A process for the production of random or impact copolymers of propylene exhibiting bimodality comprising the following steps: (a) contacting propylene and one or more alpha-olefin(s) with a catalyst system comprising (i) a catalyst precursor, which includes titanium, magnesium and an electron donor; (ii) a hydrocarbylaluminum cocatalyst; and (iii) a selectivity control agent in one or more reactors, under polymerization conditions; and (b) introducing into the reactor(s), or after polymerization into the propylene copolymer, one or more saturated alicyclic hydrocarbon(s), said hydrocarbon(s) being liquid at process temperature, non-polar, essentially amorphous, and containing less than about 15 percent by weight paraffin wax, in an amount of about 0.1 to about 20 parts by weight of hydrocarbon(s) per 100 parts by weight of propylene copolymer.
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PROCESS FOR THE PRODUCTION OF BIMODAL PROPYLENE COPOLYMERS

This application claims the benefit of United States Provisional Applications numbered 60/008367 and 60/008417, both filed on December 8, 1995.

Technical Field

This invention relates to a process for the production of polypropylene copolymers, both random and impact.

Background Information

Random copolymers of propylene and one or more alpha-olefins generally exhibit good clarity, low temperature impact strength, and melt sealing characteristics. It would be advantageous, however, for certain applications such as food containers if these random copolymers could be provided with further improvements in clarity and impact strength as well as processability.

With respect to impact polypropylene copolymers: Polypropylene homopolymers are widely used for many consumer and industrial applications where high impact strength at low temperatures is not required. For applications requiring a high level of low temperature impact strength, so-called "impact polypropylene copolymers" are used. These polypropylene copolymers are usually manufactured by the incorporation of an elastomeric impact modifier, e.g., an ethylene/propylene copolymer rubber (EPR), into a homopolymer matrix either by blending the homopolymer with the EPR or by producing the copolymer in situ. Impact copolymers generally have excellent low temperature properties, but suffer from a deficiency known as "stress whitening" or "blushing". This phenomenon occurs when a molded impact copolymer is stressed or impacted, and results
in a white mark on the surface of the molded copolymer at the point of impact. These white marks are obviously undesirable in such consumer items as housewares, appliances, and automotive parts. To overcome this deficiency and produce a stress whitening resistant product, a three reactor process was proposed. It was economically advantageous to accomplish this result in two reactors, and this was achieved, for example, by the process described in United State Patent 4,882,380.

In both the three reactor and two reactor processes, however, it was found that gains in impact strength were desirable especially in products such as automotive parts, for example, bumpers and battery casings, in which high impact strength is so important.

**Disclosure of the Invention**

An object of this invention, therefore, is to provide a process for the production of a random and impact copolymers of propylene and one or more alpha-olefins, which exhibit improved impact strength and processability.

Other objects and advantages will become apparent hereinafter.

According to the present invention, the above object is met by a process for the production of copolymers of propylene, which exhibit bimodality, comprising the following steps:

(a) contacting propylene and one or more alpha-olefin(s) with a catalyst system comprising (i) a catalyst precursor, which includes titanium, magnesium and an electron donor; (ii) a hydrocarbylaluminum cocatalyst; and (iii) a selectivity control agent in one or more reactors, under polymerization conditions; and

(b) introducing into the reactor(s), or after polymerization into the propylene copolymer, one or more saturated alicyclic hydrocarbon(s), said hydrocarbon(s) being liquid at process temperature, non-polar, essentially amorphous, and containing less
than about 15 percent by weight paraffin wax, in an amount of about 0.1 to about 20 parts by weight of hydrocarbon(s) per 100 parts by weight of propylene copolymer.

A second embodiment of the invention is represented by (i) a copolymer of propylene and one or more alpha-olefins, and blended therewith (ii) one or more saturated alicyclic hydrocarbon(s), said hydrocarbon(s) being liquid at blending temperature, non-polar, essentially amorphous, and containing less than about 15 percent by weight paraffin wax, in an amount of about 0.1 to about 20 parts by weight of hydrocarbon(s) per 100 parts by weight of component (i), said copolymer, after blending, exhibiting bimodality.

A third embodiment is an in situ process for the production of bimodal impact polypropylene copolymers comprising an ethylene/propylene or 1-butene copolymer incorporated into a matrix of propylene homopolymer or copolymer comprising the following steps:

(a) contacting propylene or propylene and one or more alpha-olefin(s) with a catalyst system comprising (i) a catalyst precursor, which includes titanium, magnesium and an electron donor; (ii) a hydrocarbylaluminum cocatalyst; and (iii) a selectivity control agent in a first reactor, under polymerization conditions, such that a matrix of homopolymer of propylene or copolymer of propylene and alpha olefin(s), which includes active catalyst, is produced;

(b) passing the matrix from step (a) into a second reactor;

(c) introducing into the second reactor, under polymerization conditions, a sufficient amount of ethylene and propylene or 1-butene to form, in the matrix, an ethylene/propylene or 1-butene copolymer;

and

(d) introducing into the first and/or second reactor or, after polymerization into the impact polypropylene copolymer, one or more saturated alicyclic hydrocarbon(s), said hydrocarbon(s) being liquid at process temperature, non-polar, essentially amorphous, and containing
less than about 15 percent by weight paraffin wax, in an amount of about 0.1 to about 20 parts by weight of hydrocarbon(s) per 100 parts by weight of impact polypropylene copolymer.

