EXHIBIT V

PART 11

US005395810A

United States Patent [19]

Shamshoum et al.

[11] Patent Number: 5,395,810

[45] Date of Patent: Mar. 7, 1995

[54] **METHOD OF MAKING A HOMOGENEOUS-HETEROGENOUS CATALYST SYSTEM FOR OLEFIN POLYMERIZATION**

[75] Inventors: **Edwar S. Shamshoum**, Houston; **Michael J. Elder**, Friendswood; **Baireddy R. Reddy**, Baytown; **David J. Rauscher**, Webster, all of Tex.

[73] Assignee: **Fina Technology, Inc.**, Dallas, Tex.

[21] Appl. No.: **9,520**

[22] Filed: **Jan. 27, 1993**

Related U.S. Application Data

[62] Division of Ser. No. 768,783, Sep. 30, 1991, abandoned.

[51] **Int. Cl.**[6] **B01J 31/00**

[52] **U.S. Cl.** **502/113**; 502/103; 502/114; 502/115; 502/117; 502/121; 502/125; 502/127; 502/134

[58] **Field of Search** 502/103, 113, 114, 115, 502/117, 121, 125, 127, 134

[56] **References Cited**

U.S. PATENT DOCUMENTS

4,701,432	10/1987	Welborn, Jr.	502/113
5,104,838	4/1992	Fujita et al.	502/108

FOREIGN PATENT DOCUMENTS

0436328	7/1991	European Pat. Off.
0436399	7/1991	European Pat. Off. .

OTHER PUBLICATIONS

Zambelli et al., "Isotactic Polymerization of Propene: Homogeneous Catalysts Based on Group 4 Metallocenes without Methylalumoxane", Macromolecules, vol. 22, pp. 2186–2189 (1989).

Fujita et al., "Production of alpha-olefin Polymer", Patent Abstracts of Japan, vol. 15, No. 231, App. No. 01-207562, (1991).

Primary Examiner—Asok Pal
Assistant Examiner—E. D. Irzinski
Attorney, Agent, or Firm—Jim Wheelington; M. Norwood Cheairs

[57] **ABSTRACT**

This invention concerns a making a catalyst system comprising at least one homogeneous catalyst and at least one heterogeneous catalyst, specifically, a metallocene catalyst and a conventional Ziegler-Natta catalyst, respectively. This invention is useful for making a catalyst for the polymerization of any polymer in which separate polymerizations with a homogeneous catalyst and with a heterogeneous catalyst are possible, but preferably, polymerization of olefins, more preferably, α-olefins, and, most preferably, propylene. This invention provides a catalyst system which facilitates use of a homogeneous catalyst but eliminates the disadvantages of such a system. This invention produces a polymer with molecular weight distribution (MWD) as broad or broader than the MWD of the heterogeneous catalyst alone. Hydrogen can be used to control molecular weight distribution of a polymer produced with this invention.

13 Claims, 3 Drawing Sheets

FIG. 1

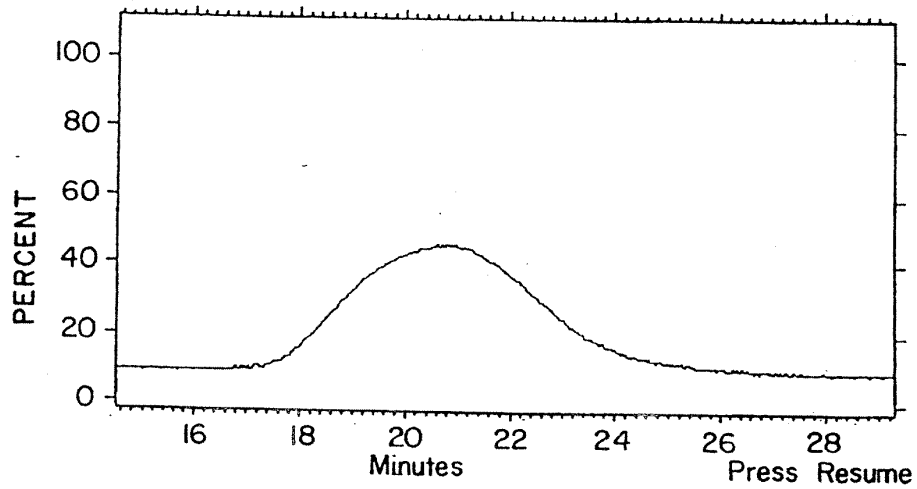

100
80
60
40
20
0
PERCENT
16
18
20
22
24
26
28
Minutes
Press Resume

FIG. 2

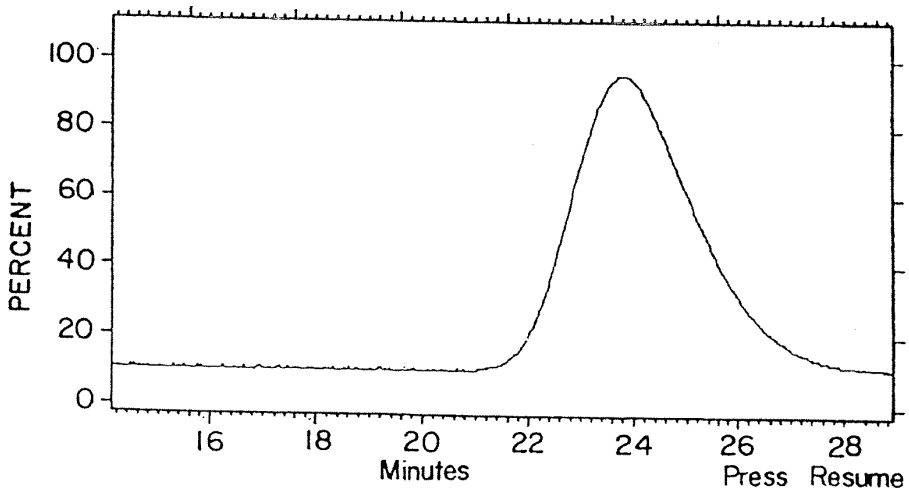

100
80
60
40
20
0
PERCENT
16
18
20
22
24
26
28
Minutes
Press Resume

FIG. 3

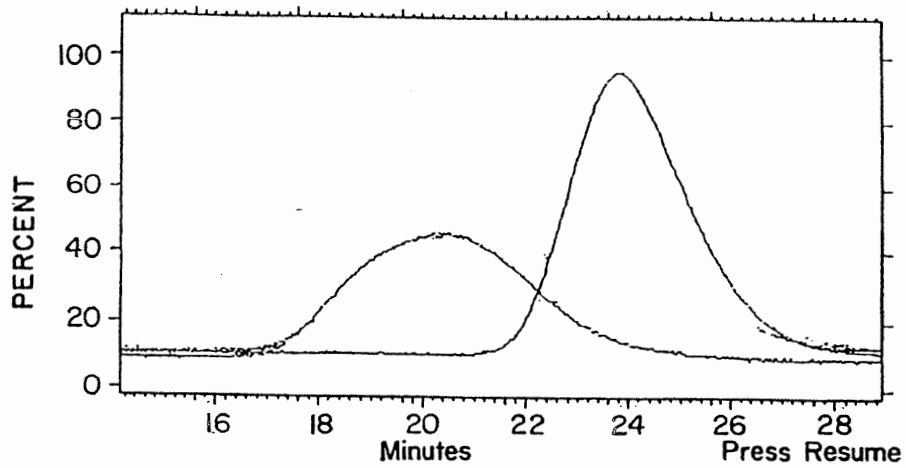

100
80
60
40
20
0
PERCENT
16
18
20
22
24
26
28
Minutes
Press Resume

FIG. 4

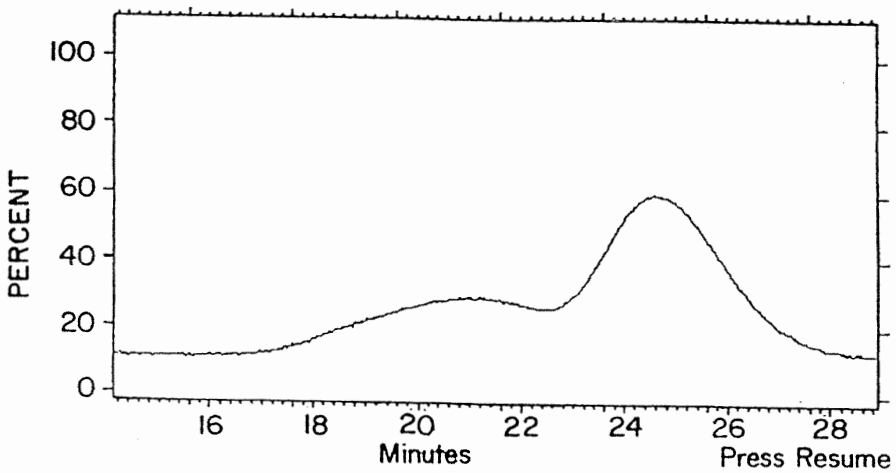

100
80
60
40
20
0
PERCENT
16
18
20
22
24
26
28
Minutes
Press Resume

FIG. 5

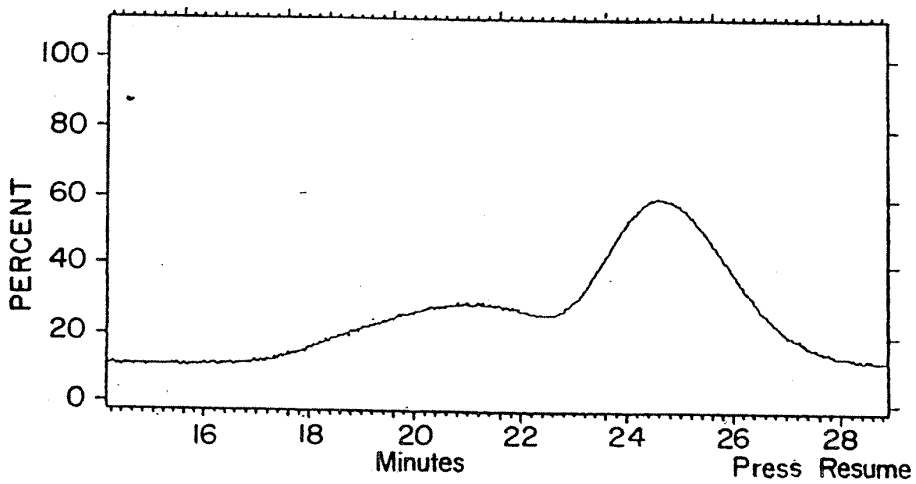
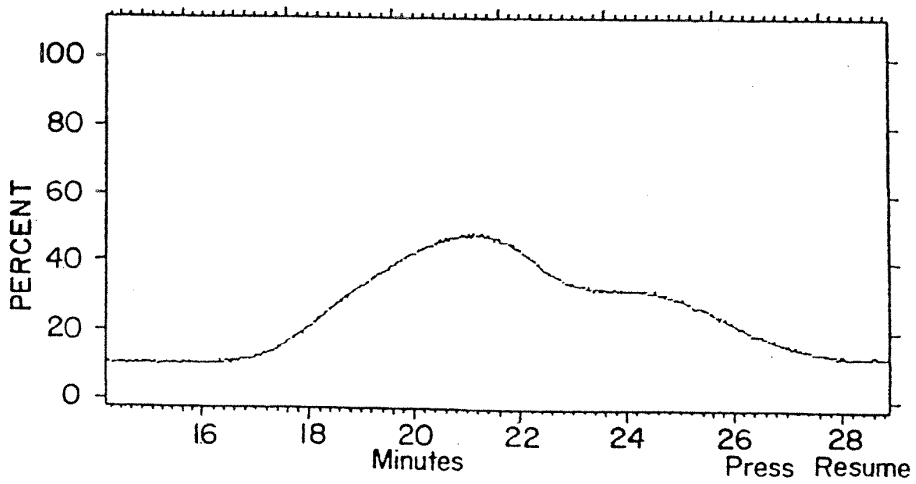

100
80
60
40
20
0
PERCENT
16
18
20
22
24
26
28
Minutes
Press Resume

FIG. 6


100
80
60
40
20
0
PERCENT
16
18
20
22
24
26
28
Minutes
Press Resume

METHOD OF MAKING A HOMOGENEOUS-HETEROGENOUS CATALYST SYSTEM FOR OLEFIN POLYMERIZATION

This is a division of application Ser. No. 07/768,783, filed on Sep. 30, 1991, and now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a catalyst system which is a combination of at least one homogeneous catalyst and at least one heterogeneous catalyst. Changing the homogeneous catalyst used with the heterogeneous catalyst effects the molecular weight distribution of the resulting polymer.

2. Description of the Prior Art

It is known that two or more homogeneous catalysts, such as those based on metallocene compounds, may be combined to effect properties, such as molecular weight distribution. U.S. Pat. No. 4,530,914 discloses use of a catalyst system comprising two or more metallocenes in the polymerization of α-olefins, primarily ethylene, to obtain a broad molecular weight distribution. The metallocenes each have different propagation and termination rate constants. The metallocenes are mixed with an alumoxane to form the catalyst system.

It is also known that metallocenes may be affixed to a support to simulate a heterogeneous catalyst. In U.S. Pat. No. 4,808,561 discloses reacting a metallocene with an alumoxane and forming a reaction product in the presence of a support. The support is a porous material like talc, inorganic oxides such as Group IIA, IIIA IVA OR IVB metal oxides like silica, alumina, silica-alumina, magnesia, titania, zirconia and mixtures thereof, and resinous material such as polyolefins like finely divided polyethylene. The metallocenes and alumoxanes are deposited on the dehydrated support material.

In U.S. Pat. No. 4,701,432 a support is treated with at least one metallocene and at least one non-metallocene transition metal compound. To form a catalyst system a cocatalyst comprising an alumoxane and an organometallic compound of Group IA, IIA, IIB and IIIA is added to the supported metallocene/non-metallocene. The support is a porous solid such as talc or inorganic oxides or resinous materials, preferably an inorganic oxide, such as silica, alumina, silica-alumina, magnesia, titania or zirconia, in finely divided form. By depositing the soluble metallocene on the support material it is converted to a heterogeneous supported catalyst. The transition metal compound, such as $TiCl_4$, is contacted with the support material prior to, after, simultaneously with or separately from contacting the metallocene with the support.

An advantage of a homogeneous (metallocene) catalyst system is the very high activity of the catalyst and the narrow molecular weight distribution of the polymer produced with a metallocene catalyst system. The metallocene catalysts suffer from a disadvantage in that the ratio of alumoxane cocatalyst to metallocene is high, requiring extensive treatment of the polymer product to remove the aluminum. Another disadvantage of the homogenous catalyst system is that the polymer product has small particle size and low bulk density. Another disadvantage of the homogeneous catalyst system is that the reactor fouls during polymerization.

It would be advantageous to provide a catalyst system which facilitates use of a homogeneous catalyst but

eliminates the disadvantages of such a system. A combination of a homogeneous catalyst with a heterogeneous catalyst in a single reactor will eliminate the disadvantages of the homogeneous catalyst alone and will facilitate use of a homogeneous catalyst. A combination of a homogeneous catalyst with a heterogeneous catalyst in a single reactor will also provide a means to control molecular weight distribution and polydispersity.

DESCRIPTION OF THE DRAWINGS

FIG. 1 is a chart of gel permeation chromatography (GPC) of a polymer produced with a conventional Ziegler-Natta heterogeneous catalyst.

FIG. 2 is a chart of GPC of a polymer produced with a metallocene homogeneous catalyst.

FIG. 3 is an overlay of FIGS. 1 and 2.

FIG. 4 is a chart of GPC of a polymer produced with a homogeneous-heterogeneous catalyst system.

FIG. 5 is a chart of GPC of a polymer produced with a homogeneous-heterogeneous catalyst system and a low level of hydrogen (3.9 mmol).

FIG. 6 is a chart of GPC of a polymer produced with a homogeneous-heterogeneous catalyst system and a high level of hydrogen (15.7 mmol).

SUMMARY OF THE INVENTION

Accordingly, an object of this invention is to provide a catalyst system which eliminates extensive treatment of the polymer product to remove impurities.

And, an object of this invention is to provide a catalyst system which produces polymer with little or no small particle size and high bulk density.

Also, an object of this invention is to provide a catalyst system which eliminates reactor fouling during polymerization.

Further, an object of this invention is to provide a catalyst system which controls the molecular weight distribution by varying the catalyst.

Additionally, an object of this invention is to provide a catalyst system which produces polymer with a bimodal molecular weight distribution.

As well, an object of this invention is to provide a catalyst system which produces a reactor blend of polymer with a broad molecular weight distribution in a single reactor.

In addition, an object of this invention is to provide a process for using hydrogen to control molecular weight distribution.

These and other objects are accomplished by a catalyst system comprising at least one homogeneous catalyst and at least one heterogeneous catalyst, i.e., metallocene catalyst and conventional Ziegler-Natta catalyst, respectively.

DETAILED DESCRIPTION OF THE INVENTION

The multi-catalyst system of the present invention is useful in the polymerization of any polymer in which separate polymerizations with a homogeneous catalyst and with a heterogeneous catalyst are possible. Preferably, the multi-catalyst system is useful in the polymerization of olefins, more preferably, α-olefins, and, most preferably, propylene.

The multi-catalyst system of the present invention is obtained by mixing the components of at least one homogeneous catalyst system and at least one heterogeneous system. The components may be combined in any order. Generally, the components of a homogeneous

catalyst system are a metallocene compound and an ionizing agent. Generally, the components of a heterogeneous catalyst system are an aluminum alkyl and a transition metal compound with, optionally, an electron donor.

Any of the conventional heterogeneous Ziegler-Natta transition metal compound catalyst components can be used as the heterogeneous catalyst of the catalyst system of the present invention. The compound is preferably of the general formula MR^{+}_{x} where M is the metal, R is a halogen or a hydrocarbyloxy and x is the valence of the metal. Preferably, M is a Group IVB, VB or VIB metal, more preferably a Group IVB, and most preferably titanium. Preferably, R is chlorine, bromine, an alkoxy or a phenoxy, more preferably chlorine or ethoxy and most preferably, chlorine. Illustrative examples of the transition metal compound catalyst components are $TiCl_4$, $TiBr_4$, $Ti(OC_2H_5)_3Cl$, $Ti(OC_2H_5)Cl_3$, $Ti(OC_4H_9)_3Cl$, $Ti(OC_3H_7)_2Cl_2$, $Ti(OC_6H_{13})_2Cl_2$, $Ti(OC_2H_5)_2Br_2$ and $Ti(OC_{12}H_{25})Cl_3$. Mixtures of the transition metal compounds may be used. No restriction on the number of transition metal compounds is made as long as at least one transition metal compound is present.

The transition metal compound may be either supported or unsupported. If supported, the support should be an inert solid which is chemically unreactive with any of the components of the heterogeneous or homogeneous catalyst.

The aluminum alkyl is of the general formula AlR'_3 where R' is an alkyl of from 1–8 carbon atoms and R' may be the same or different. Examples of aluminum alkyls are trimethyl aluminum (TMA), triethyl aluminum (TEAl) and triisobutyl aluminum (TiBAl). The preferred aluminum alkyl is TEAl.

The electron donor is any one of the electron donors which are effective with Ziegler-Natta catalysts. Typically, an electron donor is an organosilicon compound. Examples of electron donors are cyclohexylmethyl dimethoxysilane (MCDS), diphenyldimethoxysilane (DPMS) and isobutyltrimethoxysilane (IBMS). Other examples of electron donors are disclosed in U.S. Pat. Nos. 4,218,339; 4,395,360; 4,328,122; 4,473,660; 4,562,173 and 4,547,552, which are hereby incorporated by reference.

The homogeneous catalyst component may be a metallocene or cyclopentadienide, i.e., a metal derivative of a cyclopentadiene. The metallocene should contain two cyclopentadiene rings and be of the general formula:

$$R''_b(CpR_4)(CpR'_4)M'R^*_{v-2}$$

where R'' is a bridge imparting stereoridigity to the structure to the metallocene by connecting the two cyclopentadienyl rings, b is 0 or 1, Cp is a cyclopentadienyl ring, R and R' are substituents on the cyclopentadienyl rings and can be a hydride or a hydrocarbyl from 1–9 carbon atoms, each R and R' being the same or different, each (CpR_4) and (CpR'_4) being the same or different, M' is a Group IIIB, IVB, VB or VIB metal, R* is a hydride, a halogen or a hydrocarbyl from 1–20 carbon atoms, v is the valence of M'. Preferably, b is 1 and R'' is a hydrocarbyl radical, more preferably an alkenyl radical having one to four carbon atoms, a dialkyl germanium, a dialkyl silicon, an alkyl phosphine or amine radical, such as a dimethyl silyl radical, an ethylenyl radical or a isopropenyl radical and, most preferably, is an ethylenyl radical. Preferably, (CpR_4) is an substituted cyclopentadienyl ring such that it is 3-t-butyl-cyclopentadienyl, indenyl or cyclopentadienyl and (CpR'_4) is a substituted cyclopentadienyl ring such that it is fluorenyl, indenyl or fluorenyl, respectively; most preferably, (CpR_4) is indenyl and (CpR'_4) is indenyl. Preferably M' is a Group IVB metal, most preferably zirconium, which has a valence of 4. Preferably, R* is a halogen or alkyl, most preferably chlorine or methyl.

The ionizing agent is an alumoxane, an aluminum alkyl, other Lewis acid or a combination thereof which will ionize a neutral metallocene compound to form a cationic metallocene catalyst. Examples of such ionizing agents are methyl alumoxane (MAO), triethyl aluminum (TEAl) and tris(pentafluorophenyl)boron. Other ionizing agents are disclosed in U.S. patent application Ser. Nos. 07/419,057 and 07/419,222 and European Patent Publication Nos. 0-277-003 and 0-277-004 which are hereby incorporated by reference.

By using a multi-catalyst system having at least one homogeneous catalyst and at least one heterogeneous catalyst a polymer can be produced with molecular weight distribution (MWD) as broad or broader than the MWD of the heterogeneous catalyst alone. MWD can be represented by a chart of gel permeation chromatography (GPC). The homogeneous catalyst produces a polymer with a MWD which is narrow relative to a polymer produced by a heterogeneous. For example, using a heterogeneous catalyst alone produces a polymer with a MWD of approximately 5–7 (FIG. 1) and using a homogeneous catalyst alone produces a MWD of approximately 2–3.5 (FIG. 2). By superimposing FIG. 1 on FIG. 2 (FIG. 3), it can be predicted that using the two catalysts together will result in a polymer having a MWD of 5–7. When the two catalysts are used together in an actual polymerization, a polymer having a MWD of 5–7 results, as shown is FIG. 4. A comparison of FIGS. 3 and 4 show a near identity in the shape and location of the plot.

By using different ratios of the homogeneous:heterogeneous catalysts, the polydispersity, i.e., the distribution of molecular weights, can be effected. Since the molecular weight of the polymer produced with the homogeneous catalyst is different from that of the heterogeneous catalyst, changing the relative amount of one catalyst to another in a multi-catalyst system of this invention will change the polydispersity of the polymer produced.

The effect of hydrogen on a catalyst system having one or more homogeneous catalysts alone is known to be negligible. The effect of hydrogen on a catalyst system having one or more heterogeneous catalysts alone is known to have an inverse proportional effect on the peak molecular weight of the polymer, but there is no effect on molecular weight distribution. However, when a catalyst system comprises one or more homogeneous catalysts and one or more heterogeneous, the effect of hydrogen in decreasing the peak molecular weight of the polymer produced by the heterogeneous catalyst while the polymer produced by the homogeneous catalyst remains unaffected results in on overall change in the molecular weight distribution. The effect of using a relative low amount of hydrogen compared to using a relative high amount of hydrogen is shown in FIGS. 5 and 6, respectively. Therefore, hydrogen can be used to control molecular weight distribution of a

polymer produced by a multi-catalyst of the present invention.

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

EXAMPLE 1

5.0 mg of conventional Ziegler-Natta catalyst was placed in a stainless steel bomb with 0.2 mmol CMDS. 5.0 mg of $Et(Ind)_2ZrCl_2$ were placed in a mixing bottle with 2.0 mmol TEAl. The metallocene-TEAl mixture was placed in the bomb. 2.5 ml of MAO were placed in a second stainless steel bomb. 1.0 liter of propylene was placed in a 2 liter Zipperclave reactor at 30° C. Contents of the first bomb were charged to the reactor with 0.3 liter of propylene and 15.7 mmol of hydrogen. Contents of the second bomb were charged to the reactor with 0.3 liter of propylene. The reactor temperature was increased from 30° C. to 60° C. Polymerization continued for one hour during which time the reactor was maintained at the polymerization temperature. At the end of this time polymerization was terminated by rapidly venting the reactor of unreacted monomer. The polymer yield and analysis is shown in Table I.

EXAMPLE 2

The procedure of Example 1 was followed except 2.5 mg of conventional Ziegler-Natta catalyst and 5.0 mg of $Et(Ind)_2ZrCl_2$ and 3.9 mmol of hydrogen was used. The polymer yield and analysis is shown in Table I.

EXAMPLE 3

5.0 mmol of conventional Ziegler-Natta catalyst were placed in a bomb with 2.0 mmol of TEAl and 0.2 mg of CMDS. 2.5 mg of $Et(Ind)_2ZrCl_2$ were placed in a second bomb with 2.5 ml of MAO. 1.0 liter of propylene was placed in a 2 liter Zipperclave reactor at 32° C. Contents of the first bomb were charged to the reactor with 0.3 liter of propylene and 4 mmol of hydrogen. The contents of the second bomb were charged to the reactor with 0.3 liter of propylene. The reactor temperature was increased from 32° C. to 60° C. Polymerization continued for one hour during which time the reactor was maintained at the polymerization temperature. At the end of this time polymerization was terminated by rapidly venting the reactor of unreacted monomer. The polymer yield and analysis is shown in Table I.

EXAMPLE 4

5.0 mg of conventional Ziegler-Natta catalyst were placed in a stainless steel bomb with 2.0 mmol TEAl and 0.2 mmol of CMDS. 2.5 mg of $Et(Ind)_2ZrCl_2$ were placed in a mixing bottle with 2.5 ml of MAO. The metallocene-MAO mixture was placed in the bomb. 1.0 liter of propylene was placed in a 2 liter Zipperclave reactor at 31° C. Contents of the bomb were charged to the reactor with 0.3 liter of propylene and 4 mmol of hydrogen. The reactor temperature was increased from 31° C. to 60° C. Polymerization continued for one hour during which time the reactor was maintained at the polymerization temperature. At the end of this time polymerization was terminated by rapidly venting the reactor of unreacted monomer. The polymer yield and analysis is shown in Table I.

