, e.g., the alkyl groups are all above or below the plane. Another way of describing the structure is through the use of NMR. Bovey's NMR nomenclature for an isotactic pentad is ...mmmm... with each "m" representing a "meso" dyad or successive alkyl groups on the same side in the plane. As known in the art, any deviation or inversion in the structure of the chain lowers the degree of isotacticity of the polymer.

In contrast to the isotactic structure, syndiotactic polymers are those in which the alkyl groups attached to the tertiary carbon atoms of successive monomeric units in the chain lie on alternate sides of the plane of the polymer. In NMR nomenclature, this pentad is described as ...rrr... in which the "r" represents a "racemic" dyad, i.e., alkyl groups on alternate sides of the plane. The percentage of r dyads in the chain determines the degree of syndiotacticity of the polymer. A number of methods of preparing olefin homopolymers or copolymers and their structures have been reported. Preparation of syndiotactic polypropylene is disclosed and its particular microstructure is claimed in U.S. Patent

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4,892,851. However, preparation of random copolymers of propylene and olefins having from 2 to 10 carbon atoms of very high syndiotactic structure has not yet been disclosed.

5 SUMMARY OF THE INVENTION

10 The present invention provides random copolymers of propylene and olefins having from 2 to 10 carbon atoms having a very high syndiotactic index and with a novel syndiotactic microstructure. The novel microstructure for the syndiotactic copolymers included within the present invention has blocks of repeating racemic (r) dyads connected by units predominantly consisting of a pair of meso (m) dyads, i.e., a meso triad "mm". The predominant structure of each polymer in the copolymer chain is described in NMR nomenclature as ...rrrmmrrr...

15 Preferably, the degree of syndiotacticity in the polypropylene units in the copolymer chain consists of greater than 80% racemic dyads, most preferably, greater than 90% racemic dyads, and the deviations from the repeating racemic pattern are predominantly meso triads, while the degree of syndiotacticity for the polyolefins units, except polyethylene units, in the copolymer
20 consist of greater than 70% racemic dyads.

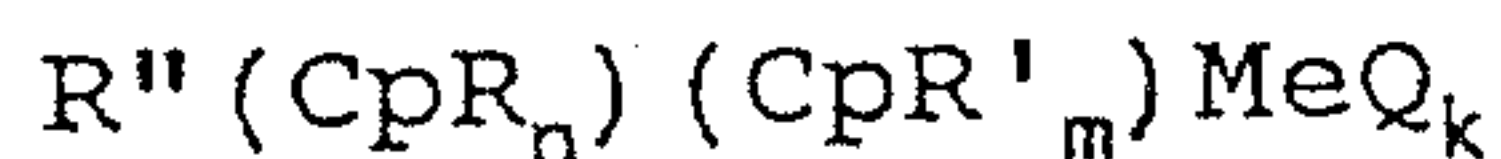
 The present invention relates to random copolymers of propylene and olefins having from 2 to 10 carbon atoms having a degree of polymerization of not less than 5 and having a

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stereoregular structure which is mainly syndiotactic.

The novel microstructure is obtained through use of a stereorigid metallocene catalyst described by the formula:



5 wherein each Cp is a cyclopentadienyl or substituted cyclopentadienyl ring; each R and each R' is the same or different and is a hydrocarbyl radical having 1-20 carbon atoms; R'' is a structural bridge between the two Cp rings imparting stereorigidity to the catalyst; Me is a transition metal; and each Q is a
 10 hydrocarbyl radical or is a halogen. Further, R'_m may be selected so that (CpR'_m) is a substantially different substituted cyclopentadienyl ring than (CpR_n). This catalyst was disclosed and claimed in U.S. Patent No. 4,892,851. It was discovered that the use of a metallocene catalyst as described above with
 15 cyclopentadienyl ligands that are substantially different in terms of their substituents, and thus their electrical and steric effects, produces not only a predominantly syndiotactic polymer rather than an isotactic polymer but also syndiotactic copolymers having the novel microstructure described above.

20

The novel microstructure of syndiotactic copolymers is obtained by utilizing at least one of the catalysts described by the above formula and introducing the catalyst into a polymerization reaction zone containing both olefin monomers. In

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addition, an electron donor compound and/or a cocatalyst such as alumoxane may be introduced into the reaction zone. Further, the catalyst may also be pre-polymerized prior to introducing it into the reaction zone and/or prior to the stabilization of reaction conditions in the reactor. A prepolymerization process is disclosed in U.S. Patent No. 4,767,735.

