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(54) **Title:** PROPYLENE BUTENE COPOLYMER AND COMPOSITIONS MADE THEREFROM

(57) **Abstract:** Propylene and butene random copolymers are disclosed that have excellent stiffness properties, low xylene soluble content, and excellent transparency characteristics especially when combined with one or more nucleating agents. The propylene-butene copolymers can be made with different melt flow characteristics making them well suited for use in injection molding, blow molding and thermoforming applications.

TITLE

PROPYLENE BUTENE COPOLYMER AND COMPOSITIONS MADE THEREFROM

RELATED APPLICATIONS

[0001] The present application is based on, and claims priority to, U.S. Provisional Patent Application Serial No. 63/050,770, filed on July 11, 2020, which is incorporated herein by reference.

BACKGROUND

[0002] Polypropylene polymers are highly versatile thermoplastic polymers that can be used in numerous and diverse applications. For example, polypropylene polymers can be extruded to form various different shapes including films and fibers and can be molded into articles having relatively simple or complex shapes. Polypropylene polymers are used to produce, for instance, carpets, carpet backing, food packaging, rigid packaging, technical parts such as automotive parts, waste and pressure pipes, and the like, and various consumer products including furniture parts, housewares, and toys. Polypropylene polymers can, for instance, have low density, high stiffness, heat resistance, chemical inertness, good transparency properties, and are recyclable. The properties of polypropylene polymers can be modified and tailored to a particular use by combining propylene monomers with other monomers in order to impart various properties.

[0003] For example, copolymerizing propylene with small amounts of ethylene produces random copolymers having unique properties. The resulting copolymer, for instance, can have a lower degree of crystallinity than a polypropylene homopolymer leading to improved transparency, impact resistance, and lower heat sealing temperatures. Transparency can be further enhanced by additives such as nucleators and clarifiers. The random propylene-ethylene copolymers also generally have a lower melting temperature which can limit their use in high temperature applications. In addition, when subjected to higher temperatures, the transparency of the polymers has a tendency to degrade. For instance, not only can further crystallization occur during aging but also blooming can occur that produces a hazy surface layer.

[0004] Although propylene-ethylene random copolymers have made great advances in the art, as described above, the polymers do have various draw backs. Further, when attempting to improve one product property, such as lowering haze, the improvement can adversely affect another property, such as mechanical strength. Thus, a need exists for a propylene polymer having an improved balance of mechanical properties and good optics. A need also exists for a propylene polymer as described above that can be used to form numerous articles through injection molding, blow molding, and thermoforming.

SUMMARY

[0005] In general, the present disclosure is directed to propylene copolymers, particularly propylene-butene random copolymers, that have been found to have an excellent balance of properties. In addition, the propylene copolymers can be made without using a phthalate-based catalyst. The propylene-butene copolymers of the present disclosure have excellent optical properties and can form clear articles. In addition, the polymer can be formulated for any suitable molding technique, such as extrusion blow molding, thermoforming, and the like. For example, articles can be formed from the nucleated/clarified propylene-butene copolymer that have lower haze and higher stiffness in comparison to articles made in the past from nucleated/clarified propylene-ethylene random copolymers.

[0006] In one embodiment, for instance, the present disclosure is directed to a propylene-butene copolymer that contains propylene as the primary monomer. The copolymer can contain butene generally in an amount from about 1% to about 12% by weight, such as in an amount from about 2% to about 10 % by weight, such as in an amount from about 5% to about 8% by weight. The propylene-butene copolymer can have a xylene soluble fraction of from about 1% to about 10% by weight, such as from about 2% to about 8% by weight. The polymer can have a xylene soluble fraction/butene content ratio of from about 0.3 to about 3.0, such as from about 0.3 to about 2.2, such as from about 0.5 to about 1.0. The propylene-butene copolymer can be made from a non-phthalate based Ziegler-Natta catalyst including a substituted aromatic phenylene diester for producing a polymer with a molecular weight distribution of greater than about 3.5, such as greater than about 4. In addition, the propylene-butene copolymer can have a heat deflection temperature of greater than about 70 ° C and even greater than about 75 ° C, especially when the copolymer contains lower amounts of butene.

[0007] Propylene-butene copolymers made in accordance with the present disclosure can be produced with a particular melt flow rate that matches later melt processing conditions for producing polymer articles. For example, in one embodiment, the propylene-butene copolymer can have a relatively low melt flow rate, such as from about 0.2 g/10 mins to about 4 g/10 mins. Alternatively, the propylene-butene copolymer can have a melt flow rate of from about 4 g/10 mins to about 220 g/10 mins.

[0008] Propylene-butene copolymers made in accordance with the present disclosure can have relatively high stiffness values. For instance, the polymer can have a flexural modulus of greater than about 1100 MPa, such as greater than about 1300 MPa, such as greater than about 1400 MPa, such as greater than about 1500 MPa. The polymer can have a relatively high melting temperature. The primary melting point, for instance, can be greater than about 135°C, such as from about 145° C to about 155 °C.

[0009] The random propylene copolymer of the present disclosure can be used to form a polymer composition for forming various molded articles. The random propylene-butene copolymer, for instance, can be present in the composition in an amount greater than about 70% by weight, such as in an amount greater than about 80% by weight, such as in an amount of about 90% by weight, such as in an amount greater than about 95% by weight, such as greater than about 98% by weight, such as greater than about 99% by weight. The composition can contain various other additives and ingredients including an antioxidant, an acid scavenger, and/or an anti-static agent. In one embodiment, the polymer composition can contain a nucleating agent. The nucleating agent, for instance, can comprise a nonitol.

[0010] The polymer composition can be formulated to have excellent transparency characteristics. For instance, the composition can display a haze at 0.7 mm of about 15% or less, such as less than about 8%.

[0011] The present disclosure is also directed to molded articles made from the polymer composition described above. For example, the polymer composition of the present disclosure, can be formulated so as to be used to produce injection molded articles, and particularly blow molded articles, and thermoformed articles. For example, the present disclosure can be used to produce blow molded bottles, thermoformed cups, and thermoformed containers. The polymer of the present disclosure is also particularly well suited to producing packaging, including food packaging. For instance, the propylene-butene copolymer of the present disclosure can be used to produce a packaging film. The polymer composition can also for fibers.

DETAILED DESCRIPTION

[0012] The present disclosure is directed to propylene-alpha olefin copolymer compositions and methods of producing the propylene copolymer compositions. The compositions can include a propylene-butene random copolymer. For example, the polymer of the present disclosure can be made only from propylene and butene monomers or can be made from propylene, butene, and relatively minor amounts of one or more other alpha olefin monomers.

[0013] Propylene-butene copolymers made in accordance with the present disclosure have been found to have an excellent balance of properties. For instance, the copolymers can display improved stiffness, high heat deflection resistance, and good optics, especially in comparison to many conventional propylene-ethylene copolymers. For example, the propylene-butene copolymers of the present disclosure can be formulated with additives to have excellent optical characteristics, displaying a very low haze even at thicknesses of 0.7 mm. The propylene-butene copolymer is also very versatile and can be formulated over a broad range of melt flow rates that makes the polymer well suited for use in all different types of molding processes, such as injection molding, extrusion blow molding, or thermoforming.

[0014] The propylene-butene copolymers of the present disclosure can also be formed using Ziegler-Natta catalysts that provide the polymer with a relatively broad molecular weight distribution. In one aspect, a non-phthalate based catalyst can be used including a substituted aromatic phenylene diester, making the polymer more suitable for contact with food and beverages. The polymer is also well suited for use in medical applications.

[0015] The propylene-butene copolymer of the present disclosure can be incorporated into various polymer compositions containing other additives and nucleating agents, including clarifying agents. The polymer composition can then be used to make diverse and numerous articles. For instance, the polymer composition of the present disclosure can be used to produce all different types of packaging products, including food packaging. For example, in one aspect, the polymer composition containing the propylene-butene copolymer can be used to produce polymer films having low haze for packaging food items. In addition, the polymer composition can be used to make all different types of rigid containers with excellent stiffness properties combined with great optical characteristics. The polymer composition of the present disclosure containing the propylene-butene copolymer can also be used to produce blow molded bottles, thermoformed cups, fibers and the like.

I. Definitions and Testing Procedures

[0016] The term "propylene-butene copolymer", as used herein, is a copolymer containing a majority weight percent propylene monomer with butene monomer as a secondary constituent. A "propylene-butene copolymer" (also sometimes referred to as a polypropylene-butene random copolymer, is a polymer having individual repeating units of the butene monomer present in a random or statistical distribution in the polymer chain.

[0017] Melt flow rate (MFR), as used herein, is measured in accordance with the ASTM D 1238 test method at 230° C with a 2.16 kg weight for propylene-based polymers. The melt flow rate can be measured in pellet form or on the reactor powder. When measuring the reactor powder, a stabilizing package can be added including 2000 ppm of CYANOX 2246 antioxidant (methylenebis(4-methyl-6-tert-butylphenol) 2000 ppm of IRGAFOS 168 antioxidant (tris(2,4-di-tert.-butylphenyl)phosphite) and 1000 ppm of acid scavenger ZnO.

[0018] Xylene solubles (XS) is defined as the weight percent of resin that remains in solution after a sample of polypropylene random copolymer resin is dissolved in hot xylene and the solution is allowed to cool to 25° C. This is also referred to as the gravimetric XS method according to ASTM D5492-06 using a 60 minute precipitation time and is also referred to herein as the "wet method".

[0019] The ASTM D5492-06 method mentioned above may be adapted to determine the xylene soluble portion. In general, the procedure consists of weighing 2 g of sample and dissolving the sample in 200 ml o-xylene in a 400 ml flask with 24/40 joint. The flask is connected to a water cooled condenser and the contents are stirred and heated to reflux under nitrogen (N2), and then maintained at reflux for an additional 30 minutes. The solution is then cooled in a temperature controlled water bath at 25° C for 60 minutes to allow the crystallization of the xylene insoluble fraction. Once the solution is cooled and the insoluble fraction precipitates from the solution, the separation of the xylene soluble portion (XS) from the xylene insoluble portion (XI) is achieved by filtering through 25 micron filter paper. One hundred ml of the filtrate is collected into a pre-weighed aluminum pan, and the o-xylene is evaporated from this 100 ml of filtrate under a nitrogen stream. Once the solvent is evaporated, the pan and contents are placed in a 100° C vacuum oven for 30 minutes or until dry. The pan is then allowed to cool to room temperature and weighed. The xylene soluble portion is calculated as XS (wt %)=[(m3−m2)*2/m1]*100, where m1 is the original weight of the sample used, m2 is the weight of empty aluminum pan, and m3 is the weight of the pan and residue (the asterisk, *, here and elsewhere in the disclosure indicates that the identified terms or values are multiplied).

[0020] XS can also be measured according to the Viscotek method, as follows: 0.4 g of polymer is dissolved in 20 ml of xylenes with stirring at 130° C for 60 minutes. The solution is then cooled to 25° C and after 60 minutes the insoluble polymer fraction is filtered off. The resulting filtrate is analyzed by Flow Injection Polymer Analysis using a Viscotek ViscoGEL H-100-3078 column with THF mobile phase flowing at 1.0 ml/min. The column is coupled to a Viscotek Model 302 Triple Detector Array, with light scattering, viscometer and refractometer detectors operating at 45° C. Instrument calibration is maintained with Viscotek PolyCAL™ polystyrene standards. A polypropylene (PP) homopolymer, such as biaxially oriented polypropylene (BOPP) grade Dow 5D98, is used as a reference material to ensure that the Viscotek instrument and sample preparation procedures provide consistent results. The value for the reference polypropylene homopolymer is initially derived from testing using the ASTM method identified above.

