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(54) Title: POLYMER BLENDS WITH ETHYLENE/α-OLEFIN INTERPOLYMERS

(57) Abstract: Embodiments of the invention provide an impact modified composition comprising ethylene/α-olefin interpolymers. The ethylene/α-olefin interpolymers are characterized by an average block index, ABI, which is greater than zero and up to about 1.0 and a molecular weight distribution, Mw/Mn, greater than about 1.3. In addition or alternatively, the block ethylene/α-olefin interpolymer is characterized by having at least one fraction obtained by Temperature Rising Elution Fractionation ("TREF"), wherein the fraction has a block index greater than about 0.3 and up to about 1.0 and the ethylene/α-olefin interpolymer has a molecular weight distribution, Mw/Mn, greater than about 1.4.

POLYMER BLENDS WITH ETHYLENE/α-OLEFIN INTERPOLYMERS

CROSS-REFERENCE TO RELATED APPLICATIONS

[1]   This application claims priority from U.S. Patent Application Serial No. 61/102635, filed on October 3, 2008. This application is related to U.S. Patent Application Serial Nos. 61/024,674 filed on January 30, 2008; 11/376,838 filed on March 15, 2006; and 11/377,046 filed on March 15, 2006. For purposes of United States patent practice, the contents of these applications are herein incorporated by reference in their entirety.

FIELD OF THE INVENTION

[2]   This invention relates to improved impact modification of thermoplastic polymers and polymer blends thereof.

BACKGROUND OF THE INVENTION

[3]   Many different polymers and materials have been added to polymer compositions in attempting to enhance the composition's impact strength or maintain the impact strength while enhancing other properties. For example, U.S. Pat. No. 5,118,753 (Hikasa et al.), incorporated herein by reference, discloses thermoplastic elastomer compositions said to have low hardness and excellent flexibility and mechanical properties consisting essentially of a mixture of an oil-extended olefinic copolymer rubber and an olefinic plastic. The olefinic plastic is polypropylene or a copolymer of polypropylene and an .alpha.-olefin of 2 or more carbon atoms. Modern Plastics Encyclopedia/89, mid October 1988 Issue, Volume 65, Number 11, pp. 110-117, the disclosure of which is incorporated herein by reference, also discusses the use of various thermoplastic elastomers (TPEs) useful for impact modification. These include: elastomeric alloys TPEs, engineering TPEs, olefinic TPEs (also known as thermoplastic olefins or TPOs), polyurethane TPEs and styrenic TPEs.

[4]   Thermoplastic olefins (TPOs) are often produced from blends of an elastomeric material such as ethylene/propylene rubber (EPM) or ethylene/propylene diene monomer terpolymer (EPDM) and a more rigid material such as isotactic polypropylene. Other materials or components can be added into the formulation depending upon the application, including oil, fillers, and cross-linking agents. TPOs are often characterized by a balance of stiffness (modulus) and low temperature impact, good chemical resistance and broad use temperatures. Because of features such as these, TPOs are used in many applications,

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including automotive facia and wire and cable operations, rigid packaging, molded articles, instrument panels, and the like.

[5]   Union Carbide Chemicals and Plastics Inc. announced in 1990 that they have developed a new cost effective class of polyolefins trademarked Flexomer™ Polyolefins that

5   could replace expensive EPM or EPDM rubbers. These new polyolefins are said to have bridged the gap between rubbers and polyethylene, having moduli between the two ranges. Modulus of the rubber and of the formulation is not, however, the only criteria for evaluating a TPO formulation. Low temperature impact performance, sometimes measured by Gardner Impact at -30°C. also is sometimes important to a TPO composition's performance.

10   According to the data contained in FIG. 4 of the paper "Flexomer™ Polyolefins: A Bridge Between Polyethylene and Rubbers" by M. R. Rifi, H. K. Ficker and M. A. Corwin, more of the Flexomer™ Polyolefin needs to be added into the TPO formulation in order to reach the same levels of low temperature Gardner Impact performance as the standard EPM rubber, thus somewhat negating the benefits of the lower cost EPM/EPDM replacement. For

15   example, using the data of FIG. 4 of the Rifi et al paper, about 20% (by weight) of the EPM in polypropylene gives a Gardner Impact of about 22 J. at -30.degree. C., while the same amount of Flexomer™ Polyolefin gives a -30°C. Gardner Impact of about 13 J.

[6]   In a paper presented on Sep. 24, 1991 at the 1991 Specialty Polyolefins Conference (SPO '91) (pp. 43-55) in Houston, Tex., Michael P. Jeffries (Exxpol Ethylene Polymers

20   Venture Manager of Exxon Chemical Company) also reports that Exxon's Exact™ polymers and Plastomers can be blended into polypropylene for impact modification. Exxon Chemical Company, in the Preprints of Polyolefins VII International Conference, page 45-66, Feb. 24-27 1991, also disclose that the narrow molecular weight distribution (NMWD) resins produced by their EXXPOL™ technology have higher melt viscosity and lower melt strength

25   than conventional Ziegler resins at the same melt index. In another recent publication, Exxon Chemical Company has also taught that NMWD polymers made using a single site catalyst create the potential for melt fracture ("New Specialty Linear Polymers (SLP) For Power Cables," by Monica Hendewerk and Lawrence Spenadel, presented at IEEE meeting in Dallas, Tex., September, 1991).

