

SEMI-CRYSTALLINE THERMOPLASTIC BLOCK COPOLYMERS

FIELD OF THE INVENTION

[0001] This invention relates to thermoplastic block copolymers, to compositions comprising such copolymers, and to a process for making such copolymers.

BACKGROUND OF THE INVENTION

[0002] US 2010/0063213 A1 describes gel fiber and film compositions comprised of narrow molecular weight distribution homopolymers, statistical copolymers, block copolymers, and graft copolymers blended with a low molecular weight diluent. However, a need stills exists for polyolefin elastomers with better elastic hysteresis.

SUMMARY OF THE INVENTION

[0003] The present disclosure refers to a semi-crystalline thermoplastic polyolefin block copolymer that combines high tensile strength with other desirable physical properties, such as high elongation at break and/or high elastic recovery. Within the semi-crystalline copolymer, crystalline domains are comprised of isotactic poly(1-butene) (iPB), the A or hard block, while the amorphous or semi-crystalline segment, the B or soft block, is comprised of a copolymer of 1-butene and ethylene or a second alpha-olefin or a terpolymer of 1-butene, ethylene, and a second alpha-olefin. In one example, two A blocks are joined to and separated from one another by the B block, i.e., an ABA block terpolymer or higher order polymer such as an ABAB tetrablock copolymer or ABABA pentablock copolymer. In one example, two B blocks are joined to and separated from one another by the A block, i.e., an BAB block terpolymer or higher order polymer such as an BABA tetrablock copolymer or BABAB pentablock copolymer. The desirable properties of the resulting segmented copolymer are superior to those obtained from blends of the individual blocks.

[0004] In one example the present disclosure refers to a semi-crystalline, thermoplastic polyolefin block copolymer comprising:

- (A) A first polyolefin A block comprising isotactic poly(1-butene) (iPB);
- (B) A polyolefin B block comprising an ethylene and/or alpha-olefin/1-butene copolymer or terpolymer; and
- (C) A second polyolefin A block comprising isotactic poly(1-butene) (iPB);

the A and B blocks bonded to one another to form the polymer in which the first and second polyolefin A blocks are joined to and separated by the polyolefin B block.

[0004a] In one aspect, the present disclosure refers to a semi-crystalline, thermoplastic polyolefin block copolymer comprising:

- (A) a first polyolefin A block comprising isotactic poly(1-butene) (iPB);
- (B) a polyolefin B block selected from the group consisting of 1-butene/ethylene copolymer, 1-butene/alpha-olefin copolymer, and 1-butene/ethylene/alpha-olefin terpolymer; and
- (C) a second polyolefin A block comprising isotactic poly(1-butene) (iPB);

the A and B blocks bonded to one another to form the polymer in which the first and second polyolefin A blocks are joined to and separated by the polyolefin B block.

[0005] In one example the present disclosure refers to a semi-crystalline, thermoplastic polyolefin block copolymer comprising:

- (A) A first polyolefin B block comprising an ethylene and/or alpha-olefin/1-butene copolymer or terpolymer;
- (B) A polyolefin A block comprising isotactic poly(1-butene) (iPB); and
- (C) A second polyolefin B block comprising an ethylene and/or alpha-olefin/1-butene copolymer or terpolymer;

the B and A blocks bonded to one another to form the polymer in which the first and second polyolefin B blocks are joined to and separated by the polyolefin A block.

[0005a] In another aspect, the present disclosure refers to a semi-crystalline, thermoplastic polyolefin block copolymer comprising:

- (A) a first polyolefin B block selected from the group consisting of 1-butene/ethylene copolymer, 1-butene/alpha-olefin copolymer, and 1-butene/ethylene/alpha-olefin terpolymer;
- (B) a polyolefin A block comprising isotactic poly(1-butene) (iPB); and
- (C) a second polyolefin B block selected from the group consisting of 1-butene/ethylene copolymer, 1-butene/alpha-olefin copolymer, and 1-butene/ethylene/alpha-olefin terpolymer;

the B and A blocks bonded to one another to form the polymer in which the first and second polyolefin B blocks are joined to and separated by the polyolefin A block.

[0006] In one example the present disclosure refers to a composition comprising a semi-crystalline, thermoplastic polyolefin block copolymer comprising a minimum block sequence of either ABA or BAB.

[0006a] In another aspect, the present disclosure refers to a composition comprising the semi-crystalline, thermoplastic polyolefin polymer as described herein.

[0006b] In another aspect, the present disclosure refers to an article comprising the composition as described herein.

[0007] In another aspect, the present disclosure refers to a process for making a semi-crystalline, thermoplastic polyolefin ABA block copolymer, the process comprising the steps of:

- (A) Feeding 1-butene to a high pressure reactor under polymerization conditions to produce a first A block of isotactic poly(1-butene) (iPB);
- (B) Adding ethylene and/or a second alpha-olefin to the reactor under copolymerization conditions to form a B block of a 1-butene/ethylene copolymer, a 1-butene/alpha-olefin copolymer, or a 1-butene/ethylene/alpha-olefin terpolymer which is attached to the first A block to form an AB block copolymer; and
- (C) Stopping the addition of ethylene and/or the second alpha-olefin, and continue feeding 1-butene to the reactor under polymerization conditions to form a second A block of iPB which is attached to the B block to form the ABA block copolymer.

[0008] In another aspect, the present disclosure refers to a process for making the semi-crystalline, thermoplastic polyolefin BAB block copolymer, the process comprising the steps of:

- (A) Feeding 1-butene and ethylene and/or a second alpha-olefin to a reactor under copolymerization conditions to form a first B block of a 1-butene/ethylene

copolymer, a 1-butene/alpha-olefin copolymer, or a 1-butene/ethylene/alpha-olefin terpolymer;

- (B) Stopping the addition of ethylene and/or the second alpha-olefin, and continue feeding 1-butene to the reactor under polymerization conditions to form an A block of isotactic poly(1-butene) (iPB) which is attached to the B block to form a BA block copolymer; and
- (C) Restarting the addition of ethylene and/or the second alpha-olefin to the reactor under copolymerization conditions to form a second B block of a 1-butene/ethylene copolymer, a 1-butene/alpha-olefin copolymer, or a 1-butene/ethylene/alpha-olefin terpolymer which is attached to the A block to form the BAB block copolymer.

BRIEF DESCRIPTION OF THE FIGURES

[0009] Figure 1 is an example ^{13}C NMR spectrum of the branch CH_2 region of a predominately isotactic poly(1-butene). This spectrum was acquired with 2560 scans to enable low level triads to be clearly observed for method development. This is 8X the number of scans used for the analysis of typical samples in the examples.