[0021] The term "tacticity" generally refers to the relative stereochemistry of adjacent chiral centers within in a macromolecule or polymer. For example, in a propylene-based polymer, the chirality of adjacent monomers, such as two propylene monomers, can be of either like or opposite configuration. The term "diad" is used to designate two contiguous monomers and three adjacent monomers are called a "triad." If the chirality of adjacent monomers is of the same relative configuration, the diad is considered isotactic; if opposite in configuration, it is termed syndiotactic. Another way to describe the configurational relationship is to term contiguous pairs of monomers having the same chirality as meso (m) and those of opposite configuration racemic (r).

[0022] Tacticity or stereochemistry of macromolecules generally and polypropylene or polypropylene random copolymers in particular can be described or quantified by referring to triad concentration. An isotactic triad, typically identified with the shorthand reference "mm", is made up of two adjacent meso diads, which have the same configuration, and so the stereoregularity of the triad is identified as "mm". If two adjacent monomers in a three-monomer sequence have the same chirality and that is different from the relative configuration of the third unit, this triad has 'mr' tacticity. An 'rr' triad has the middle monomer unit having an opposite configuration from either neighbor. The fraction of each type of triad in the polymer can be determined and when multiplied by 100 indicates the percentage of that type found in the polymer. The mm percentage is used to identify and characterize the polymers herein.

[0023] The sequence distribution of monomers in the polymer may be determined by ^{13}C-NMR, which can also locate butene residues in relation to the neighboring propylene residues. ^{13}C NMR can be used to measure butene content, triad distribution, and triad tacticity, and is performed as follows.

[0024] The samples are prepared by adding approximately 2.7 g of a 50/50 mixture of tetrachloroethane-d2/orthodichlorobenzene containing 0.025 M Cr(AcAc)3 to 0.20 g sample in a Norell 1001-7 10 mm NMR tube. The samples are dissolved and homogenized by heating the tube and its contents to 150° C using a heating block. Each sample is visually inspected to ensure homogeneity.

[0025] The data are collected using a Bruker 400 MHz spectrometer equipped with a Bruker Dual DUL high-temperature CryoProbe. The data are acquired using 512 transients per data file, a 6 sec pulse repetition delay, 90 degree flip angles, and inverse gated decoupling with a sample temperature of 120° C. All measurements are made on non-spinning samples in locked mode. Samples are allowed to thermally equilibrate for 10 minutes prior to data acquisition. Percent mm tacticity and weight % butene are calculated according to methods commonly used in the art, which is briefly summarized as follows.

[0026] With respect to measuring the chemical shifts of the resonances, the methyl group of the third unit in a sequence of 5 contiguous propylene units consisting of head-to-tail bonds and having the same relative chirality is set to 21.83 ppm. The chemical shift of other carbon resonances are determined by using the above-mentioned value as a reference. The spectrum relating to the methyl carbon region (17.0-23 ppm) can be classified into the first region (21.1-21.9 ppm), the second region (20.4-21.0 ppm), the third region (19.5-20.4 ppm) and the fourth region (17.0-17.5 ppm). Each peak in the spectrum is assigned with reference to a literature source such as the articles in, for example, Polymer, T. Tsutsui et al., Vol. 30, Issue 7, (1989) 1350-1356 and/or Macromolecules, H. N. Cheng, 17 (1984) 1950-1955, the contents of which are incorporated herein by reference.

[0027] For convenience, butene content is also measured using a Fourier Transform Infrared method (FTIR) which is correlated to butene values determined using ^{13}C NMR, noted above, as the primary method. The relationship and agreement between measurements conducted using the two methods is described in, e.g., J. R. Paxson, J. C. Randall, "Quantitative Measurement of Ethylene Incorporation into Propylene Copolymers by Carbon-13 Nuclear Magnetic Resonance and Infrared Spectroscopy", Analytical Chemistry, Vol. 50, No. 13, Nov. 1978, 1777-1780.

[0028] The Flexural modulus is determined in accordance with ASTM D790-10 Method A at 1.3 mm/min, using a Type 1 specimen per ASTM 3641 and molded according to ASTM D4101.

[0029] IZOD impact strength is measured in accordance with ASTM D 256 and D4101.

[0030] Haze is determined according to ASTM Test D1003, procedure A using the latest version of the test. Haze can be measured on a test plaque or on a molded article, such as a bottle, cup, container, or film. Haze can be measured before and after thermal aging. Haze can be measured using BYK Gardner Haze-Gard Plus 4725 instrument. Injection molded test samples that are tested for haze measurements can be injection molded at a temperature of from 200 to 230 C when a nonitol is present as a nucleating agent, at a temperature of from 250 to 260 C when a sorbitol is present as a nucleating agent, or at a temperature from 200 to 260 C when a non-soluble, particulate nucleating agent is present. Thermal aging is conducted by placing the samples in an oven at the desired temperature (e.g 121 C) and for a desired time (e.g. 30 min.) and then retested for haze.

[0031] The heat distortion temperature (HDT) is determined according to ASTM Test D648 entitled deflection temperature of plastics under flexural load, 66 psi on samples prepared/aged according to D4101.

[0032] The melting point or melting temperature and the crystallization temperature are determined using differential scanning calorimetry (DSC). The melting point is the primary peak that is formed during the test and is typically the second peak that forms. The term "crystallinity" refers to the regularity of the arrangement of atoms or molecules forming a crystal structure. Polymer crystallinity can be examined using DSC. T_{me} means the temperature at which the melting ends and T_{max} means the peak melting temperature, both as determined by one of ordinary skill in the art from DSC analysis using data from the final heating step. One suitable method for DSC analysis uses a model Q1000™ DSC from TA Instruments, Inc. Calibration of the DSC is performed in the following manner. First, a baseline is obtained by heating the cell from -90° C to 290°C without any sample in the aluminum DSC pan. Then 7 milligrams of a fresh indium sample is analyzed by heating the sample to 180°C, cooling the sample to 140° C at a cooling rate of 10° C/min followed by keeping the sample isothermally at 140° C for 1 minute, followed by heating the sample from 140°C to 180° C at a heating rate of 10°C/min. The heat of fusion and the onset of melting of the indium sample are determined and checked to be within 0.5° C from 156.6°C for the onset of melting and within 0.5 J/g from 28.71 J/g for the heat of fusion. Then deionized water is analyzed by cooling a small drop of fresh sample in the DSC pan from 25°C to -30°C at a cooling rate of 10°C/min. The sample is kept isothermally at -30° C. for 2 minutes and heated to 30° C. at a heating rate of 10°C./min. The onset of melting is determined and checked to be within 0.5°C from 0°C.

[0033] Mw/Mn (also referred to as “MWD”) and Mz/Mw are measured by GPC according to the Gel Permeation Chromatography (GPC) Analytical Method for Polypropylene. The polymers are analyzed on Polymer Char High Temperature GPC with IR5 MCT (Mercury Cadmium Telluride-high sensitivity, thermoelectrically cooled IR detector), Polymer Char four capillary viscometer, a Wyatt 8 angle MALLS and three Agilent Plgel Olexis (13um). . The oven temperature is set at 150° C. The solvent is nitrogen purged 1,2,4-trichlorobenzene (TCB) containing ~200 ppm 2,6-di-t-butyl-4-methylphenol (BHT). The flow rate is 1.0 mL/min and the injection volume was 200 μl. A 2 mg/mL sample concentration is prepared by dissolving the sample in N2 purged and preheated TCB (containing 200 ppm BHT) for 2 hrs at 160° C. with gentle agitation.

[0034] The GPC column set is calibrated by running twenty narrow molecular weight distribution polystyrene standards. The molecular weight (MW) of the standards ranges from 266 to 12,000,000 g/mol, and the standards were contained in 6 “cocktail” mixtures. Each standard mixture has at least a decade of separation between individual molecular weights. The polystyrene standards are prepared at 0.005 g in 20 mL of solvent for molecular weights equal to or greater than 1,000,000 g/mol and 0.001 g in 20 mL of solvent for molecular weights less than 1,000,000 g/mol. The polystyrene standards are dissolved at 160° C for 60 min under stirring. The narrow standards mixtures are run first and in order of decreasing highest molecular weight component to minimize degradation effect. A logarithmic molecular weight calibration is generated using a fourth-order polynomial fit as a function of elution volume. The equivalent polypropylene molecular weights are calculated by using following equation with reported Mark-Houwink coefficients for polypropylene (Th. G. Scholte, N. L. J. Meijerink, H. M. Schoffeleers, and A. M. G. Brands, J. Appl. Polym. Sci., 29, 3763-3782 (1984)) and polystyrene(E. P. Otocka, R. J. Roe, N. Y. Hellman, P. M. Muglia, Macromolecules, 4, 507 (1971)):

$$M_{PP} = \left(\frac{K_{PS} M_{PS}^{a_{PS}+1}}{K_{PP}} \right)^{\frac{1}{a_{PP}+1}}$$

where M_{pp} is PP equivalent MW, M_{PS} is PS equivalent MW, log K and a values of Mark-Houwink coefficients for PP and PS are listed below .

TABLE 2		
Polymer	A	Log K
Polypropylene	0.725	-3.721
Polystyrene	0.702	-3.900

II. Propylene-Butene Random Copolymer and Compositions

[0035] Propylene-butene copolymers of the present disclosure can include a majority weight percent propylene monomer with a butene monomer as a secondary constituent. The butene content of the propylene-butene copolymer of the present disclosure can be from about 1% to about 12% by weight including all increments of 0.1% by weight therebetween. For example, the propylene-butene copolymer can contain butene in an amount greater than about 1.5% by weight, such as greater than about 2% by weight, such as greater than about 2.3% by weight, such as greater than about 3% by weight, such as greater than about 4% by weight, such as greater than about 4.5% by weight, such as greater than about 5% by weight. The butene content of the propylene-butene copolymer is generally less than about 11% by weight, such as less than about 10% by weight, such as less than about 9% by weight, such as less than about 8% by weight, such as less than about 7.8% by weight, such as less than about 7% by weight, such as less than about 6% by weight, such as less than about 5% by weight. The amount of butene incorporated into the copolymer can be varied in order to change various physical properties of the polymer.

[0036] The xylene soluble (XS) fraction for the copolymers of the present invention can be less than or equal to (≦)8.0% by weight of the copolymer, or ≦7.0% by weight, more preferably ≦6.0% by weight, and still more preferably ≦5.0% by weight. The xylene soluble fraction is generally greater than about 0.5% by weight, such as greater than about 1% by weight. The xylene soluble (XS) fraction is preferably in the range of from 1.0% to 8.0% by weight, such as from 2% to 7% by weight. Of particular advantage, propylene-butene copolymers in accordance with the present disclosure can have xylene soluble contents of greater than about 3% by weight while still having excellent low haze properties. The polymer can have a xylene soluble fraction/butene content ratio of from about 0.3 to about 3.0, such as from about 0.3 to about 2.0, such as from about 0.5 to about 1.0 or less than 1.0.