30   [7]   It is well known that narrow molecular weight distribution linear polymers disadvantageously have low shear sensitivity or low I_{10}/I_2 value, which limits the extrudability of such polymers. Additionally, such polymers possessed low melt elasticity, causing problems in melt fabrication such as film forming processes or blow molding

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processes (e.g., sustaining a bubble in the blown film process, or sag in the blow molding process etc.). Finally, such resins also experienced surface melt fracture properties at relatively low extrusion rates thereby processing unacceptably and causing surface irregularities in the finished product.

5   [8]   Thus, while the development of new lower modulus polymers such as Flexomer™ Polyolefins by Union Carbide or Exact™ polymers by Exxon has aided the TPO marketplace, there continues to be a need for other more advanced, cost-effective polymers for compounding with thermoplastics (e.g., polyolefins such as polypropylene or HDPE) to improve or maintain modulus and/or impact performance at room temperature or below.

10   [9]   Block copolymers comprise sequences ("blocks") of the same monomer unit, covalently bound to sequences of unlike type. The blocks can be connected in a variety of ways, such as A—B in diblock and A—B—A triblock structures, where A represents one block and B represents a different block. In a multi-block copolymer, A and B can be connected in a number of different ways and be repeated multiply. It may further comprise

15   additional blocks of different type. Multi-block copolymers can be either linear multi-block, multi-block star polymers (in which all blocks bond to the same atom or chemical moiety) or comb-like polymers where the B blocks are attached at one end to an A backbone.

[10]   A block copolymer is created when two or more polymer molecules of different chemical composition are covalently bonded to each other. While a wide variety of block

20   copolymer architectures are possible, a number of block copolymers involve the covalent bonding of hard plastic blocks, which are substantially crystalline or glassy, to elastomeric blocks forming thermoplastic elastomers. Other block copolymers, such as rubber-rubber (elastomer-elastomer), glass-glass, and glass-crystalline block copolymers, are also possible.

[11]   One method to make block copolymers is to produce a "living polymer". Unlike

25   typical Ziegler-Natta polymerization processes, living polymerization processes involve only initiation and propagation steps and essentially lack chain terminating side reactions. This permits the synthesis of predetermined and well-controlled structures desired in a block copolymer. A polymer created in a "living" system can have a narrow or extremely narrow distribution of molecular weight and be essentially monodisperse (i.e., the molecular weight

30   distribution is essentially one). Living catalyst systems are characterized by an initiation rate which is on the order of or exceeds the propagation rate, and the absence of termination or transfer reactions. In addition, these catalyst systems are characterized by the presence of a single type of active site. To produce a high yield of block copolymer in a polymerization

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process, such catalysts must exhibit living characteristics to a substantial extent.

[12]   Butadiene-isoprene block copolymers have been synthesized via anionic polymerization using the sequential monomer addition technique. In sequential addition, a certain amount of one of the monomers is contacted with the catalyst. Once a first such monomer has reacted to substantial extinction forming the first block, a certain amount of the second monomer or monomer species is introduced and allowed to react to form the second block. The process may be repeated using the same or other anionically polymerizable monomers. However, ethylene and other α-olefins, such as propylene, butene, 1-octene, etc., are not directly block polymerizable by anionic techniques.

[13]   Whenever crystallization occurs under quiescent conditions, which means that the polymer is not subjected to either external mechanical forces or unusually fast cooling, homopolymers made from a highly crystallizable monomer will crystallize from a melt and form spherical structures called "spherulites". These spherulites range in size from micrometers to millimeters in diameter. A description of this phenomenon may be found in Woodward, A.E., *Atlas of Polymer Morphology*, Hanser Publishers, New York, 1988. The spherulites are composed of layer like crystallites called lamellae. Descriptions of this may be found in Keller, A., Sawada, S. *Makromol. Chem.*, 74, 190 (1964) and Basset, D.C., Hodge, A.M., Olley, R.H., *Proc. Roy. Soc. London*, A377, p 25, 39, 61 (1981). The spherulitic structure starts from a core of parallel lamellae that subsequently branch and grow outward from the core in a radial direction. Disordered polymeric chains make up the material between lamellar branches as described in Li, L., Chan, C., Yeung, K.L., Li, J., Ng, K., Lei, Y., *Macromolecules*, 34, 316 (2001).

