

COPOLYMERS AND FILMS THEREOF

The present invention relates to novel copolymers and in particular to novel copolymers of ethylene and higher alpha-olefins having C7 – C12 carbon atoms in particular to copolymers of ethylene and 1-octene and also to films produced from said
5 copolymers.

In recent years there have been many advances in the production of polyolefin copolymers due to the introduction of metallocene catalysts. Metallocene catalysts offer the advantage of generally higher activity than traditional Ziegler catalysts and are usually described as catalysts which are single-site in nature. Because of their single-site nature
10 the polyolefin copolymers produced by metallocene catalysts often are quite uniform in their molecular structure. For example, in comparison to traditional Ziegler produced materials, they have relatively narrow molecular weight distributions (MWD) and narrow Short Chain Branching Distribution (SCBD).

Although certain properties of metallocene products are enhanced by narrow
15 MWD, difficulties are often encountered in the processing of these materials into useful articles and films relative to Ziegler produced materials. In addition, the uniform nature of the SCBD of metallocene produced materials does not readily permit certain structures to be obtained.

Recently a number of patents have published directed to the preparation of films
20 based on low density polyethylenes prepared using metallocene catalyst compositions.

EP 608369 describes copolymers having a melt flow ratio (I_{10}/I_2) of ≥ 5.63 and a molecular weight distribution (MWD) satisfying the relationship $MWD \leq (I_{10}/I_2) - 4.63$. The copolymers are described as elastic substantially linear olefin polymers having improved processability and having between 0.01 to 3 long chain branches per 1000 C
25 atoms and show the unique characteristic wherein the I_{10}/I_2 is essentially independent of MWD.

WO 94/14855 discloses linear low density polyethylene (LLDPE) films prepared using a metallocene, alumoxane and a carrier. The metallocene component is typically a bis (cyclopentadienyl) zirconium complex exemplified by bis (n-butylcyclopentadienyl)
30 zirconium dichloride and is used together with methyl alumoxane supported on silica. The LLDPE's are described in the patent as having a narrow Mw/Mn of 2.5-3.0, a melt flow ratio (MFR) of 15-25 and low zirconium residues.

WO 94/26816 also discloses films prepared from ethylene copolymers having a narrow composition distribution. The copolymers are also prepared from traditional metallocenes (eg bis (1-methyl, 3-n-butylcyclopentadienyl) zirconium dichloride and methylalumoxane deposited on silica) and are also characterised in the patent as having a
5 narrow Mw/Mn values typically in the range 3-4 and in addition by a value of Mz/Mw of less than 2.0.

However, it is recognised that the polymers produced from these types of catalyst system have deficiencies in processability due to their narrow Mw/Mn. Various approaches have been proposed in order to overcome this deficiency. An effective method to regain
10 processability in polymers of narrow Mw/Mn is by the use of certain catalysts which have the ability to incorporate long chain branching (LCB) into the polymer molecular structure. Such catalysts have been well described in the literature, illustrative examples being given in WO 93/08221 and EP-A-676421.

WO 97/44371 discloses polymers and films where long chain branching is present
15 and the products have a particularly advantageous placement of the comonomer within the polymer structure. Polymers are exemplified having both narrow and broad Mw/Mn, for example from 2.19 up to 6.0, and activation energy of flow, which is an indicator of LCB, from 7.39 to 19.2 kcal/mol (31.1 to 80.8kJ/mol). However, there are no examples of polymers of narrow Mw/Mn, for example less than 3.4, which also have a low or moderate
20 amount of LCB, as indicated by an activation energy of flow less than 11.1kcal/mol (46.7kJ/mol).

WO 00/68285 exemplified copolymers of ethylene and alpha-olefins having molecular weight distributions in the range 2.3 to 3.2, melt index of 1.02 – 1.57 and activation energies of about 32 kJ/mol. The copolymers were most suitable for use in the
25 application of films showing good processability, improved optical and mechanical properties and good heat sealing properties. The copolymers were suitably prepared in the gas phase by use of monocyclopentadienyl metallocene complexes.

EP 1360213 describes metallocene film resins having good mechanical properties, excellent optical properties and very good extrusion potential. The resins exhibit melt
30 indices MI₂ the range 0.001 to 150 g/10 min and a high Dow Rheology Index (DRI) of at least 20/MI₂. The resins are suitably prepared from ethylene bis(4,5,6,7-tetrahydro-1-indenyl) zirconium dichloride/MAO catalyst systems.

EP 1260540 and EP 1225201 similarly disclose polymers having DRI of at least 8/MI₂ and 5/MI₂ respectively.

US 5674342 describes ethylene polymers having a DRI of at least 0.1 and preferably at least 0.3 and a melt flow ratio (I₁₀/I₂) in the range 8 to about 12. Specifically
 5 exemplified polymers exhibit DRI in the range 0.3 – 0.7 and molecular weight distributions (Mw/Mn) in the range 2.15 - 3.4.

WO 04/000919 describes films from LLDPE having a ratio of MD tear to TD tear of ≥ 0.9 . The films are based on copolymers produced from hafnium metallocene catalysts systems, the reported films however have dart impacts of ≤ 690 g (1013 g/mil).

10 WO 06/085051 describes copolymers of ethylene and alpha-olefins having broader molecular weight distributions (Mw/Mn) in the range 3.5 to 4.5. These copolymers exhibited a melt elastic modulus G' (G'' = 500 Pa) in the range 40 to 150 Pa and an activation energy of flow (Ea) in the range 28 – 45 kJ/mol but which had low or moderate amounts of LCB.

15 WO 08/074689 describes copolymers of ethylene and alpha-olefins having a much lower Dow Rheology Index (DRI) but with a more balanced processability with improved properties particularly those suitable for preparing films with an excellent balance of processing, optical and mechanical properties.

The copolymers described and exemplified in these prior art publications have
 20 typically been copolymers of ethylene and α -olefins having C4 – C6 carbon atoms for example 1-butene, 1-hexene and 4-methyl-1 pentane.

SUMMARY

We have now surprisingly found that copolymers comprising ethylene and higher α -olefins, in particular having C7 to C12 carbon atoms and most preferably having C8
 25 carbon atoms, show improved processability having properties particularly suitable for preparing films with an excellent balance of processing, optical and mechanical properties. In particular blown films exhibit an excellent combination of MD tear strength, TD tear strength and dart drop impact.

Thus according to a first aspect of the present disclosure there is provided a
 30 copolymer of ethylene and a α -olefin having C7 to C12 carbon atoms, said copolymer having

- (a) a density (D) in the range 0.900 – 0.940 g/cm³,
- (b) a melt index MI₂ (2.16 kg, 190°C) in the range of 0.01 - 50 g/10 min,

- (c) a melt elastic modulus G' ($G''= 500$ Pa) in the range 20 to 150 Pa, and
- (d) a tear strength (MD) of ≥ 220 g
- a tear strength (TD) of ≥ 470 g, and
- a Dart Drop Impact (DDI) of ≥ 1800 g

5 of a blown film having a thickness of 25 μm produced from the copolymer, where MD is referred to the machine direction and TD is the transverse direction of the blown film.