[0037] The melt flow rate of propylene-butene copolymers made in accordance with the present disclosure can vary. For instance, the melt flow rate can be from about 0.2 g/10 min to about 220 g/10 min, including all increments of 0.1 therebetween. The melt flow rate of the polymer, for instance, can be varied and controlled based upon various factors and the desired application. When the polymer is incorporated into the composition and blow molded or thermoformed, for instance, lower melt flow rates may be desired. For instance, in one aspect, the melt flow rate of the propylene-butene copolymer can be less than about 20 g/10 min, such as less about 15 g/10 min, such as less about 10 g/10 min, such as less than about 8 g/10 min, such as less about 6 g/10 min, such as less about 4 g/10 min, and generally greater than about 1 g/10 min, such as greater than about 1.5 g/10 min. When the polymer is used in injection molding, however, a higher melt flow rate may be desired. For example, in one aspect, the melt flow rate of the polymer can be greater than about 10 g/10 min, such as greater than about 20 g/10 min, such as greater than about 30 g/10 min, such as greater than about 40 g/10 min, and generally less than about 110 g/10 min, such as less than 80 g/10 min, such as less than about 60 g/10 min.

[0038] The copolymer of the present disclosure generally has a relatively broad molecular weight distribution. For instance, the molecular weight distribution (Mw/Mn) is generally greater than about 3.5, such as greater than about 3.8, such as greater than about 4, such as greater than about 4.3, such as greater than about 4.5, such as greater than about 4.8, such as greater than about 5, such as greater than about 5.2, such as greater than about 5.5, such as greater than about 5.7, such as greater than about 6 and is generally less than about 10, such as less than about 8, such as less than about 7.5. The weight average molecular weight is determined by GPC.

[0039] In one aspect, the propylene-butene copolymer can be formulated to have excellent stiffness properties. For instance, the copolymer can have a flexural modulus of greater than about 1100 MPa, such as greater than about 1150 MPa, such as greater than about 1200 MPa, such as greater than about 1250 MPa, such as greater than about 1300 MPa, such as greater than about 1350 MPa, such as greater than about 1400 MPa, such as greater than about 1450 MPa, such as greater than about 1500 MPa. The flexural modulus is generally less than about 3000 MPa, such as less than about 2000 MPa.

[0040] Of particular advantage, the propylene-butene random copolymer can have a high heat deflection resistance, especially when the polymer is formulated to contain butene in lower amounts. In general, the polymer can have a heat deflection temperature (HDT) of greater than about 70° C. When containing butene in an amount less than 8% by weight, such as in an amount less than 6% by weight, such as in an amount less than 5% by weight, the HDT can be greater than about 75 ° C, such as greater than about 76° C, such as greater than about 77° C, and generally less than about 90° C. In addition, the polymer can be formulated to have a melting point of greater than about 135° C, such as greater than about 145° C, such as greater than about 147° C, such as greater than about 148° C, such as greater than about 149° C, such as greater than about 150° C, such as greater than about 151° C, and generally less than about 165° C. In one aspect, the polymer can have a primary melting point of no less than 147° C.

[0041] In addition to excellent stiffness properties and heat resistance properties, the propylene-butene copolymer can also have good toughness characteristics. For instance, the copolymer can have an IZOD impact strength of greater than about 40 J/m, such as greater than about 45 J/m, such as greater than about 50 J/m, such as greater than about 55 J/m, such as greater than about 60 J/m, such as greater than about 65 J/m, such as greater than about 70 J/m, such as greater than about 75 J/m, such as greater than about 80 J/m, such as greater than about 85 J/m, such as greater than about 90 J/m. The impact strength is generally less than about 200 J/m, such as less than about 150 J/m.

III. Propylene-Butene Random Copolymer Production

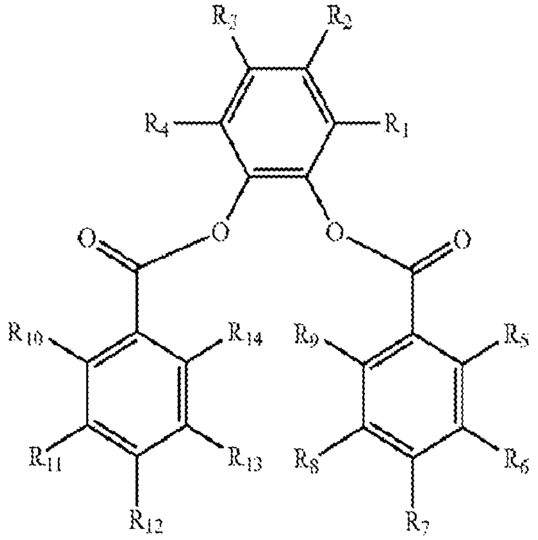
[0042] In one aspect, the propylene-butene copolymers of the present disclosure can be produced using non-phthalate based Ziegler-Natta catalysts. A non-phthalate based catalyst includes a catalyst system that contains no phthalate compounds, e.g. catalyst support, internal electron donors, external electron donors, activity limiting agent and activator are all phthalate free. Phthalates were used in the past as internal electron donors. Non-phthalate internal electron donors include diethers, succinates, ethyl benzoates, phenylene diesters, and the like. By using a non-phthalate based catalyst, the polymers are more suitable for food contact and medical applications. In addition, using a Ziegler-Natta catalyst can produce a broad molecular weight distribution that can provide numerous advantages and benefits.

[0043] Propylene-butene copolymers can generally be made in any suitable reactor using any suitable process to produce propylene based polymers. This includes the UNIPOL® PP gas phase process, using a supported Ziegler-Natta catalyst. Particularly preferable are CONSISTA® catalysts available from W.R. Grace & Co., Columbia, Maryland. Suitable polypropylene random copolymers may be produced using a single reactor or multiple reactors. Examples of processes that may be used are described in US Patent No. 9,624,323 and US Patent Publication No. 2016/0289357, which are incorporated herein by reference.

[0044] Procatalyst compositions suitable for use in producing the polypropylene random copolymers include Ziegler-Natta procatalyst compositions. In an embodiment, the Ziegler-Natta procatalyst composition contains a titanium moiety such as titanium chloride, a magnesium moiety such as magnesium chloride, and an internal electron donor.

[0045] In an embodiment, the internal electron donor comprises a substituted phenylene aromatic diester. In an embodiment, a 1,2-phenylene aromatic diester is provided. The substituted 1,2-phenylene aromatic diester has the structure (I) below:

(I)



[0046] wherein R_1-R_{14} are the same or different. Each of R_1-R_{14} is selected from a hydrogen, substituted hydrocarbyl group having 1 to 20 carbon atoms, an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms, a heteroatom, and combinations thereof. At least one of R_1-R_{14} is not hydrogen.

[0047] As used herein, the term "hydrocarbyl" and "hydrocarbon" refer to substituents containing only hydrogen and carbon atoms, including branched or unbranched, saturated or unsaturated, cyclic, polycyclic, fused, or acyclic species, and combinations thereof. Nonlimiting examples of hydrocarbyl groups include alkyl-, cycloalkyl-, alkenyl-, alkadienyl-, cycloalkenyl-, cycloalkadienyl-, aryl-, aralkyl, alkylaryl, and alkynyl-groups.

[0048] As used herein, the terms "substituted hydrocarbyl" and "substituted hydrocarbon" refer to a hydrocarbyl group that is substituted with one or more nonhydrocarbyl substituent groups. A nonlimiting example of a nonhydrocarbyl substituent group is a heteroatom. As used herein, a "heteroatom" refers to an atom other than carbon or hydrogen. The heteroatom can be a non-carbon atom from Groups IV, V, VI, and VII of the

Periodic Table. Nonlimiting examples of heteroatoms include: halogens (F, Cl, Br, I), N, O, P, B, S, and Si. A substituted hydrocarbyl group also includes a halohydrocarbyl group and a silicon-containing hydrocarbyl group. As used herein, the term "halohydrocarbyl" group refers to a hydrocarbyl group that is substituted with one or more halogen atoms. As used herein, the term "silicon-containing hydrocarbyl group" is a hydrocarbyl group that is substituted with one or more silicon atoms. The silicon atom(s) may or may not be in the carbon chain.

[0049] The procatalyst precursor can include (i) magnesium, (ii) a transition metal compound of an element from Periodic Table groups IV to VIII, (iii) a halide, an oxyhalide, and/or an alkoxide of (i) and/or (ii), and (iv) combinations of (i), (ii), and (iii). Nonlimiting examples of suitable procatalyst precursors include halides, oxyhalides, and alkoxides of magnesium, manganese, titanium, vanadium, chromium, molybdenum, zirconium, hafnium, and combinations thereof.

[0050] In an embodiment, the procatalyst precursor is a magnesium moiety compound (MagMo), a mixed magnesium titanium compound (MagTi), or a benzoate-containing magnesium chloride compound (BenMag). In an embodiment, the procatalyst precursor is a magnesium moiety ("MagMo") precursor. The "MagMo precursor" contains magnesium as the sole metal component. The MagMo precursor includes a magnesium moiety. Nonlimiting examples of suitable magnesium moieties include anhydrous magnesium chloride and/or its alcohol adduct, magnesium alkoxide or aryloxide, mixed magnesium alkoxy halide, and/or carboxylated magnesium dialkoxide or aryloxide. In one embodiment, the MagMo precursor is a magnesium di(C_{1-4})alkoxide. In a further embodiment, the MagMo precursor is diethoxymagnesium.

[0051] In an embodiment, the procatalyst precursor is a mixed magnesium/titanium compound ("MagTi"). The "MagTi precursor" has the formula $Mg_dTi(OR^e)_fX_g$ wherein R^e is an aliphatic or aromatic hydrocarbon radical having 1 to 14 carbon atoms or COR' wherein R' is an aliphatic or aromatic hydrocarbon radical having 1 to 14 carbon atoms; each OR^e group is the same or different; X is independently chlorine, bromine or iodine, preferably chlorine; d is 0.5 to 56, or 2 to 4; f is 2 to 116 or 5 to 15; and g is 0.5 to 116, or 1 to 3. The precursors are prepared by controlled precipitation through removal of an alcohol from the reaction mixture used in their preparation. In an embodiment, a reaction medium comprises a mixture of an aromatic liquid, especially a chlorinated aromatic compound, most especially chlorobenzene, with an alkanol, especially ethanol. Suitable halogenating agents include titanium tetrabromide, titanium tetrachloride or titanium trichloride, especially titanium tetrachloride. Removal of the alkanol from the solution used in the halogenation results in precipitation of the solid precursor, having especially desirable morphology and surface area. Moreover, the resulting precursors are particularly uniform in particle size.

[0052] In one embodiment, the procatalyst precursor contains magnesium as the sole metal component. Non-limiting examples include anhydrous magnesium chloride and/or its alcohol adduct, magnesium alkoxide, and or aryloxide, mixed magnesium alkoxy halide, and/or carboxylated magnesium dialkoxide or aryloxide.

[0053] In one embodiment, the procatalyst precursor is an alcohol adduct of anhydrous magnesium chloride. The anhydrous magnesium chloride adduct is generally defined as $MgCl_2$-nROH where n has a range of 1.5-6.0, preferably 2.5-4.0, and most preferably 2.8-3.5 moles total alcohol. ROH is a C_1-C_4 alcohol, linear or branched, or mixture of alcohol. Preferably ROH is ethanol or a mixture of ethanol and a higher alcohol. If ROH is a mixture, the mole ratio of ethanol to higher alcohol is at least 80:20, preferably 90:10, and most preferably at least 95:5.