A fourth embodiment of the invention is represented by an impact polypropylene copolymer comprising (i) an ethylene/propylene or 1-butene copolymer incorporated into a matrix of propylene homopolymer or copolymer and blended therewith (ii) one or more saturated alicyclic hydrocarbon(s), said hydrocarbon(s) being liquid at blending temperature, non-polar, essentially amorphous, and containing less than about 15 percent by weight paraffin wax, in an amount of about 0.1 to about 20 parts by weight of hydrocarbon(s) per 100 parts by weight of component (i), said impact copolymer exhibiting bimodality after blending.

**Description of the Preferred Embodiment(s)**

The process steps and conditions and the catalyst system used in the reactor(s) are exemplified in United States Patent 4,414,132; 4,882,380; and 5,093,415, and the reactors are preferably gas phase reactors such as the fluidized bed reactor described in United States Patent 4,482,687. Other transition metal catalyst systems useful in the preparation of polypropylene can also be used including, for example, metallocene catalyst systems such as those described in United States Patents 4,937,299 and 5,317,036. Many of the transition metal catalyst systems are referred to as Ziegler-Natta catalyst systems.

A typical catalyst system is made up of a catalyst precursor, which includes magnesium, titanium, chlorine, and an electron donor; an organoaluminum compound, which can be referred to as a cocatalyst; and a selectivity control agent. The selectivity control agent is defined as an additive, which modifies the catalyst precursor
in such a manner as to increase the overall percentage of isotactic crystalline polymer produced.

The catalyst precursor can be obtained by halogenating a magnesium compound having the formula MgR_{2-n}X_n wherein each R is independently an alkoxide, aryloxide, or carboxylate group, X is a halogen, and n is 0 or 1 with a tetravalent titanium halide in the presence of a halohydrocarbon and an electron donor; contacting the halogenated product with a tetravalent titanium halide, optionally treating the resulting solid with an aromatic acid halide; washing the halogenated product to remove unreacted titanium compounds; and recovering the solid product.

The atomic or mole ratios of catalyst components are generally as follows:

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<td>3:1 to 30:1</td>
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<td>1:1 to 5:1</td>
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<td>Cocatalyst to selectivity control agent</td>
<td>0.1:1 to 100:1</td>
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Suitable halogen containing magnesium compounds that can be used to prepare the catalyst precursor are alkox and arylox magnesium halides such as isobutoxy magnesium chloride, ethoxy magnesium bromide, phenoxy magnesium iodide, cumyloxy magnesium bromide, and naphthenoxy magnesium chloride.

Magnesium compounds which can be used are magnesium dialkoxides, diaryloxides, and carboxylates having 2 to 24 carbon atoms such as magnesium di-isopropoxide, magnesium diethoxide,
magnesium dibutoxide, magnesium diphenoxide, magnesium dinaphthenoxyde, and ethoxy magnesium isobutoxide, magnesium dioctanoate, and magnesium dipropionate.

Magnesium compounds having one alkoxide and aryloxide group can also be employed. Examples of such compounds are ethoxy magnesium phenoxide and napthenoxide magnesium isoamyloxide. Also suitable are compounds having one carboxylate group and one alkoxide, aryloxide, or halide group such as ethoxy magnesium octanoate, phenoxy magnesium propionate, and chloromagnesium docanoate.

Suitable halides of tetravalent titanium include arloxy- or alkoxy di- and tri-halides, such as dihexoxy titanium dibromide, isoproxyloxy titanium triiodide, and phenoxy titanium trichloride, are preferred.

The halohydrocarbons employed can be aromatic or aliphatic. Each aliphatic halohydrocarbon preferably contains from 1 to 12 carbon atoms and at least 2 halogen atoms. The aliphatic halohydrocarbons include carbon tetrachloride, dibromomethane, trichloromethane, 1,2-dichloroethane, dichlorobutane, 1,1,3-trichloroethane, trichlorocyclohexane, dichlorofluoroethane, trichloropropane, trichlorofluoroctane, dibromodifluorodecane, hexachloroethane, and tetrachloroisooctane. Carbon tetrachloride and 1,1,3-trichloroethane are preferred. Aliphatic halohydrocarbons containing only one halogen atom per molecule, such as butyl chloride and amyl chloride, can also be employed. Suitable aromatic halohydrocarbons include chlorobenzene, bromobenzene, dichlorobenzene, dichloro bromobenzene, naphthyl chloride, chlorotoluene, and dichlorotoluene. Chlorobenzene is the most preferred aromatic halohydrocarbon.

Suitable electron donors, which can be used in the Mg/Ti complex (as an inside electron donor) separately or complexed with the
organoaluminum compound, are ethers, mono- or polycarboxylic acid esters, ketones, phenols, amines, amides, imines, nitriles, silanes, phosphines, phosphites, stilbenes, arsines, phosphoramides, and alcoholates. The selectivity control agent (the outside electron donor) is generally different from the inside electron donor.