The present invention also includes a process for producing syndiotactic homopolymers of olefin having from 4 to 8 carbon atoms in accordance with the invention.

DETAILED DESCRIPTION OF THE INVENTION

The copolymers of propylene and olefins of the present invention have a syndiotactic structure and include syndiotactic propylene-ethylene, propylene-butene, propylene-pentene, propylene-4-methylpentene, propylene-hexene, propylene-octene and analogs. This novel syndiotactic structure of the copolymers of the invention consists predominantly of the structure described in NMR nomenclature as ...rrrmmmrrrr... and consists of a very high percentage of racemic dyads. The copolymers can be produced to varying specifications for melting points, molecular weights, and molecular weight distributions. The tacticity of the copolymers of the invention is determined by the nuclear magnetic resonance (NMR) method. In more detail, the tacticity of the homopolymers of olefins is determined by analyzing the signal of C, carbon of

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an aromatic ring and the signal of methine-methylene carbon in NMR (nuclear magnetic resonance spectrum as measured using an isometric carbon), or the proton signal o H-NMR. The tacticity can be determined by NMR for each given number of constituting units connected continuously, such as a dyad in which the number of constituting units is two, a triad in which the number of constituting units is three, and a pentad in which the number of constituting units is five. The term "copolymer having mainly a syndiotactic structure" as used herein means that each polymer units present in the random copolymer has such a syndiotactic structure that the syndiotacticity expressed in terms of the dyad ([r] value) is not less than 80% for the propylene units and 70% for the olefins units, except those formed from ethylene in which the [r] value for the propylene units and the ethylene units is not less than 80%. The metallocene catalysts of the present invention may be described by the formula $R''(CpR_n)(CpR'_m)MeQ_k$ wherein each Cp is a cyclopentadienyl or substituted cyclopentadienyl ring; R and R' are hydrocarbyl radicals having 1-20 carbon atoms and each may be the same or different; R'' is a structural bridge between the two Cp rings imparting stereorigidity to the catalyst, and R'' is preferably selected from the group consisting of an alkyl radical having 1-4 carbon atoms or a hydrocarbyl radical containing silicon, germanium, phosphorus, nitrogen, boron, or aluminum; Me is a group 4b, 5b or 6b metal from the Periodic Table of Elements;

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each Q is a hydrocarbyl radical having 1-20 carbon atoms or is a halogen; $0 \leq k \leq 3$; $0 \leq n \leq 4$; and $1 \leq m \leq 4$. In order to be syndio-specific, it was discovered that the catalyst must have substantially different Cp ring substituents. Therefore, R'_m is selected such that (CpR'_m) is a substantially different substituted ring than (CpR_n) . In order to produce a syndiotactic polymer, the characteristics of the groups substituted directly on the cyclopentadienyl rings seem to be important. Where there is a substantial difference in the characteristics of the ring substituents, either electrical, steric or other difference resulting in a substantially different effect on the metal complex as compared with symmetrical rings, then the catalyst can be expected to produce predominantly syndiotactic polymers.

In a preferred catalyst useful in producing polymers of the present invention, Me is titanium, zirconium, hafnium or vanadium; Q is preferably a halogen, and it is most preferably chlorine; and k is preferably 2, but it may vary with the valence of the metal atom. Exemplary hydrocarbyl radicals include methyl, ethyl, propyl, isopropyl, butyl, isobutyl, amyl, isoamyl, hexyl, heptyl, octyl, nonyl, decyl, cetyl, phenyl, and the like. Other hydrocarbyl radicals include other alkyl, aryl, alkenyl, alkylaryl or arylalkyl radicals. Further, R_n and R'_m may include hydrocarbyl radicals attached to a single carbon atom in the Cp ring. A preferred catalyst is isopropyl(fluorenyl) (cyclopentadienyl) Zr

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dichloride.

The catalyst may be prepared by any method known in the art. The Examples below disclose two methods of preparing the catalyst with the second method being preferred as it produces a more stable and active catalyst. It is important that the catalyst complex be "clean" as usually low molecular weight, amorphous polymer is produced by impure catalyst. Generally, the preparation of the catalyst complex consists of forming and isolating the Cp or substituted Cp ligands which are then reacted with a halogenated metal to form the complex.