[0054] In one embodiment, a substantially spherical $MgCl_2$-nEtOH adduct may be formed by a spray crystallization process. In one, embodiment the spherical $MgCl_2$ precursor has an average particle size (Malvern d_{50}) of between about 15-150 microns, preferably between 20-100 microns, and most preferably between 35-85 microns.

[0055] In one embodiment, the procatalyst precursor contains a transition metal compound and a magnesium metal compound. The transition metal compound has the general formula TrX_x where Tr is the transition metal, X is a halogen or a C_{1-10} hydrocarboxyl or hydrocarbyl group, and x is the number of such X groups in the compound in combination with a magnesium metal compound. Tr may be a Group IV, V or VI metal. In one embodiment, Tr is a Group IV metal, such as titanium. X may be chloride, bromide, C_{1-4} alkoxide or phenoxide, or a mixture thereof. In one embodiment, X is chloride.

[0056] The present procatalyst composition can also include an internal electron donor. As used herein, an "internal electron donor" is a compound added during formation of the procatalyst composition that donates a pair of electrons to one or more metals present in the resultant procatalyst composition. Not bounded by any particular theory, it is believed that the internal electron donor assists in regulating the formation of active sites and thus enhances catalyst stereoselectivity. In an embodiment, the internal electron donor includes a substituted phenylene aromatic diester of structure (I), identified above.

[0057] In an embodiment, a procatalyst composition is provided which includes a combination of a magnesium moiety, a titanium moiety and an internal electron donor. The internal electron donor includes the substituted phenylene aromatic diester. The procatalyst composition is produced by way of a halogenation procedure described in detail in U.S. Pat. No. 8,536,372, incorporated herein by reference, which converts the procatalyst precursor and the substituted phenylene aromatic diester donor into the combination of the magnesium and titanium moieties, into which the internal electron donor is incorporated. The procatalyst precursor from which the procatalyst composition is formed can be the magnesium moiety precursor, the mixed magnesium/titanium precursor, or the benzoate-containing magnesium chloride precursor.

[0058] In an embodiment, the magnesium moiety is a magnesium halide. In another embodiment, the magnesium halide is magnesium chloride, or magnesium chloride alcohol adduct. In an embodiment, the titanium moiety is a titanium halide such as a titanium chloride. In another embodiment the titanium moiety is titanium tetrachloride. In another embodiment, the procatalyst composition includes a magnesium chloride support upon which a titanium chloride is deposited and upon which the internal electron donor is incorporated.

[0059] In an embodiment, the internal electron donor of the procatalyst composition includes the substituted phenylene aromatic diester of structure (I), illustrated above, wherein R_1-R_{14} are the same or different; each of R_1-R_{14} is selected from hydrogen, a substituted hydrocarbyl group having 1 to 20 carbon atoms, an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms, a heteroatom, and combinations thereof; and at least one of R_1-R_{14} is not hydrogen.

[0060] In an embodiment, at least one (or two, or three, or four) R group(s) of R_1-R_4 is selected from a substituted hydrocarbyl group having 1 to 20 carbon atoms, an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms, a heteroatom, and combinations thereof.

[0061] In an embodiment, at least one (or some, or all) R group(s) of R_5-R_{14} is selected from a substituted hydrocarbyl group having 1 to 20 carbon atoms, an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms, a heteroatom, and combinations thereof. In another embodiment, at least one of R_5-R_9 and at least one of R_{10}-R_{14} is selected from a substituted hydrocarbyl group having 1 to 20 carbon atoms, an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms, a heteroatom, and combinations thereof.

[0062] In an embodiment, at least one of R_1-R_4 and at least one of R_5-R_{14} is selected from a substituted hydrocarbyl group having 1 to 20 carbon atoms, an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms, a heteroatom, and combinations thereof. In another embodiment, at least one of R_1-R_4 at least one R_5-R_9 of and at least one of R_{10}-R_{14} is selected from a substituted hydrocarbyl group having 1 to 20 carbon atoms, an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms, a heteroatom, and combinations thereof.

[0063] In an embodiment, any consecutive R groups in R_1-R_4, and/or any consecutive R groups in R_5-R_9, and/or any consecutive R groups in R_{10}-R_{14} may be linked to form an inter-cyclic or an intra-cyclic structure. The inter-/intra-cyclic structure may or may not be aromatic. In an embodiment, the inter-/intra-cyclic structure is a C_5 or a C_6 membered ring.

[0064] In an embodiment, at least one of R_1-R_4 is selected from a substituted hydrocarbyl group having 1 to 20 carbon atoms, an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, and combinations thereof. Optionally, at least one of R_5-R_{14} may be a halogen atom or an alkoxy group having 1 to 20 carbon atoms. Optionally, R_1-R_4, and/or R_5-R_9, and/or R_{10}-R_{14} may be linked to form an inter-cyclic structure or an intra-cyclic structure. The inter-cyclic structure and/or the intra-cyclic structure may or may not be aromatic.

[0065] In an embodiment, any consecutive R groups in R_1-R_4, and/or in R_5-R_9, and/or in R_{10}-R_{14}, may be members of a C_5-C_6-membered ring.

[0066] In an embodiment, structure (I) includes R_1, R_3 and R_4 as hydrogen. R_2 is selected from a substituted hydrocarbyl group having 1 to 20 carbon atoms, an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, and combinations thereof. R_5-R_{14} are the same or different and each of R_5-R_{14} is selected from hydrogen, a substituted hydrocarbyl group having 1 to 20 carbon atoms, an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms, a halogen, and combinations thereof.

[0067] In an embodiment, R_2 is selected from a C_1-C_8 alkyl group, a C_3-C_6 cycloalkyl, or a substituted C_3-C_6 cycloalkyl group. R_2 can be a methyl group, an ethyl group, a n-propyl group, an isopropyl group, a t-butyl group, an isobutyl group, a sec-butyl group, a 2,4,4-trimethylpentan-2-yl group, a cyclopentyl group, and a cyclohexyl group.

[0068] In an embodiment, structure (I) includes R_2 that is methyl, and each of R_5-R_{14} is hydrogen. In an embodiment, structure (I) includes R_2 that is ethyl, and each of R_5-R_{14} is hydrogen. In an embodiment, structure (I) includes R_2 that is t-butyl, and each of R_5-R_{14} is hydrogen. In an embodiment, structure (I) includes R_2 that is ethoxycarbonyl, and each of R_5-R_{14} is hydrogen.

[0069] In an embodiment, structure (I) includes R_2, R_3 and R_4 each as hydrogen and R_1 is selected from a substituted hydrocarbyl group having 1 to 20 carbon atoms, an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, and combinations thereof. R_5-

R_{14} are the same or different and each is selected from hydrogen, a substituted hydrocarbyl group having 1 to 20 carbon atoms, an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms, a halogen, and combinations thereof.

[0070] In an embodiment, structure (I) includes R_1 that is methyl, and each of R_5-R_{14} is hydrogen.

[0071] In an embodiment, structure (I) includes R_2 and R_4 that are hydrogen and R_1 and R_3 are the same or different. Each of R_1 and R_3 is selected from a substituted hydrocarbyl group having 1 to 20 carbon atoms, an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, and combinations thereof. R_5-R_{14} are the same or different and each of R_5-R_{14} is selected from a substituted hydrocarbyl group having 1 to 20 carbon atoms, an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms, a halogen, and combinations thereof.

[0072] In an embodiment, structure (I) includes R_1 and R_3 that are the same or different. Each of R_1 and R_3 is selected from a C_1-C_8 alkyl group, a C_3-C_6 cycloalkyl group, or a substituted C_3-C_6 cycloalkyl group. R_5-R_{14} are the same or different and each of R_5-R_{14} is selected from hydrogen, a C_1–C_8 alkyl group, and a halogen. Nonlimiting examples of suitable C_1-C_8 alkyl groups include methyl, ethyl, n-propyl, isopropyl, n-butyl, i-butyl, t-butyl, n-pentyl, i-pentyl, neopentyl, t-pentyl, n-hexyl, and 2,4,4-trimethylpentan-2-yl group. Nonlimiting examples of suitable C_3-C_6 cycloalkyl groups include cyclopentyl and cyclohexyl groups. In a further embodiment, at least one of R_5-R_{14} is a C_1-C_8 alkyl group or a halogen.

[0073] In an embodiment, structure (I) includes R_1 that is a methyl group and R_3 that is a t-butyl group. Each of R_2, R_4 and R_5-R_{14} is hydrogen.

[0074] In an embodiment, structure (I) includes R_1 and R_4 as methyl groups and one of R_3 or R_2 is a hydrogen and the other is a cycloalkyl group, such as a cyclohexal group.

[0075] In an embodiment, structure (I) includes R_1 and R_3 that is an isopropyl group. Each of R_2, R_4 and R_5-R_{14} is hydrogen.

[0076] In an embodiment, structure (I) includes each of R_1, R_5, and R_{10} as a methyl group and R_3 is a t-butyl group. Each of R_2, R_4, R_6-R_9 and R_{11}-R_{14} is hydrogen.

[0077] In an embodiment, structure (I) includes each of R_1, R_7, and R_{12} as a methyl group and R_3 is a t-butyl group. Each of R_2, R_4, R_5, R_6, R_8, R_9, R_{10}, R_{11}, R_{13}, and R_{14} is hydrogen.

[0078] In an embodiment, structure (I) includes R_1 as a methyl group and R_3 is a t-butyl group. Each of R_7 and R_{12} is an ethyl group. Each of R_2, R_4, R_5, R_6, R_8, R_9, R_{10}, R_{11}, R_{13}, and R_{14} is hydrogen.

[0079] In an embodiment, structure (I) includes each of R_1, R_5, R_7, R_9, R_{10}, R_{12}, and R_{14} as a methyl group and R_3 is a t-butyl group. Each of R_2, R_4, R_6, R_8, R_{11}, and R_{13} is hydrogen.

[0080] In an embodiment, structure (I) includes R_1 as a methyl group and R_3 is a t-butyl group. Each of R_5, R_7, R_9, R_{10}, R_{12}, and R_{14} is an i-propyl group. Each of R_2, R_4, R_6, R_8, R_{11}, and R_{13} is hydrogen.

[0081] In an embodiment, the substituted phenylene aromatic diester has a structure selected from the group consisting of structures (II)-(V), including alternatives for each of R_1 to R_{14}, that are described in detail in U.S. Pat. No. 8,536,372, which is incorporated herein by reference.

[0082] In an embodiment, structure (I) includes R_1 that is a methyl group and R_3 is a t-butyl group. Each of R_7 and R_{12} is an ethoxy group. Each of R_2, R_4, R_5, R_6, R_8, R_9, R_{10}, R_{11}, R_{13}, and R_{14} is hydrogen.

[0083] In an embodiment, structure (I) includes R_1 that is a methyl group and R_3 is a t-butyl group. Each of R_7 and R_{12} is a fluorine atom. Each of R_2, R_4, R_5, R_6, R_8, R_9, R_{10}, R_{11}, R_{13}, and R_{14} is hydrogen.

[0084] In an embodiment, structure (I) includes R_1 that is a methyl group and R_3 is a t-butyl group. Each of R_7 and R_{12} is a chlorine atom. Each of R_2, R_4, R_5, R_6, R_8, R_9, R_{10}, R_{11}, R_{13}, and R_{14} is hydrogen.

