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AUSTRALIA

Patents Act

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Patent Declaration

DECLARATION FOR A PATENT APPLICATION

INSTRUCTIONS

(a) Insert "Convention" if applicable
(b) Insert FULL name(s) of applicant(s)

(c) Insert "of addition" if applicable
(d) Insert TITLE of invention

(e) Insert FULL name(s) AND address(es) of declarant(s) (See headnote*)

(f) Insert FULL name(s) AND address(es) of actual inventor(s)

(g) Recite how applicant(s) derive(s) title from actual inventor(s) (See headnote**)

(h) Insert country, filing date, and basic applicant(s) for the/or EACH basic application

(k) Insert PLACE of signing

(l) Insert DATE of signing

(m) Signature(s) of declarant(s)

Note: No legalization or other witness required

In support of the (a) convention application made by

(b) THE DOW CHEMICAL COMPANY
2030 Dow Center, Abbott Road,
Midland, Michigan 48640, U.S.A.

(hereinafter called "applicant(s)" for a patent (c) for an
invention entitled (d)
CATALYST AND PROCESS FOR PREPARATION OF SYNDIOTACTIC
POLYSTYRENE

I/We (e) Richard G. Waterman, General Patent Counsel
THE DOW CHEMICAL COMPANY
2030 Dow Center, Abbott Road,
Midland, Michigan 48640, U.S.A.

do solemnly and sincerely declare as follows:

~~1. I am/We are the applicant(s).~~

(or, in the case of an application by a body corporate)

1. I am/We are authorized to make this declaration on behalf of the applicant(s).

~~2. I am/We are the actual inventor(s) of the invention.~~

(or, where the applicant(s) is/are not the actual inventor(s))

2. (f) RICHARD E. CAMPBELL, JR., 5301 Woodview Pass, Midland,
State of Michigan 48640, United States of America
JOHN G. HEFNER, 122 Cacao, Lake Jackson, State of Texas
77566, United States of America

is/are the actual inventor(s) of the invention and the facts upon which the applicant(s)
is/are entitled to make the application are as follows:

(g) The applicant Company is the assignee of the said
invention from the said actual inventor(s).

(Note: Paragraphs 3 and 4 apply only to Convention applications)

3. The basic application(s) for patent or similar protection on which the application is based
is/are identified by country, filing date, and basic applicant(s) as follows:

(b) U.S. Priority Serial No.: 064,282 (PCT/US88/021111)
Filing Date: June 17, 1987 (PCT - June 17, 1988)
Inventors: Richard E. Campbell, Jr.
John G. Hefner

4. The basic application(s) referred to in paragraph 3 hereof was/were the first application(s)
made in a Convention country in respect of the invention the subject of the application.

Declared at (k) Midland, Michigan, 48640,

Dated (l) 11 January 1989 U.S.A.

THE DOW CHEMICAL COMPANY

CORP.
SEAL

To: The Commissioner of Patents

By:

RICHARD G. WATERMAN
General Patent Counsel

Agent: Phillips, Ormonde & Fitzpatrick

(12) PATENT ABRIDGMENT (11) Document No. AU-B-20866/88
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CATALYST AND PROCESS FOR PREPARATION OF SYNDIOTACTIC POLYSTYRENE

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(71) Applicant(s)
THE DOW CHEMICAL COMPANY

(72) Inventor(s)
RICHARD E. CAMPBELL JR.; JOHN G. HEFNER

(74) Attorney or Agent
PHILLIPS ORMONDE & FITZPATRICK, 367 Collins Street, MELBOURNE VIC 3000

(56) Prior Art Documents
AU 26403/88 C08F 4/66
AU 25310/88 C08F 4/66
AU 25207/88 C08F 4/66

(57) Claim

1. A process for preparing polymers of vinyl aromatic monomers having ~~a high degree of~~ greater than 50% syndiotacticity comprising contacting one or more aromatic monomers under polymerization conditions with a catalytically effective amount of a catalyst comprising the reaction product of polymethylaluminum and a monocyclopentadienyl/titanium complex corresponding to the formula: $CpTiX_3$, wherein Cp is a π -bonded cyclopentadienyl group, a π -bonded substituted or multiply substituted cyclopentadienyl group ~~or a π -bonded monovalent oligomer of cyclopentadiene~~ and X is independently each occurrence halide, OR, or NR_2 , wherein R is independently each occurrence an aliphatic, cycloaliphatic or aromatic hydrocarbon group having from 1 to 12 carbon atoms; and provided further that in at least one occurrence X is OR or NR_2 .