EXAMPLE 5

The procedure of Example 1 was followed except 2.5 mg of conventional Ziegler-Natta catalyst, 5.0 mg of $Me_2Si(t\text{-}b\text{-}Cp)(Flu)ZrCl_2$ and 4 mmol of hydrogen were used and the initial reactor temperature was 33° C. The polymer yield and analysis is shown in Table I.

TABLE I

RUN	TEAl (mmol)	CMDS (mmol)	HETEROGENEOUS CATALYST (mg)	METALLOCENE/ AMOUNT */(mg)	MAO (ml)	H_2 (mmol)	YIELD (g)	BULK DENSITY (g/cc)	T_m (°C.)	MW** (×1000)	MWD (M_w/M_n)
1	2.0	0.2	5.0	$Et(Ind)_2ZrCl_2$/2.5	2.5	15.7	105	0.42	161	220	21.3
2	2.0	0.2	2.5	$Et(Ind)_2ZrCl_2$/5.0	2.5	3.9	164	0.50	161	294	13.7
3	2.0	0.2	5.0	$Et(Ind)_2ZrCl_2$/2.5	2.5	3.9	235	0.48	160	153	15.5
4	2.0	0.2	5.0	$Et(Ind)_2ZrCl_2$/2.5	2.5	3.9	67	0.48	163	298	13.6
5	2.0	0.2	2.5	$Me_2Si(t\text{-}b\text{-}Cp)(Flu)ZrCl_2$/5.0	2.5	3.9	54	0.31	161	224	16.4

*$Et(Ind)_2ZrCl_2$-ethylenebis(indenyl)zirconium dichloride
$Me_2Si(t\text{-}b\text{-}Cp)(Flu)ZrCl_2$-dimethylsilyl(3-t-butyl-cyclopentadienyl)(fluorenyl)zirconium dichloride
**obtained from GPC

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

What is claimed as new and desired to be secured by Letter of Patent of the United States is:

1. A method of making a catalyst system comprising:
mixing in any order the components of at least one homogeneous catalyst wherein the components of the homogeneous catalyst comprise:
a) a neutral metallocene of the general formula

$$R''_g(CpR_4)(CpR'_4)MR^*_{v-2}$$

where R'' is a bridge imparting stereorigidity to the structure to the metallocene by connecting the two cyclopentadienyl rings, b is 0 or 1, Cp is a cyclopentadienyl ring, R and R' are substituents on the cyclopentadienyl rings and can be a hydride or a hydrocarbyl from 1–9 carbon atoms, each R and R' being the same or different, each (CpR_4) and (CpR'_4) being the same or different, M is a group IIIB, IVB, VB or VIB metal, R* is a hydride, a halogen or a hydrocarbyl from 1–20 carbon atoms, v is the valence of M and
b) an ionizing agent which will ionize a neutral metallocene compound to form a cationic metallocene catalyst and the components of at least one heterogeneous catalyst wherein the components of the heterogeneous catalyst comprise:
a) a transition metal of the general formula MR^+_x where M is a Group IIIB, IVB, VB or VIB metal, R+ is a halogen or a hydrocarboxyl and x is the valence of the metal and

b) an aluminum alkyl of the general formula $AlR^{\#}_3$ where $R^{\#}$ is an alkyl of from 1–8 carbon atoms and $R^{\#}$ may be the same or different.

2. A method of making a catalyst system as recited in claim 1 wherein b is 1, R'' is a hydrocarbyl radical chosen from the group consisting of an alkenyl radical having one to four carbon atoms, a dialkyl germanium, a dialkyl silicon, an alkyl phosphine and an amine radical, M' is a Group IVB metal, R* is a halogen or alkyl.

3. A method of making a catalyst system as recited in claim 2 wherein R'' is a dimethyl silyl radical, an ethylenyl radial or a isopropenyl radical.

4. A method of making a catalyst system as recited in claim 3 wherein R'' is an ethylenyl radical.

5. A method of making a catalyst system as recited in claim 1 wherein (CpR_4) is an substituted cyclopentadienyl ring such that it is 3-t-butyl-cyclopentadienyl, indenyl or cyclopentadienyl and (CpR'_4) is a substituted cyclopentadienyl ring such that it is fluorenyl, indenyl or fluorenyl, respectively.

6. A method of making a catalyst system as recited in claim 5 wherein (CpR_4) is indenyl and (CpR'_4) is indenyl.

7. A method of making a catalyst system as recited in claim 1 wherein the ionizing agent is chosen from the group consisting of an alumoxane, an aluminum alkyl, other Lewis acids and combinations thereof.

8. A method of making a catalyst system as recited in claim 7 wherein the ionizing agent is methyl alumoxane.

9. A method of making a catalyst system as recited in claim 1 wherein M is titanium and R^+ is chlorine or ethoxy.

10. A method of making a catalyst system as recited in claim 1 wherein the heterogeneous catalyst is chosen from the group consisting of $TiCl_4$, $TiBr_4$, $Ti(OC_2H_5)_3Cl$, $Ti(OC_2H_5)Cl_3$, $Ti(OC_4H_9)_3Cl$, $Ti(OC_3H_7)_2Cl_2$, $Ti(OC_6H_{13})_2Cl_2$, $Ti(OC_2H_5)_2Br_2$ and $Ti(OC_{12}H_{25})Cl_3$.

11. A method of making a catalyst system as recited in claim 1 wherein the aluminum alkyl is chosen from the group consisting of trimethyl aluminum, triethyl aluminum and triisobutyl aluminum.

12. A method of making a catalyst system as recited in claim 1 further comprising adding an electron donor organosilicon compound.

13. A method of making a catalyst system as recited in claim 1 wherein the electron donor is chosen from the group consisting of cyclohexylmethyldimethyoxysilane, diphenyldimethoxysilane and isobutyltrimethoxysilane.

* * * * *

US005408004A

United States Patent [19]

Lai et al.

[11] Patent Number: 5,408,004

[45] Date of Patent: Apr. 18, 1995

[54] **POLYOLEFIN BLENDS AND THEIR SOLID STATE PROCESSING**

[75] Inventors: **Shih-Yaw Lai**, Sugar Land; **Morris S. Edmondson**, Alvin, both of Tex.

[73] Assignee: **The Dow Chemical Company**, Midland, Mich.

[21] Appl. No.: **107,482**

[22] Filed: **Aug. 17, 1993**

[51] **Int. Cl.**[6] **C08L 23/04**; C08L 23/10; C08J 5/00

[52] **U.S. Cl.** **525/240**; 525/198; 264/331.17; 264/322

[58] **Field of Search** 525/198, 240; 264/322, 264/331.7

[56] **References Cited**

U.S. PATENT DOCUMENTS

3,645,992	2/1972	Elston	526/348.6
3,739,052	6/1973	Ayres et al.	
3,947,204	3/1976	Ayres et al.	425/383
3,995,763	12/1976	Ayres et al.	220/74
4,005,967	2/1977	Ayres et al.	425/326
4,014,956	3/1977	Smith et al.	260/853
4,107,243	8/1978	Stearns et al.	264/13
4,115,499	9/1978	Salyer et al.	264/122
4,161,502	7/1979	Wessling et al.	264/119
4,352,766	10/1982	Bradley et al.	264/45.5
4,542,886	9/1985	Yoshimura et al.	264/22
4,607,797	8/1986	Enikolopow et al.	241/23
4,981,760	1/1991	Naito et al.	428/523
5,001,206	3/1991	Bashir et al.	526/352
5,028,633	7/1991	Ohno et al.	514/778
5,028,663	7/1991	Chung	525/198
5,091,133	2/1992	Kobayashi et al.	264/119
5,166,268	11/1992	Ficker	525/198
5,206,075	4/1993	Hodgson	525/240
5,210,142	5/1993	Kale et al.	525/240

FOREIGN PATENT DOCUMENTS

351189	1/1990	European Pat. Off.	C08F 210/16
572034	12/1993	European Pat. Off.	C08F 210/02
590739	4/1994	European Pat. Off.	C08L 23/04
53-75278	7/1978	Japan .	
WO93/13143	7/1993	WIPO	C08F 10/02

OTHER PUBLICATIONS

Schwank—Selected Applications for CGCT Polymers—Sep. 1992, Paper presented at SPO '92.

Pawloski and Raspor, "Articles with Improved Properties Via Solid Phase Forming", Conference Proceedings for the Society of Plastics Engineers, Inc., 43d Annual Technical Conference, Washington, D.C., Apr. 29–May 2, 1985.

Capaccio, et al., "The Drawing Behavior of Linear Polyethylene. I. Rate of Drawing as a Function of Polymer Molecular Weight and Initial Thermal Treatment", J. Polym. Sci., vol. 14, 1641–1658 (1976).

Hidehiko and Kuriyama, "Mechanical Relaxations in γ-Ray-Polymerized Polyethylene", J. Polym. Sci., vol. 14, 1659–1669 (1976).

Cansfield, et al., "The Preparation of Ultra-High Modulus Polypropylene Films and Fibres", Polymer Eng. and Sci., vol. 16, No. 11, 721–724 (1976).

Hope, et al., "Hydrostatic Extrusion of Linear Polyethylene in Tubular and Non-Circular Sections", Poly. Eng. and Sci., vol. 20, No. 8, 540–545, (1980).

Gibson, et al., "Hydrostatic Extrusion of Linear Polyethylene: Effects of Molecular Weight and Product Diameter", J. Poly. Sci., vol. 16, 2015–2030 (1978).

Coffman, "Stretch-forming: a simple process with a lot of potential", Plastics Engineering, 19–21 (Aug., 1977).

Coates, "Hydrostatic Extrusion of Polyoxymethylene", J. Polym. Sci., vol. 16, 2031–2047 (1978).

(List continued on next page.)

Primary Examiner—Carman J. Seccuro, Jr.

[57] **ABSTRACT**

Polyolefin blends characterized by melting and crystallization curves which exhibit either two distinct melt regions, or wherein one component of the blend has a low softening temperature relative to the individual components of the blend, provide an unusually wide window for solid state processing. The solid state processing characteristics of these blends are independent of the manner in which the blends are formulated, e.g. mechanical mixing, solvent dispersion, and the like.

6 Claims, No Drawings

OTHER PUBLICATIONS

Bigg, "A Review of Techniques for Processing Ultra-High Modulus Polymers", Polym. Eng. and Sci., vol. 16, No. 11, 725–734 (1976).

Bigg, et al., "High Modulus Semi-Crystalline Polymers by Solid State Rolling", Polym. Eng. Sci., vol. 22, No. 1, 27–33 (1982).

Krjutchkov, et al., "Solid State Extrusion of Semicrystalline Polymers", Polymer Composites, vol. 7, No. 6, 413–420 (Dec., 1986).

International Search Report, dated Nov. 11, 1994, issued by the EPO acting as the International Searching Authority in PCT/US94/08943.

Ciferri and Ward, Ultra High Modulus Polymers, Applied Science Publ., London (1979).

Krjutchkov, Polymer Composite, vol. 7, #6, pp. 413–420 (1986).

POLYOLEFIN BLENDS AND THEIR SOLID STATE PROCESSING

BACKGROUND OF THE INVENTION

This invention relates to polyolefin blends. In one aspect, the invention relates to polyolefin blends suitable for solid state processing while in another aspect, the invention relates to particular blends of various polyethylenes. In still another aspect, the invention relates to polyolefin blends characterized by melting and crystallization curves exhibiting either two distinct melt regions, or wherein one component has a softening point lower than that of a conventional polyolefin, either technique of which provides an unusually wide window for solid state processing.

While the field of metal forming offers a wide variety of solid state processing, e.g. stamping, forging, rolling, extrusion, etc., the solid state processing of semicrystalline polymers is much more limited. To process a thermoplastic in the solid state, typically the processing temperature is maintained at just a few degrees below the melting point of the polymer. If the processing temperature is above the melting point of the polymer, then the processing is simply a melt extrusion. At temperatures considerably below the melting point of the polymer, the polymer is essentially a solid and its deformation requires a tremendous amount of pressure (often in excess of one million psi). Such enormous pressures make large deformations very difficult, and result in a relatively low production rate and a generally energy inefficient process. Moreover, since the processing temperature is the most critical parameter in solid state processing, this technique has been limited to those polymers and polymer blends with relatively wide (e.g. at least about 20 degrees on the Celsius scale) ranges between their softening and melting temperatures. Since this temperature range is relatively narrow for conventional polyolefins and their blends, these materials have not been the subject of extensive, commercial-scale solid state processing.

Despite their relatively narrow processing temperature window, the sheer commercial scale of the polyolefin market has generated considerable interest in applying this technique to polyolefins. The potential benefits to be gained include energy efficiency, speed, and scrap reduction. Ciferri and Ward in "Ultra High Modulus Polymers", *Applied Science Publications*, London (1979), teach that the extrusion of polymers below the melting point is a promising method of producing highly oriented materials. Krjutchkov, et al. in *Polymer Composite*, Vol. 7, No. 6, pp. 4-13-420 (1986), disclosed the detailed investigations of the dynamics of solid state extrusion, and they have also postulated a model to correlate the flow of instability in extrudate defects to the extrusion temperature and pressure.

Chung in U.S. Pat. No. 5,028,663 teaches that certain blends of high density polyethylene (HDPE) and low density polyethylene (LDPE) prepared by solution mixing can achieve a broader operating window for certain solid state processing applications than would otherwise be achieved by mechanical mixing. The melting peak of each component in the blend is separated due to solution precipitation such that large deformation processing can be performed at a temperature between the melting peaks of the two components.

Pawloski, et al. in U.S. Pat. Nos. 4,352,766, 4,161,502 and 3,739,052 teach a unique process called Solid Phase Forming (SPF) to form polymers and composites at a pre-melt state. This unique fabrication process induces a biaxial orientation throughout the finished parts.

Enikolopow, et al. in U.S. Pat. No. 4,607,797 teach a process called Solid State Sheer Extrusion or Pulverization to perform polymer extrusion at a temperature below the peak melting temperature of the polymer. However, Shutov has observed in a 1992 I.I.T. Research Report that certain polymers, such as HDPE, polypropylene (PP) and polycarbonate (PC) did not perform well in this process.

The disclosures of each of the patents referenced above are incorporated herein by reference.

SUMMARY OF THE INVENTION

According to this invention, polyolefin blends characterized by melting and crystallization curves which exhibit either two distinct melt regions, or a low softening point relative to the high melting component of the blend, provide an unusually wide window for solid state processing. These blends comprise at least 10 percent by weight of the low melting component, and the difference between the peak melting temperature of the low melting component and the high melting component is at least about twenty degrees on the Celsius scale. These blends are processed in their solid state at a temperature above about the peak melting temperature of the low melting component and below the peak melting temperature of the high melting component. The solid state processing characteristics of the blends of this invention are independent of the manner in which the components are mixed, e.g. mechanical, solvent, etc.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The polyolefin blends of this invention comprise two or more, typically two, polyolefin components. These blends are characterized by having a solid state processing temperature (Tp) defined by

$$T_{m1} < T_p < T_{m2}$$

in which the T_{m2} is the peak melting temperature of the high melting component, and T_{m1} is the peak melting temperature of the low melting component. Typically, the difference or range between T_{m2} and T_{m1}, i.e. $T_{m2} - T_{m1}$, is greater than about twenty, preferably greater than about thirty, and most preferably greater than about forty, degrees on the Celsius scale.

The components of the blends of this invention are polyolefins, e.g. polyethylenes, polypropylenes, dienes, styrene, etc. Preferred polyolefins are the various polyethylenes and polypropylenes, and preferred blends are those containing at least one polyethylene, particularly a substantially linear ethylene polymer.

The polyethylenes can be divided into two broad classes, heterogeneously branched and homogeneously branched. The heterogeneously branched polyethylenes that can be used in the practice of this invention fall into two broad categories, those prepared with a free radical initiator at high temperature and high pressure, and those prepared with a coordination catalyst at high temperature and relatively low pressure. The former are generally known as low density polyethylenes (LDPE) and are characterized by branched chains of polymerized monomer units pendant from the polymer backbone. LDPE polymers generally have a density

between about 0.910 and 0.935 grams per cubic centimeter (g/cc).

Ethylene polymers and copolymers prepared by the use of a coordination catalyst, such as a Ziegler or Phillips catalyst, are generally known as linear polymers because of the substantial absence of branch chains of polymerized monomer units pendant from the backbone. High density polyethylene (HDPE), generally having a density of about 0.941 to about 0.965 g/cc, is typically a homopolymer of ethylene, and it contains relatively few branch chains relative to the various linear copolymers of ethylene and an α-olefin. HDPE is well known, commercially available in various grades, and is useful in this invention.

Linear copolymers of ethylene and at least one α-olefin of 3 to 12 carbon atoms, preferably of 4 to 8 carbon atoms, are also well known, commercially available and useful in this invention. As is well known in the art, the density of a linear ethylene/α-olefin copolymer is a function of both the length of the α-olefin and the amount of such monomer in the copolymer relative to the amount of ethylene, the greater the length of the α-olefin and the greater the amount of α-olefin present, the lower the density of the copolymer. Linear low density polyethylene (LLDPE) is typically a copolymer of ethylene and an α-olefin of 3 to 12 carbon atoms, preferably 4 to 8 carbon atoms (e.g., 1-butene, 1-octene, etc.), that has sufficient α-olefin content to reduce the density of the copolymer to that of LDPE. When the copolymer contains even more α-olefin, the density will drop below about 0.91 g/cc and these copolymers are known as ultra low density polyethylene (ULDPE) or very low density polyethylene (VLDPE). The densities of these linear polymers generally range from about 0.87 to 0.91 g/cc.

Both the materials made by the free radical catalysts and by the coordination catalysts are well known in the art, as are their methods of preparation. Relevant discussions of both of these classes of materials, and their methods of preparation, are found in U.S. Pat. No. 4,950,541 and the patents to which it refers, all of which are incorporated herein by reference.

The homogeneously branched polyethylenes that can be used in the practice of this invention also fall into two broad categories, the linear homogeneously branched and the substantially linear homogeneously branched. Both are known. The former and their method of preparation are described in U.S. Pat. No. 3,645,992 to Elston, and the latter and their method of preparation are fully described in U.S. Pat. Nos. 5,272,236 and 5,278,272, all of which are incorporated into and made a part of this application by reference. Examples of the former are the Tafmer TM polymer of Mitsui and the Exact TM polymer of Exxon, while an example of the latter are the polymers made by the Insite TM Technology of The Dow Chemical Company.

As here used, "substantially linear" means that the polymer backbone is substituted with about 0.01 long-chain branches/1000 carbons to about 3 long-chain branches/1000 carbons, preferably from about 0.01 long-chain branches/1000 carbons to about 1 long-chain branch/1000 carbons, and more preferably from about 0.05 long-chain branches/1000 carbons to about 1 long-chain branch/1000 carbons. In contrast, simply "linear" means that long chain branching is essentially absent from the polymer backbone. Long-chain branching is here defined as a chain length of at least about 6 carbon atoms, above which the length cannot be distinguished using ^{13}C nuclear magnetic resonance spectroscopy, yet the long-chain branch can be about the same length as the length of the polymer backbone.

These unique substantially linear homogeneously branched polymers (subsequently referred to as "substantially linear ethylene polymers") are prepared by using constrained geometry catalysts (CGC), and are characterized by a narrow molecular weight distribution and if an interpolymer, by a narrow comonomer distribution. As here used, "interpolymer" means a polymer of two or more comonomers, e.g. a copolymer, terpolymer, etc. Other basic characteristics of these substantially linear ethylene polymers include a low residuals content (i.e. low concentrations in the substantially linear ethylene polymer of the catalyst used to prepare the polymer, unreacted comonomers, if any, and low molecular weight oligomers made during the course of the polymerization), and a controlled molecular architecture which provides good processability even though the molecular weight distribution is narrow relative to conventional olefin polymers.

While the substantially linear ethylene polymers used in the practice of this invention include substantially linear ethylene homopolymers, preferably these substantially linear ethylene polymers comprise between about 95 and 50 wt % ethylene, and about 5 and 50 wt % of at least one α-olefin comonomer, more preferably 10 to 25 wt % of at least one α-olefin comonomer. Percent comonomer is measured by Infrared Spectroscopy according to ASTM D-2238 Method B. Typically, the substantially linear ethylene polymers are copolymers of ethylene and an α-olefin of 3 to about 20 carbon atoms (e.g. propylene, 1-butene, 1-hexene, 4-methyl-1-pentene, 1-heptene, 1-octene, styrene, etc.), with a density of 0.850 to about 0.960 grams per cubic centimeter (g/cm^3), preferably of 0.870 to about 0.910 g/cm^3. The melt flow ratio, measured as I_{10}/I_2 (ASTM D-1238), is greater than or equal to 5.63, and is preferably from about 6.5 to 15, more preferably from about 7 to 10. The molecular weight distribution (M_w/M_n), measured by gel permeation chromatography (GPC), is defined by the equation:

$$M_wM_n \leqq (I_{10}/I_2) - 4.63,$$

and is preferably between about 1.5 and 2.5. For the substantially linear ethylene polymers, the I_{10}/I_2 ratio indicates the degree of long-chain branching, i.e. the larger the I_{10}/I_2 ratio, the more long-chain branching in the polymer.

The "rheological processing index" (PI) is the apparent viscosity (in kpoise) of a polymer measured by a gas extrusion rheometer (GER). The gas extrusion rheometer is described by M. Shida, R. N. Shroff and L. V. Cancio in *Polymer Engineering Science*, Vol. 17, No. 11, p. 770 (1977), and in "Rheometers for Molten Plastics" by John Dealy, published by Van Nostrand Reinhold Co. (1982) on pp. 97–99, both publications of which are incorporated herein by reference. GER experiments are performed at a temperature of 190° C., at nitrogen pressures between 250 to 5500 psig using about a 7.54 cm diameter, 20:1 L/D die with an entrance angle of 180°. For the substantially linear ethylene polymers described herein, the PI is the apparent viscosity (in kpoise) of a material measured by GER at an apparent shear stress of 2.15×10^6 dyne/CM^2. These substantially linear ethylene interpolymers and homopolymers preferably have a PI in the range of about 0.01 kpoise to about 50

kpoise, preferably about 15 kpoise or less, which is less than or equal to about 70% of the PI of a comparative linear ethylene polymer (either a Ziegler polymerized polymer or a linear uniformly branched polymer as described by Elston in U.S. Pat. No. 3,645,992) at about the same I_2 and M_w/M_n.

An apparent shear stress versus apparent shear rate plot is used to identify the melt fracture phenomena. According to Ramamurthy in the *Journal of Rheology*, 30(2), 337–357, 1986, above a certain critical flow rate, the observed extrudate irregularities may be broadly classified into two main types: surface melt fracture and gross melt fracture.

Surface melt fracture occurs under apparently steady flow conditions and ranges in detail from loss of specular film gloss to the more severe form of "sharkskin." In this disclosure, the onset of surface melt fracture (OSMF) is characterized at the beginning of losing extrudate gloss at which the surface roughness of the extrudate can only be detected by 40× magnification. The critical shear rate at the onset of surface melt fracture for the substantially linear ethylene interpolymers and homopolymers is at least 50 percent greater than the critical shear rate at the onset of surface melt fracture of a comparative linear ethylene polymer (either a Ziegler polymerized polymer or a linear uniformly branched polymer as described by Elston in U.S. Pat. No. 3,645,992) having about the same I_2 and M_w/M_n.

Gross melt fracture occurs at unsteady extrusion flow conditions and ranges in detail from regular (alternating rough and smooth, helical, etc.) to random distortions. For commercial acceptability, (e.g., in blown films and bags therefrom), surface defects should be minimal, if not absent, for good film quality and properties. The critical shear stress at the onset of gross melt fracture for the substantially linear ethylene interpolymers and homopolymers used in making the biaxially oriented, heat-shrinkable film of the present invention is greater than about 4×10^6 dynes/cm^2. The critical shear rate at the onset of surface melt fracture (OSMF) and the onset of gross melt fracture (OGMF) will be used herein based on the changes of surface roughness and configurations of the extrudates extruded by a GER.

As here used, "homogeneously branched" means that the comonomer is randomly distributed within a given molecule and that substantially all of the copolymer molecules have the same ethylene/comonomer ratio. The distribution or homogeneity of comonomer branches for the substantially linear ethylene interpolymers and homopolymers is characterized by its SCBDI (Short Chain Branch Distribution Index) or CDBI (Composition Distribution Branch Index), and it is defined as the weight percent of the polymer molecules having a comonomer content within 50 percent of the median total molar comonomer content. The CDBI of a polymer is readily calculated from data obtained from techniques known in the art, such as, for example, temperature rising elution fractionation (abbreviated herein as "TREF") as described, for example, by Wild et al., *Journal of Polymer Science, Poly. Phys, Ed.*, Vol. 20, p. 441 (1982), or in U.S. Pat. No. 4,798,081, both disclosures of which are incorporated herein by reference. The SCBDI or CDBI for the substantially linear homogeneously branched interpolymers and homopolymers of the present invention is preferably greater than about 30 percent, especially greater than about 50 percent.

Both the linear homogeneously branched and the substantially linear homogeneously branched ethylene polymers used in this invention have a single melting peak, as measured using differential scanning calorimetry (DSC), in contrast to heterogeneously branched linear ethylene polymers, which have two or more melting peaks due to their broad branching distribution.

The unique characteristic of the homogeneously branched, substantially linear ethylene polymers is a highly unexpected flow property where the I_{10}/I_2 value of the polymer is essentially independent of the polydispersity index (i.e., M_w/M_n) of the polymer. This is contrasted with conventional linear homogeneously branched and linear heterogeneously branched polyethylene resins having rheological properties such that to increase the I_{10}/I_2 value the polydispersity index must also be increased.

The preferred melt index, measured as I_2 (ASTM D-1238, condition 190/2.16 (formerly condition E)), is from about 0.5 g/10 min to 20 g/10 min, more preferably 1 to 5 g/10 min. Typically, the preferred substantially linear ethylene polymers used in the construction of the plastic films used in this practice of this invention are homogeneously branched and do not have any measurable high density fraction, (i.e. short chain branching distribution as measured by Temperature Rising Elution Fractionation which is described in U.S. Pat. No. 5,089,321, and which is incorporated into and made a part of this application by reference), e.g. they do not contain any polymer fraction that has a degree of branching less than or equal to 2 methyl/1000 carbons. These preferred substantially linear ethylene polymers have a single differential scanning calorimetry (DSC) melting peak.

The polypropylene component of this invention, if present, is a homopolymer or one or more copolymers of propylene and up to about 20 mole percent ethylene or other α-olefin having up to about 12 carbon atoms. If a copolymer, it can be random, block or graft. The polypropylene component of this has a typical melt flow rate (as determined by ASTM D-1238, Condition 230/2.16 (formerly Condition L)) of between about 0.1 and 30, and preferably between about 0.8 and 30.

