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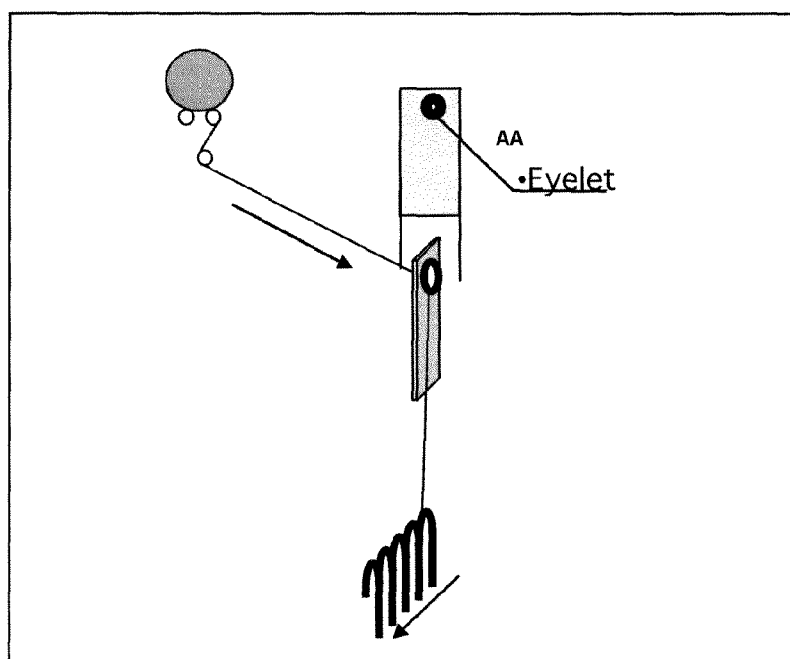
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(54) Title: KNIT FABRICS COMPRISING OLEFIN BLOCK INTERPOLYMERS



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(57) Abstract: Knit fabric compositions have now been discovered that often have a balanced combination of desirable properties. Said fabric compositions comprise olefin block interpolymers. These compositions allow for improved processability when manufacturing knitted fabrics.

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KNIT FABRICS COMPRISING OLEFIN BLOCK INTERPOLYMERS

FIELD OF THE INVENTION

[0001] This invention relates to improved polyolefin fibers and knitted fabrics.

5 BACKGROUND AND SUMMARY OF THE INVENTION

[0002] Many different materials have been used in making knit fabrics for use in, for example, garments. It is often desirable that such fabrics have a combination of desirable properties including one or more of the following: dimensional stability, heat-set properties, capability to be made stretchable in one or both dimensions, chemical, heat, and abrasion
10 resistant, tenacity, etc. It is also often important that such fabrics be able to withstand hand or machine washing without significantly degrading one or more of the aforementioned properties. Further, increased throughput with reduced defects, e.g., fiber breakage, is usually desirable. Unfortunately, the prior materials often suffer from one or more deficiencies in the aforementioned properties. In addition, the prior materials may limit the
15 knit process in some way, e.g., production may be limited to a pulley feeding system as opposed to an eyelet system.

[0003] Improved fibers have now been discovered which unwind from a spool better and reduce defects such as fabric faults and elastic filament or fiber breakage. Use of the inventive fibers may reduce buildup of fiber fragments on a needle bed – a problem that often
20 occurs in circular knit machines when polymer residue adheres to the needle surface. Thus, the inventive fibers may reduce the corresponding fabric breaks caused by the residue.

[0004] Similarly, knit fabric compositions have been discovered that often have a balanced combination of desirable properties. These compositions allow for improved processability. The knit fabric of the present invention is typically a knit fabric comprising:
25 (A) an ethylene/ α -olefin interpolpolymer, wherein the ethylene/ α -olefin interpolpolymer has one or more of the following characteristics:

(1) an average block index greater than zero and up to about 1.0 and a molecular weight distribution, M_w/M_n , greater than about 1.3; or

(2) at least one molecular fraction which elutes between 40°C and 130°C when fractionated using TREF, characterized in that the fraction has a block index of at least 0.5 and up to about 1; or

(3) an Mw/Mn from about 1.7 to about 3.5, at least one melting point, T_m , in degrees Celsius, and a density, d , in grams/cubic centimeter, wherein the numerical values of T_m and d correspond to the relationship:

$$T_m > -2002.9 + 4538.5(d) - 2422.2(d)^2; \text{ or}$$

(4) an Mw/Mn from about 1.7 to about 3.5, and is characterized by a heat of fusion, ΔH in J/g, and a delta quantity, ΔT , in degrees Celsius defined as the temperature difference between the tallest DSC peak and the tallest CRYSTAF peak, wherein the numerical values of ΔT and ΔH have the following relationships:

$$\Delta T > -0.1299(\Delta H) + 62.81 \text{ for } \Delta H \text{ greater than zero and up to } 130 \text{ J/g,}$$

$$\Delta T \geq 48^\circ\text{C for } \Delta H \text{ greater than } 130 \text{ J/g,}$$

wherein the CRYSTAF peak is determined using at least 5 percent of the cumulative polymer, and if less than 5 percent of the polymer has an identifiable CRYSTAF peak, then the CRYSTAF temperature is 30°C; or

(5) an elastic recovery, Re , in percent at 300 percent strain and 1 cycle measured with a compression-molded film of the ethylene/ α -olefin interpolpolymer, and has a density, d , in grams/cubic centimeter, wherein the numerical values of Re and d satisfy the following relationship when ethylene/ α -olefin interpolpolymer is substantially free of a cross-linked phase:

$$Re > 1481 - 1629(d); \text{ or}$$

(6) a molecular fraction which elutes between 40°C and 130°C when fractionated using TREF, characterized in that the fraction has a molar comonomer content of at least 5 percent higher than that of a comparable random ethylene interpolpolymer fraction eluting between the same temperatures, wherein said comparable random ethylene interpolpolymer has the same comonomer(s) and has a melt index, density, and molar

comonomer content (based on the whole polymer) within 10 percent of that of the ethylene/ α -olefin interpolpolymer; or

(7) a storage modulus at 25 °C, $G'(25\text{ °C})$, and a storage modulus at 100 °C, $G'(100\text{ °C})$, wherein the ratio of $G'(25\text{ °C})$ to $G'(100\text{ °C})$ is in the range of about 1:1 to about 9:1; and

(B) at least one other material;

wherein the fabric has less than about 5 percent shrinkage after wash by AATCC 135 IVAi.

[0005] Preferably, the one or more polymer characteristics are exhibited by the ethylene/ α -olefin interpolpolymer before any crosslinking has occurred. In some cases, the crosslinked ethylene/ α -olefin interpolpolymer may also exhibit one or more of the seven aforementioned properties.

[0006] The other material is often selected from the group consisting of cellulose, cotton, flax, ramie, rayon, viscose, hemp, wool, silk, linen, bamboo, tencel, viscose, mohair, polyester, polyamide, polypropylene, and mixtures thereof. Preferred fabrics include those wherein the other material comprises cellulose, wool, or mixtures thereof and wherein the fabric is knitted or woven. The improvements described above may allow increase throughput with reduced defects. Also, fabric may be made in either a conventional pulley or eyelet machine.

BRIEF DESCRIPTION OF THE DRAWINGS

[0007] Figure 1 shows the melting point/density relationship for the inventive polymers (represented by diamonds) as compared to traditional random copolymers (represented by circles) and Ziegler-Natta copolymers (represented by triangles).

[0008] Figure 2 shows plots of delta DSC-CRYSTAF as a function of DSC Melt Enthalpy for various polymers. The diamonds represent random ethylene/octene copolymers; the squares represent polymer examples 1-4; the triangles represent polymer examples 5-9; and the circles represent polymer examples 10-19. The "X" symbols represent polymer examples A*-F*.

[0009] Figure 3 shows the effect of density on elastic recovery for unoriented films made from inventive interpolpolymers (represented by the squares and circles) and traditional

copolymers (represented by the triangles which are various AFFINITY™ polymers (available from The Dow Chemical Company)). The squares represent inventive ethylene/butene copolymers; and the circles represent inventive ethylene/octene copolymers.

[0010] Figure 4 is a plot of octene content of TREF fractionated ethylene/ 1-octene copolymer fractions versus TREF elution temperature of the fraction for the polymer of Example 5 (represented by the circles) and comparative polymers E and F (represented by the “X” symbols). The diamonds represent traditional random ethylene/octene copolymers.

[0011] Figure 5 is a plot of octene content of TREF fractionated ethylene/ 1-octene copolymer fractions versus TREF elution temperature of the fraction for the polymer of Example 5 (curve 1) and for comparative F (curve 2). The squares represent Example F*; and the triangles represent Example 5.

[0012] Figure 6 is a graph of the log of storage modulus as a function of temperature for comparative ethylene/1-octene copolymer (curve 2) and propylene/ ethylene- copolymer (curve 3) and for two ethylene/1-octene block copolymers of the invention made with differing quantities of chain shuttling agent (curves 1).

[0013] Figure 7 shows a plot of TMA (1mm) versus flex modulus for some inventive polymers (represented by the diamonds), as compared to some known polymers. The triangles represent various Dow VERSIFY™ polymers(available from The Dow Chemical Company); the circles represent various random ethylene/styrene copolymers; and the squares represent various Dow AFFINITY™ polymers(available from The Dow Chemical Company).

[0014] Figure 8 shows the Electronic Constant Tension Transporter used to determine the average coefficient of friction.

[0015] Figure 9 shows the first threading configuration used to determine the average coefficient of friction.

[0016] Figure 10 shows the second threading configuration used to determine the average coefficient of friction.

[0017] Figure 11 shows an illustration of a knitting machine comprising a pulley feeder.

[0018] Figure 12 shows an illustration of knitting machine comprising an eyelet feeder.

[0019] Figure 13 shows a process map of a typical dyeing and finishing process.

[0020] Figure 14 shows a diagram of the hanger assembly as employed in ASTM D 2594.

DETAILED DESCRIPTION OF THE INVENTION

General Definitions

[0021] “Fiber” means a material in which the length to diameter ratio is greater than about 10. Fiber is typically classified according to its diameter. Filament fiber is generally defined as having an individual fiber diameter greater than about 15 denier, usually greater than about 30 denier per filament. Fine denier fiber generally refers to a fiber having a diameter less than about 15 denier per filament. Microdenier fiber is generally defined as fiber having a diameter less than about 100 microns denier per filament.

[0022] “Filament fiber” or “monofilament fiber” means a continuous strand of material of indefinite (i.e., not predetermined) length, as opposed to a “staple fiber” which is a discontinuous strand of material of definite length (i.e., a strand which has been cut or otherwise divided into segments of a predetermined length).

[0023] “Elastic” means that a fiber will recover at least about 50 percent of its stretched length after the first pull and after the fourth to 100% strain (doubled the length). Elasticity can also be described by the “permanent set” of the fiber. Permanent set is the converse of elasticity. A fiber is stretched to a certain point and subsequently released to the original position before stretch, and then stretched again. The point at which the fiber begins to pull a load is designated as the percent permanent set. “Elastic materials” are also referred to in the art as “elastomers” and “elastomeric”. Elastic material (sometimes referred to as an elastic article) includes the copolymer itself as well as, but not limited to, the copolymer in the form of a fiber, film, strip, tape, ribbon, sheet, coating, molding and the like. The preferred elastic material is fiber. The elastic material can be either cured or uncured, radiated or un-radiated, and/or crosslinked or uncrosslinked.

[0024] “Nonelastic material” means a material, e.g., a fiber, that is not elastic as defined above.

[0025] “Substantially crosslinked” and similar terms mean that the copolymer, shaped or in the form of an article, has xylene extractables of less than or equal to 70 weight percent (i.e., greater than or equal to 30 weight percent gel content), preferably less than or equal to 40 weight percent (i.e., greater than or equal to 60 weight percent gel content). Xylene extractables (and gel content) are determined in accordance with ASTM D-2765.

[0026] “Homofil fiber” means a fiber that has a single polymer region or domain, and that does not have any other distinct polymer regions (as do bicomponent fibers).

[0027] “Bicomponent fiber” means a fiber that has two or more distinct polymer regions or domains. Bicomponent fibers are also known as conjugated or multicomponent fibers. The polymers are usually different from each other although two or more components may comprise the same polymer. The polymers are arranged in substantially distinct zones across the cross-section of the bicomponent fiber, and usually extend continuously along the length of the bicomponent fiber. The configuration of a bicomponent fiber can be, for example, a sheath/core arrangement (in which one polymer is surrounded by another), a side by side arrangement, a pie arrangement or an “islands-in-the sea” arrangement. Bicomponent fibers are further described in U.S. Patents No. 6,225,243, 6,140,442, 5,382,400, 5,336,552 and 5,108,820.

[0028] “Meltblown fibers” are fibers formed by extruding a molten thermoplastic polymer composition through a plurality of fine, usually circular, die capillaries as molten threads or filaments into converging high velocity gas streams (e.g. air) which function to attenuate the threads or filaments to reduced diameters. The filaments or threads are carried by the high velocity gas streams and deposited on a collecting surface to form a web of randomly dispersed fibers with average diameters generally smaller than 10 microns.

[0029] “Meltspun fibers” are fibers formed by melting at least one polymer and then drawing the fiber in the melt to a diameter (or other cross-section shape) less than the diameter (or other cross-section shape) of the die.

[0030] “Spunbond fibers” are fibers formed by extruding a molten thermoplastic polymer composition as filaments through a plurality of fine, usually circular, die capillaries of a spinneret. The diameter of the extruded filaments is rapidly reduced, and then the filaments are deposited onto a collecting surface to form a web of randomly dispersed fibers with average diameters generally between about 7 and about 30 microns.

[0031] “Nonwoven” means a web or fabric having a structure of individual fibers or threads which are randomly interlaid, but not in an identifiable manner as is the case of a knitted fabric. The elastic fiber in accordance with embodiments of the invention can be employed to prepare nonwoven structures as well as composite structures of elastic nonwoven fabric in combination with nonelastic materials.

[0032] “Yarn” means a continuous length of twisted or otherwise entangled filaments which can be used in the manufacture of woven or knitted fabrics and other articles. Yarn can be covered or uncovered. Covered yarn is yarn at least partially wrapped within an outer covering of another fiber or material, typically a natural fiber such as cotton or wool.

[0033] "Polymer" means a polymeric compound prepared by polymerizing monomers, whether of the same or a different type. The generic term "polymer" embraces the terms "homopolymer," "copolymer," "terpolymer" as well as "interpolymer."

[0034] "Interpolymer" means a polymer prepared by the polymerization of at least two different types of monomers. The generic term "interpolymer" includes the term "copolymer" (which is usually employed to refer to a polymer prepared from two different monomers) as well as the term "terpolymer" (which is usually employed to refer to a polymer prepared from three different types of monomers). It also encompasses polymers made by polymerizing four or more types of monomers.

[0035] The term "ethylene/ α -olefin interpolymer" generally refers to polymers comprising ethylene and an α -olefin having 3 or more carbon atoms. Preferably, ethylene comprises the majority mole fraction of the whole polymer, i.e., ethylene comprises at least about 50 mole percent of the whole polymer. More preferably ethylene comprises at least about 60 mole percent, at least about 70 mole percent, or at least about 80 mole percent, with the substantial remainder of the whole polymer comprising at least one other comonomer that is preferably an α -olefin having 3 or more carbon atoms. For many ethylene/octene copolymers, the preferred composition comprises an ethylene content greater than about 80 mole percent of the whole polymer and an octene content of from about 10 to about 15, preferably from about 15 to about 20 mole percent of the whole polymer. In some embodiments, the ethylene/ α -olefin interpolymers do not include those produced in low yields or in a minor amount or as a by-product of a chemical process. While the ethylene/ α -olefin interpolymers can be blended with one or more polymers, the as-produced ethylene/ α -olefin interpolymers are substantially pure and often comprise a major component of the reaction product of a polymerization process.

[0036] The ethylene/ α -olefin interpolymers comprise ethylene and one or more copolymerizable α -olefin comonomers in polymerized form, characterized by multiple blocks or segments of two or more polymerized monomer units differing in chemical or physical properties. That is, the ethylene/ α -olefin interpolymers are block interpolymers, preferably multi-block interpolymers or copolymers. The terms "interpolymer" and "copolymer" are used interchangeably herein. In some embodiments, the multi-block copolymer can be represented by the following formula:



where n is at least 1, preferably an integer greater than 1, such as 2, 3, 4, 5, 10, 15, 20, 30, 40, 50, 60, 70, 80, 90, 100, or higher, "A" represents a hard block or segment and "B" represents a soft block or segment. Preferably, As and Bs are linked in a substantially linear fashion, as opposed to a substantially branched or substantially star-shaped fashion. In other
5 embodiments, A blocks and B blocks are randomly distributed along the polymer chain. In other words, the block copolymers usually do not have a structure as follows.



[0037] In still other embodiments, the block copolymers do not usually have a third type of block, which comprises different comonomer(s). In yet other embodiments, each of block
10 A and block B has monomers or comonomers substantially randomly distributed within the block. In other words, neither block A nor block B comprises two or more sub-segments (or sub-blocks) of distinct composition, such as a tip segment, which has a substantially different composition than the rest of the block.

[0038] The multi-block polymers typically comprise various amounts of "hard" and
15 "soft" segments. "Hard" segments refer to blocks of polymerized units in which ethylene is present in an amount greater than about 95 weight percent, and preferably greater than about 98 weight percent based on the weight of the polymer. In other words, the comonomer content (content of monomers other than ethylene) in the hard segments is less than about 5 weight percent, and preferably less than about 2 weight percent based on the weight of the
20 polymer. In some embodiments, the hard segments comprises all or substantially all ethylene. "Soft" segments, on the other hand, refer to blocks of polymerized units in which the comonomer content (content of monomers other than ethylene) is greater than about 5 weight percent, preferably greater than about 8 weight percent, greater than about 10 weight percent, or greater than about 15 weight percent based on the weight of the polymer. In some
25 embodiments, the comonomer content in the soft segments can be greater than about 20 weight percent, greater than about 25 weight percent, greater than about 30 weight percent, greater than about 35 weight percent, greater than about 40 weight percent, greater than about 45 weight percent, greater than about 50 weight percent, or greater than about 60 weight percent.

[0039] The soft segments can often be present in a block interpolymer from about 1
30 weight percent to about 99 weight percent of the total weight of the block interpolymer, preferably from about 5 weight percent to about 95 weight percent, from about 10 weight percent to about 90 weight percent, from about 15 weight percent to about 85 weight percent,

from about 20 weight percent to about 80 weight percent, from about 25 weight percent to about 75 weight percent, from about 30 weight percent to about 70 weight percent, from about 35 weight percent to about 65 weight percent, from about 40 weight percent to about 60 weight percent, or from about 45 weight percent to about 55 weight percent of the total weight of the block interpolmer. Conversely, the hard segments can be present in similar ranges. The soft segment weight percentage and the hard segment weight percentage can be calculated based on data obtained from DSC or NMR. Such methods and calculations are disclosed in a concurrently filed U.S. Patent Application Serial No. 11/376,835, Attorney Docket No. 385063999558, entitled "Ethylene/ α -Olefins Block Interpolymers", filed on March 15, 2006, in the name of Colin L.P. Shan, Lonnie Hazlitt, et. al. and assigned to Dow Global Technologies Inc., the disclosure of which is incorporated by reference herein in its entirety.

[0040] The term "crystalline" if employed, refers to a polymer that possesses a first order transition or crystalline melting point (T_m) as determined by differential scanning calorimetry (DSC) or equivalent technique. The term may be used interchangeably with the term "semicrystalline". The term "amorphous" refers to a polymer lacking a crystalline melting point as determined by differential scanning calorimetry (DSC) or equivalent technique.

[0041] The term "multi-block copolymer" or "segmented copolymer" refers to a polymer comprising two or more chemically distinct regions or segments (referred to as "blocks") preferably joined in a linear manner, that is, a polymer comprising chemically differentiated units which are joined end-to-end with respect to polymerized ethylenic functionality, rather than in pendent or grafted fashion. In a preferred embodiment, the blocks differ in the amount or type of comonomer incorporated therein, the density, the amount of crystallinity, the crystallite size attributable to a polymer of such composition, the type or degree of tacticity (isotactic or syndiotactic), regio-regularity or regio-irregularity, the amount of branching, including long chain branching or hyper-branching, the homogeneity, or any other chemical or physical property. The multi-block copolymers are characterized by unique distributions of both polydispersity index (PDI or M_w/M_n), block length distribution, and/or block number distribution due to the unique process making of the copolymers. More specifically, when produced in a continuous process, the polymers desirably possess PDI from 1.7 to 2.9, preferably from 1.8 to 2.5, more preferably from 1.8 to 2.2, and most preferably from 1.8 to 2.1. When produced in a batch or semi-batch process, the polymers

possess PDI from 1.0 to 2.9, preferably from 1.3 to 2.5, more preferably from 1.4 to 2.0, and most preferably from 1.4 to 1.8.

[0042] In the following description, all numbers disclosed herein are approximate values, regardless whether the word “about” or “approximate” is used in connection therewith. They may vary by 1 percent, 2 percent, 5 percent, or, sometimes, 10 to 20 percent. Whenever a numerical range with a lower limit, R^L and an upper limit, R^U , is disclosed, any number falling within the range is specifically disclosed. In particular, the following numbers within the range are specifically disclosed: $R = R^L + k \cdot (R^U - R^L)$, wherein k is a variable ranging from 1 percent to 100 percent with a 1 percent increment, i.e., k is 1 percent, 2 percent, 3 percent, 4 percent, 5 percent, ..., 50 percent, 51 percent, 52 percent, ..., 95 percent, 96 percent, 97 percent, 98 percent, 99 percent, or 100 percent. Moreover, any numerical range defined by two R numbers as defined in the above is also specifically disclosed.

Ethylene/ α -Olefin Interpolymers

[0043] The ethylene/ α -olefin interpolymers used in embodiments of the invention (also referred to as “inventive interpolymer” or “inventive polymer”) comprise ethylene and one or more copolymerizable α -olefin comonomers in polymerized form, characterized by multiple blocks or segments of two or more polymerized monomer units differing in chemical or physical properties (block interpolymer), preferably a multi-block copolymer. The ethylene/ α -olefin interpolymers are characterized by one or more of the aspects described as follows.

[0044] In one aspect, the ethylene/ α -olefin interpolymers used in embodiments of the invention have a M_w/M_n from about 1.7 to about 3.5 and at least one melting point, T_m , in degrees Celsius and density, d , in grams/cubic centimeter, wherein the numerical values of the variables correspond to the relationship:

$$T_m > -2002.9 + 4538.5(d) - 2422.2(d)^2, \text{ and preferably}$$

$$T_m \geq -6288.1 + 13141(d) - 6720.3(d)^2, \text{ and more preferably}$$

$$T_m \geq 858.91 - 1825.3(d) + 1112.8(d)^2.$$

[0045] Such melting point/density relationship is illustrated in Figure 1. Unlike the traditional random copolymers of ethylene/ α -olefins whose melting points decrease with decreasing densities, the inventive interpolymers (represented by diamonds) exhibit melting

points substantially independent of the density, particularly when density is between about 0.87 g/cc to about 0.95 g/cc. For example, the melting point of such polymers are in the range of about 110 °C to about 130 °C when density ranges from 0.875 g/cc to about 0.945 g/cc. In some embodiments, the melting point of such polymers are in the range of about 115 °C to about 125 °C when density ranges from 0.875 g/cc to about 0.945 g/cc.

[0046] In another aspect, the ethylene/ α -olefin interpolymers comprise, in polymerized form, ethylene and one or more α -olefins and are characterized by a ΔT , in degree Celsius, defined as the temperature for the tallest Differential Scanning Calorimetry ("DSC") peak minus the temperature for the tallest Crystallization Analysis Fractionation ("CRYSTAF") peak and a heat of fusion in J/g, ΔH , and ΔT and ΔH satisfy the following relationships:

$$\Delta T > -0.1299(\Delta H) + 62.81, \text{ and preferably}$$

$$\Delta T \geq -0.1299(\Delta H) + 64.38, \text{ and more preferably}$$

$$\Delta T \geq -0.1299(\Delta H) + 65.95,$$

for ΔH up to 130 J/g. Moreover, ΔT is equal to or greater than 48 °C for ΔH greater than 130 J/g. The CRYSTAF peak is determined using at least 5 percent of the cumulative polymer (that is, the peak must represent at least 5 percent of the cumulative polymer), and if less than 5 percent of the polymer has an identifiable CRYSTAF peak, then the CRYSTAF temperature is 30°C, and ΔH is the numerical value of the heat of fusion in J/g. More preferably, the highest CRYSTAF peak contains at least 10 percent of the cumulative polymer. Figure 2 shows plotted data for inventive polymers as well as comparative examples. Integrated peak areas and peak temperatures are calculated by the computerized drawing program supplied by the instrument maker. The diagonal line shown for the random ethylene octene comparative polymers corresponds to the equation $\Delta T = -0.1299 (\Delta H) + 62.81$.

[0047] In yet another aspect, the ethylene/ α -olefin interpolymers have a molecular fraction which elutes between 40°C and 130°C when fractionated using Temperature Rising Elution Fractionation ("TREF"), characterized in that said fraction has a molar comonomer content higher, preferably at least 5 percent higher, more preferably at least 10 percent higher, than that of a comparable random ethylene interpolymers fraction eluting between the same temperatures, wherein the comparable random ethylene interpolymers contains the same comonomer(s), and has a melt index, density, and molar comonomer content (based on the

whole polymer) within 10 percent of that of the block interpolmer. Preferably, the Mw/Mn of the comparable interpolmer is also within 10 percent of that of the block interpolmer and/or the comparable interpolmer has a total comonomer content within 10 weight percent of that of the block interpolmer.

- 5 [0048] In still another aspect, the ethylene/ α -olefin interpolymers are characterized by an elastic recovery, Re, in percent at 300 percent strain and 1 cycle measured on a compression-molded film of an ethylene/ α -olefin interpolmer, and has a density, d, in grams/cubic centimeter, wherein the numerical values of Re and d satisfy the following relationship when ethylene/ α -olefin interpolmer is substantially free of a cross-linked phase:

10 Re > 1481-1629(d); and preferably

Re $\geq$ 1491-1629(d); and more preferably

Re $\geq$ 1501-1629(d); and even more preferably

Re $\geq$ 1511-1629(d).

- [0049] Figure 3 shows the effect of density on elastic recovery for unoriented films made from certain inventive interpolymers and traditional random copolymers. For the same density, the inventive interpolymers have substantially higher elastic recoveries.

- [0050] In some embodiments, the ethylene/ α -olefin interpolymers have a tensile strength above 10 MPa, preferably a tensile strength $\geq$ 11 MPa, more preferably a tensile strength $\geq$ 13 MPa and/or an elongation at break of at least 600 percent, more preferably at least 700 percent, highly preferably at least 800 percent, and most highly preferably at least 900 percent at a crosshead separation rate of 11 cm/minute.

- [0051] In other embodiments, the ethylene/ α -olefin interpolymers have (1) a storage modulus ratio, $G'(25^\circ\text{C})/G'(100^\circ\text{C})$, of from 1 to 50, preferably from 1 to 20, more preferably from 1 to 10; and/or (2) a 70°C compression set of less than 80 percent, preferably less than 70 percent, especially less than 60 percent, less than 50 percent, or less than 40 percent, down to a compression set of 0 percent.

- [0052] In still other embodiments, the ethylene/ α -olefin interpolymers have a 70°C compression set of less than 80 percent, less than 70 percent, less than 60 percent, or less than 50 percent. Preferably, the 70°C compression set of the interpolymers is less than 40 percent, less than 30 percent, less than 20 percent, and may go down to about 0 percent.

[0053] In some embodiments, the ethylene/ α -olefin interpolymers have a heat of fusion of less than 85 J/g and/or a pellet blocking strength of equal to or less than 100 pounds/foot² (4800 Pa), preferably equal to or less than 50 lbs/ft² (2400 Pa), especially equal to or less than 5 lbs/ft² (240 Pa), and as low as 0 lbs/ft² (0 Pa).

5 [0054] In other embodiments, the ethylene/ α -olefin interpolymers comprise, in polymerized form, at least 50 mole percent ethylene and have a 70°C compression set of less than 80 percent, preferably less than 70 percent or less than 60 percent, most preferably less than 40 to 50 percent and down to close to zero percent.

[0055] In some embodiments, the multi-block copolymers possess a PDI fitting a
10 Schultz-Flory distribution rather than a Poisson distribution. The copolymers are further characterized as having both a polydisperse block distribution and a polydisperse distribution of block sizes and possessing a most probable distribution of block lengths. Preferred multi-block copolymers are those containing 4 or more blocks or segments including terminal blocks. More preferably, the copolymers include at least 5, 10 or 20 blocks or segments
15 including terminal blocks.

[0056] Comonomer content may be measured using any suitable technique, with techniques based on nuclear magnetic resonance ("NMR") spectroscopy preferred. Moreover, for polymers or blends of polymers having relatively broad TREF curves, the polymer desirably is first fractionated using TREF into fractions each having an eluted
20 temperature range of 10°C or less. That is, each eluted fraction has a collection temperature window of 10°C or less. Using this technique, said block interpolymers have at least one such fraction having a higher molar comonomer content than a corresponding fraction of the comparable interpolpolymer.