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8. A composition of matter comprising the reaction product of polymethylaluminoxane and a complex corresponding to the formula: CpTiX_3 , wherein Cp is a π -bonded cyclopentadienyl group, a π -bonded substituted cyclopentadienyl group or a π -bonded monovalent oligomer of cyclopentadiene and X is independently each occurrence halide, OR, or NR_2 , wherein R is independently each occurrence an aliphatic, cycloaliphatic or aromatic hydrocarbon group having from 1 to 12 carbon atoms and provided further that in at least one occurrence X is OR or NR_2 .

9. A composition of matter according to Claim 8, wherein X is NR_2 and R is CH_3 .

PCT

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International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(21) International Application Number: PCT/US88/02111 (22) International Filing Date: 17 June 1988 (17.06.88) (31) Priority Application Number: 064,282 (32) Priority Date: 17 June 1987 (17.06.87) (33) Priority Country: US (71) Applicant: THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Abbott Road, Midland, MI 48640 (US). (72) Inventors: CAMPBELL, Richard, E., Jr. ; 5301 Woodview Pass, Midland, MI 48640 (US). HEFNER, John, G. ; 122 Cacao, Lake Jackson, TX 77566 (US). (74) Agent: MACLEOD, Roderick, B.; The Dow Chemical Company, P.O. Box 1967, Midland, MI 48641-1967 (US).		(81) Designated States: AT (European patent), AU, BE (European patent), CH (European patent), DE (European patent), FR (European patent), GB (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (European patent). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i> A.O.J.P. 16 MAR 1989 AUSTRALIAN 19 JAN 1989 PATENT OFFICE

(54) Title: CATALYST AND PROCESS FOR PREPARATION OF SYNDIOTACTIC POLYSTYRENE

(57) Abstract

Syndiotactic polymers of vinyl aromatic monomers are prepared by conducting the polymerization in the presence of a catalytic amount of the reaction product of polymethylaluminoxane and a specific monocyclopentadienyl/titanium complex.

This document contains the amendments made under Section 49 and is correct for printing.

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CATALYST AND PROCESS FOR PREPARATION OF
SYNDIOTACTIC POLYSTYRENE

The present invention pertains to a catalyst and a process for polymerizing vinyl aromatic monomers, particularly styrene, to produce syndiotactic polymers. The catalyst is the reaction product of polymethyl
5 aluminoxane and a specific monocyclopentadienyl/-
titanium complex

It has recently been reported by N. Ishihara, T. Seimiya, M. Kuramoto and M. Uoi in "Crystalline
10 Syndiotactic Polystyrene", Macromolecules, pp 2164-5, (1986) that syndiotactic polystyrene having high stereo regularity had been prepared in the presence of a titanium compound and an organoaluminum compound.

15 In EPO 210,615 syndiotactic polystyrene polymers were prepared utilizing titanium tetraethoxide, and cyclopentadienyltitanium trichloride complexes in combination with a polymethylaluminoxane cocatalyst.
20

According to the present invention there is now provided a process for preparing polymers of vinyl aromatic monomers having a high degree of
25 syndiotacticity comprising contacting one or more

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aromatic monomers under polymerization conditions with a catalytically effective amount of a catalyst comprising the reaction product of polymethylaluminum and a monocyclopentadienyl/titanium complex corresponding to the formula: CpTiX_3 , wherein Cp is a π -bonded cyclopentadienyl group, a π -bonded substituted or multiply substituted cyclopentadienyl group or a π -bonded monovalent oligomer of cyclopentadiene and X is independently each occurrence halide, OR, or NR_2 , wherein R is independently each occurrence an aliphatic, cycloaliphatic or aromatic hydrocarbon group having from 1 to 12 carbon atoms; and provided further that in at least one occurrence X is OR or NR_2 . By the term aromatic is included both substituted and unsubstituted aryl groups. Most suitably X is in each occurrence OR and R is selected from the group consisting of phenyl, and C_{1-6} alkyl or cycloalkyl. In a preferred embodiment X is in each occurrence phenoxy.