[14]   Polyethylene and random α-olefin copolymers of ethylene can be forced to assume non-spherulitic morphologies in certain cases. One situation occurs when the crystallization conditions are not quiescent, such as during blown or cast film processing. In both cases, the melts are subjected to strong external forces and fast cooling, which usually produce row-nucleated or "shish-kebab" structures as described in A. Keller, M.J. Machin, *J. Macromol. Sci. Phys.*, 1, 41 (1967). A non-spherulitic morphology will also be obtained when the molecules contain enough of an α-olefin or another type of comonomer to prevent the formation of lamellae. This change in crystal type occurs because the comonomers are usually too bulky to pack within an ethylene crystal and, therefore, a sequence of ethylene units in between comonomers cannot form a crystal any thicker than the length of that

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sequence in an all-trans conformation. Eventually, the lamellae would have to become so thin that chain folding into lamellar structures is no longer favorable. In this case, fringed micellar or bundled crystals are observed as described in S. Bensason, J. Minick, A. Moet, S. Chum, A. Hiltner, E. Baer, *J. Polym. Sci. B: Polym. Phys.*, 34, 1301 (1996). Studies of low

5   molecular weight polyethylene fractions provide an understanding of the number of consecutive ethylene units that are required to form a chain folded lamellae. As described in L. Mandelkern, A. Prasad, R.G. Alamo, G.M. Stack, *Macromolecules*, 23, 3696 (1990) polymer chain segments of at least 100 ethylene units are required for chain folding. Below this number of ethylene units, low molecular weight fractions form extended chain crystals

10   while polyethylene at typical molecular weights forms fringed micelles and creates a granular type morphology.

[15]   A fourth type of solid state polymer morphology has been observed in α-olefin block copolymers made by batch anionic polymerization of butadiene followed by hydrogenation of the resulting polymer. At the crystallization temperature of the ethylene segments, the

15   amorphous blocks can be either glassy or elastic. Studies of crystallization within a glassy matrix have used styrene-ethylene (S-E) diblocks as described in Cohen, R.E., Cheng, P.L., Douzinas, K., Kofinas, P., Berney, C.V., *Macromolecules*, 23, 324 (1990) and ethylene-vinylcyclohexane (E-VCH) diblocks as described in Loo, Y.L., Register, R.A., Ryan, A.J., Dee G.T., *Macromolecules* 34, 8968 (2001). Crystallization within an elastic matrix has been

20   studied using ethylene-(3-methyl-butene) diblocks as described in Quiram, D.J., Register, R.A., Marchand, G.R., Ryan, A.J., *Macromolecules* 30, 8338 (1997) and using ethylene-(styrene-ethylene-butene) diblocks as described in Loo, Y.L., Register, R.A., Ryan, A.J., *Macromolecules* 35, 2365 (2002). When the matrix was either glassy or was elastic but with a high degree of segregation between the blocks, the solid state structure showed the classical

25   morphology of amorphous block copolymers such as styrene-butadiene-styrene (SBS), in which the different polymer segments were constrained into microdomains of approximately 25 nm in diameter. Crystallization of the ethylene segments in these systems was primarily constrained to the resulting microdomains. Microdomains can take the form of spheres, cylinders, lamellae, or other morphologies. The narrowest dimension of a microdomain, such

30   as perpendicular to the plane of lamellae, is constrained to < 60 nm in these systems. It is more typical to find constraints on the diameter of the spheres and cylinders, and the thickness of the lamellae to < 30 nm. Such materials may be referred to as microphase separated. Figure 28 shows the predicted lamellar domain thickness for monodisperse

ethylene/octene diblock copolymers at different values of total molecular weight and Δ octene mole %. The figure demonstrates that, even at very large differences in octene content of the blocks, molecular weights in excess of 180,000 g/mol are necessary to achieve domain sizes of 50 nm. The high viscosity which is unavoidable at such high molecular weights

5   greatly complicates the production and processing of these materials. The calculation applied the theoretical results of Matsen, M.W.; Bates, F.S. *Macromolecules* (1996) 29, 1091 at a temperature of 140 °C, a characteristic ratio of 7.5, and a melt density of 0.78 g/cm^3. The correlation between octene mole % and χ was determined using the experimental results of Reichart, G.C. et al, *Macromolecules* (1998) 31, 7886.

10   **[16]**   Block copolymers containing both crystalline and amorphous blocks can crystallize from disordered, rather than microphase separated, melts and produce a regular arrangement of crystalline lamellae as described in Rangarajan, P., Register, R.A., Fetters, L.J. *Macromolecules*, 26, 4640 (1993). The lamellar thickness of these materials is controlled by the composition and molecular weight of both blocks as described in theories by Dimarzio,

15   E.A., Guttmann, C.M., Hoffman, J.D., *Macromolecules*, 13, 1194 and Whitmore, M.D., Noolandi, J., *Macromolecules*, 21, 1482 (1988). For an ethylene based block copolymer, the maximum thickness of the crystalline region of these morphologies is the same as the maximum thickness of a high density polyethylene crystal which is about 22 nm.