For the avoidance of doubt all references to density refer to the non-annealed density unless otherwise stated.

10 According to another aspect, there is provided a film comprising a copolymer of ethylene and an α -olefin having C7 to C12 carbon atoms as defined above.

According to another aspect, there is provided a blown film comprising a copolymer of ethylene and an α -olefin having C7 to C12 carbon atoms, said copolymer having

- (a) a density in the range $0.900 - 0.940 \text{ g/cm}^3$,
- (b) a melt index MI_2 (2.16 kg, 190°C) in the range of 0.01 - 50 g/10 min, and
- 15 (c) a melt elastic modulus G' ($G''= 500$ Pa) in the range 20 to 150 Pa

wherein said film when having a thickness of 25 μm exhibits :

- a tear strength (MD) of ≥ 220 g
- a tear strength (TD) of ≥ 470 g, and
- a Dart Drop Impact (DDI) ≥ 1800 g

20 wherein MD is referred to the machine direction and TD is the transverse direction of the film.

DETAILED DESCRIPTION

The novel copolymers of the present invention may also be suitably described by reference to the relationship between density (D) and the Dart Drop Impact (DDI).

25 Thus according to another aspect of the present invention there is provided a copolymer of ethylene and a α -olefin having C7 to C12 carbon atoms, said copolymer having

- (a) a density (D) in the range $0.900 - 0.940 \text{ g/cm}^3$,
- (b) a melt index MI_2 (2.16 kg, 190°C) in the range of 0.01 - 50 g/10 min,

(c) a tear strength (TD) of ≥ 470 g, and a Dart Drop Impact (DDI) in g of a blown film having a thickness of 25 μm produced from the copolymer satisfying the equation:

$$\text{DDI} \geq 21500 \times \{1 - \text{Exp} [-750(D - 0.908)^2]\} \times \{\text{Exp} [(0.919 - D)/0.0045]\}$$

5

The novel polymers of the present invention may also be defined by means of their Composition Distribution Breadth Index (CDBI) which has been well defined, for example in US 5206075 and PCT publication WO93/03090, as a measure of the composition distribution. The CDBI may be suitably determined by means of Temperature Rising

10 Elution Fractionation (TREF).

The novel copolymers of the present invention exhibit a relationship between the Composition Distribution Breadth Index (CDBI) and density (D) that satisfy the relationship of

$$\text{CDBI} \leq (-192 \text{ D} + 241.5)$$

15

The novel copolymers of the present invention typically exhibit a CDBI in the range 50 – 63%.

The novel copolymers of the present invention also exhibit a comonomer partitioning factor $C_{pf} \geq 1.20$.

The aforementioned WO 97/44371 describes the comonomer partitioning factor C_{pf} the relevant parts of which are incorporated herein by reference.

5 Thus according to a further aspect of the present invention there is provided a copolymer of ethylene and a α -olefin having C7 to C12 carbon atoms, said copolymer having :

- (a) a density (D) in the range $0.900 - 0.940 \text{ g/cm}^3$,
- (b) a melt index MI_2 (2.16 kg, 190°C) in the range of $0.01 - 50 \text{ g/10 min}$,
- 10 (c) a melt elastic modulus G' ($G'' = 500 \text{ Pa}$) in the range 20 to 150 Pa ,
- (d) a composition Distribution Breadth Index (CDBI) and density (D) that satisfy the relationship of $\text{CDBI} \leq (-192 D + 241.5)$, and
- (e) a comonomer partitioning factor $C_{pf} \geq 1.20$.

The copolymers preferably have a density in the range $0.910 - 0.935 \text{ g/cm}^3$ and most
15 preferably in the range $0.915 - 0.925 \text{ g/cm}^3$

The copolymers preferably have a melt index in the range $0.05 - 20 \text{ g/10 min}$ and most preferably in the range $0.5 - 5 \text{ g/10 min}$.

The copolymers preferably have a melt elastic modulus G' ($G'' = 500 \text{ Pa}$) in the range $35 - 80 \text{ Pa}$. and most preferably in the range $35 - 45 \text{ Pa}$.

20 The copolymers preferably have an activation energy of flow (E_a) in the range $28 - 45 \text{ kJ/mol}$.

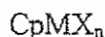
The copolymers typically have a molecular weight distribution in the range $2.5 - 4.5$ and preferably in the range $3.0 - 4.0$.

The preferred α -olefin of the present invention has C8 carbon atoms and comprises
25 1-octene.

The novel copolymers of the present invention may suitably be prepared by use of a metallocene catalyst system comprising, preferably a monocyclopentadienyl metallocene complex having a 'constrained geometry' configuration together with a suitable activator.

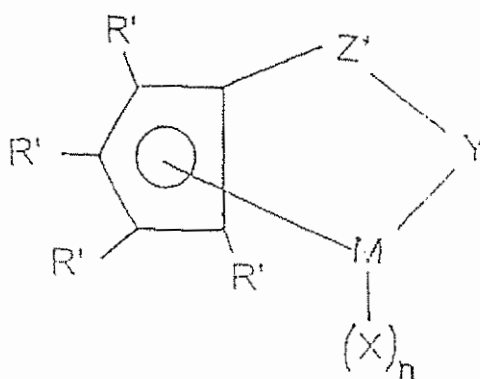
Examples of monocyclopentadienyl or substituted monocyclopentadienyl complexes
30 suitable for use in the present invention are described in EP 416815, EP 418044, EP 420436 and EP 551277.

Suitable complexes may be represented by the general formula:



wherein Cp is a single cyclopentadienyl or substituted cyclopentadienyl group optionally covalently bonded to M through a substituent, M is a Group VIA metal bound in a η^5 bonding mode to the cyclopentadienyl or substituted cyclopentadienyl group, X each occurrence is hydride or a moiety selected from the group consisting of halo, alkyl, aryl, aryloxy, alkoxy, alkoxyalkyl, amidoalkyl, siloxyalkyl etc. having up to 20 non-hydrogen atoms and neutral Lewis base ligands having up to 20 non-hydrogen atoms or optionally one X together with Cp forms a metallocycle with M and n is dependent upon the valency of the metal.