The catalyst is normally formed in the presence of an aliphatic, cycloaliphatic or aromatic solvent or a combination of such solvents. The components are employed in quantities which provide an atomic ratio of Al:Ti suitably from 10:1 to 50,000:1, more suitably from 50:1 to 10,000:1, most suitably from 100:1 to 1000:1.

Another aspect of the present invention pertains to a process for preparing syndiotactic polymers of vinyl aromatic monomers which process comprises contacting at least one polymerizable vinyl aromatic monomer under polymerization conditions in the presence of the previously disclosed catalyst. As used herein, the term "syndiotactic" refers to such polymers having a stereo regular structure of greater than

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50 percent syndiotactic as determined by C¹³ nuclear magnetic resonance spectroscopy. Such polymers may be usefully employed in the preparation of articles and objects (eg., via compression molding or other suitable technique) having an extremely high resistance to deformation due to the effects of temperature. Compared to processes employing cyclopentadienyl-titanium trichloride containing catalysts, the present invention achieves improved yields.

The polymethylaluminoxane may be prepared according to any known technique. One such technique includes the reaction of trimethylaluminum and a hydrated metal salt as disclosed by Kaminsky in U.S. Patent 4,544,762, the teachings of which are herein incorporated in their entirety by reference thereto. For purposes of calculating the molar ratio of aluminum:titanium in the catalysts of the present invention, the polymethylaluminoxane is assigned a repeating unit structure corresponding to the formula: $(Al(CH_3)O)$.

Following preparation of polymethylaluminoxane a cyclopentadienyltitanium complex, as previously defined, is added to the polymethylaluminoxane along with additional diluent if desired. In addition to unsubstituted cyclopentadienyl derivatives, the metal complexes employed to prepare the catalysts of the present invention illustratively include cyclopentadienyl derivatives containing from 1 to 5 alkyl, aryl or silyl substituents having up to 18 carbons, eg., pentamethylcyclopentadienyl derivatives, penta(trimethylsilyl)cyclopentadienyl derivatives, etc. and ring fused derivatives such as indenyl titanium complexes and substituted indenyl

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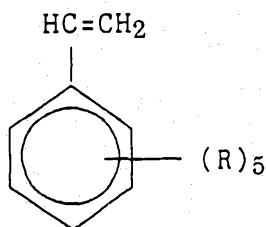
titanium complexes. It is understood that the complex may be employed in the form of a precursor that is capable of generating the desired cyclopentadienyl/titanium complex in situ. An example includes such complexes additionally incorporating one or more molecules of any nature in the crystal structure, such as alcohol molecules associated with the crystal structure via Van der Waals forces. In the preparation of the catalyst composition, the cyclopentadienyl/titanium complex and the polymethylaluminoxane can be combined in any order. The catalyst components may be suitably mixed in an inert atmosphere such as nitrogen, argon, xenon, or combinations thereof. The components are mixed at any suitable temperature, preferably from 0°C to 50°C, more suitably 25°C.

The polymerization is conducted at temperatures of from 25°C to 100°C, preferably from 30°C to 60°C, for a time sufficient to produce the desired polymer. Typical reaction times are from several minutes to several hours, preferably from 1 to 10 hours. The optimum time will vary depending upon the temperature, solvent and other reaction conditions employed. The polymerization is generally conducted under slurry polymerization conditions.

The polymerization can be conducted at subatmospheric pressure as well as superatmospheric pressure, suitably at reduced pressures such that the lowest boiling component(s) of the polymerization mixture does not vaporize up to about 1000 psig. However, it is preferable that near atmospheric pressure be employed.