The metallocene catalyst of the present invention are useful in many of the polymerization processes known in the art including many of those disclosed especially for the use of isotactic copolymers of propylene and other olefins. When the catalyst of the present invention are used in these types of processes, syndiotactic copolymers are produced rather than isotactic copolymers. A preferred polymerization procedure includes the step of prepolymerizing the catalyst and/or precontacting the catalyst with a cocatalyst and the olefin monomers prior to introducing the catalyst into a reaction zone.

Consistent with the prior disclosures of metallocene catalysts for the production of isotactic polymers, the catalysts of the present invention are particularly useful in combination with an aluminum cocatalyst, preferably an alumoxane, an alkyl aluminum,

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or a mixture thereof. In addition, a complex may be isolated between a metallocene catalyst as described herein and an aluminum cocatalyst in accordance with the teachings of European Patent Publication no. 226,463 published on June 24, 1987 and assigned to
5 Exxon Chemical Patents Inc. with Howard Turner listed as the inventor. The alumoxanes useful in combination with the catalysts of the present invention may be represented by the general formula $(R-Al-O-)$ in the cyclic form and $R(R-Al-O)_n-ALR_2$ in the linear form wherein R is an alkyl group with one to five carbon atoms and n is
10 an integer from 1 to about 20. Most preferably, R is a methyl group. The alumoxanes can be prepared by various methods known in the art. Preferably, they are prepared by contacting water with a solution of trialkyl aluminum, such as trimethyl aluminum, in a suitable solvent such as benzene. Another preferred method includes
15 the preparation of alumoxane in the presence of a hydrated copper sulfate as described in U.S. Patent no. 4,404,344. This method comprises treating a dilute solution of trimethyl aluminum in toluene with copper sulfate. The preparation of other aluminum cocatalysts useful in the present invention may be prepared by
20 methods known to those skilled in the art.

The invention having been generally described, the following examples are given as particular embodiments of the invention and

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to demonstrate the practice and advantages thereof. It is understood that the examples are given by way of illustration and are not intended to limit the specification or the claims to follow in any manner. The examples given below illustrate the present invention and its various advantages and benefits in more detail. Synthesis procedures are described for zirconium metallocene catalysts. The general catalyst formula for the catalyst produced by these methods is iso-propyl(fluorenyl)(cyclopentadienyl) $ZrCl_2$.

PREPARATION OF THE CATALYST - METHOD A

The synthesis procedures for the catalyst were performed under an inert gas atmosphere using a Vacuum Atmospheres glove box or Schlenk techniques. The synthesis process generally comprises the steps of 1) preparing the halogenated or alkylated metal compound, 2) preparing the ligand, 3) synthesizing the complex, and 4) purifying the complex.

In Method A, a halogenated metal compound was prepared using tetrahydrofuran ("THF") as a solvent resulting in THF bound in with the final catalyst complex. Specifically, $MeCl_4 \cdot THF$ was prepared as described in Manzer, L., Inorg. Synth., 21, 135-36 (1982). In the Examples below, Me is zirconium and hafnium, but it may also include titanium or other transition metals.

The substituted dicyclopentadienyl ligand may be prepared using various processes known in the art depending upon the selection of the specific bridge or ring substituents. In the

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preferred embodiments shown in the Examples below, the ligand is 2,2-isopropyl-(fluorene)cyclopentadiene. To prepare this ligand, 44 gms (0.25 mol) of fluorene were dissolved in 350 ml THF in a round bottom flask equipped with a side arm and dropping funnel. Contained within the funnel were 0.25 mol of tri-methyl lithium (CH_3Li) in ether (1.4M). The CH_3Li was added dropwise to the fluorene solution and the deep orange-red solution was stirred for several hours. After gas evolution had ceased, the solution was cooled to -78°C and 100 ml of THF containing 26.5 mgs (0.25 mol) of 6,6-dimethylfulvene was added dropwise to the solution. The red solution was gradually warmed to room temperature and stirred overnight. The solution was treated with 200 ml of water and stirred for ten minutes. The organic fraction of the solution was extracted several times with 100 ml portions of diethylether, and the combined organic phases were dried over magnesium sulfate. Removal of the ether from the organic phases left a yellow solid which was dissolved in 500 ml of chloroform and recrystallized by addition of excess methanol at 2°C to yield a white powder.

The elemental analysis of the ligand showed carbon to be 91.8% by weight of the compound and hydrogen to be 7.4% by weight. This corresponds to the weight percentages for $\text{C}_{21}\text{H}_{20}$, of 92.6% for carbon and 7.4% for hydrogen. The NMR spectrum for the ligand establishes the structure to include one cyclopentadienyl ring attached by an isopropyl bridge to a second cyclopentadienyl ring that is

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substituted to form a fluorenyl radical.