     [17]   These materials based on batch anionic polymerization can be additionally

20   characterized as having very narrow molecular weight distributions, typically with Mw/Mn < 1.2, and correspondingly narrow molecular weight distributions of their individual segments. They have also only been examined in the form of diblock and triblock copolymers since these are more readily synthesized via living anionic polymerization than structures with higher numbers of blocks.

25   **[18]**   Block copolymers from olefin monomers prepared using living polymerization catalysts were recently reviewed by Domski, G. J.; Rose, J. M.; Coates, G. W.; Bolig, A. D.; Brookhart, M., in *Prog. Polym. Sci.* 32, 30–92, (2007). Some of these monodisperse block copolymers also showed the classical morphology of amorphous block copolymers such as styrene-butadiene-styrene (SBS). Several of these block copolymers contain crystallizable

30   segments or blocks, and crystallization of the segments in these systems was primarily constrained to the resulting microdomains. Syndiotactic polypropylene-block-poly(ethylene-co-propylene) and syndiotactic polypropylene-block-polyethylene, as described in

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Ruokolainen, J., Mezzenga, R., Fredrickson, G. H., Kramer, E. J., Hustad, P. D., and Coates,

G. W., in *Macromolecules*, 38(3); 851-86023 (2005), form microphase separated

morphologies with domain sizes consistent with monodisperse block copolymers (<60 nm).

Similarly, polyethylene-block-poly(ethylene-co-propylene)s, as described by Matsugi, T.;

5   Matsui, S.; Kojoh, S.; Takagi, Y.; Inoue, Y.; Nakano, T.; Fujita, T.; Kashiwa, N. in

Macromolecules, 35(13); 4880-4887 (2002), are described as having microphase separated

morphologies. Atactic polypropylene-block-poly(ethylene-co-propylene)s with narrow

molecular weight distributions (Mw/Mn = 1.07 – 1.3), as described in Fukui Y, Murata M.

Appl. Catal. A 237, 1–10 (2002), are claimed to form microphase separated morphologies

10   when blended with isotactic polypropylenes, with domains of amorphous poly(ethylene-co-

propylene) between 50 – 100 nm. No microphase separation was observed in the bulk block

copolymer.

[19]   Microphase separated diblock and triblock olefin block copolymers in which both

block types are amorphous have also been prepared using living olefin polymerization

15   techniques. A triblock poly(1-hexene)-block-poly(methylene-1,3-cyclopentene)-block-

poly(1-hexene) copolymer, as described by Jayaratne K. C., Keaton R. J., Henningsen D. A.,

Sita L.R., *J. Am. Chem. Soc.* 122, 10490–10491 (2000), with Mn = 30,900 g/mol and Mw/Mn

= 1.10 displayed a microphase separated morphology with cylinders of poly(methylene-1,3-

cyclopentane) sized about 8 nm wide. Poly(methylene-1,3-cyclopentane-co-

20   vinyltetramethylene)-block-poly(ethylene-co-norbornene) and poly(ethylene-co-propylene)-

block-poly(ethylene-co-norbornene), as described by Yoon, J.; Mathers, R. T.; Coates, G. W.;

Thomas, E. L. in *Macromolecules*, 39(5), 1913-1919 (2006), also display microphase

separated morphologies. The poly(methylene-1,3-cyclopentane-co-vinyltetramethylene)-

block-poly(ethylene-co-norbornene), with Mn = 450,000 g/mol and Mw/Mn = 1.41, has

25   alternating domains of 68 and 102 nm, while the poly(ethylene-co-propylene)-block-

poly(ethylene-co-norbornene), with Mn = 576,000 g/mol and Mw/Mn = 1.13, has domains

sized 35 – 56 nm. These samples demonstrate the difficulty in achieving domain sizes > 60

nm, as very high molecular weights are required to achieve such large domains.

[20]   Achieving microphase separated block copolymer morphologies usually requires

30   unfavorable dispersive interactions between the segments of the different blocks, as

characterized by the Flory-Huggins χ parameter, and high molecular weights. Representing

the average block molecular weight as N, a typical narrow polydispersity diblock containing

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equal amounts by volume of the two blocks requires a value of χ times N greater than 5.25 for the melt to display an ordered microphase morphology as shown by L. Leibler, *Macromolecules* 13, 1602 (1980). This minimum value of χN to achieve order increases to about 6 for triblock copolymers with equal volumes of the two block types. As the number of

5   blocks per molecule increases further, the required χN also increases and asymptotically approaches 7.55 in the limit of a large number of blocks per molecule as shown by T.A. Kavassalis, M.D. Whitmore, *Macromolecules* 24, 5340 (1991). Although multiblocks such as pentablocks have been shown to provide a substantial improvement in mechanical properties as described in T.J. Hermel, S.F. Hahn, K.A. Chaffin, W.W. Gerberich, F.S. Bates,

10   *Macromolecules* 36, 2190 (2003), the overall molecular weight of these multiblocks has to be large in order to meet the requirements for ordered melt morphologies. Since the energy requirements to process a polymer increase sharply with molecular weight, the commercial opportunities of such multiblocks may be limited.