[0085] In an embodiment, structure (I) includes R_1 that is a methyl group and R_3 is a t-butyl group. Each of R_7 and R_{12} is a bromine atom. Each of R_2, R_4, R_5, R_6, R_8, R_9, R_{10}, R_{11}, R_{13}, and R_{14} is hydrogen.

[0086] In an embodiment, structure (I) includes R_1 that is a methyl group and R_3 is a t-butyl group. Each of R_7 and R_{12} is an iodine atom. Each of R_2, R_4, R_5, R_6, R_8, R_9, R_{10}, R_{11}, R_{13}, and R_{14} is hydrogen.

[0087] In an embodiment, structure (I) includes R_1 that is a methyl group and R_3 is a t-butyl group. Each of R_6, R_7, R_{11}, and R_{12} is a chlorine atom. Each of R_2, R_4, R_5, R_8, R_9, R_{10}, R_{13}, and R_{14} is hydrogen.

[0088] In an embodiment, structure (I) includes R_1 that is a methyl group and R_3 is a t-butyl group. Each of R_6, R_8, R_{11}, and R_{13} is a chlorine atom. Each of R_2, R_4, R_5, R_7, R_9, R_{10}, R_{12}, and R_{14} is hydrogen.

[0089] In an embodiment, structure (I) includes R_1 that is a methyl group and R_3 is a t-butyl group. Each of R_2, R_4 and R_5-R_{14} is a fluorine atom.

[0090] In an embodiment, structure (I) includes R_1 that is a methyl group and R_3 is a t-butyl group. Each of R_7 and R_{12} is a trifluoromethyl group. Each of R_2, R_4, R_5, R_6, R_8, R_9, R_{10}, R_{11}, R_{13}, and R_{14} is hydrogen.

[0091] In an embodiment, structure (I) includes R_1 that is a methyl group and R_3 is a t-butyl group. Each of R_7 and R_{12} is an ethoxycarbonyl group. Each of R_2, R_4, R_5, R_6, R_8, R_9, R_{10}, R_{11}, R_{13}, and R_{14} is hydrogen.

[0092] In an embodiment, R_1 is methyl group and R_3 is a t-butyl group. Each of R_7 and R_{12} is an ethoxy group. Each of R_2, R_4, R_5, R_6, R_8, R_9, R_{10}, R_{11}, R_{13}, and R_{14} is hydrogen.

[0093] In an embodiment, structure (I) includes R_1 that is a methyl group and R_3 is a t-butyl group. Each of R_7 and R_{12} is a diethylamino group. Each of R_2, R_4, R_5, R_6, R_8, R_9, R_{10}, R_{11}, R_{13}, and R_{14} is hydrogen.

[0094] In an embodiment, structure (I) includes R_1 that is a methyl group and R_3 is a 2,4,4-trimethylpentan-2-yl group. Each of R_2, R_4 and R_5-R_{14} is hydrogen.

[0095] In an embodiment, structure (I) includes R_1 and R_3, each of which is a sec-butyl group. Each of R_2, R_4 and R_5-R_{14} is hydrogen.

[0096] In an embodiment, structure (I) includes R_1 and R_4 that are each a methyl group. Each of R_2, R_3, R_5-R_9 and R_{10}-R_{14} is hydrogen.

[0097] In an embodiment, structure (I) includes R_1 that is a methyl group. R_4 is an i-propyl group. Each of R_2, R_3, R_5-$R_9$and R_{10}-R_{14} is hydrogen.

[0098] In an embodiment, structure (I) includes R_1, R_3, and R_4, each of which is an i-propyl group. Each of R_2, R_5-R_9 and R_{10}-R_{14} is hydrogen.

[0099] In an embodiment, another procatalyst composition is provided. The procatalyst composition includes a combination of a magnesium moiety, a titanium moiety and a mixed internal electron donor. As used herein, a "mixed internal electron donor" is (i) a substituted phenylene aromatic diester, (ii) an electron donor component that donates a pair of electrons to one or more metals present in the resultant procatalyst composition, and (iii) optionally other components. In an embodiment, the electron donor component is a diether, a benzoate, and combinations thereof. The procatalyst composition with the mixed internal electron donor can be produced by way of the procatalyst production procedure as disclosed in the previously granted patents and publications identified herein.

[0100] For example, suitable catalyst compositions comprise a pro-catalyst composition, a co-catalyst, and an external electron donor or a mixed external electron donor (M-EED) of two or more different components. Suitable external donors include one or more activity limiting agents (ALA), one or more selectivity control agents (SCA) or both an ALA and an SCA. As used herein, an "external electron donor" is a component or a composition comprising a mixture of components added independent of procatalyst formation that modifies the catalyst performance. As used herein, an "activity limiting agent" is a composition that decreases catalyst activity as the polymerization temperature in the presence of the catalyst rises above a threshold temperature (e.g., temperature greater than about 85° C). A "selectivity control agent" is a composition that improves polymer tacticity, wherein improved tacticity is generally understood to mean increased tacticity or reduced xylene solubles or both. It should be understood that the above definitions are not mutually exclusive and that a single compound may be classified, for example, as both an activity limiting agent and a selectivity control agent.

[0101] In an embodiment, the external electron donor includes an alkoxysilane. The alkoxysilane has the general formula:

$$SiR_m(OR')_{4-m} \qquad (I)$$

where R independently each occurrence is hydrogen or a hydrocarbyl or an amino group optionally substituted with one or more substituents containing one or more Group 14, 15, 16, or 17 heteroatoms, said R containing up to 20 atoms not counting hydrogen and halogen; R' is a C_{1-4} alkyl group; and m is 0, 1, 2 or 3. In an embodiment, R is C_{6-12} arylalkyl or aralkyl, C_{3-12} cycloalkyl, C_{3-12} branched alkyl, or C_{3-12} cyclic or acyclic amino group, R' is C_{1-4} alkyl, and m is 1 or 2.

[0102] Nonlimiting examples of suitable silane compositions include dicyclopentyldimethoxysilane; di-tert-butyldimethoxysilane; methylcyclohexyldimethoxysilane; methylcyclohexyldiethoxysilane; ethylcyclohexyldimethoxysilane; diphenyldimethoxysilane; diisopropyldimethoxysilane; di-n-propyldimethoxysilane; diisobutyldimethoxysilane; diisobutyldiethoxysilane; isobutylisopropyldimethoxysilane; di-n-butyldimethoxysilane; cyclopentyltrimethoxysilane; isopropyltrimethoxysilane; n-propyltrimethoxysilane; n-propyltriethoxysilane; ethyltriethoxysilane; tetramethoxysilane; tetraethoxysilane; diethylaminotriethoxysilane; cyclopentylpyrrolidinodimethoxysilane; bis(pyrrolidino)dimethoxysilane; bis(perhydroisoquinolino)dimethoxysilane; and dimethyldimethoxysilane. In an embodiment, the silane composition is dicyclopentyldimethoxysilane (DCPDMS);

methylcyclohexyldimethoxysilane (MChDMS); or n-propyltrimethoxysilane (NPTMS); and any combination of thereof.

[0103] In an embodiment, the selectivity control agent component can be a mixture of 2 or more alkoxysilanes. In a further embodiment, the mixture can be dicyclopentyldimethoxysilane and methylcyclohexyldimethoxysilane, dicyclopentyldimethoxysilane and tetraethoxysilane, or dicyclopentyldimethoxysilane and n-propyltriethoxysilane. In an embodiment, the mixed external electron donor may include a benzoate, a succinate, and/or a diol ester. In an embodiment, the mixed external electron donor includes 2,2,6,6-tetramethylpiperidine as an SCA. In another embodiment, the mixed external electron donor includes a diether as both an SCA and an ALA.

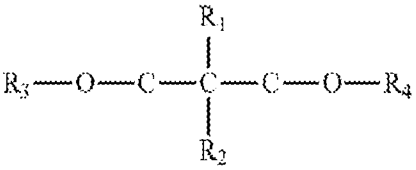
[0104] A mixed external electron donor system can also include an activity limiting agent (ALA). An ALA inhibits or otherwise prevents polymerization reactor upset and ensures continuity of the polymerization process. Typically, the activity of Ziegler-Natta catalysts increases as the reactor temperature rises. Ziegler-Natta catalysts also typically maintain high activity near the melting point temperature of the polymer produced. The heat generated by the exothermic polymerization reaction may cause polymer particles to form agglomerates and may ultimately lead to disruption of continuity for the polymer production process. The ALA reduces catalyst activity at elevated temperature, thereby preventing reactor upset, reducing (or preventing) particle agglomeration, and ensuring continuity of the polymerization process.

[0105] The activity limiting agent may be a carboxylic acid ester, a diether, a poly(alkene glycol), a diol ester, and combinations thereof. The carboxylic acid ester can be an aliphatic or aromatic, mono- or poly-carboxylic acid ester. Nonlimiting examples of suitable monocarboxylic acid esters include ethyl and methyl benzoate; ethyl p-methoxybenzoate; methyl p-ethoxybenzoate; ethyl p-ethoxybenzoate; ethyl p-isopropoxybenzoate; ethyl acrylate; methyl methacrylate; ethyl acetate; ethyl p-chlorobenzoate; hexyl p-aminobenzoate; isopropyl naphthenate; n-amyl toluate; ethyl cyclohexanoate and propyl pivalate.

[0106] The aliphatic carboxylic acid ester may be a C_6 aliphatic acid ester, may be a mono- or a poly- (two or more) ester, may be straight chain or branched, may be saturated or unsaturated, and any combination thereof. The C_6-C_{30} aliphatic acid ester may also be substituted with one or more Group 14, 15 or 16 heteroatom containing substituents. Nonlimiting examples of suitable C_6-C_{30} aliphatic acid esters include C_{i-2}O alkyl esters of aliphatic C_{6-30} monocarboxylic acids, C_{1-20} alkyl esters of aliphatic C_{8-20} monocarboxylic acids, C_{1-4} allyl mono- and diesters of aliphatic C_{4-20} monocarboxylic acids and dicarboxylic acids, C_{1-4} alkyl esters of aliphatic C_{8-20}monocarboxylic acids and dicarboxylic acids, and C_{6-20} mono- or polycarboxylate derivatives of C_{2-100} (poly) glycols or C_{2-100} (poly)glycol ethers. In a further embodiment, the C_6-C_{30} aliphatic acid ester may be a laurate, a myristate, a palmitate, a stearate, an oleate, a sebacate, (poly)(alkylene glycol) mono- or diacetates, (poly)(alkylene glycol) mono- or di-myristates, (poly)(alkylene glycol) mono- or di-laurates, (poly)(alkylene glycol) mono- or di-oleates, glyceryl tri(acetate), glyceryl tri-ester of C_{2-40} aliphatic carboxylic acids, and mixtures thereof. In a further embodiment, the C_6-C_{20} aliphatic ester is isopropyl myristate or di-n-butyl sebacate.