Preferred monocyclopentadienyl complexes have the formula:



wherein:-

R' each occurrence is independently selected from hydrogen, hydrocarbyl, silyl, germyl, halo, cyano, and combinations thereof, said R' having up to 20 nonhydrogen atoms, and optionally, two R' groups (where R' is not hydrogen, halo or cyano) together form a divalent derivative thereof connected to adjacent positions of the cyclopentadienyl ring to form a fused ring structure;

X is hydride or a moiety selected from the group consisting of halo, alkyl, aryl, aryloxy, alkoxy, alkoxyalkyl, amidoalkyl, siloxyalkyl etc. having up to 20 non-hydrogen atoms and neutral Lewis base ligands having up to 20 non-hydrogen atoms,

Y is -O-, -S-, -NR*-, -PR*-,

M is hafnium, titanium or zirconium,

Z* is SiR^*_2 , CR^*_2 , $\text{SiR}^*_2\text{SiR}^*_2$, $\text{CR}^*_2\text{CR}^*_2$, $\text{CR}^*=\text{CR}^*$, $\text{CR}^*_2\text{SiR}^*_2$, or

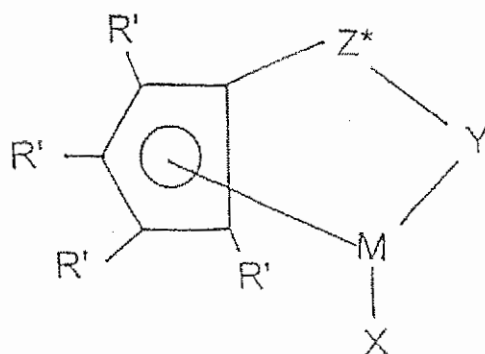
GeR^*_2 , wherein:

R* each occurrence is independently hydrogen, or a member selected from
 5 hydrocarbyl, silyl, halogenated alkyl, halogenated aryl, and combinations thereof, said
 R* having up to 10 non-hydrogen atoms, and optionally, two R* groups from Z*
 (when R* is not hydrogen), or an R* group from Z* and an R* group from Y form a ring
 system,

and n is 1 or 2 depending on the valence of M.

10 Examples of suitable monocyclopentadienyl complexes are (tert-butylamido)
 dimethyl (tetramethyl- η^5 -cyclopentadienyl) silanetitanium dichloride and (2-
 methoxyphenylamido) dimethyl (tetramethyl- η^5 -cyclopentadienyl) silanetitanium
 dichloride.

15 Particularly preferred metallocene complexes for use in the preparation of the
 copolymers of the present invention may be represented by the general formula:



wherein:-

R' each occurrence is independently selected from hydrogen, hydrocarbyl, silyl,
 germlyl, halo, cyano, and combinations thereof, said R' having up to 20 nonhydrogen
 20 atoms, and optionally, two R' groups (where R' is not hydrogen, halo or cyano) together
 form a divalent derivative thereof connected to adjacent positions of the cyclopentadienyl
 ring to form a fused ring structure;

X is a neutral η^4 bonded diene group having up to 30 non-hydrogen atoms, which forms a π -complex with M;

Y is -O-, -S-, -NR*-, -PR*-;

M is titanium or zirconium in the + 2 formal oxidation state;

5 Z* is SiR^*_2 , CR^*_2 , $\text{SiR}^*_2\text{SiR}^*_2$, $\text{CR}^*_2\text{CR}^*_2$, $\text{CR}^*=\text{CR}^*$, $\text{CR}^*_2\text{SiR}^*_2$, or GeR^*_2 , wherein:

R* each occurrence is independently hydrogen, or a member selected from hydrocarbyl, silyl, halogenated alkyl, halogenated aryl, and combinations thereof, said

10 R* having up to 10 non-hydrogen atoms, and optionally, two R* groups from Z* (when R* is not hydrogen), or an R* group from Z* and an R* group from Y form a ring system.

Examples of suitable X groups include s-trans- η^4 -1,4-diphenyl-1,3-butadiene, s-trans- η^4 -3-methyl-1,3-pentadiene; s-trans- η^4 -2,4-hexadiene; s-trans- η^4 -1,3-pentadiene; s-trans- η^4 -1,4-ditolyl-1,3-butadiene; s-trans- η^4 -1,4-bis(trimethylsilyl)-1,3-butadiene; s-cis- η^4 -3-methyl-1,3-pentadiene; s-cis- η^4 -1,4-dibenzyl-1,3-butadiene; s-cis- η^4 -1,3-pentadiene; s-cis- η^4 -1,4-bis(trimethylsilyl)-1,3-butadiene, said s-cis diene group forming a π -complex as defined herein with the metal.

Most preferably R' is hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, benzyl, or phenyl or 2 R' groups (except hydrogen) are linked together, the entire
20 $\text{C}_5\text{R}'_4$ group thereby being, for example, an indenyl, tetrahydroindenyl, fluorenyl, tetrahydrofluorenyl, or octahydrofluorenyl group.

Highly preferred Y groups are nitrogen or phosphorus containing groups containing a group corresponding to the formula -N(R'')- or -P(R'')- wherein R'' is C_{1-10} hydrocarbyl.

Most preferred complexes are amidosilane - or amidoalkanediyl complexes.

25 Most preferred complexes are those wherein M is titanium.

Specific complexes are those disclosed in WO 95/00526 and are incorporated herein by reference.

A particularly preferred complex is (t-butylamido) (tetramethyl- η^5 -cyclopentadienyl) dimethyl silanetitanium - η^4 -1,3-pentadiene.

30 Suitable cocatalysts for use in the preparation of the novel copolymers of the present invention are those typically used with the aforementioned metallocene complexes.

These include aluminoxanes such as methyl aluminoxane (MAO), boranes such as tris(pentafluorophenyl) borane and borates.

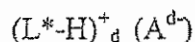
Aluminoxanes are well known in the art and preferably comprise oligomeric linear and/or cyclic alkyl aluminoxanes. Aluminoxanes may be prepared in a number of ways and preferably are prepared by contacting water and a trialkylaluminium compound, for example trimethylaluminium, in a suitable organic medium such as benzene or an aliphatic hydrocarbon.

A preferred aluminoxane is methyl aluminoxane (MAO).

Other suitable cocatalysts are organoboron compounds in particular triarylboron compounds. A particularly preferred triarylboron compound is tris(pentafluorophenyl) borane.

Other compounds suitable as cocatalysts are compounds which comprise a cation and an anion. The cation is typically a Bronsted acid capable of donating a proton and the anion is typically a compatible non-coordinating bulky species capable of stabilizing the cation.

Such cocatalysts may be represented by the formula:



wherein:-

L^* is a neutral Lewis base

$(L^*-H)^+_d$ is a Bronsted acid

A^{d-} is a non-coordinating compatible anion having a charge of d^- , and

d is an integer from 1 to 3.

The cation of the ionic compound may be selected from the group consisting of acidic cations, carbonium cations, silylium cations, oxonium cations, organometallic cations and cationic oxidizing agents.

Suitably preferred cations include trihydrocarbyl substituted ammonium cations eg. triethylammonium, tripropylammonium, tri(n-butyl)ammonium and similar. Also suitable are N,N-dialkylanilinium cations such as N,N-dimethylanilinium cations.

The preferred ionic compounds used as cocatalysts are those wherein the cation of the ionic compound comprises a hydrocarbyl substituted ammonium salt and the anion comprises an aryl substituted borate.

Typical borates suitable as ionic compounds include:

triethylammonium tetraphenylborate
triethylammonium tetraphenylborate,
tripropylammonium tetraphenylborate,
5 tri(n-butyl)ammonium tetraphenylborate,
tri(t-butyl)ammonium tetraphenylborate,
N,N-dimethylanilinium tetraphenylborate,
N,N-diethylanilinium tetraphenylborate,
trimethylammonium tetrakis(pentafluorophenyl) borate,
10 triethylammonium tetrakis(pentafluorophenyl) borate,
tripropylammonium tetrakis(pentafluorophenyl) borate,
tri(n-butyl)ammonium tetrakis(pentafluorophenyl) borate,
N,N-dimethylanilinium tetrakis(pentafluorophenyl) borate,
N,N-diethylanilinium tetrakis(pentafluorophenyl) borate.