Examples are esters of carboxylic acids such as ethyl and methyl benzoate, p-methoxy ethyl benzoate, ethylacrylate, methyl methacrylate, ethyl acetate, p-chloroethyl benzoate, p-amino hexyl benzoate, isopropyl napthenate, n-amyl toluate, ethyl cyclohexanoate, and propyl pivalate. Examples of amines are N,N,N',N' - tetramethylethylene diamine, 1,24-trimethyl piperazine, and 2,2,6,6-tetramethyl piperidine.

The preferred electron donor for use in preparing the catalyst precursor (the inside electron donor) is ethyl benzoate. The preferred electron donor for use as a selectivity control agent (the outside electron donor) is para-ethoxy ethyl benzoate.

Another preferred combination of inside and outside electron donors follows:

(i) inside electron donor = a polycarboxylic acid ester containing two coplanar ester groups attached to adjacent carbon atoms; and

(ii) outside electron donor = a silicon compound containing a silicon oxygen carbon linkage

wherein the atomic ratio of aluminum in the hydrocarbyl aluminum cocatalyst to silicon in the silicon compound is in the range of about 0.5:1 to about 100:1 and the atomic ratio of said aluminum to the titanium in the catalyst precursor is in the range of about 5:1 to about 300:1.

The polycarboxylic acid ester is characterized by a molecularly rigid structure wherein two ester groups are attached to adjacent carbon atoms of the molecule and lie in a single plane. Such esters include: (a) polycarboxylic acid esters containing two ester groups
which are attached to ortho carbon atoms of a monocyclic or polycyclic aromatic ring, each of said ester groups being further linked to a branched or unbranched chain hydrocarbon radical; (b) polycarboxylic acid esters containing two ester groups which are attached to vicinal carbon atoms of a non-aromatic monocyclic or polycyclic ring and which lie in a syn configuration with respect to each other, each of said ester groups being further linked to a branched or unbranched chain hydrocarbon radical; and (c) polycarboxylic acid esters containing two ester groups which are attached to vicinal double bonded carbon atoms of an unsaturated aliphatic compound and which lie in a syn configuration which respect to each other, each of said ester groups being further linked to a branched or unbranched chain hydrocarbon radical.

Among the polycarboxylic acid esters which can be employed as inside electron donors are dimethyl phthalate, diethyl phthalate, di-n-propyl phthalate, diisobutyl phthalate, di-tert-butyl phthalate, diisooamyl phthalate, di-tertamyl phthalate, dineopentyl phthalate, di-e-ethylhexyl phthalate, di-2-ethyldecal phthalate, diethyl-1,2-fluorenedicarboxylate, diisoprophyl-1,2-ferrocenedicarboxylate, cis-diisobutyl-cyclobutane-1,2-dicarboxylate, endo-diisobutyl-5-norbornene-2,3-dicarboxylate and endo-diisobutyl-bicyclo [2.2.2]oct-5-ene-2,3-dicarboxylate, diisobutyl maleate, and diisooamyl citraconate. Diisobutyl phthalate is most preferred.

The silicon compounds employed as selectivity control agents (outside electron donors) in the catalyst system employed in the process of the invention contain at least one silicon-oxygen-carbon linkage. Suitable silicon compounds include compounds having the formula:

R<sub>m</sub>SiY<sub>n</sub>X<sub>p</sub>

wherein:

R is a hydrocarbon radical having 1 to 20 carbon atoms,
Y is -OR' or -OCOR' wherein R' is a hydrocarbon radical having 1 to 20 carbon atoms,

X is hydrogen or halogen,
m is an integer having a value of 0 to 3,
n is an integer having a value of 1 to 4,
p is an integer having a value of 0 or 1, and
m + n + p is equal to 4.

Each of R and R' can be the same or different, and, if desired, substituted with any substituent which is inert under the reaction conditions employed during polymerization. Preferably, R and R' contain from 1 to 10 carbon atoms when they are aliphatic or cycloaliphatic, and from 6 to 10 carbon atoms when they are aromatic.

Silicon compounds in which two or more silicon atoms are linked to each other by an oxygen atom may also be employed, provided that the requisite silicon-oxygen-carbon linkage is also present.

The hydrocarbyl aluminum cocatalyst can be represented by the formula R₃Al wherein each R is an alkyl, cycloalkyl, aryl, or hydride radical; at least one R is a hydrocarbyl radical; two or three R radicals can be joined in a cyclic radical forming a heterocyclic structure; each R can be alike or different; and each R, which is a hydrocarbyl radical, has 1 to 20 carbon atoms, and preferably 1 to 10 carbon atoms. Further, each alkyl radical can be straight or branched chain and such hydrocarbyl radical can be a mixed radical, i.e., the radical can contain alkyl, aryl, and/or cycloalkyl groups. Examples of suitable radicals are: methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tert-butyl, pentyl, neopentyl, hexyl, 2-methylpentyl, heptyl, octyl, isoctyl, 2-ethylhexyl, 5,5-dimethylhexyl, nonyl, decyl, isodecyl, undecyl, dodecyl, phenyl, phenethyl, methoxyphenyl, benzyl, tolyl, xylyl, naphthyl, naphthal, methylnaphthyl, cyclohexyl, cyclohexyl, and cyclooctyl.