[0010] Figure 2 is an example ^{13}C NMR spectrum of the branch CH_2 region of a predominately isotactic poly(1-butene) (adapted from Tetsuo, A.; Demura, M.; Yamamoto, K.; Chûjô, R. "Polymerization Mechanism and Conformation of Poly(1-butene)," *Polymer* 1987, 28, 1037-1040).

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

Definitions

[0011] Unless stated to the contrary, implicit from the context, or customary in the art, all parts and percents are based on weight and all test methods are current as of the filing date of this disclosure. For purposes of United States patent practice, the contents of any referenced patent, patent application or publication are incorporated by reference in their entirety (or its equivalent US version is so incorporated by reference), especially with respect to the disclosure of definitions (to the extent not inconsistent with any definitions specifically provided in this disclosure) and general knowledge in the art.

[0012] The numerical ranges disclosed herein include all values from, and including, the lower and upper value. For ranged containing explicit values (e.g., 1 or 2; or 3 to 5; or 6; or 7),

any subrange between any two explicit values is included (e.g., 1 to 2; 2 to 6; 5 to 7; 3 to 7; 5 to 6; etc.).

[0013] "Polymerization conditions", "copolymerization conditions", and like terms refer to process parameters under which a procatalyst entering the reactor zone will be activated using a suitable activator, which results in an open coordination site on the metal center, thereby initiating the coordination polymerization or copolymerization. These conditions include, for example, pressure, temperature, concentrations of reagents and polymer, residence time and distribution, influencing the composition, molecular weight, molecular weight distribution (also known as polydispersity index, PDI) and polymer structure.

[0014] A "polymer" is a compound prepared by polymerizing monomers, whether of the same or a different type, that in polymerized form provide the multiple and/or repeating "units" or "mer units" that make up a polymer. The generic term polymer thus embraces the term homopolymer, usually employed to refer to polymers prepared from only one type of monomer, the term copolymer, usually employed to refer to polymers prepared from at least two types of monomers, and the term terpolymer, usually employed to refer to polymers prepared from three different types of monomers. It also embraces all forms of copolymer, e.g., random, block, etc.

[0015] "Block copolymer", "block polymer" and like terms mean a polymer in which units derived from like monomers group together in a polymer chain, e.g., units derived from monomers A and B group together to form a polymer with a configuration of AAAABBBB, or ABA, or BAB, etc. Each block of a block copolymer can comprise mer units derived from a single monomer, e.g., ethylene, or 1-butene, etc., or the block can comprise mer units derived from two or more monomers, e.g., 1-butene and ethylene, or 1-butene and 1-hexene and/or 1-octene.

Hard (Crystalline) Block A

[0016] Block A is isotactic poly(1-butene) (iPB), and it has an isotacticity of meso triad percent (mm%) greater than (>) 90%. The melting temperature (T_m) of the A block can vary, but typically it is from 60 to 120 °C, or from 70 to 110 °C, or from 75 to 100 °C. The melting enthalpy (ΔH_m) of the A block can vary, but typically it is from 5 to 120 J/g, or from 8 to 90 J/g, or from 10 to 40 J/g, as measured after 1 week of aging at room temperature (23 °C). The weight average molecular weight (M_w) of the A block can vary widely, but typically it is from 8,000 to 90,000 grams per mole (g/mol), or from 15,000 to 70,000 g/mol, or from 25,000 to 60,000

g/mol. The number average molecular weight (M_n) of the A block can also vary widely, but typically it is from 5,000 to 50,000 grams per mole (g/mol), or from 8,000 to 40,000 g/mol, or from 10,000 to 30,000 g/mol. The polydispersity index (PDI, or M_w/M_n) of the A block can also vary widely, but typically it is from 1 to 3, or from 1.1 to 2, or from 1.3 to 1.8. In one embodiment the semi-crystalline, thermoplastic polyolefin block copolymers of this invention have at least two A blocks separated by and joined to a B block, and each A block can be the same or different in molecular weight and/or PDI. In one embodiment the semi-crystalline, thermoplastic polyolefin block copolymers of this invention have only one A block separating two B blocks.

Soft (Amorphous or Semi-Crystalline) Block B

[0017] Block B comprises a copolymer or terpolymer of 1-butene and one or more of ethylene and/or one or more of a second alpha-olefin. The second alpha-olefin typically has 3 to 12 carbon atoms, more typically 3 to 10 carbon atoms and even more typically 3 to 8 carbon atoms. Representative second alpha-olefins include propylene, 1-pentene, 1-hexene and 1-octene. In one embodiment the B block consists of 1-butene and ethylene. In one embodiment the B block consists of 1-butene and ethylene with the following properties: amorphous—a glass transition temperature (T_g) less than 0 °C, preferably less than -20 °C, and more preferably less than -40 °C; semi-crystalline—less than (<) 25% ethylene crystallinity (T_m <80 °C), preferably < 20% ethylene crystallinity (T_m <70 °C), and more preferably <15% ethylene crystallinity (T_m <50 °C). In one embodiment the B block consists of 1-butene and a second alpha-olefin. In one embodiment, the B block consists of 1-butene, ethylene, and a second alpha-olefin.

[0018] The amount of 1-butene in the B block can vary widely, but typically the B block comprises from 15 to 90 weight percent (wt%), more typically from 30 to 80 wt%, and even more typically from 40 to 65 wt%, 1-butene.

[0019] The weight average molecular weight (M_w) of the B block can vary widely, but typically it is from 20,000 to 300,000 g/mol, or from 30,000 to 200,000 g/mol, or from 65,000 to 120,000 g/mol. The number average molecular weight (M_n) of the B block can also vary widely, but typically it is from 10,000 to 250,000 grams per mole (g/mol), or from 20,000 to 150,000 g/mol, or from 40,000 to 75,000 g/mol. The PDI of the B block can also vary widely, but typically it is from 1 to 3, or from 1 to 2, or from 1 to 1.5.

[0020] The butene crystallinity of the B block is always less than the butene crystallinity of the A block. In one embodiment the B block is amorphous with a glass transition temperature (T_g) of less than $-20\text{ }^{\circ}\text{C}$, and more typically less than $-40\text{ }^{\circ}\text{C}$.