A syndiospecific catalyst complex was synthesized using the ligand and the metal tetrachloride-THF complex. The catalyst was formed by adding 0.05 mol of N-butyl lithium and hexane (1.6M) was added dropwise to a 100 ml THF solution containing 6.8 mgs (0.025 mol) of the Cp ligand described above. The solution was stirred at 35°C for twelve hours after which 9.4 gms (0.025 mol) of $ZrCl_4 \cdot 2THF$ contained in 200 ml of THF were rapidly cannulated together with the ligand solution into a 500 ml round bottom flask with vigorous stirring. The deep orange-red solution was stirred for twelve hours under reflux. A mixture of LiCl and a red solid were isolated by removing the solvents under vacuum.

Catalyst complexes produced in accordance with Method A are noted to be somewhat impure and extremely air and moisture sensitive. In the Examples below, Method A catalysts were purified using one or more of the following purification procedures:

1. Extraction with pentane. Trace quantities of a yellow impurity contained in the solid red catalyst complex were repeatedly extracted with pentane until the pentane became colorless.

2. Fractional recrystallization. The red complex was separated from the white LiCl by dissolving it in 100 ml of toluene, filtering it through a fine porosity sintered glass frit, and forming a saturated solution by adding pentane. The red

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zirconium complex was isolated using crystallization at -20°C .

3. Chromotography on bio-beads. 50 gms of bio-beads SM-2 (20-50 mesh spherical, macroreticular styrene-divinylbenzene copolymer from Bio-Rad laboratories) were dried under vacuum at 70°C for 48 hours in a 30 x 1.5 centimeter column. The beads were then equilibrated with toluene for several hours. A concentrated solution of the red catalyst complex in toluene was eluded down the column with 150-200 ml of toluene. The complex was recovered by evaporating the toluene under vacuum.

PREPARATION OF THE CATALYST - METHOD B

As an alternative synthesis procedure, Method B provides catalyst that are more air stable, more active, and produce a higher percentage of syndiotactic polypropylene. In this process, methylene chloride is used as a non-coordinating solvent. The process described below uses hafnium as the transition metal, but the procedure is adaptable for use with zirconium, titanium or other transition metals. The substituted dicyclopentadienyl ligand was synthesized in THF in the same manner as described in Method A above. The red dilithio salt of the ligand (0.025 mol) was isolated as disclosed in Method A by removing the solvents under vacuum and by washing with pentane. The isolated red dilithio salt was dissolved in 125 ml of cold methylene chloride at -78°C . The HfCl_4 slurry was rapidly cannulated into the flask containing the ligand solution. The mixture was stirred for two hours at -78°C .

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allowed to warm slowly to 25°C and stirred for an additional 12 hours. An insoluble white sale (LiCl) was filtered off. A moderately air sensitive, yellow powder was obtained by cooling the brown/yellow methylene chloride solution to -20°C for 12 hours and cannulating away the supernatant. The bright yellow product was washed on the sintered glass filter by repeatedly filtering off cold supernatant that had been cannulated back over it. The catalyst complex was isolated by pumping off the solvents using a vacuum, and it was stored under dry, deoxygenated argon. The process yielded 5.5 mgs of catalyst complex.

The elemental analysis of the hafnium catalyst complex prepared using Method B showed that the catalyst consisted of 48.79% by weight of carbon, 3.4% hydrogen, 15.14% chlorine and 33.2% hafnium. These percentages compare with the theoretical analysis for $\text{C}_{21}\text{H}_{18}\text{HfCl}_2$ which is 48.39% carbon, 3.45% hydrogen, 13.59% chlorine and 34.11% hafnium. Similarly, zirconium catalysts produced using Method B show elemental analysis close to the expected or theoretical values. Further, some of the hafnium complexes illustrated in the Examples below were made using 96% pure HfCl_4 which also contains about 4% ZrCl_4 . Still other catalyst samples were made using 99.99% pure HfCl_4 . Differences can be seen in the molecular weight distributions of the polymers produced with the pure Hf catalyst compared with the polymers produced using the catalysts which contain a small percentage of zirconium. The mixed

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catalyst produces a polymer with a broader molecular weight distribution than that produced by a pure catalyst system.