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Suitable vinyl aromatic monomers which can be polymerized in the process of the present invention include those represented by the formula:



wherein each R is independently hydrogen, an aliphatic, cycloaliphatic or aromatic hydrocarbon group having suitably from 1 to 10, more suitably from 1 to 6, most suitably from 1 to 4, carbon atoms; or a halogen atom. Suitably such monomers include, for example styrene, chlorostyrene, n-butyl styrene, t-butyl styrene and p-vinyl toluene, etc. with styrene being especially suitable.

The polymerization is normally conducted in the presence of an inert diluent. Examples include aliphatic, cycloaliphatic, aromatic and halogenated aromatic hydrocarbons, as well as mixtures thereof. Preferred diluents comprise the C_{4-20} alkanes, especially branched chain alkanes, toluene and mixtures thereof. A particularly desirable diluent for the polymerization is isooctane, or blends thereof such as Isopar-E®, available from Exxon. Suitable amounts of solvent are employed to provide a monomer concentration from 5 percent to 100 percent by weight. During the polymerization, polymer may precipitate from the reaction mixture as it is formed.

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As in other similar polymerizations it is highly desirable that the monomers and solvents employed be of sufficiently high purity that catalyst deactivation does not occur. Any suitable technique for monomer purification such as devolatilization at reduced pressures, contacting with molecular sieves or high surface area alumina, deaeration, etc. may be employed.

Purification of the resulting polymer to remove entrained catalyst may also be desired by the practitioner. Entrained catalyst may generally be identified by residues of ash on pyrolysis of the polymer that are attributable to aluminum and titanium values. A suitable technique for removing such compounds is by solvent extraction, eg. extraction utilizing hot, high boiling chlorinated solvents, followed by filtration.

Having described the invention, the following examples are provided as further illustrative and are not to be construed as limiting.

Example 1

In a nitrogen atmosphere glovebox, a dry 2 oz (59 ml) bottle is charged with 32 ml of ISOPAR-E™ (hereinafter IPE), a solution of polymethylaluminoxane (0.325 g., 5.6 mmole, in 7.2 ml IPE), and 220 μ l, 22.4 μ mole, of a 0.051 M toluene solution of cyclopentadienyltitanium trisphenoxide (formed by the reaction of cyclopentadienyl trichloride and phenol in a 1:3 molar ratio in the presence of an acid scavenger). The molar ratio of styrene:Al:Ti is 6,000:500:1. The resulting solution is then stirred at room temperature for 30 seconds and is then treated

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with purified, deaerated styrene (7.0 g., 67.3 mmole). The bottle is then sealed with a sure seal cap which is then sealed again with electrical tape and the thus sealed container is placed in a shaker/hot water bath which is maintained at a temperature of 51°C for 20 hours. The reaction mixture is then hydrolyzed with the addition of 20 ml of methanol, and slurried in 50 ml of 1N aqueous HCl for 5 minutes. The water is then removed with the use of a separatory funnel. The resultant polystyrene is collected by filtration, washed with methanol and vacuum dried at 110°C for 24 hours. The yield is 6.78 g (97 percent). The resultant polystyrene has a melting point of 246°C, >95 percent syndiotacticity by C¹³ analysis, and has a weight average molecular weight (Mw) as determined by gel permeation chromatography utilizing atactic polystyrene standards of 166,400. Number average molecular weight (Mn) determined similarly is 50,600. Results are summarized in Table I.

Examples 2-13

The reaction conditions of Example 1 are substantially repeated excepting that the titanium complexes, solvents, ratios and reaction temperatures of Table I are employed. Results are contained in Table I.

Comparative Examples 14 and 15

These comparative Examples are summarized in Table I. They are not prior art. Note the low yields obtained (in contrast to Examples 1-13).

Examples 16-53

These examples are summarized in Table I, and essentially repeated Example 1 except for the different indications listed in Table I. Examples relating to the preparation of syndiotactic tertiary butylstyrene are of particular interest because the polymers obtained had a molecular weight (Mw) that was too high to measure by gel permeation chromatography (Examples 16, 18, 19, 20, 39, 40, 41 and 42).