Examples of suitable hydrocarbyl aluminum compounds are as follows: triisobutylaluminum, trihexylaluminum, di-
isobutylaluminum dihydride, hexylaluminum dihydride, di-
isobutylhexylaluminum, isobutyl dihexylaluminum, trimethylaluminum, triethylaluminum, tripropylaluminum, triisopropylaluminum, tri-n-butylaluminum, trioctylaluminum, tridecylaluminum, tridodecylaluminum, tribenzylaluminum, triphenylaluminum, trinaphthylaluminum, and tritoxyaluminum. The preferred hydrocarbyl aluminums are triethylaluminum, triisobutylaluminum, trihexylaluminum, di-isobutylaluminum hydride, and dihexylaluminum hydride.

The acid halide mentioned above as optional is the derivative of the ester compound used as an inside electron donor. Preferably, the halide is a chloride or bromide. The acid halide can contain 7 to 22 carbon atoms and one or more aromatic rings.

For random copolymers, the polymerization can be conducted in one or more reactors using gas phase, slurry, or solution processes; however, the polymerization is preferably carried out in one reactor and in the gas phase. For gas phase polymerizations, fluidized bed reactors are the reactors of choice. For impact copolymers, the same applies except that two or more reactors are used, preferably two reactors, and the second reactor, in particular, is preferably operated in the gas phase.

A typical fluidized bed reactor can be described as follows:

The bed is usually made up of the same granular resin that is to be produced in the reactor. Thus, during the course of the polymerization, the bed comprises formed polymer particles, growing polymer particles, and catalyst particles fluidized by polymerizable and modifying gaseous components introduced at a flow rate or velocity sufficient to cause the particles to separate and act as a fluid. The fluidizing gas is made up of the initial feed, feed, and cycle (recycle) gas, i.e., monomers and, if desired, modifiers and/or an inert carrier gas.
The essential parts of the reaction system are the vessel, the bed, the gas distribution plate, inlet and outlet piping, a compressor, a cycle gas cooler, and a product discharge system. In the vessel, above the bed, there is a velocity reduction zone, and in the bed a reaction zone. Both are above the gas distribution plate.

Each fluidized bed reactor is, generally, operated at a temperature in the range of about 40°C to about 150°C, and preferably about 60°C to about 120°C, and a pressure of about 50 psig to about 700 psig and preferably about 250 psig to about 550 psig. The velocity of the fluidizing gas is in the range of about 0.1 to about 3.0 feet per second and preferably about 0.5 to about 2.0 feet per second. The weight flow ratio of monomer to catalyst in the first reactor is about 1000:1 to about 100,000:1 and is preferably about 10,000:1 to about 100,000:1.

In a typical process for random copolymers:

(i) A mixture of propylene and one or more alpha-olefin(s) is introduced together with hydrogen and catalyst into a reactor. The alpha-olefin comonomers can each have 2 or 4 to 12 carbon atoms, and preferably have 2 or 4 to 8 carbon atoms, which can be, for example, ethylene, 1-butene, or 1-hexene, or various mixtures of alpha-olefins. The mole ratio of alpha-olefin to propylene is about 0.01 to about 0.06 and, preferably, is about 0.015 to about 0.04. The mole ratio of hydrogen to propylene alone or combined propylene and alpha-olefin is in the range of about 0.001 to about 0.45 and is preferably about 0.004 to about 0.1.

(ii) The combination of components and conditions, previously mentioned, lead to a random copolymer of propylene.

(iii) Hydrogen can be introduced into the reactor as a chain control agent. The mole ratio of hydrogen to combined propylene and alpha-olefin is about 0.1 to about 1.0 and is preferably about 0.1 to about 0.4.
(iv) The process of the invention calls for the addition of a hydrocarbon or mixture of hydrocarbons. On addition of the hydrocarbon(s), the random propylene copolymer increases its modality from monomodal to bimodal. Thus, the post-blend propylene copolymers can be characterized as bimodal.

In a typical process for the preparation of impact copolymers:

(i) Propylene or a mixture of propylene and one or more alpha-olefin(s) is introduced together with hydrogen and catalyst into the first reactor. The alpha-olefins can each have 2 or 3 to 12 carbon atoms, and preferably have 2 or 4 to 8 carbon atoms. Examples of alpha-olefin comonomers are ethylene, 1-butene, or 1-hexene, or various mixtures of alpha-olefins. The mole ratio of alpha-olefin to propylene is about 0.01 to about 0.06 and, preferably, is about 0.015 to about 0.04. The mole ratio of hydrogen to propylene alone or combined propylene and alpha-olefin is in the range of about 0.001 to about 0.45 and is preferably about 0.004 to about 0.1.