[0057] In another aspect, the inventive polymer is an olefin interpolpolymer, preferably
25 comprising ethylene and one or more copolymerizable comonomers in polymerized form, characterized by multiple blocks (i.e., at least two blocks) or segments of two or more polymerized monomer units differing in chemical or physical properties (blocked interpolpolymer), most preferably a multi-block copolymer, said block interpolpolymer having a peak (but not just a molecular fraction) which elutes between 40°C and 130°C (but without
30 collecting and/or isolating individual fractions), characterized in that said peak, has a comonomer content estimated by infra-red spectroscopy when expanded using a full width/half maximum (FWHM) area calculation, has an average molar comonomer content higher, preferably at least 5 percent higher, more preferably at least 10 percent higher, than

that of a comparable random ethylene interpolymer peak at the same elution temperature and expanded using a full width/half maximum (FWHM) area calculation, wherein said comparable random ethylene interpolymer has the same comonomer(s) and has a melt index, density, and molar comonomer content (based on the whole polymer) within 10 percent of that of the blocked interpolymer. Preferably, the Mw/Mn of the comparable interpolymer is also within 10 percent of that of the blocked interpolymer and/or the comparable interpolymer has a total comonomer content within 10 weight percent of that of the blocked interpolymer. The full width/half maximum (FWHM) calculation is based on the ratio of methyl to methylene response area $[CH_3/CH_2]$ from the ATREF infra-red detector, wherein the tallest (highest) peak is identified from the base line, and then the FWHM area is determined. For a distribution measured using an ATREF peak, the FWHM area is defined as the area under the curve between T_1 and T_2 , where T_1 and T_2 are points determined, to the left and right of the ATREF peak, by dividing the peak height by two, and then drawing a line horizontal to the base line, that intersects the left and right portions of the ATREF curve. A calibration curve for comonomer content is made using random ethylene/ α -olefin copolymers, plotting comonomer content from NMR versus FWHM area ratio of the TREF peak. For this infra-red method, the calibration curve is generated for the same comonomer type of interest. The comonomer content of TREF peak of the inventive polymer can be determined by referencing this calibration curve using its FWHM methyl : methylene area ratio $[CH_3/CH_2]$ of the TREF peak.

[0058] Comonomer content may be measured using any suitable technique, with techniques based on nuclear magnetic resonance (NMR) spectroscopy preferred. Using this technique, said blocked interpolymer has higher molar comonomer content than a corresponding comparable interpolymer.

[0059] Preferably, for interpolymers of ethylene and 1-octene, the block interpolymer has a comonomer content of the TREF fraction eluting between 40 and 130°C greater than or equal to the quantity $(-0.2013) T + 20.07$, more preferably greater than or equal to the quantity $(-0.2013) T + 21.07$, where T is the numerical value of the peak elution temperature of the TREF fraction being compared, measured in °C.

[0060] Figure 4 graphically depicts an embodiment of the block interpolymers of ethylene and 1-octene where a plot of the comonomer content versus TREF elution temperature for several comparable ethylene/1-octene interpolymers (random copolymers) are fit to a line representing $(-0.2013) T + 20.07$ (solid line). The line for the equation (-

0.2013) $T + 21.07$ is depicted by a dotted line. Also depicted are the comonomer contents for fractions of several block ethylene/1-octene interpolymers of the invention (multi-block copolymers). All of the block interpolymer fractions have significantly higher 1-octene content than either line at equivalent elution temperatures. This result is characteristic of the inventive interpolymer and is believed to be due to the presence of differentiated blocks within the polymer chains, having both crystalline and amorphous nature.

[0061] Figure 5 graphically displays the TREF curve and comonomer contents of polymer fractions for Example 5 and Comparative F discussed below. The peak eluting from 40 to 130°C, preferably from 60°C to 95°C for both polymers is fractionated into three parts, each part eluting over a temperature range of less than 10°C. Actual data for Example 5 is represented by triangles. The skilled artisan can appreciate that an appropriate calibration curve may be constructed for interpolymers containing different comonomers and a line used as a comparison fitted to the TREF values obtained from comparative interpolymers of the same monomers, preferably random copolymers made using a metallocene or other homogeneous catalyst composition. Inventive interpolymers are characterized by a molar comonomer content greater than the value determined from the calibration curve at the same TREF elution temperature, preferably at least 5 percent greater, more preferably at least 10 percent greater.

[0062] In addition to the above aspects and properties described herein, the inventive polymers can be characterized by one or more additional characteristics. In one aspect, the inventive polymer is an olefin interpolymer, preferably comprising ethylene and one or more copolymerizable comonomers in polymerized form, characterized by multiple blocks or segments of two or more polymerized monomer units differing in chemical or physical properties (blocked interpolymer), most preferably a multi-block copolymer, said block interpolymer having a molecular fraction which elutes between 40°C and 130°C, when fractionated using TREF increments, characterized in that said fraction has a molar comonomer content higher, preferably at least 5 percent higher, more preferably at least 10, 15, 20 or 25 percent higher, than that of a comparable random ethylene interpolymer fraction eluting between the same temperatures, wherein said comparable random ethylene interpolymer comprises the same comonomer(s), preferably it is the same comonomer(s), and a melt index, density, and molar comonomer content (based on the whole polymer) within 10 percent of that of the blocked interpolymer. Preferably, the M_w/M_n of the comparable interpolymer is also within 10 percent of that of the blocked interpolymer and/or the

comparable interpolymer has a total comonomer content within 10 weight percent of that of the blocked interpolymer.

[0063] Preferably, the above interpolymers are interpolymers of ethylene and at least one α -olefin, especially those interpolymers having a whole polymer density from about 0.855 to about 0.935 g/cm³, and more especially for polymers having more than about 1 mole percent comonomer, the blocked interpolymer has a comonomer content of the TREF fraction eluting between 40 and 130°C greater than or equal to the quantity $(-0.1356) T + 13.89$, more preferably greater than or equal to the quantity $(-0.1356) T + 14.93$, and most preferably greater than or equal to the quantity $(-0.2013) T + 21.07$, where T is the numerical value of the peak ATREF elution temperature of the TREF fraction being compared, measured in °C.

[0064] Preferably, for the above interpolymers of ethylene and at least one alpha-olefin especially those interpolymers having a whole polymer density from about 0.855 to about 0.935 g/cm³, and more especially for polymers having more than about 1 mole percent comonomer, the blocked interpolymer has a comonomer content of the TREF fraction eluting between 40 and 130°C greater than or equal to the quantity $(-0.2013) T + 20.07$, more preferably greater than or equal to the quantity $(-0.2013) T + 21.07$, where T is the numerical value of the peak elution temperature of the TREF fraction being compared, measured in °C.

[0065] In still another aspect, the inventive polymer is an olefin interpolymer, preferably comprising ethylene and one or more copolymerizable comonomers in polymerized form, characterized by multiple blocks or segments of two or more polymerized monomer units differing in chemical or physical properties (blocked interpolymer), most preferably a multi-block copolymer, said block interpolymer having a molecular fraction which elutes between 40°C and 130°C, when fractionated using TREF increments, characterized in that every fraction having a comonomer content of at least about 6 mole percent, has a melting point greater than about 100°C. For those fractions having a comonomer content from about 3 mole percent to about 6 mole percent, every fraction has a DSC melting point of about 110°C or higher. More preferably, said polymer fractions, having at least 1 mole percent comonomer, has a DSC melting point that corresponds to the equation:

$$T_m \geq (-5.5926)(\text{mole percent comonomer in the fraction}) + 135.90.$$

[0066] In yet another aspect, the inventive polymer is an olefin interpolymer, preferably comprising ethylene and one or more copolymerizable comonomers in polymerized form, characterized by multiple blocks or segments of two or more polymerized monomer units differing in chemical or physical properties (blocked interpolymer), most preferably a multi-

block copolymer, said block interpolymers having a molecular fraction which elutes between 40°C and 130°C, when fractionated using TREF increments, characterized in that every fraction that has an ATREF elution temperature greater than or equal to about 76°C, has a melt enthalpy (heat of fusion) as measured by DSC, corresponding to the equation:

$$\text{Heat of fusion (J/gm)} \leq (3.1718)(\text{ATREF elution temperature in Celsius}) - 136.58,$$

[0067] The inventive block interpolymers have a molecular fraction which elutes between 40°C and 130°C, when fractionated using TREF increments, characterized in that every fraction that has an ATREF elution temperature between 40°C and less than about 76°C, has a melt enthalpy (heat of fusion) as measured by DSC, corresponding to the equation:

$$\text{Heat of fusion (J/gm)} \leq (1.1312)(\text{ATREF elution temperature in Celsius}) + 22.97.$$

ATREF Peak Comonomer Composition Measurement by Infra-Red Detector

[0068] The comonomer composition of the TREF peak can be measured using an IR4 infra-red detector available from Polymer Char, Valencia, Spain (<http://www.polymerchar.com/>).

[0069] The “composition mode” of the detector is equipped with a measurement sensor (CH₂) and composition sensor (CH₃) that are fixed narrow band infra-red filters in the region of 2800-3000 cm⁻¹. The measurement sensor detects the methylene (CH₂) carbons on the polymer (which directly relates to the polymer concentration in solution) while the composition sensor detects the methyl (CH₃) groups of the polymer. The mathematical ratio of the composition signal (CH₃) divided by the measurement signal (CH₂) is sensitive to the comonomer content of the measured polymer in solution and its response is calibrated with known ethylene alpha-olefin copolymer standards.

[0070] The detector when used with an ATREF instrument provides both a concentration (CH₂) and composition (CH₃) signal response of the eluted polymer during the TREF process. A polymer specific calibration can be created by measuring the area ratio of the CH₃ to CH₂ for polymers with known comonomer content (preferably measured by NMR). The comonomer content of an ATREF peak of a polymer can be estimated by applying the reference calibration of the ratio of the areas for the individual CH₃ and CH₂ response (i.e. area ratio CH₃/CH₂ versus comonomer content).

[0071] The area of the peaks can be calculated using a full width/half maximum (FWHM) calculation after applying the appropriate baselines to integrate the individual signal responses from the TREF chromatogram. The full width/half maximum calculation is

based on the ratio of methyl to methylene response area $[CH_3/CH_2]$ from the ATREF infra-red detector, wherein the tallest (highest) peak is identified from the base line, and then the FWHM area is determined. For a distribution measured using an ATREF peak, the FWHM area is defined as the area under the curve between T1 and T2, where T1 and T2 are points
 5 determined, to the left and right of the ATREF peak, by dividing the peak height by two, and then drawing a line horizontal to the base line, that intersects the left and right portions of the ATREF curve.

[0072] The application of infra-red spectroscopy to measure the comonomer content of polymers in this ATREF-infra-red method is, in principle, similar to that of GPC/FTIR
 10 systems as described in the following references: Markovich, Ronald P.; Hazlitt, Lonnie G.; Smith, Linley; "Development of gel-permeation chromatography-Fourier transform infrared spectroscopy for characterization of ethylene-based polyolefin copolymers". Polymeric Materials Science and Engineering (1991), 65, 98-100.; and Deslauriers, P.J.; Rohlfing, D.C.; Shieh, E.T.; "Quantifying short chain branching microstructures in ethylene-1-olefin
 15 copolymers using size exclusion chromatography and Fourier transform infrared spectroscopy (SEC-FTIR)", Polymer (2002), 43, 59-170., both of which are incorporated by reference herein in their entirety.

[0073] In other embodiments, the inventive ethylene/ α -olefin interpolymers are characterized by an average block index, ABI, which is greater than zero and up to about 1.0
 20 and a molecular weight distribution, M_w/M_n , greater than about 1.3. The average block index, ABI, is the weight average of the block index ("BI") for each of the polymer fractions obtained in preparative TREF from 20°C and 110°C, with an increment of 5°C:

$$ABI = \sum (w_i BI_i)$$

where BI_i is the block index for the i th fraction of the inventive ethylene/ α -olefin
 25 interpolymers obtained in preparative TREF, and w_i is the weight percentage of the i th fraction.

[0074] For each polymer fraction, BI is defined by one of the two following equations (both of which give the same BI value):

$$BI = \frac{1/T_X - 1/T_{XO}}{1/T_A - 1/T_{AB}} \quad \text{or} \quad BI = -\frac{\ln P_X - \ln P_{XO}}{\ln P_A - \ln P_{AB}}$$

30 where T_X is the preparative ATREF elution temperature for the i th fraction (preferably expressed in Kelvin), P_X is the ethylene mole fraction for the i th fraction, which can be

measured by NMR or IR as described above. P_{AB} is the ethylene mole fraction of the whole ethylene/ α -olefin interpolmer (before fractionation), which also can be measured by NMR or IR. T_A and P_A are the ATREF elution temperature and the ethylene mole fraction for pure “hard segments” (which refer to the crystalline segments of the interpolmer). As a first
 5 order approximation, the T_A and P_A values are set to those for high density polyethylene homopolymer, if the actual values for the “hard segments” are not available. For calculations performed herein, T_A is 372°K, P_A is 1.

[0075] T_{AB} is the ATREF temperature for a random copolymer of the same composition and having an ethylene mole fraction of P_{AB} . T_{AB} can be calculated from the following
 10 equation:

$$\ln P_{AB} = \alpha/T_{AB} + \beta$$

where α and β are two constants which can be determined by calibration using a number of known random ethylene copolymers. It should be noted that α and β may vary from instrument to instrument. Moreover, one would need to create their own calibration curve
 15 with the polymer composition of interest and also in a similar molecular weight range as the fractions. There is a slight molecular weight effect. If the calibration curve is obtained from similar molecular weight ranges, such effect would be essentially negligible. In some embodiments, random ethylene copolymers satisfy the following relationship:

$$\ln P = -237.83/T_{ATREF} + 0.639$$

[0076] T_{XO} is the ATREF temperature for a random copolymer of the same composition and having an ethylene mole fraction of P_X . T_{XO} can be calculated from $\ln P_X = \alpha/T_{XO} + \beta$. Conversely, P_{XO} is the ethylene mole fraction for a random copolymer of the same composition and having an ATREF temperature of T_X , which can be calculated from $\ln P_{XO} = \alpha/T_X + \beta$.

[0077] Once the block index (BI) for each preparative TREF fraction is obtained, the weight average block index, ABI, for the whole polymer can be calculated. In some embodiments, ABI is greater than zero but less than about 0.3 or from about 0.1 to about 0.3. In other embodiments, ABI is greater than about 0.3 and up to about 1.0. Preferably, ABI should be in the range of from about 0.4 to about 0.7, from about 0.5 to about 0.7, or from
 30 about 0.6 to about 0.9. In some embodiments, ABI is in the range of from about 0.3 to about 0.9, from about 0.3 to about 0.8, or from about 0.3 to about 0.7, from about 0.3 to about 0.6,

from about 0.3 to about 0.5, or from about 0.3 to about 0.4. In other embodiments, ABI is in the range of from about 0.4 to about 1.0, from about 0.5 to about 1.0, or from about 0.6 to about 1.0, from about 0.7 to about 1.0, from about 0.8 to about 1.0, or from about 0.9 to about 1.0.

5 [0078] Another characteristic of the inventive ethylene/ α -olefin interpolymer is that the inventive ethylene/ α -olefin interpolymer comprises at least one polymer fraction which can be obtained by preparative TREF, wherein the fraction has a block index greater than about 0.1 and up to about 1.0 and a molecular weight distribution, M_w/M_n , greater than about 1.3. In some embodiments, the polymer fraction has a block index greater than about 0.6 and up to about 1.0, greater than about 0.7 and up to about 1.0, greater than about 0.8 and up to about 1.0, or greater than about 0.9 and up to about 1.0. In other embodiments, the polymer fraction has a block index greater than about 0.1 and up to about 1.0, greater than about 0.2 and up to about 1.0, greater than about 0.3 and up to about 1.0, greater than about 0.4 and up to about 1.0, or greater than about 0.4 and up to about 1.0. In still other embodiments, the polymer fraction has a block index greater than about 0.1 and up to about 0.5, greater than about 0.2 and up to about 0.5, greater than about 0.3 and up to about 0.5, or greater than about 0.4 and up to about 0.5. In yet other embodiments, the polymer fraction has a block index greater than about 0.2 and up to about 0.9, greater than about 0.3 and up to about 0.8, greater than about 0.4 and up to about 0.7, or greater than about 0.5 and up to about 0.6.

20 [0079] For copolymers of ethylene and an α -olefin, the inventive polymers preferably possess (1) a PDI of at least 1.3, more preferably at least 1.5, at least 1.7, or at least 2.0, and most preferably at least 2.6, up to a maximum value of 5.0, more preferably up to a maximum of 3.5, and especially up to a maximum of 2.7; (2) a heat of fusion of 80 J/g or less; (3) an ethylene content of at least 50 weight percent; (4) a glass transition temperature, T_g , of less than -25°C, more preferably less than -30°C; and/or (5) one and only one T_m .

[0080] Further, the inventive polymers can have, alone or in combination with any other properties disclosed herein, a storage modulus, G' , such that $\log(G')$ is greater than or equal to 400 kPa, preferably greater than or equal to 1.0 MPa, at a temperature of 100°C. Moreover, the inventive polymers possess a relatively flat storage modulus as a function of temperature in the range from 0 to 100°C (illustrated in Figure 6) that is characteristic of block copolymers, and heretofore unknown for an olefin copolymer, especially a copolymer of ethylene and one or more C_{3-8} aliphatic α -olefins. (By the term "relatively flat" in this

context is meant that $\log G'$ (in Pascals) decreases by less than one order of magnitude between 50 and 100°C, preferably between 0 and 100°C).

[0081] The inventive interpolymers may be further characterized by a thermomechanical analysis penetration depth of 1 mm at a temperature of at least 90°C as well as a flexural modulus of from 3 kpsi (20 MPa) to 13 kpsi (90 MPa). Alternatively, the inventive interpolymers can have a thermomechanical analysis penetration depth of 1 mm at a temperature of at least 104°C as well as a flexural modulus of at least 3 kpsi (20 MPa). They may be characterized as having an abrasion resistance (or volume loss) of less than 90 mm³. Figure 7 shows the TMA (1 mm) versus flex modulus for the inventive polymers, as compared to other known polymers. The inventive polymers have significantly better flexibility-heat resistance balance than the other polymers.

[0082] Additionally, the ethylene/ α -olefin interpolymers can have a melt index, I_2 , from 0.01 to 2000 g/10 minutes, preferably from 0.01 to 1000 g/10 minutes, more preferably from 0.01 to 500 g/10 minutes, and especially from 0.01 to 100 g/10 minutes. In certain embodiments, the ethylene/ α -olefin interpolymers have a melt index, I_2 , from 0.01 to 10 g/10 minutes, from 0.5 to 50 g/10 minutes, from 1 to 30 g/10 minutes, from 1 to 6 g/10 minutes or from 0.3 to 10 g/10 minutes. In certain embodiments, the melt index for the ethylene/ α -olefin polymers is 1 g/10 minutes, 3 g/10 minutes or 5 g/10 minutes.

[0083] The polymers can have molecular weights, M_w , from 1,000 g/mole to 5,000,000 g/mole, preferably from 1000 g/mole to 1,000,000, more preferably from 10,000 g/mole to 500,000 g/mole, and especially from 10,000 g/mole to 300,000 g/mole. The density of the inventive polymers can be from 0.80 to 0.99 g/cm³ and preferably for ethylene containing polymers from 0.85 g/cm³ to 0.97 g/cm³. In certain embodiments, the density of the ethylene/ α -olefin polymers ranges from 0.860 to 0.925 g/cm³ or 0.867 to 0.910 g/cm³.

[0084] The process of making the polymers has been disclosed in the following patent applications: U.S. Provisional Application No. 60/553,906, filed March 17, 2004; U.S. Provisional Application No. 60/662,937, filed March 17, 2005; U.S. Provisional Application No. 60/662,939, filed March 17, 2005; U.S. Provisional Application No. 60/662,938, filed March 17, 2005; PCT Application No. PCT/US2005/008916, filed March 17, 2005; PCT Application No. PCT/US2005/008915, filed March 17, 2005; and PCT Application No. PCT/US2005/008917, filed March 17, 2005, all of which are incorporated by reference herein in their entirety. For example, one such method comprises contacting ethylene and

optionally one or more addition polymerizable monomers other than ethylene under addition polymerization conditions with a catalyst composition comprising:

the admixture or reaction product resulting from combining:

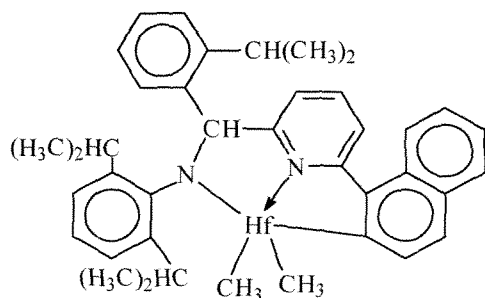
(A) a first olefin polymerization catalyst having a high comonomer incorporation index,

(B) a second olefin polymerization catalyst having a comonomer incorporation index less than 90 percent, preferably less than 50 percent, most preferably less than 5 percent of the comonomer incorporation index of catalyst (A), and

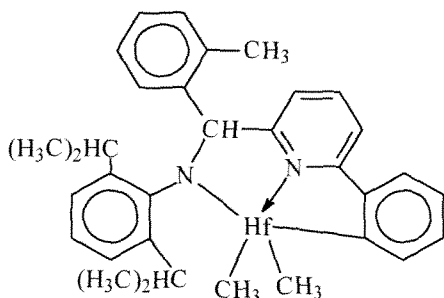
(C) a chain shuttling agent.

[0085] Representative catalysts and chain shuttling agent are as follows.

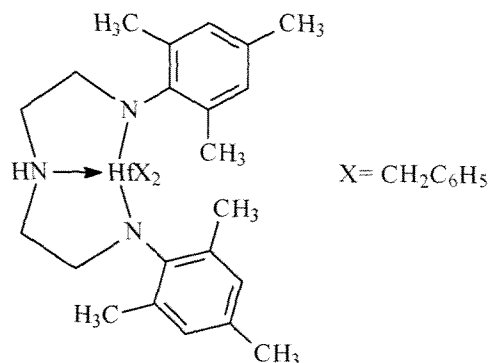
[0086] Catalyst (A1) is [N-(2,6-di(1-methylethyl)phenyl)amido)(2-isopropylphenyl)(α -naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium dimethyl, prepared according to the teachings of WO 03/40195, 2003US0204017, USSN 10/429,024, filed May 2, 2003, and WO 04/24740.



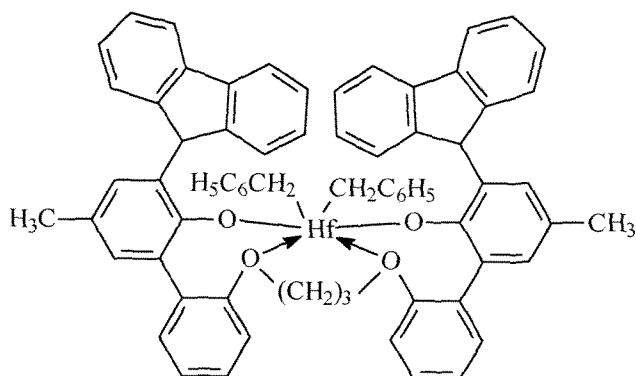
[0087] Catalyst (A2) is [N-(2,6-di(1-methylethyl)phenyl)amido)(2-methylphenyl)(1,2-phenylene-(6-pyridin-2-diyl)methane)]hafnium dimethyl, prepared according to the teachings of WO 03/40195, 2003US0204017, USSN 10/429,024, filed May 2, 2003, and WO 04/24740.



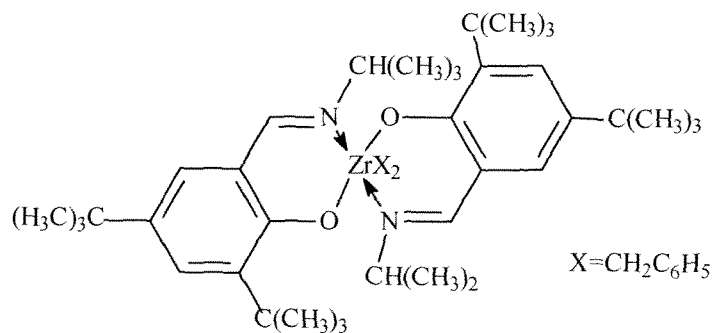
[0088] Catalyst (A3) is bis[N,N''-(2,4,6-tri(methylphenyl)amido)ethylenediamine]hafnium dibenzyl.



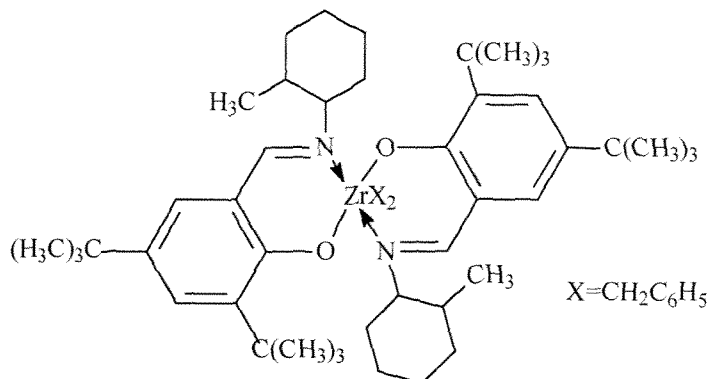
[0089] Catalyst (A4) is bis((2-oxoyl-3-(dibenzo-1H-pyrrole-1-yl)-5-(methyl)phenyl)-2-phenoxy)methyl)cyclohexane-1,2-diyl zirconium (IV) dibenzyl, prepared substantially according to the teachings of US-A-2004/0010103.



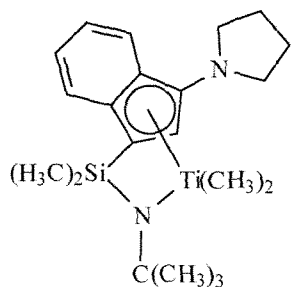
[0090] Catalyst (B1) is 1,2-bis-(3,5-di-t-butylphenylene)(1-(N-(1-methylethyl)immino)methyl)(2-oxoyl) zirconium dibenzyl



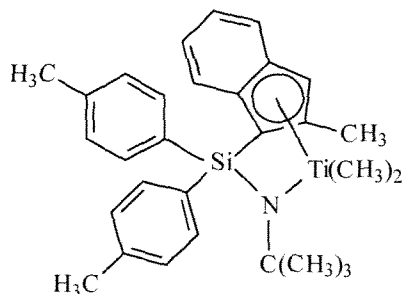
[0091] Catalyst (B2) is 1,2-bis-(3,5-di-*t*-butylphenylene)(1-(*N*-(2-methylcyclohexyl)-immino)methyl)(2-oxoyl) zirconium dibenzyl



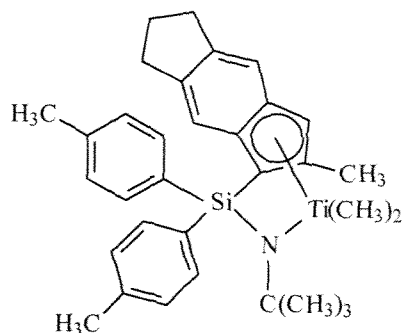
[0092] Catalyst (C1) is (t-butylamido)dimethyl(3-N-pyrrolyl-1,2,3,3a,7a- η -inden-1-yl)silanetitanium dimethyl prepared substantially according to the techniques of USP 6,268,444:



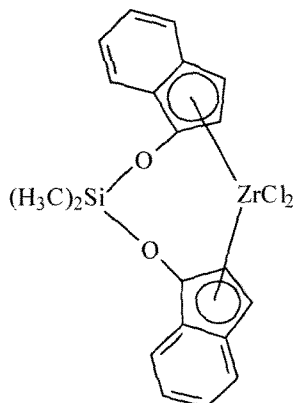
[0093] Catalyst (C2) is (t-butylamido)di(4-methylphenyl)(2-methyl-1,2,3,3a,7a- η -inden-1-yl)silanetitanium dimethyl prepared substantially according to the teachings of US-A- 2003/004286:



[0094] Catalyst (C3) is (t-butylamido)di(4-methylphenyl)(2-methyl-1,2,3,3a,8a-η-s-indacen-1-yl)silanetitanium dimethyl prepared substantially according to the teachings of US-A-2003/004286:



5 [0095] Catalyst (D1) is bis(dimethyldisiloxane)(indene-1-yl)zirconium dichloride available from Sigma-Aldrich:



[0096] **Shuttling Agents** The shuttling agents employed include diethylzinc, di(i-butyl)zinc, di(n-hexyl)zinc, triethylaluminum, trioctylaluminum, triethylgallium, i-butylaluminum bis(dimethyl(t-butyl)siloxane), i-butylaluminum bis(di(trimethylsilyl)amide),
 10 n-octylaluminum di(pyridine-2-methoxide), bis(n-octadecyl)i-butylaluminum, i-butylaluminum bis(di(n-pentyl)amide), n-octylaluminum bis(2,6-di-t-butylphenoxide), n-octylaluminum di(ethyl(1-naphthyl)amide), ethylaluminum bis(t-butyl dimethylsiloxide), ethylaluminum di(bis(trimethylsilyl)amide), ethylaluminum bis(2,3,6,7-dibenzo-1-
 15 azacycloheptaneamide), n-octylaluminum bis(2,3,6,7-dibenzo-1-azacycloheptaneamide), n-octylaluminum bis(dimethyl(t-butyl)siloxide, ethylzinc (2,6-diphenylphenoxide), and ethylzinc (t-butoxide).

[0097] Preferably, the foregoing process takes the form of a continuous solution process for forming block copolymers, especially multi-block copolymers, preferably linear multi-
 20 block copolymers of two or more monomers, more especially ethylene and a C₃₋₂₀ olefin or

cycloolefin, and most especially ethylene and a C₄₋₂₀ α -olefin, using multiple catalysts that are incapable of interconversion. That is, the catalysts are chemically distinct. Under continuous solution polymerization conditions, the process is ideally suited for polymerization of mixtures of monomers at high monomer conversions. Under these
5 polymerization conditions, shuttling from the chain shuttling agent to the catalyst becomes advantaged compared to chain growth, and multi-block copolymers, especially linear multi-block copolymers are formed in high efficiency.