Table I

Ex	Complex	Ratio Styrene:Al:Ti	Solvent ¹	% Styrene ²	temp °C	time hr.	yield %	% syndio- tactic ¹³ C	Mw x10 ³	melt pt.°C
1	CpTi(OPh) ₃	6,000:500:1	IPE	20	51	20	97	>95	166.4	249
2	CpTi(OPh) ₃	6,000:500:1	IPE	5	51	2.5	56.5	88	60.6	249
3	CpTi(OPh) ₃	18,000:500:1	"	20	"	"	60.3	95	145	250
4	CpTi(OPh) ₃	6,000:500:1	toluene	40	"	"	93.6	84	60.6	253
5	CpTi(OPh) ₃	"	IPE	20	"	"	82.1	>94	90.0	250
6	CpTi(OEt) ₃	"	"	"	25	"	67.4	91	123	251
7	CpTi(OEt) ₃	"	"	"	51	"	91.1	--	86.4	251
8	Indenyl- Ti(NMe ₂) ₃	6,000:1,000:1	"	40	50	20	86.2	>95	160	263
9	CpTi(NMe ₂) ₃	6,000:500:1	"	"	51	2.5	71.7	>84	102.9	255
10	CpTi(OPh) ₃	6,000:125:1	IPE	20	51	20	74.7	95	98.1	--
11	CpTi(OPh) ₃	6,000:500:1	IPE	20	51	2.25	96.7	93	180.9	250
12	Me ₅ C ₅ Ti(OPh) ₃	"	"	"	"	"	95.1	>95	343.0	268
13	Me ₅ C ₅ - Ti(OPh)Cl ₂	"	"	"	"	"	53.3	91	83.0	254

Table I Continued

Ex	Complex	Ratio Styrene:Al:Ti	Solvent ¹	% styrene ²	temp °C	time hr.	yield %	% syndio- tactic 13C	Mw x10 ³	Melt pt.°C
14	Me ₅ C ₅ TiCl ₃ ³	6,000:500:1	IPE	20	51	2.25	30.6	>95	333.1	--
15	CpTiCl ₃ ³	6,000:500:1	"	20	"	2.5	27.7	--	--	255.4
16	CpTi(NMe ₂) ₃	6,000:500:1	IPE	TBS 20	50	2.25	34.4	>90	--	306
17	CpTi(NMe ₂) ₃	"	"	PVT 20	50	2.25	34.4	>90	--	165
18	Me ₅ C ₅ Ti(OPH) ₃	"	"	TBS 20	50	2.25	98	>95	--	308
19	Me ₅ C ₅ Ti(O-i-Pr) ₃	"	"	TBS 20	50	2.25	99.2	>95	--	308
20	CpTi(OPH) ₃	"	"	TBS 20	50	2.25	99.8	>90	--	291
21	CpTi(OPH) ₃	"	"	PVT 70	50	2.0	96.9	--	88.9	142
22	Me ₅ C ₅ Ti(OPH) ₃	"	"	PVT 20	"	"	99.6	>95	750.0	167
23	Me ₅ C ₅ Ti(O-i-Pr) ₃	"	"	PVT 20	"	"	99.8	>95	723.0	167
24	Me ₅ C ₅ Ti(OPH) ₃	6,000:500:1	IPE	20	50	2.25	83.1	>95	509.0	271
25	Me ₅ C ₅ Ti(O-i-Pr) ₃	"	"	"	"	"	89.8	>95	544.0	271
26	Me ₄ CpTi(O-i-Pr) ₃	"	"	"	"	"	80.9	>93	201.0	271
27	EtMe ₄ C ₅ Ti- (O-i-Pr) ₃	"	"	"	"	2.0	76.5	--	556.0	--
28	[(Me ₃ Si)Cp]- Ti(O-i-Pr) ₃	"	"	"	"	2.0	74.2	--	83.4	--