The blends of this invention can also include polyolefins derived from post-consumer recycle (PCR) sources. These materials will vary in composition, but include HDPE derived from milk bottle recycled resin and LLDPE derived from recycled grocery sacks. The PCR resins used in this invention usually have a polyethylene content of at least about 70 wt %, based on the weight of the resin, up to about 100 wt %. The polyethylenes in the PCR resins usually have a melt index between about 0.1 and about 10, and a density between about 0.86 and about 0.97 g/cm^3.

Typically, the polyolefin blends of this invention comprise at least about 10 percent, preferably at least about 20 percent and more preferably at least about 30 percent, based on the weight of the blend, of the low melting component. In a preferred embodiment of this invention, the component with the low melting or softening temperature is at least one linear or substantially linear homogeneously branched polyethylene, e.g. at least one of a Tafmer TM , Exact TM or a polymer made by Insite TM Technology, or an ethylene-propylene rubber, or an ethylene-propylene-diene monomer terpolymer. More preferably, the low melting temperature component of the blend is a substantially linear homogeneously branched polymer, e.g. a polymer made by Insite TM . In these embodiments, the remainder of the

blend comprises one or more, preferably one, heterogeneously branched polyethylene.

The solid state processing temperature of these blends is usually at least about 5, and preferably at least about 10, degrees on the Celsius scale below the peak melting temperature of the blend component with the highest melting temperature, and it is usually at least about 5, preferably at least about 10, degrees on the Celsius scale above the melting or softening temperature of the blend component with the lowest melting or softening temperature.

The polyolefin blends of this invention can be prepared by any one of a number of different methods that ensures a relatively homogenous blend, the particular method employed being a matter of convenience. Illustrative methods include roller milling, extrusion, solvent mixing, and the like. Similarly, the blends can be processed by any conventional solid state technique, e.g. stamping, forging, rolling, extrusion, etc.

The following examples are illustrative of certain specific embodiments of this invention. All parts and percentages are by weight unless otherwise noted.

SPECIFIC EMBODIMENTS

EXAMPLE 1

Sample E-1 is prepared from a 50/50 blend of CGC resin (Sample C-1) and HDPE resin (Sample C-2) using a Haake blender operated for 4 minutes at 180° C. Sample C-5 is prepared in the same manner except that it is prepared from a 50/50 blend of conventional LLDPEs (Samples C-3 and C-4). All the samples except Sample C-1 are subjected to solid state extrusion evaluation by using an Instron Capillary Rheometer (ICR) at 105° C. using a Number 8 die (0.0494 inches in diameter, length/diameter ratio of 5.10). Sample E-1 (with a T_p of 50 (133-83)) is successfully extruded at a plunger speed of 0.1 inch per minute and at a pressure of 250 psi. The other samples (including Sample C-5 with a T_p of (122-132)) can not be extruded at these conditions, even at the maximum safe extrusion pressure of the I of 4500 psi. These results are reported in Table I.

TABLE I

Sample #	Composition	MI (g/10 min)	Density (g/cm³)	Peak Melt Temp (C.)	Solid St Extrudal
E-1	CGC/HDPE*	1.33	0.926	—	Yes
C-1	CGC	1.33	0.893	83	NA±
C-2	HDPE	1.0	0.959	133	No
C-3	LLD-3	1.0	0.920	122	No
C-4	LLD-4	2.0	0.930	122	No
C-5	LLD-3/LLD-4*	1.4	0.925	—	No

*50/50/Blend based on weight.
±NA = Not applicable: above melting point

EXAMPLE 2

The procedures of Example 1 are repeated with d ferent samples (although the composition of Sample C is the same as the composition of Sample C-1). Sampl E-2 (a blend of C-6 and C-7) (with a T_p of 51) and E (a blend of C-8 and C-9) (with a T_p of 79) are succes fully extruded on the ICR at a plunger speed of 0.1 in per minute, a pressure of about 2800 psi, a temperatu of about 105° C., and using a Number 2 die (0.030 inc length/diameter ratio of 33.3). Neither the Tafmer T A-4085 resin nor the polypropylene resin could be e truded at these conditions, or even at the maximum sa extrusion pressure of 4500 psi. The results are report in Table II.

TABLE II

Sample #	Composition	MI (g/10 min)	Density (g/cm³)	Peak Melt Temp (C.)	Solid Stat Extrudabl
E-2	CGC/HDPE*	2.33	0.926	—	Yes
C-6	CGC	1.78	0.893	83	NA***
C-7	HDPE	10.	0.962	134	NM±
E-3	Tafmer TM /PP**	1.4	0.925	—	Yes
C-8	Tafmer TM A-4085	1.0	0.88	88	No
C-9	PP	35.0	—	167	No

*50/50 Blend based on weight.
**30/70 Blend based on weight.
±NM = Not measured.
***NA = Not applicable: above melting point

EXAMPLE 3

The procedures of Example 1 are repeated with dif ferent samples. The compositions of Samples C-10 an C-12 are the same. The PCR resin of Sample C-13 i post-consumer recycled grocery sack resin from Ad vanced Environmental Recycling Technology of Littl Rock, Ark., and the PCR resin of Sample C-11 is post consumer recycled milk bottle resin FR-120 flake fron Akron WTE Corp of Akron, Ohio. Both the resins o Samples E-4 (a blend of C-10 and C-11) and E-5 (a blen of C-12 and C-13) (with a T_p of 49) were successfull extruded under the same conditions as those used i Example 2. Neither the resin of C-11 nor the resin o C-13 are extruded under these conditions, and they cannot be extruded under these conditions even at th maximum safe extrusion pressure of 4500 psi. The re sults are reported in Table III.

TABLE III

Sample #	Composition	MI (g/10 min)	Density (g/cm³)	Peak Melt Temp (C.)	Solid State Extrudable
E-4	CGC/PCR*	—	0.912	—	Yes
C-10	CGC	1.0	0.882	86	NA**

TABLE III-continued

Sample #	Composition	MI (g/10 min)	Density (g/cm^3)	Peak Melt Temp (C.)	Solid State Extrudable
C-11	PCR	0.75	0.955	132	No
E-5	CGC/PCR*	1.4	0.935	—	Yes
C-12	CGC	1.0	0.882	86	NA**
C-13	PCR	0.4	0.962	135	No

*30/70 Blend based on weight.
**NA — Not applicable: above melting point.

EXAMPLE 4

The procedures of Example 1 are repeated with different samples. Sample C-14 (which is the same as Sample C-3) is a conventional LLDPE with a similar melt index and density as Sample E-6 (a blend of C-16 and C-15) (with a T_p of 107). Both Samples E-6 and C-14 are compression molded into a 125 mil thick plaque according to the procedures of ASTM-1238. The plaques are heated to 65° C., and then compressed in a 40 ton (2075 psi) solid phase forming machine for 3 minutes. The samples are then cooled under the same pressure, removed at room temperature, and the modulus and percent deformation determined. These results are reported in Table IV, and the modulus and percent deformation characteristics of Sample E-6 are clearly superior to those of Sample C-14.

TABLE IV

Sample #	Composition	MI (g/10 min)	Density (g/cm^3)	Peak Melt Temp (C.)	% Modulus Deformed	% Modulus (psi)
E-6	HDPE/LD*	1.01	0.922	—	203	39,900
C-14	LLD-3	1.0	0.920	122	162	16,120
C-15	LD	1.01	0.856	26	NM±	NM±
C-16	HDPE	1.0	0.959	133	NM±	NM±

*35/65 Blend based on weight.
± NM = Not measured.

Although the invention has been described in considerable detail through the preceding examples, this detail is for illustration purposes only, and it is not to be construed as a limitation on the spirit and scope of the invention as described in the following claims.

What is claimed is:

1. A process for shaping a solid polyolefin blend, the process comprising the steps of:

A. Heating a solid polyolefin blend which comprises at least a first and second polyolefin, the first of which is a substantially linear homogeneously branched polyethylene characterized as having:

a) a melt flow ratio, I_{10}/I_2, $\geqq$ 5.63,

b) a molecular weight distribution, M_w/M_n, defined by the equation:

$$M_w/M_n \leqq (I_{10}/I_2) - 4.63, \text{ and}$$

c) a critical shear stress at onset of gross melt fracture of greater than about 4×10^6 dyne/cm^2, with a softening temperature of at least about 10 degrees on the Celsius scale lower than the softening temperature of the second polyolefin, the first polyolefin comprising at least about 10 percent of the total weight of the polyolefin blend, the polyefin blend heated to a processing temperature above the softening temperature of the first polyolefin but below the softening temperature of the second polyolefin;

B. Shaping the blend at the processing temperature; and

C. Cooling the shaped blend of (B) to a temperature below the processing temperature.

2. The process of claim 1 in which the second polyolefin is at least one of high density polyethylene, low density polyethylene, linear low density polyethylene, and ultra low density polyethylene.

3. The process of claim 2 in which the first polyolefin comprises at least about 20 percent of the total weight of the polyolefin blend.

4. The process of claim 3 in which the process temperature is a temperature of at least about 5 degrees on the Celsius scale lower than the softening temperature of the first polyolefin, and at least about 5 degrees on the Celsius scale higher than the softening temperature of the second polyolefin.

5. The process of claim 3 in which the processing temperature is at least about 10 degrees on the Celsius scale lower than the softening temperature of the second polyolefin, and at least about 10 degrees higher than the softening temperature of the first polyolefin.

6. The process of claim 5 in which the polyolefin blend is prepared by mechanically mixing the first and second polyolefins with one another.

* * * * *

US005444145A

United States Patent [19]

Brant et al.

[11] Patent Number: 5,444,145

[45] Date of Patent: Aug. 22, 1995

[54] ETHYLENE/BRANCHED OLEFIN COPOLYMERS

[75] Inventors: **Patrick Brant**, Seabrook; **Jo Ann M. Canich**; **Natalie A. Merrill**, both of Webster, all of Tex.

[73] Assignee: **Exxon Chemical Patents Inc.**, Wilmington, Del.

[21] Appl. No.: **81,960**

[22] Filed: **Jun. 24, 1993**

Related U.S. Application Data

[63] Continuation of Ser. No. 871,248, Apr. 20, 1992, abandoned.

[51] Int. Cl.[6] **C08F 10/14**; C08F 210/14

[52] U.S. Cl. **526/348.3**; 526/348.1; 526/348.2; 526/348.4; 526/348.6; 526/127; 526/160

[58] Field of Search 526/348.1, 348.2, 348.3, 526/348.4, 348.6

[56] References Cited

U.S. PATENT DOCUMENTS

4,205,021	5/1980	Morita et al.	526/348.4
4,287,328	9/1981	Kikuta et al.	526/115
4,321,345	3/1982	Sato et al.	526/115
4,405,774	9/1983	Miwa et al.	526/348.4
4,411,854	10/1983	Maurer et al.	526/348.1
4,436,689	3/1984	Smith et al.	526/348.1
4,438,238	3/1984	Fukushima et al.	525/240
4,668,752	5/1987	Tominari et al.	526/348.4
4,883,853	11/1989	Hobes et al.	526/329
5,017,665	5/1991	Chang	526/129
5,087,677	2/1992	Brekner et al.	526/160
5,153,157	10/1992	Hlatky et al.	502/117
5,272,236	12/1993	Lai et al.	526/348.5

FOREIGN PATENT DOCUMENTS

0273654	12/1987	European Pat. Off. .
254022	1/1988	European Pat. Off. .
283958	9/1988	European Pat. Off. .
420436	4/1991	European Pat. Off. .
57-195704	12/1982	Japan .
195704	12/1982	Japan .
61-221206	3/1985	Japan .
63039905	4/1986	Japan .

OTHER PUBLICATIONS

Shirayama, K, et al. Die. Makrol. Chemie 151 (1972) 97–120.

A. H. Willbourn, J. Polym. Sci. 34 (1959) 569.

D. A. Boyle, et al. Polymer 2 (1961) 335.

K. Casey, et al. J. Polym. Sci. B2 (1964) 1053.

Primary Examiner—David W. Wu

Attorney, Agent, or Firm—Catherine Bell

[57] ABSTRACT

High molecular weight copolymers of ethylene and 0.5–10 mole percent branched α-olefins are disclosed. The polymers have M_w of 30,000–1,000,000, MWD of 2–4, a density of 0.85–0.95 g/cm^3, and a high composition distribution breadth index. Also disclosed are a method for making the polymers with a cyclopentadienyl metallocene catalyst system, and films, fibers, molded articles and other products made from the copolymers.

30 Claims, 11 Drawing Sheets

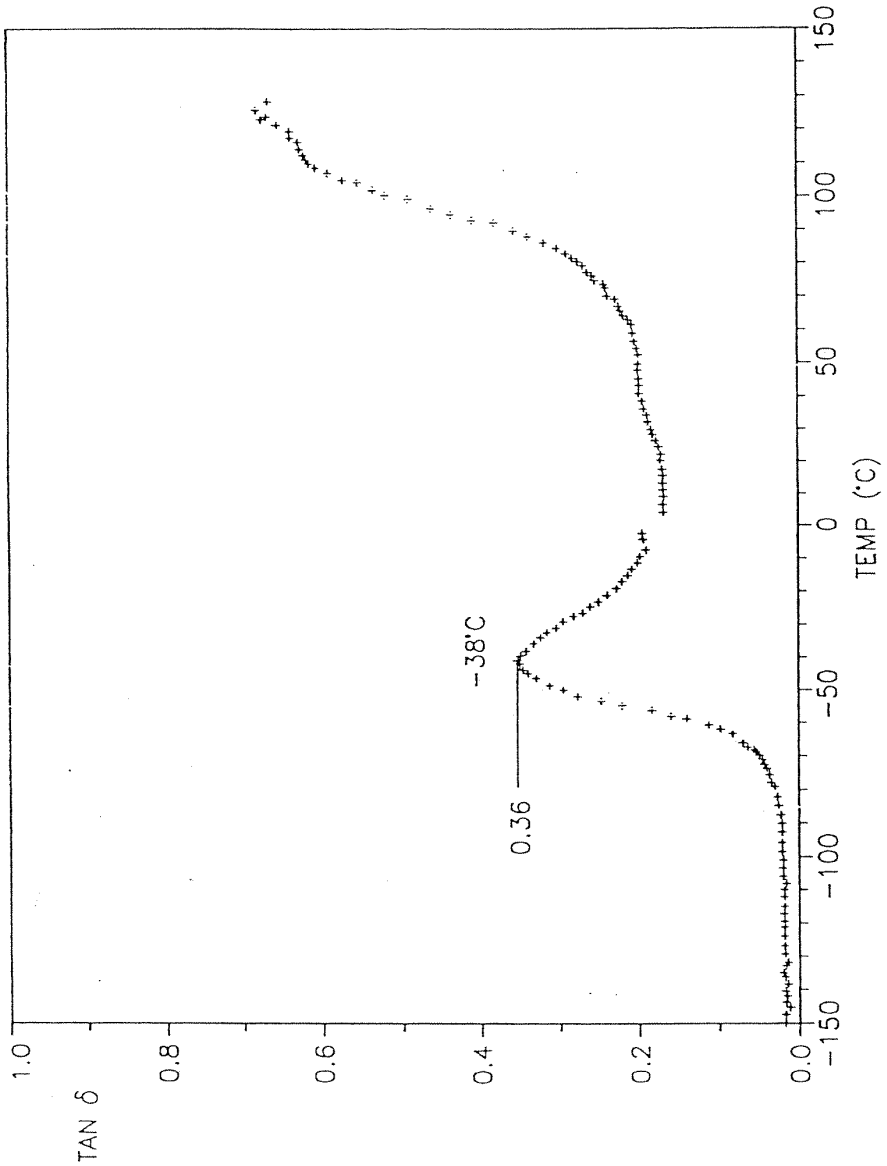


FIG. 1

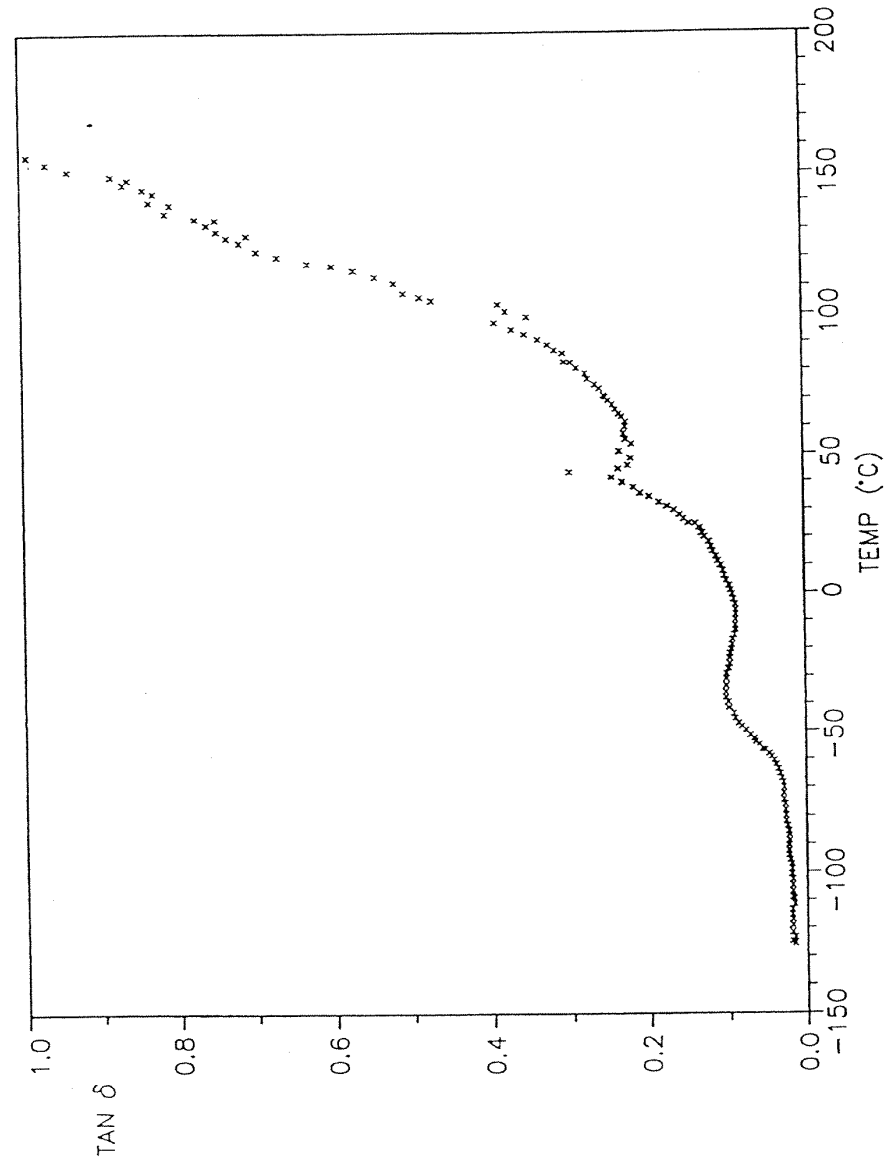


FIG. 2

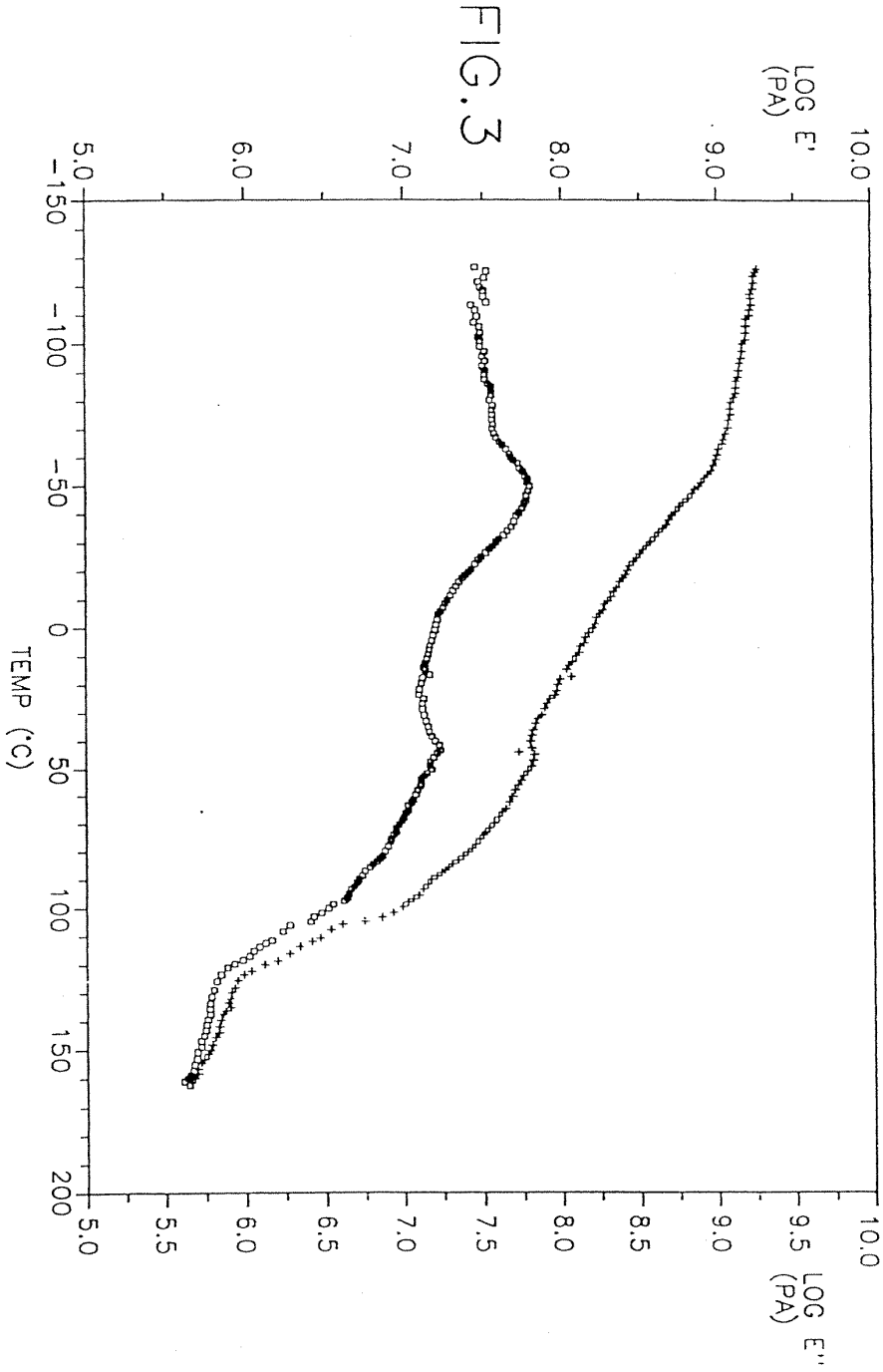

LOG E' (PA)
10.0
9.0
8.0
7.0
6.0
5.0
-150
-100
-50
0
50
100
150
200
TEMP (°C)
LOG E'' (PA)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0

FIG. 3

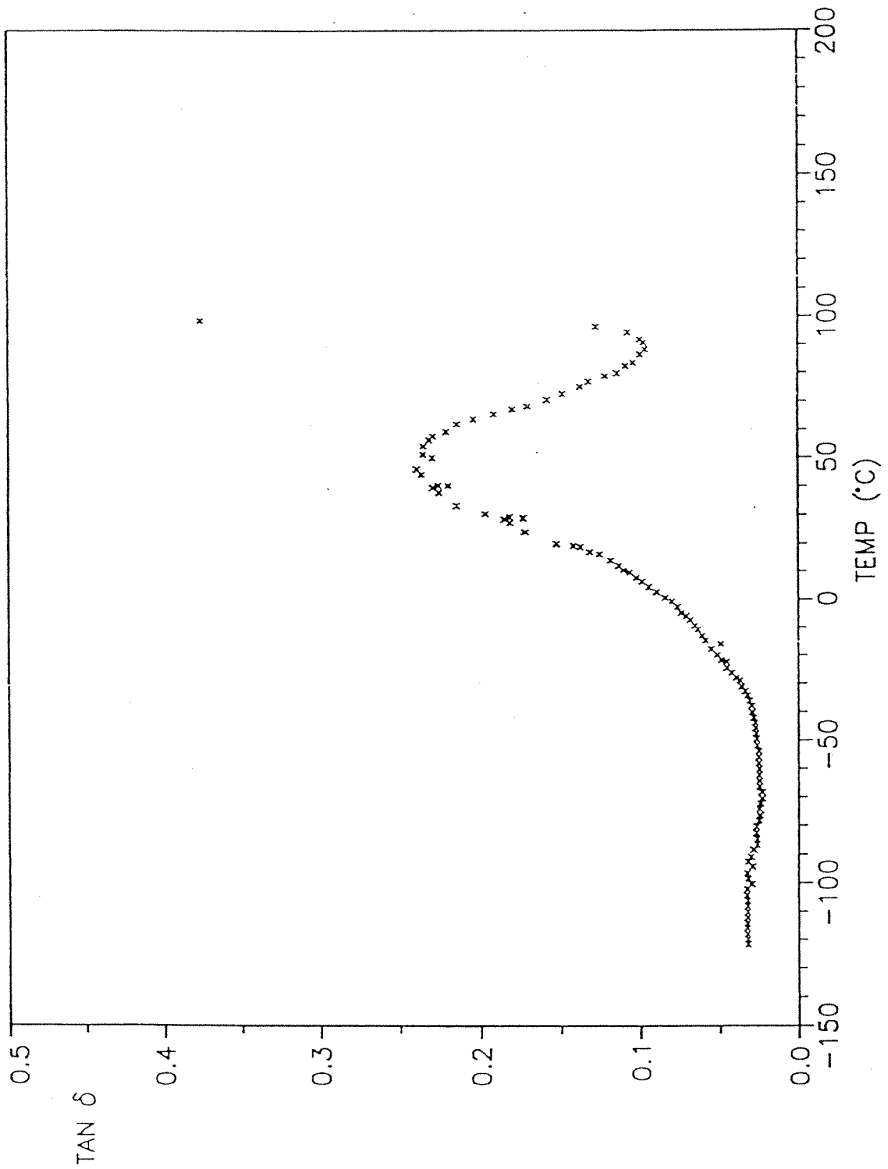


FIG. 4

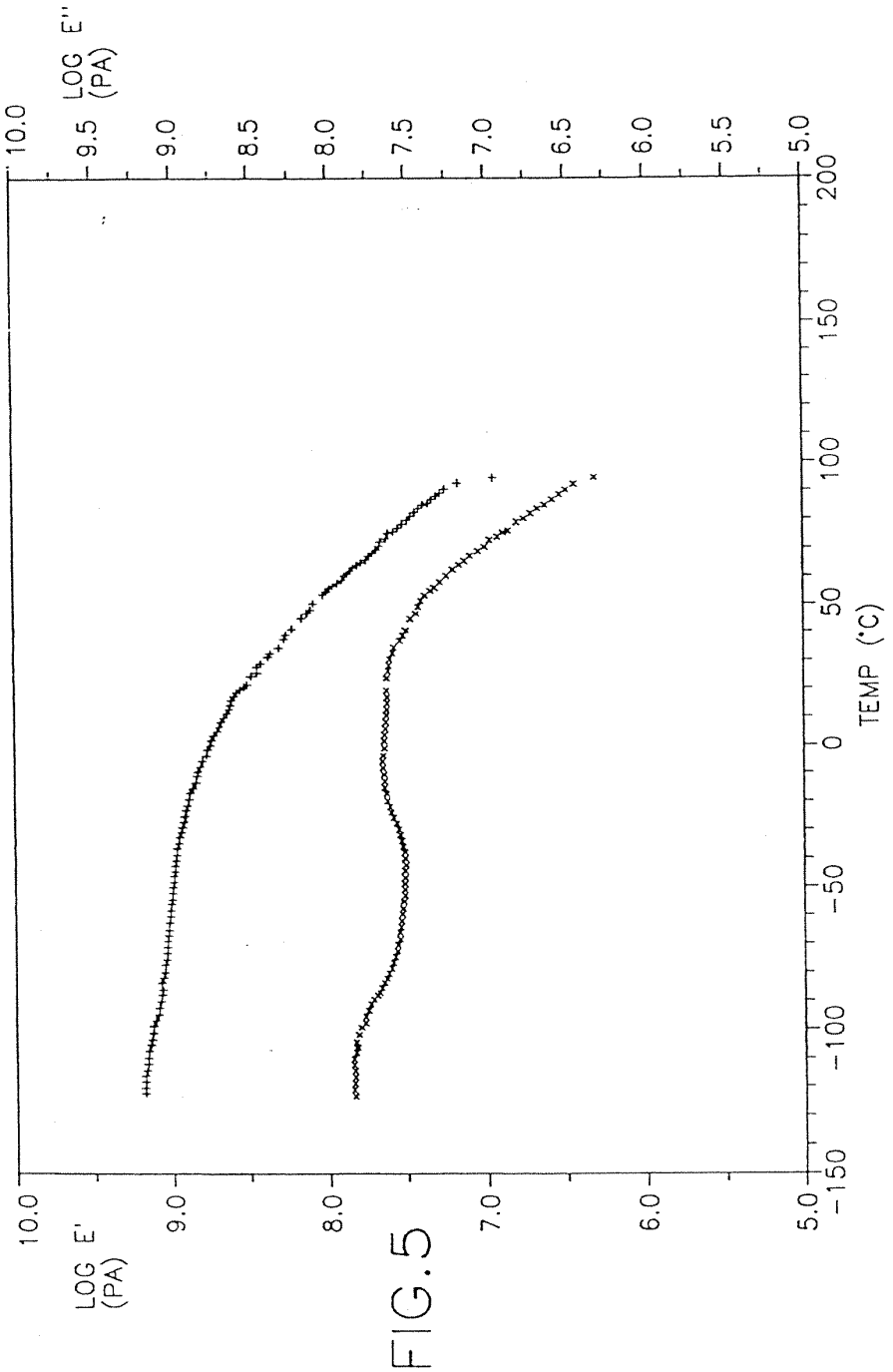

LOG E''
(PA)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
200
150
100
50
0
−50
−100
−150
TEMP (°C)
LOG E'
(PA)
10.0
9.0
8.0
7.0
6.0
5.0