[0098] The inventive interpolymers may be differentiated from conventional, random copolymers, physical blends of polymers, and block copolymers prepared via sequential
10 monomer addition, fluxional catalysts, anionic or cationic living polymerization techniques. In particular, compared to a random copolymer of the same monomers and monomer content at equivalent crystallinity or modulus, the inventive interpolymers have better (higher) heat resistance as measured by melting point, higher TMA penetration temperature, higher high-temperature tensile strength, and/or higher high-temperature torsion storage modulus as
15 determined by dynamic mechanical analysis. Compared to a random copolymer containing the same monomers and monomer content, the inventive interpolymers have lower compression set, particularly at elevated temperatures, lower stress relaxation, higher creep resistance, higher tear strength, higher blocking resistance, faster setup due to higher crystallization (solidification) temperature, higher recovery (particularly at elevated
20 temperatures), better abrasion resistance, higher retractive force, and better oil and filler acceptance.

[0099] The inventive interpolymers also exhibit a unique crystallization and branching distribution relationship. That is, the inventive interpolymers have a relatively large difference between the tallest peak temperature measured using CRYSTAF and DSC as a
25 function of heat of fusion, especially as compared to random copolymers containing the same monomers and monomer level or physical blends of polymers, such as a blend of a high density polymer and a lower density copolymer, at equivalent overall density. It is believed that this unique feature of the inventive interpolymers is due to the unique distribution of the comonomer in blocks within the polymer backbone. In particular, the inventive
30 interpolymers may comprise alternating blocks of differing comonomer content (including homopolymer blocks). The inventive interpolymers may also comprise a distribution in number and/or block size of polymer blocks of differing density or comonomer content, which is a Schultz-Flory type of distribution. In addition, the inventive interpolymers also

have a unique peak melting point and crystallization temperature profile that is substantially independent of polymer density, modulus, and morphology. In a preferred embodiment, the microcrystalline order of the polymers demonstrates characteristic spherulites and lamellae that are distinguishable from random or block copolymers, even at PDI values that are less than 1.7, or even less than 1.5, down to less than 1.3.

[0100] Moreover, the inventive interpolymers may be prepared using techniques to influence the degree or level of blockiness. That is the amount of comonomer and length of each polymer block or segment can be altered by controlling the ratio and type of catalysts and shuttling agent as well as the temperature of the polymerization, and other polymerization variables. A surprising benefit of this phenomenon is the discovery that as the degree of blockiness is increased, the optical properties, tear strength, and high temperature recovery properties of the resulting polymer are improved. In particular, haze decreases while clarity, tear strength, and high temperature recovery properties increase as the average number of blocks in the polymer increases. By selecting shuttling agents and catalyst combinations having the desired chain transferring ability (high rates of shuttling with low levels of chain termination) other forms of polymer termination are effectively suppressed. Accordingly, little if any β -hydride elimination is observed in the polymerization of ethylene/ α -olefin comonomer mixtures according to embodiments of the invention, and the resulting crystalline blocks are highly, or substantially completely, linear, possessing little or no long chain branching.

[0101] Polymers with highly crystalline chain ends can be selectively prepared in accordance with embodiments of the invention. In elastomer applications, reducing the relative quantity of polymer that terminates with an amorphous block reduces the intermolecular dilutive effect on crystalline regions. This result can be obtained by choosing chain shuttling agents and catalysts having an appropriate response to hydrogen or other chain terminating agents. Specifically, if the catalyst which produces highly crystalline polymer is more susceptible to chain termination (such as by use of hydrogen) than the catalyst responsible for producing the less crystalline polymer segment (such as through higher comonomer incorporation, regio-error, or atactic polymer formation), then the highly crystalline polymer segments will preferentially populate the terminal portions of the polymer. Not only are the resulting terminated groups crystalline, but upon termination, the highly crystalline polymer forming catalyst site is once again available for reinitiation of polymer formation. The initially formed polymer is therefore another highly crystalline

polymer segment. Accordingly, both ends of the resulting multi-block copolymer are preferentially highly crystalline.

[0102] The ethylene α -olefin interpolymers used in the embodiments of the invention are preferably interpolymers of ethylene with at least one C₃-C₂₀ α -olefin. Copolymers of ethylene and a C₃-C₂₀ α -olefin are especially preferred. The interpolymers may further comprise C₄-C₁₈ diolefin and/or alkenylbenzene. Suitable unsaturated comonomers useful for polymerizing with ethylene include, for example, ethylenically unsaturated monomers, conjugated or nonconjugated dienes, polyenes, alkenylbenzenes, etc. Examples of such comonomers include C₃-C₂₀ α -olefins such as propylene, isobutylene, 1-butene, 1-hexene, 1-pentene, 4-methyl-1-pentene, 1-heptene, 1-octene, 1-nonene, 1-decene, and the like. 1-butene and 1-octene are especially preferred. Other suitable monomers include styrene, halo- or alkyl-substituted styrenes, vinylbenzocyclobutane, 1,4-hexadiene, 1,7-octadiene, and naphthenics (e.g., cyclopentene, cyclohexene and cyclooctene).

[0103] While ethylene/ α -olefin interpolymers are preferred polymers, other ethylene/olefin polymers may also be used. Olefins as used herein refer to a family of unsaturated hydrocarbon-based compounds with at least one carbon-carbon double bond. Depending on the selection of catalysts, any olefin may be used in embodiments of the invention. Preferably, suitable olefins are C₃-C₂₀ aliphatic and aromatic compounds containing vinylic unsaturation, as well as cyclic compounds, such as cyclobutene, cyclopentene, dicyclopentadiene, and norbornene, including but not limited to, norbornene substituted in the 5 and 6 position with C₁-C₂₀ hydrocarbyl or cyclohydrocarbyl groups. Also included are mixtures of such olefins as well as mixtures of such olefins with C₄-C₄₀ diolefin compounds.

[0104] Examples of olefin monomers include, but are not limited to propylene, isobutylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, and 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene, 1-eicosene, 3-methyl-1-butene, 3-methyl-1-pentene, 4-methyl-1-pentene, 4,6-dimethyl-1-heptene, 4-vinylcyclohexene, vinylcyclohexane, norbornadiene, ethylidene norbornene, cyclopentene, cyclohexene, dicyclopentadiene, cyclooctene, C₄-C₄₀ dienes, including but not limited to 1,3-butadiene, 1,3-pentadiene, 1,4-hexadiene, 1,5-hexadiene, 1,7-octadiene, 1,9-decadiene, other C₄-C₄₀ α -olefins, and the like. In certain embodiments, the α -olefin is propylene, 1-butene, 1-pentene, 1-hexene, 1-octene or a combination thereof. Although any hydrocarbon containing

a vinyl group potentially may be used in embodiments of the invention, practical issues such as monomer availability, cost, and the ability to conveniently remove unreacted monomer from the resulting polymer may become more problematic as the molecular weight of the monomer becomes too high.

5 [0105] The polymerization processes described herein are well suited for the production of olefin polymers comprising monovinylidene aromatic monomers including styrene, o-methyl styrene, p-methyl styrene, t-butylstyrene, and the like. In particular, interpolymers comprising ethylene and styrene can be prepared by following the teachings herein.

Optionally, copolymers comprising ethylene, styrene and a C₃-C₂₀ alpha olefin, optionally
10 comprising a C₄-C₂₀ diene, having improved properties can be prepared.

[0106] Suitable non-conjugated diene monomers can be a straight chain, branched chain or cyclic hydrocarbon diene having from 6 to 15 carbon atoms. Examples of suitable non-conjugated dienes include, but are not limited to, straight chain acyclic dienes, such as 1,4-hexadiene, 1,6-octadiene, 1,7-octadiene, 1,9-decadiene, branched chain acyclic dienes, such
15 as 5-methyl-1,4-hexadiene; 3,7-dimethyl-1,6-octadiene; 3,7-dimethyl-1,7-octadiene and mixed isomers of dihydromyricene and dihydroocinene, single ring alicyclic dienes, such as 1,3-cyclopentadiene; 1,4-cyclohexadiene; 1,5-cyclooctadiene and 1,5-cyclododecadiene, and multi-ring alicyclic fused and bridged ring dienes, such as tetrahydroindene, methyl tetrahydroindene, dicyclopentadiene, bicyclo-(2,2,1)-hepta-2,5-diene; alkenyl, alkylidene,
20 cycloalkenyl and cycloalkylidene norbornenes, such as 5-methylene-2-norbornene (MNB); 5-propenyl-2-norbornene, 5-isopropylidene-2-norbornene, 5-(4-cyclopentenyl)-2-norbornene, 5-cyclohexylidene-2-norbornene, 5-vinyl-2-norbornene, and norbornadiene. Of the dienes typically used to prepare EPDMs, the particularly preferred dienes are 1,4-hexadiene (HD), 5-ethylidene-2-norbornene (ENB), 5-vinylidene-2-norbornene (VNB), 5-methylene-2-
25 norbornene (MNB), and dicyclopentadiene (DCPD). The especially preferred dienes are 5-ethylidene-2-norbornene (ENB) and 1,4-hexadiene (HD).

[0107] One class of desirable polymers that can be made in accordance with embodiments of the invention are elastomeric interpolymers of ethylene, a C₃-C₂₀ α-olefin, especially propylene, and optionally one or more diene monomers. Preferred α-olefins for
30 use in this embodiment of the present invention are designated by the formula CH₂=CHR*, where R* is a linear or branched alkyl group of from 1 to 12 carbon atoms. Examples of suitable α-olefins include, but are not limited to, propylene, isobutylene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, and 1-octene. A particularly preferred α-olefin is propylene.

The propylene based polymers are generally referred to in the art as EP or EPDM polymers. Suitable dienes for use in preparing such polymers, especially multi-block EPDM type polymers include conjugated or non-conjugated, straight or branched chain-, cyclic- or polycyclic- dienes comprising from 4 to 20 carbons. Preferred dienes include 1,4-pentadiene, 1,4-hexadiene, 5-ethylidene-2-norbornene, dicyclopentadiene, cyclohexadiene, and 5-butylidene-2-norbornene. A particularly preferred diene is 5-ethylidene-2-norbornene.

[0108] Because the diene containing polymers comprise alternating segments or blocks containing greater or lesser quantities of the diene (including none) and α -olefin (including none), the total quantity of diene and α -olefin may be reduced without loss of subsequent polymer properties. That is, because the diene and α -olefin monomers are preferentially incorporated into one type of block of the polymer rather than uniformly or randomly throughout the polymer, they are more efficiently utilized and subsequently the crosslink density of the polymer can be better controlled. Such crosslinkable elastomers and the cured products have advantaged properties, including higher tensile strength and better elastic recovery.

[0109] In some embodiments, the inventive interpolymers made with two catalysts incorporating differing quantities of comonomer have a weight ratio of blocks formed thereby from 95:5 to 5:95. The elastomeric polymers desirably have an ethylene content of from 20 to 90 percent, a diene content of from 0.1 to 10 percent, and an α -olefin content of from 10 to 80 percent, based on the total weight of the polymer. Further preferably, the multi-block elastomeric polymers have an ethylene content of from 60 to 90 percent, a diene content of from 0.1 to 10 percent, and an α -olefin content of from 10 to 40 percent, based on the total weight of the polymer. Preferred polymers are high molecular weight polymers, having a weight average molecular weight (Mw) from 10,000 to about 2,500,000, preferably from 20,000 to 500,000, more preferably from 20,000 to 350,000, and a polydispersity less than 3.5, more preferably less than 3.0, and a Mooney viscosity (ML (1+4) 125°C.) from 1 to 250. More preferably, such polymers have an ethylene content from 65 to 75 percent, a diene content from 0 to 6 percent, and an α -olefin content from 20 to 35 percent.

[0110] The ethylene/ α -olefin interpolymers can be functionalized by incorporating at least one functional group in its polymer structure. Exemplary functional groups may include, for example, ethylenically unsaturated mono- and di-functional carboxylic acids, ethylenically unsaturated mono- and di-functional carboxylic acid anhydrides, salts thereof and esters thereof. Such functional groups may be grafted to an ethylene/ α -olefin

interpolymer, or it may be copolymerized with ethylene and an optional additional comonomer to form an interpolymer of ethylene, the functional comonomer and optionally other comonomer(s). Means for grafting functional groups onto polyethylene are described for example in U.S. Patents Nos. 4,762,890, 4,927,888, and 4,950,541, the disclosures of these patents are incorporated herein by reference in their entirety. One particularly useful functional group is malic anhydride.

[0111] The amount of the functional group present in the functional interpolymer can vary. The functional group can typically be present in a copolymer-type functionalized interpolymer in an amount of at least about 1.0 weight percent, preferably at least about 5 weight percent, and more preferably at least about 7 weight percent. The functional group will typically be present in a copolymer-type functionalized interpolymer in an amount less than about 40 weight percent, preferably less than about 30 weight percent, and more preferably less than about 25 weight percent.

Testing Methods

[0112] In the examples that follow, the following analytical techniques are employed:

GPC Method for Samples 1-4 and A-C

[0113] An automated liquid-handling robot equipped with a heated needle set to 160°C is used to add enough 1,2,4-trichlorobenzene stabilized with 300 ppm Ionol to each dried polymer sample to give a final concentration of 30 mg/mL. A small glass stir rod is placed into each tube and the samples are heated to 160°C for 2 hours on a heated, orbital-shaker rotating at 250 rpm. The concentrated polymer solution is then diluted to 1 mg/ml using the automated liquid-handling robot and the heated needle set to 160°C.

[0114] A Symyx Rapid GPC system is used to determine the molecular weight data for each sample. A Gilson 350 pump set at 2.0 ml/min flow rate is used to pump helium-purged 1,2-dichlorobenzene stabilized with 300 ppm Ionol as the mobile phase through three Plgel 10 micrometer (µm) Mixed B 300mm x 7.5mm columns placed in series and heated to 160°C. A Polymer Labs ELS 1000 Detector is used with the Evaporator set to 250°C, the Nebulizer set to 165°C, and the nitrogen flow rate set to 1.8 SLM at a pressure of 60-80 psi (400-600 kPa) N₂. The polymer samples are heated to 160°C and each sample injected into a 250 µl loop using the liquid-handling robot and a heated needle. Serial analysis of the polymer samples using two switched loops and overlapping injections are used. The sample

data is collected and analyzed using Symyx Epoch™ software. Peaks are manually integrated and the molecular weight information reported uncorrected against a polystyrene standard calibration curve.

Standard CRYSTAF Method

- 5 **[0115]** Branching distributions are determined by crystallization analysis fractionation (CRYSTAF) using a CRYSTAF 200 unit commercially available from PolymerChar, Valencia, Spain. The samples are dissolved in 1,2,4 trichlorobenzene at 160°C (0.66 mg/mL) for 1 hour and stabilized at 95°C for 45 minutes. The sampling temperatures range from 95 to 30°C at a cooling rate of 0.2°C/min. An infrared detector is used to measure the polymer solution concentrations. The cumulative soluble concentration is measured as the polymer crystallizes while the temperature is decreased. The analytical derivative of the cumulative profile reflects the short chain branching distribution of the polymer.
- 10 **[0116]** The CRYSTAF peak temperature and area are identified by the peak analysis module included in the CRYSTAF Software (Version 2001.b, PolymerChar, Valencia, Spain). The CRYSTAF peak finding routine identifies a peak temperature as a maximum in the dW/dT curve and the area between the largest positive inflections on either side of the identified peak in the derivative curve. To calculate the CRYSTAF curve, the preferred processing parameters are with a temperature limit of 70°C and with smoothing parameters above the temperature limit of 0.1, and below the temperature limit of 0.3.

20 **DSC Standard Method (Excluding Samples 1-4 and A-C)**

- [0117]** Differential Scanning Calorimetry results are determined using a TAI model Q1000 DSC equipped with an RCS cooling accessory and an autosampler. A nitrogen purge gas flow of 50 ml/min is used. The sample is pressed into a thin film and melted in the press at about 175°C and then air-cooled to room temperature (25°C). 3-10 mg of material is then cut into a 6 mm diameter disk, accurately weighed, placed in a light aluminum pan (ca 50 mg), and then crimped shut. The thermal behavior of the sample is investigated with the following temperature profile. The sample is rapidly heated to 180°C and held isothermal for 3 minutes in order to remove any previous thermal history. The sample is then cooled to -40°C at 10°C/min cooling rate and held at -40°C for 3 minutes. The sample is then heated to 150°C at 10°C/min. heating rate. The cooling and second heating curves are recorded.
- 25
- 30

[0118] The DSC melting peak is measured as the maximum in heat flow rate (W/g) with respect to the linear baseline drawn between -30°C and end of melting. The heat of fusion is measured as the area under the melting curve between -30°C and the end of melting using a linear baseline.

5 GPC Method (Excluding Samples 1-4 and A-C)

[0119] The gel permeation chromatographic system consists of either a Polymer Laboratories Model PL-210 or a Polymer Laboratories Model PL-220 instrument. The column and carousel compartments are operated at 140°C. Three Polymer Laboratories 10-micron Mixed-B columns are used. The solvent is 1,2,4 trichlorobenzene. The samples are prepared at a concentration of 0.1 grams of polymer in 50 milliliters of solvent containing 200 ppm of butylated hydroxytoluene (BHT). Samples are prepared by agitating lightly for 2 hours at 160°C. The injection volume used is 100 microliters and the flow rate is 1.0 ml/minute.

[0120] Calibration of the GPC column set is performed with 21 narrow molecular weight distribution polystyrene standards with molecular weights ranging from 580 to 8,400,000, arranged in 6 "cocktail" mixtures with at least a decade of separation between individual molecular weights. The standards are purchased from Polymer Laboratories (Shropshire, UK). The polystyrene standards are prepared at 0.025 grams in 50 milliliters of solvent for molecular weights equal to or greater than 1,000,000, and 0.05 grams in 50 milliliters of solvent for molecular weights less than 1,000,000. The polystyrene standards are dissolved at 80°C with gentle agitation for 30 minutes. The narrow standards mixtures are run first and in order of decreasing highest molecular weight component to minimize degradation. The polystyrene standard peak molecular weights are converted to polyethylene molecular weights using the following equation (as described in Williams and Ward, J. Polym. Sci., Polym. Let., 6, 621 (1968)): $M_{\text{polyethylene}} = 0.431(M_{\text{polystyrene}})$.

[0121] Polyethylene equivalent molecular weight calculations are performed using Viscotek TriSEC software Version 3.0.

Compression Set

[0122] Compression set is measured according to ASTM D 395. The sample is prepared by stacking 25.4 mm diameter round discs of 3.2 mm, 2.0 mm, and 0.25 mm thickness until a total thickness of 12.7 mm is reached. The discs are cut from 12.7 cm x 12.7 cm compression

molded plaques molded with a hot press under the following conditions: zero pressure for 3 minutes at 190°C, followed by 86 MPa for 2 minutes at 190°C, followed by cooling inside the press with cold running water at 86 MPa.

Density

- 5 [0123] Samples for density measurement are prepared according to ASTM D 1928. Measurements are made within one hour of sample pressing using ASTM D792, Method B.

Flexural/Secant Modulus/ Storage Modulus

- [0124] Samples are compression molded using ASTM D 1928. Flexural and 2 percent secant moduli are measured according to ASTM D-790. Storage modulus is measured
10 according to ASTM D 5026-01 or equivalent technique.

Optical properties

- [0125] Films of 0.4 mm thickness are compression molded using a hot press (Carver Model #4095-4PR1001R). The pellets are placed between polytetrafluoroethylene sheets, heated at 190 °C at 55 psi (380 kPa) for 3 minutes, followed by 1.3 MPa for 3 minutes, and
15 then 2.6 MPa for 3 minutes. The film is then cooled in the press with running cold water at 1.3 MPa for 1 minute. The compression molded films are used for optical measurements, tensile behavior, recovery, and stress relaxation.
- [0126] Clarity is measured using BYK Gardner Haze-gard as specified in ASTM D 1746.
- [0127] 45° gloss is measured using BYK Gardner Glossmeter Microgloss 45° as
20 specified in ASTM D-2457.
- [0128] Internal haze is measured using BYK Gardner Haze-gard based on ASTM D 1003 Procedure A. Mineral oil is applied to the film surface to remove surface scratches.

Mechanical Properties - Tensile, Hysteresis, and Tear

- [0129] Stress-strain behavior in uniaxial tension is measured using ASTM D 1708
25 microtensile specimens. Samples are stretched with an Instron at 500% min⁻¹ at 21°C. Tensile strength and elongation at break are reported from an average of 5 specimens.
- [0130] 100% and 300% Hysteresis is determined from cyclic loading to 100% and 300% strains using ASTM D 1708 microtensile specimens with an Instron™ instrument. The sample is loaded and unloaded at 267 % min⁻¹ for 3 cycles at 21°C. Cyclic experiments at

300% and 80°C are conducted using an environmental chamber. In the 80°C experiment, the sample is allowed to equilibrate for 45 minutes at the test temperature before testing. In the 21°C, 300% strain cyclic experiment, the retractive stress at 150% strain from the first unloading cycle is recorded. Percent recovery for all experiments are calculated from the first unloading cycle using the strain at which the load returned to the base line. The percent recovery is defined as:

$$\% \text{ Recovery} = \frac{\varepsilon_f - \varepsilon_s}{\varepsilon_f} \times 100$$

where ε_f is the strain taken for cyclic loading and ε_s is the strain where the load returns to the baseline during the 1st unloading cycle.

[0131] Stress relaxation is measured at 50 percent strain and 37°C for 12 hours using an Instron™ instrument equipped with an environmental chamber. The gauge geometry was 76 mm x 25 mm x 0.4 mm. After equilibrating at 37°C for 45 min in the environmental chamber, the sample was stretched to 50% strain at 333% min⁻¹. Stress was recorded as a function of time for 12 hours. The percent stress relaxation after 12 hours was calculated using the formula:

$$\% \text{ Stress Relaxation} = \frac{L_0 - L_{12}}{L_0} \times 100$$

where L_0 is the load at 50% strain at 0 time and L_{12} is the load at 50 percent strain after 12 hours.

[0132] Tensile notched tear experiments are carried out on samples having a density of 0.88 g/cc or less using an Instron™ instrument. The geometry consists of a gauge section of 76 mm x 13 mm x 0.4 mm with a 2 mm notch cut into the sample at half the specimen length. The sample is stretched at 508 mm min⁻¹ at 21 °C until it breaks. The tear energy is calculated as the area under the stress-elongation curve up to strain at maximum load. An average of at least 3 specimens are reported.

TMA

[0133] Thermal Mechanical Analysis (Penetration Temperature) is conducted on 30mm diameter x 3.3 mm thick, compression molded discs, formed at 180°C and 10 MPa molding pressure for 5 minutes and then air quenched. The instrument used is a TMA 7, brand

available from Perkin-Elmer. In the test, a probe with 1.5 mm radius tip (P/N N519-0416) is applied to the surface of the sample disc with 1N force. The temperature is raised at 5°C/min from 25°C. The probe penetration distance is measured as a function of temperature. The experiment ends when the probe has penetrated 1 mm into the sample.

5 DMA

[0134] Dynamic Mechanical Analysis (DMA) is measured on compression molded disks formed in a hot press at 180°C at 10 MPa pressure for 5 minutes and then water cooled in the press at 90°C / min. Testing is conducted using an ARES controlled strain rheometer (TA instruments) equipped with dual cantilever fixtures for torsion testing.

- 10 [0135] A 1.5mm plaque is pressed and cut in a bar of dimensions 32x12mm. The sample is clamped at both ends between fixtures separated by 10mm (grip separation ΔL) and subjected to successive temperature steps from -100°C to 200°C (5°C per step). At each temperature the torsion modulus G' is measured at an angular frequency of 10 rad/s, the strain amplitude being maintained between 0.1 percent and 4 percent to ensure that the torque
- 15 is sufficient and that the measurement remains in the linear regime.

- [0136] An initial static force of 10 g is maintained (auto-tension mode) to prevent slack in the sample when thermal expansion occurs. As a consequence, the grip separation ΔL increases with the temperature, particularly above the melting or softening point of the polymer sample. The test stops at the maximum temperature or when the gap between the
- 20 fixtures reaches 65 mm.

Melt Index

[0137] Melt index, or I_2 , is measured in accordance with ASTM D 1238, Condition 190°C/2.16 kg. Melt index, or I_{10} is also measured in accordance with ASTM D 1238, Condition 190°C/10 kg.

25 ATREF

- [0138] Analytical temperature rising elution fractionation (ATREF) analysis is conducted according to the method described in U.S. Patent No. 4,798,081 and Wilde, L.; Ryle, T.R.; Knobloch, D.C.; Peat, I.R.; *Determination of Branching Distributions in Polyethylene and Ethylene Copolymers*, J. Polym. Sci., 20, 441-455 (1982), which are incorporated by
- 30 reference herein in their entirety. The composition to be analyzed is dissolved in

trichlorobenzene and allowed to crystallize in a column containing an inert support (stainless steel shot) by slowly reducing the temperature to 20°C at a cooling rate of 0.1°C/min. The column is equipped with an infrared detector. An ATREF chromatogram curve is then generated by eluting the crystallized polymer sample from the column by slowly increasing the temperature of the eluting solvent (trichlorobenzene) from 20 to 120°C at a rate of 1.5°C/min.

¹³C NMR Analysis

[0139] The samples are prepared by adding approximately 3g of a 50/50 mixture of tetrachloroethane-d₂/orthodichlorobenzene to 0.4 g sample in a 10 mm NMR tube. The samples are dissolved and homogenized by heating the tube and its contents to 150°C. The data are collected using a JEOL Eclipse™ 400MHz spectrometer or a Varian Unity Plus™ 400MHz spectrometer, corresponding to a ¹³C resonance frequency of 100.5 MHz. The data are acquired using 4000 transients per data file with a 6 second pulse repetition delay. To achieve minimum signal-to-noise for quantitative analysis, multiple data files are added together. The spectral width is 25,000 Hz with a minimum file size of 32K data points. The samples are analyzed at 130 °C in a 10 mm broad band probe. The comonomer incorporation is determined using Randall's triad method (Randall, J.C.; JMS-Rev. Macromol. Chem. Phys., C29, 201-317 (1989), which is incorporated by reference herein in its entirety.

Polymer Fractionation by TREF

[0140] Large-scale TREF fractionation is carried by dissolving 15-20 g of polymer in 2 liters of 1,2,4-trichlorobenzene (TCB) by stirring for 4 hours at 160°C. The polymer solution is forced by 15 psig (100 kPa) nitrogen onto a 3 inch by 4 foot (7.6 cm x 12 cm) steel column packed with a 60:40 (v:v) mix of 30-40 mesh (600-425 µm) spherical, technical quality glass beads (available from Potters Industries, HC 30 Box 20, Brownwood, TX, 76801) and stainless steel, 0.028" (0.7mm) diameter cut wire shot (available from Pellets, Inc. 63 Industrial Drive, North Tonawanda, NY, 14120). The column is immersed in a thermally controlled oil jacket, set initially to 160°C. The column is first cooled ballistically to 125°C, then slow cooled to 20°C at 0.04°C per minute and held for one hour. Fresh TCB is introduced at about 65 ml/min while the temperature is increased at 0.167°C per minute.

[0141] Approximately 2000 ml portions of eluant from the preparative TREF column are collected in a 16 station, heated fraction collector. The polymer is concentrated in each

fraction using a rotary evaporator until about 50 to 100 ml of the polymer solution remains. The concentrated solutions are allowed to stand overnight before adding excess methanol, filtering, and rinsing (approx. 300-500 ml of methanol including the final rinse). The filtration step is performed on a 3 position vacuum assisted filtering station using 5.0 μm polytetrafluoroethylene coated filter paper (available from Osmonics Inc., Cat# Z50WP04750). The filtrated fractions are dried overnight in a vacuum oven at 60°C and weighed on an analytical balance before further testing.

Melt Strength

[0142] Melt Strength (MS) is measured by using a capillary rheometer fitted with a 2.1 mm diameter, 20:1 die with an entrance angle of approximately 45 degrees. After equilibrating the samples at 190°C for 10 minutes, the piston is run at a speed of 1 inch/minute (2.54 cm/minute). The standard test temperature is 190°C. The sample is drawn uniaxially to a set of accelerating nips located 100 mm below the die with an acceleration of 2.4 mm/sec². The required tensile force is recorded as a function of the take-up speed of the nip rolls. The maximum tensile force attained during the test is defined as the melt strength. In the case of polymer melt exhibiting draw resonance, the tensile force before the onset of draw resonance was taken as melt strength. The melt strength is recorded in centiNewtons (“cN”).

Catalysts

[0143] The term “overnight”, if used, refers to a time of approximately 16-18 hours, the term “room temperature”, refers to a temperature of 20-25 °C, and the term “mixed alkanes” refers to a commercially obtained mixture of C₆₋₉ aliphatic hydrocarbons available under the trade designation Isopar E[®], from ExxonMobil Chemical Company. In the event the name of a compound herein does not conform to the structural representation thereof, the structural representation shall control. The synthesis of all metal complexes and the preparation of all screening experiments were carried out in a dry nitrogen atmosphere using dry box techniques. All solvents used were HPLC grade and were dried before their use.

[0144] MMAO refers to modified methylalumoxane, a triisobutylaluminum modified methylalumoxane available commercially from Akzo-Noble Corporation.

[0145] The preparation of catalyst (B1) is conducted as follows.

a) Preparation of (1-methylethyl)(2-hydroxy-3,5-di(t-butyl)phenyl)methylimine

3,5-Di-t-butylsalicylaldehyde (3.00 g) is added to 10 mL of isopropylamine. The solution rapidly turns bright yellow. After stirring at ambient temperature for 3 hours, volatiles are removed under vacuum to yield a bright yellow, crystalline solid (97 percent yield).

b) Preparation of 1,2-bis-(3,5-di-t-butylphenylene)(1-(N-(1-methylethyl)imino)methyl)(2-oxoyl) zirconium dibenzyl

A solution of (1-methylethyl)(2-hydroxy-3,5-di(t-butyl)phenyl)imine (605 mg, 2.2 mmol) in 5 mL toluene is slowly added to a solution of $\text{Zr}(\text{CH}_2\text{Ph})_4$ (500 mg, 1.1 mmol) in 50 mL toluene. The resulting dark yellow solution is stirred for 30 minutes. Solvent is removed under reduced pressure to yield the desired product as a reddish-brown solid.