[0021] In one embodiment the semi-crystalline, thermoplastic polyolefin block copolymers of this invention contain at least one B block that is joined to and separates two A blocks. In one embodiment the semi-crystalline, thermoplastic polyolefin block copolymers of this invention have at least two B blocks separated by and joined to an A block, and each B block can be the same or different in molecular weight and/or PDI. In one embodiment, the semi-crystalline, thermoplastic polyolefin block copolymers of this invention contain two or more B blocks, with the B blocks alternating with the A blocks to form a block polymer with an ABAB or BABA configuration. Each B block can be the same or different in molecular weight and/or PDI.

Semi-crystalline, Thermoplastic Polyolefin Block Copolymers

[0022] The polyolefin block copolymers of this invention comprise an ABA or BAB block structure. In one embodiment the block copolymer is a terpolymer with an ABA block structure. In one embodiment the block copolymer is a terpolymer with an BAB block structure. In one embodiment the block copolymer is a tetrablock copolymer with an ABAB or BABA block structure. In one embodiment the block copolymer is a pentablock copolymer with an ABABA or BABAB block structure.

[0023] The weight average molecular weight (M_w) of the block copolymer of this invention can vary widely, but typically it is from 40,000 to 500,000 g/mol, or from 50,000 to 350,000 g/mol, or from 100,000 to 250,000 g/mol. The number average molecular weight (M_n) of the block copolymer can also vary widely, but typically it is from 20,000 to 350,000 grams per mole (g/mol), or from 30,000 to 250,000 g/mol, or from 70,000 to 160,000 g/mol. The PDI of the block copolymer can also vary widely, but typically it is from 1 to 3, or from 1 to 2, or from 1.3 to 2.

[0024] The relative amount of A block to B block in the block copolymers of this invention can vary widely but typically the weight ratio of the A blocks to B block(s) is from 4:96 to 70:30, or from 15:85 to 60:40, or from 30:70 to 45:55, based on the weight of the block copolymer.

Process for Making Polyolefin Block Copolymers

[0025] In one embodiment, an ABA block terpolymer is made in a three-step process in which the first step comprises feeding 1-butene to a high pressure reactor under polymerization conditions to produce the first A block (iPB) at a desired M_w , M_n and/or PDI. The second step comprises adding ethylene and/or a second alpha-olefin to the reactor (with 1-butene still present in the reactor and/or with additional 1-butene fed to the reactor) under copolymerization conditions to grow the B block through chain extension from the active end of the first A block. The third step comprises stopping the addition of ethylene and/or second alpha-olefin feed to the reactor, and, if necessary, purging the reactor of unreacted ethylene and/or second alpha-olefin, but continuing the feed of 1-butene under polymerization conditions to grow the second A block from the active end of the B block. The final block polymer is recovered using conventional equipment and protocols. The process for producing a BAB block copolymer is essentially the same except that the first B block is first made, followed by the making of the A block, followed by the making of the second block, i.e., *mutatis mutandis*.

[0026] The inventive copolymers can be produced *via* solution living polymerization at low temperature ($< 0\text{ }^{\circ}\text{C}$) using a suitable catalyst (e.g., a metallocene, salen-type, etc.), that can produce iPB (A block) with high tacticity ($\text{mm}\% > 90\%$, preferably $>96\%$) and ethylene or a second alpha olefin/1-butene copolymer or terpolymer (B block) in a living manner in a Parr reactor, continuous stirred tank reactor (CSTR) or loop reactor. This is the method illustrated in the examples.

[0027] Alternatively, the block copolymers of this invention can be produced in a high temperature solution process ($> 120\text{ }^{\circ}\text{C}$) using a combination of two catalysts and a chain shuttling agent. Both catalysts are capable of chain shuttling, and one produces iPB (A block) and the other produces the B block. The A and B blocks are produced in separate reactors. For triblocks, a series of 3 reactors can be used (Parr reactors, CSTR or loop reactors).

[0028] Another potential method using high temperature solution polymerization involves the synthesis of iPB with high isotacticity and high chain-end unsaturation using a suitable catalyst (e.g., CGC catalysts) followed by a series of steps to functionalize the double bonds (e.g., install amine functional groups) and couple the resulting polymer with a suitable functionalized soft copolymer (e.g., maleic anhydride-grafted ethylene-octene (EO) copolymer).

Applications

[0029] The thermoplastic polyolefin block copolymers of this invention may be used neat or as a formulated blend in injected molded parts, cast or blown films. The desirable properties of the resulting segmented copolymers are superior to those obtained from blends of the individual blocks. Representative end uses include, but are not limited to, airbeds, medical cushions, artificial leather (sporting bags, upholstery), cap liners, medical and other tubing, grips, lids, toys, tooth brushes, elastic film (diapers, etc.) and the like. Additional uses are identified in USP 7,858,706 and USP 7,893,166.

SPECIFIC EMBODIMENTS

*Test Methods**Gel Permeation Chromatography (GPC)*

[0030] A high temperature Triple Detector Gel Permeation Chromatography (3D-GPC) system equipped with Robotic Assistant Delivery (RAD) system for sample preparation and sample injection was used. The concentration detector was an infrared concentration detector (IR4 from Polymer Char *Inc.*, Valencia, Spain). The other two detectors were 1) a Precision Detectors 2-angle laser light scattering detector, Model 2040, from Agilent, and 2) a 4-capillary differential viscometer detector, Model 150R, from Viscotek (Houston, TX). The 15-degree angle of the light scattering detector was used for absolute molecular weight calculation purposes.

[0031] Data collection was performed using the Polymer Char DM 100 Data acquisition box. The chromatographic and the sample preparation solvent was 1,2,4-trichlorobenzene (TCB) containing 200 ppm of butylated hydroxytoluene (BHT). TCB was sparged with nitrogen. The columns were four Olexis 13 micron columns or four Mixed A LS 20 um columns. The injection volume was 200 μ l, and the flow rate was 1.0 mL/minute. The column compartment was operated at 150°C. Solid samples were made at a concentration 1 – 2 mg/mL in TCB, and solution samples were diluted with TCB targeting 1 – 2 mg/mL. All samples were filtered hot through a layer of Perlite to remove color and/or catalyst residues prior to running HT GPC.

[0032] Calibration of the GPC column set was performed with 21 narrow molecular weight distribution polystyrene standards, with molecular weights ranging from 580 to 8,400,000 g/mol. The polystyrene standard peak molecular weights were converted to polyethylene molecular weights using the following equation (Williams, T. and Ward, I. M. “The Construction of a

Polyethylene Calibration Curve for Gel Permeation Chromatography Using Polystyrene Fractions” *J. Polym. Sci., Polym. Let.* 1968, 6, 621.):

$$M_{pe} = A(M_{ps})^B \quad (\text{Eq. 1})$$

where $B = 1.0$, and the experimentally determined value of A is approximately 0.38.