FIG. 5

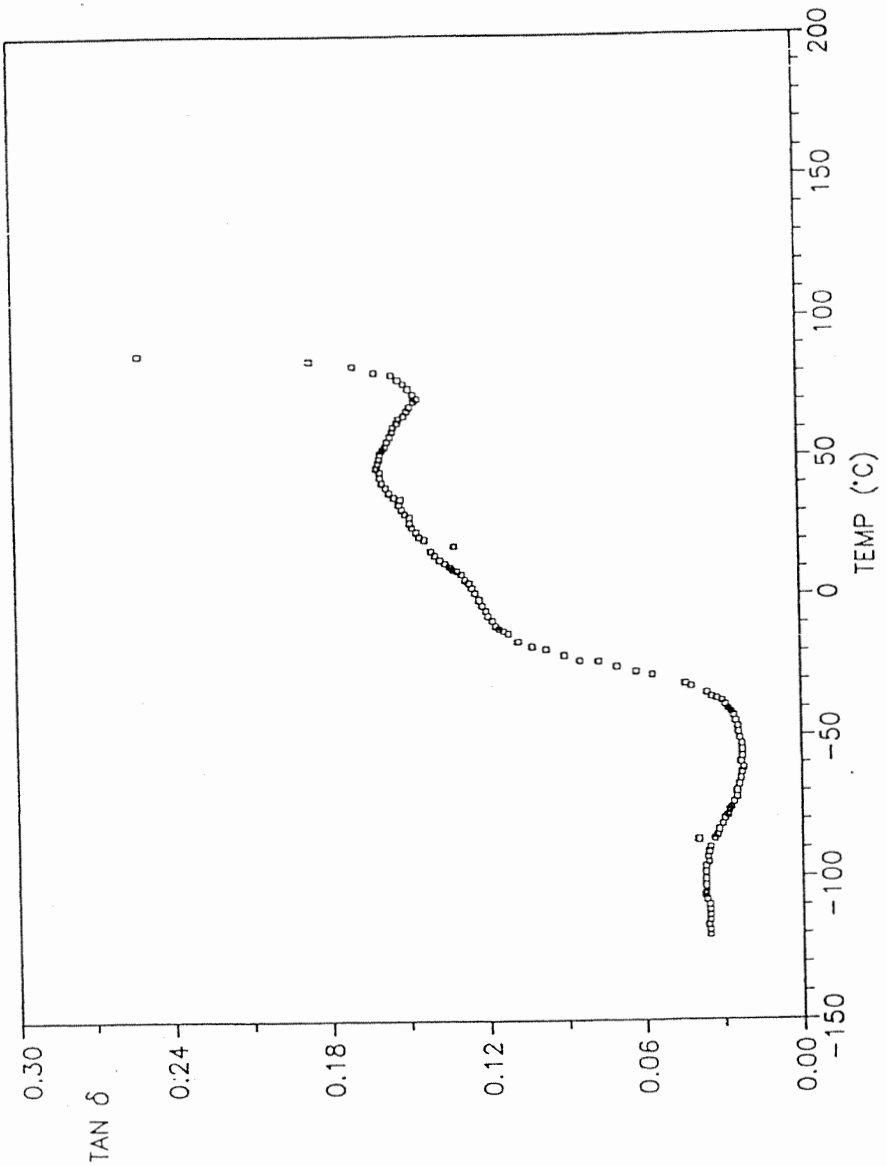


FIG. 6

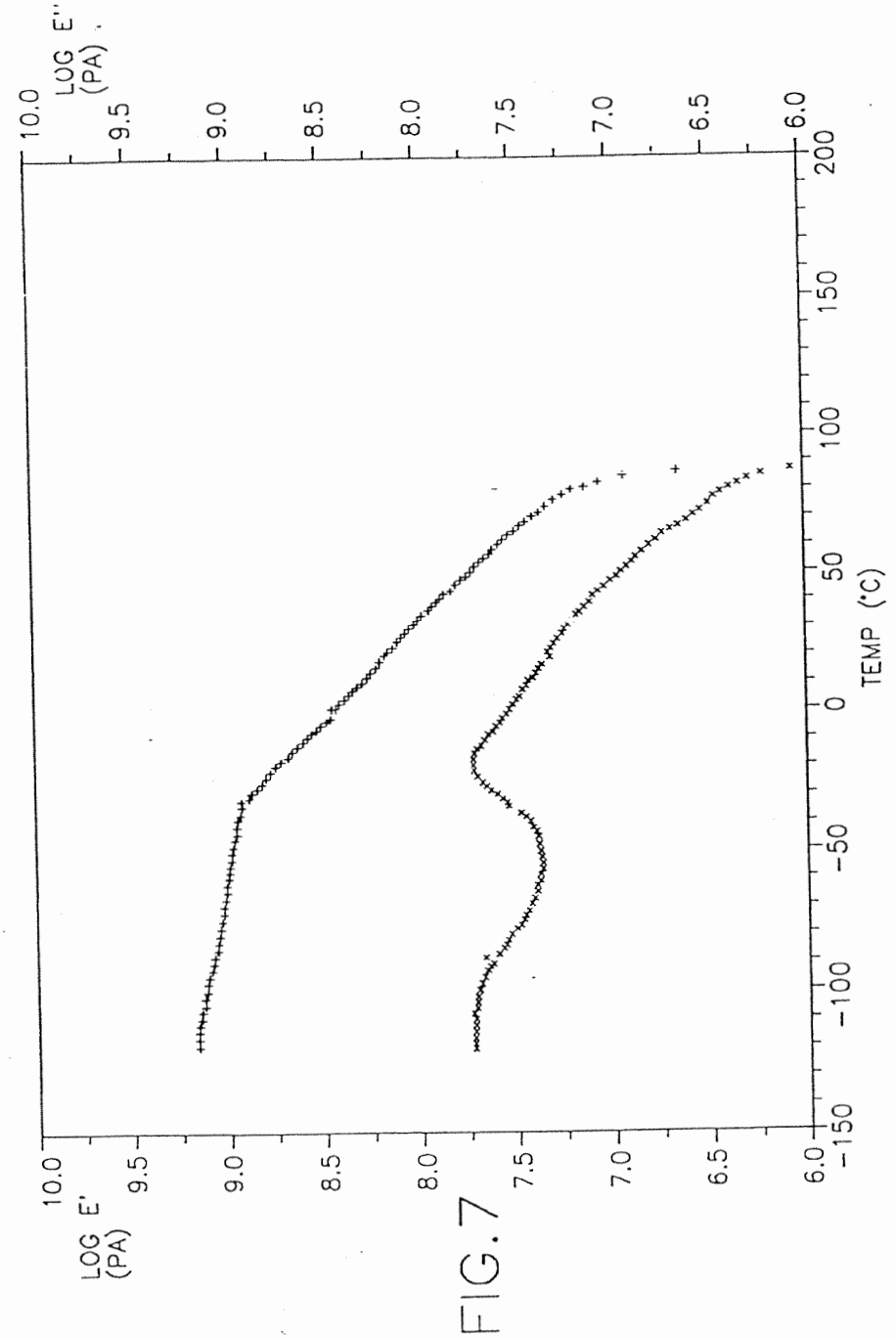

LOG E''
(PA)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
200
150
100
50
0
−50
−100
−150
TEMP (°C)
LOG E'
(PA)

FIG. 7

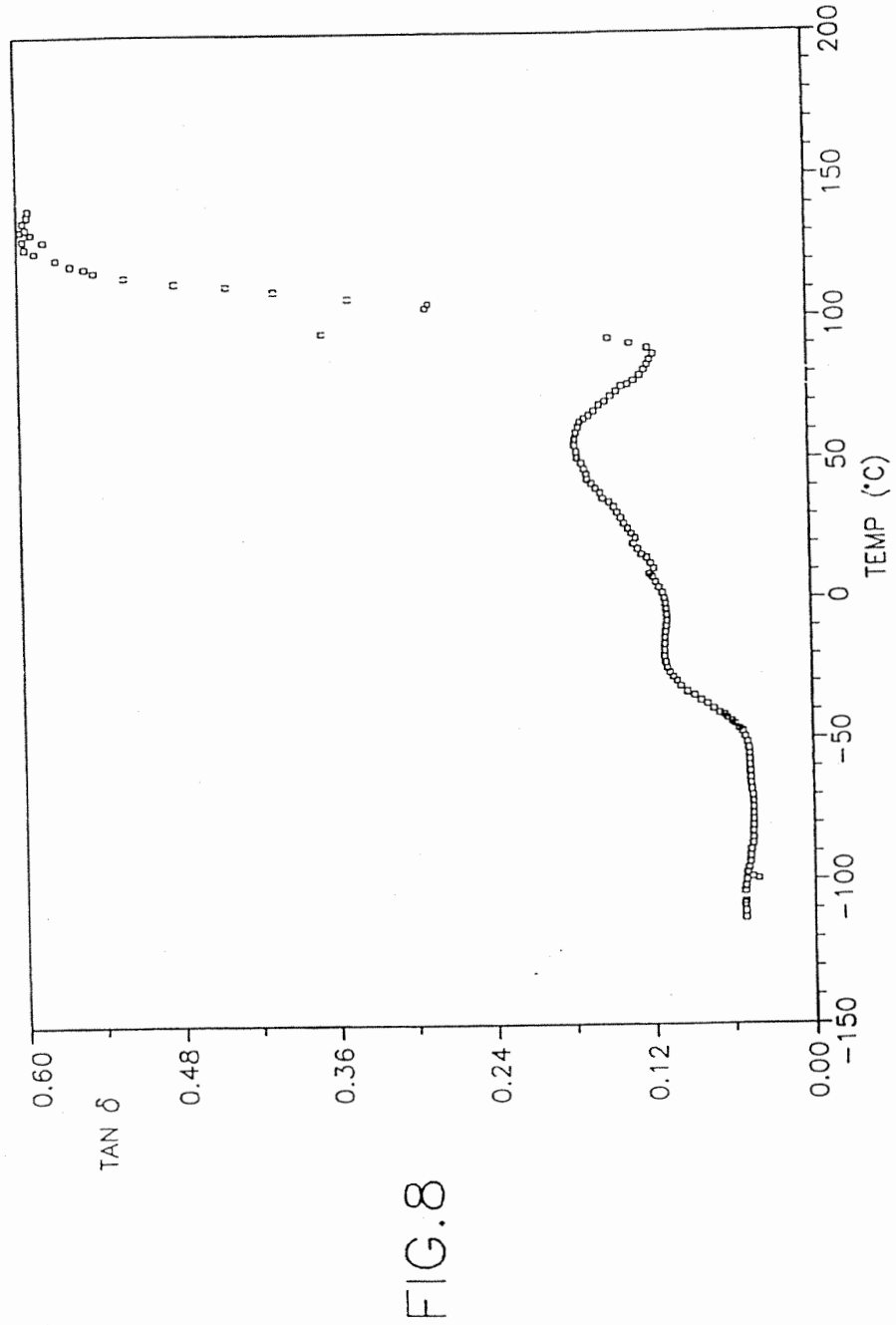


FIG. 8

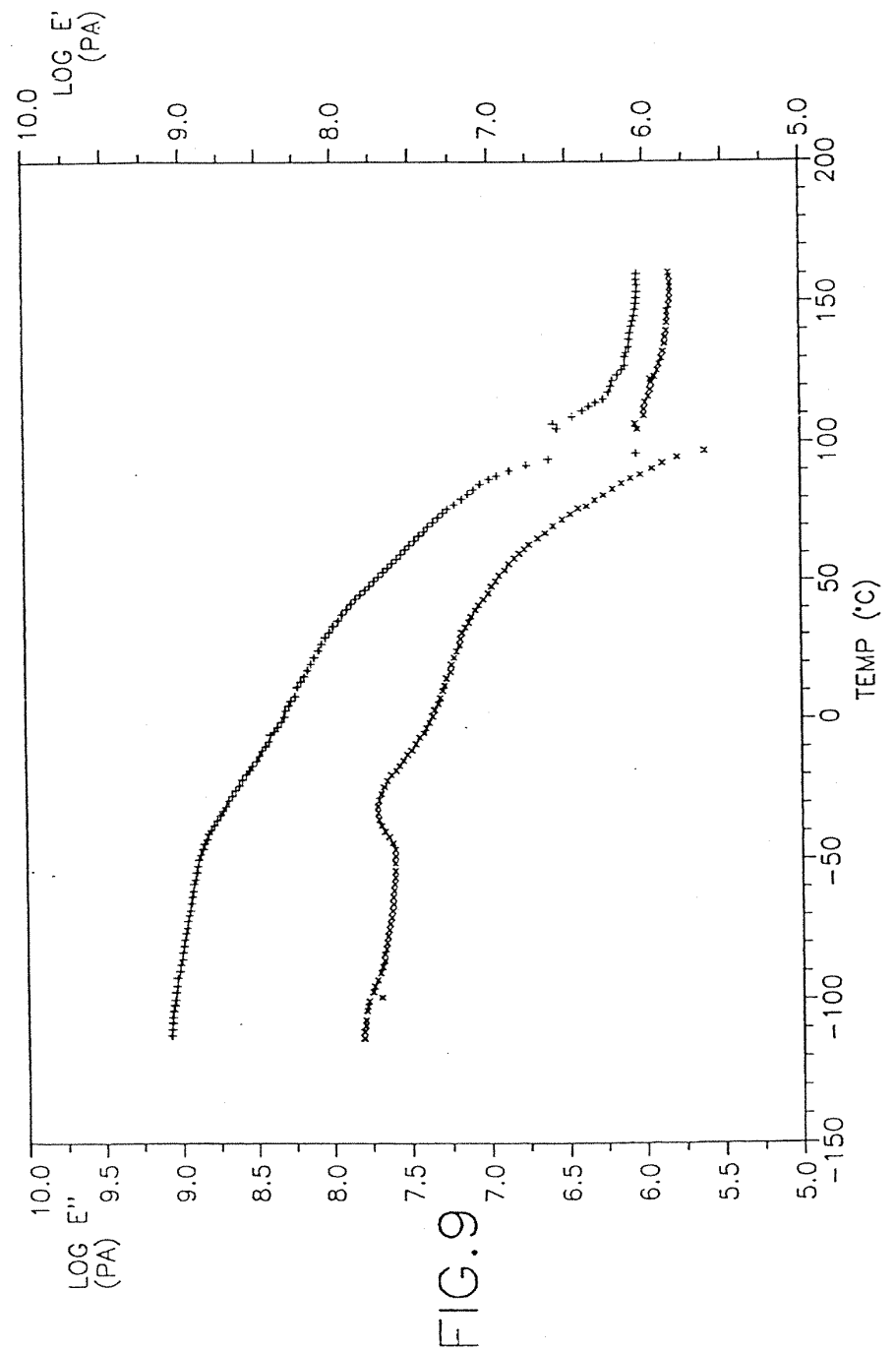

LOG E'
(PA)
10.0
9.0
8.0
7.0
6.0
5.0
200
150
100
50
0
-50
-100
-150
TEMP (°C)
LOG E''
(PA)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0

FIG. 9

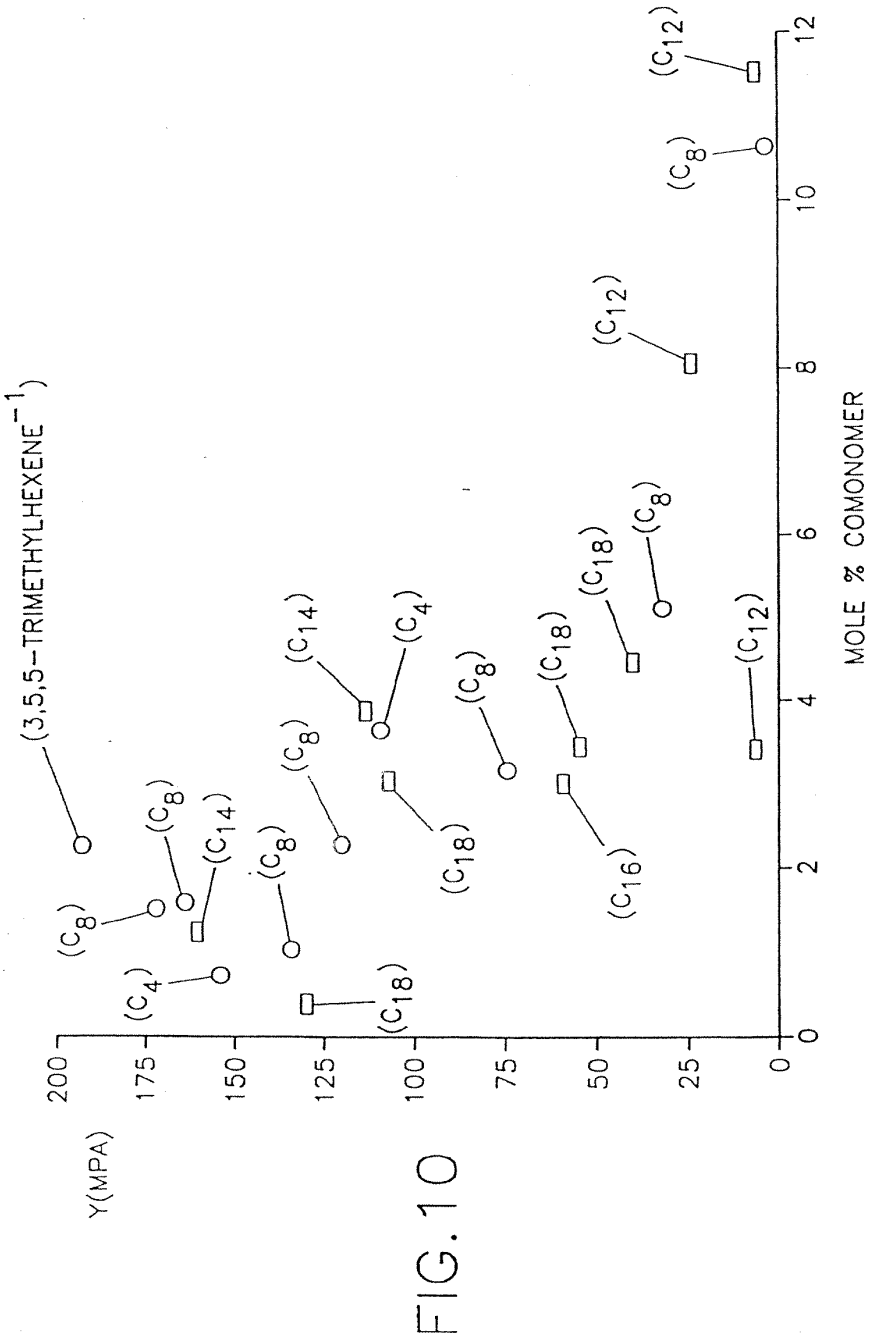

(3,5,5-TRIMETHYLHEXENE^{-1})
Y(MPA)
MOLE % COMONOMER
200
175
150
125
100
75
50
25
0
0
2
4
6
8
10
12
(C$_8$)
(C$_4$)
(C$_8$)
(C$_{14}$)
(C$_8$)
(C$_{18}$)
(C$_8$)
(C$_{14}$)
(C$_4$)
(C$_{18}$)
(C$_8$)
(C$_{18}$)
(C$_{16}$)
(C$_{18}$)
(C$_8$)
(C$_{12}$)
(C$_{12}$)
(C$_8$)
(C$_{12}$)

FIG. 10

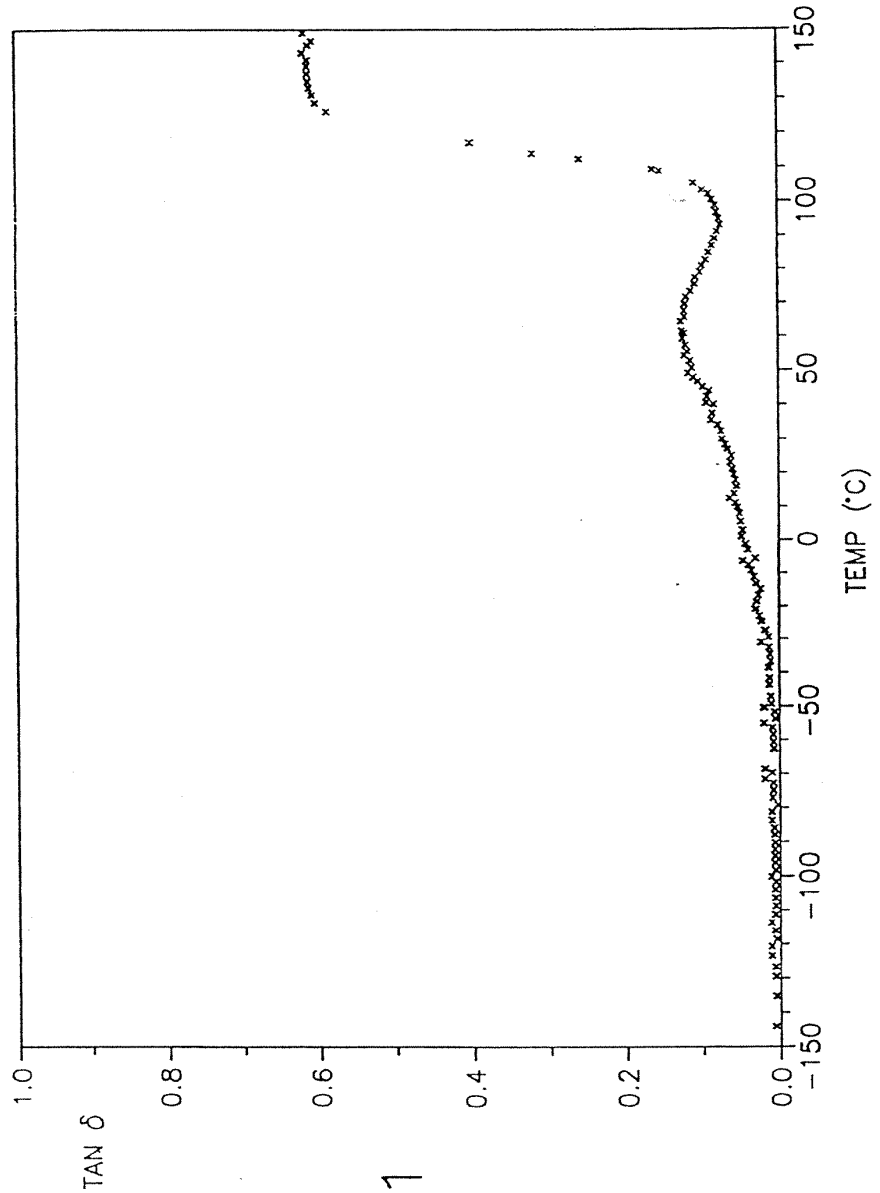


FIG. 11

ETHYLENE/BRANCHED OLEFIN COPOLYMERS

This is a continuation of application Ser. No. 07/871,248, filed Apr. 20, 1992 now abandoned.

FIELD OF THE INVENTION

This invention relates to copolymers of ethylene and branched α-olefins, and more particularly to tough, high strength copolymers thereof. This invention also relates to a process for copolymerizing ethylene with branched α-olefins utilizing certain transition metal compounds from Group IV B of the Periodic Table of Elements that produces high molecular weight copolymers.