[0107] In an embodiment, the activity limiting agent includes a diether. The diether can be a 1,3-diether compound represented by the following structure (VI):

(VI)

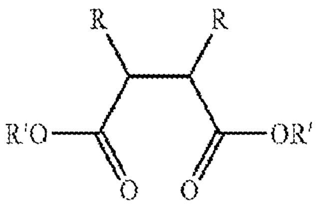


$$R_3-O-C-\overset{R_1}{\underset{R_2}{C}}-C-O-R_4$$

wherein R_1 to R_4 are independently of one another an alkyl, aryl or aralkyl group having up to 20 carbon atoms, which may optionally contain a group 14, 15, 16, or 17 heteroatom, and R_1 and R_2 may be a hydrogen atom. The dialkylether may linear or branched, and may include one or more of the following groups: alkyl, cycloaliphatic, aryl, alkylaryl or arylalkyl radicals with 1-18 carbon atoms, and hydrogen. R_1 and R_2 may be linked to form a cyclic structure, such as cyclopentadiene or fluorene.

[0108] In an embodiment, the activity limiting agent includes a succinate composition having the following structure (VII):

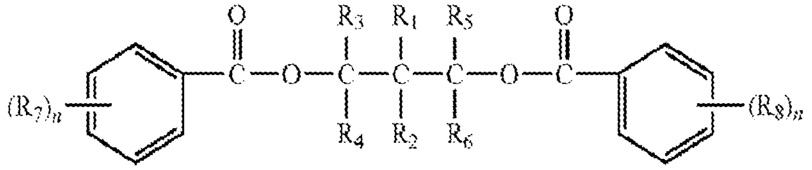
(VII)



wherein R and R' may be the same or different, R and/or R' including one or more of the following groups: hydrogen, linear or branched alkyl, alkenyl, cycloalkyl, aryl, arylalkyl or alkylaryl group, optionally containing heteroatoms. One or more ring structures can be formed via one or both 2- and 3-position carbon atom.

[0109] In an embodiment, the activity limiting agent includes a diol ester as represented by the following structure (VIII):

(VIII)



wherein n is an integer from 1 to 5. R_1 and R_2, may be the same or different, and each may be selected from hydrogen, methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, t-butyl, allyl, phenyl, or halophenyl group. R_3, R_4, R_5, R_6, R_7, and R_8 may be the same or different, and each may be selected from hydrogen, halogen, substituted, or unsubstituted hydrocarbyl having 1 to 20 carbon atoms. R_1-R_6 groups may optionally contain one or more heteroatoms replacing carbon, hydrogen or both, the hetero-atom selected from nitrogen, oxygen, sulfur, silicon, phosphorus and a halogen. R_7 and R_8, may be the same or different, and may be bonded to any carbon atom of the 2-, 3-, 4-, 5-, and 6-position of either phenyl ring.

[0110] Individual external electron donor components can be added into the reactor separately or two or more can be mixed together in advance and then added into the reactor as a mixture. In the mixture, more than one selectivity control agent or more than one activity limiting agent can be used. In an embodiment, the mixture is dicyclopentyldimethoxysilane and isopropyl myristate; diisopropyldimethoxysilane and isopropyl myristate; dicyclopentyldimethoxysilane and poly(ethylene glycol) laurate; dicyclopentyldimethoxysilane and isopropyl myristate and poly(ethylene glycol) dioleate; methylcyclohexyldimethoxysilane and isopropyl myristate; n-propyltrimethoxysilane and isopropyl myristate; dimethyldimethoxysilane and methylcyclohexyldimethoxysilane and isopropyl myristate; dicyclopentyldimethoxysilane and n-propyltriethoxysilane and isopropyl myristate; diisopropyldimethoxysilane and n-propyltriethoxysilane and isopropyl myristate; and dicyclopentyldimethoxysilane and tetraethoxysilane and isopropyl myristate; dicyclopentyldimethoxysilane and diisopropyldimethoxysilane and n-propyltriethoxysilane and isopropyl myristate; and combinations thereof.

[0111] The catalyst composition includes a cocatalyst. The cocatalyst for use with the Ziegler-Natta procatalyst composition may be an aluminum containing composition. Nonlimiting examples of suitable aluminum containing compositions include organoaluminum compounds, such as trialkylaluminum; dialkylaluminum hydride; alkylaluminum dihydride; dialkylaluminum halide; alkylaluminumdihalide; dialkylaluminum alkoxide; and alkylaluminum dialkoxide-compounds containing from 1-10, or 1-6 carbon atoms in each alkyl- or alkoxide-group. In an embodiment, the cocatalyst is a C_{1-4} trialkylaluminum compound, such as triethylaluminum (TEA). The catalyst composition includes a mole ratio of aluminum (Al) to (SCA(s)+ALA(s)) of 0.5-25:1; or 1.0-20:1; or 1.5-15:1; or less than about 6.0; or less than about 5; or less than 4.5. In an embodiment, the Al:(SCA(s)+ALA(s)) mole ratio is 0.5-4.0:1. The total-SCA to ALA mole ratio is 0.01-20:1; 0.10-5.00:1; 0.43-2.33:1; or 0.54-1.85:1; or 0.67-1.5:1.

IV. Applications

[0112] The propylene-butene copolymers of the present disclosure can be used in numerous and diverse applications. As described above, the nucleated/clarified propylene-butene copolymers have excellent stiffness characteristics and excellent transparency properties.

[0113] In one embodiment, the propylene-butene copolymers of the present disclosure can be incorporated into a composition for forming injection molded articles, such as containers. When used for injection molding, the polymer can have a melt flow rate of greater than about 4 g/10 min, such as greater than about 10 g/10 min, such as greater than about 20 g/10 min, such as greater than about 30 g/10 min, such as greater than about 35 g/10 min. The containers can have a bottom that defines a hollow interior and a top that includes a flange that seals to the bottom. In addition to containers, in general any injection moldable article can be produced in accordance with the present disclosure that requires a certain degree of rigidity in combination with good optics. For instance, the propylene-butene copolymer of the present disclosure is particularly well suited to producing packaging, including all different types food packaging.

[0114] In addition to injection molded articles, the propylene-butene copolymer of the present disclosure can also be used in extrusion blow molding and thermoforming applications. When used for blow molding or thermoforming, the polymer can have a melt flow rate of less than about 5 g/10 min, such as less than about 4.5 g/10 min, such as less than about 4 g/10 min, such as less than about 3.5 g/10 min. The polymer can have a melt flow rate of greater than about 0.2 g/10 min, such as greater than about 1 g/10 min. When formulated with a relatively low melt flow rate, the copolymer displays excellent melt strength allowing for the formation of various different blow molded articles having relatively uniform wall thickness. For instance, the propylene-butene copolymer can be used to produce all different types of plastic bottles for containing, for instance, beverages. As described above, because the polymer can be formed from non-phthalate based catalysts, the polymer is exceptionally well suited for food contact applications.

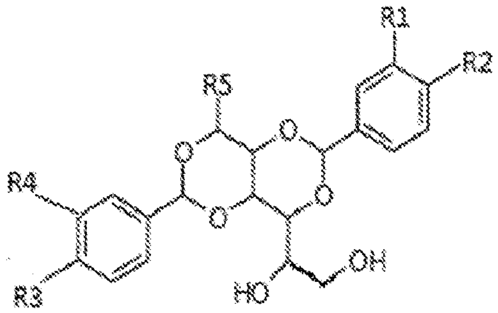
[0115] In still another embodiment, the propylene-butene copolymer of the present disclosure can be used in thermoforming applications. For instance, the polymer can be used to produce thermoformed containers including drink cups. Drink cups made according to the present disclosure, for instance, can be display lower haze and higher stiffness in comparison to cups made with ethylene random copolymers.

[0116] The propylene-butene copolymers of the present disclosure can be combined with various other components and ingredients in formulating a polymer composition for making molded articles as described above. For instance, in one embodiment, the polymer composition can contain antioxidants and acid scavengers, and in some applications may preferably also contain other additives such as nucleators, mold release agents, anti-stats, slip agents, anti-block agents, processing aids, UV stabilizers, and colorants (pigments). The antioxidant can be a hindered phenol, which may be used with a phosphite stabilizer. Acid scavengers that may be used include a metal stearate such as calcium stearate, a hydrotalcite, or mixtures thereof. Each additive can be present in the composition in an amount of from about 0.01% to about 2% by weight, such as from about 0.1% to about 1% by weight.

[0117] In one embodiment, the copolymer composition can further contain a nucleating agent. The nucleating agent can be added to further improve the transparency properties of the composition. In one aspect, the nucleating agent can be a clarifying agent that can comprise a compound capable of producing a gelation network within the composition.

[0118] In one embodiment, the nucleating agent may comprise a sorbitol compound, such as a sorbitol acetal derivative. In one embodiment, for instance, the nucleating agent may comprise a dibenzyl sorbitol.

[0119] With regard to sorbitol acetal derivatives that can be used as an additive in some embodiments, the sorbitol acetal derivative is shown in Formula (I):



(I)

wherein R1-R5 comprise the same or different moieties chosen from hydrogen and a C1-C3 alkyl.

[0120] In some embodiments, R1-R5 are hydrogen, such that the sorbitol acetal derivative is 2,4-dibenzylidene sorbitol ("DBS"). In some embodiments, R1, R4, and R5 are hydrogen, and R2 and R3 are methyl groups, such that the sorbitol acetal derivative is 1,3:2,4-di-p-methyldibenzylidene-D-sorbitol ("MDBS"). In some embodiments, R1-R4 are methyl groups and R5 is hydrogen, such that the sorbitol acetal derivative is 1,3:2,4-Bis (3,4-dimethylbenzylidene) sorbitol ("DMDBS"). In some embodiments, R2, R3, and R5 are propyl groups (-CH2-CH2-CH3), and R1 and R4 are hydrogen, such that the sorbitol acetal derivative is 1,2,3-trideoxy-4,6:5,7-bis-O-(4-propylphenyl methylene) nonitol ("TBPMN").

[0121] Other embodiments of nucleating agents that may be used include:

1,3:2,4-dibenzylidenesorbitol;

1,3:2,4-bis(p-methylbenzylidene)sorbitol;

Di(p-methylbenzylidene)Sorbitol;

Di(p-ethylbenzylidene)Sorbitol; and

Bis(5',6',7',8'-tetrahydro-2-naphtylidene)Sorbitol.

[0122] In one embodiment, the nucleating agent may also comprise a bisamide, such as benzenetrisamide. The nucleating agents described above can be used alone or in combination.

[0123] The one or more nucleating agents can be present in the polymer composition in an amount greater than about 100 ppm, such as in an amount greater than about 300 ppm, such as in an amount greater than about 1000 ppm, such as in an amount greater than about 2000 ppm, and generally less than about 20,000 ppm, such as less than about 10,000 ppm, such as less than about 4000 ppm.

[0124] When the one or more nucleating agents are clarifying agents, the clarifying agents can be added in an amount greater than about 1,500 ppm, such as in an amount greater than about 1,800 ppm, such as in an amount greater than about 2,000 ppm, such as in an amount greater than about 2,200 ppm. One or more clarifying agents are generally present in an amount less than about 20,000 ppm, such as less than about 15,000 ppm, such as less than about 10,000 ppm, such as less than about 8,000 ppm, such as less than about 5,000 ppm.

[0125] As described above, polymer compositions containing the propylene-butene copolymer of the present disclosure have excellent low haze characteristics, which can be enhanced when one or more nucleating agents are added and combined with the polymer. For example, when measured at a thickness of 0.7 mm, the propylene-butene copolymer or polymer composition containing the propylene-butene copolymer can have a haze of less than about 12%, such as less than about 10%, such as less than about 8%. Molded articles, such as bottles, containers, films, and cups made with the polymer can have a haze of less than about 10%, such as less than about 7.5%, such as less than about 7 %, such as less than about 6.5%, such as less than about 6 %, such as less than about 5.5 %. The haze is generally greater than about 1%.