[0033] A fifth-order polynomial was used to fit the respective polyethylene-equivalent calibration points obtained from Eq. 1 to their observed elution volumes for each polystyrene standard. Number average and weight average molecular weights (M_n and M_w respectively) were calculated according to the following equations:

$$M_n = \frac{\sum Wf_i}{\sum \left(\frac{Wf_i}{M_i} \right)} \quad (\text{Eq. 2})$$

$$M_w = \frac{\sum (Wf_i * M_i)}{\sum Wf_i} \quad (\text{Eq. 3})$$

[0034] Where Wf_i and M_i are the weight fraction and molecular weight of elution component i , respectively. The accurate A value was determined by adjusting its value in Eq 1 until the M_w of a linear PE homopolymer reference (Dow 53494-38-4) calculated using Eq 3 agreed with its known M_w of 115,000 g/mol. The polydispersity index (PDI) was expressed as M_w/M_n . Conventional GPC results were determined by this method.

[0035] The absolute molecular weights were determined by the LS and IR4 concentration detectors using the following equation:

$$Mw(abs) = K_{LS} * \frac{\sum (LS_i)}{\sum (IR_i)} \quad (\text{Eq. 4})$$

where $\sum (LS_i)$ is the response area of LS detector, $\sum (IR_i)$ is the response area of the IR4 detector, and K_{LS} is the instrument constant, that was determined using a standard (NBS 1475) with known concentration and the certificated value for the weight average molecular weight (52,000 g/mol).

[0036] The composition detector (IR5) measures infrared response of carbon-hydrogen bond stretches of the methyl groups from the polymerized 1-butene comonomer, and the methylene/methine groups from both the polymerized ethylene and 1-butene comonomers. The ratio of the methyl and methylene infrared responses was used to determine the butene content at each elution volume. The IR5 detector composition mode was calibrated with modal poly(ethylene-co-1-butene) random copolymers with known 1-butene content determined by

^{13}C NMR spectroscopy. The calibration curve was built by first order fitting of the response ratio of methyl to methylene at the peak position to the weight percentage of 1-butene for each sample.

[0037] The comonomer wt% at each elution component of each characterized sample was calculated using the measured ratio of the methyl over methylene responses and the established calibration curve, while the molecular weight of the same elution component was calculated as discussed previously. The molecular weight and comonomer content at each elution component were plotted as two dimensional plots.

Carbon 13 Nuclear Magnetic Resonance (^{13}C NMR)

Sample Preparation

[0038] Samples were prepared by adding approximately 2.7 g of a 50/50 (by wt) mixture of tetrachloroethane- d_2 /orthodichlorobenzene containing 0.025 M $\text{Cr}(\text{acac})_3$ to 0.10 to 0.25 g of the polymer sample in the NMR tube. Each sample was dissolved and homogenized by heating the tube and its contents to approximately 145 °C using a heating block and heat gun. Each sample was visually inspected to ensure homogeneity.

Data Acquisition Parameters

[0039] The data were collected using a Bruker 400 MHz spectrometer equipped with a Bruker Dual DUL high-temperature CryoProbe. The data were acquired using 320 scans, a 6 sec pulse repetition delay (1.3 s at and 4.7 s D1), 90 degree flip angles, and inverse gated decoupling with a sample temperature of 120°C. All measurements were made on non-spinning samples in locked mode. Samples were allowed to thermally equilibrate for 7 minutes prior to data acquisition. The ^{13}C NMR chemical shifts were internally referenced to the *mmmm* + *mmmr* CH_3 's at 11.0 ppm (for iPB homopolymer) or the *EEE* triads at 30.0 ppm (for EB and block polymers).

Data Analysis for Tacticity in iPB Homopolymers

[0040] Tacticity for iPB homopolymers was determined from the C2 branch CH_2 region of the ^{13}C NMR spectrum (~26.5 to 28 ppm) as shown in Table 1 (Tetsuo, A.; Demura, M.; Yamamoto, K.; Chûjô, R. "Polymerization Mechanism and Conformation of Poly(1-butene)," *Polymer* 1987, 28, 1037-1040.). 1.0 Hz line broadening was applied prior to the Fourier transformation of the data. The integral for the entire branch CH_2 region from ~26.5 to 28 ppm

was set to a value of 100 to establish nominal values. The following regions were then integrated: *mmmm* = 27.8 to 28.3 ppm, *mm* = 27.4 to 28.3 ppm.

Table 1

Integral regions and assignments used for tacticity determination in iPB homopolymers.*
The chemical shifts are referenced to 11.0 ppm for the *mm* methyls.

Peak #	Pentad	Triad	ppm	Δ ppm (ref.) approx.	Δ ppm (observed)
1	<i>mmmm</i>	<i>mm</i>	27.878	0.00	0.000
2	<i>mmmr</i>		27.714	0.20	-0.164
3	<i>rmmr</i>		27.513	0.40	-0.365
4	<i>mmrr</i>	<i>mr</i>	27.389	0.46	-0.489
5	<i>mmrm</i>		27.330	0.55	-0.548
6	<i>rmrr</i>		27.296	0.65	-0.582
7	<i>mrmr</i>		27.092	0.75	-0.786
8	<i>rrrr</i>	<i>rr</i>	26.896	0.90	-0.982
9	<i>mrrr</i>		26.789	1.02	-1.089
10	<i>mrrm</i>		26.699	1.15	-1.179

*Tetsuo, A.; Demura, M.; Yamamoto, K.; Chûjô, R. "Polymerization Mechanism and Conformation of Poly(1-butene)" *Polymer* 1987, 28, 1037-1040.

Data Analysis for Comonomer Content in the EB Block

[0041] The 1-butene content of EB random copolymers was determined using the simple method of setting the full polymer integral (~40 to 10 ppm) to a value of 1000, and integrating all butene methyls from ~12 to 10 ppm. The wt% and mol% 1-butene values were then calculated directly from these two integrals. This method is accurate for the typical EB compositions in these examples with near 50 mol% comonomer content. Other methods are more appropriate when the amount of either monomer is less than 5-10 mol%.