(ii) The combination of components and conditions, previously mentioned, lead to a mixture of homopolymer or copolymer of propylene together with active catalyst embedded in the polymer matrix. This mixture from the first reactor is transferred to the second reactor to which additional catalyst, cocatalyst, and selectivity control agent can be added although it is preferred that only cocatalyst be added to the second reactor. For some catalysts, none of these three components need be added.

(iii) In the second reactor, ethylene and propylene or 1-butene are introduced in a mole ratio of about 10 to about 100 moles of ethylene per mole of propylene or 1-butene, and preferably about 10 to about 50 moles of ethylene per mole of propylene or 1-butene. The combined ethylene/propylene or 1-butene addition is sufficient to provide a copolymer fraction of about 20 to about 45 percent by weight of copolymer based on the weight of the product, and preferably a
copolymer fraction of about 25 to about 30 percent by weight. As noted above, the product i.e., the final product, is an ethylene/propylene or 1-butene copolymer incorporated into a matrix of propylene homopolymer or copolymer. Hydrogen is also introduced into the second reactor together with the ethylene and propylene or 1-butene. The mole ratio of hydrogen to combined ethylene and propylene or 1-butene is about 0.1 to about 1.0 and is preferably about 0.1 to about 0.4. It should be noted that some or all of the propylene or 1-butene in the second reactor can come from the first reactor. The two reactors are operated continuously, in series.

In addition to adding the ethylene/propylene or 1-butene mixture to the second reactor, the process of the invention calls for the addition of a hydrocarbon or mixture of hydrocarbons. On addition of the hydrocarbon(s), the impact polypropylene copolymer increases its modality from monomodal to bimodal. Thus, the post-blend impact polypropylene copolymers can be characterized as bimodal.

The hydrocarbon(s) are saturated alicyclic hydrocarbon. They are unsubstituted. Alicyclic hydrocarbons are mixtures of aliphatic and cycloaliphatic hydrocarbons. The hydrocarbon(s) are generally liquid at ambient temperatures; are liquid at process temperature, non-polar, essentially amorphous, and contain less than 15 percent by weight paraffin wax, preferably less than one percent by weight paraffin wax. No paraffin wax would be most preferable, but this is not considered practical or necessary for the composition applications. The liquid hydrocarbons can have a viscosity in the range of about 200 to about 1000 SUS (Saybolt Universal Seconds) at 100°F (37.8°C) and preferably have a viscosity in the range of about 250 to about 800 SUS at 100°F. Examples of these hydrocarbons are Kaydol® 350, 380, and 550 hydrocarbons. Other examples are Tufflo® 6056 and 6026 hydrocarbons. It is noted that these Tufflo® hydrocarbons do not comply with the FDA regulations for food contact.
Kaydol® 350 is reported to contain 11.8 percent by weight paraffin wax and Kaydol® 550 is reported to contain less than one percent by weight paraffin wax. The molecular weight of these hydrocarbons is in the range of about 200 to about 5000. The hydrocarbon(s) can be present in the mixture of polypropylene copolymer and hydrocarbon(s) in an amount of about 0.1 to about 20 parts by weight of hydrocarbon(s) per 100 parts by weight of polypropylene copolymer, and are preferably present in an amount of about 1 to about 15 parts by weight. These values refer to total hydrocarbons and total polypropylene copolymer. In any case, the amount of hydrocarbon(s) should be such that the surface of each particle of propylene copolymer resin is essentially free of these hydrocarbon(s). The hydrocarbon(s) are also miscible with the propylene copolymer at process temperatures, and, in the suggested proportions, reside in the amorphous phase of the propylene copolymer.

For the purposes of this specification, extrusion processes shall be considered to include conventional extrusion processes such as blown tubular film extrusion (see discussion in United States Patent 4,814,135), and pipe and sheet extrusion, and blow molding, injection molding, rotational molding, and slot casting.

In the event that it is desired to use blending techniques other than in situ blending, the hydrocarbon(s) are usually dry blended with the propylene copolymer post-polymerization and prior to extrusion (preblending), but the hydrocarbon(s) and resin can be blended in the extruder itself under melt processing conditions, if desired. Preblending is preferable, however, since it shortens the mixing time and is a key factor in achieving uniform distribution of the hydrocarbon in the resin. In the case of pelletized propylene copolymer, the propylene copolymer is in the molten state when the blending is initiated. The propylene copolymer mixes readily with the hydrocarbon(s) without the use of heat except, as noted, when it is in
pelletized form. Preblending can be carried out at ambient or elevated temperatures, however. Useful mixers and extruders are conventional off-the-shelf equipment. Mixers, which can be used to blend the resin and the liquid hydrocarbon, are, for example, Banbury™ or other internal mixers, two roll mills, Baker Perkins™ or similar sigma blade mixers, ribbon blenders, and Henschel™ mixers. As noted, extruders can also be used to mix the resin and the hydrocarbon(s). Blending can also be effected by injecting the hydrocarbon(s) into fluidized propylene copolymer.