V. Examples

Example Set No. 1

[0126] Propylene-butene random copolymer samples were produced and their properties tested in accordance with the procedures outlined above. The properties and experimental results are outlined in the table below.

[0127] The propylene-butene random copolymers were produced with a stereospecific 6th generation Ziegler-Natta magnesium supported/titanium-based catalyst. The catalyst contained a non-phthalate internal donor producing polymers having a broader molecular weight distribution than polymers made using a metallocene catalyst. The process used to produce the polymers is described in the art as the UNIPOL gas phase process. The catalyst used to produce the polymers included a substituted phenylene aromatic diester internal electron donor. The catalyst used is commercially available from W.R. Grace and Company and sold under the trade name CONSISTA. All copolymers were made using an external electron donor and triethylaluminum as a cocatalyst.

[0128] The various different random copolymers that were produced were combined with a nucleating agent except for Sample Nos. 1, 6, 10, and 14 where no nucleating agent was added. Two different nucleating agents were used. The nucleating agents were (1) TPBMN (a clarifier) and (2) HYPERFORM HPN-600ei (a nucleator) marketed by Milliken Chemical. Sample Nos. 2, 7, 11, and 15 contained HYPERFORM HPN-600ei at a concentration of 400 ppm. Sample Nos. 3, 8, 12, and 16 contained TPBMN at a concentration of 2000 ppm and Sample Nos. 4, 5, 9, 13, and 17 contained TPBMN at a concentration of 4000 ppm. Each sample also contained a hindered phenol antioxidant, a phosphite antioxidant, and an acid scavenger (hydrotalcite).

[0129] The following results were obtained:

Sample No.	MFR (g/10 min)	IZOD (J/M) @23°C	Flex Mod @1% Sec (psi)	Tensile Strength @ yield (psi)	Tensile Elongation @ Yield (%)	%XS Viscotek	Bt (% wt)
1	3.47	41.922	192990	5252	11.5645	4.963	2.32
2	3.24	71.993	213640	5528	10.2826	5.16	2.43
3	3.00	48.697	213740	5499	10.8095	5.115	2.69
4	3.14	59.595	220430	5569	10.8818	5.268	2.47
5	3.14	39.868	213390	5536	10.8089	5.119	2.62
6	2.83	39.729	188330	4873	11.065	4.632	4.23
7	2.76	83.778	202670	5359	10.6176	4.759	4.22
8	2.84	82.035	203440	5358	11.0179	4.75	4.19
9	3.30	56.806	211460	5431	11.2834	4.939	4.51
10	2.68	62.442	175320	4624	11.400	4.902	5.80
11	2.47	85.453	187410	4839	10.798	4.684	5.90
12	2.52	79.571	190630	4793	11.377	5.065	6.00
13	2.66	93.884	196950	4854	11.018	4.806	6.15
14	2.74	69.173	164140	4431	11.415	4.347	7.66
15	2.85	99.446	173650	4614	11.010	4.506	7.73
16	2.82	90.03	175420	4556	11.862	4.83	7.75
17	3.05	90.514	180360	4632	11.462	4.615	7.75

Sample No.	ΔH Tc (J/g)	Tc (°C)	ΔH Tm (J/g)	Tm (°C)	1 mm	1.5 mm	3 mm
1	103.7	111.59	100.4	153.34	65.74	78.40	97.58
2	103.8	122.94	101.5	156.65	25.28	37.42	80.30
3	103.2	125.71	103.1	157.21	23.00	42.84	64.44
4	110.1	126.7	105.5	157.21	15.62	29.36	56.58
5	100.2	125.07	98.35	157.2	21.72	39.50	63.60
6	92.58	114.42	88.31	150.93	54.76	66.74	96.86
7	99.31	120.14	97.85	152.69	23.08	33.76	74.98
8	100.7	122.86	100.3	153.39	22.66	40.72	60.30
9	101.1	124.26	96.27	153.31	6.19	10.04	35.28
10	84.95	111.56	93.85	147.17	56.28	67.72	96.68
11	93.67	117.21	93.14	149.2	21.8	31.26	71.26
12	96.79	120.88	93.91	150.09	14.42	26.88	47.06
13	96.91	121.44	94.6	150.04	6.12	9.72	31.44
14	90.3	108.39	91.14	143.85	59.28	70.46	96.38
15	91.94	114.08	90.57	145.77	23.4	33.1	74.14
16	92.26	118.37	87.47	147.31	15.18	25.9	47.32
17	94.09	118.96	98.15	147.21	6.24	9.94	31.48

Example Set No. 2

[0130] Propylene-butene random copolymer samples were produced and their properties tested in accordance with the procedures outlined above. The properties and experimental results are outlined in the tables below.

[0131] The propylene-butene random copolymers were produced with a stereospecific 6th generation Ziegler-Natta magnesium supported/titanium-based catalyst. The catalyst contained a non-phthalate internal donor producing polymers having a broader molecular weight distribution than polymers made using a metallocene catalyst. The process used to produce the polymers is described in the art as the UNIPOL gas phase process. The catalyst used to produce the polymers included a substituted phenylene aromatic diester internal electron donor. The catalyst used is commercially available from W.R. Grace and Company and sold under the trade name CONSISTA. All copolymers were made using an external electron donor and triethylaluminum as a cocatalyst.

[0132] Propylene-ethylene random copolymers were also produced. In the table below, for instance, Sample Nos. 20-28, and 32-36 are directed to propylene-butene random copolymers while Sample Nos. 18, 19, 29-31, and 37-40 are directed to propylene-ethylene random copolymers. Sample Nos. 18, 19, 37, and 38 were made with the same catalyst that was used to produce the propylene-butene copolymers. Sample Nos. 29-31, 39, and 40 were made using a phthalate-based catalyst. Some of the polymers produced were combined with either 2000 ppm or 4000 ppm of a nucleating agent, namely TBPMN, while Sample Nos. 20, 23, 26, 29, and 32 did not contain a nucleating agent. The polymer compositions where then injection molded into containers or blow molded into bottles. The following results were obtained:

			Anti-oxident 1	Anti-oxident 2	Antacid	Clarifier	Test																	
Sample	Catalyst Type	Tested Application	Irgan 1010 Hindered Phenol	Irgafos 168 Phosphite	DHT-4A hydro talcite	TPBMN	Viskotek	Pellet MFR	IZOD 23°C	Flex Mod 1% sec 23°C	Tensile Strength @yield	Elongation @yield	Haze			Clarity			Gloss		FTIR	FTIR	DSC Tc	DSC Tm	HDT
			ppm	ppm	ppm	ppm	%XS	dg/min	Avg (J/m)	Avg Mpa	Strength MPa	%	1.0 mm	1.6 mm	3.0 mm	1.0 mm	1.6 mm	3.0 mm	45°	60°	Et%	Bt%	C	C	C
18	non-pthalate	Injection Molding	500	750	180	2000	8.65	47.33	51.45	1069.30	29.45	13.48	13.86	18.74	41.72	99.48	99.62	89.86	90.98	103.22	3.54		102.40	146.90	70.8
19	non-pthalate	Injection Molding	500	750	180	4000	6.46	50.68	39.83	1093.20	30.52	12.65	6.87	11.06	33.90	56.50	28.67	9.64	102.40	152.38	3.61		120.23	146.67	70.7
20	non-pthalate	Injection Molding	500	750	180	0	4.49	42.13	20.75	1117.70	31.39	10.71	58.10	79.62	99.00	95.68	37.12	9.24	62.54	79.08		7.60	108.22	143.58	80.8
21	non-pthalate	Injection Molding	500	750	180	2000	4.56	42.41	33.62	1301.80	33.40	11.42	14.54	19.86	45.40	99.40	99.62	94.20	89.76	107.18		7.72	120.61	147.57	77.6
22	non-pthalate	Injection Molding	500	750	180	4000	4.69	44.67	26.40	1360.40	34.09	10.61	7.11	11.54	35.98	99.50	99.72	91.52	102.06	151.34		7.74	120.79	147.16	75.6
23	non-pthalate	Injection Molding	500	750	180	0	4.58	46.22	20.72	1204.10	32.67	10.52	60.94	81.20	99.08	93.74	80.94	7.36	62.38	101.20		5.61	111.38	147.02	85.3
24	non-pthalate	Injection Molding	500	750	180	2000	4.82	45.95	22.75	1417.30	35.42	10.83	16.22	22.18	48.58	99.64	99.52	90.64	99.16	135.22		5.73	123.12	150.88	84.4
25	non-pthalate	Injection Molding	500	750	180	4000	4.63	49.19	33.56	1472.20	36.09	10.00	7.11	11.94	37.72	99.44	99.58	90.08	101.34	150.24		5.79	123.32	150.78	82.4
26	non-pthalate	Injection Molding	500	750	180	0	3.96	38.47	18.57	1202.00	33.02	10.52	16.96	79.68	98.68	90.96	79.10	7.78	62.52	78.46		5.62	110.61	146.84	85.7
27	non-pthalate	Injection Molding	500	750	180	2000	4.40	42.61	22.06	1424.40	35.23	10.62	16.30	22.80	49.40	99.62	99.62	96.06	86.62	104.22		5.71	123.04	150.69	84.3
28	non-pthalate	Injection Molding	500	750	180	4000	4.26	42.80	35.27	1491.20	35.93	10.18	7.59	12.16	38.24	99.26	99.56	95.42	99.60	116.96		5.76	123.38	150.74	83.9
29	pthalate	Injection Molding	500	750	180	0	6.09	13.14	26.12	950.63	28.44	12.06	57.86	73.02	97.86	83.04	75.40	8.40	66.22	80.20	3.41		106.33	142.69	75.7
30	pthalate	Injection Molding	500	750	180	2000	6.27	13.23	36.90	1091.60	33.30	12.77	17.68	24.72	47.98	99.58	99.74	95.48	85.68	103.00	3.58		120.28	147.82	73.2
31	pthalate	Injection Molding	500	750	180	4000	6.16	13.28	48.43	1120.70	31.08	12.43	6.56	11.18	33.60	99.26	99.66	96.56	101.18	117.88	3.61		120.56	148.19	71.3
32	non-pthalate	Injection Molding	500	750	180	0	5.13	13.31	26.19	1195.80	31.90	10.99	62.00	76.46	98.26	86.44	76.30	8.56	64.78	80.14		5.75	109.91	148.29	80.3
33	non-pthalate	Injection Molding	500	750	180	2000	5.24	13.21	41.23	1377.00	33.67	11.51	14.14	21.54	48.16	99.60	99.62	94.48	89.30	106.38		5.72	121.95	151.08	80.1
34	non-pthalate	Injection Molding	500	750	180	4000	5.33	13.97	54.49	1396.30	34.44	10.84	6.04	12.06	36.84	99.30	99.28	96.28	100.86	118.62		5.84	122.12	150.99	79.6
35	non-pthalate	Extrusion Blow Moulding	Unknown	Unknown	Unknown	2000	6.09	2.53	96.64	1232.20	31.75	11.80	10.70	16.58	41.70	99.42	99.42	96.40	97.48	113.56		7.26	118.47	148.51	74.1
36	non-pthalate	Extrusion Blow Moulding	Unknown	Unknown	Unknown	2000	5.36	2.84	126.98	1216.80	31.74	12.10	10.58	17.00	41.22	99.44	99.48	96.54	96.86	113.00		7.38	118.45	148.20	73.1
37	non-pthalate	Extrusion Blow Moulding	Unknown	Unknown	Unknown	2000	9.13	2.69	369.24	966.22	28.19	14.04	9.46	15.76	37.14	99.60	99.50	96.42	96.98	112.98	3.17		119.23	147.33	69.5
38	non-pthalate	Extrusion Blow Moulding	Unknown	Unknown	Unknown	2500	9.65	2.52	338.05	961.67	28.06	14.30	6.10	12.68	35.32	99.58	99.56	96.62	99.82	115.98	3.21		117.17	147.16	68.7
39	pthalate	Extrusion Blow Moulding	Unknown	Unknown	Unknown	2000	6.50	2.03	344.38	1067.50	30.39	13.01	11.40	19.72	45.72	98.96	98.86	95.16	94.30	109.38	3.08		120.29	149.76	74.1
40	pthalate	Extrusion Blow Moulding	Unknown	Unknown	Unknown	2000	6.90	2.26	351.75	1044.40	29.84	13.29	11.48	19.72	44.00	99.00	98.98	96.12	96.02	111.30	3.04		120.50	149.60	74.4

[0133] Sample Nos. 19 and 22 above were also tested for haze on the injection molded article after one year of production and compared to a commercial grade propylene-ethylene random copolymer having the following characteristics.