Data Analysis for Block Copolymers

[0042] The diblock, triblock and tetrablock copolymer spectra were analyzed using the method described above for overall wt% and mol% 1-butene. The amount of iPB present was determined using the integral of the *mm* branch CH₂'s at 27.9 ppm. This peak was fairly well resolved in most samples. Due to the high ethylene content of the EB component, the number of 1-butene sequences of three or more units, which are necessary to create an isotactic *mm* triad, was very small, and could be treated as zero. From these two integrals, and having set the full polymer integral to 1000, one can readily calculate the wt% EB, wt% iPB, and wt% B in the EB values.

Differential Scanning Calorimetry (DSC)

[0043] Glass transition temperature (T_g), melting enthalpy (ΔH_m), and melting temperature (T_m) were measured by DSC. Samples were analyzed using a TA Instruments Q2000 DSC approximately 1 week after the polymers were produced. Samples were cut from compression molded films. Approximately 5 mg of polymer was placed into an aluminum pan and capped with an aluminum lid. Samples were analyzed by cooling to $-100\text{ }^{\circ}\text{C}$ at $10\text{ }^{\circ}\text{C}/\text{min}$, then heating to $180\text{ }^{\circ}\text{C}$ at $10\text{ }^{\circ}\text{C}/\text{min}$, cooling to $-100\text{ }^{\circ}\text{C}$ at $10\text{ }^{\circ}\text{C}/\text{min}$, and heating to $180\text{ }^{\circ}\text{C}$ at $10\text{ }^{\circ}\text{C}/\text{min}$. The data was analyzed using TA Universal Analysis software. The T_g was measured using the 1st heat cycle data using the inflection method. The melting enthalpy (ΔH_m) and melting temperature (T_m) was measured using the 1st heat cycle data.

[0044] Tensile measurements were measured on an INSTRON™ 4201 using ASTM D638 with Type V sample geometry with a $2''/\text{min}$ extension rate. All reported values represent the average of 2-3 sample bars and are reported in terms of engineering stress and strain unless otherwise noted. Samples were compression molded at approximately $150\text{ }^{\circ}\text{C}$ and allowed to age at ambient conditions for approximately seven days prior to testing. Tensile hysteresis measurements were performed at 300% elongation with no relaxation period between loading/unloading cycles at a $2''/\text{min}$ rate using the same sample geometry. The percentage energy loss and tensile set observed during the first loading/unloading cycle was determined [$\{(\text{area under the 1}^{\text{st}} \text{ stress-strain extension curve}) - (\text{area under the 1}^{\text{st}} \text{ stress-strain retraction curve})\}/(\text{area under the 1}^{\text{st}} \text{ stress-strain extension curve})$]. All reported values represent the average of 3 sample bars. Small delays in stress response (typically $<10\%$ strain) resulting from residual “slack” in the specimen after loading into the INSTRON™ sample holder and zeroing the load were compensated for in the reported tensile set values. Compression set was measured based on ASTM D395B. Due to limited sample quantities, the procedure was modified to utilize specimens of approximately $1'' \times 0.25''$ (diameter $\times$ thickness), which were obtained by stacking four $1'' \times 1/16''$ (diameter $\times$ thickness) samples. Specimens were compressed by 25% of their initial thickness at 23 and $70\text{ }^{\circ}\text{C}$ for 24 hrs. All reported values were obtained from a single specimen. The tensile set was reported as the % strain at which the stress returned to a value of zero upon the 1st retraction cycle.

[0045] Ultimate tensile strength was measured according to ASTM D638 (Type V).

[0046] Elongation at break was measured according to ASTM D638 (Type V).

- [0047] Young's modulus was measured according to ASTM D638 (Type V).
- [0048] Tensile strength at 100% was measured according to ASTM D638 (Type V).
- [0049] Tensile strength at 300% was measured according to ASTM D638 (Type V).

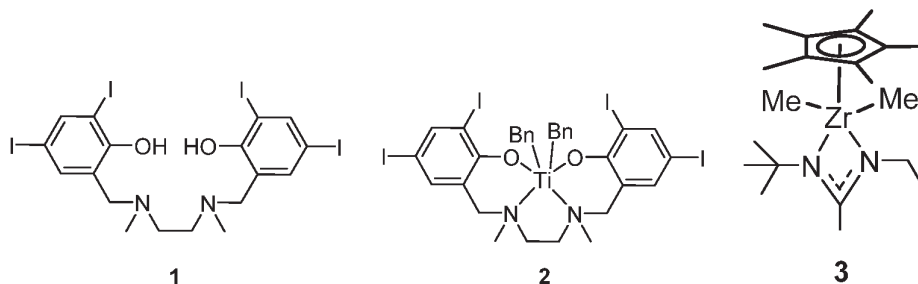
Materials

[0050] Chlorobenzene (HPLC grade, 99.9%) and toluene were obtained from Aldrich, degassed by sparging with dry nitrogen and dried over molecular sieves and activated alumina beads prior to use. The activated alumina beads (F-200, 1/8" bead size, product of BASF) were obtained from Coastal Chemical and dried at 250 °C for several days, then stored under a dry nitrogen atmosphere prior to use. Methanol was purchased from Aldrich and used as received. Tris(pentafluorophenyl)boron (FAB), trityl tetrakis(pentafluoro-phenyl)borate and reagents for the synthesis of ligand 1 were obtained from commercial sources and used as received. Ligand 1 was synthesized according to the reported procedure (Cohen, A.; Kopilov, J.; Lamberti, M.; Venditto, V.; Kol, M. *Macromolecules* 2010, 43, 1689-1691).

[0051] Procatalyst 2 was prepared in situ by mixing ligand 1 and tetrabenzyltitanium shortly before each polymerization run. Procatalyst 3 used for the synthesis of the iPB sample used to prepare the polymer blends in the Comparative Examples was synthesized using the general synthetic method described in Kissounko, D. A.; Fettinger, J. C.; Sita, L. R. "Structure/Activity Relationships for the Living Ziegler-Natta Polymerization of 1-Hexene by the Series of Cationic Monocyclopentadienyl Zirconium Acetamidinate Complexes" *Inorg. Chim. Acta* 2003, 345, 121-129. The ¹H NMR data for procatalyst 2 can be found in Jayaratne, K. C.; Sita, L. R. "Stereospecific Living Ziegler-Natta Polymerization of 1-Hexene" *J. Am. Chem. Soc.* 2000, 122, 958-959.