BACKGROUND OF THE INVENTION

As far as Applicants are aware, it has not been possible to prepare ethylene copolymers with many branched α-olefin comonomers, particularly where the branch is in the 3-position, with sufficiently high molecular weight for most applications, using a traditional Ziegler-Natta catalyst.

It has been proposed to use certain metallocenes such as bis(cyclopentadienyl) titanium or zirconium dialkyls in combination with aluminum alkyl/water cocatalyst as a homogeneous catalyst system for the polymerization of olefins in general. For example: German Patent Application 2,608,863 teaches the use of a catalyst system for the polymerization of ethylene consisting of bis(cyclopentadienyl) titanium dialkyl, aluminum trialkyl and water; German Patent Application 2,608,933 teaches an ethylene polymerization catalyst system consisting of zirconium metallocenes of the general formula $(cyclopentadienyl)_nZrY_{4-n}$, wherein n stands for an integer in the range of 1 to 4, Y for R, CH_2AlR_2, $CH_2CH_2AlR_2$ and $CH_2CH(AlR_2)_2$, wherein R stands for alkyl or metallo alkyl, an aluminum trialkyl cocatalyst and water; European Patent Application No. 0035242 teaches a process for preparing ethylene and atactic propylene polymers in the presence of a halogen-free Ziegler catalyst system of (1) cyclopentadienyl compound of the formula $(cyclopentadienyl)_nMY_{4-n}$ in which n is an integer from 1 to 4, M is a transition metal, especially zirconium, and Y is either hydrogen, a C_1–C_5 alkyl or metallo alkyl group or a radical having the following general formula CH_2AlR_2, $CH_2CH_2AlR_2$, and $CH_2CH(AlR_2)_2$ in which R represents a C_1—C_5 alkyl or metallo alkyl group, and (2) an alumoxane; and U.S. Pat. No. 4,564,647 teaches a low pressure process for polymerizing ethylene, either alone or in combination with small amounts of other α-olefins, in the presence of a catalyst which may comprise a cyclopentadienyl compound, represented by the formula $(Cp)MR^2R^3R^4$ wherein (Cp) represents a cyclopentadienyl group, M represents titanium, vanadium, zirconium or hafnium, and R^2, R^3 and R^4 are each an alkyl group having from 1 to 6 carbon atoms, a cyclopentadienyl group, a halogen atom or a hydrogen atom, an alumoxane, which can be prepared by reacting trialkyl aluminum or dialkyl aluminum monohalide with water and a filler. Each of the above patents also teach that the polymerization process employing the homogeneous catalyst system is hydrogen sensitive thereby providing a means to control polymer molecular weight.

As is well known in the prior art, catalyst systems comprising a cyclopentadienyl compound, hereinafter frequently referred to as a metallocene or metallocene catalyst component, and an alumoxane offer several distinct advantages when compared to the more conventional Ziegler-type catalyst systems. For example, the cyclopentadienyl-transition metal/alumoxane catalyst systems, particularly those wherein the cyclopentadienyl compound contains at least one halogen atom, have demonstrated extremely high activity in the polymerization of α-olefins, particularly ethylene. Moreover, these catalyst systems produce relatively high yields of polymer product having a relatively narrow molecular weight distribution. However, these catalyst systems, when used to prepare copolymers of ethylene with branched α-olefins in anything more than a very minor proportion, still suffer from the drawbacks of low incorporation rates, and low molecular weights.

For many applications it is of primary importance for a polyolefin to have a high weight average molecular weight while having a relatively narrow molecular weight distribution. A high weight average molecular weight, when accompanied by a narrow molecular weight distribution, provides a polyolefin or an ethylene-lower-α-olefin copolymer with high strength properties. Traditional Ziegler-Natta catalyst systems—a transition metal compound cocatalyzed by an aluminum alkyl—are in general capable of producing polyolefins having a high molecular weight but with a broad molecular weight distribution.

More recently a catalyst system has been developed wherein the transition metal compound has two or more cyclopentadienyl ring ligands, such transition metal compound also referred to as a metallocene, which catalyzes the production of olefin monomers to polyolefins. Accordingly, metallocene compounds of the Group IV B metals, particularly, titanocene and zirconocene have been utilized as the transition metal component in such "metallocene" containing catalyst system for the production of polyolefins and ethylene-α-olefin copolymers. When such metallocenes are cocatalyzed with an aluminum alkyl—as is the case with a traditional type Ziegler-Natta catalyst system—the catalytic activity of such metallocene catalyst system is generally too low to be of any commercial interest. It has since become known that such metallocenes may be cocatalyzed with an alumoxane—rather than an aluminum alkyl—to provide a metallocene catalyst system of high activity which catalyzes the production of polyolefins. The zirconium metallocene species, as cocatalyzed or activated with alumoxane are commonly more active than their hafnium or titanium analogues for the general polymerization of ethylene alone or together with an α-olefin comonomer.

A wide variety of Group IV B transition metal compounds of the metallocene type have been named as possible candidates for an alumoxane cocatalyzed catalyst system. Hence, although bis(cyclopentadienyl) Group IV B transition metal compounds have been the most preferred and heavily investigated type metallocenes for use in metallocene/alumoxane catalyst for polyolefin production, suggestions have appeared that mono and tris(cyclopentadienyl) transition metal compounds may also be useful. See, for example, U.S. Pat. Nos. 4,522,982; 4,530,914 and 4,701,431. Such mono(cyclopentadienyl) transition metal compounds as have heretofore been suggested as candidates for a metallocene/alumoxane catalyst are mono(cyclopentadienyl) transition metal trihalides and trialkyls.

More recently International Publication No. WO 87/03887 described the use of a composition comprising

a transition metal coordinated to at least one cyclopentadienyl and at least one heteroatom ligand as a metallocene type component for use in a metallocene/alumoxane catalyst system for α-olefin polymerization. The composition is broadly defined as a transition metal, preferably of Group IV B of the Periodic Table which is coordinated with at least one cyclopentadienyl ligand and one to three heteroatom ligands, the balance of the coordination requirement being satisfied with cyclopentadienyl or hydrocarbyl ligands. The metallocene/alumoxane catalyst system described is illustrated solely with reference to transition metal compounds which are bis(cyclopentadienyl) Group IV B transition metal compounds.

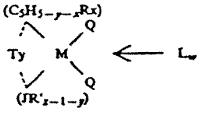
SUMMARY OF THE INVENTION

In accordance with the present invention, branched α-olefins are copolymerized with ethylene in the presence of a catalyst system comprising an activated cyclopentadienyl transition metal compound. Quite surprisingly, it has been found that the branched α-olefins have a reactivity ratio with ethylene which is sufficiently low to obtain substantial incorporation when these catalysts are employed, despite the bulky "tail" of the branched α-olefin. As a result, the branched α-olefin is unexpectedly incorporated into the copolymer at a competitive rate with the ethylene, and the composition distribution is substantially uniform and generally random.

The present invention resides, at least in part, in the discovery that branched α-olefins can be polymerized with ethylene using certain monocyclopentadienyl metallocene catalysts to obtain a high molecular weight copolymer with a high proportion of branched α-olefin incorporation, a narrow molecular weight distribution and a relatively random and uniform branched α-olefin comonomer distribution. The present invention also resides, in part, in the discovery that certain of these novel copolymers have very surprising properties, such as, for example, modulus, strain to break, rheological properties, storage and loss moduli, dissipative characteristics, and the like. In particular the preferred copolymers of the present invention exhibit surprising toughness, have suppressed or nonexistent secondary phase transitions in the temperature ranges conventional for ethylene/linear α-olefin copolymers, and have a secondary phase transition temperature and/or magnitude different from such conventional copolymers.

In one aspect, then, the present invention provides a substantially compositionally uniform copolymer of ethylene and preferably from about 0.5 to about 10 mole percent, more preferably from about 1 to about 8, and especially from about 1 to about 5 mole percent, of a branched α-olefin incorporated substantially randomly in the copolymer. The copolymer is generally semicrystalline and has a density of from about 0.85 to about 0.95 g/cm^3. The copolymer preferably has a weight average molecular weight from about 30,000 to about 1,000,000 daltons or more, more preferably from about 80,000 to about 500,000 daltons, and a molecular weight distribution substantially between about 2 and about 4. The copolymer has a generally uniform comonomer composition distribution. The present invention also provides useful articles made from the foregoing copolymers, including fibers, films, sheets, coatings and molded articles. In particular, the invention provides fibers, films and other forms of the copolymer wherein the copolymer is axially oriented by physical or mechanical processing such as, for example, drawing, extrusion, and the like.

In a further aspect, the present invention provides a method of preparing a copolymer by contacting ethylene and the branched α-olefin comonomer with a catalyst at polymerization conditions wherein the ethylene:comonomer reactivity ratio is less than about 75. In a preferred embodiment, the foregoing copolymers are prepared by contacting ethylene and a branched α-olefin with a catalyst system comprising a Group IV B transition metal component and an activating component for the catalyst at polymerization conditions, and recovering a high molecular weight, narrow molecular weight distribution copolymer having a generally uniform, random α-olefin composition distribution. The "Group IV B transition metal component" of the catalyst system is represented by the general formula:



wherein:

M is Zr, Hf or Ti and is in its highest formal oxidation state (+4, d^0 complex);

$(C_5H_{5-y-x}R_x)$ is a cyclopentadienyl ring which is substituted with from zero to five substituent groups R, "x" is 0, 1, 2, 3, 4 or 5 denoting the degree of substitution, and each substituent group R is, independently, a radical selected from a group consisting of C_1–C_{20} hydrocarbyl radicals, substituted C_1–C_{20} hydrocarbyl radicals wherein one or more hydrogen atoms is replaced by a halogen radical, an amido radical, a phosphido radical, an alkoxy radical, an alkylborido radical, or any other radical containing a Lewis acidic or basic functionality, C_1–C_{20} hydrocarbyl-substituted metalloid radicals wherein the metalloid is selected from the Group IV A of the Periodic Table of Elements, and halogen radicals, amido radicals, phosphido radicals, alkoxy radicals, alkylborido radicals or any other radical containing Lewis acidic or basic functionality or $(C_5H_{5-y-x}R_x)$ is a cyclopentadienyl ring in which two adjacent R-groups are joined forming a C_4–C_{20} ring to give a saturated or unsaturated polycyclic cyclopentadienyl ligand such as indenyl, tetrahydroindenyl, fluorenyl or octahydrofluorenyl;

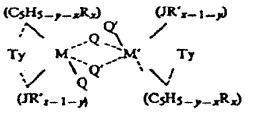
(JR'_{z-1-y}) is a heteroatom ligand in which J is an element with a coordination number of three from Group V A or an element with a coordination number of two from Group VIA of the Periodic Table of Elements, preferably nitrogen, phosphorus, oxygen or sulfur, and each R' is, independently a radical selected from the group consisting of C_1–C_{20} hydrocarbyl radicals, substituted C_1–C_{20} hydrocarbyl radicals wherein one or more hydrogen atoms is replaced by a halogen radical, an amido radical, a phosphido radical, an alkoxy radical, an alkylborido radical or any other radical containing a Lewis acidic or basic functionality and "z" is the coordination number of the element J;

Each Q may be independently any univalent anionic ligand such as halogen, hydride, or substituted or unsubstituted C_1–C_{20} hydrocarbyl, alkoxide, ary-

loxide, amide, arylamide, phosphide or arylphosphide, provided that where any Q is a hydrocarbyl such Q is different from $(C_5H_{5-y-x}R_x)$ or both Q together may be an alkylidene or a cyclometallated hydrocarbyl or any other divalent anionic chelating ligand;

"y" is 0 or 1 when w is greater than 0; y is 1 when w is 0; when "y" is 1, T is a covalent bridging group containing a Group IV A or V A element such as, but not limited to, a dialkyl, alkylaryl or diaryl silicon or germanium radical, alkyl or aryl phosphine or amine radical, or a hydrocarbyl radical such as methylene, ethylene and the like;

L is a Lewis base such as diethylether, tetraethylammonium chloride, tetrahydrofuran, dimethylaniline, aniline, trimethylphosphine, n-butylamine, and the like; and "w" is a number from 0 to 3; L can also be a second transition metal compound of the same type such that the two metal centers M and M' are bridged by Q and Q', wherein M' has the same meaning as M and Q' has the same meaning as Q. Such compounds are represented by the formula:



The activating component for the metallocene catalyst component can be an alumoxane component represented by the formulas: $(R^3—Al—O)_m$; $R^4(R^5—Al—O)_m—AlR^6_2$ or mixtures thereof, wherein R^3–R^6 are, independently, a univalent anionic ligand such as a C_1–C_5 alkyl group or halide and "m" is an integer ranging from 1 to about 50 and preferably is from about 13 to about 25. Alternatively, the activating component for the metallocene catalyst component can comprise a cation capable of irreversibly reacting with a substituent of the metallocene component and a bulky, non-coordinating anion capable of stabilizing the metal cation formed by the reaction between the irreversibly-reacting cation and the metallocene component substituent.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a plot of tan δ(loss modulus (E")/storage modulus (E'), 1 Hz, 10% torsion strain) versus temperature for the ethylene/5-ethyl-nonene-1 copolymer of Example 6.

FIG. 2 is a plot of tan δ(1 Hz, 10% torsion strain) versus temperature for the ethylene/5-ethyl-nonene-1 copolymer of Example 5.

FIG. 3 is a plot of log (storage modulus E') (+-+-+) and log (loss modulus E") (O-O-O) (1 Hz, 10% torsion strain) versus temperature for the ethylene/5-ethylnonene-1 copolymer of Example 5.

FIG. 4 is a plot of tan δ(1 Hz, 10% torsion strain) versus temperature for the ethylene/3-methylpentene-1 copolymer of Example 7.

FIG. 5 is a plot of log (storage modulus E') (+-+-+) and log (loss modulus E") (x-x-x) (10 Hz, 10% torsion strain) versus temperature for the ethylene/3-methylpentene-1 copolymer of Example 7.

FIG. 6 is a plot of tan δ(10 Hz, 10% torsion strain) versus temperature for the ethylene/3methylpentene copolymer of Example 8.

FIG. 7 is a plot of log (storage modulus E') (+-+-+) and log (loss modulus E") (x-x-x) (10 Hz, 10% torsion strain) versus temperature for the ethylene/3-methylpentene-1 copolymer of Example 8.

FIG. 8 is a plot of tan δ(10 Hz, 10% strain) versus temperature for the ethylene/5-ethylnonene-1 copolymer of Example 4.

FIG. 9 is a plot of log (storage modulus E') (+-+-+) and log (loss modulus E") (x-x-x) (10 Hz, 10% torsion strain) versus temperature for the ethylene/5-ethylnonene-1 copolymer of Example 4.

FIG. 10 is a plot comparing initial modulus (Y) versus comonomer content for the ethylene/3,5,5-trimethylhexene-1 copolymer of Example 3 and several ethylene/linear-α-olefin (C_4–C_{18}) copolymers having molecular weights between 80,000 and 125,000.

FIG. 11 is a plot of tan δ(1 Hz, 10% torsion strain) versus temperature for the ethylene/3,5,5-trimethylhexane copolymer of Example 3.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to copolymers of ethylene with branched α-olefins. The branched α-olefin comonomer is generally not copolymerizable at a competitive rate with ethylene when conventional Ziegler-Natta catalysts are used. The branched α-olefin generally has at least one alkyl branch adjacent to the ethylenic unsaturation of the comonomer, and thus, when copolymerized with ethylene, forms a copolymer having a backbone or main chain and pendant side chains randomly interspersed along the backbone, with alkyl branches on the side chain adjacent the backbone. The alkyl branches on the side chains are preferably closer to the polymer backbone than the terminal carbon in the side chain, or stated another way, the alkyl branch on the comonomer is preferably closer to the ethylenic unsaturation than the terminal carbon of the longest straight chain of the comonomer. The comonomer contains at least one alkyl branch, and more preferably has from 2 to 4 alkyl branches along the longest straight chain. Preferred branches have from 1 to 3 carbon atoms each, such as methyl, ethyl, propyl and isopropyl. The branched α-olefin comonomer must have at least 5 carbon atoms, more preferably has at least 6 carbon atoms, and most preferably has at least 8 carbon atoms. The branched comonomer is not, in general, restricted at any particular upper limit of size and C_{100} or larger could be used, although as a practical matter, the branched comonomer preferably contains less than about 30 carbon atoms, more preferably up to about 14, and especially up to about 12 carbon atoms.

In accordance with a preferred embodiment, the branched α-olefin comonomer has the formula:

$$H_2C{=}CH—CHR^aR^b$$

wherein R^a is C_{1-3} alkyl and R^b is C_{2+} aliphatic hydrocarbyl, and wherein the branched α-olefin has up to about 30 carbon atoms, preferably 6 to 14 carbon atoms and more preferably 8 to 12 carbon atoms.

Specific representative examples of suitable branched α-olefins include 3-methylpentene-1, 3-ethylpentene-1, 3,4-dimethylpentene-1, 4-methyl-3-ethylpentene-1, 3,4,4-trimethylpentene-1, 4,4-dimethyl-3-ethylpentene-

1, 3-methylhexene-1, 3-ethylhexene-1, 3-propylhexene-1, 3-isopropylhexene-1, 3,4-dimethylhexene-1, 3,5-dimethylhexene-1, 4-methyl-3-ethylhexene-1, 5-methyl-3-ethylhexene-1, 3-methyl-4-ethylhexene-1, 4-methyl-3-propylhexene-1, 5-methyl-3-propylhexene-1, 3,4-diethylhexene-1, 4-methyl-3-isopropylhexene-1, 5-methyl-3-isopropylhexene-1, 3,4,4-trimethylhexene-1, 3,4,5-trimethylhexene-1, 3,5,5-trimethylhexene-1, 4,4-dimethyl-3-ethylhexene-1, 4,5-dimethyl-3-ethylhexene-1, 5,5-dimethyl-3-ethylhexene-1, 5,5-dimethyl-3-ethylhexene-1, 3,4-dimethyl-4-ethylhexene-1, 3,5-dimethyl-4-ethylhexene-1, 4-methyl-3,4-diethylhexene-1, 5-methyl-3,4-diethylhexene-1, 3-methyl-4,4-diethylhexene-1, 3,4,4-triethylhexene-1, 4,4-dimethyl-3-propylhexene-1, 4,5-dimethyl-3-propylhexene-1, 5,5-dimethyl-3-propylhexene-1, 4,4-dimethyl-3-isopropylhexene-1, 4,5-dimethyl-3-isopropylhexene-1, 5,5-dimethyl-3-isopropylhexene-1, 3,4,4,5-tetramethylhexene-1, 3,4,5,5-tetramethylhexene-1, 4,4,5-trimethyl-3-ethylhexene-1, 4,5,5-trimethyl-3-ethylhexene-1, 3,4,5-trimethyl-4-ethylhexene-1, 3,5,5-trimethyl-4-ethylhexene-1, 4,5-dimethyl-3,4-diethylhexene-1, 5,5-dimethyl-3,4-diethylhexene-1, 3,5-dimethyl-4,4-diethylhexene-1, 5-methyl-3,4,4-triethylhexene-1, 5-ethylnonene-1 and the like.

The copolymer can further contain additional monomers, usually in relatively minor amounts, which do not substantially adversely affect the novel properties of the copolymers. Such termonomers include vinyl and vinylidene compounds, for example, generally linear α-olefins having from 3 to 100 carbon atoms, preferably from 3 to 20 carbon atoms, and particularly from 3 to 10 carbon atoms, such as propylene, 1-butene, isobutene, 1-pentene, 4-methylpentene-1, 1-hexene, 1-heptene, 1-octene, 1-nonene, and the like; dienes, such as 1,3-butadiene, 2-methyl-1,4-pentadiene, 1,4-hexadiene, 1,5-hexadiene and the like; vinyl aromatic and alicyclic monomers, such as styrene, alkyl-substituted styrene, cyclopentene, vinyl cyclohexane, vinyl cyclohexene phenyl butadiene, vinyl norbornene, and the like; and combinations thereof. Specifically contemplated are terpolymers of ethylene, the branched α-olefin and from about 2 to about 25 mole percent, preferably 2 to 10 mole percent, of a linear C_3 to C_8 α-olefin.

Preferably, the ethylene is interpolymerized with from about 0.5 to about 10 mole percent of the branched α-olefin, more preferably from about 1 to about 8 mole percent branched α-olefin, and especially from about 1 to about 5 mole percent branched α-olefin. In general, at an increased branched α-olefin content, the properties imparted by the branched α-olefin are more pronounced, e.g., toughness and strain hardening increase.

The polymers of the present invention are generally semicrystalline, but can be amorphous if more than about 12 mole percent of a linear C_3–C_8 α-olefin termonomer is incorporated. The ethylene/branched α-olefin copolymers generally have a density from about 0.85 to about 0.95 g/cm^3.

The polymers of the present invention have a surprisingly high molecular weight, preferably from about 30,000 to about 1,000,000 daltons or more, depending on the desired end-use application. As used herein, molecular weight refers to the weight average molecular weight (M_w), unless otherwise indicated. The unique characteristics of the ethylene/branched α-olefin copolymers are not generally observed at lower molecular weights where there is limited chain entanglement. Polymers having a molecular weight higher than this range, while theoretically possible, are difficult to prepare as a practical matter. Most commercially useful polymers, e.g. in film, fiber and molding applications, have M_w in the range of from about 80,000 to about 500,000 daltons.

The copolymers of the present invention have a narrow molecular weight distribution (MWD). This surprising fact is reflected in a low polydispersity, i.e. a ratio of M_w to number average molecular weight (M_n). The MWD (M_w/M_n) is generally in the range of from about 2 to about 4, even in the copolymers of very high molecular weight.

The copolymers of the present invention are substantially random and quite surprisingly should have a fairly uniform branched α-olefin distribution throughout the copolymer. This uniform composition can be reflected in a relatively high composition distribution breadth index (CDBI). As used herein, CDBI is defined as the percentage by weight of the copolymer molecules having a branched α-olefin comonomer content within 50 percent of the median molar comonomer content, i.e. ±50 percent of the median C_{10}–C_{100} olefin content. Homopolymers such as polyethylene, which do not contain a comonomer, thus have a CDBI of 100%. The CDBI of a copolymer is readily calculated from data obtained by techniques known in the art, such as, for example, temperature rising elution fractionation (TREF) as described in U.S. Ser. No. 151,350 or Wild et al., *J. Poly. Sci. Poly. Phys. Ed.*, vol. 20, p. 441 (1982). The ethylene/branched α-olefin copolymers herein generally should preferably have a CDBI on the order of about 50 percent or more, i.e. about 50 percent or more of the copolymer having a molar branched α-olefin comonomer content within 50 percent of the median comonomer content. In contrast, linear low density polyethylene prepared using conventional Ziegler-Natta catalyst has a CDBI on the order of 30 to 40 percent.

The present polymers comprise linear, comb-like molecules, wherein each of the side chains are of short, controlled branching which reflects the configuration of the branched α-olefin comonomer, as opposed to uncontrolled long chain branched polymers which are generally obtained by free-radically initiated, high pressure ethylene polymerization conventionally used to obtain low density polyethylene (LDPE). This derives from the use of a single-site coordination catalyst as opposed to a free radical catalyst. The olefin polymerizes in a predominantly head-to-tail fashion so that the polymer molecule has a generally linear main chain formed by polymerization at the carbon-carbon double bond, and a plurality of side chains of controlled length and branching corresponding to the aliphatic "tails" of the branched α-olefin.

The branched side chains in the present copolymers can have a profound effect on the crystalline behavior of the copolymers. For example, linear low density polyethylenes invariably have secondary phase transitions at from about −120° C. to about −90° C. (generally known as T_γ) and at from about −30° C. to about 20° C. (generally known as T_β). In semicrystalline LLDPE, these T_β and T_γ phenomena appear to be relatively unaffected, or only slightly affected, by the size of the C_3–C_8 linear α-olefin comonomer, as well as comonomer content. However, in the case of the present copolymers where the side chains are branched adjacent the generally linear polymer the T_β and T_γ are at least highly suppressed, and usually entirely eliminated, at the conventional LLDPE temperatures at

which they are normally observed. Instead, a secondary phase transition temperature (which could be an altered or shifted T_β and/or T_γ owing to the branching of the side chains) appears outside the conventional ranges. For example, in a copolymer containing a 3-methyl branched α-olefin such as 3,5,5-trimethylhexene-1, the T_γ disappears completely, the copolymer is essentially free of any phase transition at −30° C. to 20° C., and a secondary phase transition temperature is seen at about 70°–80° C. This copolymer is also observed to exhibit very high toughness and profound strain hardening. As the position of the branch is moved away from the backbone, say to the 5-position as in, for example, 5-ethylnonene copolymers, the T_β can be observed somewhat, although significantly suppressed, T_β is still not apparent in the −30° C. to 20° C. range, and a secondary phase transition is observed at about −35° C. to about −40° C. Also, the toughness is decreased and strain hardening much less pronounced than with the 3,5,5-trimethylhexene-1 copolymers.

The novel characteristics of the ethylene/branched α-olefin copolymers of the present invention, i.e. simultaneously high branched α-olefin content, high M_w, narrow MWD and a relatively good degree of random comonomer incorporation, impart a number of unique and, in some cases, rather surprising physical, rheological and other properties to the copolymers. As a consequence, the copolymers have a wide number of uses, particularly where high toughness is desirable.

For structural film applications, the generally semicrystalline copolymers preferably have a density from about 0.88 to about 0.93 g/cm^3. The present films have high strength and a high Young's modulus, but have exceptionally high toughness (generally taken as the integrated area under the stress-strain curve) at increasing strain or elongation, and excellent processability due to rheological properties.

The copolymer can be used in a monolayer film, e.g., a film comprised of a single layer of the copolymer without adjacent layers made of a different polymer. Alternatively, the copolymer can be used as one or more layers in a multi-layer film, e.g. as a structural and/or skin layer.

The film can include one or more conventional additives, e.g. antiblock (slip and/or antiblock) additives which may be added during the production of the copolymer or subsequently blended in. Such additives are well-known in the art and include, for example, silicas, silicates, diatomaceous earths, talcs and various lubricants. These additives are preferably utilized in amounts ranging from about 100 ppm to about 20,000 ppm, more preferably between about 500 ppm to about 10,000 ppm by weight based upon the weight of the copolymer. The copolymer can, if desired, also include one or more other well-known additives such as, for example, tackifiers, oils, viscosity modifiers, waxes, antioxidants, ultraviolet absorbers, antistatic agents, release agents, pigments, colorants, crosslinking agents, coupling agents, fillers, or the like; however, this again should not be considered a limitation of the present invention.