The preferred blending technique is to add the hydrocarbon(s) to the polymerization reactor. The advantage of this technique is improved homogeneity of the blend with an attendant improvement in many of the improved properties achieved in dry or melt blending. It will be understood that sufficient hydrocarbon(s) have to be added to the reactor to provide the amount set forth above for the blend. In the case of impact copolymers, it is preferred to add the hydrocarbon(s) to the first reactor or prior to the second reactor.

Extruders and processes for extrusion are described in United States patents 4,169,679; 4,814,135; 4,857,600; 5,076,988; and 5,153,382. Examples of various extruders are a single screw type such as one modified with a blown film die and air ring and continuous take off equipment; a blown film extruder; and a slot cast extruder. Twin screw extruders can also be considered. A typical single screw type extruder can be described as one having a hopper at its upstream end and a die at its downstream end. The hopper feeds into a barrel, which contains a screw. At the downstream end, between the end of the screw and the die, is a screen pack and a breaker plate. The screw portion of the extruder is considered to be divided up into three sections, the feed section, the compression section, and the metering section, and multiple heating zones from the rear heating zone to the front heating zone, the multiple sections and zones running from
upstream to downstream. If it has more than one barrel, the barrels are connected in series. The length to diameter ratio of each barrel is in the range of about 16:1 to about 30:1. The extrusion can take place at temperatures in the range of about 160 to about 270 degrees C, and is preferably carried out at temperatures in the range of about 180 to about 240 degrees C. In wire coating, where the material is crosslinked after extrusion, the die of the crosshead feeds directly into a heating zone, and this zone can be maintained at a temperature in the range of about 130°C to about 260°C, and preferably in the range of about 170°C to about 220°C.


An important advantage of this invention is the improvement in the Notched Izod Impact Strength at 23 degrees C and 0 degrees C as measured under ASTM D-256. Further, there is an improvement in clarity. In the case where the hydrocarbon(s) are introduced into the reactor(s), it is noted that the product is not sticky and does not foul the reactor; and the static is reduced. In addition, the copolymers exhibit bimodality.

Other advantages of the blend of propylene copolymer and hydrocarbon(s) are that the processability and one or more properties of the ultimate product (as measured on films or plaques) are improved when the blend is compared with the same or similar propylene copolymers having, for example, similar densities, melt indices, and/or melt flow ratios, without the hydrocarbon(s), i.e., there is essentially no bleeding; there are essentially no hydrocarbon(s) on the surface of each resin particle or on the surface of the articles of manufacture
produced by the extrusion of the polypropylene(s); the ESCR; die swell, diameter swell, shrinkage, and melt fracture are reduced; surfaces are smooth; and gels are reduced in in situ blends. Further, there is improvement in extensional viscosity; tangent delta (enhanced chain entanglement/less orientation/higher dart drop); beta transition temperature; spiral flow; and shear thinning. The accompanying bimodality is considered at least partially responsible for improved processability and lower density.

Conventional additives can be added to the hydrocarbon modified propylene copolymer during the preblending step and/or the extrusion step, and, in some cases, directly to the polymerization reactor. One method for addition involves first blending the desired additive(s) with the hydrocarbon(s) and then blending the mixture with the propylene copolymer. Stabilization packages are advantageously added in this way. The amount of additive is usually in the range of about 0.01 to about 5 percent by weight based on the weight of the resin. The amount of filler can reach 60 percent or higher. Useful additives are antioxidants, ultraviolet absorbers, antistatic agents, pigments, dyes, fillers, slip agents, fire retardants, plasticizers, processing aids, lubricants, stabilizers, smoke inhibitors, viscosity control agents, vulcanizing agents, crosslinking agents, crosslinking catalysts, and crosslinking boosters.

The product produced by the process of this invention can be a propylene copolymer blend comprising:

(a) a random copolymer of propylene and one or more alpha-olefins wherein the portion of the random copolymer based on alpha-olefins other than propylene is not greater than about 10 percent by weight based on the weight of the random copolymer and is preferably about 2 to about 8 percent by weight; and, blended therewith,

(b) one or more saturated alicyclic hydrocarbon(s), said hydrocarbon(s) being liquid at process temperature, non-polar,
essentially amorphous, and containing less than about 15 percent by weight paraffin wax, in an amount of about 0.1 to about 20 parts by weight of hydrocarbon(s) per 100 parts by weight of component (a), defined above, and preferably in an amount of about 0.5 to about 15 parts by weight,

said copolymer exhibiting bimodality after blending.

The bimodal random propylene copolymer of this invention preferably has the following physical properties:

(i) a melt flow (MF) in the range of about 0.5 to about 50 grams per 10 minutes, and preferably about 1 to about 30 grams per 10 minutes (melt flow is determined under ASTM D-1238 at 230 degrees C and at 2.16 kilograms);

(ii) a density is in the range of 0.890 to 0.905 gram per cubic centimeter, and is preferably in the range of 0.895 to 0.903 gram per cubic centimeter; and

(iii) a DSC Melting Point attributable to the polypropylene crystalline fraction in the range of about 125°C to about 150°C.