[0052] Air-sensitive compounds were manipulated in a glovebox under a dry nitrogen atmosphere and stored at -30°C. The monomers were obtained from Airgas (ethylene: 99.9%, 1-butene: 99.95%, 3.5 grade). The 1-butene monomer was passed through a purification bed containing molecular sieves and SELEXSORBTM CD (a smooth, spherical adsorbent customized to provide optimum adsorption for several polar organic compounds including: oxygenated hydrocarbons, mercaptans, and nitrogen-based molecules, available from BASF) both dried at 250 °C under nitrogen before use. Given the air- and moisture-sensitive nature of the catalyst, the dry solvent and reagents were fed into the polymerization reactor using pressurized nitrogen,

and extra care was taken to avoid exposure of the reactor contents to oxygen and moisture at all times.



Synthesis of Tetrabenzyltitanium (TiBn_4)

[0053] In a nitrogen-filled drybox BnMgCl (120 mL, 91.2 mmol, 0.76 M in Et_2O) was cooled to $-30\text{ }^\circ\text{C}$ in an amber bottle. TiCl_4 (4.325 g, 22.8 mmol) was dissolved in 40 mL pentane and the solution was cooled to $-30\text{ }^\circ\text{C}$. The cold TiCl_4 solution was slowly added to the cold BnMgCl solution while stirring. Cold pentane (40 mL) was added and the deep red mixture was stirred for 2 hours at $-30\text{ }^\circ\text{C}$. The reaction mixture was filtered and the filter cake was rinsed with cold pentane. The combined filtrate was pumped off to give a somewhat sticky red material, which was triturated with 20 mL of pentane, cooled to $-30\text{ }^\circ\text{C}$, filtered and dried under vacuum. The triturated solid showed impure product by ^1H NMR. Trituration with pentane was repeated two more times affording the pure desired product in 30% yield.

[0054] ^1H NMR (400 MHz, C_6D_6) δ 7.08 (m, 8H), 6.95 (m, 4H), 6.61 (m, 8H), 2.81 (s, 8H).

Reactor Setup

[0055] A high-pressure Parr reactor was used for these examples. Key reactor specifications included:

- 600 mL Parr reactor
- Siemens PCS-7 control system
- Solvent loading cylinder (600 mL)
- Catalyst loading cylinder (60 mL)
- Monomer-specific mass flow control
- Pressure control
- Internal cooling coil
- Glycol chiller/band heater control (-20 to $200\text{ }^\circ\text{C}$)
- Glass kettle dump tank

2000 psig rupture disc and knockout pot

Due to the fact that the internal cooling coil and the agitator occupied some of the total reactor volume, the polymerization solutions were limited to 250 mL and the hot wash between runs to 400 mL. In an effort to keep the solvents used for runs and washes dry and free of oxygen, each solvent was loaded into a cylinder inside of a nitrogen-purged glovebox and added to the reactor from the cylinder using pressurized nitrogen.

Polymer Synthesis Using Procatalyst 2 – General Procedure

Synthesis of the iPB Block

[0056] The polymerization was carried out in a 600 milliliter (mL) Parr reactor controlled by a Siemens process control system and equipped with an internal cooling coil. Chlorobenzene (200 mL) was added to the reactor from a solvent cylinder pressurized with nitrogen. The agitator was turned on at 700 revolutions per minute (rpm) and the reactor was cooled to about -7°C using a chiller. The 1-butene monomer was added at 1800 milligrams per minute (mg/min). The FAB activator was dissolved in 10 mL of chlorobenzene was added to the reactor via a small bomb pressurized with nitrogen. A fresh solution of ligand 1 mixed with TiBn_4 in 20 mL of chlorobenzene was added to the reactor via the same small bomb pressurized with nitrogen. The bomb was flushed with 20 mL chlorobenzene. The reactor contents were agitated for a specified length of time to produce the iPB block.

Synthesis of the Ethylene/1-Butene (EB) Block

[0057] In order to achieve chain extension via the addition of an EB block, ethylene was added to the reactor either by quickly pressurizing the reactor with ethylene to a set pressure and then allowing ethylene to flow at 0.2 grams per minute (g/min) to maintain pressure. The vent valve was controlled to open in the event of a pressure rise above the setpoint to maintain the target pressure. After completing the synthesis of the EB block with a specific block length, the ethylene flow was stopped and the reactor was quickly purged with nitrogen to remove residual ethylene from the solution. This was done by venting the reactor quickly, then pressurizing it to about 50 pounds per square inch (psig) (344.74 kilopascals (kPa)) with nitrogen through a tube reaching down to the bottom of the reactor and venting quickly again.

Synthesis of the Third Block (iPB)

[0058] After the ethylene flow was shut off and the solution was quickly purged with nitrogen, generally extra 1-butene was added to make up for the amount consumed during the

polymerization and lost during the nitrogen purge. Allowing the reaction to proceed for a specified length of time facilitated chain extension via the growth of the third block (iPB).

Sampling the Reactor for GPC Analysis

[0059] In order to accelerate sample turnaround, we developed the following method of preparing samples for gel permeation chromatography (GPC) analysis: each polymerization reaction mixture was sampled directly into 30 mL of 1,2,4-trichlorobenzene (TCB) containing 200 parts per million (ppm) of the butylated hydroxytoluene (BHT) inhibitor. Lower sample volume was required at higher conversion due to higher polymer concentration. Next, in order to remove the orange color caused by catalyst decomposition products, the TCB solution was mixed with a small amount of silica gel (about 100-200 mg) and heated to 90 °C for 30 minutes while stirring. Stirring was then stopped allowing the silica gel to settle. The resulting colorless liquid phase was decanted into a syringe equipped with a 1 micron polytetrafluoroethylene (PTFE) syringe filter and quickly filtered into a vial. The solution obtained this way was suitable for GPC analysis without further filtration, thereby dramatically accelerating the GPC turnaround time. Samples did require heating before transferring the solutions into GPC vials in order to ensure that the entire polymer was in the solution phase.

Isolation of the Final Polymer Product

[0060] The final polymer product was isolated by draining the reactor into 600 mL of methanol. The polymer precipitate was filtered and dried at 130 °C under vacuum overnight. Each polymerization was followed by a hot wash using dry, degassed toluene (400 mL) at 170 °C under about 50 psig (344.74 kPa) pressure for a minimum of 4 hours.

Inventive Examples 1-3

[0061] All three Inventive Examples (IE) were iPB-EB-iPB triblock copolymers prepared according to the general method described above. All samples were subjected to four weeks of aging at 25 °C prior to mechanical testing. Specific run details and polymer characterization data are reported in Table 2.