Sample No.	MFR (g/10min)	XS (wt%)	Et% (wt%)
41	50	6.3	3.7

[0134] The following results were obtained:

Sample	Haze % (1 year later)	Aged haze % (50 C, 24h)	Aged haze change % after 1 year
19	3.8	4.9	33%
22	4.2	4.6	10%
41	7.9	11.8	94%

[0135] These and other modifications and variations to the present invention may be practiced by those of ordinary skill in the art, without departing from the spirit and scope of the present invention, which is more particularly set forth in the appended claims. In addition, it should be understood that aspects of the various embodiments may be interchanged both in whole or in part. Furthermore, those of ordinary skill in the art will appreciate that the foregoing description is by way of example only, and is not intended to limit the invention so further described in such appended claims.

What Is Claimed:

1. A propylene-butene copolymer comprising:
propylene as a primary monomer;
a butene content of from about 1% to about 12% by weight;
a xylene soluble fraction of from about 1.0% to about 8.0% by weight;
a molecular weight distribution (Mw/Mn) of greater than about 3.5; and
a substituted phenylene aromatic diester.

2. A propylene-butene copolymer as defined in claim 1, wherein the butene content is from about 2% to about 8% by weight, such as from about 2% to about 6% by weight.

3. A propylene-butene copolymer as defined in claim 2, wherein the copolymer has a heat deflection temperature of greater than about 75 ° C.

4. A propylene-butene copolymer as defined in any of the preceding claims, wherein the copolymer has a melting temperature of from about 147° C to about 155° C.

5. A propylene-butene copolymer as defined in any of the preceding claims, wherein the xylene soluble content is from about 2% to about 7% by weight.

6. A propylene-butene copolymer as defined in any of the preceding claims, wherein the copolymer has a melt flow rate of from about 0.2 g/10 min to about 8 g/10 min.

7. A propylene-butene copolymer as defined in any of claims 1-3, wherein the copolymer has a melt flow rate of from about 8 g/10 min to about 220 g/10 min.

8. A propylene-butene copolymer as defined in any of the preceding claims, wherein the copolymer has a flexural modulus of greater than about 1200 MPa, such as greater than about 1300 MPa, such as greater than about 1400 MPa, and generally less than about 2000 MPa.

9. A propylene-butene copolymer as defined in any of the preceding claims, wherein the polymer has been Ziegler-Natta catalyzed using a non-phthalate catalyst.

10. A propylene-butene copolymer as defined in any of the preceding claims, wherein the polymer has a xylene soluble fraction/butene content ratio of from about 0.3 to about 3.0, such as from about 0.3 to about 2.0 or from 0.5 to about 1.0.

11. A polymer composition containing the propylene-butene copolymer as defined in any of the preceding claims, the propylene-butene copolymer being present in the polymer composition in an amount greater than about 70% by weight, such as in an amount greater

than about 80% by weight, such as in an amount greater than about 90% by weight, such as in an amount greater than about 95% by weight.

12. A polymer composition as defined in claim 11, wherein the composition further comprises a nucleating agent.

13. A polymer composition as defined in claim 12, wherein the nucleating agent comprises a nonitol.

14. A polymer composition as defined in any of claims 11 - 13, wherein the polymer composition displays a haze at 0.7 mm of about 8% or less, such as about 6% or less.

15. An article made from the polymer composition as defined in any of the preceding claims, the article comprising an injection molded article, a blow molded article, a thermoformed article, a film or a fiber.

16. An article comprising a blow molded article, a thermoformed article, a film or a fiber made from a polymer composition comprising a propylene-butene copolymer comprising:

propylene as a primary monomer;
a butene content of from about 1% to about 12% by weight;
a xylene soluble fraction of from about 1.0% to about 8.0% by weight; and
a molecular weight distribution (Mw/Mn) of greater than about 3.5.
an antioxidant and antacid

17. An article as defined in claim 16, comprising a cup, a bottle, or a container.

18. An article as defined in claim 16, comprising packaging.

19. An article as defined in claim 16, wherein the butene content of the copolymer is from about 2% to about 8% by weight, such as from about 2% to about 6% by weight.

20. An article as defined in claim 19, wherein the copolymer has a heat deflection temperature of greater than about 75 ° C.

21. An article as defined in any of claims 19 or 20, wherein the copolymer has a melting temperature of from about 145° C to about 155° C, such as from 147° C to about 155° C.

22. An article as defined in any of claims 16 - 21, wherein the xylene soluble content is from about 2% to about 7% by weight.

23. An article as defined in any of claims 16 - 22, wherein the copolymer has a melt flow rate of from about 0.2 g/10 min to about 4 g/10 min.

24. An article as defined in any of claims 16 - 23, wherein the polymer has a xylene soluble fraction/butene content ratio of from about 0.3 to about 3.0, such as from about 0.3 to about 2.0.

25. An article as defined in any of claims 16 - 24, wherein the propylene-butene copolymer is present in the polymer composition in an amount greater than about 70% by weight, such as in an amount greater than about 80% by weight, such as in an amount greater than about 90% by weight, such as in an amount greater than about 95% by weight.

26. An article as defined in any of claims 16 - 25, wherein the composition further comprises a nucleating agent.

27. An article as defined in claim 26, wherein the nucleating agent comprises a nonitol.

28. An article as defined in any of claims 16 - 27, wherein the polymer composition displays a haze at 0.7 mm of about 8% or less, such as about 6% or less.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 21/40822

A. CLASSIFICATION OF SUBJECT MATTER
IPC - B32B 27/32; C08F 210/06; C08J 5/18 (2021.01)

CPC - B32B 27/32; C08F 210/06; C08J 5/18

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)
See Search History document

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 2016/0280808 A1 (W.R. Grace & Co. - Conn.) 29 September 2016 (29.09.2016) - entire document especialy para[0135], [0148], [0149], and [0150]	1-3, 7 ---- 4
Y	US 2011/0293867 A1 (Bernreitner et al.) 01 December 2011 (01.12.2011) - entire document especially para[0020]	4
A	WO 2017/108644 A1 (Borealis AG) 29 June 2017 (29.06.2017) - entire document	1-4, 7
A	US 2016/0311951 A1 (Borealis AG) 27 October 2016 (27.10.2016) - entire document	1-4, 7
A	US 2016/0009836 A1 (Toho Titanium Co. LTD) 14 January 2016 (14.01.2016) - entire document	1-4, 7

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"D" document cited by the applicant in the international application

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 22 September 2021 (22.09.2021)	Date of mailing of the international search report DEC 21 2021
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Authorized officer Kari Rodriquez Telephone No. PCT Helpdesk: 571-272-4300

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 5-6, 8-15, and 22-28
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:
This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I: Claims 1-4, 7 directed to a propylene-butene copolymer comprising: propylene as a primary monomer; a butene content of from about 1% to about 12% by weight; a xylene soluble fraction of from about 1.0% to about 8.0% by weight; a molecular weight distribution (Mw/Mn) of greater than about 3.5; and a substituted phenylene aromatic diester.

Group II: Claims 16-21 directed to an article comprising a blow molded article, a thermoformed article, a film or a fiber made from a polymer composition comprising a propylene-butene copolymer comprising: propylene as a primary monomer; a butene content of from about 1% to about 12% by weight; a xylene soluble fraction of from about 1.0% to about 8.0% by weight; and a molecular weight distribution (Mw/Mn) of greater than about 3.5; an antioxidant and antacid.

---see supplemental box---

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-4, 7

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

---Box No. III Cont.---

The inventions listed as Groups I-II do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

Special Technical Features:

Group I requires a substituted phenylene aromatic diester; not required by Group II.

Group II requires an article comprising a blow molded article, a thermoformed article, a film or a fiber made from a polymer composition comprising a propylene-butene copolymer comprising: an antioxidant and antacid; not required by Group I.

Common Technical Features:

Groups I and II share the technical feature of a propylene-butene copolymer comprising: propylene as a primary monomer; a butene content of from about 1% to about 12% by weight; a xylene soluble fraction of from about 1.0% to about 8.0% by weight; and a molecular weight distribution (Mw/Mn) of greater than about 3.5.

However, these shared technical features do not represent a contribution over prior art, because the shared technical feature is obvious over US 2016/0280808 A1 to W.R. Grace & Co. - Conn. (hereinafter "Grace"). Grace teaches a propylene-butene copolymer (para[0149] "a polymerization process is provided and includes contacting propylene and ethylene and/or 1-butene with a catalyst composition under polymerization conditions"; para[0159] "Polymer includes homopolymers, copolymers, terpolymers, interpolymers, and so on") comprising: propylene as a primary monomer (para[0022] "a propylene-based polymer"; para[0164] "propylene-based polymer...refers to a polymer that comprises a majority weight percent polymerized propylene monomer"); a butene content of from about 1% to about 12% by weight (para[0135] "One or more olefin monomers can be introduced into a polymerization reactor to...form a polymer...monomers include...1-butene"; "para[0150] "formant propylene-based interpolymer has a weight percent comonomer content relative to propylene of...about 0.001% to about 20%"); a xylene soluble fraction of from about 1.0% to about 8.0% by weight (para[0149] "The formant propylene-based interpolymer has a xylene solubles content from about 0.5% to about 40%"); a molecular weight distribution (Mw/Mn) of greater than about 3.5(para[0148] "forming a propylene-based polymer having a polydispersity index (PDI) from about 4 to about 15"; para[0222] "molecular weight distribution (PDI)"); and a substituted phenylene aromatic diester (para[0151] "olefin-based polymer (i.e., propylene-based polymer) produced by any of the foregoing processes comprises a substituted phenylene aromatic diester"), but does not teach a specific embodiment comprising a propylene-butene copolymer. However, it would have been obvious to one skilled in the art through routine experimentation to use the propylene based copolymer taught by Grace wherein the comonomer is butene.

As the shared technical features were known in the art at the time of the invention, they cannot be considered common technical features that would otherwise unify the groups. Therefore, Groups I-II lack unity under PCT Rule 13.

Note: Claims 5-6, 8-15 and 22-28 determined unsearchable because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).