[21]   However, theoretical studies by S.W. Sides, G.H. Fredrickson, *J. Chem. Phys.* 121,

15   4974 (2004) and D.M. Cooke, A. Shi, *Macromolecules* 39, 6661 (2006) have shown that the minimum χN for ordered morphologies decreases as the polydispersity of one or both of the block types is increased. When both block types have a most probable distribution of length, i.e. the ratio of weight average to number average block molecular weight is 2, the minimum value of χN, where N is the number average block length, in order to achieve an ordered

20   morphology is 2 for equal volumes of the two block types as shown by I.I. Potemkin, S.V. Panyukov, *Phys. Rev. E.* 57, 6902 (1998) for multiblocks in the mean-field limit. This lower value in χN translates to a substantial reduction in overall molecular weight for a melt ordered multiblock and, therefore, a drop in processing costs.

[22]   Another prediction of interest made by Potemkin, Panyukov and also by Matsen,

25   M.W., *Phys. Rev. Lett.* 99, 148304 (2007) is that each transition in morphology, including the transition from disorder to order, does not occur abruptly as in monodisperse block copolymers. Instead, there are regions of coexisting phases along each boundary. Along the order-order boundaries, the overall composition of a molecule may determine how it partitions between phases. For example, polydisperse diblocks along the boundary between

30   cylindrical and lamellar phases may have the more symmetric diblocks form lamellae while the asymmetric ones will tend to form cylinders. In the vicinity of the order-disorder boundary, molecules with longer blocks may form an ordered morphology while those with

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shorter blocks remain disordered. In some cases, these disordered molecules may form a distinct macrophase. Alternatively, the location of these molecules could be directed to the center of the ordered domains in a similar manner to the domain swelling that occurs when a homopolymer is blended with a block copolymer (Matsen, M.W., *Macromolecules* **28**, 5765

5   (1995)).

[23] In addition to achieving microphase separation at lower values of χN, block length polydispersity has also been hypothesized to have a pronounced effect on the domain spacing of the ordered structures. The size of the microdomains in monodisperse block copolymers is largely a function of the average molecular weight of a block, N, and is typically on the order

10 of ~20-50 nm. However, it has been predicted that polydispersity leads to larger domain spacings as compared with equivalent monodisperse block copolymers (Cooke, D. M.; Shi, A. C. *Macromolecules*, *39*, 6661-6671 (2006); Matsen, M.W., *Eur. Phys. J. E*, *21*, 199-207 (2006)). The effects of polydispersity on phase behavior have also been demonstrated experimentally. Matsushita and coworkers approximated polydispersity by blending a series

15 of monodisperse polystyrene-*b*-poly(2-vinylpyridine)s (Noro, A.; Cho, D.; Takano, A.; Matsushita, Y. *Macromolecules*, *38*, 4371-4376 (2005)). Register and coworkers found ordered morphologies in a series of polystyrene-*b*-poly(acrylic acid)s synthesized using a controlled radical polymerization technique (Bendejacq, D.; Ponsinet, V.; Joanicot, M.; Loo, Y. L.; Register, R. A. *Macromolecules*, *35*, 6645-6649 (2002)). Most recently, Lynd and

20 Hillmyer (Lynd, N. A.; Hillmyer, M. A. *Macromolecules*, *38*, 8803-8810 (2005)) evaluated a series of monodisperse poly(ethylene-*alt*-propylene)s that were chain extended with a block of poly(DL-lactide) using synthetic techniques that introduced polydispersity in the poly(DL-lactide) block. In all of these examples polydispersity led to increased domain spacings, suggesting that the longer blocks have a greater role in determining domain size. In some

25 instances, polydispersity also produced changes in the type of ordered morphology. The range of techniques for synthesis of polydisperse block copolymers is extremely limited, and it is especially difficult to introduce polydispersity in multiple blocks while maintaining a high fraction of block copolymer.

[24] The tendency for longer block lengths to have a greater role in determining domain

30 size, combined with the ability to swell domains, creates the potential for domain sizes that are much larger than what is observed in typical monodisperse block copolymers. The ability for some molecules to be ordered and others disordered contributes to the formation of swollen domains. The morphology of these systems can be termed block copolymer-directed

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mesophase separation.

[25]   It would be useful to provide an olefin block copolymer with an overall molecular weight distribution and segment molecular weight distribution such that Mw/Mn > 1.4, that is mesophase separated. It would also be useful to provide such a material that is a multi-block copolymer with a distribution in the number of blocks.

[26]   In addition, there is an unfulfilled need for mesophase separated block copolymers which are based on ethylene and α-olefins. There is also a need for block copolymers with low molecular weights (Mw<250,000 g/mol) that form domains larger than those from monodisperse block copolymers of the prior art, namely greater than 60 nm in the smallest dimension. There is also a need for a method of making such block copolymers.