Table 2
Run Details and Polymer Data of IE 1-3

Ex.	Polymer type	1-Butene (g)	C ₂ H ₄ (psig)	Segment run time (min)	Polymer Yield (g)	GPC (triple detector, absolute MW)			¹³ C NMR		T _g (°C)	DSC T _m (°C)	ΔH _m (J/g)
						M _w	M _n	PDI	wt% iPB	wt% B in EB			
1	iPB	20		30m		17,864	12,393	1.44					
	diblock		30	30m		86,911	55,323	1.57					
	triblock	+10		30m	5.47	113,914	76,643	1.49	39.2	58.2	-59.9	80.1	13.2
2	iPB	30		30m		27,402	18,574	1.48					
	diblock		30	90m		202,557	128,711	1.57					
	triblock	+10		30m	12.22	234,956	152,029	1.55	34.3	61.0	-54.2	83.1	10.8
3	iPB	20		70m		41,183	28,532	1.44					
	diblock		70	25m		158,488	101,965	1.55					
	triblock	+5		70m	11.61	215,564	120,420	1.79	34.7	47.1	-61.7	94.1	3.6

TiBn₄: 120 micromoles (μmol).

Ligand 1: TiBn₄:FAB = 1.2:1:1.2 (mole ratio).

Reactor temperature: -7 °C.

*Comparative Examples (CE) 1-3**Synthesis Random Poly(ethylene-co-1-butene) Copolymer (EB) Using Procatalyst 2*

[0062] Chlorobenzene (200 mL) was added to the reactor from a solvent cylinder pressurized with nitrogen. The agitator was turned on at 700 rpm and the reactor was cooled to about -7°C using a chiller. The 1-butene monomer was added at 1800 mg/min. The FAB activator was dissolved in 10 mL of chlorobenzene was added to the reactor via a small bomb pressurized with nitrogen. A fresh solution of ligand **1** mixed with TiBn_4 in 20 mL of chlorobenzene was added to the reactor via the same small bomb pressurized with nitrogen. The bomb was flushed with 20 mL chlorobenzene. The reactor was quickly pressurized with ethylene to 50 psig (344.74 kPa). An ethylene flow was established at 0.2 g/min to maintain pressure. The vent valve was controlled to open in the event of a pressure rise above the setpoint to maintain the target pressure. The reactor contents were agitated for 90 minutes to produce the EB sample. Specific run details and polymer characterization data are reported in Table 3.

Table 3

Run Details and Polymer Data of EB Copolymer

Polymer type	1-Butene (g)	C_2H_4 (psig)	Run time (min)	Polymer Yield (g)	GPC (triple detector, absolute MW)			^{13}C NMR wt% B	DSC		
					M_w	M_n	PDI		T_g ($^{\circ}\text{C}$)	T_m ($^{\circ}\text{C}$)	ΔH_m (J/g)
EB	30	50	90	16.60	295,235	188,815	1.56	57	-62.1	ND	ND

TiBn_4 : 120 μmol .

Reactor temperature: -7°C .

Ligand 1: TiBn_4 :FAB = 1.2:1:1.2 (mole ratio).

ND = none detected.

Synthesis of iPB Homopolymer Using Procatalyst 3

[0063] The polymerization was carried out in a 600 mL Parr reactor controlled by a Siemens process control system and equipped with an internal cooling coil. A solution of the trityl tetrakis(pentafluorophenyl) borate activator in 220 mL of chlorobenzene was added to the reactor from a solvent cylinder pressurized with nitrogen. The agitator was turned on at 700 rpm and the reactor was cooled to -6°C using a chiller. The 1-butene monomer was added at 1800 mg/min. A solution of Procatalyst 3 in 15 mL of chlorobenzene was added to the reactor via a small bomb pressurized with nitrogen. The bomb was flushed with 15 mL chlorobenzene. The reactor contents were agitated for 25 hours to produce the iPB homopolymer. Specific run details and polymer characterization data are reported in Table 4.

Table 4
Run Details and Polymer Data of iPB Homopolymer

Polymer type	1-Butene (g)	Run time (h)	Polymer Yield (g)	GPC (triple detector, absolute MW)			¹³ C NMR		T _g (°C)	DSC T _m (°C)	ΔH _m (J/g)
				M _w	M _n	PDI	% mmmm	% mm			
iPB	80	25	19	48,163	20,203	2.38	85	96	-21.4	113.4	87.5

Procatalyst 3: 453 μmol.

Activator: Procatalyst 3 = 1.08 (mole ratio).

Reactor pressurized to 50 psig (344.74 kPa) with N₂.

Reactor temperature: -6 °C.

Comparative Example 1 (CE-1) (20/80 w/w blend of iPB/EB)

[0064] A 20/80 blend of an iPB homopolymer (20 kg/mol, 2.38 PDI, 96% [mm], 85% [4m]) and random poly(ethylene-*co*-1-butene) (EB) copolymer (189 kg/mol, 1.56 PDI, 57 wt% 1-butene) was prepared by dissolving the two polymers in hot toluene, precipitating in methanol, and drying under vacuum. The blend has a total 1-butene composition of 65 wt% (¹³C NMR). Tensile specimens were prepared by compression molding and samples measured according to ASTM D638 (Type V) at an extension rate of 2"/min after 28 days of aging at room temperature. Hysteresis and tensile set were recorded after elongating the sample to 300%. The data is reported in Table 5.

Comparative Example 2 (CE-2) (25/75 w/w blend of iPB/EB)

[0065] A 25/75 blend of an iPB homopolymer (20 kg/mol, 2.38 PDI, 96% [mm], 85% [4m]) and random poly(ethylene-*co*-1-butene) (EB) copolymer (189 kg/mol, 1.56 PDI, 57 wt% 1-butene) was prepared by dissolving the two polymers in hot toluene, precipitating in methanol, and drying under vacuum. The blend has a total 1-butene composition of 67 wt% (¹³C NMR). Tensile specimens were prepared by compression molding and samples measured according to ASTM D638 (Type V) at an extension rate of 2"/min after 28 days of aging at room temperature. Hysteresis and tensile set were recorded after elongating the sample to 300%. The data is reported in Table 5.

Comparative Example 3 (CE-3) (40/60 w/w blend of iPB/EB)

[0066] A 40/60 blend of an iPB homopolymer (20 kg/mol, 2.38 PDI, 96% [mm], 85% [4m]) and random poly(ethylene-*co*-1-butene) (EB) copolymer (189 kg/mol, 1.56 PDI, 57 wt% 1-butene) was prepared by dissolving the two polymers in hot toluene, precipitating in methanol, and drying under vacuum. The blend has a total 1-butene composition of 74 wt% (¹³C NMR). Tensile specimens were prepared by compression molding and samples measured according to ASTM D638 (Type V) at an extension rate of 2"/min after 28 days of aging at room temperature. Hysteresis and tensile set were recorded after elongating the sample to 300%. The data is reported in Table 5.