The examples below illustrate the present invention in more details. The results of the polymerization process and the analysis of the polymer are shown in Table 1 for Examples 1-4 and in Table 2 for Examples 5-9.

EXAMPLES 1-4

1 liter of liquid propylene was added into a dried 1.5 liter glass reactor equipped with inclined stirrer.

To this, were injected a solution of 3 mg isopropyl fluorenyl cyclopentadienyl titanium dichloride in 5 ml of a 10 wt% solutions of MAO in toluene previously precontacted in a glove box under nitrogen. The reactor was thermostated at 60°C (and was left polymerizing for 1 hour under four different ethylene pressures).

The polymers were recovered by venting off the monomer gas.

Approximately 120 g of polymeric material were respectively collected. Their characteristics are shown on table 1.

^{13}C NMR analysis of the different propylene-ethylene sequences indicate that the ethylene incorporation is predominantly random and that even for the copolymer with the highest ethylene content (Example 4) the number of sequences having a length longer than 2 monomer units is only about 20% of the total amount of sequences (see SDE 2).

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EXAMPLES 5-9

A dried 1.5 liter glass reactor equipped with inclined stirrer was filled under nitrogen flow with 1 liter of five different liquid monomer mixtures of propylene and hexene. To this, were injected a solution of 8 mg isopropyl fluorenyl cyclopentadienyl titanium dichloride in 40 ml of a 10 wt% solutions of MAO in toluene previously precontacted in a glove box under nitrogen. The reactor was thermostated at 60°C and was left polymerizing for 1 hour. All copolymers proved to be soluble in the monomer mixture and were recovered by distilling of the monomer under reduced pressure. Approximately 200 g of polymeric material were respectively collected. Their characteristics are shown on Table 2.

The ratio of the ^{13}C NMR peak at 41.0 to 41.9 ppm (CH_2 for hexene-hexene blocks) with the peak at 23.5 ppm ($\text{CH}_2(2)$ in the hexene branch) is an indication for the randomness or block type incorporation of the 1-hexene. For example 2 this ratio is only 13.7% indicating that the majority of the 1-hexene is incorporated as isolated comonomer between two propylene monomers. This ratio increase to 71.8% for example 3 and to 81.1% for example 4 indicating the block formation of polyhexene at increased hexene concentration.

Obviously, numerous modifications and variations of the present invention are possible in light of the above teachings.

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It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described herein.

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TABLE 1

Ex	C ₂ (mole%)	C ₂ (mole%)	Mn	MWD	Tm(°C)	Hm(cal/gr)	Tg(°C)	SDE2
	Starting	in	Mw/Mn					
	Reactants	Polymers						

1	0	0	42549	2.396	136.2	10.05	0	0
2	4	19.75	18791	2.466	-	-	-25.32	10.24
3	8	27.93	16731	2.257	-	-	-29.62	13.12
4	25	57.19	12656	2.51	125.3	1.16	-51.02	21.24

MWD - Molecular Weight Distribution

Tm - Melting Point

Hm - Melt Enthalpy

Tg - Glass Transition Temperature

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TABLE 2

Ex.	C ₆ (mole%) in monomer mixture	C ₆ (mole%) in polymer	Mn	MWD Mw/Mn	Tg (°C)	Ratio of ¹³ C NMR peaks (%)
5	0	0	42549	2.396	0	-
6	16.7	17.8	22136	2.754	-24.27	13.7
7	83.3	86.7	16786	2.996	-34.49	71.8
8	90.9	95.5	14480	2.981	-40.42	81.1
9	100	100	8569	1.905	-32.19	-

MWD - Molecular Weight Distribution
Tg - Glass Transition Temperature

WE CLAIM:

1. Syndiotactic random copolymer of propylene and olefin having from 2 to 10 carbon atoms having a degree of polymerization of not less than 5 in which the microstructure of the polypropylene units and the polyolefin units, except the polyethylene units, of the polymer chain are each consisting of blocks of repeating racemic (r) dyads being about equal to or greater than 80% connected by units consisting of a meso triad (mm).
2. Syndiotactic random copolymer of claim 1 wherein the structure of the polypropylene units of the polymer chain consists of greater than 80% racemic (r) dyads.
3. Syndiotactic random copolymer of claim 1 wherein the structure of the polyolefin units, except the polyethylene units, of the polymer chain consists of greater than 70% racemic (r) dyads.
4. Syndiotactic random copolymer of claim 1 wherein the olefin has from 4 to 8 carbon atoms.
5. Syndiotactic random copolymer of claim 1 wherein the olefin is selected from the group consisting of ethylene,

1-butene, 1-pentene, 4-methylpentene, 1-hexene, 1-heptene, 1-octene, 1-nonene and 1-decene.