SUMMARY OF THE INVENTION

[27]   The invention provides a composition comprising:

A)   a thermoplastic polymer composition, and

B) impact modifying amount of an ethylene/α-olefin block interpolymer comprising hard blocks and soft blocks, wherein the ethylene/α-olefin block interpolymer is characterized by a molecular weight distribution, M_w/M_n, in the range of from about 1.4 to about 2.8 and:

(a)   has 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:

$T_m > -6553.3 + 13735(d) - 7051.7(d)^2$, or

(b)   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,

$\Delta T \geq 48°C$ 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

(c)   is characterized by 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

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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

5   (d)   has 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 10   on the whole polymer) within 10 percent of that of the ethylene/α-olefin interpolymer; or

(e)   has a storage modulus at 25°C, G'(25°C), and a storage modulus at 100°C, G'(100°C), wherein the ratio of G'(25°C) to G'(100°C) is in the range of about 1:1 to about 9:1; or

(f)   is characterized by an average block index greater than zero and up to about 1.0; and, wherein the ethylene/α-olefin block interpolymer is mesophase separated.

15   [28]   In addition, the invention provides a composition comprising an ethylene/α-olefin block copolymer wherein the copolymer is characterized by an average molecular weight of greater than 40,000 g/mol, a molecular weight distribution, Mw/Mn, in the range of from about 1.4 to about 2.8, and a difference in mole percent α-olefin content between the soft block and the hard block of greater than about 20 mole percent; and, one or more olefin 20   copolymers.

[29]   The invention also provides an article made from the above described compositions.

BRIEF DESCRIPTION OF THE DRAWINGS

[30]   Figure 1 shows the melting point/density relationship for mesophase separated olefin 25   block copolymers (represented by diamonds) as compared to traditional random copolymers (represented by squares).

[31]   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; and the circles represent polymer Examples 29-40.

30   [32]   Figure 3 shows the effect of density on elastic recovery for unoriented films made from olefin block copolymers (represented by the squares and circles) and traditional copolymers (represented by the triangles which are AFFINITY® polymers (The Dow Chemical Company)). The squares represent inventive ethylene/butene copolymers; and the

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circles represent inventive ethylene/octene copolymers.

[33]   Figure 4 is a plot of octene content of Temperature Rising Elution Fractionation

("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

5   comparative polymers E and F (represented by the "X" symbols). The diamonds represent

traditional random ethylene/octene copolymers.

[34]   Figure 5 is a plot of octene content of TREF fractionated ethylene/1-octene copolymer

fractions versus ATREF elution temperature of the fraction for the polymer of Example 5 and

for comparative F*. The squares represent Polymer Example F*; and the triangles represent

10   Polymer Example 5. Also shown is the ATREF temperature distribution for Example 5

(curve 1) and comparative F* (curve 2).

[35]   Figure 6 is a graph of log 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 made with differing quantities of

15   chain shuttling agent (curves 1).

[36]   Figure 7 is a plot of natural log ethylene mole fraction for random ethylene/α-olefin

copolymers as a function of the inverse of DSC peak melting temperature or ATREF peak

temperature. The filled squares represent data points obtained from random homogeneously

branched ethylene/α-olefin copolymers in ATREF; and the open squares represent data points

20   obtained from random homogeneously branched ethylene/α-olefin copolymers in DSC. "P"

is the ethylene mole fraction; "T" is the temperature in Kelvin.

[37]   Figure 8 is a plot constructed on the basis of the Flory equation for random

ethylene/α-olefin copolymers to illustrate the definition of "block index." "A" represents the

whole, perfect random copolymer; "B" represents a pure "hard segment"; and "C" represents

25   the whole, perfect block copolymer having the same comonomer content as "A". A, B, and C

define a triangular area within which most TREF fractions would fall.

[38]   Figure 9 is a plot of the block index calculated for each TREF fraction for four

polymers. The diamonds represent Polymer F* with an average block index of 0; the

triangles represent Polymer 5 with an average block index of 0.53; the squares represent

30   Polymer 8 with an average block index of 0.59; and the "X" represents Polymer 20 with an

average block index of 0.20.

[39]   Figure 10 is a plot of the block index calculated for each TREF fraction for two block

copolymers: the filled bars represent Polymer 18B; and the open bars represent Polymer 5.

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[40]   Figure 11 is a plot of the average block index calculated for nine different polymers as a function of the diethyl zinc concentration during polymerization in terms of "[Zn/C₂H₄]*1000." "x" represents an ethylene/propylene block copolymer (Polymer 23); the two triangles represent two ethylene/butene block copolymers (Polymer 21 and Polymer 22); and the squares represent ethylene/octene copolymers made at different levels of diethyl zinc (including one made without any diethyl zinc).

[41]   Figure 12 is a plot of the square root of the second moment about the mean weight average block index as a function of [Zn/C₂H₄]*1000.

[42]   Figure 13 is a representation of a normal DSC profile for an olefin block copolymer.