15 A preferred type of cocatalyst suitable for use with the metallocene complexes comprise ionic compounds comprising a cation and an anion wherein the anion has at least one substituent comprising a moiety having an active hydrogen.

Suitable cocatalysts of this type are described in WO 98/27119 the relevant portions of which are incorporated herein by reference.

20 Examples of this type of anion include:

triphenyl(hydroxyphenyl) borate
tri (p-tolyl)(hydroxyphenyl) borate
tris (pentafluorophenyl)(hydroxyphenyl) borate
tris (pentafluorophenyl)(4-hydroxyphenyl) borate

25 Examples of suitable cations for this type of cocatalyst include triethylammonium, triisopropylammonium, diethylmethylanmonium, dibutylethylanmonium and similar.

Particularly suitable are those cations having longer alkyl chains such as dihexyldecylmethylanmonium, dioctadecylmethylanmonium, ditetradecylmethylanmonium, bis(hydrogentated tallow alkyl) methylanmonium
30 and similar.

Particular preferred cocatalysts of this type are alkylanmonium tris(pentafluorophenyl) 4-(hydroxyphenyl) borates. A particularly preferred cocatalyst is

bis(hydrogenated tallow alkyl) methyl ammonium tris (pentafluorophenyl) (4-hydroxyphenyl) borate.

With respect to this type of cocatalyst, a preferred compound is the reaction product of an alkylammonium tris(pentafluorophenyl)-4-(hydroxyphenyl) borate and an
5 organometallic compound, for example triethylaluminium or an aluminoxane such as tetraisobutylaluminoxane.

The catalysts used to prepare the novel copolymers of the present invention may suitably be supported.

Suitable support materials include inorganic metal oxides or alternatively
10 polymeric supports may be used for example polyethylene, polypropylene, clays, zeolites, etc.

The most preferred support material for use with the supported catalysts according to the method of the present invention is silica. Suitable silicas include Ineos ES70 and Grace Davison 948 silicas.

15 The support material may be subjected to a heat treatment and/or chemical treatment to reduce the water content or the hydroxyl content of the support material. Typically chemical dehydration agents are reactive metal hydrides, aluminium alkyls and halides. Prior to its use the support material may be subjected to treatment at 100°C to 1000°C and preferably at 200 to 850°C in an inert atmosphere under reduced pressure.

20 The porous supports are preferably pretreated with an organometallic compound preferably an organoaluminium compound and most preferably a trialkylaluminium compound in a dilute solvent.

The support material is pretreated with the organometallic compound at a temperature of -20°C to 150°C and preferably at 20°C to 100°C.

25 Particularly suitable catalysts for use in the preparation of the copolymers of the present invention are metallocene complexes which have been treated with polymerisable monomers. Our earlier applications WO 04/020487 and WO 05/019275 describe supported catalyst compositions wherein a polymerisable monomer is used in the catalyst preparation.

30 Polymerisable monomers suitable for use in this aspect of the present invention include ethylene, propylene, 1-butene, 1-hexene, 1-octene, 1-decene, styrene, butadiene, and polar monomers for example vinyl acetate, methyl methacrylate, etc. Preferred

monomers are those having 2 to 10 carbon atoms in particular ethylene, propylene, 1-butene or 1-hexene.

Alternatively a combination of one or more monomers may be used for example ethylene and 1-hexene.

5 The preferred polymerisable monomer is 1-hexene.

The polymerisable monomer is suitably used in liquid form or alternatively may be used in a suitable solvent. Suitable solvents include for example heptane.

The polymerisable monomer may be added to the cocatalyst before addition of the metallocene complex or alternatively the complex may be pretreated with the
10 polymerisable monomer.

The novel copolymers of the present invention may suitably be prepared in processes performed in either the slurry or the gas phase.

A slurry process typically uses an inert hydrocarbon diluent and temperatures from about 0°C up to a temperature just below the temperature at which the resulting polymer
15 becomes substantially soluble in the inert polymerisation medium. Suitable diluents include toluene or alkanes such as hexane, propane or isobutane. Preferred temperatures are from about 30°C up to about 200°C but preferably from about 60°C to 100°C. Loop reactors are widely used in slurry polymerisation processes.

The novel copolymers are most suitably prepared in a gas phase process.

20 Gas phase processes for the polymerisation of olefins, especially for the homopolymerisation and the copolymerisation of ethylene and α -olefins for example 1-butene, 1-hexene, 4-methyl-1-pentene are well known in the art.

Typical operating conditions for the gas phase are from 20°C to 100°C and most preferably from 40°C to 85°C with pressures from subatmospheric to 100 bar.

25 Preferred gas phase processes are those operating in a fluidised bed. Particularly preferred gas phase processes are those operating in "condensed mode" as described in EP 89691 and EP 699213 the latter being a particularly preferred process.

By "condensed mode" is meant the "process of purposefully introducing a recycle stream having a liquid and a gas phase into a reactor such that the weight percent of liquid
30 based on the total weight of the recycle stream is typically greater than about 2.0 weight percent".

The novel copolymers of the present invention may thus be suitably prepared by the copolymerisation of ethylene with α -olefins having C7 – C12 carbon atoms.

The most preferred α -olefin is 1-octene.

Thus according to another preferred aspect of the present invention there is provided
 5 a method for the preparation of copolymers of ethylene and α -olefins having C7 – C12 carbon atoms having :

- (a) a density (D) in the range 0.900 – 0.940 g/cm³,
- (b) a melt index MI₂ (2.16 kg, 190°C) in the range of 0.01 - 50 g/10 min, and
- (c) a melt elastic modulus G' (G'' = 500 Pa) in the range 20 to 150 Pa

10 said method comprising copolymerising ethylene and the α -olefin in the presence of a catalyst system as hereinbefore described.

According to a preferred aspect of the present invention there is further provided a method for the preparation of copolymers of ethylene and α -olefins having C7 – C12 carbon atoms having :

- 15 (a) a density (D) in the range 0.900 – 0.940 g/cm³,
- (b) a melt index MI₂ (2.16 kg, 190°C) in the range of 0.01 - 50 g/10 min, and
- (c) a melt elastic modulus G' (G'' = 500 Pa) in the range 20 to 150 Pa,
- (d) a composition Distribution Breadth Index (CDBI) and density (D) that satisfy the relationship of $CDBI \leq (-192 D + 241.5)$, and
- 20 (e) a comonomer partitioning factor $C_{pf} \geq 1.20$.

said method comprising copolymerising ethylene and the α -olefin in the presence of a catalyst system as hereinbefore described.

The most preferred α -olefin is 1-octene.

The copolymers are particularly suitable for the production of films and sheets
 25 prepared using traditional methods well known in the art. Examples of such methods are film blowing, film casting and orientation of the partially crystallised product. The films exhibit good balance of processability, optical and mechanical properties and good heat sealing properties.