[0146] The preparation of catalyst (B2) is conducted as follows.

a) Preparation of (1-(2-methylcyclohexyl)ethyl)(2-oxoyl-3,5-di(t-butyl)phenyl)imine

2-Methylcyclohexylamine (8.44 mL, 64.0 mmol) is dissolved in methanol (90 mL), and di-t-butylsalicylaldehyde (10.00 g, 42.67 mmol) is added. The reaction mixture is stirred for three hours and then cooled to -25°C for 12 hours. The resulting yellow solid precipitate is collected by filtration and washed with cold methanol (2 x 15 mL), and then dried under reduced pressure. The yield is 11.17 g of a yellow solid. ^1H NMR is consistent with the desired product as a mixture of isomers.

b) Preparation of bis-(1-(2-methylcyclohexyl)ethyl)(2-oxoyl-3,5-di(t-butyl)phenyl)imino)zirconium dibenzyl

A solution of (1-(2-methylcyclohexyl)ethyl)(2-oxoyl-3,5-di(t-butyl)phenyl)imine (7.63 g, 23.2 mmol) in 200 mL toluene is slowly added to a solution of $\text{Zr}(\text{CH}_2\text{Ph})_4$ (5.28 g, 11.6 mmol) in 600 mL toluene. The resulting dark yellow solution is stirred for 1 hour at 25°C . The solution is diluted further with 680 mL toluene to give a solution having a concentration of 0.00783 M.

[0147] Cocatalyst 1 A mixture of methyldi(C_{14-18} alkyl)ammonium salts of tetrakis(pentafluorophenyl)borate (here-in-after armeenium borate), prepared by reaction of a

long chain trialkylamine (Armeen™ M2HT, available from Akzo-Nobel, Inc.), HCl and Li[B(C₆F₅)₄], substantially as disclosed in USP 5,919,9883, Ex. 2.

[0148] Cocatalyst 2 Mixed C₁₄₋₁₈ alkyldimethylammonium salt of bis(tris(pentafluorophenyl)-alumane)-2-undecylimidazolid, prepared according to USP

6,395,671, Ex. 16.

[0149] Shuttling Agents The shuttling agents employed include diethylzinc (DEZ, SA1), di(i-butyl)zinc (SA2), di(n-hexyl)zinc (SA3), triethylaluminum (TEA, SA4),

trioctylaluminum (SA5), triethylgallium (SA6), i-butylaluminum bis(dimethyl(t-

butyl)siloxane) (SA7), i-butylaluminum bis(di(trimethylsilyl)amide) (SA8), n-octylaluminum

di(pyridine-2-methoxide) (SA9), bis(n-octadecyl)i-butylaluminum (SA10), i-butylaluminum

bis(di(n-pentyl)amide) (SA11), n-octylaluminum bis(2,6-di-t-butylphenoxide) (SA12), n-

octylaluminum di(ethyl(1-naphthyl)amide) (SA13), ethylaluminum bis(t-

butyldimethylsiloxide) (SA14), ethylaluminum di(bis(trimethylsilyl)amide) (SA15),

ethylaluminum bis(2,3,6,7-dibenzo-1-azacycloheptaneamide) (SA16), n-octylaluminum

bis(2,3,6,7-dibenzo-1-azacycloheptaneamide) (SA17), n-octylaluminum bis(dimethyl(t-

butyl)siloxide(SA18), ethylzinc (2,6-diphenylphenoxide) (SA19), and ethylzinc (t-butoxide)

(SA20).

Examples 1-4, Comparative A-C

General High Throughput Parallel Polymerization Conditions

[0150] Polymerizations are conducted using a high throughput, parallel polymerization reactor (PPR) available from Symyx Technologies, Inc. and operated substantially according

to US Patents No. 6,248,540, 6,030,917, 6,362,309, 6,306,658, and 6,316,663. Ethylene

copolymerizations are conducted at 130°C and 200 psi (1.4 MPa) with ethylene on demand

using 1.2 equivalents of cocatalyst 1 based on total catalyst used (1.1 equivalents when

MMAO is present). A series of polymerizations are conducted in a parallel pressure reactor

(PPR) contained of 48 individual reactor cells in a 6 x 8 array that are fitted with a pre-

weighed glass tube. The working volume in each reactor cell is 6000 µL. Each cell is

temperature and pressure controlled with stirring provided by individual stirring paddles.

The monomer gas and quench gas are plumbed directly into the PPR unit and controlled by

automatic valves. Liquid reagents are robotically added to each reactor cell by syringes and

the reservoir solvent is mixed alkanes. The order of addition is mixed alkanes solvent (4 ml),

ethylene, 1-octene comonomer (1 ml), cocatalyst 1 or cocatalyst 1/MMAO mixture, shuttling

agent, and catalyst or catalyst mixture. When a mixture of cocatalyst 1 and MMAO or a mixture of two catalysts is used, the reagents are premixed in a small vial immediately prior to addition to the reactor. When a reagent is omitted in an experiment, the above order of addition is otherwise maintained. Polymerizations are conducted for approximately 1-2 minutes, until predetermined ethylene consumptions are reached. After quenching with CO, the reactors are cooled and the glass tubes are unloaded. The tubes are transferred to a centrifuge/vacuum drying unit, and dried for 12 hours at 60°C. The tubes containing dried polymer are weighed and the difference between this weight and the tare weight gives the net yield of polymer. Results are contained in Table 1. In Table 1 and elsewhere in the application, comparative compounds are indicated by an asterisk (*).

[0151] Examples 1-4 demonstrate the synthesis of linear block copolymers by the present invention as evidenced by the formation of a very narrow MWD, essentially monomodal copolymer when DEZ is present and a bimodal, broad molecular weight distribution product (a mixture of separately produced polymers) in the absence of DEZ. Due to the fact that Catalyst (A1) is known to incorporate more octene than Catalyst (B1), the different blocks or segments of the resulting copolymers of the invention are distinguishable based on branching or density.

Table 1

Ex.	Cat. (A1) (μ mol)	Cat (B1) (μ mol)	Cocat (μ mol)	MMAO (μ mol)	shuttling agent (μ mol)	Yield (g)	Mn	Mw/Mn	hexyls ¹
A*	0.06	-	0.066	0.3	-	0.1363	300502	3.32	-
B*	-	0.1	0.110	0.5	-	0.1581	36957	1.22	2.5
C*	0.06	0.1	0.176	0.8	-	0.2038	45526	5.30 ²	5.5
1	0.06	0.1	0.192	-	DEZ (8.0)	0.1974	28715	1.19	4.8
2	0.06	0.1	0.192	-	DEZ (80.0)	0.1468	2161	1.12	14.4
3	0.06	0.1	0.192	-	TEA (8.0)	0.208	22675	1.71	4.6
4	0.06	0.1	0.192	-	TEA (80.0)	0.1879	3338	1.54	9.4

¹ C₆ or higher chain content per 1000 carbons

² Bimodal molecular weight distribution

[0152] It may be seen the polymers produced according to the invention have a relatively narrow polydispersity (Mw/Mn) and larger block-copolymer content (trimer, tetramer, or larger) than polymers prepared in the absence of the shuttling agent.

[0153] Further characterizing data for the polymers of Table 1 are determined by reference to the figures. More specifically DSC and ATREF results show the following:

[0154] The DSC curve for the polymer of example 1 shows a 115.7°C melting point (T_m) with a heat of fusion of 158.1 J/g. The corresponding CRYSTAF curve shows the tallest

peak at 34.5°C with a peak area of 52.9 percent. The difference between the DSC T_m and the Tcrystaf is 81.2°C.

[0155] The DSC curve for the polymer of example 2 shows a peak with a 109.7°C

melting point (T_m) with a heat of fusion of 214.0 J/g. The corresponding CRYSTAF curve shows the tallest peak at 46.2°C with a peak area of 57.0 percent. The difference between the DSC T_m and the Tcrystaf is 63.5°C.

[0156] The DSC curve for the polymer of example 3 shows a peak with a 120.7°C

melting point (T_m) with a heat of fusion of 160.1 J/g. The corresponding CRYSTAF curve shows the tallest peak at 66.1°C with a peak area of 71.8 percent. The difference between the DSC T_m and the Tcrystaf is 54.6°C.

[0157] The DSC curve for the polymer of example 4 shows a peak with a 104.5°C

melting point (T_m) with a heat of fusion of 170.7 J/g. The corresponding CRYSTAF curve shows the tallest peak at 30 °C with a peak area of 18.2 percent. The difference between the DSC T_m and the Tcrystaf is 74.5°C.

[0158] The DSC curve for comparative A shows a 90.0°C melting point (T_m) with a heat

of fusion of 86.7 J/g. The corresponding CRYSTAF curve shows the tallest peak at 48.5°C with a peak area of 29.4 percent. Both of these values are consistent with a resin that is low in density. The difference between the DSC T_m and the Tcrystaf is 41.8°C.

[0159] The DSC curve for comparative B shows a 129.8°C melting point (T_m) with a

heat of fusion of 237.0 J/g. The corresponding CRYSTAF curve shows the tallest peak at 82.4°C with a peak area of 83.7 percent. Both of these values are consistent with a resin that is high in density. The difference between the DSC T_m and the Tcrystaf is 47.4°C.

[0160] The DSC curve for comparative C shows a 125.3°C melting point (T_m) with a

heat of fusion of 143.0 J/g. The corresponding CRYSTAF curve shows the tallest peak at 81.8 °C with a peak area of 34.7 percent as well as a lower crystalline peak at 52.4 °C. The separation between the two peaks is consistent with the presence of a high crystalline and a low crystalline polymer. The difference between the DSC T_m and the Tcrystaf is 43.5°C.

Examples 5-19, Comparatives D-F, Continuous Solution Polymerization, Catalyst A1/B2 + DEZ

[0161] Continuous solution polymerizations are carried out in a computer controlled autoclave reactor equipped with an internal stirrer. Purified mixed alkanes solvent (Isopar™

E available from ExxonMobil Chemical Company), ethylene at 2.70 lbs/hour (1.22 kg/hour), 1-octene, and hydrogen (where used) are supplied to a 3.8 L reactor equipped with a jacket for temperature control and an internal thermocouple. The solvent feed to the reactor is measured by a mass-flow controller. A variable speed diaphragm pump controls the solvent flow rate and pressure to the reactor. At the discharge of the pump, a side stream is taken to provide flush flows for the catalyst and cocatalyst 1 injection lines and the reactor agitator. These flows are measured by Micro-Motion mass flow meters and controlled by control valves or by the manual adjustment of needle valves. The remaining solvent is combined with 1-octene, ethylene, and hydrogen (where used) and fed to the reactor. A mass flow controller is used to deliver hydrogen to the reactor as needed. The temperature of the solvent/monomer solution is controlled by use of a heat exchanger before entering the reactor. This stream enters the bottom of the reactor. The catalyst component solutions are metered using pumps and mass flow meters and are combined with the catalyst flush solvent and introduced into the bottom of the reactor. The reactor is run liquid-full at 500 psig (3.45 MPa) with vigorous stirring. Product is removed through exit lines at the top of the reactor. All exit lines from the reactor are steam traced and insulated. Polymerization is stopped by the addition of a small amount of water into the exit line along with any stabilizers or other additives and passing the mixture through a static mixer. The product stream is then heated by passing through a heat exchanger before devolatilization. The polymer product is recovered by extrusion using a devolatilizing extruder and water cooled pelletizer. Process details and results are contained in Table 2. Selected polymer properties are provided in Table 3.

Table 2 Process details for preparation of exemplary polymers

Ex.	C ₈ H ₁₆ kg/hr	Solv. kg/hr	H ₂ scm ¹	T °C	Cat Al ² ppm	Cat Al ¹ Flow kg/hr	Cat B ³ ppm	B2 Flow kg/hr	DEZ Conc %	DEZ Flow kg/hr	Cocat Conc. ppm	Cocat Flow kg/hr	[C ₂ H ₄]/ [DEZ] ⁴	Poly Rate ⁵ kg/hr	Conv % ⁶	Solids %	Eff. ⁷
D*	1.63	12.7	29.90	120	142.2	0.14	-	--	0.19	0.32	820	0.17	536	1.81	88.8	11.2	95.2
E*	"	9.5	5.00	"	--	--	109	0.10	0.19	"	1743	0.40	485	1.47	89.9	11.3	126.8
F*	"	11.3	251.6	"	71.7	0.06	30.8	0.06	--	--	"	0.11	-	1.55	88.5	10.3	257.7
5	"	"	-	"	"	0.14	30.8	0.13	0.17	0.43	"	0.26	419	1.64	89.6	11.1	118.3
6	"	"	4.92	"	"	0.10	30.4	0.08	0.17	0.32	"	0.18	570	1.65	89.3	11.1	172.7
7	"	"	21.70	"	"	0.07	30.8	0.06	0.17	0.25	"	0.13	718	1.60	89.2	10.6	244.1
8	"	"	36.90	"	"	0.06	"	"	"	0.10	"	0.12	1778	1.62	90.0	10.8	261.1
9	"	"	78.43	"	"	"	"	"	"	0.04	"	"	4596	1.63	90.2	10.8	267.9
10	"	"	0.00	123	71.1	0.12	30.3	0.14	0.34	0.19	1743	0.08	415	1.67	90.31	11.1	131.1
11	"	"	"	120	71.1	0.16	"	0.17	0.80	0.15	1743	0.10	249	1.68	89.56	11.1	100.6
12	"	"	"	121	71.1	0.15	"	0.07	"	0.09	1743	0.07	396	1.70	90.02	11.3	137.0
13	"	"	"	122	71.1	0.12	"	0.06	"	0.05	1743	0.05	653	1.69	89.64	11.2	161.9
14	"	"	"	120	71.1	0.05	"	0.29	"	0.10	1743	0.10	395	1.41	89.42	9.3	114.1
15	2.45	"	"	"	71.1	0.14	"	0.17	"	0.14	1743	0.09	282	1.80	89.33	11.3	121.3
16	"	"	"	122	71.1	0.10	"	0.13	"	0.07	1743	0.07	485	1.78	90.11	11.2	159.7
17	"	"	"	121	71.1	0.10	"	0.14	"	0.08	1743	"	506	1.75	89.08	11.0	155.6
18	0.69	"	"	121	71.1	"	"	0.22	"	0.11	1743	0.10	331	1.25	89.93	8.8	90.2
19	0.32	"	"	122	71.1	0.06	"	"	"	0.09	1743	0.08	367	1.16	90.74	8.4	106.0

* Comparative, not an example of the invention

1 standard cm³/min2 [N-(2,6-di(1-methylethyl)phenyl)amido](2-isopropylphenyl)(α -naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium dimethyl

3 bis-(1-(2-methylcyclohexyl)ethyl)(2-oxoyl-3,5-di(t-butyl)phenyl)imino) zirconium dibenzyl

4 molar ratio in reactor

5 polymer production rate

6 percent ethylene conversion in reactor

7 efficiency, kg polymer/g M where g M = g Hf + g Zr

Table 3 Properties of exemplary polymers

Ex.	Density (g/cm ³)	I ₂	I ₁₀	I ₁₀ /I ₂	Mw (g/mol)	Mn (g/mol)	Mw/Mn	Heat of Fusion (J/g)	T _m (°C)	T _c (°C)	T _{CRYSTAF} (°C)	T _m - T _{CRYSTAF} (°C)	CRYSTAF Peak Area (percent)
D*	0.8627	1.5	10.0	6.5	110,000	55,800	2.0	32	37	45	30	7	99
E*	0.9378	7.0	39.0	5.6	65,000	33,300	2.0	183	124	113	79	45	95
F*	0.8895	0.9	12.5	13.4	137,300	9,980	13.8	90	125	111	78	47	20
5	0.8786	1.5	9.8	6.7	104,600	53,200	2.0	55	120	101	48	72	60
6	0.8785	1.1	7.5	6.5	109,600	53,300	2.1	55	115	94	44	71	63
7	0.8825	1.0	7.2	7.1	118,500	53,100	2.2	69	121	103	49	72	29
8	0.8828	0.9	6.8	7.7	129,000	40,100	3.2	68	124	106	80	43	13
9	0.8836	1.1	9.7	9.1	129,600	28,700	4.5	74	125	109	81	44	16
10	0.8784	1.2	7.5	6.5	113,100	58,200	1.9	54	116	92	41	75	52
11	0.8818	9.1	59.2	6.5	66,200	36,500	1.8	63	114	93	40	74	25
12	0.8700	2.1	13.2	6.4	101,500	55,100	1.8	40	113	80	30	83	91
13	0.8718	0.7	4.4	6.5	132,100	63,600	2.1	42	114	80	30	81	8
14	0.9116	2.6	15.6	6.0	81,900	43,600	1.9	123	121	106	73	48	92
15	0.8719	6.0	41.6	6.9	79,900	40,100	2.0	33	114	91	32	82	10
16	0.8758	0.5	3.4	7.1	148,500	74,900	2.0	43	117	96	48	69	65
17	0.8757	1.7	11.3	6.8	107,500	54,000	2.0	43	116	96	43	73	57
18	0.9192	4.1	24.9	6.1	72,000	37,900	1.9	136	120	106	70	50	94
19	0.9344	3.4	20.3	6.0	76,800	39,400	1.9	169	125	112	80	45	88

[0162] The resulting polymers are tested by DSC and ATREF as with previous examples. Results are as follows:

[0163] The DSC curve for the polymer of example 5 shows a peak with a 119.6 °C melting point (T_m) with a heat of fusion of 60.0 J/g. The corresponding CRYSTAF curve shows the tallest peak at 47.6°C with a peak area of 59.5 percent. The delta between the DSC T_m and the T_{crystaf} is 72.0°C.

[0164] The DSC curve for the polymer of example 6 shows a peak with a 115.2 °C melting point (T_m) with a heat of fusion of 60.4 J/g. The corresponding CRYSTAF curve shows the tallest peak at 44.2°C with a peak area of 62.7 percent. The delta between the DSC T_m and the T_{crystaf} is 71.0°C.

[0165] The DSC curve for the polymer of example 7 shows a peak with a 121.3 °C melting point with a heat of fusion of 69.1 J/g. The corresponding CRYSTAF curve shows the tallest peak at 49.2°C with a peak area of 29.4 percent. The delta between the DSC T_m and the T_{crystaf} is 72.1°C.

[0166] The DSC curve for the polymer of example 8 shows a peak with a 123.5 °C melting point (T_m) with a heat of fusion of 67.9 J/g. The corresponding CRYSTAF curve shows the tallest peak at 80.1°C with a peak area of 12.7 percent. The delta between the DSC T_m and the T_{crystaf} is 43.4°C.

[0167] The DSC curve for the polymer of example 9 shows a peak with a 124.6 °C melting point (T_m) with a heat of fusion of 73.5 J/g. The corresponding CRYSTAF curve shows the tallest peak at 80.8°C with a peak area of 16.0 percent. The delta between the DSC T_m and the T_{crystaf} is 43.8°C.

[0168] The DSC curve for the polymer of example 10 shows a peak with a 115.6 °C melting point (T_m) with a heat of fusion of 60.7 J/g. The corresponding CRYSTAF curve shows the tallest peak at 40.9°C with a peak area of 52.4 percent. The delta between the DSC T_m and the T_{crystaf} is 74.7°C.

[0169] The DSC curve for the polymer of example 11 shows a peak with a 113.6 °C melting point (T_m) with a heat of fusion of 70.4 J/g. The corresponding CRYSTAF curve shows the tallest peak at 39.6°C with a peak area of 25.2 percent. The delta between the DSC T_m and the T_{crystaf} is 74.1°C.

[0170] The DSC curve for the polymer of example 12 shows a peak with a 113.2 °C melting point (T_m) with a heat of fusion of 48.9 J/g. The corresponding CRYSTAF curve

shows no peak equal to or above 30 °C. (Tcrystaf for purposes of further calculation is therefore set at 30°C). The delta between the DSC Tm and the Tcrystaf is 83.2°C.

[0171] The DSC curve for the polymer of example 13 shows a peak with a 114.4 °C melting point (Tm) with a heat of fusion of 49.4 J/g. The corresponding CRYSTAF curve shows the tallest peak at 33.8 °C with a peak area of 7.7 percent. The delta between the DSC Tm and the Tcrystaf is 84.4°C.

[0172] The DSC for the polymer of example 14 shows a peak with a 120.8 °C melting point (Tm) with a heat of fusion of 127.9 J/g. The corresponding CRYSTAF curve shows the tallest peak at 72.9 °C with a peak area of 92.2 percent. The delta between the DSC Tm and the Tcrystaf is 47.9°C.

[0173] The DSC curve for the polymer of example 15 shows a peak with a 114.3 °C melting point (Tm) with a heat of fusion of 36.2 J/g. The corresponding CRYSTAF curve shows the tallest peak at 32.3 °C with a peak area of 9.8 percent. The delta between the DSC Tm and the Tcrystaf is 82.0°C.

[0174] The DSC curve for the polymer of example 16 shows a peak with a 116.6 °C melting point (Tm) with a heat of fusion of 44.9 J/g. The corresponding CRYSTAF curve shows the tallest peak at 48.0 °C with a peak area of 65.0 percent. The delta between the DSC Tm and the Tcrystaf is 68.6°C.

[0175] The DSC curve for the polymer of example 17 shows a peak with a 116.0 °C melting point (Tm) with a heat of fusion of 47.0 J/g. The corresponding CRYSTAF curve shows the tallest peak at 43.1 °C with a peak area of 56.8 percent. The delta between the DSC Tm and the Tcrystaf is 72.9°C.

[0176] The DSC curve for the polymer of example 18 shows a peak with a 120.5 °C melting point (Tm) with a heat of fusion of 141.8 J/g. The corresponding CRYSTAF curve shows the tallest peak at 70.0 °C with a peak area of 94.0 percent. The delta between the DSC Tm and the Tcrystaf is 50.5 °C.

[0177] The DSC curve for the polymer of example 19 shows a peak with a 124.8 °C melting point (Tm) with a heat of fusion of 174.8 J/g. The corresponding CRYSTAF curve shows the tallest peak at 79.9 °C with a peak area of 87.9 percent. The delta between the DSC Tm and the Tcrystaf is 45.0 °C.

[0178] The DSC curve for the polymer of comparative D shows a peak with a 37.3°C melting point (Tm) with a heat of fusion of 31.6 J/g. The corresponding CRYSTAF curve

shows no peak equal to and above 30°C. Both of these values are consistent with a resin that is low in density. The delta between the DSC T_m and the T_{crystaf} is 7.3°C.

[0179] The DSC curve for the polymer of comparative E shows a peak with a 124.0 °C melting point (T_m) with a heat of fusion of 179.3 J/g. The corresponding CRYSTAF curve shows the tallest peak at 79.3°C with a peak area of 94.6 percent. Both of these values are consistent with a resin that is high in density. The delta between the DSC T_m and the T_{crystaf} is 44.6°C.

[0180] The DSC curve for the polymer of comparative F shows a peak with a 124.8 °C melting point (T_m) with a heat of fusion of 90.4 J/g. The corresponding CRYSTAF curve shows the tallest peak at 77.6°C with a peak area of 19.5 percent. The separation between the two peaks is consistent with the presence of both a high crystalline and a low crystalline polymer. The delta between the DSC T_m and the T_{crystaf} is 47.2°C.

Physical Property Testing

[0181] Polymer samples are evaluated for physical properties such as high temperature resistance properties, as evidenced by TMA temperature testing, pellet blocking strength, high temperature recovery, high temperature compression set and storage modulus ratio, G'(25°C)/G'(100°C). Several commercially available polymers are included in the tests: Comparative G* is a substantially linear ethylene/1-octene copolymer (AFFINITY®, available from The Dow Chemical Company), Comparative H* is an elastomeric, substantially linear ethylene/ 1-octene copolymer (AFFINITY®EG8100, available from The Dow Chemical Company), Comparative I is a substantially linear ethylene/1-octene copolymer (AFFINITY®PL1840, available from The Dow Chemical Company), Comparative J is a hydrogenated styrene/butadiene/styrene triblock copolymer (KRATON™ G1652, available from KRATON Polymers), Comparative K is a thermoplastic vulcanizate (TPV, a polyolefin blend containing dispersed therein a crosslinked elastomer). Results are presented in Table 4.

Table 4 High Temperature Mechanical Properties

Ex.	TMA-1mm penetration (°C)	Pellet Blocking Strength lb/ft ² (kPa)	G'(25°C)/G'(100°C)	300 % Strain Recovery (80°C) (percent)	Compression Set (70°C) (percent)
D*	51	-	9	Failed	-
E*	130	-	18	-	-
F*	70	141 (6.8)	9	Failed	100
5	104	0 (0)	6	81	49
6	110	-	5	-	52
7	113	-	4	84	43
8	111	-	4	Failed	41
9	97	-	4	-	66
10	108	-	5	81	55
11	100	-	8	-	68
12	88	-	8	-	79
13	95	-	6	84	71
14	125	-	7	-	-
15	96	-	5	-	58
16	113	-	4	-	42
17	108	0 (0)	4	82	47
18	125	-	10	-	-
19	133	-	9	-	-
G*	75	463 (22.2)	89	Failed	100
H*	70	213 (10.2)	29	Failed	100
I*	111	-	11	-	-
J*	107	-	5	Failed	100
K*	152	-	3	-	40

[0182] In Table 4, Comparative F (which is a physical blend of the two polymers resulting from simultaneous polymerizations using catalyst A1 and B1) has a 1 mm penetration temperature of about 70°C, while Examples 5-9 have a 1 mm penetration temperature of 100°C or greater. Further, examples 10-19 all have a 1 mm penetration temperature of greater than 85°C, with most having 1 mm TMA temperature of greater than 90°C or even greater than 100°C. This shows that the novel polymers have better dimensional stability at higher temperatures compared to a physical blend. Comparative J (a commercial SEBS) has a good 1 mm TMA temperature of about 107°C, but it has very poor (high temperature 70°C) compression set of about 100 percent and it also failed to recover (sample broke) during a high temperature (80°C) 300 percent strain recovery. Thus the exemplified polymers have a unique combination of properties unavailable even in some commercially available, high performance thermoplastic elastomers.

[0183] Similarly, Table 4 shows a low (good) storage modulus ratio, $G'(25^\circ\text{C})/G'(100^\circ\text{C})$, for the inventive polymers of 6 or less, whereas a physical blend (Comparative F) has a storage modulus ratio of 9 and a random ethylene/octene copolymer

(Comparative G) of similar density has a storage modulus ratio an order of magnitude greater (89). It is desirable that the storage modulus ratio of a polymer be as close to 1 as possible. Such polymers will be relatively unaffected by temperature, and fabricated articles made from such polymers can be usefully employed over a broad temperature range. This feature of low storage modulus ratio and temperature independence is particularly useful in elastomer applications such as in pressure sensitive adhesive formulations.

[0184] The data in Table 4 also demonstrate that the polymers of the invention possess improved pellet blocking strength. In particular, Example 5 has a pellet blocking strength of 0 MPa, meaning it is free flowing under the conditions tested, compared to Comparatives F and G which show considerable blocking. Blocking strength is important since bulk shipment of polymers having large blocking strengths can result in product clumping or sticking together upon storage or shipping, resulting in poor handling properties.

[0185] High temperature (70°C) compression set for the inventive polymers is generally good, meaning generally less than about 80 percent, preferably less than about 70 percent and especially less than about 60 percent. In contrast, Comparatives F, G, H and J all have a 70°C compression set of 100 percent (the maximum possible value, indicating no recovery). Good high temperature compression set (low numerical values) is especially needed for applications such as gaskets, window profiles, o-rings, and the like.

Table 5 Ambient Temperature Mechanical Properties

Ex.	Flex Modulus (MPa)	Tensile Modulus (MPa)	Tensile Strength (MPa) ¹	Elongation at Break ¹ (%)	Tensile Strength (MPa)	Elongation at Break (%)	Abrasion: Volume Loss (mm ³)	Tensile Notched Tear Strength (mJ)	100 % Strain Recovery 21°C (percent)	300 % Strain Recovery 21°C (percent)	Retractive Stress at 150 % Strain (kPa)	Compression Set 21°C (Percent)	Stress Relaxation at 50 % Strain ²
D*	12	5	-	-	10	1074	-	-	91	83	760	-	-
E*	895	589	-	-	31	1029	-	-	-	-	-	-	-
F*	57	46	-	-	12	824	93	339	78	65	400	42	-
5	30	24	14	951	16	1116	48	-	87	74	790	14	33
6	33	29	-	-	14	938	-	-	-	75	861	13	-
7	44	37	15	846	14	854	39	-	82	73	810	20	-
8	41	35	13	785	14	810	45	461	82	74	760	22	-
9	43	38	-	-	12	823	-	-	-	-	-	25	-
10	23	23	-	-	14	902	-	-	86	75	860	12	-
11	30	26	-	-	16	1090	-	976	89	66	510	14	30
12	20	17	12	961	13	931	-	1247	91	75	700	17	-
13	16	14	-	-	13	814	-	691	91	-	-	21	-
14	212	160	-	-	29	857	-	-	-	-	-	-	-
15	18	14	12	1127	10	1573	-	2074	89	83	770	14	-
16	23	20	-	-	12	968	-	-	88	83	1040	13	-
17	20	18	-	-	13	1252	-	1274	13	83	920	4	-
18	323	239	-	-	30	808	-	-	-	-	-	-	-
19	706	483	-	-	36	871	-	-	-	-	-	-	-
G*	15	15	-	-	17	1000	-	746	86	53	110	27	50
H*	16	15	-	-	15	829	-	569	87	60	380	23	-
I*	210	147	-	-	29	697	-	-	-	-	-	-	-
J*	-	-	-	-	32	609	-	-	93	96	1900	25	-
K*	-	-	-	-	-	-	-	-	-	-	-	30	-

1. Tested at 51 cm/minute

2. measured at 38°C for 12 hours

[0186] Table 5 shows results for mechanical properties for the new polymers as well as for various comparison polymers at ambient temperatures. It may be seen that the inventive polymers have very good abrasion resistance when tested according to ISO 4649, generally showing a volume loss of less than about 90 mm³, preferably less than about 80 mm³, and especially less than about 50 mm³. In this test, higher numbers indicate higher volume loss and consequently lower abrasion resistance.