The film is produced from the ethylene copolymer by any one of a number of well-known extrusion or coextrusion techniques. As preferred examples, any of the blown or chill roll cast processes known in the art, with or without axial or biaxial orientation obtained by mechanically working the film, as by stretching, drawing, extrusion or the like, can be used.

As previously mentioned, the semicrystalline films of the present invention have properties making them especially well suited for use in a variety of applications. For example, these films can be used in stretch/cling films or made into other forms, such as a tape, by any one of a number of well-known cutting, slitting and/or rewinding operations. Physical properties including, but not limited to, tensile strength, tear strength and elongation can be adjusted over wide ranges by altering the copolymer properties and specifications, as well as additive packages, as appropriate to meet the requirements to a given structural, wrapping, bundling, taping or other application.

The copolymer of the present invention can also be blended with another polymer such as LLDPE, LDPE, HDPE, polypropylene or the like to improve the properties of the blend polymer. The copolymer of the present invention can, for example, be blended with another polymer to enhance the toughness of the blend polymer. The improvement in toughness generally depends on the toughness of the ethylene/branched α-olefin copolymer and the relative properties of the blend polymer, and can be balanced against the other properties of the blend.

The copolymer of the present invention is also contemplated to be used in fibers, particularly to make high tenacity fibers. It is contemplated that the copolymer can be formed into fiber using conventional fiber formation equipment, such as, for example, equipment commonly employed for melt spinning or to form melt blown fiber, or the like. In melt spinning, either monofilaments or fine denier fibers, a relatively high melt strength is generally required, and the copolymer preferably has a melt index (MI) of from about 10 to about 100 dg/min. (As used herein, MI is determined in accordance with ASTM D-1238, condition E (190° C./2.16 kg)). Typical melt spinning equipment includes a mixing extruder which feeds a spinning pump which supplies polymer to mechanical filters and a spinnerette with a plurality of extrusion holes therein. The filament or filaments formed from the spinnerette are taken up on a take up roll after the polyolefin has solidified to form fibers. If desired, the fiber may be subjected to further drawing or stretching, either heated or cold, and also to texturizing, such as, for example, air jet texturing, steam jet texturing, stuffing box treatment, cutting or crimping into staples, and the like.

In the case of melt blown fiber, the copolymer is generally fed to an extrusion die along with a high pressure source of air or other inert gas in such a fashion as to cause the melt to fragment at the die orifice and to be drawn by the passage of the air into short fiber which solidifies before it is deposited and taken up as a mat or web on a screen or roll which may be optionally heated. Melt blown fiber formation generally requires low melt viscosity material, and for this reason, it is desirable to use a copolymer in melt blown fiber formation which has a MI in the range from about 400 to about 1000 dg/min.

In a preferred embodiment, the copolymer of the present invention can be used to form nonwoven fabric. The fiber can be bonded using conventional techniques, such as, for example, needle punch, adhesive binder, binder fibers, hot embossed roll calendaring and the like.

It is also contemplated that the copolymer of the present invention can be used as one component of a biconstituent or bicomponent fiber wherein the fiber

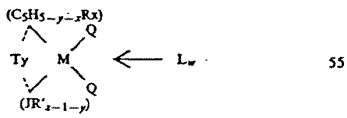
includes a second component in a side-by-side or sheath-core configuration. For example, the copolymer and LLDPE, LDPE, HDPE, polypropylene, polyethylene terephthalate (PET) or the like can be formed into a side-by-side or sheath-core bicomponent fiber by using equipment and techniques known for formation of bicomponent fibers. Alternatively, the copolymer of the present invention can be used as the dispersed or matrix phase in a biconstituent fiber.

The copolymer of the present invention has a wide number of uses because of its unique properties which can be varied to suit particular applications. The copolymer can have utility, for example, in film, fiber and molding applications, as previously mentioned; in applications requiring super tough polymers with the unique morphology of the present copolymer; in film surface modifications wherein the copolymer is added to or coated on, e.g. a conventional polyethylene, and the film surface can also be subjected to corona discharge or other surface treatment; in polymer processing as an additive to enhance the melt viscosity of the thermoplastic, elastomer or thermoplastic elastomer being processed; in elastomer applications, particularly vulcanizable elastomers wherein the copolymer includes a termonomer which imparts vulcanizability; in applications requiring a tough polymer; in laminates and coating applications as a hydrophobic, corrosion-resistant coating; in curable coatings, where the copolymer includes a termonomer which imparts vulcanizability through residual unsaturation (e.g. a diene termonomer), which are crosslinkable by the action of an acrylate crosslinking agent (e.g. 2-ethyl-2-hydroxymethyl-1,3-propanediol trimethacrylate), a silane coupling agent, irradiation (e.g. electron beam or gamma rays), or the like; in various molding applications, e.g. injection molding, rotational molding, blow molding and thermoforming; and the like.

CATALYST COMPONENT

The present invention relates to copolymers of ethylene and branched α-olefins made by a process comprising polymerizing branched α-olefins with ethylene in the presence of a catalyst providing a low ethylene:comonomer reactivity ratio, preferably a ratio less than about 75, more preferably less than about 50, and especially from about 25 to about 50. A preferred catalyst comprises an activated cyclopentadienyl-transition metal compound wherein the transition metal component is from Group IV B.

The Group IV B transition metal component of the catalyst system is represented by the general formula:



wherein:

M is Zr, Hf or Ti and is in its highest formal oxidation state (+4, d^0 complex);

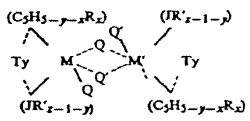
$(C_5H_{5-y-x}R_x)$ is a cyclopentadienyl ring which is substituted with from zero to five substituent groups R, "x" is 0, 1, 2, 3, 4 or 5 denoting the degree of substitution, and each substituent group R is, independently, a radical selected from a group consisting of C_1–C_{20} hydrocarbyl radicals, substituted C_1–C_{20} hydrocarbyl radicals wherein one or more hydrogen atoms is replaced by a halogen radical, an amido radical, a phosphido radical, an alkoxy radical or any other radical containing a Lewis acidic or basic functionality, C_1–C_{20} hydrocarbyl-substituted metalloid radicals wherein the metalloid is selected from the Group IV A of the Periodic Table of Elements, and halogen radicals, amido radicals, phosphido radicals, alkoxy radicals, alkylborido radicals or any other radical containing a Lewis acidic or basic functionality or $(C_5H_{5-y-x}R_x)$ is a cyclopentadienyl ring in which two adjacent R-groups are joined forming C_4–C_{20} ring to give a saturated or unsaturated polycyclic cyclopentadienyl ligand such as indenyl, tetrahydroindenyl, fluorenyl or octahydrofluorenyl;

(JR'_{z-1-y}) is a heteroatom ligand in which J is an element with a coordination number of three from Group V A or an element with a coordination number of two from Group VIA of the Periodic Table of Elements, preferably nitrogen, phosphorus, oxygen or sulfur with nitrogen being preferred, and each R' is, independently a radical selected from a group consisting of C_1–C_{20} hydrocarbyl radicals, substituted C_1–C_{20} hydrocarbyl radicals wherein one or more hydrogen atoms is replaced by a halogen radical, an amido radical, a phosphido radical, an alkoxy radical or any other radical containing a Lewis acidic or basic functionality, and "z" is the coordination number of the element J;

Each Q is, independently any univalent anionic ligand such as halogen, hydride, or substituted or unsubstituted C_1–C_{20} hydrocarbyl, alkoxide, aryloxide, amide, arylamide, phosphide or arylphosphide, provided that where any Q is a hydrocarbyl such Q is different from $(C_5H_{5-y-x}R_x)$ or both Q together may be an alkylidene or a cyclometallated hydrocarbyl or any other divalent anionic chelating ligand.

"y" is 0 or 1 when w is greater than 0; y is 1 when w is 0; when "y" is 1, T is a covalent bridging group containing a Group IV A or V A element such as, but not limited to, a dialkyl, alkylaryl or diaryl silicon or germanium radical, alkyl or aryl phosphine or amine radical, or a hydrocarbyl radical such as methylene, ethylene and the like.

L is a Lewis base such as diethylether, tetraethylammonium chloride, tetrahydrofuran, dimethylaniline, aniline, trimethylphosphine, n-butylamine, and the like; and "w" is a number from 0 to 3; L can also be a second transition metal compound of the same type such that the two metal centers M and M' are bridged by Q and Q', wherein M' has the same meaning as M and Q' has the same meaning as Q. Such compounds are represented by the formula:



A preferred activator is an alumoxane component which may be represented by the formulas: $(R^3—Al—O)_m$; $R^4(R^5—Al—O)_m—AlR^6_2$ or mixtures thereof,

wherein R^3–R^6 are, independently, a univalent anionic ligand such as a C_1—C_5 alkyl group or halide and "m" is an integer ranging from 1 to about 50 and preferably is from about 13 to about 25.

Examples of the T group which are suitable as a constituent group of the Group IV B transition metal component of the catalyst system are identified in Column 1 of Table 1 under the heading "T".

nent of the catalyst system are identified in Column 4 of Table 1 under the heading "Q".

Suitable hydrocarbyl and substituted hydrocarbyl radicals, which may be substituted as an R group for at least one hydrogen atom in the cyclopentadienyl ring, will contain from 1 to about 20 carbon atoms and include straight and branched alkyl radicals, cyclic hydrocarbon radicals, alkyl-substituted cyclic hydrocar-

TABLE 1

T (when y = 1)	$(C_5H_{5-y-x}R_x)$	(JR'_{z-1-y})	Q	M
dimethylsilyl	cyclopentadienyl	t-butylamido	hydride	zirconium
diethylsilyl	methylcyclopentadienyl	phenylamido	chloro	hafnium
di-n-propylsilyl	1,2-dimethylcyclopentadienyl	p-n-butylphenylamido	methyl	titanium
diisopropylsilyl	1,3-dimethylcyclopentadienyl	cyclohexylamido	ethyl	
di-n-butylsilyl	indenyl	perfluorophenylamido	phenyl	
di-t-butylsilyl	1,2-diethylcyclopentadienyl	n-butylamido	fluoro	
di-n-hexylsilyl	tetramethylcyclopentadienyl	methylamido	bromo	
methylphenylsilyl	ethylcyclopentadienyl	ethylamido	iodo	
ethylmethylsilyl	n-butylcyclopentadienyl	n-propylamido	n-propyl	
diphenylsilyl	cyclohexylmethylcyclopentadienyl	isopropylamido	isopropyl	
di(p-t-butylphenethylsilyl)	n-octylcyclopentadienyl	benzylamido	n-butyl	
n-hexylmethylsilyl	beta-phenylpropylcyclopentadienyl	t-butylphosphido	amyl	
cyclopentamethylenesilyl	tetrahydroindenyl	ethylphosphido	isoamyl	
cyclotetramethylenesilyl	propylcyclopentadienyl	phenylphosphido	hexyl	
cyclotrimethylenesilyl	t-butylcyclopentadienyl	cyclohexylphosphido	isobutyl	
dimethylgermanyl	benzylcyclopentadienyl	oxo (when y = 1)	heptyl	
diethylgermanyl	diphenylmethylcyclopentadienyl	sulfido (when y = 1)	octyl	
phenylamido	trimethylgermylcyclopentadienyl	methoxide (when y = 0)	nonyl	
t-butylamido	trimethylstannylcyclopentadienyl	ethoxide (when y = 0)	decyl	
methylamido	triethylplumbylcyclopentadienyl	methylthio (when y = 0)	cetyl	
t-butylphosphido	trifluoromethylcyclopentadienyl	ethylthio (when y = 0)	methoxy	
ethylphosphido	trimethylsilylcyclopentadienyl		ethoxy	
phenylphosphido	pentamethylcyclopentadienyl (when y = 0)		propoxy	
methylene	fluorenyl		butoxy	
dimethylmethylene	octahydrofluorenyl		phenoxy	
diethylmethylene	N,N-dimethylamidocyclopentadienyl		dimethylamido	
ethylene	dimethylphosphidocyclopentadienyl		diethylamido	
dimethylethylene	methoxycyclopentadienyl		methylethylamido	
dipropylethylene	(N,N-dimethylamidomethyl) cyclopentadienyl		diphenylamido	
propylene			diphenylphosphido	
dimethylpropylene			dicyclohexylphosphido	
diethylpropylene			dimethylphosphido	
1,1-dimethyl-3,3-dimethylpropylene			methylidene (both Q)	
tetramethyldisiloxane			ethylidene (both Q)	
1,1,4,4-tetramethyldisilylethylene			propylidene (both Q)	
			ethyleneglycoldianion (both Q)	

Exemplary hydrocarbyl radicals for the Q are methyl, ethyl, propyl, butyl, amyl, isoamyl, hexyl, isobutyl, heptyl, octyl, nonyl, decyl, cetyl, 2-ethylhexyl, phenyl and the like, with methyl being preferred. Exemplary halogen atoms for Q include chlorine, bromine, fluorine, and iodine, with chlorine being preferred. Exemplary alkoxides and aryloxides for Q are methoxide, phenoxide and substituted phenoxides such as 4-methylphenoxide. Exemplary amides for Q are dimethylamide, diethylamide, methylethylamide, di-t-butylamide, diisopropylamide and the like. Exemplary amides for Q are dimethylamide, diethylamide, methylethylamide, di-t-butylamide, diisopropylamide and the like. Exemplary aryl amides are diphenylamide and any other substituted phenyl amides. Exemplary phosphides for Q are diphenylphosphide, dicyclohexylphosphide, diethylphosphide, dimethylphosphide and the like. Exemplary alkyldiene radicals for both Q together are methylidene, ethylidene and propylidene. Examples of the Q group which are suitable as a constituent group or element of the Group IV B transition metal compo-

bon radicals, aromatic radicals, alkyl-substituted aromatic radicals, phosphido substituted hydrocarbon radicals, alkoxy substituted hydrocarbon radicals, alkylborido substituted radicals and cyclopentadienyl rings containing one or more fused saturated or unsaturated rings. Suitable organometallic radicals, which may be substituted as an R group for at least one hydrogen atom in the cyclopentadienyl ring include trimethylsilyl, triethylsilyl, ethyldimethylsilyl, methyldiethylsilyl, triphenylgermyl, trimethylgermyl and the like. Other suitable radicals that may be substituted for one or more hydrogen atom in the cyclopentadienyl ring include halogen radicals, amido radicals, phosphido radicals, alkoxy radicals, alkylborido radicals and the like. Examples of cyclopentadienyl ring groups $(C_5H_{5-y-x}R_x)$ which are suitable as a constituent group of the Group IV B transition metal component of the catalyst system are identified in Column 2 of Table 1 under the heading $(C_5H_{5-y-x}R_x)$.

Suitable hydrocarbyl and substituted hydrocarbyl radicals, which may be used as an R' group in the heteroatom J ligand group, will contain from 1 to about 20

carbon atoms and include straight and branched alkyl radicals, cyclic hydrocarbon radicals, alkyl-substituted cyclic hydrocarbon radicals, aromatic radicals, alkyl-substituted aromatic radicals, halogen radicals, amido radicals, phosphido radicals, alkylborido radicals and the like. Examples of heteroatom ligand groups (JR'_{z-1-y}) which are suitable as a constituent group of the Group IV B transition metal component of the catalyst system are identified in Column 3 of Table 1 under the heading (JR'z-1-y).

Table 1 depicts representative constituent moieties for the "Group IV B transition metal component", the list is for illustrative purposes only and should not be construed to be limiting in any way. A number of final components may be formed by permuting all possible combinations of the constituent moieties with each other. Illustrative compounds are: dimethylsilyltetramethylcyclopentadienyl-tert-butylamido zirconium dichloride, dimethylsilytetramethylcyclopentadienyl-tert-butylamido hafnium dichloride, dimethylsilyl-tert-butylcyclopentadienyl-tert-butylamido hafnium dichloride, dimethylsilyltrimethylsilylcyclopentadienyl-tert-butylamido zirconium dichloride, dimethylsilyltetramethylcyclopentadienylphenylamido zirconium dichloride, dimethylsilyltetramethylcyclopentadienyl-phenylamido hafnium dichloride, methylphenylsilyltetramethylcyclopentadienyl-tert-butylamido zirconium dichloride, methylphenylsilyltetramethylcyclopentadienyl-tert-butylamido hafnium dichloride, methylphenylsilyltetramethylcyclopentadienyl-tert-butylamido hafnium dimethyl, dimethylsilyltetramethylcyclopentadienyl-p-n-butylphenylamido zirconium dichloride, dimethylsilyltetramethylcyclopentadienyl-p-n-butylphenylamido hafnium dichloride.

As noted, titanium species of the Group IV B transition metal compound have generally been found to yield catalyst systems which in comparison to their zirconium or hafnium analogues, are of higher activity and α-olefin comonomer incorporating ability. Illustrative, but not limiting of the titanium species which exhibit such superior properties are methylphenylsilyltetramethylcyclopentadienyl-tert-butylamido titanium dichloride, dimethylsilyltetramethylcyclopentadienyl-p-n-butylphenylamido titanium dichloride, dimethylsilyltetramethylcyclopentadienyl-p-methoxyphenylamido titanium dichloride, dimethylsilyl-tert-butylcyclopentadienyl-2,5-di-tert-butylphenylamido titanium dichloride, dimethylsilylindenyl-tert-butylamido titanium dichloride, dimethylsilyltetramethylcyclopentadienylcyclohexylamido titanium dichloride, dimethylsilylfluorenylcyclohexylamido titanium dichloride, dimethylsilyltetramethylcyclopentadienylphenylamido titanium dichloride, dimethylsilyltetramethylcyclopentadienyl-tert-butylamido titanium dichloride, dimethylsilyltetramethylcyclopentadienylcyclododecylamido titanium dichloride, and the like.

For illustrative purposes, the above compounds and those permuted from Table 1 do not include the Lewis base ligand (L). The conditions under which complexes containing Lewis base ligands such as ether or those which form dimers is determined by the steric bulk of the ligands about the metal center. For example, the t-butyl group in $Me_2Si(Me_4C_5)(N\text{-}t\text{-}Bu)ZrCl_2$ has greater steric requirements than the phenyl group in $Me_2Si(Me_4C_5)$ (NPh) $ZrCl_2.Et_2O$ thereby not permitting ether coordination in the former compound. Similarly, due to the decreased steric bulk of the trimethylsilylcyclopentadienyl group in $[Me_2Si(Me_3SiC_5H_3)(N\text{-}t\text{-}Bu)ZrCl_2]_2$ versus that of the tetramethylcyclopentadienyl group in Me_2Si $(Me_4C_5)(N\text{-}t\text{-}Bu)ZrCl_2$, the former compound is dimeric and the latter is not.

Generally the bridged species of the Group IV B transition metal compound ("y" = 1) are preferred. These compounds can be prepared by reacting a cyclopentadienyl lithium compound with a dihalo compound whereupon a lithium halide salt is liberated and a monohalo substituent is covalently bound to the cyclopentadienyl compound. The substituted cyclopentadienyl reaction product is next reacted with a lithium salt of a phosphide, oxide, sulfide or amide (for the sake of illustrative purposes, a lithium amide) whereupon the halo element of the monohalo substituent group of the reaction product reacts to liberate a lithium halide salt and the amine moiety of the lithium amide salt is covalently bound to the substituent of the cyclopentadienyl reaction product. The resulting amine derivative of the cyclopentadienyl product is then reacted with an alkyl lithium reagent whereupon the labile hydrogen atoms, at the carbon atom of the cyclopentadienyl compound and at the nitrogen atom of the amine moiety covalently bound to the substituent group, react with the alkyl of the lithium alkyl reagent to liberate the alkane and produce a dilithium salt of the cyclopentadienyl compound. Thereafter the bridged species of the Group IV B transition metal compound is produced by reacting the dilithium salt cyclopentadienyl compound with a Group IV B transition metal preferably a Group IV B transition metal halide.

Unbridged species of the Group IV B transition metal compound can be prepared from the reaction of a cyclopentadienyl lithium compound and a lithium salt of an amine with a Group IV B transition metal halide.

Suitable, but not limiting, Group IV B transition metal compounds which may be utilized in the catalyst system of this invention include those bridged species ("y" = 1) wherein the T group bridge is a dialkyl, diaryl or alkylaryl silane, or methylene or ethylene. Exemplary of the more preferred species of bridged Group IV B transition metal compounds are dimethylsilyl, methylphenylsilyl, diethylsilyl, ethylphenylsilyl, diphenylsilyl, ethylene or methylene bridged compounds. Most preferred of the bridged species are dimethylsilyl, diethylsilyl and methylphenylsilyl bridged compounds.

Suitable Group IV B transition metal compounds which are illustrative of the unbridged ("y"=0) species which may be utilized in the catalyst systems of this invention are exemplified by pentamethylcyclopentadienyldi-t-butylphosphinodimethyl hafnium; pentamethylcyclopentadienyldi-t-butylphosphinomethylethyl hafnium; cyclopentadienyl-2-methylbutoxide dimethyl titanium.

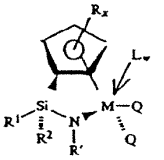
To illustrate members of the Group IV B transition metal component, select any combination of the species in Table 1. An example of a bridged species would be dimethylsilylcyclopentadienyl-t-butylamidodichloro zirconium; an example of an unbridged species would be cyclopentadienyldi-t-butylamidodichloro zirconium.

Those species of the Group IV B transition metal component wherein the metal is titanium have been found to impart beneficial properties to a catalyst system which are unexpected in view of what is known about the properties of bis(cyclopentadienyl) titanium compounds which are cocatalyzed by alumoxanes. Whereas titanocenes in their soluble form are generally unstable in the presence of aluminum alkyls, the monocyclopentadienyl titanium metal components of

this invention, particularly those wherein the heteroatom is nitrogen, generally exhibit greater stability in the presence of aluminum alkyls and higher catalyst activity rates.

Further, the titanium species of the Group IV B transition metal component catalyst of this invention generally exhibit higher catalyst activities and the production of polymers of greater molecular weight than catalyst systems prepared with the zirconium or hafnium species of the Group IV B transition metal component.

Generally, wherein it is desired to produce an α-olefin copolymer which incorporates a high content of α-olefin, while maintaining high molecular weight polymer the species of Group IV B transition metal compound preferred is one of titanium. The most preferred species of titanium metal compounds are represented by the formula:



wherein Q, L, R', R, "x" and "w" are as previously defined and R^1 and R^2 are each independently a C_1 to C_{20} hydrocarbyl radicals, substituted C_1 and C_{20} hydrocarbyl radicals wherein one or more hydrogen atom is replaced by a halogen atom; R^1 and R^2 may also be joined forming a C_3 to C_{20} ring which incorporates the silicon bridge. Suitable hydrocarbyl and substituted hydrocarbyl radicals which may be used as an R' group have been described previously. Preferred R' groups include those bearing primary carbons bonded directly to the nitrogen atom such as methyl; ethyl, n-propyl, n-butyl, n-hexyl, n-octyl, n-decyl, n-dodecyl, n-tetradecyl, n-hexadecyl, n-octadecyl, benzyl and the like, and those bearing secondary carbons bonded directly to the nitrogen atom such as 2-propyl, 2-butyl, 3-pentyl, 2-heptyl, 2-octyl, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclododecyl, 2-norbornyl and the like.

Also, the most preferred cyclopentadienyl ring is tetramethylcyclopentadiene (R=Me and x=4).

The alumoxane component of the catalyst system is an oligomeric compound which may be represented by the general formula $(R^3—Al—O)_m$ which is a cyclic compound, or may be $R^4(R^5—Al—O)_m—AlR^6_2$ which is a linear compound. An alumoxane is generally a mixture of both the linear and cyclic compounds. In the general alumoxane formula R^3, R^4, R^5, and R^6 are, independently a univalent anionic ligand such as a C_1–C_5 alkyl radical, for example, methyl, ethyl, propyl, butyl, pentyl or halide and "m" is an integer from 1 to abut 50. Most preferably, R^3, R^4, R^5 and R^6 are each methyl and "m" is at least 4. When an alkyl aluminum halide is employed in the preparation of alumoxane, one or more of R^{3-6} could be halide.

As is now well known, alumoxanes can be prepared by various procedures. For example, a trialkyl aluminum may be reacted with water, in the form of a moist inert organic solvent; or the trialkyl aluminum may be contacted with a hydrated salt, such as hydrated copper sulfate suspended in an inert organic solvent, to yield an alumoxane. Generally, however prepared, the reaction of a trialkyl aluminum with a limited amount of water yields a mixture of both the linear and cyclic species of alumoxane.

Suitable alumoxanes which may be utilized in the catalyst systems of this invention are those prepared by the hydrolysis of a alkylaluminum reagent; such as trimethylaluminum, triethyaluminum, tripropylaluminum, triisobutylaluminum, dimethylaluminumchloride, diisobutylaluminumchloride, diethylaluminumchloride, and the like. Mixtures of different alkyl aluminum reagents in preparing an alumoxane may also be used. The most preferred alumoxane for use is methylalumoxane (MAO), particularly methylalumoxanes having a reported average degree of oligomerization of from about 4 to about 25 ("m"=4 to 25) with a range of 13 to 25 being most preferred.

As an alternative to the alumoxane activation, the metallocene component can be ionically activated using the procedures and techniques set forth in Turner et al., U.S. Ser. No. 133,052, filed Dec. 21, 1987 now abandoned; Turner et al., U.S. Ser. No. 133,480, filed Dec. 22, 1987 now abandoned; Canich et al., U.S. Ser. No 542,236, filed Jun. 22, 1990; and EP Publication Nos. 277,004; 418,044; and 426,637; all of which are hereby incorporated by reference. Briefly, for ionic activation, the metallocene has at least one substituent capable of reacting with a proton. The metallocene is activated by reaction with a proton-donating cation and a bulky, non-coordinating anion which stabilizes the metal cation formed by the metallocene-proton reaction. Typically, Q in the above formula is hydrocarbyl, the cation is trialkylammonium, for example, and the anion is tetraperfluorophenyl borate, for example.

CATALYST SYSTEMS

The catalyst systems employed in the method of the invention comprise a complex formed upon admixture of the Group IV B transition metal component with an activating component. The catalyst system may be prepared by addition of the requisite Group IV B transition metal and alumoxane components, or a previously cationically activated Group IV B transition metal component, to an inert solvent in which olefin polymerization can be carried out by a solution, slurry or bulk phase polymerization procedure.