The copolymers are particularly suitable for the production of blown films.

30 The films typically exhibit a tear strength (MD) of ≥ 220 g and more preferably ≥ 240 g and a tear strength (TD) ≥ 470 g and more preferably ≥ 475 g; where MD is referred to

the machine direction and TD is the transverse direction of the blown film of thickness 25 μm .

The films typically exhibit a Dart Drop Impact (DDI) of a 25 μm film thickness of $\geq 1800\text{g}$, and more preferably $\geq 2000\text{g}$ and most preferably $\geq 2200\text{g}$.

5 The films typically also exhibit a 1% secant modulus (MD) of $\geq 200\text{ MPa}$ and a 1% secant modulus (TD) of $\geq 170\text{ MPa}$; where MD is again referred to the machine direction and TD is the transverse direction of the blown film.

The films may be suitable for a number of applications for example industrial, retail, food packaging, non-food packaging and medical applications. Examples include films for
10 bags, garment bags, grocery sacks, merchandise bags, self-serve bags, grocery wet pack, food wrap, pallet stretch wrap, bundling and overwrap, industrial liners, refuse sacks, heavy duty bags, agricultural films, daiper liners, etc.

The films may also be utilised as shrink film, cling film, stretch film, sealing film or other suitable type of film.

15 The novel copolymers of the present invention are however particularly suitable for use in the manufacture of blown films.

Thus according to another aspect of the present invention there is provided a blown film comprising a copolymer of ethylene and an α -olefin having C7 to C12 carbon atoms, said copolymer having :

- 20 (a) a density in the range $0.900 - 0.940\text{ g/cm}^3$,
(b) a melt index MI_2 (2.16 kg, 190°C) in the range of $0.01 - 50\text{ g/10 min}$, and
(c) a melt elastic modulus G' ($G'' = 500\text{ Pa}$) in the range 20 to 150 Pa

wherein said film when having a thickness of $25\text{ }\mu\text{m}$ exhibits :

- a tear strength (MD) of $\geq 220\text{ g}$
25 a tear strength (TD) of $\geq 470\text{ g}$, and
a Dart Drop Impact (DDI) $\geq 1800\text{ g}$

wherein MD is referred to the machine direction and TD is the transverse direction of the film.

According to another aspect of the present invention there is provided a blown film
30 comprising a copolymer of ethylene and an α -olefin having C7 to C12 carbon atoms, said copolymer having

(a) a density (D) in the range 0.900 – 0.940 g/cm³, and

(b) a melt index MI₂ (2.16 kg, 190°C) in the range of 0.01 - 50 g/10 min,

wherein said film when having a thickness of 25 µm exhibits a tear strength (TD) of ≥ 470 g, and a Dart Drop Impact (DDI) in g satisfying the equation

$$DDI \geq 21500 \times \{1 - \text{Exp}[-750(D - 0.908)^2]\} \times \{\text{Exp}[(0.919 - D)/0.0045]\}$$

wherein TD is the transverse direction of the film.

The films of the present invention show an excellent balance of processing, optical and mechanical properties compared with films prepared from prior art copolymers in particular form copolymers of ethylene and 1-hexene. In particular the blown films of the present invention exhibit an excellent combination of MD tear strength, TD tear strength and dart drop impact.

The present invention will now be further illustrated with reference to the following examples:

Examples 1 and 2

A supported catalyst was prepared according to the general procedure described in the aforementioned WO 06/085051 and WO 08/074689. The catalyst comprised the following components:

support material – silica D984 (Grace-Davison)

metallocene – (C₅Me₄SiMe₂N^tBu)Ti(h⁴-1,3-pentadiene) premixed with 1-hexene

activator - [N(H)Me(C₁₈₋₂₂H₃₇₋₄₅)₂][B(C₆F₅)₃(p-OHC₆H₄)]

Details of the final catalyst composition was as follows:

Parameter	Catalyst
Ti loading (mmol/g)	48.2
B:Ti ratio	1.07
Al:B (TEA:activator)	1.00
hexene:Ti ratio	35
Stadis content (ppm)	500

Polymerisations

- Polymerization of ethylene and 1-octene was carried out continuously using the above catalyst system in a fluidized bed gas phase reactor of 0.74 m diameter with a vertical section of 7 m. The polymerisation conditions are shown below in Table 1 for the preparation of two ethylene/1-octene copolymers and also for the preparation of an ethylene/1-hexene copolymer as comparative example 3 (CE3).

TABLE 1

Condition	Example 1	Example 2	CE3
Reaction Temperature ($^{\circ}\text{C}$)	76	80	74
C2 partial pressure (bar)	11.2	12.5	13.0
H2 partial pressure (bar)	0.034	0.035	0.0533
C8 partial pressure (bar)	0.027	0.023	
C6 partial pressure (Bar)			0.0857
C5 (pentane) partial pressure (bar)	2.51	2.5	2.4
Residence time (hrs)	2.9	4.2	6.4
Condensation rate wt (%)	2.7	1.4	6.0

Product Characteristics

- The product characteristics of Examples 1 and 2 are shown below in Table 2.

TABLE 2

Property	Example 1	Example 2
Non - annealed Density (g/cm^3)	0.918	0.918
MI ₂ (2.16 kg/190 $^{\circ}\text{C}$)	1.13	1.07
Melt elastic modulus $G'(G''=500\text{Pa})$ Pa	39.9	39.60
Activation energy of flow Ea (kJ/mol)	34.1	35.3
CDBI (%)		54.06
C _{pf}		1.38
Mw/Mn (Standard GPC - uncorrected for LCB)	3.0	3.3

Methods of test

Melt index (190/2.16) was measured according to ISO 1133.

Density (non-annealed) was measured using a density column according to ISO 1872/1 method except that the melt index extrudates were conditioned on a plastic plaque for 30 minutes at 23°C before immersion in the density gradient columns. 2 samples were taken, and put in the density gradient column. The density value of the sample that sunk deeper was taken after 20 minutes.

Density (annealed) was measured using a density column according to ISO 1872/1 method except that the melt index extrudates were annealed in boiling water for 30 minutes. It was then cooled down in the water without further heating for 60 minutes. 2 samples were taken, washed with isopropanol and put in the density gradient column. The density value of the sample that sunk deeper was taken after 20 minutes.

15 **Standard Gel Permeation Chromatography Analysis for Molecular Weight**

Distribution (Mw/Mn) determination

Apparent molecular weight distribution and associated averages, uncorrected for long chain branching, were determined by Gel Permeation Chromatography using a GPCV 2000 from Waters. Acquisition is done using Alliance software from the same supplier.

20 The apparatus settings were the following:

Column temperature: 150°C

Injector temperature: 150°C

Pump temperature: 50°C

Injection volume: 217,5 µl

25 Elution time: 60 min

Eluant: 1,2,4-Trichlorobenzene stabilised with 0.05% BHT

Flow rate: 1 ml/min

Columns set: 2 Shodex AT806MS + 1 Waters HT2 with a plate count (at half height) of typically 26,000

30 Detector: differential refractometer

Prior the elution, the polyethylene samples were dissolved at 150°C for 2 hours with stirring in 1,2,4 Trichlorobenzene stabilised with 0.05% BHT. The polyethylene concentration is 0.1% w/w.