Table I Continued

Ex	Complex	Ratio Styrene:Al:Ti	Solvent ¹	% Styrene ²	Temp °C	Time hr.	Yield %	% Syndio- tactic ¹³ C	Mw x10 ³	Melt pt.°C
29	Me ₅ C ₅ Ti(OPH) ₃	6,000:500:1	IPE	20	50	2.0	72.0	--	784.0	--
30	Me ₅ C ₅ Ti(O-i-Pr) ₃	"	"	"	"	"	48.2	--	864.0	--
31	EtMe ₄ C ₅ Ti- (O-i-Pr) ₃	"	"	"	"	"	44.0	--	1,070.0	--
32	[(Me ₃ Si)Cp]- Ti(O-i-Pr) ₃	"	"	"	"	"	33.8	--	69.8	--
33	Me ₅ C ₅ Ti(OPH) ₃	6,000:500:1	IPE	Para-Br- Styrene 20	50	2.25	3.3	--	--	298
34	Me ₅ C ₅ Ti(O-i-Pr) ₃	"	"	"	"	"	3.8	--	--	296
35	CpTi(OPh) ₃	"	"	"	"	"	2.3	--	--	--
36	Me ₅ C ₅ Ti(OPH) ₃	6,000:500:1	IPE	Para-Cl- Styrene 20	50	4.0	2.8	--	--	296
37	Me ₅ C ₅ Ti(O-i-Pr) ₃	"	"	"	"	"	2.8	--	--	--
38	CpTi(OPh) ₃	"	"	"	"	"	3.8	--	--	292
39	Me ₅ C ₅ Ti(OPH) ₃	6,000:500:1	MCH	20	50	2	98.6	--	--	307
40	Indenyl- Ti(NMe ₂) ₃	6,000:500/1	MCH	20	50	7	63.0	--	--	308

Table I Continued

Ex	Complex	Ratio Styrene:Al:Ti	Solvent ¹	% Styrene ²	Temp °C	Time hr.	Yield %	% Syndio- tactic ¹³ C	Mw x10 ³	Melt pt.°C
41	MeCpTi(NMe ₂) ₃	"	"	"	"	"	87.9	--	--	300
42	CpTi(NMe ₂) ₃	"	"	"	"	"	93.4	--	--	291
43	Me ₅ C ₅ Ti (OPH) ₃	6,000:500:1	MCH	20	50	2	98.8	--	--	158 ⁴ 181
44	Indenyl- Ti(NMe ₂) ₃	"	"	"	"	7	49.9	--	--	165 ⁴ 183
45	MeCpTi(NMe ₂) ₃	"	"	"	"	"	38.4	--	--	168 ⁴ 182
46	CpTi(NMe ₂) ₃	"	"	"	"	"	31.4	--	--	155 ⁴ 174
47	Me ₅ C ₅ Ti (OPH) ₃	"	"	"	"	2	99.6	--	--	271
48	Indenyl- Ti(NMe ₂) ₃	"	"	"	"	2.75	49.6	--	--	265

Table I Continued

Ex	Complex	Ratio styrene:Al:Ti	Solvent ¹	% Styrene ²	Temp °C	Time hr.	Yield %	% Syndio- tactic 13C	Mw x10 ³	Melt pt.°C
49	MeCpTi(NMe ₂) ₃	6,000:500:1	MCH	20	50	2.75	46.0	--	--	264
50	CpTi(NMe ₂) ₃	"	"	"	"	"	44.2	--	--	266
51	CpTi(NPh ₂) ₃	"	"	"	"	4	--	--	--	--
52	CpTi(N(Butyl) ₂) ₃	"	"	"	"	4	--	--	--	--
53	Me ₅ C ₅ Ti(OPh) ₃	"	"	OVT 20	"	4	--	--	--	--

¹IPE = Isopar - E™, MCH - Methylcyclohexane

²Weight Percent of reaction mixture

TBS = p-tert butyl styrene

PVT = p-vinyl toluene

OVT = Ortho-vinyl toluene

³Comparative examples

⁴Two melting peaks

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1. A process for preparing polymers of vinyl aromatic monomers having ~~a high degree of~~ greater than 50% syndiotacticity comprising contacting one or more aromatic monomers under polymerization conditions with a catalytically effective amount of a catalyst comprising the reaction product of polymethylaluminum and a monocyclopentadienyl/titanium complex corresponding to the formula: $CpTiX_3$, wherein Cp is a η -bonded cyclopentadienyl group, a η -bonded substituted or multiply substituted cyclopentadienyl group ~~or a~~ ~~η -bonded monovalent oligomer of cyclopentadiene~~ and X is independently each occurrence halide, OR, or NR_2 , wherein R is independently each occurrence an aliphatic, cycloaliphatic or aromatic hydrocarbon group having from 1 to 12 carbon atoms; and provided further that in at least one occurrence X is OR or NR_2 .