The catalyst system may be conveniently prepared by placing the selected Group IV B transition metal component and the selected alumoxane or ionic activating component(s), in any order of addition, in an alkane or aromatic hydrocarbon solvent, preferably one which is also suitable for service as a polymerization diluent. Where the hydrocarbon solvent utilized is also suitable for use as a polymerization diluent, the catalyst system may be prepared in situ in the polymerization reactor. Alternatively, the catalyst system may be separately prepared, in concentrated form, and added to the polymerization diluent in a reactor. Or, if desired, the components of the catalyst system may be prepared as separate solutions and added to the polymerization diluent in a reactor, in appropriate ratios, as is suitable for a continuous liquid polymerization reaction procedure. Alkane and aromatic hydrocarbons suitable as solvents for formation of the catalyst system and also as a polymerization diluent are exemplified by, but are not necessarily limited to, straight and branched chain hydrocarbons such as isobutane, butane, pentane, hexane, heptane, octane and the like, cyclic and alicyclic hydrocar-

bons such as cyclohexane, cycloheptane, methylcyclohexane, methylcycloheptane and the like, and aromatic and alkyl-substituted aromatic compounds such as benzene, toluene, xylene and the like. Suitable solvents also include liquid olefins which may act as monomers or comonomers, including ethylene, propylene, 1-butene, 1-hexene and the like, particularly when the catalyst components are prepared as separate solutions, in which case prepared catalyst is added to the monomer mixture in the reactor and polymerization is effected essentially in neat monomer.

In accordance with this invention optimum results are generally obtained wherein the Group IV B transition metal compound is present in the polymerization diluent in a concentration of preferably from abut 0.00001 to about 10.0 millimoles/liter of diluent and the alumoxane component, when used, is present in an amount to provide a molar aluminum to transition metal ratio of from about 0.5:1 to about 20,000:1. Sufficient solvent is normally used so as to provide adequate heat transfer away from the catalyst components during reaction and to permit good mixing.

The catalyst system ingredients, that is, the Group IV B transition metal, the alumoxane and/or ionic activators, and polymerization diluent, can be added to the reaction vessel rapidly or slowly. The temperature maintained during the contact of the catalyst components can vary widely, such as, for example, from −100° C. to 300° C. Greater or lesser temperatures can also be employed. Preferably, during formation of the catalyst system, the reaction is maintained within a temperature of from about 25° C. to 100° C., most preferably about 25° C.

At all times, the individual catalyst system components, as well as the catalyst system once formed, are protected from oxygen and moisture. Therefore, the reactions are performed in an oxygen and moisture free atmosphere and, where the catalyst system is recovered separately it is recovered in an oxygen and moisture free atmosphere. Preferably, therefore, the reactions are performed in the presence of an inert dry gas such as, for example, helium or nitrogen. Inhibitor-free monomers are preferred. Thus, any monomer inhibitors can usually be removed from the monomer just prior to polymerization.

POLYMERIZATION PROCESS

In a preferred embodiment of the process of this invention the catalyst system is utilized in the liquid phase (slurry, solution, suspension or bulk phase or combination thereof), high pressure fluid phase or gas phase copolymerization of ethylene and the branched α-olefin monomer. These processes may be employed singularly or in series. The liquid phase process comprises the steps of contacting a branched α-olefin monomer and ethylene with the catalyst system in a suitable polymerization diluent and reacting said monomers in the presence of said catalyst system for a time and at a temperature sufficient to produce a copolymer of high molecular weight. Conditions most preferred for the copolymerization of ethylene are those wherein ethylene is submitted to the reaction zone at pressures of from about 0.019 psia to about 50,000 psia and the reaction temperature is maintained at from about −100° C. to about 300° C. The aluminum to transition metal molar ratio is preferably from about 1:1 to 18,000 to 1. A more preferable range would be 1:1 to 2000:1. The reaction time can be from 10 seconds to 48 hours, or more, preferably from about 10 seconds to about 4 hours.

Without limiting in any way the scope of the invention, one means for carrying out the process of the present invention for production of a copolymer is as follows: in a stirred-tank reactor liquid α-olefin monomer is introduced, such as 3,5,5-trimethylhexene-1. The catalyst system is introduced via nozzles in either the vapor or liquid phase. Feed ethylene gas is introduced either into the vapor phase of the reactor, or sparged into the liquid phase as is well known in the art. The reactor contains a liquid phase composed substantially of liquid α-olefin comonomer, together with dissolved ethylene gas, and a vapor phase containing vapors of all monomers. The reactor temperature and pressure may be controlled via reflux of vaporizing α-olefin monomer (autorefrigeration), as well as by cooling coils, jackets etc. The polymerization rate is generally controlled by the concentration of catalyst. The ethylene content of the polymer product is determined by the ratio of ethylene to α-olefin comonomer in the reactor, which is controlled by manipulating the relative feed rates of these components to the reactor.

In accordance with another preferred embodiment, the copolymer is prepared by a high pressure process. The high pressure polymerization is completed at a temperature from abut 120° C. to about 350° C., preferably from about 120° C. to about 250° C., and at a pressure of from about 500 bar to about 3500 bar, preferably from about 800 bar to about 2000 bar, in a tubular or stirred autoclave reactor. After polymerization and catalyst deactivation, the product copolymer can be recovered using conventional equipment for polymer recovery, such as, for example, a series of high and low pressure separators wherein unreacted ethylene and branched α-olefin comonomer are flashed off for recycle to the reactor and the polymer obtained extruded in an underwater pelletizer. An advantage of the high pressure process is that the flashing off of the comonomer is relatively effective, particularly at the ratio of comonomer:ethylene used in the copolymerization to obtain the desired higher comonomer incorporation in the copolymer, in distinction from the available prior art catalyst which required a much higher, generally impractical ratio of comonomer:ethylene to facilitate such a separation and recycle (and it was still generally not possible to obtain the high M_w, narrow MWD copolymers of the present invention). Pigments, antioxidants and other known additives, as are known in the art, can be added to the polymer, generally subsequent to the polymerization step.

As before noted, a catalyst system wherein the Group IV B transition metal component is a titanium species has the ability to incorporate relatively high contents of branched α-olefin comonomers. Accordingly, the selection of the Group IV B transition metal component is another parameter which may be utilized as a control over the ethylene content of a copolymer within a reasonable ratio of ethylene to branched α-olefin comonomer.

EXAMPLES

CATALYST PREPARATION EXAMPLE 1

All catalyst preparation and polymerization procedures were performed under an inert atmosphere of helium or nitrogen. Solvent choices were often optional, for example, in most cases either pentane or

petroleum ether could be interchanged. The choice between tetrahydrofuran (THF) and diethyl ether was a bit more restricted, but in several reactions, either could be used. The lithiated amides were prepared from the corresponding amines and either n-butyllithium (n-BuLi) or methyllithium (MeLi). Tetramethylcyclopentadienyllithium (C_5Me_4HLi) was prepared according to the procedures of C. M. Fendrick et al., *Organometallics*, 1984, 3, 819 and F. H. Kohler and K. H. Doll, Z *Naturforsch.* 1982, 376, 144. Other lithiated substituted cyclopentadienyl compounds were generally prepared from the corresponding cyclopentadienyl ligand and n-BuLi or MeLi, or by reaction of MeLi with the proper fulvene. $TiCl_4$ was typically used in its etherate form. The etherate was generally prepared by simply adding $TiCl_4$ to ether, filtering off the solid product and vacuum drying. $TiCl_4$, $ZrCl_4$, $HfCl_4$, amines, silanes, substituted and unsubstituted cyclopentadienyl compounds or precursors, and lithium reagents were purchased from Aldrich Chemical Company or Petrarch Systems. Methylalumoxane was supplied by either Schering or Ethyl Corporation.

C_5Me_4HLi (10.0 g, 0.078 mol) was slowly added to Me_2SiC_2 (11.5 ml, 0.095 mol, in 225 ml of THF solution). The solution was stirred for 1 hour to assure a complete reaction. The solvent was then removed in vacuo. Pentane was added to precipitate the LiCl. The mixture was filtered through diatomaceous earth and the solvent was removed from the filtrate in vacuo. Tetramethylcyclopentadienyldimethylchlorosilane, $(C_5Me_4H)SiMe_2Cl$, (15.34 g, 0.071 mol) was recovered as a pale yellow liquid.

$(C_5Me_4H)SiMe_2Cl$ (8.0 g, 0.037 mol) was slowly added to a suspension of lithium cyclododecylamine ($LiHNCl_{12}H_{23}$) (7.0 g, 0.037 mol, ~80 ml THF). The mixture was stirred overnight. The THF was then removed by vacuum to a cold trap held at −196° C. A mixture of petroleum ether and toluene was added to precipitate the LiCl. The mixture was filtered through diatomaceous earth. The solvent was removed from the filtrate. Tetramethylcyclopentadienyl amidocyclododecyldimethylsilane, $Me_2Si(C_5Me_4H)(NHC_{12}H_{23})$, (11.8 g, 0.033 mol) was isolated as a pale yellow liquid.

$Me_2Si(C_5ME_4H)(NHC_{12}H_{23})$ (11.9 g, 0.033 mol) was diluted with ~150 ml of ether. MeLi (1.4M, 47 ml, 0.066 mol) was added slowly, and the mixture was stirred for 2 hours. The ether was reduced in volume by evaporation. The product was filtered off. The product $[Me_2Si(C_5Me_4)(NC_{12}H_{23})]Li_2$, was washed with several small portions of ether, then vacuum dried to yield 11.1 g (0.030 mol).

$[Me_2Si(C_5Me_4)(NC_{12}H_{23})]Li_2$ (3.0 g, 0.008 mol) was suspended in cold ether. $TiCl_4.2Et_2O$ (2.7 g, 0.008 mol) was slowly added and the resulting mixture was stirred overnight. The ether was removed via a vacuum to a cold trap held at −196° C. Methylene chloride was added to precipitate the LiCl. The mixture was filtered through diatomaceous earth. The solvent was significantly reduced in volume by evaporation and petroleum ether was added to precipitate the product. This mixture was refrigerated prior to filtration in order to maximize precipitation. The solid collected was recrystallized from methylene chloride and $Me_2Si(C_5Me_4)(NC_{12}H_{23})TiCl_2$ was isolated (1.0 g, 2.1 mmol).

POLYMERIZATION EXAMPLES

Polymerization was done in a 1-liter autoclave reactor equipped with a paddle stirrer, an external water jacket for temperature control, a regulated supply of dry nitrogen, ethylene, propylene, 1-butene and hexane, and a septum inlet for introduction of other solvents or comonomers, transition metal compound and alumoxane solutions. The reactor was dried and degassed thoroughly prior to use. A typical run consisted of injecting a quantity of freshly distilled solvent (typically toluene), the comonomer and 6.0 ml of 1.0M methylalumoxane (MAO) into the reactor. The reactor was then heated to 80° C. and the transition metal compound solution and the ethylene at a pressure of 4.08 atm were introduced into the system. The polymerization reaction was limited to 30 minutes. The reaction was ceased by rapidly cooling and venting the system, and the resulting polymer was recovered by evaporating the solvent under a stream of nitrogen.

Remaining process run conditions are given in Table 2 including the amount of transition metal catalyst solution (TMC) used, the amount of methylalumoxane solution used, the Al/Ti molar ratio, the amount of toluene and comonomer used, the polymerization temperature, polymer yield, catalyst efficiencies in terms of kg polymer per mole catalyst-atm-hr and kg polymer per mole catalyst-hr and catalyst reactivity ratio.

For example (see Example 2 in Tables 2 and 3), 390 ml of toluene, 6 ml of 1M MAO and 10 ml of 3,5,5-trimethylhexene-1 were added to the reactor described above. The reactor was heated to 80° C. prior to introducing 1.0 ml of the catalyst stock solution made by dissolving 13.5 mg of the transition metal compound in 10 ml of toluene. The reactor was then immediately pressurized with 4.08 atm of ethylene. The polymerization reaction was limited to 30 minutes after which time the reaction was ceased by rapidly cooling and venting the system. The resulting polymer (40 g) was recovered by solvent evaporation and drying in a vacuum at 30°–60° C., typically 50°–60° C. for 48 hours to 5 days. Catalyst productivity was calculated at 6,950 (kg polymer/mol TMC·atm-hr) and 28,354 (kg polymer/mol TMC·hr). Polymer characteristics include a GPC/DRI PE molecular weight of 103,500 daltons, a molecular weight distribution of 3.6, 2.5 mole percent incorporated 3,5,5-trimethylhexene-1 giving a catalyst reactivity ratio of 24.6 ethylene to 3,5,5-trimethylhexene-1, a polymer density of 0.930 g/ml, and a melting point of 114° C.

TABLE 2

Ex.	Olefin Used	TMC Stock (mg/10 ml)	TMC Stock Used (ml)	TMC Stock Used (mg)	Al/M	Toluene (ml)	Olefin (ml)	Polymer Yield (g)	Productivity (kg P/mol TMC · atm · hr)	Productivity (kg P/mol TMC · hr)
2	3,5,5-trimethyl-hexene-1	13.5	1	1.35	2127	390	10	40	6950	28,354
3	3,5,5-trimethyl-	13.5	1	1.35	2127	380	20	24	4170	17,013

TABLE 2-continued

Ex.	Olefin Used	TMC Stock (mg/10 ml)	TMC Stock Used (ml)	TMC Stock Used (mg)	Al/M	Toluene (ml)	Olefin (ml)	Polymer Yield (g)	Productivity (kg P/mol TMC - atm - hr)	Productivity (kg P/mol TMC - hr)
	hexene-1									
4	5-ethyl-nonene-1	13	1	1.3	2208	395	5	23	4150	16,931
5	5-ethyl-nonene-1	13	1	1.3	2208	390	10	35	6225	25,396
6	5-ethyl-nonene-1	13	1	1.3	2208	380	20	36	6495	26,500
7	3-methyl-pentene-1	13	1	1.3	2208	390	10	35	6315	25,764
8	3-methyl-pentene-1	13	1	1.3	2208	380	20	24	4430	17,667

Resulting polymer characteristics are given in Table 3 including weight average molecular weight, molecular weight distribution, comonomer concentration, polymer density, melting point and secondary phase transition temperature (T_2).

peratures. Isochronal experiments were conducted at a frequency of 10 rad/s and 1 Hz on the SYSTEM IV and the DMTA rheometer, respectively. The storage modulus (E') is determined according to a Polymer Laboratories, Inc. dynamic mechanical thermal analyzer

TABLE 3

Ex.	Olefin Used	MW[a] (daltons)	MWD	mol % α Olefin	r_1	Polymer Density (g/ml)	T_m (°C.)	T_2[b] (°C.)	Modulus (kpsi)	Strain to Break (%)
2	3,5,5-trimethyl-hexene-1	103,500	3.6	2.5	24.6	0.930	114	50	>28	577
3	3,5,5-trimethyl-hexene-1	84,100	2.5	2.1	58.7	0.931	105	62	—	—
4	5-ethyl-nonene-1	114,400/151,000	2.3/2.8	3.8	6.8	0.928	114	−20; 55[c]	11.65	511
5	5-ethyl-nonene-1	201,000/173,000	2.6/3.1	6.0	8.4	0.920	—	−38; 42[c]	5.08	648
6	5-ethyl-nonene-1	113,400/181,000	2.4/2.7	9.0	10.9	0.889	96	−38; 40[c]	0.564	549
7	3-methyl-pentene-1	62,000	2.1	1.8	46.8	0.933	112	−17; 50[c]	28.07	572
8	3-methyl-pentene-1	51,000	2.8	4.2	39.2	0.924	99/127	−10; 48[c]	10.87	538

[a]First (or only, where no second figure appears) figure from GPC-Differential Refractive Index (DRI) calibrated to polyethylene universal standards; second figure from GPC-viscometer.
[b]Secondary phase transition temperature.
[c]From tan δ data.

The gel permeation chromatography (GPC) data for the present copolymer is very unusual in that the M_w as determined by GPC with differential refractive index (DRI) measurement yielded artificially low results as compared to the more accurate (but more difficult) viscosity (VIS) measurements. This is apparently due to the size of the comonomer side chain distributed throughout the polymer backbone.

The stress-strain properties of the Example 2 copolymer as reported in Table 3 indicate that the copolymers are extremely tough materials. The modulus of elasticity is very high, and the strain to break is unusual in that it is also high. See FIG. 10 When the material of Example 2 was evaluated in a conventional Instron tensile testing machine, it exhibited unusual strain hardening to the extreme point where the material stiffened and pulled out of the specimen holder before any break could be observed.

Measurements of viscoelastic properties were performed using a PHEOMETRICS SYSTEM IV rheometer or a POLYMER LABORATORIES DMTA rheometer. Isothermal measurements were performed on the SYSTEM IV rheometer over a wide range of temperatures. Isochronal experiments were conducted at a frequency of 10 rad/s and 1 Hz on the SYSTEM IV and the DMTA rheometer, respectively. The storage modulus (E') is determined according to a Polymer Laboratories, Inc. dynamic mechanical thermal analyzer (DMTA) procedures at ambient temperature. The specimen is cast in a Teflon-coated mold, and 12 mm diameter disks are die cut for DMTA testing. E' is understood in the art to be a measurement of the elastic or storage modulus (stress/strain) measured in phase with sinusoidal torsional displacement of the material.

The unusual characteristics of the present copolymers are also seen in the storage modulus (E'), loss modulus (E") and tan δ data developed for Examples 3–8 and presented in FIGS. 1–9 and 11 and Table 4. A comparison of the tan δ data in FIGS. 1, 2, 4, 8 and 11 indicates an effect of the positioning of the branches on the side chains with respect to the copolymer backbone. The secondary phase transition temperatures (T_2) of the ethylene/5-ethyl-1-nonene copolymer (relatively distant ethyl branch) are generally lower than the conventional LLDPE T_β. However, steric hindrances created by methyl branches right up against the backbone of the copolymer are thought to be the reason for the appearance of the secondary phase transition temperatures at about 50° C. in the 3-methylpentene copolymer (FIGS. 4 and 6) and at about 70° C. in the 3,5,5-trimethylhexene-1 copolymer (FIG. 11).

TABLE 4

POLY-MER	STRAIN (%)	TEMP (°C.)		FREQUENCY (rad/sec) 0.10	0.20	0.40	1.00	2.51	10.0	39.8	100	200	398
Ex. 5	10	25° C.	G' (dyne × 10^5/cm^2)	27.8	33.3	38.6	45.6	52.0	60.0	65.7	70.5	73.3	75.9
			G" (dyne × 10^5/cm^2)	12.2	12.0	12.1	11.7	11.0	9.66	8.73	9.15	10.5	12.9
			G"/G'	0.44	0.36	0.31	0.26	0.21	0.16	0.13	0.13	0.14	0.17
	10	45° C.	G'	11.4	15.3	19.6	26.2	33.1	43.4	32.7	58.0	61.0	63.6
			G"	8.21	9.16	10.3	11.4	11.9	11.7	10.6	8.73	9.28	9.00
			G"/G'	0.72	0.60	0.52	0.43	0.36	0.27	0.20	0.17	0.15	0.14
	10	85° C.	G'	4.44	6.70	9.46	14.1	19.7	29.4	39.5	46.0	50.3	54.0
			G"	4.42	5.70	7.02	8.71	10.1	11.6	11.5	11.0	10.5	9.96
			G"/G'	0.99	0.85	0.74	0.62	0.50	0.39	0.29	0.29	0.21	0.18
	10	95° C.	G'	1.12	1.90	3.06	5.33	8.57	15.3	23.9	30.1	34.8	39.1
			G"	1.74	2.49	3.42	4.89	6.51	8.84	10.4	10.9	10.9	10.7
			G"/G'	1.56	1.31	1.12	0.92	0.76	0.58	0.44	0.36	0.31	0.27
	10	120° C.	G'	0.383	0.675	1.23	2.48	4.54	9.42	16.4	21.9	26.2	30.5
			G"	0.829	1.27	1.90	3.03	4.49	6.94	9.12	9.12	10.5	10.7
			G"/G'	2.16	1.88	1.55	1.22	0.99	0.74	0.56	0.46	0.40	0.35

Many modifications and variations besides the embodiments specifically mentioned may be made in the compositions and methods described herein without substantially departing from the concept of the present invention. Accordingly, it should be clearly understood that the form of the invention described herein is exemplary only, and is not intended as a limitation of the scope thereof.

What is claimed is:

1. A copolymer comprising ethylene and at least about 2.5 to less than 50 mole percent of an α-olefin comonomer having at least two C_1 to C_3 branches and said copolymer having a composition distribution breadth index within the range of 50% to less than 100%.

2. The copolymer of claim 1 exhibiting a strain hardening characteristic.

3. The copolymer of claim 1 having suppressed phase transitions in the temperature ranges of from about −120° C. to about −90° C. and from about −30° C. to about 20° C.

4. The copolymer of claim 3 having a secondary phase transition temperature in the range of from about −50° C. up to about −30° C.

5. The copolymer of claim 3 having a secondary phase transition temperature in the range of from above about 20° C. to about 80° C.

6. The copolymer of claim 1 comprising at least about 3.0 mole % comonomer.

7. The copolymer of claim 1, wherein the comonomer having two or more branches has at least one alkyl branch adjacent to the α-olefinic unsaturation thereof.

8. The copolymer of claim 7, wherein the alkyl branch has from 1 to 3 carbon atoms and is closer to the α-olefinic unsaturation than a terminal carbon of the longest straight chain of the comonomer.

9. The copolymer of claim 7, wherein the comonomer has from 6 to 14 carbon atoms.

10. The copolymer of claim 1, wherein said branched alpha-olefin has two, three or four alkyl branches and from 6 to 14 carbon atoms.

11. A copolymer of ethylene and from about 0.5 to about 10 mole percent of a branched C_6 to C_{30} α-olefin comonomer having three or four branches wherein at least one of the branches is a C_3, C_4 or c_5 lower alkyl and said copolymer having a composition distribution breadth index of within the range of 50% to less than 100%.

12. The copolymer of claim 11, comprising from about 3.0 to about 8 mole percent of the branched α-olefin.

13. The copolymer of claim 1 or 11, further comprising from about 2 to about 25 mole percent of a straight-chained α-olefin.

14. The copolymer of claim 13, wherein the alpha olefin has 3 to 8 carbon atoms and is present at about 2.5 to about 10 mole percent.

15. The copolymer of claim 1 or 11, wherein the comonomer has from 6 to 14 carbon atoms and the branching substituents are selected from the group consisting of methyl, ethyl, propyl and isopropyl.

16. The copolymer of claim 1, wherein the comonomer is selected from the group consisting of 3,4-dimethylpentene-1, 4-methyl-3-ethylpentene-1, and 4,4-dimethyl-3-ethylpentene-1.

17. The copolymer of claim 1, wherein the comonomer is selected from the group consisting of 3,4-dimethylhexene-1, 3,5-dimethylhexene-1, 4-methyl-3-ethylhexene-1, 5-methyl-3-ethylhexene-1, 3-methyl-4-ethylhexene-1, 4-methyl-3-propylhexene-1, 5-methyl-3-propylhexene-1, 3,4-diethylhexene-1, 4-methyl-3-isopropylhexene-1, and 5-methyl-3-isopropylhexene-1.

18. The copolymer of claim 1 or 11, wherein the comonomer is selected from the group consisting of 3,4,4-trimethylhexene-1, 3,4,5-trimethylhexene-1, 3,5,5-trimethylhexene-1, 4,4-dimethyl-3-ethylhexene-1, 4,5-dimethyl-3-ethylhexene-1, 5,5-dimethyl-3-ethylhexene-1, 3,4-dimethyl-4-ethylhexene-1, 3,5-dimethyl-4-ethylhexene-1, 4-methyl-3,4-diethylhexene-1, 5-methyl-3,4-diethylhexene-1, 3-methyl-4,4-diethylhexene-1, 3,4,4-triethylhexene-1, 4,4-dimethyl-3-propylhexene-1, 4,5-dimethyl-3-propylhexene-1, 5,5-dimethyl-3-propylhexene-1, 4,4-dimethyl-3-isopropylhexene-1, 4,4-dimethyl-3-ethylpentene-1 and 5,5-dimethyl-3-isopropylhexene-1.

19. The copolymer of claim 1 or 11, wherein the comonomer is selected from the group consisting of 3,4,4,5-tetramethylhexene-1, 3,4,5,5-tetramethylhexene-1, 4,4,5-trimethyl-3-ethylhexene-1, 4,5,5-trimethyl-3-ethylhexene-1, 3,4,5-trimethyl-4-ethylhexene-1, 3,5,5-trimethyl-4-ethylhexene-1, 4,5-dimethyl-3,4-diethylhexene-1, 5,5-dimethyl-3,4-diethylhexene-1, 3,5-dimethyl-4,4-diethylhexene-1, and 5-methyl-3,4,4-triethylhexene-1.

20. The copolymer of claim 1 or 11, wherein the molecular weight is from about 80,000 to about 500,000 daltons.

21. A copolymer of ethylene and 3,5,5-trimethylhexene-1 wherein the content of 3,5,5-trimethylhexene-1 is at least 2.5 to less than 50 mole percent, and said copolymer has a composition distribution breadth index of within the range of 50% to less than 100%.

22. A film comprising the copolymer of claim 1 or 11.

23. A fiber comprising the copolymer of claim 1 or 11.

24. A molded article comprising the copolymer of claim 1 or 11.

25. A film comprising the copolymer of claim 21.

26. A fiber comprising the copolymer of claim 21.

27. A molded article comprising the copolymer of claim 21.

28. The copolymer of claim 1 or 11 wherein the copolymer has a M_w of from about 30,000 to about 1,000,000.

29. The copolymer of claim 1 or 11 wherein the copolymer has a M_w/M_n of from about 2 to about 4.

30. The copolymer of claim 21 having at least about 3.0 mole % comonomer.

* * * * *

PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : C08L 23/08 — A1

(11) International Publication Number: WO 94/12568

(43) International Publication Date: 9 June 1994 (09.06.94)

(21) International Application Number: PCT/EP93/03355

(22) International Filing Date: 26 November 1993 (26.11.93)

(30) Priority Data:
9224876.4 27 November 1992 (27.11.92) GB

(71) Applicant *(for all designated States except US)*: EXXON CHEMICAL PATENTS INC. [US/US]; 1900 East Linden Avenue, Linden, NJ 07036 (US).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: CHAMBON, François, Henri [FR/BE]; Rue de Tulipe 2, B-1950 Kraainem (BE). TRUDELL, Barry, Colin [CA/US]; 16019 Greenwood Pines, Houston, TX 77062 (US).

(74) Agents: VELDHUIZEN, Albert, Dirk, Willem et al.; Exxon Chemical Limited, Exxon Chemical Technology Centre, P.O. Box 1, Abingdon, Oxfordshire OX13 6BB (GB).