[0187] Tear strength as measured by tensile notched tear strength of the inventive polymers is generally 1000 mJ or higher, as shown in Table 5. Tear strength for the inventive polymers can be as high as 3000 mJ, or even as high as 5000 mJ. Comparative polymers generally have tear strengths no higher than 750 mJ.

[0188] Table 5 also shows that the polymers of the invention have better retractive stress at 150 percent strain (demonstrated by higher retractive stress values) than some of the comparative samples. Comparative Examples F, G and H have retractive stress value at 150 percent strain of 400 kPa or less, while the inventive polymers have retractive stress values at 150 percent strain of 500 kPa (Ex. 11) to as high as about 1100 kPa (Ex. 17). Polymers having higher than 150 percent retractive stress values would be quite useful for elastic applications, such as elastic fibers and fabrics, especially nonwoven fabrics. Other applications include diaper, hygiene, and medical garment waistband applications, such as tabs and elastic bands.

[0189] Table 5 also shows that stress relaxation (at 50 percent strain) is also improved (less) for the inventive polymers as compared to, for example, Comparative G. Lower stress relaxation means that the polymer retains its force better in applications such as diapers and other garments where retention of elastic properties over long time periods at body temperatures is desired.

Optical Testing

Table 6 Polymer Optical Properties

Ex.	Internal Haze (percent)	Clarity (percent)	45° Gloss (percent)
F*	84	22	49
G*	5	73	56
5	13	72	60
6	33	69	53
7	28	57	59
8	20	65	62
9	61	38	49
10	15	73	67
11	13	69	67
12	8	75	72
13	7	74	69
14	59	15	62
15	11	74	66
16	39	70	65
17	29	73	66
18	61	22	60
19	74	11	52
G*	5	73	56
H*	12	76	59
I*	20	75	59

[0190] The optical properties reported in Table 6 are based on compression molded
5 films substantially lacking in orientation. Optical properties of the polymers may be varied over wide ranges, due to variation in crystallite size, resulting from variation in the quantity of chain shuttling agent employed in the polymerization.

Extractions of Multi-Block Copolymers

[0191] Extraction studies of the polymers of examples 5, 7 and Comparative E are
10 conducted. In the experiments, the polymer sample is weighed into a glass fritted extraction thimble and fitted into a Kumagawa type extractor. The extractor with sample is purged with nitrogen, and a 500mL round bottom flask is charged with 350 mL of diethyl ether. The flask is then fitted to the extractor. The ether is heated while being stirred. Time is noted when the ether begins to condense into the thimble, and the extraction is allowed to
15 proceed under nitrogen for 24 hours. At this time, heating is stopped and the solution is allowed to cool. Any ether remaining in the extractor is returned to the flask. The ether in the flask is evaporated under vacuum at ambient temperature, and the resulting solids are purged dry with nitrogen. Any residue is transferred to a weighed bottle using successive

washes of hexane. The combined hexane washes are then evaporated with another nitrogen purge, and the residue dried under vacuum overnight at 40°C. Any remaining ether in the extractor is purged dry with nitrogen.

[0192] A second clean round bottom flask charged with 350 mL of hexane is then connected to the extractor. The hexane is heated to reflux with stirring and maintained at reflux for 24 hours after hexane is first noticed condensing into the thimble. Heating is then stopped and the flask is allowed to cool. Any hexane remaining in the extractor is transferred back to the flask. The hexane is removed by evaporation under vacuum at ambient temperature, and any residue remaining in the flask is transferred to a weighed bottle using successive hexane washes. The hexane in the flask is evaporated by a nitrogen purge, and the residue is vacuum dried overnight at 40°C.

[0193] The polymer sample remaining in the thimble after the extractions is transferred from the thimble to a weighed bottle and vacuum dried overnight at 40°C. Results are contained in Table 7.

Table 7

Sample	wt. (g)	ether soluble (g)	ether soluble (percent)	C ₈ mole percent ¹	hexane soluble (g)	hexane soluble (percent)	C ₈ mole percent ¹	residue C ₈ mole percent ¹
Comp. F*	1.097	0.063	5.69	12.2	0.245	22.35	13.6	6.5
Ex. 5	1.006	0.041	4.08	-	0.040	3.98	14.2	11.6
Ex. 7	1.092	0.017	1.59	13.3	0.012	1.10	11.7	9.9

¹ Determined by ¹³C NMR

Additional Polymer Examples 19 A-J, Continuous Solution Polymerization, Catalyst A1/B2 + DEZ

For Examples 19A-I

[0194] Continuous solution polymerizations are carried out in a computer controlled well-mixed reactor. Purified mixed alkanes solvent (Isopar™ E available from Exxon Mobil, Inc.), ethylene, 1-octene, and hydrogen (where used) are combined and fed to a 27 gallon reactor. The feeds to the reactor are measured by mass-flow controllers. The temperature of the feed stream is controlled by use of a glycol cooled heat exchanger before entering the reactor. The catalyst component solutions are metered using pumps and mass flow meters. The reactor is run liquid-full at approximately 550 psig pressure. Upon exiting the reactor, water and additive are injected in the polymer solution. The water

hydrolyzes the catalysts, and terminates the polymerization reactions. The post reactor solution is then heated in preparation for a two-stage devolatilization. The solvent and unreacted monomers are removed during the devolatilization process. The polymer melt is pumped to a die for underwater pellet cutting.

5 For Example 19J

[0195] Continuous solution polymerizations are carried out in a computer controlled autoclave reactor equipped with an internal stirrer. Purified mixed alkanes solvent (Isopar™ E available from ExxonMobil Chemical Company), ethylene at 2.70 lbs/hour (1.22 kg/hour), 1-octene, and hydrogen (where used) are supplied to a 3.8 L reactor
10 equipped with a jacket for temperature control and an internal thermocouple. The solvent feed to the reactor is measured by a mass-flow controller. A variable speed diaphragm pump controls the solvent flow rate and pressure to the reactor. At the discharge of the pump, a side stream is taken to provide flush flows for the catalyst and cocatalyst injection lines and the reactor agitator. These flows are measured by Micro-Motion mass flow meters
15 and controlled by control valves or by the manual adjustment of needle valves. The remaining solvent is combined with 1-octene, ethylene, and hydrogen (where used) and fed to the reactor. A mass flow controller is used to deliver hydrogen to the reactor as needed. The temperature of the solvent/monomer solution is controlled by use of a heat exchanger before entering the reactor. This stream enters the bottom of the reactor. The catalyst
20 component solutions are metered using pumps and mass flow meters and are combined with the catalyst flush solvent and introduced into the bottom of the reactor. The reactor is run liquid-full at 500 psig (3.45 MPa) with vigorous stirring. Product is removed through exit lines at the top of the reactor. All exit lines from the reactor are steam traced and insulated. Polymerization is stopped by the addition of a small amount of water into the exit line along
25 with any stabilizers or other additives and passing the mixture through a static mixer. The product stream is then heated by passing through a heat exchanger before devolatilization. The polymer product is recovered by extrusion using a devolatilizing extruder and water cooled pelletizer.

[0196] Process details and results are contained in Table 8. Selected polymer properties
30 are provided in Tables 9A-C.

[0197] In Table 9B, inventive examples 19F and 19G show low immediate set of around 65 – 70 % strain after 500% elongation.

Table 8 Polymerization Conditions

Ex.	C ₂ H ₄ lb/hr	C ₈ H ₁₆ lb/hr	Solv. lb/hr	H ₂ scm ¹	T °C	Cat Al ² Conc. ppm	Cat Al ¹ Flow lb/hr	Cat B ³ Conc. ppm	Cat B ² Flow lb/hr	DEZ Conc wt%	DEZ Flow lb/hr	Cocat 1 Conc. ppm	Cocat 1 Flow lb/hr	Cocat 2 Conc. ppm	Cocat 2 Flow lb/hr	Zn ⁴ in polymer ppm	Poly Rate ⁵ lb/hr	Conv wt%	Polymer wt%	Eff. ⁷
19A	55.29	32.03	323.03	101	120	600	0.25	200	0.42	3.0	0.70	4500	0.65	0.33	525	248	83.94	88.0	17.28	297
19B	53.95	28.96	325.3	577	120	600	0.25	200	0.55	3.0	0.24	4500	0.63	0.11	525	90	80.72	88.1	17.2	295
19C	55.53	30.97	324.37	550	120	600	0.216	200	0.609	3.0	0.69	4500	0.61	0.33	525	246	84.13	88.9	17.16	293
19D	54.83	30.58	326.33	60	120	600	0.22	200	0.63	3.0	1.39	4500	0.66	0.66	525	491	82.56	88.1	17.07	280
19E	54.95	31.73	326.75	251	120	600	0.21	200	0.61	3.0	1.04	4500	0.64	0.49	525	368	84.11	88.4	17.43	288
19F	50.43	34.80	330.33	124	120	600	0.20	200	0.60	3.0	0.74	4500	0.52	0.35	525	257	85.31	87.5	17.09	319
19G	50.25	33.08	325.61	188	120	600	0.19	200	0.59	3.0	0.54	4500	0.51	0.16	525	194	83.72	87.5	17.34	333
19H	50.15	34.87	318.17	58	120	600	0.21	200	0.66	3.0	0.70	4500	0.52	0.70	525	259	83.21	88.0	17.46	312
19I	55.02	34.02	323.59	53	120	600	0.44	200	0.74	3.0	1.72	4500	0.70	1.65	525	600	86.63	88.0	17.6	275
19J	7.46	9.04	50.6	47	120	150	0.22	76.7	0.36	0.5	0.19	-	-	-	-	-	-	-	-	-

standard cm³/min² [N-(2,6-di(1-methylethyl)phenyl)amido](2-isopropylphenyl)(α-naphthalen-2-yl)(6-pyridin-2-yl)methane]hafnium dimethyl³ bis-(1-(2-methylcyclohexyl)ethyl)(2-oxo-3,5-di(t-butyl)phenyl)imino) zirconium dimethyl⁴ ppm in final product calculated by mass balance⁵ polymer production rate⁶ weight percent ethylene conversion in reactor⁷ efficiency, kg polymer/g M where g M = g Hf + g Z

Table 9A Polymer Physical Properties

Ex.	Density (g/cc)	I2	I10	I10/I2	Mw (g/mol)	Mn (g/mol)	Mw/Mn	Heat of Fusion (J/g)	Tm (°C)	Tc (°C)	TCRYSTAF (°C)	Tm- TCRYSTAF (°C)	CRYSTAF Peak Area (wt%)
19A	0.8781	0.9	6.4	6.9	123700	61000	2.0	56	119	97	46	73	40
19B	0.8749	0.9	7.3	7.8	133000	44300	3.0	52	122	100	30	92	76
19C	0.8753	5.6	38.5	6.9	81700	37300	2.2	46	122	100	30	92	8
19D	0.8770	4.7	31.5	6.7	80700	39700	2.0	52	119	97	48	72	5
19E	0.8750	4.9	33.5	6.8	81800	41700	2.0	49	121	97	36	84	12
19F	0.8652	1.1	7.5	6.8	124900	60700	2.1	27	119	88	30	89	89
19G	0.8649	0.9	6.4	7.1	135000	64800	2.1	26	120	92	30	90	90
19H	0.8654	1.0	7.0	7.1	131600	66900	2.0	26	118	88	-	-	-
19I	0.8774	11.2	75.2	6.7	66400	33700	2.0	49	119	99	40	79	13
19J	0.8995	5.6	39.4	7.0	75500	29900	2.5	101	122	106	-	-	-

Table 9B Polymer Physical Properties of Compression Molded Film

Example	Density (g/cm ³)	Melt Index (g/10 min)	Immediate Set after 100% Strain (%)	Immediate Set after 300% Strain (%)	Immediate Set after 500% Strain (%)	Recovery after 100% (%)	Recovery after 300% (%)	Recovery after 500% (%)
19A	0.878	0.9	15	63	131	85	79	74
19B	0.877	0.88	14	49	97	86	84	81
19F	0.865	1	-	-	70	-	87	86
19G	0.865	0.9	-	-	66	-	-	87
19H	0.865	0.92	-	39	-	-	87	-

Table 9C Average Block Index For exemplary polymers¹

Example	Zn/C ₂ ²	Average BI
Polymer F	0	0
Polymer 8	0.56	0.59
Polymer 19a	1.3	0.62
Polymer 5	2.4	0.52
Polymer 19b	0.56	0.54
Polymer 19h	3.15	0.59

1. Additional information regarding the calculation of the block indices for various polymers is disclosed in U.S. Patent Application Serial No. 11/376,835, entitled "Ethylene/ α -Olefin Block Interpolymers", filed on March 15, 2006, in the name of Colin L.P. Shan, Lonnie Hazlett, et. al. and assigned to Dow Global Technologies Inc., the disclose of which is incorporated by reference herein in its entirety.

2. Zn/C₂ * 1000 = (Zn feed flow * Zn concentration / 1000000 / Mw of Zn) / (Total Ethylene feed flow * (1-fractional ethylene conversion rate) / Mw of Ethylene) * 1000. Please note that "Zn" in "Zn/C₂ * 1000" refers to the amount of zinc in diethyl zinc ("DEZ") used in the polymerization process, and "C₂" refers to the amount of ethylene used in the polymerization process.

Examples 20 and 21

[0198] The ethylene/ α -olefin interpolymers of Examples 20 and 21 were made in a substantially similar manner as Examples 19A-I above with the polymerization conditions shown in Table 11 below. The polymers exhibited the properties shown in Table 10. Table 10 also shows any additives to the polymer.

Table 10 – Properties and Additives of Examples 20-21

	Example 20		Example 21	
Density (g/cc)	0.8800		0.8800	
MI	1.3		1.3	
Additives	DI Water	100	DI Water	75
	Irgafos 168	1000	Irgafos 168	1000
	Irganox 1076	250	Irganox 1076	250
	Irganox 1010	200	Irganox 1010	200
	Chimmasorb		Chimmasorb	
	2020	100	2020	80
Hard segment split (wt%)	35%		35%	

[0199] Irganox 1010 is Tetrakis(methylene(3,5-di-*t*-butyl-4-hydroxyhydrocinnamate)methane. Irganox 1076 is Octadecyl-3-(3',5'-di-*t*-butyl-4'-hydroxyphenyl)propionate. Irgafos 168 is Tris(2,4-di-*t*-butylphenyl)phosphite. Chimmasorb 2020 is 1,6-Hexanediamine, N,N'-bis(2,2,6,6-tetramethyl-4-piperidinyl)-polymer with 2,3,6-trichloro-1,3,5-triazine, reaction products with, N-butyl-1-butanamine and N-butyl-2,2,6,6-tetramethyl-4-piperidinamine.

Table 11 – Polymerization Conditions for Examples 20-21

Ex.	C ₂ H ₄ lb/hr	C ₈ H ₁₆ lb/hr	Solv. lb/hr	H ₂ scm ¹	T °C	Cat Al ² Conc. ppm	Cat Al ¹ Flow lb/hr	Cat B ³ Conc. ppm	Cat B ² Flow lb/hr	DEZ Conc. wt%	DEZ Flow lb/hr	Cocat 1 Conc. ppm	Cocat 1 Flow lb/hr	Cocat 2 Conc. ppm	Cocat 2 Flow lb/hr	Zn ⁴ in polymer ppm	Poly Rate ⁵ lb/hr	Conv ⁶ wt%	Polymer wt%	Eff. ⁷
20	130.7	196.17	712.68	1767	120	499.98	1.06	298.89	0.57	4.809423	0.48	5634.36	1.24	402.45	0.478	131	177	89.25	16.94	252.04
21	132.13	199.22	708.23	1572	120	462.4	1.71	298.89	0.6	4.999847	0.47	5706.4	1.61	289.14	1.36	129	183	89.23	17.52	188.11

* Comparative, not an example of the invention

1 standard cm³/min2 [N-(2,6-di(1-methyl(ethyl)phenyl)amido)(2-isopropylphenyl)(α -naphthalen-2-yl)(6-pyridin-2-yl)methane)]hafnium dimethyl

3 bis-(1-(2-methylcyclohexyl)ethyl)(2-oxo-1,3,5-di(t-butyl)phenyl)imino) zirconium dibenzyl

4 ppm Zn in final product calculated by mass balance

5 polymer production rate

6 weight percent ethylene conversion in reactor

7 efficiency, kg polymer/g M where g M = g Hf + g Z.

Fibers Suitable for Fabrics and Textile Articles

[0200] The present invention relates to fibers suitable for fabrics such as textile articles wherein said fiber comprises at least about 1% polyolefin according to ASTM D629-99 and wherein the filament elongation to break of said fiber is greater than about 200%, preferably greater than about 210%, preferably greater than about 220%, preferably greater than about 230%, preferably greater than about 240%, preferably greater than about 250%, preferably greater than about 260%, preferably greater than about 270%, preferably greater than about 280%, and may be as high as 600% according to ASTM D2653-01 (elongation at first filament break test). The fibers of the present invention are further characterized by having (1) ratio of load at 200% elongation / load at 100% elongation of greater than or equal to about 1.5, preferably greater than or equal to about 1.6, preferably greater than or equal to about 1.7, preferably greater than or equal to about 1.8, preferably greater than or equal to about 1.9, preferably greater than or equal to about 2.0, preferably greater than or equal to about 2.1, preferably greater than or equal to about 2.2, preferably greater than or equal to about 2.3, preferably greater than or equal to about 2.4, and may be as high as 4 according to ASTM D2731-01 (under force at specified elongation in the finished fiber form); or (2) an average coefficient of friction of less than or equal to about 0.8, preferably less than or equal to about 0.78, preferably less than or equal to about 0.76, preferably less than or equal to about 0.74, preferably less than or equal to about 0.73, preferably less than or equal to about 0.72, preferably less than or equal to about 0.71, preferably less than or equal to about 0.7; preferably less than or equal to about 0.6; preferably less than or equal to about 0.5; and may be as low as 0.3 or (3) both (1) and (2).

[0201] The polyolefin may be selected from any suitable polyolefin or blend of polyolefins. Such polymers include, for example, random ethylene homopolymers and copolymers, ethylene block homopolymers and copolymers, polypropylene homopolymers and copolymers, ethylene/vinyl alcohol copolymers, and mixtures thereof. A particularly preferable polyolefin is an ethylene/ α -olefin interpolymers, wherein the ethylene/ α -olefin interpolymers has one or more of the following characteristics:

(1) an average block index greater than zero and up to about 1.0 and a molecular weight distribution, M_w/M_n , greater than about 1.3; or

(2) at least one molecular fraction which elutes between 40°C and 130°C when fractionated using TREF, characterized in that the fraction has a block index of at least 0.5 and up to about 1; or

(3) an Mw/Mn from about 1.7 to about 3.5, at least one melting point, T_m , in degrees Celsius, and a density, d , in grams/cubic centimeter, wherein the numerical values of T_m and d correspond to the relationship:

$$T_m > -2002.9 + 4538.5(d) - 2422.2(d)^2; \text{ or}$$

(4) an Mw/Mn from about 1.7 to about 3.5, and is characterized by a heat of fusion, ΔH in J/g, and a delta quantity, ΔT , in degrees Celsius defined as the temperature difference between the tallest DSC peak and the tallest CRYSTAF peak, wherein the numerical values of ΔT and ΔH have the following relationships:

$$\Delta T > -0.1299(\Delta H) + 62.81 \text{ for } \Delta H \text{ greater than zero and up to } 130 \text{ J/g,}$$

$$\Delta T \geq 48^\circ\text{C for } \Delta H \text{ greater than } 130 \text{ J/g,}$$

wherein the CRYSTAF peak is determined using at least 5 percent of the cumulative polymer, and if less than 5 percent of the polymer has an identifiable CRYSTAF peak, then the CRYSTAF temperature is 30°C; or

(5) an elastic recovery, Re , in percent at 300 percent strain and 1 cycle measured with a compression-molded film of the ethylene/ α -olefin interpolymer, and has a density, d , in grams/cubic centimeter, wherein the numerical values of Re and d satisfy the following relationship when ethylene/ α -olefin interpolymer is substantially free of a cross-linked phase:

$$Re > 1481 - 1629(d); \text{ or}$$

(6) a molecular fraction which elutes between 40°C and 130°C when fractionated using TREF, characterized in that the fraction has a molar comonomer content of at least 5 percent higher than that of a comparable random ethylene interpolymer fraction eluting between the same temperatures, wherein said comparable random ethylene interpolymer has the same comonomer(s) and has a melt

index, density, and molar comonomer content (based on the whole polymer) within 10 percent of that of the ethylene/ α -olefin interpolpolymer; or

(7) a storage modulus at 25 °C, $G'(25\text{ °C})$, and a storage modulus at 100 °C, $G'(100\text{ °C})$, wherein the ratio of $G'(25\text{ °C})$ to $G'(100\text{ °C})$ is in the range of about 1:1 to about 9:1.

[0202] The fibers may be made into any desirable size and cross-sectional shape depending upon the desired application. For many applications approximately round cross-section is desirable due to its reduced friction. However, other shapes such as a trilobal shape, or a flat (i.e., “ribbon” like) shape can also be employed. Denier is a textile term which is defined as the grams of the fiber per 9000 meters of that fiber's length. Preferred sizes include a denier from at least about 1, preferably at least about 20, preferably at least about 50, to at most about 180, preferably at most about 150, preferably at most about 100 denier, preferably at most about 80 denier.

[0203] The fiber is usually elastic and usually cross-linked. The fiber comprises the reaction product of ethylene/ α -olefin interpolpolymer and any suitable cross-linking agent, i.e., a cross-linked ethylene/ α -olefin interpolpolymer. As used herein, “cross-linking agent” is any means which cross-links one or more, preferably a majority, of the fibers. Thus, cross-linking agents may be chemical compounds but are not necessarily so. Cross-linking agents as used herein also include electron-beam irradiation, beta irradiation, gamma irradiation, corona irradiation, silanes, peroxides, allyl compounds and UV radiation with or without crosslinking catalyst. U.S. Patents No. 6,803,014 and 6,667,351 disclose electron-beam irradiation methods that can be used in embodiments of the invention. In some embodiments, the percent of cross-linked polymer is at least 10 percent, preferably at least about 20, more preferably at least about 25 weight percent to about at most 75, preferably at most about 50 percent, as measured by the weight percent of gels formed.

[0204] Depending upon the application the fiber may take any suitable form including a staple fiber or binder fiber. Typical examples may include a homofil fiber, a bicomponent fiber, a meltblown fiber, a meltspun fiber, or a spunbond fiber. In the case of a bicomponent fiber it may have a sheath-core structure; a sea-island structure; a side-by-side structure; a matrix-fibril structure; or a segmented pie structure. Advantageously, conventional fiber forming processes may be employed to

make the aforementioned fibers. Such processes include those described in, for example, U.S. Patents No. 4,340,563; 4,663,220; 4,668,566; 4,322,027; and 4,413,110).

[0205] The fibers of the present invention facilitate processing in a number of respects. First, the inventive fibers unwind better from a spool than conventional fibers. Ordinary fibers when in round cross section often fail to provide satisfactory unwinding performance due to their base polymer excessive stress relaxation. This stress relaxation is proportional to the age of the spool and causes filaments located at the very surface of the spool to lose grip on the surface, becoming loose filament strands. Later, when such a spool containing conventional fibers is placed over the rolls of positive feeders, i.e. Memminger-IRO, and starts to rotate to industrial speeds, i.e. 100 to 300 rotations/minute, the loose fibers are thrown to the sides of the spool surface and ultimately fall off the edge of the spool. This failure is known as derails which denotes the tendency of conventional fibers to slip off the shoulder or edge of the package which disrupts the unwinding process and ultimately causes machine stops. The inventive fibers exhibit derailing to a much less significant degree which allows greater throughput.

[0206] Another advantage of the inventive fibers is that defects such as fabric faults and elastic filament or fiber breakage are reduced. That is, use of the inventive fibers may reduce buildup of fiber fragments on a needle bed – a problem that often occurs in circular knit machines when polymer residue adheres to the needle surface. Thus, the inventive fibers may reduce the corresponding fabric breaks caused by the residue when the fibers are being made into, e.g. fabrics on a circular knitting machine.

[0207] Another advantage is that the inventive fibers may be knitted in circular machines where the elastic guides that drive the filament all the way from spool to the needles are stationary such as ceramic and metallic eyelets. In contrast, conventional elastic olefin fibers required that these guides were made of rotating elements such as pulleys as to minimize friction as machine parts, such as eyelets, are heated up so that machine stops or filament breaks could be avoided during the circular knitting process. That is, the friction against the guiding elements of the machine is reduced by using the inventive fibers. Further information concerning circular knitting is found in, for example, Bamberg Meisenbach, *“Circular Knitting: Technology*

Process, Structures, Yarns, Quality ", 1995, incorporated herein by reference in its entirety.

[0208] The fibers of the present invention may be made into fabrics, nonwovens, yarns, or carded webs. The yarn can be covered or not covered. When covered, it may be covered by cotton yarns or nylon yarns. The inventive fibers are particularly useful for fabrics such as circular knit fabrics and warp knitted fabrics due to the aforementioned advantages.

Additives

[0209] Antioxidants, e.g., IRGAFOS® 168, IRGANOX® 1010, IRGANOX® 3790, and CHIMASSORB® 944 made by Ciba Geigy Corp., may be added to the ethylene polymer to protect against undo degradation during shaping or fabrication operation and/or to better control the extent of grafting or crosslinking (i.e., inhibit excessive gelation). In-process additives, e.g. calcium stearate, water, fluoropolymers, etc., may also be used for purposes such as for the deactivation of residual catalyst and/or improved processability. TINUVIN® 770 (from Ciba-Geigy) can be used as a light stabilizer.

[0210] The copolymer can be filled or unfilled. If filled, then the amount of filler present should not exceed an amount that would adversely affect either heat-resistance or elasticity at an elevated temperature. If present, typically the amount of filler is between 0.01 and 80 wt % based on the total weight of the copolymer (or if a blend of a copolymer and one or more other polymers, then the total weight of the blend). Representative fillers include kaolin clay, magnesium hydroxide, zinc oxide, silica and calcium carbonate. In a preferred embodiment, in which a filler is present, the filler is coated with a material that will prevent or retard any tendency that the filler might otherwise have to interfere with the crosslinking reactions. Stearic acid is illustrative of such a filler coating.

[0211] To reduce the friction coefficient of the fibers, various spin finish formulations can be used, such as metallic soaps dispersed in textile oils (see for example U.S. Patent No. 3,039,895 or U.S. Patent No. 6,652,599), surfactants in a base oil (see for example US publication 2003/0024052) and polyalkylsiloxanes (see for example U.S. Patent No. 3,296,063 or U.S. Patent No. 4,999,120). U.S. Patent Application No. 10/933,721 (published as US20050142360) discloses spin finish compositions that can also be used.

Knitted Fabrics

[0212] The present invention is directed to improved knit textile articles comprising a polyolefin polymer. For purposes of the present invention, "textile articles" includes fabric as well as articles, i.e., garments, made from the fabric including, for example, clothes, bed sheets and other linens. By knitting it is meant intertwining yarn or thread in a series of connected loops either by hand, with knitting needles, or on a machine. The present invention may be applicable to any type of knitting including, for example, warp or weft knitting, flat knitting, and circular knitting. However, the invention is particularly advantageous when employed in circular knitting, i.e., knitting in the round, in which a circular needle is employed.

[0213] The knit fabrics of the present invention comprise:

(A) an ethylene/ α -olefin interpolymers, wherein the ethylene/ α -olefin interpolymers has one or more of the following characteristics:

(1) an average block index greater than zero and up to about 1.0 and a molecular weight distribution, Mw/Mn, greater than about 1.3; or

(2) at least one molecular fraction which elutes between 40°C and 130°C when fractionated using TREF, characterized in that the fraction has a block index of at least 0.5 and up to about 1; or

(3) an Mw/Mn from about 1.7 to about 3.5, at least one melting point, T_m , in degrees Celsius, and a density, d , in grams/cubic centimeter, wherein the numerical values of T_m and d correspond to the relationship:

$$T_m > -2002.9 + 4538.5(d) - 2422.2(d)^2; \text{ or}$$

(4) an Mw/Mn from about 1.7 to about 3.5, and is characterized by a heat of fusion, ΔH in J/g, and a delta quantity, ΔT , in degrees Celsius defined as the temperature difference between the tallest DSC peak and the tallest CRYSTAF peak, wherein the numerical values of ΔT and ΔH have the following relationships:

$$\Delta T > -0.1299(\Delta H) + 62.81 \text{ for } \Delta H \text{ greater than zero and up to } 130 \text{ J/g,}$$

$$\Delta T \geq 48^\circ\text{C for } \Delta H \text{ greater than } 130 \text{ J/g,}$$

wherein the CRYSTAF peak is determined using at least 5 percent of the cumulative polymer, and if less than 5 percent of the polymer has an identifiable CRYSTAF peak, then the CRYSTAF temperature is 30°C; or

(5) an elastic recovery, Re , in percent at 300 percent strain and 1 cycle measured with a compression-molded film of the ethylene/ α -olefin interpolymer, and has a density, d , in grams/cubic centimeter, wherein the numerical values of Re and d satisfy the following relationship when ethylene/ α -olefin interpolymer is substantially free of a cross-linked phase:

$$Re > 1481 - 1629(d); \text{ or}$$

(6) a molecular fraction which elutes between 40°C and 130°C when fractionated using TREF, characterized in that the fraction has a molar comonomer content of at least 5 percent higher than that of a comparable random ethylene interpolymer fraction eluting between the same temperatures, wherein said comparable random ethylene interpolymer has the same comonomer(s) and has a melt index, density, and molar comonomer content (based on the whole polymer) within 10 percent of that of the ethylene/ α -olefin interpolymer; or

(7) a storage modulus at 25 °C, $G'(25\text{ °C})$, and a storage modulus at 100 °C, $G'(100\text{ °C})$, wherein the ratio of $G'(25\text{ °C})$ to $G'(100\text{ °C})$ is in the range of about 1:1 to about 9:1; and

(B) at least one other material.