A relative calibration was constructed using narrow polystyrene standards. The molecular weight and the solution concentrations are listed in the below table.

PS Standard (Vial number)	Molecular weight (PS)	Polydispersity (PD)	Mass (mg) for 30 ml of solvent
1	76600	1.03	34.125
2	3900000 50400	1.05 1.03	6.75 42.75
3	1950000 30300	1.04 1.02	8.625 42.75
4	995000 21000	1.04 1.02	8.625 42.75
5	488400 9860	1.05 1.02	17.25 51.375
6	195000 2100	1.02 1.05	25.5 68.25

The elution volume, V , was recorded for each PS standards.

The PS molecular weight was converted in PE equivalent using the following Mark Houwink constants:

$$\alpha_{PS} = 0.67 \quad K_{PS} = 0.000175$$

$$\alpha_{PE} = 0.706 \quad K_{PE} = 0.00051$$

The calibration curve $Mw_{PE} = f(V)$ was then fitted with a 3rd polynomial equation.

All the calculations are done with Millennium 32 software from Waters.

This calibration has been checked against the NIST certified polyethylene BRPE0 the values obtained being 53,000 for Mw and 19,000 for Mn .

Dynamic rheological measurements are carried out, according to ASTM D 4440, on a dynamic rheometer (e.g., ARES) with 25 mm diameter parallel plates in a dynamic mode under an inert atmosphere. For all experiments, the rheometer has been thermally stable at 190°C for at least 30 minutes before inserting the appropriately stabilised (with anti-

oxidant additives), compression-moulded sample onto the parallel plates. The plates are then closed with a positive normal force registered on the meter to ensure good contact. After about 5 minutes at 190°C, the plates are lightly compressed and the surplus polymer at the circumference of the plates is trimmed. A further 10 minutes is allowed for thermal stability and for the normal force to decrease back to zero. That is, all measurements are carried out after the samples have been equilibrated at 190°C for about 15 minutes and are run under full nitrogen blanketing.

Two strain sweep (SS) experiments are initially carried out at 190°C to determine the linear viscoelastic strain that would generate a torque signal which is greater than 10% of the lower scale of the transducer, over the full frequency (e.g. 0.01 to 100 rad/s) range. The first SS experiment is carried out with a low applied frequency of 0.1 rad/s. This test is used to determine the sensitivity of the torque at low frequency. The second SS experiment is carried out with a high applied frequency of 100 rad/s. This is to ensure that the selected applied strain is well within the linear viscoelastic region of the polymer so that the oscillatory rheological measurements do not induce structural changes to the polymer during testing. In addition, a time sweep (TS) experiment is carried out with a low applied frequency of 0.1 rad/s at the selected strain (as determined by the SS experiments) to check the stability of the sample during testing.

20 Measurement of Melt Elastic Modulus G' ($G''=500$ Pa) at 190°C:

The frequency sweep (FS) experiment is then carried out at 190°C using the above appropriately selected strain level and the dynamic rheological data thus measured are then analysed using the rheometer software (viz., Rheometrics RHIOS V4.4 or Orchestrator Software) to determine the melt elastic modulus G' ($G'' = 500$ Pa) at a constant, reference value (500 Pa) of melt viscous modulus (G'').

Flow Activation Energy (E_a) Measurement

The bulk dynamic rheological properties (e.g., G' , G'' and η^*) of all the polymers were then measured at 170°, 190° and 210°C. At each temperature, scans were performed as a function of angular shear frequency (from 100 to 0.01 rad/s) at a constant shear strain appropriately determined by the above procedure.

The dynamic rheological data was then analysed using the Rheometrics Software. The following conditions were selected for the time-temperature (t-T) superposition and the determination of the flow activation energies (E_a) according to an Arrhenius equation, $a_T = \exp(E_a/kT)$, which relates the shift factor (a_T) to E_a :

5

Rheological Parameters:	$G'(\omega)$, $G''(\omega)$ & $\eta^*(\omega)$
Reference Temperature:	190°C
Shift Mode:	2D (i.e., horizontal & vertical shifts)
Shift Accuracy:	High
Interpolation Mode:	Spline

10

Determination of CDBI (as Determined by Temperature Rising Elution Fractionation (TREF)).

Temperature Rising Elution Fractionation (TREF), as described for example in Wild *et al.*, *J. Poly. Sci., Poly. Phys. Ed.*, vol. 20, p. 441 (1982), is a technique used for the analysis of the comonomer (composition) distribution in semi-crystalline polymers and more specifically for the analysis of the short chain branching distribution (SCBD) in linear low density polyethylene (LLDPE) and tacticity in polypropylene (PP).

In particular, the TREF solubility distribution curve for a copolymer can be readily used to determine a "Composition Distribution Breadth Index" ("CDBI") which has been defined (e.g., in US Patent No. 5206075 and PCT publication WO93/03090) as a measure of composition distribution. The solubility distribution curve is a plot of the weight fraction of the copolymer that is solubilised as a function of temperature. This is then converted to a weight fraction versus composition distribution curve, where the CDBI is determined by establishing the weight percentage of a sample that has comonomer content within 50% of the median comonomer content on each side of the median. It is also commonly assumed that all fractions have $M_n \geq 15000$ in the CDBI measurement for simplifying the correlation of composition with elution temperature.

The TREF apparatus was supplied by the PolymerChar Company with the following components:

30

- 5 ○ A special oven to perform the crystallization and elution temperature ramps. An Agilent GC 7890 oven which is split in two parts: the top oven (where the Valco valves, a vapor sensor are installed) and the main oven where the five 60 mL vessels as well as the TREF column are installed. The polymer samples are dissolved in these vessels.
- 10 ○ The TREF column, size: 7.8 mm (internal diameter) x 15 cm (length), packed with stainless steel beads (HPLC column).
- An infrared detector.
- A dispenser (25 mL syringe).
- An Agilent Isocratic 1200 series pump.
- A 2.5 L solvent bottle (TCB).
- A 2.5 L waste bottle for the contaminated solvent.
- A computer with the software developed by PolymerChar to program analysis, for acquisition and data processing.