6. A process for copolymerizing propylene and an olefin monomer having from 2 to 10 carbon atoms having a degree of polymerization of not less than 5 to form a syndiotactic random copolymer in which the microstructure of the polypropylene units and the polyolefin units, except polyethylene units, of the polymer chain are each consisting of blocks of repeating racemic (r) dyads being about equal to or greater than 80% connected by units consisting of a meso triad (mm), said process comprising:

- a) selecting a metallocene catalyst described by the formula $R''(CpR_n)(CpR'_m)MeQ_k$ wherein each Cp is a cyclopentadienyl or substituted cyclopentadienyl ring, each R_n is the same or different and is a hydrocarbyl radical having 1-20 carbon atoms; each R'_m is the same or different and is a hydrocarbyl radical having 1-20 carbon atoms; R'' is a structural bridge between the Cp rings imparting stereorigidity to the catalyst; Me is a group 4b, 5b, or 6b metal from the Periodic Table of Elements; each Q is a hydrocarbyl radical having 1-20 carbon atoms or is a halogen; where k, n and m may be the following

integers, respectively, $0 \leq k \leq 3$; $0 \leq n \leq 4$; $1 \leq m \leq 4$; and wherein R'_m is selected such that (CpR'_m) is a sterically different ring than (CpR_n) ;

b) introducing the metallocene catalyst into a polymerization reaction zone containing propylene and an olefin monomer having from 2 to 10 carbon atoms, and an aluminum compound as co-catalyst; and

c) maintaining the reaction zone under polymerization reaction conditions.

7. The process of claim 6 wherein the structure of the polypropylene units of the polymer chain consists greater than 80% racemic (r) dyads.

8. The process of claim 6 wherein the structure of the polyolefin units, except the polyethylene units, of the polymer chain consists of greater than 70% racemic (r) dyad.

9. The process of claim 6 wherein the olefin is selected from the group comprising ethylene, 1-butene, 1-pentene, 4-methylpentene, 1-hexene, 1-heptene, 1-octene, 1-nonene and 1-decene.

10. Syndiotactic random copolymer of propylene and olefin having from 2 to 10 carbon atoms having a degree of polymerization of not less than 5 in which the microstructure of the polypropylene units and the polyolefin units, except polyethylene units, of the polymer chain are each consisting of blocks of repeating racemic (r) dyads being about equal to or greater than 80% connected by units consisting of a meso triad (mm) produced by the process of copolymerization comprising:

- a) selecting a metallocene catalyst described by the formula $R''(CpR_n)(CpR'_mMeQ_k)$ wherein each Cp is a cyclopentadienyl or substituted cyclopentadienyl ring, each R_n is the same or different and is a hydrocarbyl radical having 1-20 carbon atoms; each R'_m is the same or different and is a hydrocarbyl radical having 1-20 carbon atoms; R'' is a structural bridge between the Cp rings imparting stereorigidity to the catalyst; Me is a group 4b, 5b, or 6b metal from the Periodic Table of Elements; each Q is a hydrocarbyl radical having 1-20 carbon atoms or is a halogen; where k, n and m may be the following integers, respectively, $0 \leq k \leq 3$; $0 \leq n \leq 4$; $1 \leq m \leq 4$; and wherein R'_m is selected such that (CpR'_m) is a sterically different ring than (CpR_n) ;

- b) introducing the metallocene catalyst into a polymerization reaction zone containing propylene and an olefin monomer having from 2 to 10 carbon atoms, and an aluminum compound as co-catalyst; and
- 5 c) maintaining the reaction zone under polymerization reaction conditions.

11. The syndiotactic random copolymer of claim 10 wherein the structure of the polypropylene units of the polymer chain consists greater than 80% racemic (r) dyads.

- 10 12. The syndiotactic random copolymer of claim 10 wherein the structure of the polyolefin units, except the polyethylene units, of the polymer chain consists of greater than 70% racemic (r) dyad.

- 15 13. The syndiotactic random copolymer of claim 10 wherein the olefin is selected from the group comprising ethylene, 1-butene, 1-pentene, 4-methylpentene, 1-haxone, 1-haptene, 1-octene, 1-nonene and 1-decene.