[0214] The amount of ethylene/ α -olefin interpolymer in the knit fabric varies depending upon the application and desired properties. The fabrics typically comprises at least about 1, preferably at least about 2, preferably at least about 5, preferably at least about 7 weight percent ethylene/ α -olefin interpolymer. The fabrics typically comprise less than about 50, preferably less than about 40, preferably less than about 30, preferably less than about 20, more preferably less than about 10 weight percent ethylene/ α -olefin interpolymer. The ethylene/ α -olefin interpolymer may be in the form of a fiber and may be blended with another suitable polymer, e.g. polyolefins such as random ethylene copolymers, HDPE, LLDPE, LDPE, ULDPE,

polypropylene homopolymers, copolymers, plastomers and elastomers, lastol, a polyamide, etc.

[0215] The ethylene/ α -olefin interpolmer of the fabric may have any density but is usually at least about 0.85 and preferably at least about 0.865 g/cm³ (ASTM D 792). Correspondingly, the density is usually less than about 0.93, preferably less than about 0.92 g/cm³ (ASTM D 792). The ethylene/ α -olefin interpolmer of the fabric is characterized by an uncrosslinked melt index of from about 0.1 to about 10 g/10 minutes. If crosslinking is desired, then the percent of cross-linked polymer is often at least 10 percent, preferably at least about 20, more preferably at least about 25 weight percent to about at most 90, preferably at most about 75, as measured by the weight percent of gels formed.

[0216] The knit fabric typically comprises at least one other material. The other material may be any suitable material, including, but not limited to, cellulose, cotton, flax, ramie, rayon, viscose, hemp, wool, silk, linen, bamboo, tencel, viscose, mohair, polyester, polyamide, polypropylene, and mixtures thereof. Often the other material comprises the majority of the fabric. In such case it is preferred that the other material comprise from at least about 50, preferably at least about 60, preferably at least about 70, preferably at least about 80, sometimes as much as 90-95, percent by weight of the fabric.

[0217] The ethylene/ α -olefin interpolmer, the other material or both may be in the form of a fiber. Preferred sizes include a denier from at least about 1, preferably at least about 20, preferably at least about 50, to at most about 180, preferably at most about 150, preferably at most about 100, preferably at most about 80 denier.

[0218] Particularly preferred circular knit fabrics comprise ethylene/ α -olefin interpolmer in the form of a fiber in an amount of from about 5 to about 20 percent (by weight) of the fabric. Particularly preferred warp knit fabrics comprise ethylene/ α -olefin interpolmer in the form of a fiber in an amount of from about 10 to about 30 percent (by weight) of the fabric in the form of a fiber. Often such warp knit and circular knit fabrics also comprise polyester.

[0219] The knit fabric typically has less than about 5, preferably less than 4, preferably less than 3, preferably less than 2, preferably less than 1, preferably less than 0.5, preferably less than 0.25, percent shrinkage after wash according to AATCC 135 in either the horizontal direction, the vertical direction, or both. More

specifically, the fabric (after heat setting) often has a dimensional stability of from about -5% to about +5%, preferably from about -3% to about +3%, preferably -2% to about +2%, more preferably -1% to about +1% in the lengthwise direction, the widthwise direction, or both according to AATCC135 IVAi.

[0220] The knit fabric can be made to stretch in two dimensions if desired by controlling the type and amount of ethylene/ α -olefin interpolymer and other materials. Similarly, the fabric can be made such that the growth in the lengthwise and widthwise directions is less than about 5%, preferably less than about 4, preferably less than about 3, preferably less than about 2, preferably less than about 1, to as little as 0.5 percent according to ASTM D 2594. Using the same test (ASTM D 2594) the lengthwise growth at 60 seconds can be less than about 15, preferably less than about 12, preferably less than about 10, preferably less than about 8%. Correspondingly, using the same test (ASTM D 2594) the widthwise growth at 60 seconds can be less than about 20, preferably less than about 18, preferably less than about 16, preferably less than about 13%. In regard to the 60 minute test of ASTM D 2594, the widthwise growth can be less than about 10, preferably less than about 9, preferably less than about 8, preferably less than about 6% while the lengthwise growth at 60 minutes can be less than about 8, preferably less than about 7, preferably less than about 6, preferably less than about 5%. The lower growth described above allows the fabrics of the invention to be heat set at temperatures from less than about 180, preferably less than about 170, preferably less than about 160, preferably less than about 150°C while still controlling size.

[0221] Advantageously, the knit fabrics of the present invention can be made without breaks and using a knitting machine comprising an eyelet feeder system, a pulley system, or a combination thereof. Thus, the circular knitted stretch fabrics having improved dimensional stability (lengthwise and widthwise), low growth and low shrinkage, the ability to be heat set at low temperatures while controlling size, low moisture regain can be made without significant breaks, with high throughput, and without derailing in a wide variety of circular knitting machines.

Determining “average coefficient of friction” as used herein

[0222] The “average coefficient of friction” as used herein is determined at higher temperature as opposed to room temperature. Specifically, “average coefficient of

friction” is determined using the following test method. The test makes use of elastic drawing equipment - namely Electronic Constant Tension Transporter, or ECTT (by Lawson Hemphill – Figure 8), details attached – where the elastic feeding and take-up speeds are controlled to accommodate any desired draft ratio (take-up speed/feeding speed) and a Tensiometer is placed in between these two rolls.

[0223] On the way from positive feeder to take-up roll there are two threading possibilities: (Threading A – Figure 9) the elastic runs from feeder to take-up roll without any constrain but frictionless pulley guides; (Threading B – Figure 10) the elastic, after passing through the tensionmeter is forced to slide through a metallic polished heated pin at a 45 degrees wrapping angle before reaching the take-up roll. This pin is constantly heated to $(90 \pm 5) ^\circ\text{C}$.

[0224] The method applied stipulates the following:

Threading A

[0225] Feeding Speed: 50 meters/minute; Take-up Speed: 150 meters/minute; Draft Ratio: 3.0X; Length of Drafted Filament: 300 meters (or 100m undrafted); Tensionmeter Reading Frequency: 1 reading/5 meters of filament; Total Number of Tension Readings:60; 1 Reading Average = Average of each 2 consecutive readings; Total Number of Tensiometer Averages: 30

[0226] The test is performed in spools containing 15% of its commercial net weight. For the test to start-up, 85% of the original (commercial) net weight of filaments on the spool has to be removed, thus, for instance, if the spool is to be commercialized with a net weight of filaments equal to 400 grams, filament layers are to be removed from the spool until 60 grams of net weight are left so that the test can be performed. The elimination of the 85% content should take place not earlier than 10min from the test start-up. And this 85% content should be removed at one single step.

[0227] Maximum spool age from its date of spinning is 45 days and without any exposure of the spool to temperatures higher than 30°C during the course of these 45 days.

Threading B

[0228] Same as per “Threading A”, except the filament slides through pin after its tension is read and before it is taken-up. “Threading B” measurements are made immediately after the measurements made by “Threading A” “Threading B” measurements are taken from the same spool “Threading A” ones were and the 100 meters filament length to be used are subsequent to the 100 meters filament length utilized by “Threading A”; +/- 5 meters of waste.

[0229] Therefore, the 30 tension averages for “Threading A” reveals the filament dynamic stress at 3.0X draft; and the relationship: (average of the 30 averages by “Threading A” / average of the 30 averages by “Threading B”); is hereafter considered for the calculation of the average coefficient of friction of a given filament. Each individual average among the 30 ones by “Threading A” is divided by each individual average among the 30 ones by “Threading B” to reveal the mean variance of the coefficient of friction of a given fiber. The order by which each of the 30 values of “Threading A” is divided by each of the 30 values of “Threading B” obeys the order by which they are generated by the tensionmeter; thus, the first value measured by “Threading A” is divided by the first value measured by “Threading B”; the second of “Threading A” by the second of “Threading B”, ..., the thirtieth of “Threading A” by the thirtieth of “Threading B”.

[0230] As a result, 30 values of “Threading A” and 30 values of “Threading B” will generate 30 values of coefficient of friction by applying the following Capstan equation (for a 45 degrees wrapping angle): $\ln(\text{“Threading A Tension Reading”}/\text{“Threading B Tension Reading”})/0.79$; where “ln” stands for natural logarithm.

EXAMPLES

Example 22 – Average Coefficient of Friction for fibers of elastic ethylene/ α -olefin interpolymer vs. random ethylene copolymer

[0231] The elastic ethylene/ α -olefin interpolymer of Example 21 was used to make monofilament fibers of 70 denier having an approximately round cross-section. Before the fiber was made the following additives were added to the polymer: 7000 ppm PDMSO(polydimethyl siloxane), 3000 ppm CYANOX 1790 (1,3,5-tris-(4-t-butyl-3-hydroxy-2,6-dimethylbenzyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione, and

3000 ppm CHIMASORB 944 Poly-[[6-(1,1,3,3-tetramethylbutyl)amino]-s-triazine-2,4-diyl][2,2,6,6-tetramethyl-4-piperidyl]imino]hexamethylene[(2,2,6,6-tetramethyl-4-piperidyl)imino]] and 0.5% by weight Talc. The fibers were produced using a die profile with circular 0.8 mm diameter, a spin temperature of 295°C, a winder speed of 900m/minute, a spin finish of 1%, a cold draw of 6%, and a spool weight of 300g. The fibers were then crosslinked using 176.4 kGy irradiation as the crosslinking agent. These fibers are referred to as “low friction fiber elastic olefin fiber” in the Table below.

[0232] A random copolymer having the generic name AFFINITY™ KC8852G (available from The Dow Chemical Company) was used to make monofilament fibers of 70 denier having an approximately rectangular cross-section. AFFINITY™ KC8852G is characterized by having a melt index of 3 g/10min., a density of 0.875 g/cm³ and similar additives as Example 21. Before the fiber was made the following additives were added to the polymer: 7000 ppm PDMSO(polydimethyl siloxane), 3000 ppm CYANOX 1790 (1,3,5-tris-(4-t-butyl-3-hydroxy-2,6-dimethylbenzyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione, and 3000 ppm CHIMASORB 944 Poly-[[6-(1,1,3,3-tetramethylbutyl)amino]-s-triazine-2,4-diyl][2,2,6,6-tetramethyl-4-piperidyl]imino]hexamethylene[(2,2,6,6-tetramethyl-4-piperidyl)imino]], 0.5% by weight Talc, and 0.2% by weight TiO₂. The fibers were produced using a die profile with a rectangular 3:1, a spin temperature of 295°C, a winder speed of 500m/minute, a spin finish of 1%, a cold draw of 18%, and a spool weight of 300g. The fibers were then crosslinked using 176.4 kGy irradiation as the crosslinking agent. These fibers are referred to as “ordinary olefin elastic fiber” in the Table below.

[0233] The “low friction fiber elastic olefin fibers” and the “ordinary olefin elastic fibers” were tested for “average coefficient of friction” using the test described above. The data is shown below.

Reading Sequence	Threading A Tension Readings, cN Ordinary Olefin Elastic Fiber			Threading B Tension Readings, cN Ordinary Olefin Elastic Fiber			Cof Ordinary Olefin Elastic Fiber		
	Spool 1	Spool 2	Spool 3	Spool 1	Spool 2	Spool 3	Spool 1	Spool 2	Spool 3
1	9.12	8.83	8.98	4.26	4.51	4.69	0.93	0.85	0.85
2	8.97	8.86	9.15	4.14	4.38	4.46	0.98	0.89	0.91
3	8.80	8.95	9.10	4.12	4.39	4.41	0.96	0.90	0.92
4	9.07	8.98	8.59	4.34	4.31	4.60	0.93	0.83	0.79
5	8.83	8.93	9.25	4.17	4.21	4.61	0.85	0.85	0.88
6	8.37	8.90	8.91	4.56	4.51	4.45	0.77	0.86	0.91
7	8.91	8.90	8.87	4.34	4.51	4.51	0.91	0.86	0.86
8	8.98	8.85	9.00	4.34	4.58	4.16	0.92	0.83	0.98
9	8.25	8.88	8.66	4.60	4.49	4.25	0.74	0.86	0.90
10	9.42	8.98	9.05	4.56	4.36	4.73	0.92	0.91	0.82
11	8.26	8.90	8.71	3.90	4.21	4.49	0.95	0.95	0.84
12	9.14	9.02	9.10	4.41	4.29	4.26	0.92	0.94	0.96
13	8.55	8.97	8.93	4.19	4.39	4.88	0.90	0.90	0.76
14	8.57	9.03	8.90	4.29	4.34	4.57	0.88	0.93	0.84
15	9.19	8.90	8.90	4.34	4.32	4.38	0.95	0.91	0.90
16	8.35	8.72	8.88	4.54	4.48	4.42	0.77	0.84	0.88
17	9.12	8.93	8.90	3.88	4.46	4.54	1.08	0.88	0.85
18	8.72	8.94	8.90	4.48	4.73	4.24	0.84	0.81	0.94
19	9.08	8.96	8.93	4.09	4.60	4.61	1.01	0.84	0.84
20	8.34	9.00	8.81	4.39	4.63	4.49	0.81	0.84	0.85
21	8.84	8.87	9.08	4.75	4.46	4.49	0.79	0.87	0.89
22	9.14	8.86	8.78	4.12	4.19	4.38	1.01	0.95	0.88
23	8.97	8.77	9.03	4.34	4.31	4.51	0.92	0.90	0.88
24	8.90	8.81	8.68	4.15	4.46	4.57	0.97	0.86	0.81
25	9.02	8.84	8.91	4.41	4.56	4.44	0.91	0.84	0.88
26	8.66	8.88	8.93	4.71	4.70	4.37	0.77	0.81	0.90
27	8.50	9.00	8.76	4.17	4.49	4.39	0.90	0.88	0.87
28	9.27	8.91	9.05	4.43	4.51	4.63	0.93	0.86	0.85
29	8.78	9.04	8.90	4.15	4.48	4.48	0.85	0.89	0.87
30	8.90	9.03	8.83	3.95	4.51	4.44	1.03	0.88	0.87
							Average Cof		
							0.888		
							STD ERROR		
							0.006		
							Average -2sig		
							0.875		
							Average +2sig		
							0.901		

Reading Sequence	Threading A Tension Readings, cN			Threading B Tension Readings, cN			CoF		
	Low Friction Fiber Elastic Olefin Fiber			Low Friction Fiber Elastic Olefin Fiber			Low Friction Fiber Elastic Olefin Fiber		
	Speed 1	Speed 2	Speed 3	Speed 1	Speed 2	Speed 3	Speed 1	Speed 2	Speed 3
1	7.69	7.81	8.05	4.19	4.17	4.41	0.77	0.79	0.76
2	7.84	7.93	7.78	4.32	4.46	4.94	0.75	0.73	0.57
3	7.72	8	8.02	4.02	4.22	4.68	0.83	0.81	0.68
4	7.62	8.05	7.73	4.12	4.29	4.02	0.78	0.80	0.83
5	7.27	7.94	7.37	4.17	4.36	3.77	0.70	0.76	0.85
6	7.75	7.75	7.90	4.39	4.48	4.00	0.72	0.69	0.86
7	7.82	8.11	7.49	4.29	4.09	4.29	0.76	0.87	0.71
8	7.50	8.05	7.73	4.19	4.34	4.43	0.74	0.78	0.70
9	7.38	7.86	7.91	4.22	4.51	4.41	0.71	0.70	0.74
10	7.67	7.81	7.97	4.56	4.46	4.53	0.66	0.71	0.72
11	7.50	7.99	7.88	4.46	4.17	4.43	0.66	0.82	0.73
12	7.77	7.93	7.85	4.61	4.17	4.95	0.66	0.81	0.56
13	7.84	8	7.83	4.61	4.29	4.95	0.67	0.79	0.58
14	7.99	7.58	7.76	4.41	4.41	4.77	0.75	0.69	0.62
15	7.62	7.98	7.90	3.80	4.14	3.88	0.88	0.83	0.90
16	7.56	7.56	7.95	3.78	4.39	3.61	0.88	0.69	1.00
17	7.38	7.67	7.47	3.84	4.58	3.83	0.83	0.65	0.85
18	7.81	7.68	7.61	4.05	4.31	4.09	0.83	0.73	0.79
19	7.56	7.75	7.98	4.19	4.14	4.02	0.75	0.79	0.87
20	7.80	7.75	8.05	4.34	4.26	4.29	0.74	0.76	0.80
21	7.62	7.93	7.93	4.48	4.70	4.92	0.67	0.66	0.60
22	7.59	7.93	7.86	4.80	4.43	4.85	0.56	0.74	0.61
23	7.50	8.05	7.85	4.51	4.36	4.65	0.64	0.78	0.66
24	7.81	7.91	7.76	4.73	4.75	4.70	0.63	0.63	0.63
25	7.78	7.99	8.05	4.90	4.58	4.63	0.58	0.70	0.70
26	7.62	7.79	7.83	4.14	4.24	4.29	0.77	0.77	0.76
27	7.68	7.67	7.95	3.73	4.56	4.09	0.91	0.66	0.84
28	7.62	7.89	7.73	3.85	4.68	4.29	0.86	0.66	0.75
29	7.80	7.92	7.83	4.21	4.53	4.36	0.73	0.71	0.74
30	7.62	7.74	7.86	4.36	4.39	4.14	0.71	0.72	0.81
							Average CoF		
							0.740		
							STD ERROR		
							0.009		
							Average +2sig		
							0.758		

Example 23 – Fabrics of fibers of elastic ethylene/ α -olefin interpolymers vs. random ethylene copolymer vs. Spandex™

[0234] Three circular knitted fabrics were produced and were then finished in a conventional manner. The first fabric, Fabric A, comprised fibers referred to as “low friction fiber elastic olefin fiber” in Example 22 above. The second fabric, Fabric B, comprised fibers referred to as “ordinary olefin elastic fiber” in Example 22 above. The third fabric comprised fibers of Spandex™. A summary of the fabric content, knitting conditions, finishing steps, and finished fabric properties is as follows:

[0235] Inventive Fabric A content:

elastic ethylene/ α -olefin interpolymers
70den, Block Copolymer Ethylene
Round profile, monofilament
176.4 kGy cross-linking dose
Load at 200%/Load at 100% > 1.5
140den Polyamide 6.6 textured (2 cables of 70den/68filaments) supplied by DEFIBER, S.A., Spain

[0236] Fabric B content:

random ethylene copolymer
70den supplied by TDCC, Random Copolymer Ethylene
Rectangular cross-section of 3:1 profile, monofilament
176.4 kGy cross-linking dose
Load at 200%/Load at 100% < 1.5
140den Polyamide 6.6 textured (2 cables of 70den/68filaments) supplied by DEFIBER, S.A., Spain

[0237] Fabric C content:

Spandex
40den Creora H250
Multifilament
140den Polyamide 6.6 textured (2 cables of 70den/68filaments) supplied by DEFIBER, S.A., Spain

[0238] Knitting Conditions:

Machine 28G, Mayer Relanit, 30” diameter, 20RPM, eyelet elastic guides
Single Jersey construction
Polyamide Stitch Length = 3.0mm/needle - a.k.a. feeding rate =
(polyamide speed/machine RPM)/machine number of needles.
Elastic Draft (as measured by the relationship polyamide speed/elastic feeding speed): 3.0X
Number of machine revolutions: 4000/fabric type

[0239] Therefore, according to knitting conditions above all fabrics made of elastic olefin had as elastic filament content 14.3% and 85.7% of polyamide 6.6 in mass. The one made with Spandex had this elastic content at 8.7% in mass.

[0240] Finishing Steps:

Continuous Scouring: scouring bath at 80°C max
Pre Heat setting of Polyamide
Stenter frame speed: 16m/min
Overfeeding: 15%
Set Width: 156cm
Max Stenter Frame Set Temperature: 180°C
Residence Time Inside Heating Chambers: 60sec

Dyeing

Machine: Softflow Jet
Dyestuff Type: Disperse
Color: Black
Drying
Stenter frame speed: 16m/min
Overfeeding: 15%
Set Width: 156cm
Max Stenter Frame Set Temperature: 160°C
Residence Time Inside Heating Chambers: 60sec

[0241] Finished Fabric Properties:

Fabric A
Width 147cm
Density 237g/m²
Elongation at 2nd loading cycle*: 125%**

Fabric B
Width 152cm
Density 208g/m²
Elongation at 2nd loading cycle*: 130%**

Fabric C
Width 147 cm
Weight 235g/m²
Elongation at 2nd loading cycle*: 172%**

* method for specifying fabric elongation: M&S15A

** resultant elongation values = square root [(width elongation²)+(length elongation²)]

Counting of Breaks

[0242] These finished fabrics were taken for inspection aimed at spotting elastic breaks. One hundred linear meters of each of the three finished fabrics had a square

cut at every five linear meter randomly across the width. Therefore, 20 squares of fabric / 100m linear fabric length were made available for counting elastic breaks for each of the three types of fabric. The fabric square dimensions were 25cmx25cm resulting in 0.0625m²/square or 1.25m²/20 squares. The number of breaks was visually counted with the help of magnifying lens and backlighting for each one of the squares.

Table 12

Square #	Number of Breaks	
	Fabric A	Fabric C
1	0	0
2	0	0
3	0	0
4	0	0
5	0	0
6	0	1
7	0	0
8	0	0
9	0	2
10	0	0
11	0	0
12	0	0
13	0	0
14	0	0
15	0	0
16	0	0
17	0	0
18	0	0
19	0	0
20	0	0

Table 12 above shows that the “Low Friction Elastic Olefin Fiber” (in Fabric A) is able to render break-free fabrics.

EXAMPLE 24 – KNIT FABRICS

[0243] The elastic ethylene/ α -olefin interpolymer of Example 20 was used to make monofilament fibers of 40 denier having an approximately round cross-section. Before the fiber was made the following additives were added to the polymer: 7000 ppm PDMSO(polydimethyl siloxane), 3000 ppm CYANOX 1790 (1,3,5-tris-(4-t-butyl-3-hydroxy-2,6-dimethylbenzyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione, and 3000 ppm CHIMASORB 944 Poly-[[6-(1,1,3,3-tetramethylbutyl)amino]-s-triazine-

2,4-diyl[[2,2,6,6-tetramethyl-4-piperidyl)imino]hexamethylene[(2,2,6,6-tetramethyl-4-piperidyl)imino]], 0.5% by weight Talc, and 0.5% by weight TiO₂. The fibers were produced using a die profile with circular 0.8 mm diameter, a spin temperature of 299°C, a winder speed of 1000m/minute, a spin finish of 2%, a cold draw of 6%, and a spool weight of 150g. The fibers were then crosslinked using 166.4 kGy irradiation from an e-beam as the crosslinking agent. These fibers are referred to as EXP 1 and employed in the tests below as EXP 1-1, 1-2, 1-3, 1-4, 1-A, and 1-B.

[0244] EXP 2 was made in the same manner as EXP 1 described above except that the fibers were crosslinked using 70.4 kGy irradiation from an e-beam as the crosslinking agent. These fibers are referred to as EXP 2 and employed in the tests below as EXP 2-1, 2-2, 2-3, 2-4, 2-A, and 2-B.

[0245] EXP 1 and EXP 2 were knitted into fabrics containing 8~10% of ethylene/ α -olefin interpolymer fiber and 90-92 % of polyester. As described above EXP 1 contains a greater degree of crosslinking than EXP 2.

The elastic core used in this study is given in Table 13.

Table 13 Elastic core fiber materials

Sample	Denier	Profile	Fiber Formulation	Line speed m/min	Average MI (g/10 min)	Average Density (g/cm ³)	Dosage kGy
EXP 1	40	Round	ethylene/ α -olefin interpolymer	650	1.0	0.88	166.4
EXP 2	40	Round	ethylene/ α -olefin interpolymer	1000	1.0	0.88	70.6

Two Types of polyester were used in this work as hard yarn in Table 14.

Table 14 Hard yarn material

Hard yarn	Material	Denier	Filament
1	Polyester	150	96
2	Polyester	150	288

Knitting Machine

[0246] Table 15 shows the two types knitting machines used in this study. Type 1 is pulley yarn guide feeder illustrated in Figure 11. Type 2 comprises an eyelet feeder such as shown in Figure 12.

Table 15 Knitting machine type

Type	Type 1 (pulley guide)	Type 2 (eyelet feeder)
	San Da Single jersey 4F	SANTEC Single jersey
Structure	Platting	Platting
Needle Gauge	24G 2260T	28G ; 2808T
Cylinder	30in	32 in
Feeder	96F	96F
Feeder guide	pulley	Eyelet

[0247] The resulting unfinished fabric, i.e., greige, were dyed and finished in a typical manner such as that shown in the process map of Figure 13. The scouring process was done in discontinuous jet. Since the base fiber is polyester, 130°C dyeing temperature was employed. Heat-setting was done at 165°C with a speed of 15 yds/min with 20% overfeed applied.

[0248] Table 16 shows the results of the knitting trial and shows that there is no need to preselect the knitting machine. No derailing during knitting was found. EXP. 1 with high crosslink level fiber can be run in pulley feeder or eyelet yarn guide under draft range between 2.7~3.2X and knitting speed ranges from 16 to 20 rpm. The greige and dyed fabrics were inspected on an inspection table. Neither missed stitches nor breaks occurred within this operation window. EXP. 2 with low crosslink level breaks after dyeing when it is run through an eyelet system. As shown in Table 16, samples EXP. 1-1 through 1-4 and EXP. 2-1 through EXP. 2-4 has different composition of ethylene/ α -olefin interpolymers fiber and polyester fiber that is controlled by draft difference during knitting. Samples EXP. 1-A&B and EXP. 2-A&B are run by eyelet feeder that differs from the others that were run by pulley feeder. All samples in Table 16 were heat set; the first 8 samples were heat set via tumble drying without over-feed, while the next 4 samples were heat set using over-feed.

Table 16 Result of knitting trial

No.	Crosslink level kGy	Machine type	R.P.M	Draft	derailing	miss stitch	Breaks on greige	Breaks on finished
EXP. 1-1	176.4	pulley	16	2.7	NO	NO	NO	NO
EXP. 1-2	176.4	pulley	20.	2.7	NO	NO	NO	NO

No.	Crosslink level kGy	Machine type	R.P.M	Draft	derailing	miss stitch	Breaks on greige	Breaks on finished
EXP. 1-3	176.4	pulley	16	3.2	NO	NO	NO	NO
EXP. 1-4	176.4	pulley	20	3.2	NO	NO	NO	NO
EXP. 2-1	70.6	pulley	16	2.7	NO	NO	NO	NO
EXP. 2-2	70.6	pulley	20	2.7	NO	NO	NO	NO
EXP. 2-3	70.6	pulley	16	3.2	NO	NO	NO	NO
EXP. 2-4	70.6	pulley	20	3.2	NO	NO	NO	NO
EXP. 1-A	176.4	eyelet	18	2.8	NO	NO	NO	NO
EXP. 1-B	176.4	eyelet	18	3.2	NO	NO	NO	NO
EXP. 2-A	70.6	eyelet	18	2.8	NO	NO	NO	YES
EXP. 2-B	70.6	eyelet	18	3.2	NO	NO	NO	YES

[0249] To determine the fabric composition, polyester fibers were dissolved. The weight of remaining elastic fiber was compared with original fabric weight. The fabrics were conditioned according to AATCC 20A-2000.

Table 17 Fabric composition (AATCC 20A-2000)

Specimen ID.	Polyester (%)	ethylene/ α -olefin interpolymer (%)
EXP. 1-1	90.1%	9.9%
EXP. 1-2	90.2%	9.8%
EXP. 1-3	90.9%	9.1%
EXP. 1-4	91.2%	8.8%
EXP. 2-1	91.2%	8.8%
EXP. 2-2	90.8%	9.2%
EXP. 2-3	91.9%	8.1%
EXP. 2-4	91.7%	8.3%
EXP. 1-A	90.0%	10.0%
EXP. 1-B	90.9%	9.1%
EXP. 2-A	90.1%	9.9%
EXP. 2-B	91.2%	8.8%

Improved dimensional stability & Heat setting ability

[0250] The dimensional stability after heat setting is measured according to AATCC 135 IVAi that wash at 120 and tumble dry for 3 times. The results are show in Table 18.

Table 18 Result of Dimensional stability

Sample ID	Length wise	Width wise
EXP. 1-A	-0.5%	-0.5%
EXP. 1-B	-0.5%	-0.5%

Lower Growth

[0251] **Table 19** shows stretch and recovery properties measured according to ASTM D 2594. The stretch properties of knitted fabric have low power (ASTM D 2594). ASTM D 2594 is a standard test method for stretch properties of knitted fabrics having low stretching power. This test method specifies the conditions for measuring the fabric growth and fabric stretch of knitted fabrics intended for use in swimwear, anchored slacks, and other form-fitting apparel applications, as well as test conditions for measuring the fabric growth of knitted fabric intended for use in sportswear and other loose-fitting apparel (also commonly known as comfort stretch apparel) applications.