Table 5

Tensile and Compressive Strength Performance of IE and CE Samples

Example	Ultimate Tensile Strength (psi)	Elongation at Break (%)	Young's Modulus (psi)	TS @100% (psi)	TS @300% (psi)	Hysteresis (%)	Tensile Set (%)
1	1211	3700	2876	209	221	57	54
2	999	4130	605	133	158	40	49
3	1580	2585	624	190	239	47	48
Comp. 1	122	98	581	30	--	--	--
Comp. 2	122	87	618	--	--	--	--
Comp. 3	190	45	1429	--	--	--	--

-- indicates no data available as sample failed to reach sufficient strain.

Discussion of Results

[0067] Table 5 shows the mechanical testing data for Examples 1–3 and Comparative Examples 1–3. The iPB-EB-iPB triblock copolymers (Examples 1–3) showed significantly higher elongation than the blends of homopolymers (Comparative Examples 1–3) indicating that they are much more extensible than the blends. This elasticity results in the hysteresis and tensile set values shown in Table 5, which represent good elastic recovery. The Comparative Examples were too brittle and failed during elastic hysteresis testing.

[0068] Without being bound by this theory, it is believed that the elastic results of the inventive examples are derived, in part, from the low creep properties of the iPB blocks. As one of ordinary skill in the art would know, iPB can have good creep resistance as compared to other semi-crystalline polyolefins, but the good creep resistance requires high isotacticity.

What is claimed is:

1. A semi-crystalline, thermoplastic polyolefin block copolymer comprising:
 - (A) a first polyolefin A block comprising isotactic poly(1-butene) (iPB);
 - (B) a polyolefin B block selected from the group consisting of 1-butene/ethylene copolymer, 1-butene/alpha-olefin copolymer, and 1-butene/ethylene/alpha-olefin terpolymer; and
 - (C) a second polyolefin A block comprising isotactic poly(1-butene) (iPB);

the A and B blocks bonded to one another to form the polymer in which the first and second polyolefin A blocks are joined to and separated by the polyolefin B block.

2. A semi-crystalline, thermoplastic polyolefin block copolymer comprising:
 - (A) a first polyolefin B block selected from the group consisting of 1-butene/ethylene copolymer, 1-butene/alpha-olefin copolymer, and 1-butene/ethylene/alpha-olefin terpolymer;
 - (B) a polyolefin A block comprising isotactic poly(1-butene) (iPB); and
 - (C) a second polyolefin B block selected from the group consisting of 1-butene/ethylene copolymer, 1-butene/alpha-olefin copolymer, and 1-butene/ethylene/alpha-olefin terpolymer;

the B and A blocks bonded to one another to form the polymer in which the first and second polyolefin B blocks are joined to and separated by the polyolefin A block.

3. The semi-crystalline, thermoplastic polyolefin polymer of claim 1 or 2 in which the polyolefin B block has a glass transition temperature (T_g) of less than $-20\text{ }^{\circ}\text{C}$.

4. The semi-crystalline, thermoplastic polyolefin polymer of claim 1 or 2 in which the polyolefin B block comprises ethylene and 1-butene.

5. A composition comprising the semi-crystalline, thermoplastic polyolefin polymer of any of the preceding claims.

6. An article comprising the composition of claim 5.

7. The article of claim 6 in the form of an injected molded part, or a cast or blown film.

8. A process for making a semi-crystalline, thermoplastic polyolefin ABA block copolymer, the process comprising the steps of:

- (A) feeding 1-butene to a high pressure reactor under polymerization conditions to produce a first A block of isotactic poly(1-butene) (iPB);
- (B) adding ethylene and/or a second alpha-olefin to the reactor under copolymerization conditions to form a B block of a 1-butene/ethylene copolymer, a 1-butene/alpha-olefin copolymer, or a 1-butene/ethylene/alpha-olefin terpolymer which is attached to the first A block to form an AB block copolymer; and
- (C) stopping the addition of ethylene and/or the second alpha-olefin, and continue feeding 1-butene to the reactor under polymerization conditions to form a second A block of iPB which is attached to the B block to form the ABA block copolymer.

9. A process for making the semi-crystalline, thermoplastic polyolefin BAB block copolymer, the process comprising the steps of:

- (A) feeding 1-butene and ethylene and/or a second alpha-olefin to a reactor under copolymerization conditions to form a first B block of 1-butene/ethylene copolymer, a 1-butene/alpha-olefin copolymer, or a 1-butene/ethylene/alpha-olefin terpolymer;
- (B) stopping the addition of ethylene and the second alpha-olefin, and continue feeding 1-butene to the reactor under polymerization conditions to form an A block of isotactic poly(1-butene) (iPB) which is attached to the B block to form a BA block copolymer; and
- (C) restarting the addition of ethylene and/or a second alpha-olefin to the reactor under copolymerization conditions to form a second B block of a 1-butene/ethylene, a 1-butene/alpha-olefin copolymer, or a 1-butene/ethylene/alpha-olefin terpolymer which is attached to the A block to form the BAB block copolymer.

10. The process of claim 8 or 9 in which the polyolefin B block has a glass transition temperature (T_g) of less than $-20\text{ }^{\circ}\text{C}$.

11. The process of claims 8-10 in which the polyolefin B block comprises ethylene and 1-butene.

12. The semi-crystalline, thermoplastic polyolefin polymer of claim 1 or 2 in which the polyolefin B block contains from 30 wt% to 80 wt% of 1-butene.

13. The process of claim 8 or 9 in which the polyolefin B block contains from 30 wt% to 80 wt% of 1-butene.

SEMI-CRYSTALLINE THERMOPLASTIC BLOCK COPOLYMERS

ABSTRACT

Semi-crystalline, thermoplastic polyolefin block copolymers comprising:

- (A) A first polyolefin A block comprising isotactic poly(1-butene) (iPB);
- (B) A polyolefin B block comprising an ethylene and/or alpha-olefin/1-butene copolymer or terpolymer; and
- (C) A second polyolefin A block comprising isotactic poly(1-butene) (iPB);

the A and B blocks bonded to one another to form a block copolymer in which the first and second polyolefin A blocks are joined to and separated by the polyolefin B block. In one embodiment the polyolefin block copolymer is a BAB block copolymer.

[No suitable figure]