<u>Equipment</u>	
Column size (mm)	7.8 (diameter) x 150 (length)
Solvent	TCB
Packing beads	Stainless steel
Detector	IR
Wavelength (μm)	3.42
<u>Sample preparation</u>	
Concentration of the PE solution (mg/ml)	3.2
Injected volume on the column (ml)	0.4
Dissolution temperature (°C)	150
<u>Crystallization step</u>	
Temperature range (°C)	95 – 35
Crystallization rate (°C/min)	0.5
Annealed time (min)	20 min at 35°C
<u>Elution step</u>	
Elution rate (ml/min)	0.5 (continuous)
Temperature range (°C)	35 - 120

Determination of C_{pf} **(a) Comonomer or Short Chain Branching (SCB) Distribution by GPC/FTIR****5 Measurement of Comonomer (SCB) Content vs. Molecular Weight**

The comonomer content as a function of molecular weight was measured by coupling a Nicolet ESP protégé 460 Fourier transform infrared spectrometer (FTIR) to Polymer Laboratories (PL 210) Gel Permeation Chromatograph (GPC) with a transfer line thermally controlled at 160°C. The setting up, calibration and operation of this system together with the method for data treatment are summarised below:

10

Preparation of polymer solution (in a heat block with constant agitation) :

- Polymer Concentration: 2 g/l (20 mg in a vial of 10 ml)
- Solvent: 1,2,4 trichlorobenzene « dry » of Biosolve and stabilized with BHT (ionol CP) at 0.2 g/l
- 15 ○ Dissolution temperature: 160 °C
- Duration : 1 h (30 minutes without agitation and 30 minutes with agitation at 150 revolutions/minute)

GPC Conditions (PL 210 Polymer Laboratories)

- Columns set: 2 PL mixed-B (30 cm length 30; 10 µm beads; 5 µm sintered)
- 20 ○ Mobile Phase: 1,2,4 trichlorobenzene « dry » of Biosolve and non-stabilised
- Oven Temperature: 160 °C
- Flow rate : 1 ml/ min
- Injection Volume: 500 µl
- Transfer line temperature: 160 °C.

25 FTIR (Nicolet Protégé 460) Spectrometer

Flow cell commercialised by PL Laboratories and placed inside the Nicolet spectrometer:

- Flow cell volume: 70 µl
- Flow cell path: 1 mm
- 30 ○ Flow cell window : calcium fluoride
- FTIR Detector: InSb cooled by liquid nitrogen
- Number of scan : 16

- Resolution : 4 cm⁻¹
- Spectral Range : 3000 to 2700 cm⁻¹

Software

Software acquisition spectres: OMNIC (version 6.0) from Thermo-Nicolet

- 5 Software exploitation: CIRRUS from Polymer Laboratories (Cirrus GPC/multidetector 2001-2003).

Calibration

The apparent molecular weights, and the associated averages and distribution, uncorrected for long chain branching, were determined by Gel Permeation

- 10 Chromatography using a PL210, with 2 PL mixed-B and a FTIR (InSb) detector. The solvent used was 1,2,4 Trichlorobenzene at 160°C, which is stabilised with BHT, of 0.2 g/litre concentration and filtered with a 0.45 µm Osmonics Inc. silver filter. Polymer solutions of 2.0 g/litre concentration were prepared at 160°C for one hour with stirring only at the last 30 minutes. The nominal injection volume was set at 500 µl and the nominal
- 15 flow rate was 1 ml/min.

A relative calibration was constructed using 10 narrow molecular weight linear polystyrene standards:

PS Standard	Molecular Weight
1	7 500 000
2	2 560 000
3	841 700
4	280 500
5	143 400
6	63 350
7	31 420
8	9 920
9	2 930
10	580

- The elution volume, V, was recorded for each PS standards. The PS molecular
- 20 weight was then converted to PE equivalent using the following Mark Houwink parameters

$k_{ps}=1.21 \times 10^{-4}$, $\alpha_{ps}=0.707$, $k_{pe}=3.92 \times 10^{-4}$, $\alpha_{pe}=0.725$. The calibration curve $M_w_{PE} = f(V)$ was then fitted with a first order linear equation.

Calibration IR for Short Chain Branching (SCB)

The chemometric model employed within the Polymer Laboratories Softwares (e.g., CIRRUS, GPC/Multidetector) involved the calibration of the FTIR detector using Standards, including the following:

Standard	CH ₃ /1000 C
CF24-7	15.4
CF24-10	11.1
CF 25-24	9.4
CF25-1	1.3
CF25-3	2.7
CF25-5	3.7
CF25-6	4.2

In order to characterize the degree to which the comonomer is concentrated in the high molecular weight part of the polymer, the GPC/FTIR data were used to calculate a parameter named comonomer partitioning factor, C_{pf} .

(b) Comonomer Partitioning Factor (C_{pf})

The comonomer partitioning factor (C_{pf}) is calculated from GPC/FTIR data, as has previously been described in WO 97/44371 which is herein incorporated by reference. It characterizes the ratio of the average comonomer content of the higher molecular weight fractions to the average comonomer content of the lower molecular weight fractions. Higher and lower molecular weight are defined as being above or below the median molecular weight respectively, that is, the molecular weight distribution is divided into two parts of equal weight. C_{pf} is calculated from the following Equation:

$$C_{pf} = \frac{\frac{\sum_{i=1}^n w_i \cdot c_i}{\sum_{i=1}^n w_i}}{\frac{\sum_{j=1}^m w_j \cdot c_j}{\sum_{j=1}^m w_j}}$$

where c_i is the mole fraction comonomer content and w_i is the normalized weight fraction as determined by GPC/FTIR for the n FTIR data points above the median molecular weight. c_j is the mole fraction comonomer content and w_j is the normalized weight fraction as determined by GPC/FTIR for the m FTIR data points below the median molecular weight. Only those weight fractions, w_i or w_j which have associated mole fraction comonomer content values are used to calculate C_{pf} . For a valid calculation, it is required that n and m are greater than or equal to 3. FTIR data corresponding to molecular weight fractions below 5,000 are not included in the calculation due to the uncertainties present in such data.

Film Characteristics

Blown films of 25 μm thickness were prepared from the copolymers prepared in the above examples 1 and 2 of the invention. The details of the extrusion conditions and the mechanical and optical properties of the resultant films are given below in Table 3. Comparative films based on examples 5 and 6 of WO 08/074689 (CE1 and CE2) and also CE3 described above are shown below in Table 4.

Dart Drop Impact strength (DDI) was measured by ASTM D1709-98 (Method A), using a Tufnol (Carp Brand to BS.6128) 60g Dart Head and the diameter of the incremental weights is equal to the diameter of the dart head (38.10 mm), **haze** by ASTM D1003, **gloss (45°)** by ASTM D2457, **tear strength** (Elmendorf) by ASTM 1922, **tensile properties** and **secant modulus** (1%) according to ISO 1184.