1. Lay the specimen on a flat surface and place two bench marks 125 mm apart on the central section of one face of the looped specimen establishing a gage length along the length of the specimen recorded as length (A).
2. Stretch fabrics to a certain strain (15% for measurement in length direction and 30% for measurement in width direction) and hold for 2 hours. At the end of relaxation, the fabrics are released for recovery. Measure the distance between the two benchmarks after 60 seconds (B) and 1 hour (C) recovery.

$$\text{Fabric Growth}_{60s}, \% = 100 \times (B-A)/A$$

$$\text{Fabric Growth}_{1h}, \% = 100 \times (C-A)/A$$

3. Place a new specimen in the hanger assembly and attach a tensiometer to the lower hanger, grasp and manually load and unload the loop specimen between 0 to 5 lb for 4 cycles.

4. Next, stretch the loop to a specific tension force and hold for 5 to 10 seconds, then measure the new distance between the two bench marks, recorded as length (D). Fabric Stretch, % = $100 \times (D-A)/A$. A diagram of the hanger assembly is shown in Figure 14.

[0252] Customer specifications often require growth in length to be less than 15% after 60 seconds and 8% after 1 hour, the growth in width- to be less than 20% in 60 seconds and 10% after 1 hour. All knits comprising ethylene/ α -olefin interpolymer fiber had lower growth than most industry specifications.

Table 19 Result of stretch and recovery test-ASTM D 2594

Lengthwise			EXP. 1-1	EXP. 1-2	EXP. 1-3	EXP. 1-4	EXP. 2-1	EXP. 2-2	EXP. 2-3	EXP. 2-4	EXP. 1-A	EXP. 1-B
Stretch@5lb load			43.0	43.8	48.5	47.5	33.5	33.5	36	32.5	65	75
Stretch 15%	Growth	60sec	4.0	4.0	5.2	5.0	4.3	5.3	3	2.7	3.3	4.0
		1hr	2.3	2.5	3.3	3.3	2.8	3.3	1.3	2.5	1	1
Widthwise			EXP. 1-1	EXP. 1-2	EXP. 1-3	EXP. 1-4	EXP. 2-1	EXP. 2-2	EXP. 2-3	EXP. 2-4	EXP. 1-A	EXP. 1-B
Stretch@5lb load			73.3	74.8	77.0	74.5	78.5	88.5	91	99.5	66	62
Stretch 30%	Growth	60sec	5.3	5.5	6.3	6.3	5.8	7.0	3.7	3.8	4.0	4.5
		1hr	3.2	3.7	3.5	4.0	3.3	4.0	2.7	2.7	2	2

We claim:

1. A knitted fabric comprising:

(A) an ethylene/ α -olefin interpolymers, wherein the ethylene/ α -olefin interpolymers has one or both of the following characteristics:

(1) an average block index greater than zero and up to about 1.0 and a molecular weight distribution, Mw/Mn, greater than about 1.3; or

(2) at least one molecular fraction which elutes between 40°C and 130°C when fractionated using TREF, characterized in that the fraction has a block index of at least 0.5 and up to about 1; and

(B) at least one other material;

wherein the fabric has less than about 5 percent shrinkage after wash according to AATCC 135 IVAi.

2. A knitted fabric comprising:

(A) a fiber comprising the reaction product of at least one ethylene/ α -olefin interpolymers and at least one cross-linking agent, wherein the ethylene/ α -olefin interpolymers has one or both of the following characteristics:

(1) an average block index greater than zero and up to about 1.0 and a molecular weight distribution, Mw/Mn, greater than about 1.3; or

(2) at least one molecular fraction which elutes between 40°C and 130°C when fractionated using TREF, characterized in that the fraction has a block index of at least 0.5 and up to about 1; and

(B) at least one other fiber comprising at least one other material;

wherein the fabric has less than about 5 percent shrinkage after wash according to AATCC 135 IVAi.

3. The knitted fabric of Claim 1 wherein the ethylene/ α -olefin interpolymers is further characterized by having one or more of the following characteristics:

(1) an Mw/Mn from about 1.7 to about 3.5, at least one melting point, T_m , in degrees Celsius, and a density, d , in grams/cubic centimeter, wherein the numerical values of T_m and d correspond to the relationship:

$$T_m > -2002.9 + 4538.5(d) - 2422.2(d)^2; \text{ or}$$

(2) an Mw/Mn from about 1.7 to about 3.5, and is characterized by a heat of fusion, ΔH in J/g, and a delta quantity, ΔT , in degrees Celsius defined as the temperature difference between the tallest DSC peak and the tallest CRYSTAF peak, wherein the numerical values of ΔT and ΔH have the following relationships:

$$\Delta T > -0.1299(\Delta H) + 62.81 \text{ for } \Delta H \text{ greater than zero and up to } 130 \text{ J/g,}$$

$$\Delta T \geq 48^\circ\text{C for } \Delta H \text{ greater than } 130 \text{ J/g,}$$

wherein the CRYSTAF peak is determined using at least 5 percent of the cumulative polymer, and if less than 5 percent of the polymer has an identifiable CRYSTAF peak, then the CRYSTAF temperature is 30°C ; or

(3) an elastic recovery, Re , in percent at 300 percent strain and 1 cycle measured with a compression-molded film of the ethylene/ α -olefin interpolpolymer, and has a density, d , in grams/cubic centimeter, wherein the numerical values of Re and d satisfy the following relationship when ethylene/ α -olefin interpolpolymer is substantially free of a cross-linked phase:

$$Re > 1481 - 1629(d); \text{ or}$$

(4) a molecular fraction which elutes between 40°C and 130°C when fractionated using TREF, characterized in that the fraction has a molar comonomer content of at least 5 percent higher than that of a comparable random ethylene interpolpolymer fraction eluting between the same temperatures, wherein said comparable random ethylene interpolpolymer has the same comonomer(s) and has a melt index, density, and molar comonomer content (based on the whole polymer) within 10 percent of that of the ethylene/ α -olefin interpolpolymer; or

(5) a storage modulus at 25 °C, $G'(25\text{ °C})$, and a storage modulus at 100 °C, $G'(100\text{ °C})$, wherein the ratio of $G'(25\text{ °C})$ to $G'(100\text{ °C})$ is in the range of about 1:1 to about 9:1.

4. The knitted fabric of Claim 2 wherein the ethylene/ α -olefin interpolymer is further characterized by having one or more of the following characteristics:

(1) an Mw/Mn from about 1.7 to about 3.5, at least one melting point, T_m , in degrees Celsius, and a density, d , in grams/cubic centimeter, wherein the numerical values of T_m and d correspond to the relationship:

$$T_m > -2002.9 + 4538.5(d) - 2422.2(d)^2; \text{ or}$$

(2) an Mw/Mn from about 1.7 to about 3.5, and is characterized by a heat of fusion, ΔH in J/g, and a delta quantity, ΔT , in degrees Celsius defined as the temperature difference between the tallest DSC peak and the tallest CRYSTAF peak, wherein the numerical values of ΔT and ΔH have the following relationships:

$$\Delta T > -0.1299(\Delta H) + 62.81 \text{ for } \Delta H \text{ greater than zero and up to } 130 \text{ J/g,}$$

$$\Delta T \geq 48^\circ\text{C for } \Delta H \text{ greater than } 130 \text{ J/g,}$$

wherein the CRYSTAF peak is determined using at least 5 percent of the cumulative polymer, and if less than 5 percent of the polymer has an identifiable CRYSTAF peak, then the CRYSTAF temperature is 30°C; or

(3) an elastic recovery, Re , in percent at 300 percent strain and 1 cycle measured with a compression-molded film of the ethylene/ α -olefin interpolymer, and has a density, d , in grams/cubic centimeter, wherein the numerical values of Re and d satisfy the following relationship when ethylene/ α -olefin interpolymer is substantially free of a cross-linked phase:

$$Re > 1481 - 1629(d); \text{ or}$$

(4) a molecular fraction which elutes between 40°C and 130°C when fractionated using TREF, characterized in that the fraction has a molar comonomer content of at least 5 percent higher than that of a comparable random ethylene interpolymer fraction eluting between the same temperatures, wherein said

comparable random ethylene interpolymer has the same comonomer(s) and has a melt index, density, and molar comonomer content (based on the whole polymer) within 10 percent of that of the ethylene/ α -olefin interpolymer; or

(5) a storage modulus at 25 °C, $G'(25\text{ °C})$, and a storage modulus at 100 °C, $G'(100\text{ °C})$, wherein the ratio of $G'(25\text{ °C})$ to $G'(100\text{ °C})$ is in the range of about 1:1 to about 9:1.

5. The fabric of any of Claims 1-4 wherein the other material is selected from the group consisting of cellulose, cotton, flax, ramie, rayon, viscose, hemp, wool, silk, linen, bamboo, tencel, viscose, mohair, polyester, polyamide, polypropylene, and mixtures thereof.

6. The fabric of any of Claims 1-4 wherein cellulose comprises from about 60 to about 97 percent by weight of the fabric.

7. The fabric of any of Claims 1-4 wherein polyester comprises at least about 80 percent by weight of the fabric.

8. The fabric of any of Claims 1-4 wherein the ethylene/ α -olefin interpolymer is blended with another polymer.

9. The fabric of any of Claims 1-4 wherein the ethylene/ α -olefin interpolymer comprises from about 2 percent to about 30 percent by weight of the fabric.

10. The fabric of any of Claims 1-4 wherein the fabric has less than about 2 percent shrinkage after wash by AATCC 135 IVAi.

11. The fabric of any of Claims 1-4 wherein the ethylene/ α -olefin interpolymer is characterized by a density of from about 0.865 to about 0.92 g/cm³ (ASTM D 792) and an uncrosslinked melt index of from about 0.1 to about 10 g/10 minutes.

12. The fabric of any of Claims 1-4 wherein the growth in the lengthwise and widthwise directions is from about 0.5 to about 5% according to ASTM D 2594.

13. The fabric of any of Claims 1-4 wherein the fabric is capable of being heat set at a temperature of 180°C or below while controlling the size.

14. The fabric of any of Claims 1-4 wherein the fabric can be stretched in two dimensions.

15. The fabric of any of Claims 1-4 wherein the fabric has been made using an eyelet feeder system.

16. The fabric of any of Claims 1-4 wherein the fabric has been made using a pulley system.

17. The fabric of any of Claims 1-4 wherein the fabric is a circular knit fabric.
18. The fabric of any of Claims 1-4 wherein the fabric is a warp knit fabric.
19. A garment comprising the fabric of any of Claims 1-4.
20. A fiber suitable for textile articles wherein said fiber comprises a reaction product of at least about 1% polyolefin according to ASTM D629-99 and at least one crosslinking agent and wherein the filament elongation to break of said fiber is greater than about 200% according to ASTM D2653-01 (elongation at first filament break test) and wherein the fiber is further characterized by having (1) ratio of load at 200% elongation / load at 100% elongation of greater than or equal to about 1.5 according to ASTM D2731-01 (under force at specified elongation in the finished fiber form); or (2) an average coefficient of friction of less than or equal to about 0.8; or (3) both (1) and (2).
21. The fiber of Claim 20 wherein the polyolefin is an ethylene/ α -olefin interpolpolymer, wherein the ethylene/ α -olefin interpolpolymer has one or both of the following characteristics:

- (1) an average block index greater than zero and up to about 1.0 and a molecular weight distribution, Mw/Mn, greater than about 1.3; or
- (2) at least one molecular fraction which elutes between 40°C and 130°C when fractionated using TREF, characterized in that the fraction has a block index of at least 0.5 and up to about 1.

22. The fiber of Claim 21 wherein the ethylene/ α -olefin interpolpolymer is further characterized by having one or more of the following characteristics:

- (1) an Mw/Mn from about 1.7 to about 3.5, at least one melting point, T_m , in degrees Celsius, and a density, d , in grams/cubic centimeter, wherein the numerical values of T_m and d correspond to the relationship:

$$T_m > -2002.9 + 4538.5(d) - 2422.2(d)^2; \text{ or}$$

- (2) an Mw/Mn from about 1.7 to about 3.5, and is characterized by a heat of fusion, ΔH in J/g, and a delta quantity, ΔT , in degrees Celsius defined as the temperature difference between the tallest DSC peak and the tallest CRYSTAF peak, wherein the numerical values of ΔT and ΔH have the following relationships:

$\Delta T > -0.1299(\Delta H) + 62.81$ for ΔH greater than zero and up to 130 J/g,

$\Delta T \geq 48^\circ\text{C}$ for ΔH greater than 130 J/g ,

wherein the CRYSTAF peak is determined using at least 5 percent of the cumulative polymer, and if less than 5 percent of the polymer has an identifiable CRYSTAF peak, then the CRYSTAF temperature is 30°C ; or

(3) an elastic recovery, Re , in percent at 300 percent strain and 1 cycle measured with a compression-molded film of the ethylene/ α -olefin interpolymer, and has a density, d , in grams/cubic centimeter, wherein the numerical values of Re and d satisfy the following relationship when ethylene/ α -olefin interpolymer is substantially free of a cross-linked phase:

$Re > 1481 - 1629(d)$; or

(4) a molecular fraction which elutes between 40°C and 130°C when fractionated using TREF, characterized in that the fraction has a molar comonomer content of at least 5 percent higher than that of a comparable random ethylene interpolymer fraction eluting between the same temperatures, wherein said comparable random ethylene interpolymer has the same comonomer(s) and has a melt index, density, and molar comonomer content (based on the whole polymer) within 10 percent of that of the ethylene/ α -olefin interpolymer; or

(5) a storage modulus at 25°C , $G'(25^\circ\text{C})$, and a storage modulus at 100°C , $G'(100^\circ\text{C})$, wherein the ratio of $G'(25^\circ\text{C})$ to $G'(100^\circ\text{C})$ is in the range of about 1:1 to about 9:1.

23. A warp knitted article comprising one or more of the fibers of any of Claims 20-22.

24. A circular knitted article comprising one or more of the fibers of any of Claims 20-22.

25. A knitted fabric comprising:

(A) a crosslinked fiber comprising an ethylene/ α -olefin interpolymer, wherein the ethylene/ α -olefin interpolymer has one or both of the following characteristics before crosslinking:

(1) an average block index greater than zero and up to about 1.0 and a molecular weight distribution, Mw/Mn, greater than about 1.3; or

(2) at least one molecular fraction which elutes between 40°C and 130°C when fractionated using TREF, characterized in that the fraction has a block index of at least 0.5 and up to about 1; and

(B) at least one other fiber comprising at least one other material;

wherein the fabric has less than about 5 percent shrinkage after wash according to AATCC 135 IVAi.

26. The knitted fabric of Claim 25 wherein the ethylene/ α -olefin interpolpolymer is further characterized by having one or more of the following characteristics before crosslinking:

(1) an Mw/Mn from about 1.7 to about 3.5, at least one melting point, T_m , in degrees Celsius, and a density, d , in grams/cubic centimeter, wherein the numerical values of T_m and d correspond to the relationship:

$$T_m > -2002.9 + 4538.5(d) - 2422.2(d)^2; \text{ or}$$

(2) an Mw/Mn from about 1.7 to about 3.5, and is characterized by a heat of fusion, ΔH in J/g, and a delta quantity, ΔT , in degrees Celsius defined as the temperature difference between the tallest DSC peak and the tallest CRYSTAF peak, wherein the numerical values of ΔT and ΔH have the following relationships:

$$\Delta T > -0.1299(\Delta H) + 62.81 \text{ for } \Delta H \text{ greater than zero and up to } 130 \text{ J/g,}$$

$$\Delta T \geq 48^\circ\text{C for } \Delta H \text{ greater than } 130 \text{ J/g,}$$

wherein the CRYSTAF peak is determined using at least 5 percent of the cumulative polymer, and if less than 5 percent of the polymer has an identifiable CRYSTAF peak, then the CRYSTAF temperature is 30°C; or

(3) an elastic recovery, Re , in percent at 300 percent strain and 1 cycle measured with a compression-molded film of the ethylene/ α -olefin interpolpolymer, and has a density, d , in grams/cubic centimeter, wherein the numerical values of Re and d

satisfy the following relationship when ethylene/ α -olefin interpolymers are substantially free of a cross-linked phase:

$Re > 1481 - 1629(d)$; or

(4) a molecular fraction which elutes between 40°C and 130°C when fractionated using TREF, characterized in that the fraction has a molar comonomer content of at least 5 percent higher than that of a comparable random ethylene interpolymers fraction eluting between the same temperatures, wherein said comparable random ethylene interpolymers has the same comonomer(s) and has a melt index, density, and molar comonomer content (based on the whole polymer) within 10 percent of that of the ethylene/ α -olefin interpolymers; or

(5) a storage modulus at 25 °C, $G'(25\text{ °C})$, and a storage modulus at 100 °C, $G'(100\text{ °C})$, wherein the ratio of $G'(25\text{ °C})$ to $G'(100\text{ °C})$ is in the range of about 1:1 to about 9:1.

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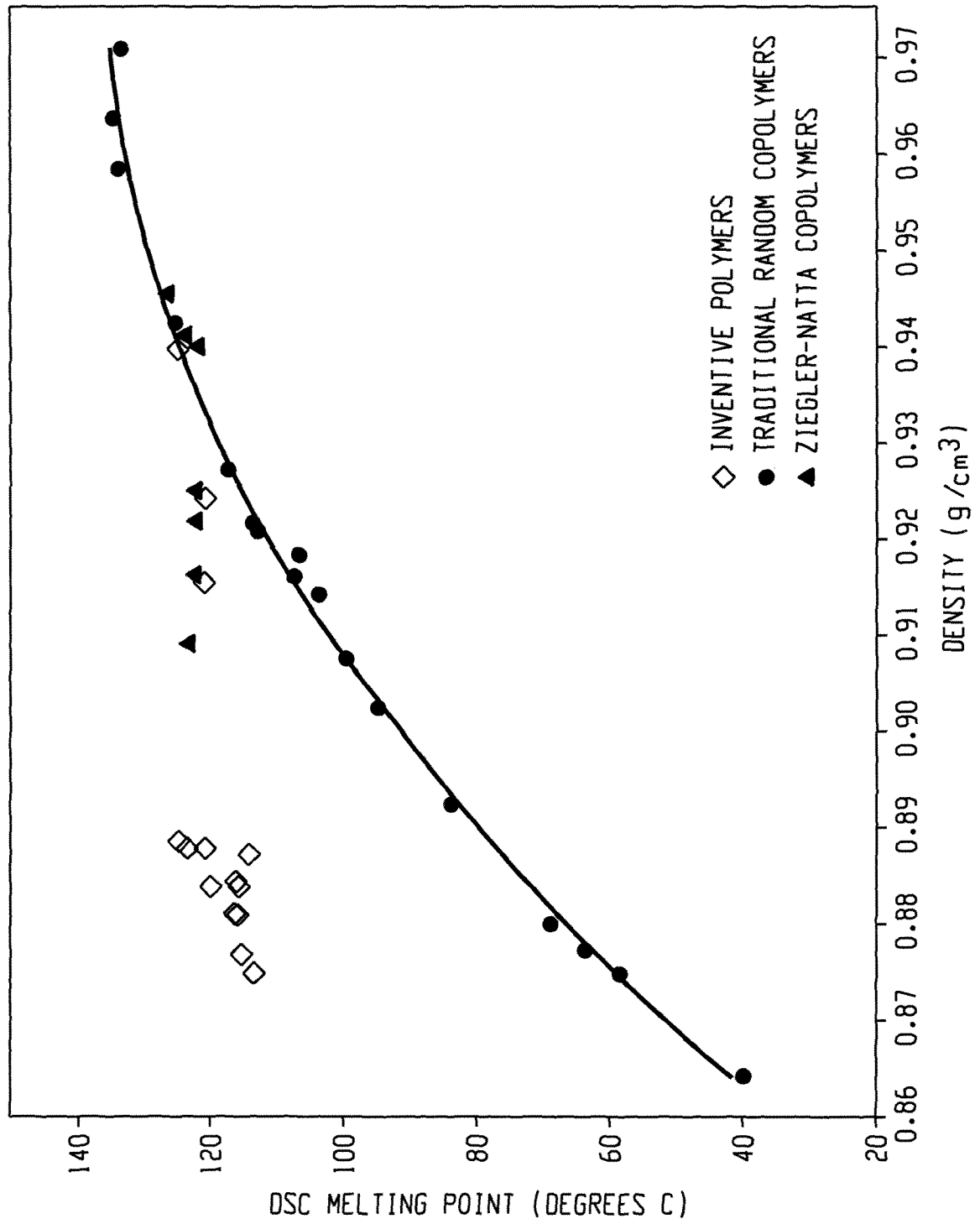


Fig. 1

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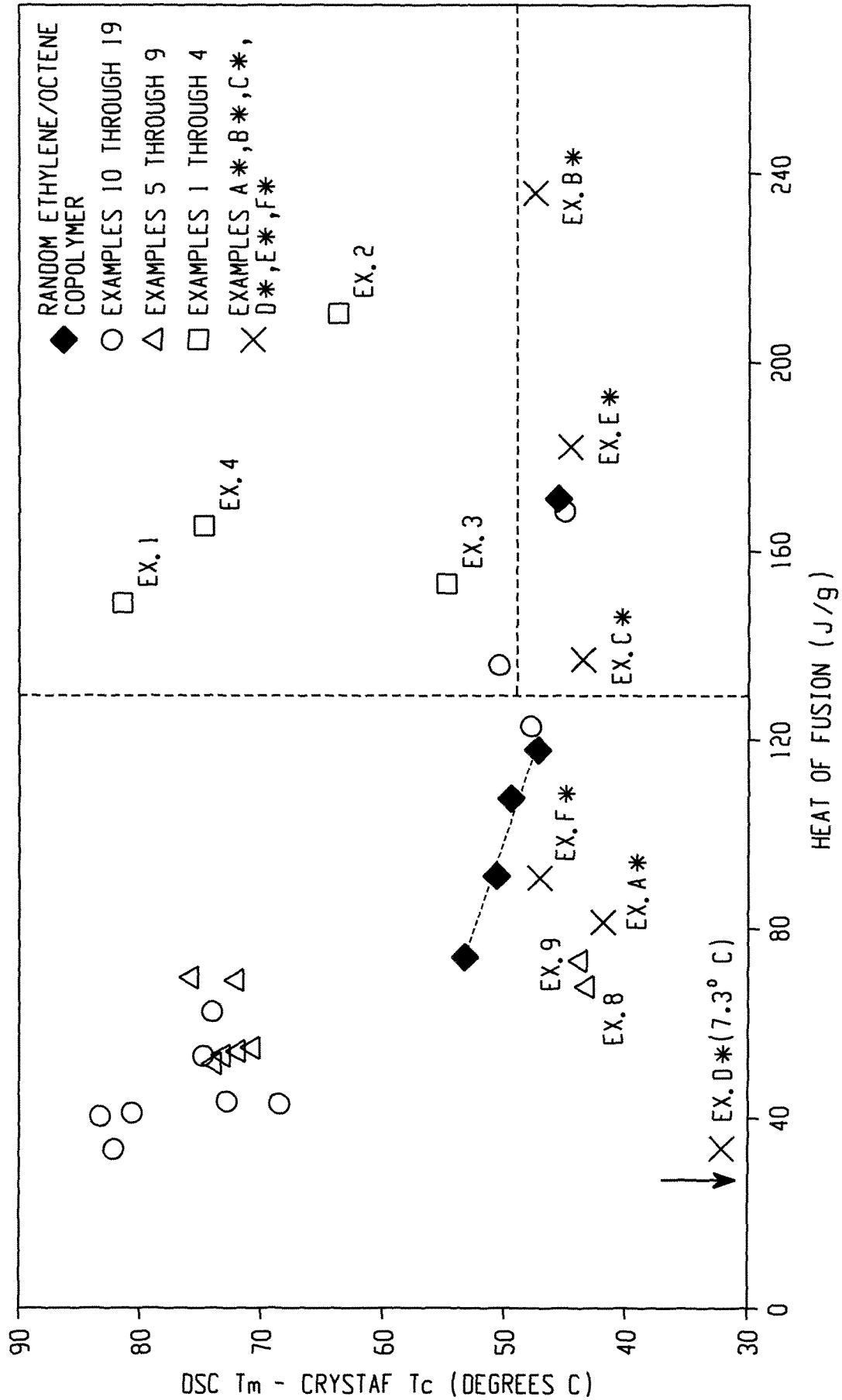


Fig. 2

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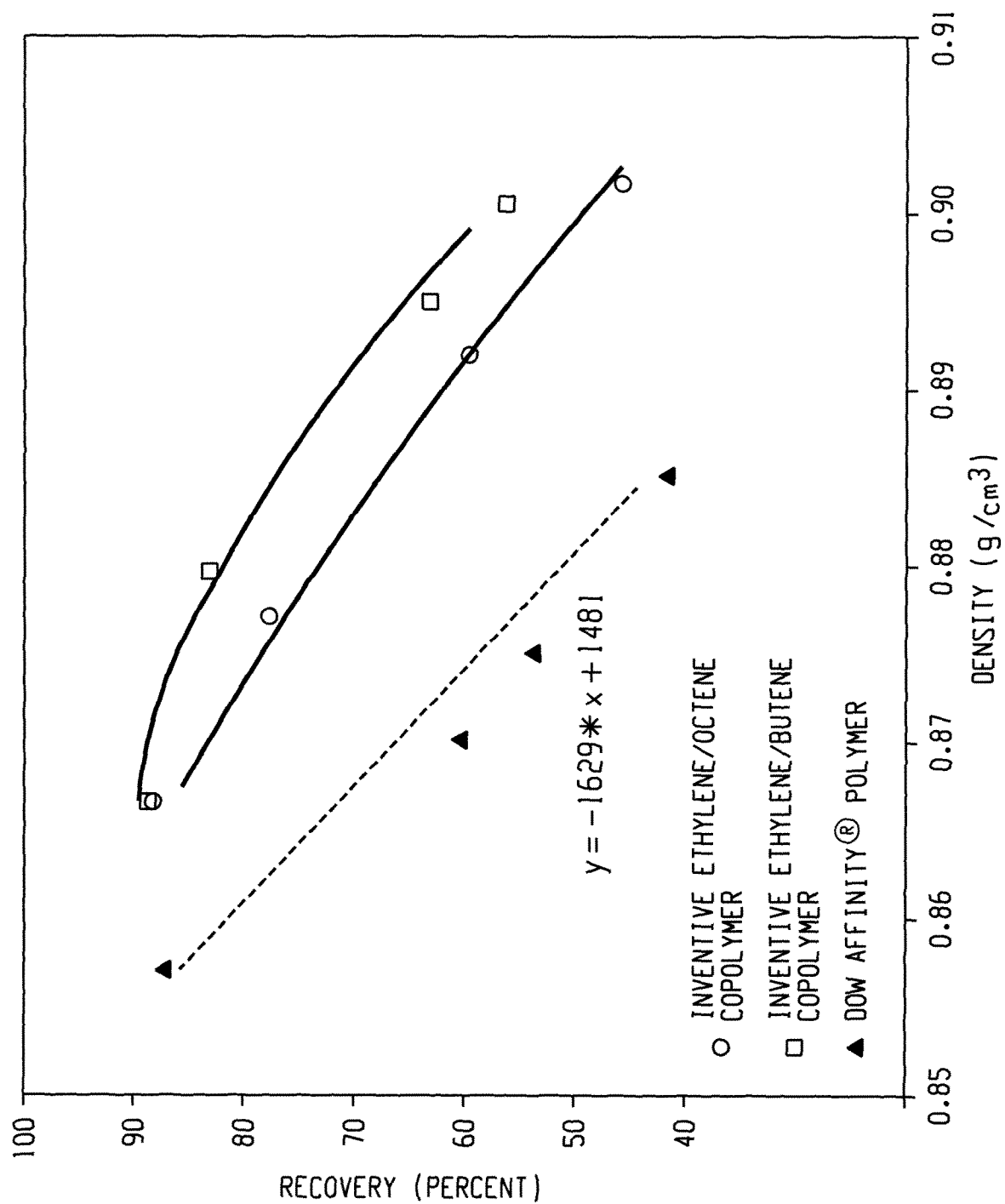