DSC Melting Point (m.p.) for polyethylene crystalline fraction (PE) and polypropylene crystalline fraction (PP) is given in degrees Centigrade (°C.). The delta H (Heat of Fusion) for polyethylene can be measured in calories per gram (cal/g). The tests used are ASTM 3417 and 3418. The PE value stands for the endotherm peak associated with the melting of the polyethylene crystalline fraction. The PP value stands for the endotherm peak associated with the melting of the polypropylene crystalline fraction. The delta H PE represents the energy required to melt the polyethylene crystalline fraction.

A typical process is carried out as follows:

To the fluidized bed is charged liquid propylene and the comonomer ethylene in a mole ratio of about 7:1, and a prepared catalyst precursor having the following approximate composition:
TiCl₄•12 MgCl₂• 2 C₆H₅COOC₂H₅. The weight ratio of liquid propylene to catalyst precursor is 10 kilograms of propylene per gram of catalyst precursor. A cocatalyst, triethylaluminum, and a selectivity control agent, para-ethoxy ethyl benzoate, in a mole ratio of about 2:1, are fed into the reactor at the same time as the catalyst precursor. The atomic ratio of aluminum to titanium is about 60. A hydrocarbon, as defined above, is also added to the fluidized bed in an amount sufficient to provide 10 parts by weight of hydrocarbon per 100 parts by weight of resin product. Conditions under which the fluidized bed reactor is operated are approximately as follows: temperature: 65 degrees C; pressure: 40 pounds per square inch absolute (psia); and fluidizing gas velocity: 1.0 foot per second.

The product produced by the invention can also be an impact polypropylene copolymer blend comprising:

(a) a polymer matrix selected from the group consisting of a homopolymer of propylene and a random copolymer of propylene and at least one alpha-olefin having 2 or 4 to 8 carbon atoms wherein (i) the polymer is present in an amount of about 55 to about 90 percent by weight based on the weight of the impact polypropylene copolymer, and is preferably present in an amount of about 60 to about 75 percent by weight; and (ii) the portion of the random copolymer based on alpha-olefins other than propylene is not greater than about 7 percent by weight based on the weight of the random copolymer and is preferably about 1 to about 3 percent by weight;

(b) a copolymer of ethylene and propylene or 1-butene within the matrix wherein (i) the copolymer is present in an amount of about 10 to about 45 percent by weight based on the weight of the impact polypropylene copolymer, and is preferably present in an amount of about 25 to about 40 percent by weight; and (ii) the portion of the copolymer based on ethylene is at least about 90 percent be weight
based on the weight of the copolymer and is preferably at least about 95 percent by weight; and, blended therewith,

(c) one or more saturated alicyclic hydrocarbon(s), said hydrocarbon(s) being liquid at process temperature, non-polar, essentially amorphous, and containing less than about 15 percent by weight paraffin wax, in an amount of about 0.1 to about 20 parts by weight of hydrocarbon(s) per 100 parts by weight of the impact polypropylene copolymer comprising components (a) and (b) defined above, and preferably in an amount of about 0.5 to about 15 parts by weight,

said impact copolymer exhibiting bimodality after blending.

Copolymer Fraction is the percent by weight of ethylene/propylene copolymer based on the weight of total polymer produced, i.e., product. This refers to the copolymer produced in the second reactor. The amount of copolymer is determined by conventional infrared spectrophotometric techniques.

The bimodal impact polypropylene copolymer of this invention, whether or not formed in situ, preferably has the following physical properties:

(i) a melt flow (MF) in the range of about 0.5 to about 50 grams per 10 minutes, and preferably about 1 to about 30 grams per 10 minutes (melt flow is determined under ASTM D-1238 at 230 degrees C and at 2.16 kilograms);

(ii) a density is in the range of 0.890 to 0.905 gram per cubic centimeter, and is preferably in the range of 0.895 to 0.903 gram per cubic centimeter; and

(iii) two DSC Melting Point attributable to polypropylene crystalline fractions in the range of about 125; C to about 132; C and in the range of about 155; C to about 170; C.

DSC Melting Point (m.p.) for polyethylene crystalline fraction (PE) and polypropylene crystalline fraction (PP) is given in
degrees Centigrade (°C.). The delta H (Heat of Fusion) for polyethylene can be determined in calories per gram (cal/g). The tests used are ASTM 3417 and 3418. The PE value stands for the endotherm peak associated with the melting of the polyethylene crystalline fraction. The PP value stands for the endotherm peak associated with the melting of the polypropylene crystalline fraction. The delta H PE represents the energy required to melt the polyethylene crystalline fraction.