TABLE 3

Copolymer		Example 1	Example 2
Non - annealed density (pellets) g/cm ³		0.918	0.918
MI (2.16) g/10min (pellets)		1.13	1.07
<u>Extrusion parameters</u>			
Melt pressure (bar)		221	227
Melt temperature (°C)		216	215
Motor load (A)		80	73
Screw speed (rpm)		55	58
Air temperature (°C)		24	19
Specific output (calculated from Output/Motor load (kg/h/A))		0.63	0.68
<u>Mechanical properties</u>			
Dart Drop Impact (g)		2075	2208
Elmendorf tear strength (g)	MD	243	221
	TD	485	477
Tensile stress at yield (MPa)	MD	10.8	
	TD	10.9	
Tensile stress at break (MPa)	MD	65.7	
	TD	66.8	
Elongation at break (%) (MPa)	MD	570	
	TD	678	
Secant modulus 1% (MPa)	MD	210	
	TD	178	
<u>Optical properties</u>			
Haze (%)		11.3	10.2
Gloss 45° (%)		51.5	58.3

TABLE 4

Copolymer		CE 1	CE 2	CE3
Annealed density (pellets) g/cm ³		0.921	0.919	0.918*
MI (2.16) g/10min (pellets)		1.3	1.24	2.00
<u>Extrusion parameters</u>				
Melt pressure (bar)		163	184	190
Melt temperature (°C)		216	216	197
Motor load (A)		70	76	71
Screw speed (rpm)		54	54	55
Air temperature (°C)		18	18	21
Specific output (calculated from Output/Motor load (kg/h/A))		0.71	0.66	0.70
<u>Mechanical properties</u>				
Dart Drop Impact (g)		1550	1707	1602
Elmendorf tear strength (g/25µm)	MD	235	216	284
	TD	470	445	519
Tensile stress at yield (MPa)	MD	10.9	9.6	
	TD	10.3	9.7	
Tensile stress at break (MPa)	MD	64.9	66.0	
	TD	60.8	60.5	
Elongation at break (%) (MPa)	MD	588	566	
	TD	697	669	
Secant modulus 1% (MPa)	MD	164	155	
	TD	168	166	
<u>Optical properties</u>				
Haze (%)		8.8	6.0	20.0
Gloss 45° (%)		62	69	53.5

5 *Note: density reported for CE3 is non-annealed

Extruder & extrusion characteristics**Extruder:**

CMG (Costruzione Meccaniche Gallia) 1200 TSA

5	Screw diameter	55mm
	Screw L/D ratio	30
	Die diameter/gap	150/2.2 mm
	Screen pack	flat

10 **Extrusion:**

Temperature profile:

	Screw	200/210/210/210/210°C
	Die	210/210/220/225°C
	Output	50kg/h
15	Take-off speed	30m/min
	Blow-up ratio	2.5:1
	Frostline height	430mm
	Film thickness	25µm

20

Claims

1. A copolymer of ethylene and an α -olefin having C7 to C12 carbon atoms, said copolymer having
 - (a) a density (D) in the range 0.900 – 0.940 g/cm³,
 - (b) a melt index MI₂ (2.16 kg, 190°C) in the range of 0.01 - 50 g/10 min,
 - (c) a melt elastic modulus G' (G'' = 500 Pa) in the range 20 to 150 Pa, and
 - (d) a tear strength (MD) of ≥ 220 g,
 a tear strength (TD) of ≥ 470 g, and
 a Dart Drop Impact (DDI) of ≥ 1800 g
 of a blown film having a thickness of 25 μ m produced from the copolymer, where MD is referred to the machine direction and TD is the transverse direction of the blown film.

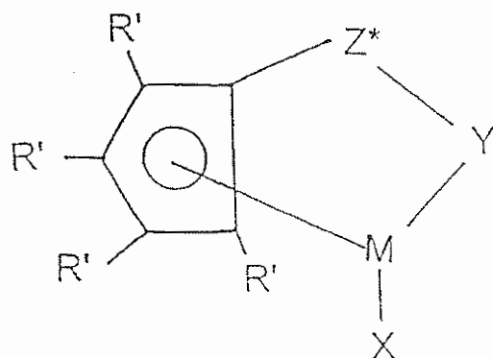
2. A copolymer according to claim 1 wherein the copolymer has a Compositional Distribution Breadth Index (CDBI) in % satisfying the equation

$$\text{CDBI} \leq (-192\text{D} + 241.5)$$

3. A copolymer according any of preceding claims having a comonomer partitioning factor Cpf ≥ 1.20 .

4. A copolymer according to any of the preceding claims wherein the density (D) is in the range 0.910 – 0.935 and preferably in the range 0.915 – 0.925.
5. A copolymer according to any of the preceding claims wherein the melt index MI_2 is in the range 0.05 – 20 g/10 min and preferably in the range 0.5 – 5 g/10 min.
6. A copolymer according to any of the preceding claims wherein the Dart Drop Impact (DDI) is ≥ 2000 g and preferably ≥ 2200 g.
7. A copolymer according to any of the preceding claims wherein the melt elastic modulus G' ($G'' = 500$ Pa) in the range 35 to 80 Pa and preferably in the range 35 – 45 Pa.
8. A copolymer according to any of the preceding claims having an activation energy of flow (E_a) in the range 28 – 45 kJ/mol.
9. A copolymer according to any of the preceding claims wherein the molecular weight distribution (MWD) is in the range 2.5 – 4.5 and preferably in the range 3.0 – 4.0.
10. A copolymer according to any of the preceding claims wherein the α -olefin is 1-octene.

11. A copolymer according to any of the preceding claims prepared by polymerization in the presence of a metallocene catalyst system.
12. A copolymer according to claim 11 wherein the metallocene catalyst system comprises a monocyclopentadienyl metallocene complex.
13. A copolymer according to claim 12 wherein the metallocene complex has the general formula:



wherein:-

R' each occurrence is independently selected from hydrogen, hydrocarbyl, silyl, germyl, halo, cyano, and combinations thereof, said R' having up to 20 nonhydrogen atoms, and optionally, two R' groups (where R' is not hydrogen, halo or cyano) together form a divalent derivative thereof connected to adjacent positions of the cyclopentadienyl ring to form a fused ring structure;

X is a neutral η^4 bonded diene group having up to 30 non-hydrogen atoms, which forms a π -complex with M;

Y is -O-, -S-, -NR*-, -PR*-;

M is titanium or zirconium in the + 2 formal oxidation state;

Z* is SiR*₂, CR*₂, SiR*₂SiR*₂, CR*₂CR*₂, CR*=CR*, CR*₂SiR*₂, or GeR*₂, wherein:

R* each occurrence is independently hydrogen, or a member selected from hydrocarbyl, silyl, halogenated alkyl, halogenated aryl, and combinations thereof, said

R* having up to 10 non-hydrogen atoms, and optionally, two R* groups from Z* (when R* is not hydrogen), or an R* group from Z* and an R* group from Y form a ring system.

14. A copolymer according to claim 11 wherein the polymerization is performed in the gas phase.
15. A copolymer according to claim 12 wherein the gas phase polymerization is performed in a fluidised bed reactor.
16. A film comprising a copolymer of ethylene and an α -olefin having C7 to C12 carbon atoms according to any of the preceding claims.
17. A blown film comprising a copolymer of ethylene and an α -olefin having C7 to C12 carbon atoms, said copolymer having
 - (a) a density in the range 0.900 – 0.940 g/cm³,
 - (b) a melt index MI₂ (2.16 kg, 190°C) in the range of 0.01 - 50 g/10 min, and
 - (c) a melt elastic modulus G' (G'' = 500 Pa) in the range 20 to 150 Pa
 wherein said film when having a thickness of 25 μ m exhibits :
 - a tear strength (MD) of $\geq$ 220 g
 - a tear strength (TD) of $\geq$ 470 g, and
 - a Dart Drop Impact (DDI) $\geq$ 1800 g
 wherein MD is referred to the machine direction and TD is the transverse direction of the film.

18. A blown film according to claim 17 wherein the α -olefin is 1-octene.