[43]   Figure 14 is a weighted DSC profile obtained by converting Figure 13.

[44]   Figure 15 is a ^{13}C NMR spectrum of Polymer 19A.

[45]   Figure 16 is an AFM image of Ex. 32 at ~3,000X magnification.

[46]   Figure 17 is an AFM image of Ex. 33 at a ~3,000X magnification.

[47]   Figure 18 shows an AFM image at ~3,000X magnification of Ex. 34.

[48]   Figure 19 shows a TEM image at ~30,000X magnification of Ex. 34.

[49]   Figure 20 is an AFM image of a styrenic block copolymer (SBC, 28 wt% styrene, 83 mol% "butane" in the B-block, M_n = 64,000 g/mol) at 30,000X magnification.

[50]   Figure 21 is a plot of Shore A vs Density for Examples 26, 27, 30 and 31.

[51]   Figure 22 is a plot of Modulus vs Density for Examples 26, 27, 30 and 31.

[52]   Figure 23 is a plot of 70 °C Compression Set vs Shore A for Examples 26, 27, 30 and 31.

[53]   Figure 24 is a plot of log storage modulus as a function of temperature for Examples 27 and 31.

[54]   Figure 25 is a plot of Tan δ as a function of temperature for Examples 26 and 30.

[55]   Figure 26 is a plot of Tan δ as a function of temperature for Examples 27 and 31.

[56]   Figure 27 is a plot of 70 °C Compression Set vs Shore A for Blends 1, 2, 3 and 4. Blends 1 and 2 comprise 35% OBC, 50% oil and 15% hPP and Blends 3 and 4 comprise 28% OBC, 60% oil and 12% hPP.

[57]   Figure 28 is a plot of the predicted thickness of each domain for a monodisperse ethylene/octene diblock copolymer made with 50% of each block type at different values of the backbone molecular weight, as measured by conventional GPC, and different levels of Δ octene mole %.

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[58]   Figure 29 shows reflectance spectra for Examples 35 - 38 and a comparative random copolymer AFFINITY® 1280G, available from The Dow Chemical Company. The random copolymer shows little reflectance (<10%) of the light in the explored range, while the inventive examples show higher reflectance across this range.

[59]   Figure 30 shows reflectance spectra for Examples 29, 30, 32, and 33 and the comparative AFFINITY® 1280G, available from The Dow Chemical Company. The random copolymer shows little reflectance (<10%) of the light in the explored range, while the inventive examples show higher reflectance across this range.

[60]   Figure 31 shows reflectance spectra for Examples 34, 39, and 40 and the comparative AFFINITY® 1280G, available from The Dow Chemical Company. The random copolymer shows little reflectance (<10%) of the light in the explored range, while the inventive examples show higher reflectance across this range.

[61]   Figure 32 shows reflectance spectra for Examples 25 and 26. These examples show little reflectance (<12%) of the light in the explored range.

[62]   Figure 33 is a plot of I_{10}/I_2 as a function of the difference in octene content (mol%) of the hard and soft segments, referred to as Δ octene.

[63]   Figure 34 shows a plot of Heat of Fusion vs. ATREF Elution Temperature for fractions of random ethylene-octene copolymers and for fractions of inventive Example 34.

[64]   Figure 35 shows a plot of DSC Tm vs. mol % octene for ATREF fractions of random ethylene-octene copolymers and for fractions of inventive Example 34.

[65]   Figure 36 compares the morphology of inventive formulation F15 as compared to comparative formulation CF9.

DESCRIPTION OF EMBODIMENTS OF THE INVENTION

General Definitions

[66]   "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."

[67]   "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

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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.

[68]   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 75 mole percent of the whole polymer and an octene content of from about 5 to about 25, preferably from about 10 to about 20 mole percent of the whole polymer, and more preferably from about 15 to about 20 mole percent of the whole polymer. For many ethylene/butene copolymers, the preferred composition comprises an ethylene content greater than about 60 mole percent of the whole polymer and a butene content of from about 10 to about 40, preferably from about 20 to about 35 mole percent of the whole polymer, and more preferably from about 25 to about 30 mole percent of the whole polymer. For many ethylene/propylene copolymers, the preferred composition comprises an ethylene content greater than about 40 mole percent of the whole polymer and a propylene content of from about 15 to about 60, preferably from about 25 to about 50 mole percent of the whole polymer, and more preferably from about 35 to about 45 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.

[69]   The term "crystalline" if employed, refers to a polymer or a segment that possesses a first order transition or crystalline melting point (Tm) as determined by differential scanning calorimetry (DSC) or equivalent technique. The term may be used interchangeably with the term "semicrystalline". The crystals may exist as stacks of closely packed lamellar crystals, lamellae forming the arms of spherulites, or as isolated lamellar or fringed micellar crystals. The term "amorphous" refers to a polymer lacking a crystalline melting point as determined

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by differential scanning calorimetry (DSC) or equivalent technique.