2. A process according to Claim 1, wherein the polymethylaluminum and titanium complex are employed in quantities which provide an atomic ratio of Al:Ti of from 50:1 to 10,000:1.

3. A process according to Claim 1, wherein the polymethylaluminum and titanium complex are employed in quantities which provide an atomic ratio of Al:Ti of from 100:1 to 1000:1.



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4. A process according to Claim 1, wherein the monomer is contacted with the catalyst at a temperature from 25°C to 100°C.

5 5. A process according to Claim 1, wherein an inert diluent is additionally present.

6. A process according to Claim 1, wherein the polymer has a molecular structure containing greater
10 than 70 percent syndiotactic.

7. A process according to Claim 1, wherein X is OR in each occurrence and R is selected from the group consisting of phenyl and C1-6 alkyl.

15 8. A composition of matter comprising the reaction product of polymethylaluminoxane and a complex corresponding to the formula: CpTiX_3 , wherein Cp is a π -bonded cyclopentadienyl group, a π -bonded substituted
20 cyclopentadienyl group or a π -bonded monovalent oligomer of cyclopentadiene and X is independently each occurrence halide, OR, or NR_2 , wherein R is independently each occurrence an aliphatic, cycloaliphatic or aromatic hydrocarbon group having
25 from 1 to 12 carbon atoms and provided further that in at least one occurrence X is OR or NR_2 .

9. A composition of matter according to Claim 8, wherein X is NR_2 and R is CH_3 .

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10. A process as claimed in claim 1 substantially as hereinbefore described with reference to any one of the examples.

DATED: 14 August 1990

PHILLIPS ORMONDE & FITZPATRICK

Attorneys for:

THE DOW CHEMICAL COMPANY

David B Fitzpatrick



INTERNATIONAL SEARCH REPORT

International Application No PCT/US88/02111

I. CLASSIFICATION & SUBJECT MATTER (If several classification symbols apply, indicate all) ¹		
According to International Patent Classification (IPC) or to both National Classification and IPC		
INT. CL. ⁴	C08F 4/64	
U.S. CL.	502/103; 526/160	
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁴		
Classification System ¹	Classification Symbols	
U.S.	502/103; 526/160	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁵		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴		
Category ¹⁵	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸
Y	US, A, 3,306,919, (Brantley et al), 28 February 1967, See col. 1, lines 23-26, col. 1, line 70 to col. 2, line 26, col. 2, line 36, Example IV	1-9
Y	US, A, 4,542,199, (Kaminsky et al.), 17 September 1985, See the Abstract, col. 2, lines 8-33	8,9
Y	US, A, 3,242,099, (Manyik et al.), 22 March 1966, See col. 1, line 37 to col. 2, line 26, col. 3, lines 54-55	8,9
Y	FR, A, 1,392,785, (Scholven-Chemie), 08 February 1965, See the Abstract	1-9
Y	JP, B, 41-5379, (Toyo), 25 March 1966, See the Abstract	1-9
Y	JP, B, 42-22691, (Toyo), 06 November 1967, See the Abstract	1-9
¹ Special categories of cited documents: ¹⁵ "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 "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "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 "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		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search ²		Date of Mailing of this International Search Report ²
08 September 1988		09 NOV 1988
International Searching Authority ¹		Signature of Authorizing Officer ²⁴
ISA/US		Patrick P. Garvin

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
Y	US, A, 3,663,635, (Lassau et al.), 16 May 1972, See col. 2, lines 7-11, 25-48	1-9
Y,P	US, A, 4,680,353, (Ishihara et al.), 14 July 1987, See the Abstract, col. 2, line 6 to col. 3, line 4, col. 3, lines 32-61, col. 4, lines 25-35, the examples	1-9