A typical in situ process is carried out as follows:

To the first fluidized bed is charged liquid polypropylene and a prepared catalyst precursor having the following approximate composition: TiCl$_4$•12 MgCl$_2$•2 C$_6$H$_5$COOC$_2$H$_5$. The weight ratio of liquid polypropylene to catalyst precursor is 10 kilograms of propylene per gram of catalyst precursor. A cocatalyst, triethylaluminum, and a selectivity control agent, para-ethoxy ethyl benzoate, in a mole ratio of about 2:1, are fed into the reactor at the same time as the catalyst precursor. The atomic ratio of aluminum to titanium is about 60. Conditions under which the first fluidized bed reactor is operated are approximately as follows: temperature: 65 degrees C; pressure: 40 pounds per square inch absolute (psia); and fluidizing gas velocity: 1.0 foot per second. The mixture from the first reactor is transferred to the second reactor and ethylene, propylene, and hydrogen are introduced into the second reactor. Conditions under which the second fluidized bed reactor is operated are approximately as follows: temperature: 70°C; pressure: 165 psi (except 240 psi in examples 1 and 5); and fluidizing gas velocity: 1.2 foot per second. A hydrocarbon, as defined above, is added to either fluidized bed, but preferably the first reactor or prior to the second reactor, in an amount sufficient to provide 10 parts by weight of hydrocarbon per 100 parts by weight of resin product.
The patents mentioned in this specification are incorporated by reference herein.
Claims

1. A process for the production of bimodal random copolymers of propylene comprising the following steps:
   (a) contacting propylene and one or more alpha-olefin(s) with a catalyst system comprising (i) a catalyst precursor, which includes titanium, magnesium and an electron donor; (ii) a hydrocarbylaluminum cocatalyst; and (iii) a selectivity control agent in one or more reactors, under polymerization conditions; and
   (b) introducing into the reactor(s), or after polymerization into the propylene copolymer, one or more saturated alicyclic hydrocarbon(s), said hydrocarbon(s) being liquid at process temperature, non-polar, essentially amorphous, and containing less than about 15 percent by weight paraffin wax, in an amount of about 0.1 to about 20 parts by weight of hydrocarbon(s) per 100 parts by weight of propylene copolymer.

2. The process defined in claim 1 wherein the viscosity of each hydrocarbon is in the range of about 200 to about 1000 SUS at 100 degrees F and the molecular weight of each hydrocarbon is in the range of about 200 to about 5000.

3. A composition comprising (i) a random copolymer of propylene and one or more alpha-olefins, and blended therewith (ii) one or more saturated alicyclic hydrocarbon(s), said hydrocarbon(s) being liquid at blending temperature, non-polar, essentially amorphous, and containing less than about 15 percent by weight paraffin wax, in an amount of about 0.1 to about 20 parts by weight of hydrocarbon(s) per 100 parts by weight of component (i), said copolymer exhibiting bimodality after blending.
4. The composition defined in claim 3 wherein component (ii) is blended into component (i) during the production of the copolymer.

5. The composition defined in claim 3 wherein the copolymer is particulate, each particle has a crystalline phase and an amorphous phase, and the surface of each particle is essentially free of said hydrocarbon(s).

6. An in situ process for the production of an impact polypropylene copolymer exhibiting bimodality comprising ethylene/propylene or 1-butene copolymer incorporated into a matrix of propylene homopolymer or copolymer comprising the following steps:
   (a) contacting propylene or propylene and one or more alpha-olefins with a catalyst system comprising (i) a catalyst precursor, which includes titanium, magnesium and an electron donor; (ii) a hydrocarbylaluminum cocatalyst; and (iii) a selectivity control agent in a first reactor, under polymerization conditions, such that a matrix of homopolymer of propylene or a copolymer of propylene and alpha olefin(s), which includes active catalyst, is produced;
   (b) passing the matrix from step (a) into a second reactor; and
   (c) introducing into the second reactor, under polymerization conditions, a sufficient amount of ethylene and propylene or 1-butene to form, in the matrix, an ethylene/propylene copolymer; and
   (d) introducing into the first and/or second reactor or, after polymerization, into the impact polypropylene copolymer, one or more saturated alicyclic hydrocarbon(s), said hydrocarbon(s) being liquid at process temperature, non-polar, essentially amorphous, and containing less than about 15 percent by weight paraffin wax, in an amount of about 0.1 to about 20 parts by weight of hydrocarbon(s) per 100 parts by weight of impact polypropylene copolymer.
7. The process defined in claim 6 wherein the viscosity of each hydrocarbon is in the range of about 200 to about 1000 SUS at 100 degrees F and the molecular weight of each hydrocarbon is in the range of about 200 to about 5000.

8. A composition comprising (i) an ethylene/propylene or 1-butene copolymer incorporated into a matrix of propylene homopolymer or copolymer to form an impact polypropylene copolymer, and blended therewith (ii) one or more saturated alicyclic hydrocarbon(s), said hydrocarbon(s) being liquid at blending temperature, non-polar, essentially amorphous, and containing less than about 15 percent by weight paraffin wax, in an amount of about 0.1 to about 20 parts by weight of hydrocarbon(s) per 100 parts by weight of component (i), said impact copolymer exhibiting bimodality after blending.

9. The composition defined in claim 8 wherein component (ii) is blended into component (i) during the production of the impact copolymer in situ.

10. The composition defined in claim 8 wherein the impact copolymer is particulate, each particle has a crystalline phase and an amorphous phase, and the surface of each particle is essentially free of said hydrocarbon(s).
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

IPC 5 C08F297/08 C08F210/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 C08F C08K C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where praceical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents:
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Date of the actual completion of the international search

25 March 1997

Date of mailing of the international search report

21.04.97

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Authorized officer

Schueler, D

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