Fig. 3

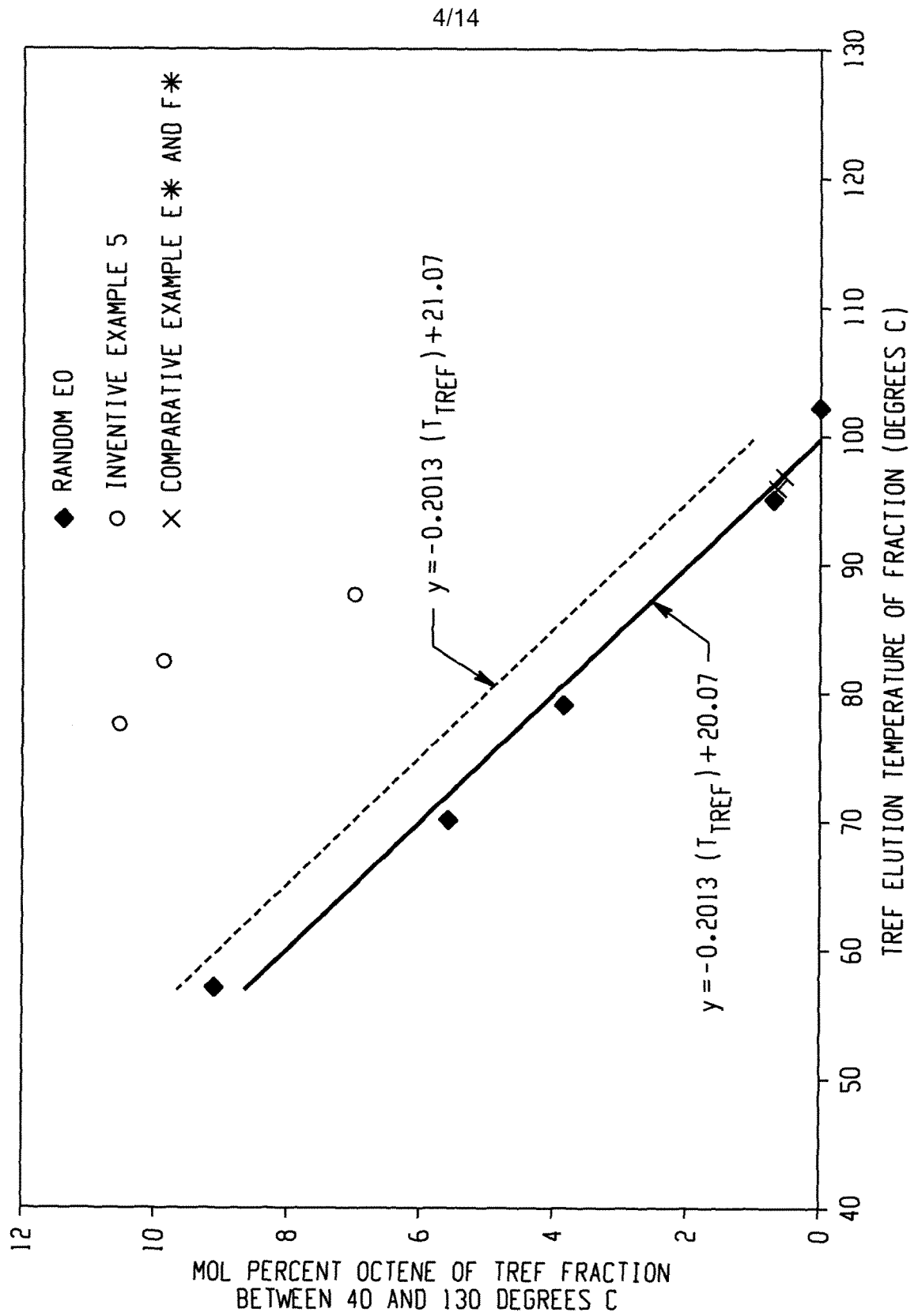


Fig. 4

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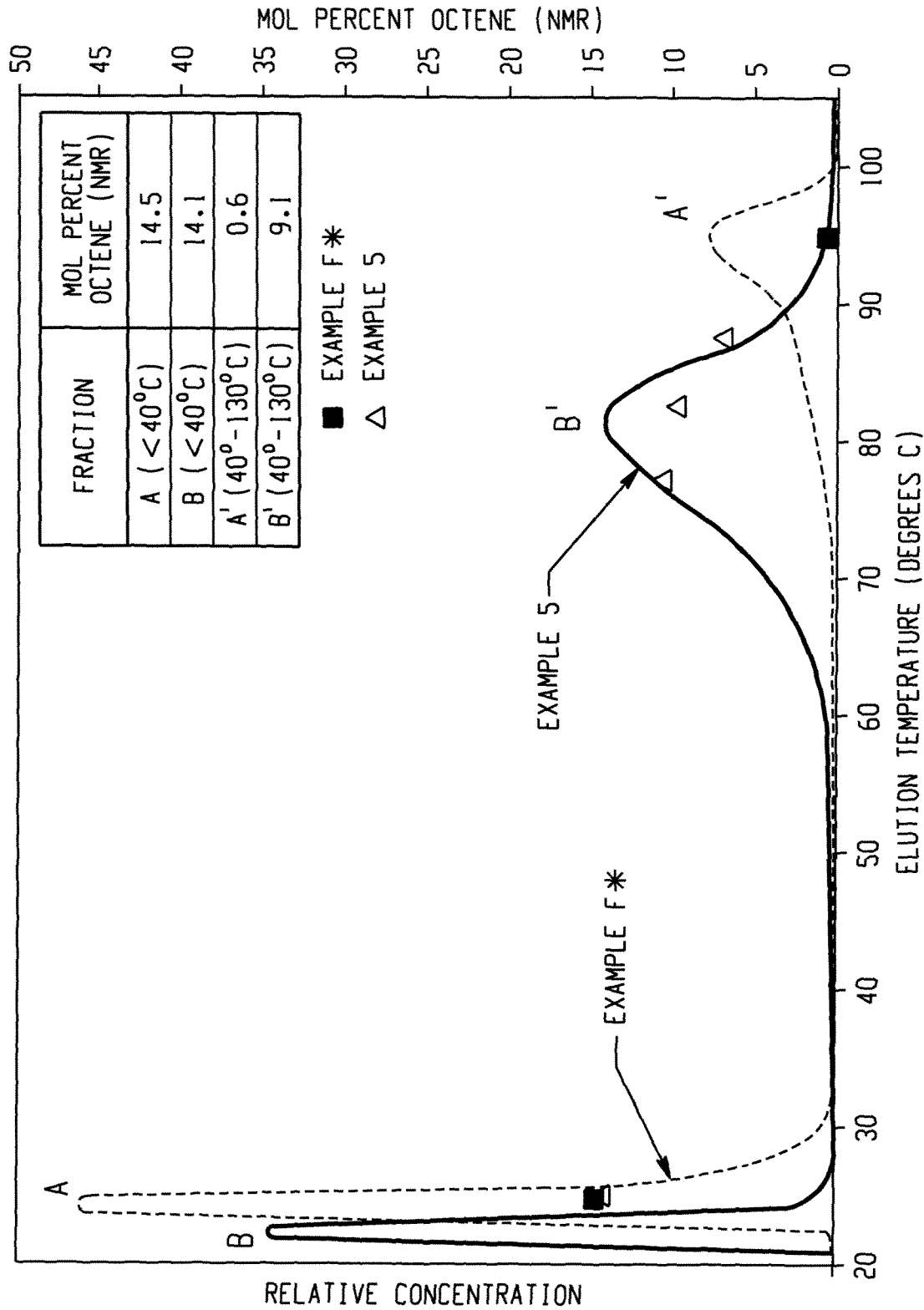


Fig. 5

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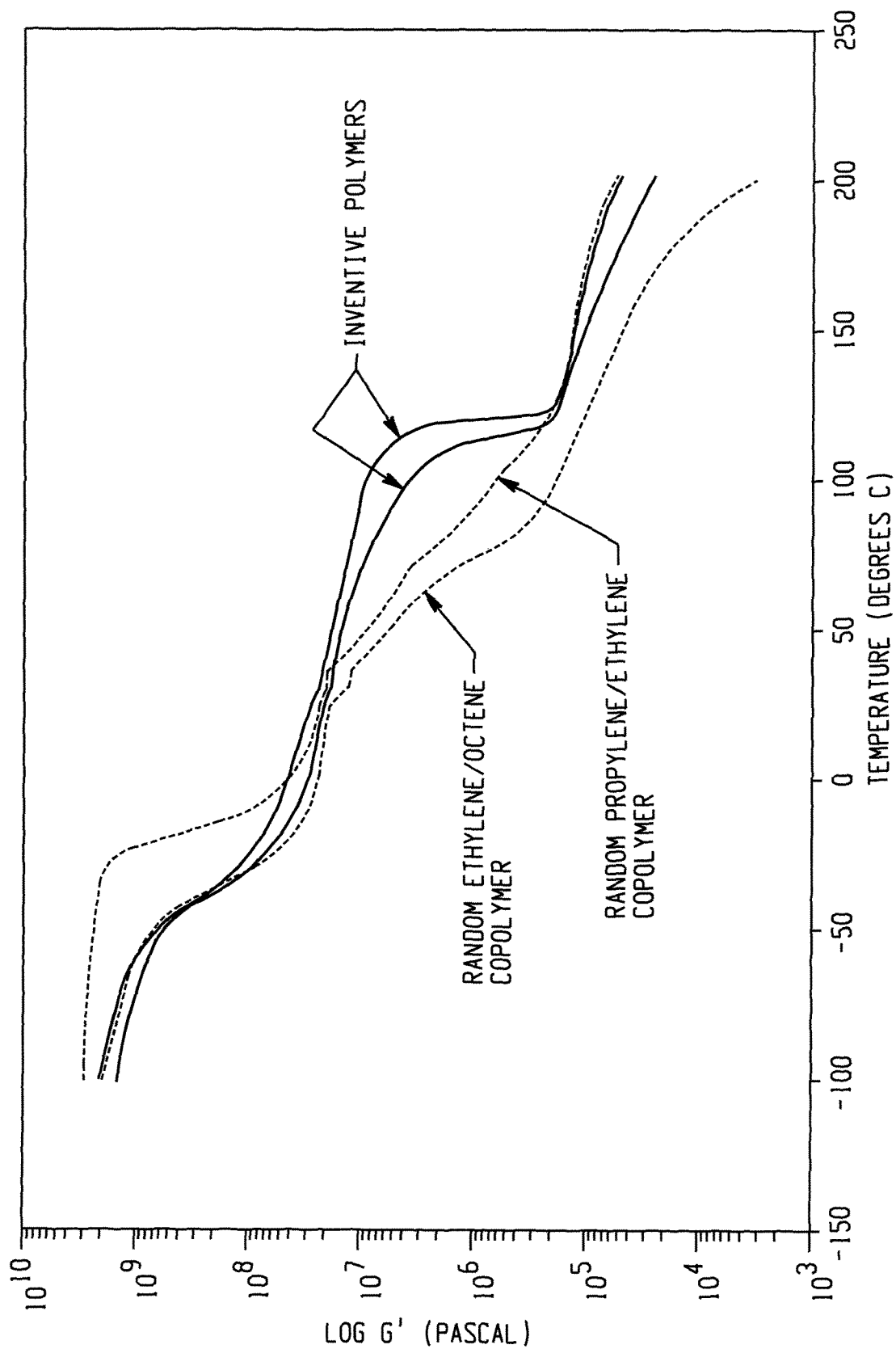


Fig. 6

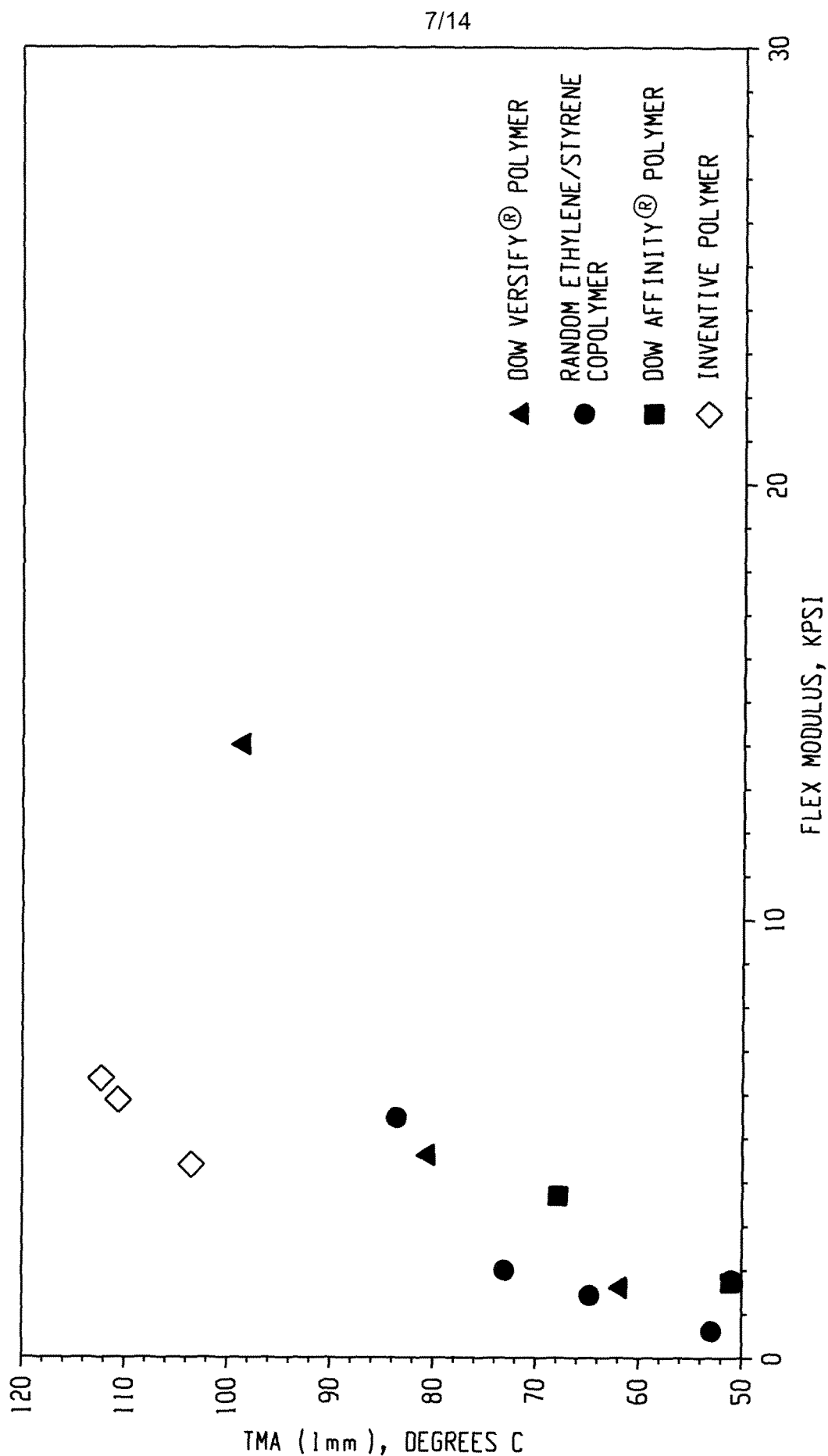


Fig. 7

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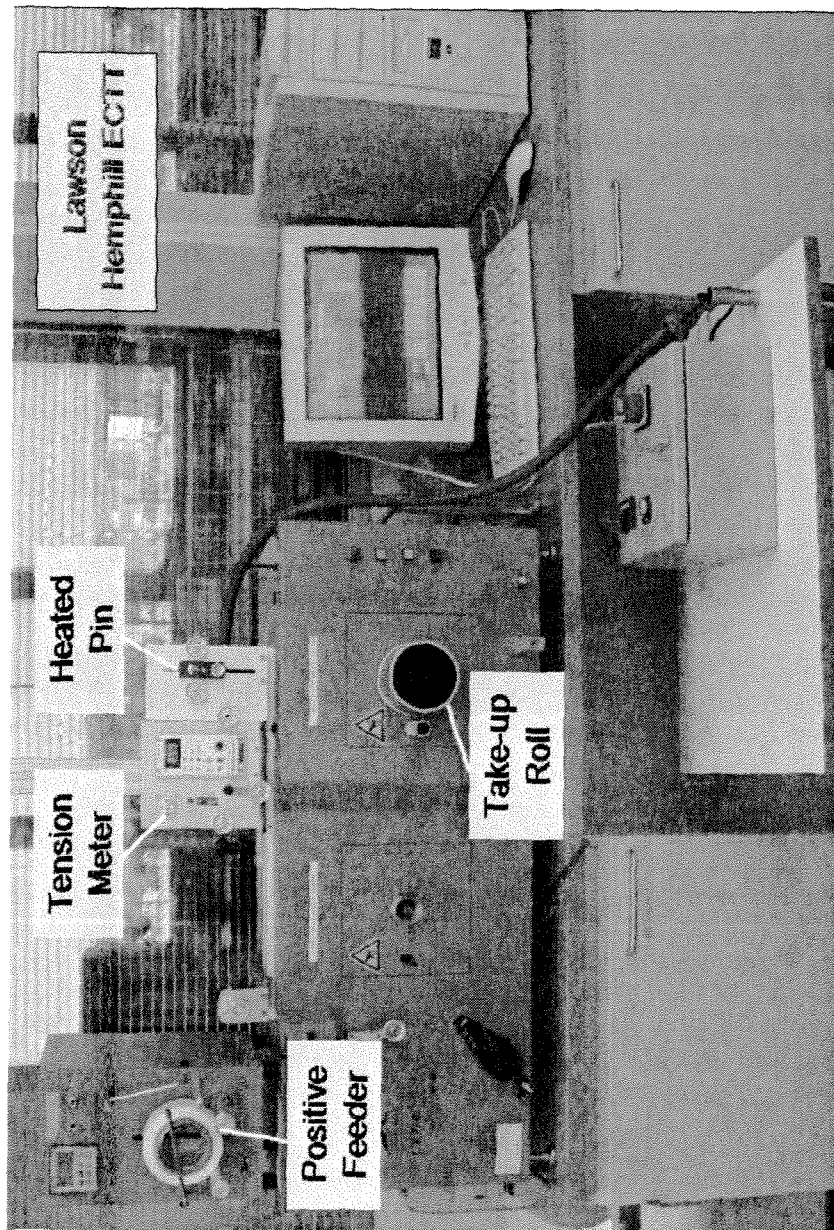


Fig. 8

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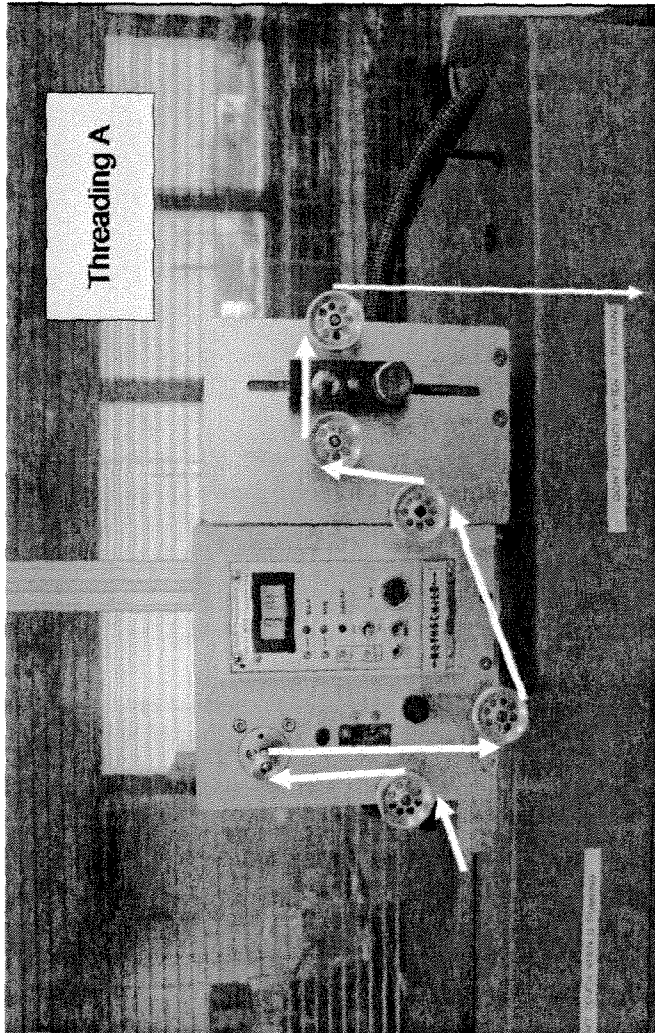


Fig. 9

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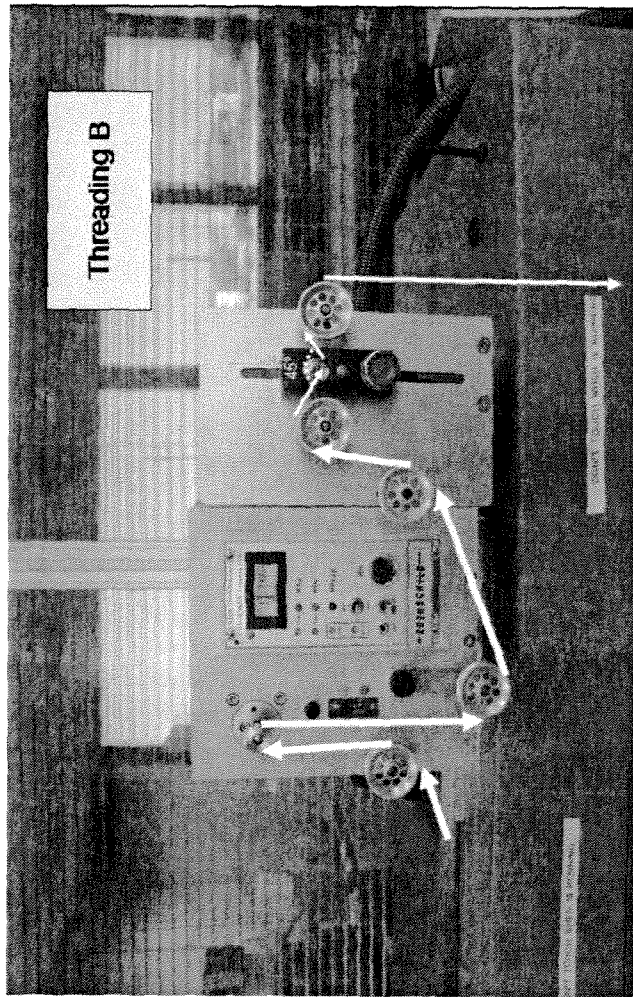


Fig. 10

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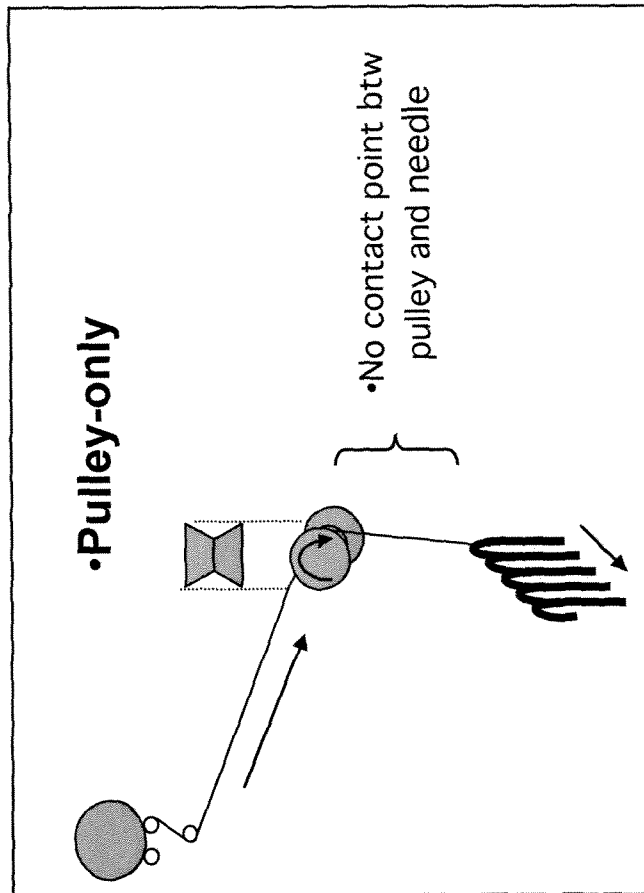


Fig. 11

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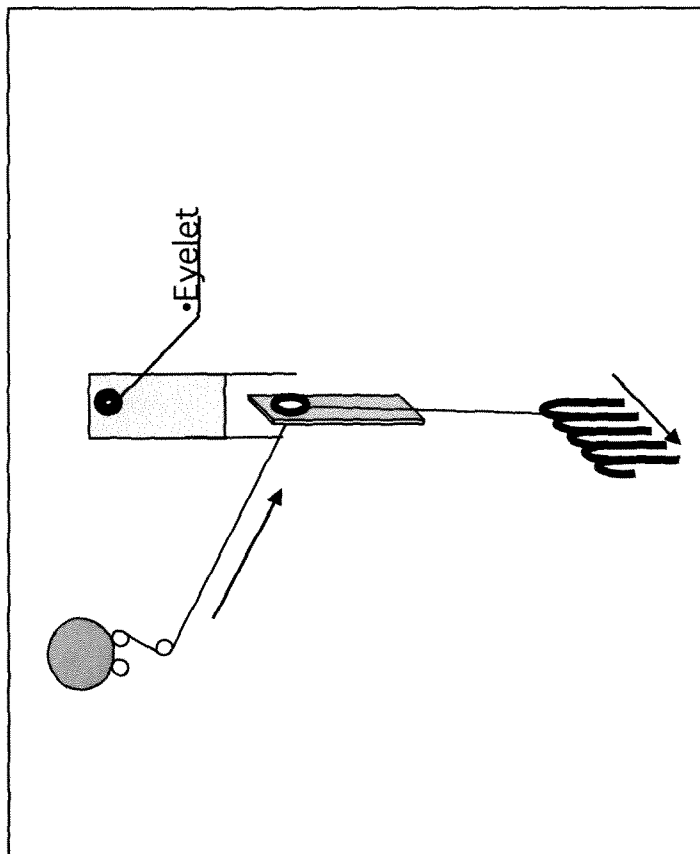


Fig. 12

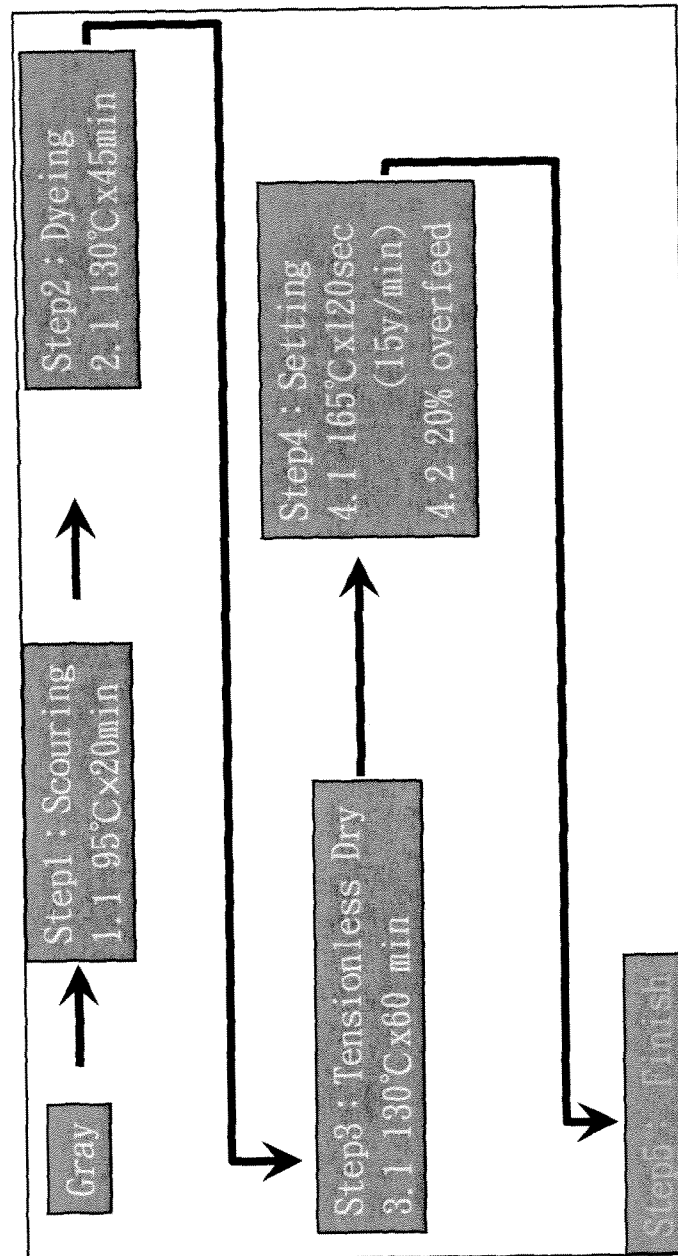


Fig. 13

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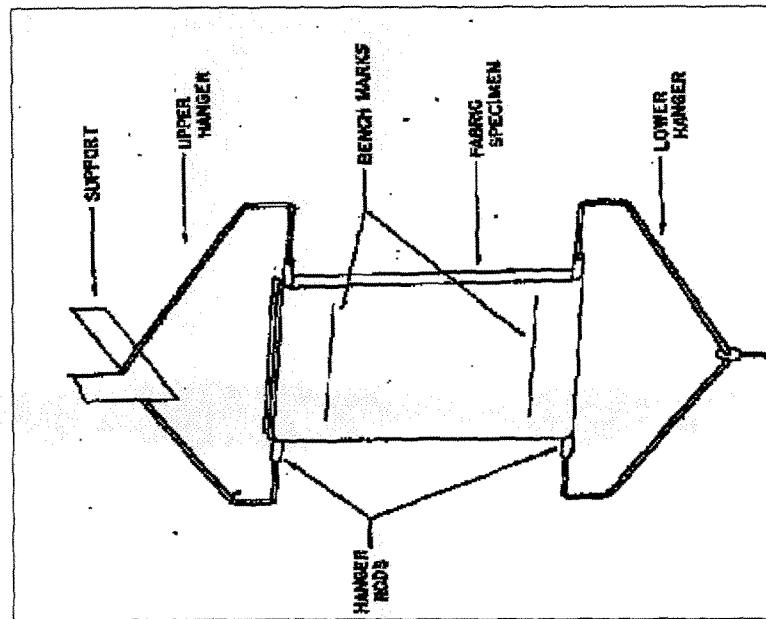


Figure 14 Hanger assembly used for ASTM D 2594

Fig. 14

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2007/077782

A. CLASSIFICATION OF SUBJECT MATTER
INV. D04B1/18 D04B21/18

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)
D04B

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 01/85843 A (DOW CHEMICAL CO [US]) 15 November 2001 (2001-11-15) page 35, line 13 – page 60, line 20; claims 2,16,19,20 -----	1-9,11, 13-17, 19,25,26
A	WO 2005/028724 A (HONEYWELL INT INC [US]) 31 March 2005 (2005-03-31) claim 23; figures 2,3 -----	1

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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Date of the actual completion of the international search

17 January 2008

Date of mailing of the international search report

30/01/2008

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2007/077782

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