(81) Designated States: CA, JP, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) Title: IMPROVED PROCESSING POLYOLEFIN BLENDS

(57) Abstract

Using effective amounts of low weight-average molecular weight polyethylene having a density greater than or equal to 0.900 g/cm^3 in polyolefin blends such as to have a blend polydispersity index of greater than 3.5 are shown to achieve improved surface properties after higher shear processing of the blends, largely eliminating or effectively minimizing the occurrence of surface distortions.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria
AU	Australia
BB	Barbados
BE	Belgium
BF	Burkina Faso
BG	Bulgaria
BJ	Benin
BR	Brazil
BY	Belarus
CA	Canada
CF	Central African Republic
CG	Congo
CH	Switzerland
CI	Côte d'Ivoire
CM	Cameroon
CN	China
CS	Czechoslovakia
CZ	Czech Republic
DE	Germany
DK	Denmark
ES	Spain
FI	Finland
FR	France
GA	Gabon
GB	United Kingdom
GE	Georgia
GN	Guinea
GR	Greece
HU	Hungary
IE	Ireland
IT	Italy
JP	Japan
KE	Kenya
KG	Kyrgystan
KP	Democratic People's Republic of Korea
KR	Republic of Korea
KZ	Kazakhstan
LI	Liechtenstein
LK	Sri Lanka
LU	Luxembourg
LV	Latvia
MC	Monaco
MD	Republic of Moldova
MG	Madagascar
ML	Mali
MN	Mongolia
MR	Mauritania
MW	Malawi
NE	Niger
NL	Netherlands
NO	Norway
NZ	New Zealand
PL	Poland
PT	Portugal
RO	Romania
RU	Russian Federation
SD	Sudan
SE	Sweden
SI	Slovenia
SK	Slovakia
SN	Senegal
TD	Chad
TG	Togo
TJ	Tajikistan
TT	Trinidad and Tobago
UA	Ukraine
US	United States of America
UZ	Uzbekistan
VN	Viet Nam

TITLE: Improved Processing Polyolefin Blends

Technical Field

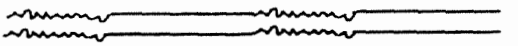
This invention relates to polyolefin blends capable of high shear extrusion into extruded compositions exhibiting improved surface properties of gloss and smoothness. More particularly, it relates to polyolefin blend compositions containing from about 30 wt.% to about 80 wt.% low weight-average molecular weight polyethylene having a density greater than or equal to 0.900 g/cm^3, and having a blend polydispersity index of greater than 3.5.

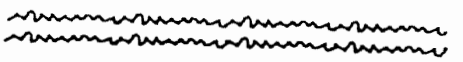
Background of the Invention

Flow instabilities in polymer processing often dramatically limit the maximum throughput possible in common converting operations. They produce irregularities of the polymer surface which are generally referred to as "melt fracture". Depending on the periodicity and the amplitude of the distortion, they can be classified as : slip-stick, sharkskin and wavy fracture. Slipstick is an observed result of the phenomena that at characteristic throughput-pressure required to extrude the resin, the pressure often begins to oscillate. Under oscillating pressure conditions, the extrudate exhibits alternating regions of smooth and rough surface making it of essentially no use. Over the recent past, slip-stick has been a very severe limiting factor for the wide utilization of neat polyethylene resins based upon LLDPE. Sharkskin is shear-stress induced surface irregularity of high frequency and low magnitude that reduces surface gloss, increases apparent roughness and accordingly limits the use of the compositions or limits the processing conditions such that the process is not commercially attractive. Numerous patents have addressed these phenomena, e.g. US-A-4 859 398 discloses extrusion

process parameters that are said to reduce sharkskin. However, this description also indicates that shear-stress and exit die temperature are to be kept at low values, thus limiting the utility of such solutions.

The following visual representation illustrates examples of the surface characteristics of extrudate having slip-stick and sharkskin :

Slip-stick 

Sharkskin 

In view of these problems with processing and resulting surface properties, various processing aids and/or flow improvers have been utilized or proposed. See generally, Ency. of Poly.Sci. and Eng. (2d Ed.), Index vol., pp. 307-324 (J. Wiley & Sons, 1990). Polyethylene wax is listed as a lubricating processing aid for LLDPE on p. 320. However these additives can lead to other problems because of their general incompatibility with the polyolefin resins being processed. Traditional processing aids such as silicone oils and other low molecular weight, non-hydrocarbon compounds are often prohibited from use in medical and food packaging applications. Additionally, the use of the traditional low molecular weight compounds can cause "blooming", the exudation of the low molecular weight materials during use or storage over time, which results in an oily feel or even discoloration of the final extruded compositions.

Additionally it is known generally for polyolefin polymers that the use of broad molecular weight distribution (MWD, or polydispersity index) blend compositions can allow increased processing speeds while maintaining or improving various properties, including surface properties. In particular, PCT-A-WO 90/03414 (and

surface properties. In particular, PCT-A-WO 90/03414 (and corresponding U.S. application number 07/916,738) addresses a broad class of linear ethylene interpolymer blends having improved mechanical, physical or chemical properties wherein the blends have M_w/M_n > 3 and wherein each blend component has a higher comonomer content than any other component of lower average molecular weight (described as a narrow composition distribution having composition distribution breadth index, "CDBI", of >50%). Samples 9D, 21F and 22E of Example 3 illustrate blends having approximately 33wt.% of a polyethylene blend component having 0.0wt.% comonomer and M_w of 13,400. Though, in general, poor surface properties are said to be minimized, and improved properties of reduced coefficients of friction and lower extractables are said to be achieved by the broad class of interpolymer blends described, the examples address only compression molded sheets and the properties thereof, not including extrudate properties.

Additionally, in co-pending U.S. application number 07/817,701, not published as of the date of the filing of this case, polyolefin blends shown to have improved heat sealing properties are described. These blends are described to comprise A and B components wherein the A component is linear ethylene interpolymers said to have a density of from 0.86 to 0.96 g/cm^3, and may include high density polyethylene with density above about 0.940 g/cm^3; a weight average molecular weight of 10^3 to 10^6; and, preferably having a CDBI >50%. The B component is said to include any of the traditional polyethylene copolymers known in the prior art. It is disclosed therein that by formulating blends of differing molecular weights of the A interpolymers to make up the A component such properties as tear strength, modulus, yield strength, clarity, gloss, haze, and heat sealibility may be retained as with the individual interpolymers, or improved. The description addresses heat-sealable

articles and the examples address films having improved heat-sealing performance, extrudate properties are not described.

The effects of higher speed melt processing have also been recently addressed in the technical literature. Extrudate surface defects in linear polydimethylsiloxane are addressed by simulation methods to postulate that hydrostatic tension cavitates the polymer melt within 1 micron of the die exit to create conditions for sharkskin formation in "Sharkskin defects of polymer melts: The role of cohesion and adhesion", B. Tremblay, J. Rheol. 35 (6), pp. 989-975 (August, 1991). The author also postulates, p. 997, that the known phenomena of decreasing sharkskin with increase of MWD may possibly be explained by the diffusion of low molecular weight species and filling of micrcoscopic voids produced so as to prevent cavitation. In "Effects of Polymer Structure on the Onset of Processing Defects in Linear Low Density Polyethylene", L.Kale et al, Poly. Eng. and Sci., v.31, no. 22 (Nov. 1991), it was concluded that the severity of the melt processing defects appears to be inversely related to the amount of low molecular weight, highly branched material.

Figures

FIG. 1 is a graphic plot of the measurement of amplitude of distortion against shear rate for Examples 1 and 2 blends in accordance with the invention and comparison examples A and B blends representing the prior art.

Invention Disclosure

It has been discovered that by using effective amounts of a low weight-average molecular weight thermoplastic polyethylene having a density greater than or equal to 0.900 g/cm^3 ("PE modifier") in polyolefin blends and that by achieving a blend polydispersity index

of greater than 3.5 for the resulting blends, surface properties resulting from high shear processing of the blends are improved by largely eliminating or effectively minimizing the occurrence of surface distortions. Thus the invention is directed to a polyolefin blend suitable for high shear-stress extrusion characterized by comprising : a) at least 30 wt.%, particularly more than about 45 wt.%, or even 60 wt % and higher, to about 80 wt.% of total polymer blend of low M_w polyethylene having a density greater than or equal to 0.900 g/cm^3; and, b) 70 to 20 wt.% of total polymer blend at least one of ethylene homopolymers or copolymers wherein the ethylene content is at least 70 mol.%, preferably at least 80 mol.%, where C_3-C_{16} α-olefins are copolymerized, and wherein the M.I. of the b) component is selected such that the blend of a) and b) exhibits an MWD of greater than 3.5.

By means of the present invention, surface distortion of polyolefin extrudate is controlled in two ways :

- it is eliminated or at least shifted outside the processing window, thus making the region of higher extrusion rates practically useful ;

- it can be finely tuned so that slip-stick is eliminated while surface distortion of low amplitude is retained. This is in recognition of the fact that for some applications surface distortion may be desirable, i.e. light sharkskin provides non-glossy, improved feel extrudates.

Accordingly, increased processing speeds are made possible for applications of polyolefin extruded products where surface defects or distortions were previously detriments to the desired end use. Also means provided for selecting the polyolefin blends of the invention permit tailoring of blend melt index ("M.I.") to achieve M.I. ranges that will be most suitable for existing equipment to maximize processing speeds while avoiding

the surface distortions previously observed at such speeds on that equipment.

Best Mode and Examples of the Invention

The invention will typically comprise the use of about 30 wt.% to about 80 wt.% of the PE modifier of the invention in a polyolefin blend, which with the provision of said PE modifier has a polydispersity index of > 3.5, for the purpose of improving the surface distortion of polyolefin blends subjected to high shear rate extrusion. Alternatively, the invention can be defined as a process for producing an extruded polyolefin composition having improved surface properties of gloss and smoothness characterized by comprising the steps of a) providing a polyolefin blend comprising at least about 30 wt.% to about 80 wt.% PE modifier and having a blend polydispersity index of greater than 3.5; and, b) extruding the blend of step a) under high shear conditions.

For the purposes of describing the invention and results of its use the term surface roughness index (R_A) is defined to mean the first moment of the amplitude of surface distortion as measured by a SURFCOM 110B, from TOKYO SEIMITSU CO. Ltd., Tokyo, Japan, and expressed in units of micrometers (μm). Typically the R_A of polyolefin blends extruded under the higher shear rate conditions of the invention will be less than 10μm, preferably less than 9μm, and even more preferable less than 3μm. The term "high shear rate extrusion" in the description of the invention is meant as understood in the polymers processing and converting art and is to encompass shear rate of not less than 500 s^{-1}($second^{-1}$ or 1/second), for example, 500-1900 s^{-1}, and above. Melt index (M.I.) as referred to in the description and claims refers to that measured in g/10 min. at 190°C and 2.16 kg (ASTM D1238). Density is reported in g/cm^3.

The PE modifier of the invention is one having a low weight-average molecular weight (M_w), typically characterized by an M.I. greater than or equal to 50 but less than or equal to 1000, preferably from 100 to 650, and a density of at least 0.900 g/cm^3, preferably from 0.910, more preferably from 0.920, up to about 0.945 or even up to 0.975. It will be comprised of polyethylene homopolymer or copolymer, or blends, of ethylene and one or more monomers copolymerizable therewith, having sufficient degree of crystallinity to achieve the density range described. Preferred copolymerizable monomers include the C_3 - C_{16} α-olefins or diolefins, particularly the C_4 - C_8 α-olefins. Level of incorporation of the comonomers determines density variation and can be either random or more regular. The density limitations are critical to the invention in that incorporation of the copolymerizable monomers disrupts the crystalline order of the copolymer formed, due to creation of branching in the otherwise linear ethylene-based polymer, and thus operates to decrease the apparent density with increased comonomer incorporation.

Methods of preparation of the PE modifier of the invention are well-known in the art. One method is in PCT-A1-WO 90/03414, which is based upon U.S. application Ser. No. 252,094 filed 30.09.88, the disclosure of which is incorporated by reference for purposes of U.S. patent practice. Catalysts and means of preparation of suitable polyethylene homo- and copolymers appear in the patent literature, see e.g., U.S. patents 4,429,079 and 4,461,873, and the co-pending U.S. application 07/817,701 which are also incorporated by reference for purposes of U.S. patent practice. Additionally, such publications as Ency. of Poly. Sci. and Eng., vol. 6, pp. 383-490 (J. Wiley & Sons, 1986), and Textbook of Polymer Science (3d ed.), F.W. Billmeyer, Jr., Pages 361-370 (J. Wiley & Sons, 1984) can be consulted for background information as to comonomers, methods of preparation and sources of

commercial products. Low M_W high-density polyethylene (HDPE) is suitable and can be prepared by metal-catalysed coordination polymerization, typically with either a co-catalyst system based on one or more transition metals and one or more of an aluminum alkyl or aluminum haloalkyl or by supported metal oxide compositions, and more recently by metallocene catalyst systems. Such HDPE typically has up to about 2 wt.% comonomer, e.g. 1-butene, 1-hexene or 1-octene. Inclusion of more, up to about 10 wt.%, results in polyethylene copolymer having densities less than about 0.941 g/cm^3 but still within the density range defined for the purposes of this invention.

The polyolefin blend ot the invention comprises, in addition to the PE Modifier of the invention, at least one of ethylene homopolymers or copolymers, as defined above, wherein the ethylene content is at least 70 mol.%, preferably at least 80 mol.%, where C_3-C_{16} α-olefins and/or diolefins are copolymerized, and the M.I. is less than 50, preferably less than 10, more preferably less than 3. This polyolefin blend may comprise any one or more of LLDPE, ULDPE, or LDPE as those terms are understood in the art and appear in such as Ency. of Poly. Sci. and Eng. and Textbook of Polymer Science, see above. Blends comprising either or both of LLDPE and VLDPE are particularly suitable. Also, HDPE can be effectively modified by the PE modifier of the invention, or included in blends so modified, so long as the HDPE is of significantly higher M_W, e.g. or having M.I. less than 10, preferably less than 3, and of equivalent or lower density than the PE modifier. Additionally these blends will encompass any of the polyethylene polymers and blends emerging from new technologies relating to metallocene coordination catalysis, such as those exemplified in the prior art description of this application, that have the monomer content and M.I. specified.

Low-density polyethylene ("LDPE") is a well-known commodity product and includes both low and medium density polyethylene having densities of about 0.910 to 0.940 g/cm^3. The term as used herein includes copolymers and terpolymers of ethylene which are thermoplastic resins. Comonomers typically include C_3-C_{10} α-olefins. The C_2 content will typically exceed about 80 wt% of the polyethylene co- and terpolymers. These polymers and copolymers are typically prepared by metal catalysed coordination polymerization in accordance with processes well known in the polymers art. A typical LDPE is available commercially as ESCORENE® LD 180 through EXXON Chemical International Marketing B.V., BELGIUM. LDPE with densities of 0.930 g/cm^3 and lower are particularly suitable in accordance with the invention.

The linear low-density polyethylene ("LLDPE") of the invention are copolymers of ethylene with at least one alphaolefin having at least four carbon atoms, e.g., 1-butene, 1-hexene, 1-octene, etc. The processes for producing LLDPE are typically based on coordination polymerization and are well known in the art. Commercial grades are widely available. A typical LLDPE is available commercially as ESCORENE® LL 6301 RQ through EXXON Chemical International Marketing B.V., BELGIUM. Preferably the LLDPE of the inventon will have a density of less than 0.930.

High density polyethylene ("HDPE") has a density of about 0.941 to 0.975 g/cm^3 and is an established product of commerce. Suitable HDPE has molecular weights in the range of 150,000 to 300,000, and includes high molecular weight ("HMW") HDPE which has molecular weights in the range of 300,000 to 500,000. Its manufacture and general properties are well known in the art.

Blends of the invention are prepared by blending the described components in the desired proportions using conventional melt-processing blending techniques and apparatus, for example, Banbury mixers, single or

multiple screw extruders and the like. To achieve the described MWD for the invention blends, components are selected meeting the above criteria and provided in such proportions as empirically result in both of targetted M.I. and MWD for the blend as is conventionally done in the polymer processing industry. Conversion of M.I. to M_W for initial target proportions, from which iteration is conducted for fine tuning, is typically done by use of empirically derived relationships for the specific polymers as is known in the art. See, for example, "Melt Flow Index : More Than Just A Quality Control Rheological Parameter. Part I." , A. Shenoy and D. Saini, Advances in Polymer Technology, Vol. 6, No. 1, 1-58 (1986).

Alternatively, blends may be made by direct polymerization, using, for example, two or more catalysts in a single reactor or one or more catalysts in parallel or series reactors, where the catalysts, monomer feeds, and reactor conditions are provided that are suitable for the preparation of polymer components meeting the invention description. Such direct polymerization blends are known in the polyolefin art, see for example PCT-A-WO 90/03414. The disclosures addressing polyolefin blends of both of U.S. application Ser. No. 252,094 filed 30 September 1988 and U.S. application Ser. No. 07/817,701 filed 7 January 1992 are incorporated by reference for purposes of U.S. patent practice.

By use of the invention, the rate of surface roughness increase of the extruded polyolefin compositons with extrusion throughput can be accurately controlled by the extent to which MWD is broadened and the difference in density, between the PE Modifier and remaining polyolefin component, is increased. More specifically, based on the present invention, resins with comparably useful MIs can be tailored by selection of component M.I. and density such that R_A remain constant over a wide range of extrusion rates. In Examples 1 and 2, below, increasing the difference in measured densities between

the PE Modifier and the other polyolefin component decreased the measured R_A in addition to flattening for both the curve of RA vs. shear rate, see Fig. 1.

Without intending to be present limitations to the invention, it is believed that the presence of the PE modifier in the polyolefin blends of the invention permits the improved processing with decreased surface defects due to a migration of at least an effective amount of the PE modifier to the surface of the blend during the high shear stress processing. Both of the low M_w and the low levels of chain branching, as is reflected in the density, permit improved dispersion and ease of migration to the surface. However the fact that the PE modifier is still of a high enough M_w to permit of some level of chain entanglement likely prevents its being significantly extractable and helps prevent reduction of blend viscosity below that typically necessary for effective extrusion.

In conclusion, the combination of the density effects and MWD described in the present invention will allow the polymer manufacturer to design resins which can be processed at unusually higher converting rates retaining simultaneously a complete control over the surface aspect of the extrudate. It will be apparent to those of skill in polymer science given the disclosure herein that the principles of this invention will be extendable to other polymer systems, that is inclusion of one, or more, miscible polymer species that is of lower molecular weight and higher in density than the matrix polymer or polymer blend to be processed by extrusion will enable improvement of the surface appearance and smoothness.

The industrial applicability of this invention will arise principally in the polymer processing and converting industry where polyolefin films, laminations, coatings, extrusion molded parts and articles, injection molded parts and articles, and the like, are made. Particular advantage can be obtained for those

applications where the traditional use of process aids or flow improvers was needed to utilize high shear rates, with the instant invention such process aids or flow improvers can be essentially eliminated or minimized, if not altogether omitted. For example, in blown film applications the desired shear rate for processing can be 500-1,000 s^{-1}, in film casting and coating up to 2000 s^{-1}, and cable coating up to 10,000 s^{-1}. As with other polyolefin blends, additives such as reinforcing fillers, pigments or colorants, UV stabilizers, antioxidants, etc., can be provided in conventional amounts in accordance with conventional methods to achieve specifically desired end product properties.

The following examples are presented to illustrate the foregoing discussion. All parts, proportions and percentages are by weight unless otherwise indicated. Although the examples may be directed to certain embodiments of the present invention, they are not to be viewed as limiting the invention in any specific respect.

Example 1

A blend of polyolefin resin and PE modifier in accordance with the invention was provided in which the polyolefin constituted 30 wt.% and was a polyethylene copolymer resin with 20 mol.% 1-butene, having a M.I. of 0.14 and a density of 0.876, and the PE Modifier was a polyethylene copolymer, with 4 mol.% 1-butene, having a M.I. of 122 and a density of 0.925. The polydispersity of the blend as measured by GPC was 4.3 and the M.I. was 5.2. Both polymers were prepared separately by gas-phase polymerization utilizing bis(n-butylcyclopentadienyl)zirconium dichloride with alumoxane-treated silica as described for Example II of co-pending U.S. application 07/817,901 filed 7 January 1992.

Generally speaking, the M.I. of both the ethylene copolymers prepared were controlled by adjustment of the amount of H_2 present and the density was controlled by

the amount of comonomer present, both during polymerization. In particular, the polymerization was conducted for the PE Modifier in a continuous gas-phase reactor at a temperature of 145°C., pressure of about 2.07 x 10^6 Pa (300 psi), H2 concentration 460 ppm, C_2 concentration 52.0 mol.% , C_4 concentration 2.85 mol.%. The polyolefin component was polymerized similarly at a temperature of 111.7°C., pressure of about 2.07 x 10^6 Pa (300 psi), H2 concentration 84 ppm, C_2 concentration 42.0 mol.% , C_4 concentration 6.45 mol.%. Residence times ranged between 2 and 5 hours. Both polymers exhibited narrow MWD (2.0-2.7) and narrow composition distribution (CD) (approximately equal comonomer content and molecular weight in each polymer chain of each component respectively).

The blend components were fed to a Werner Pfleiderer ZSK 57 twin screw extruder under melt processing conditions in which the processing temperature was 199°C., the extruder speed was 295 rpm and the applied torque was 91% maximum. The blend was mixed under these conditions, extruded and cut into pellets. These were fed to a Gottfert Rheograph 2002 for measurement of shear stress vs. shear rate using a circular die with L/D of 30/1 at 190°C. The extrudate of the Rheograph was collected, cooled and examined with the Surfcom 110B.

The blend of Example 1 was subjected to increase in shear stress, and accordingly shear rate, with the resulting observation that R_A remained essentially constant at about 1-2 µm over shear rate increase from about 100 s^{-1} to about 2000 s^{-1}. Up to about 10,000 s^{-1}, RA steadily increased to about 10 µm.

Example 2

A blend of polyolefin resin and a PE Modifier in accordance with the invention was provided in which the polyolefin constituted 30 wt.% and was a polyethylene copolymer resin with 8 mol.% 1-butene, having a M.I. of 0.09 and a density of 0.910, and the PE modifier

constituted 70 wt.% and was a polyethylene copolymer, with 8 mol.% 1-butene, having a M.I. of 97 and a density of 0.910. The polydispersity of the blend as measured by GPC was 4.6 and the M.I. was 4.7. Both polymers were prepared separately by gas-phase polymerization utilizing bis(n-butylcyclopentadienyl)zirconium dichloride with alumoxane treated silica generally as described in Example 1.

The blend blend components were melt processed and extruded for shear stress vs. shear strain analysis and R_A also in accordance with Example 1.

The R_A as measured in the Surfcom 110B remained essentially constant at about 4-6 μm over shear rate increases from about 70 s^{-1} to about 2000 s^{-1}. . From 2000 s^{-1} to 4500 s^{-1}, R_A increased to about 10 μm. See again FIG. 1.

Example 3

A blend of polyolefin resin and PE modifier in accordance with the invention was provided in which the polyolefin constituted 60 wt % and was a polyethylene copolymer resin with 8 mol % 1-butene, having a M.I. of 1.1 and a density of 0.910. The PE modifier constituted 40 wt % and was a polyethylene copolymer, with 8 mol % 1-butene, having a M.I. of 612 and a density of 0.910. The polydispersity of the blend as measured by GPC was 4.1 and the M.I. was 4.0. Both polymers were prepared separately by gas-phase polymerization, as described in Example 1.

The blend components were melt processed and extruded for testing as done for Examples 1 and 2.

The R_A as measured in the Surfcom 110B increased steadily from 0.2 to about 3 μm over shear rate increase from about 60 to about 1000s^{-1}. From 1000 to 3000s^{-1}, R_A increased essentially on a decreased slope to about 3-4 μm.

Comparison Example A

A polyolefin blend having a narow MWD (2.1) was prepared having an M.I of 5.0 as a comparison for Examples 1 and 2. It consisted of two components in equal amounts (50 wt.% each), the A component was a polyethylene copolymer resin with 10 mol.% 1-butene, having a M.I. of 5.1 and a density of 0.897, and the B component was a polyethylene copolymer, with 5 mol.% 1-butene, having a M.I. of 4.6 and a density of 0.922. Both polymers were prepared by gas-phase polymerization utilizing bis(n-butylcyclopentadienyl)zirconium dichloride with alumoxane treated silica generally as described for Example 1.

The blend was melt processed and extruded for shear stress vs. shear strain analysis and R_A in accordance with Example 1.

The polyolefin blend exhibited essentially constant rate of increase of R_A from about 0.2 μm to 20 μm for shear rate increase from 150 s^{-1} to 1900 s^{-1}. The R_A at a shear rate of 500 s^{-1} was 3 μm and increasingly rapidly, FIG. 1.

Comparison Example B

A commercial LLDPE sold for moulding applications and ready processability was provided having a MWD above about 3.5, density of 0.935 and also an M.I. of 5.0. This Escorene® LL 6301 RQ LLDPE (Exxon Chem. Inter. Inc.) was similarly melt processed and extruded for shear stress vs. shear strain and R_A analysis in accordance with Example 1. The graph of FIG. 1 illustrates the rapid increase in R_A as a function of shear rate. The LLDPE exhibited essentially constant rate of increase of R_A from about 0.3 μm to 8 μm for shear rate increase from 190 s^{-1} to 1900 s^{-1}. The R_A at a shear rate of 10,000 s^{-1} was about 20 μm. This example illustrates that though lower high shear rate processing with some standard LLDPE products may yield acceptable R_A, the increase in shear rate resulted in rapid deterioration of R_A.

Although the invention has been described with respect to particular materials, means and embodiments it is to be understood that the invention is not limited to the particulars disclosed and extends to all equivalents within the scope of the appended claims.

The following subject matter is claimed:

Claims :

1. A use of about 30 wt.% to about 80 wt.% of low M_w polyethylene having a density greater than or equal to 0.900 g/cm^3 in a polyolefin blend, which with the provision of said polyethylene has a polydispersity index of > 3.5, for the purpose of improving the surface distortion of polyolefin blends subjected to high shear rate extrusion.

2. The use according to claim 1 wherein said polyethylene has a M.I. (g/10 min., 190°C, 2.16 kg) greater than or equal to 50 but less than or equal to 1000.

3. The use according to claims 1 - 2 wherein said polyolefin blend comprises, in addition to said polyethylene, at least one of ethylene homopolymers or copolymers wherein the ethylene content is at least 70 mol.%.

4. The use according to any of claims 1 - 3 wherein said higher shear rate extrusion is not less than 500 s^{-1}.

5. The use according to claim 4 wherein said surface roughness (R_A) is greater than 0 but less than 2 µm.

6. The use according to any of claims 1 - 5 wherein after extrusion at shear rates not less than 1900 s^{-1}, the surface distortion as measured by surface roughness (R_A) is less than 10 µm.

7. A process for producing an extruded polylefin composition having improved surface properties of gloss and smoothness characterized by comprising the steps of :