[70]   The term "multi-block copolymer" or "segmented copolymer" refers to a polymer comprising two or more chemically distinct regions or segments (also referred to as "blocks") preferably joined in a linear manner, that is, a polymer comprising chemically differentiated

5   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

10   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 of making the copolymers. More specifically, when produced in a continuous process, the polymers desirably possess PDI

15   from about 1.4 to about 8, preferably from about 1.4 to about 3.5, more preferably from about 1.5 to about 2.5, and most preferably from about 1.6 to about 2.5 or from about 1.6 to about 2.1. When produced in a batch or semi-batch process, the polymers possess PDI from about 1.4 to about 2.9, preferably from about 1.4 to about 2.5, more preferably from about 1.4 to about 2.0, and most preferably from about 1.4 to about 1.8. It is noted that "block(s)" and

20   "segment(s)" are used herein interchangeably. In addition, the blocks of the polymer have a PDI in the range of from about 1.4 to about 2.5, preferably in the range of from about 1.4 to about 2.3, and more preferably in the range of from about 1.5 to about 2.3.

[71]   "Impact-modifying amount of ethylene/α-olefin multi-block interpolymer" is a quantity of ethylene/α-olefin multi-block interpolymer added to a given polymer composition

25   such that the composition's notched Izod impact strength at room temperature or below is maintained or increased as compared to said given composition's notched Izod impact strength at the same temperature without the added ethylene/α-olefin multi-block interpolymer or such that the percent ductile for the composition is greater than or equal to 50% at -20 °C.

30   [72]   As used herein, "mesophase separation" means a process in which polymeric blocks are locally segregated to form ordered domains. Crystallization of the ethylene segments in these systems is primarily constrained to the resulting mesodomains and such systems may be referred to as "mesophase separated". These mesodomains can take the form of spheres,

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cylinders, lamellae, or other morphologies known for block copolymers. The narrowest dimension of a domain, such as perpendicular to the plane of lamellae, is generally greater than about 40 nm in the mesophase separated block copolymers of the instant invention.

[73]   The ethylene/α-olefin block interpolymer may have a value of χN, where N is the number average block length, in the range of from about 2 to about 20, preferably in the range of from about 2.5 to about 15, and more preferably in the range of from about 3 to about 10.

[74]   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: $R=R^L+k*(R^U-R^L)$, 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.

[75]   Embodiments of the invention provide a new class of ethylene/α-olefin block interpolymers (hereinafter "inventive polymer", "ethylene/α-olefin interpolymers", or variations thereof). 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, wherein the polymers are mesophase separated. 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:

$(AB)_n$

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 linear fashion, not in a branched or a star fashion. "Hard" segments refer to blocks of polymerized units in which ethylene is present in an amount greater than 95 weight percent, and preferably greater than 98 weight percent. In other words, the comonomer content in the hard segments is less than 5

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weight percent, and preferably less than 2 weight percent. In some embodiments, the hard segments comprise all or substantially all ethylene. "Soft" segments, on the other hand, refer to blocks of polymerized units in which the comonomer content is greater than 5 weight percent, preferably greater than 8 weight percent, greater than 10 weight percent, or greater

5 than 15 weight percent. In some embodiments, the comonomer content in the soft segments can be greater than 20 weight percent, greater than 25 weight percent, greater than 30 weight percent, greater than 35 weight percent, greater than 40 weight percent, greater than 45 weight percent, greater than 50 weight percent, or greater than 60 weight percent.

[76]   In some embodiments, A blocks and B blocks are randomly distributed along the

10 polymer chain. In other words, the block copolymers usually do not have a structure like: AAA—AA-BBB—BB.

[77]   In other embodiments, the block copolymers usually do not have a third type of block. In still other embodiments, each of block A and block B has monomers or comonomers randomly distributed within the block. In other words, neither block A nor block B

15 comprises two or more segments (or sub-blocks) of distinct composition, such as a tip segment, which has a different composition than the rest of the block.

[78]   The melt index of the ethylene/α-olefin interpolymers can range from 0.1- 15 dg/min at 190°C. The composite density may range from 0.855 g/cc to 0.890 g/cc, preferably from 0.860 g/cc to 0.880 g/cc, and more preferably from 0.865 g/cc to 0.875 g/cc. In some

20 embodiments, the amount of hard block ranges from about 10 wt% to 40 wt%, preferably from about 15wt% to 25 wt% and more preferably from about 15 wt% to 17 wt%. In other embodiments, the amount of hard block preferably ranges from about 5 wt% to about 15 wt%. The content of alpha olefin in the soft block may range from about 20 mol% to about 40 mol%, preferably from about 25 to about 35 mole% and in some embodiments, from

25 about 23 wt% to about 30 wt%. 1-butene, 1-hexene, and 1-octene are preferred alpha olefins. 1-octene is the most preferred alpha olefin.

[79]   The ethylene/α-olefin interpolymers of the invention may be characterized as mesophase separated. Domain sizes are typically in the range of from about 40 nm to about 300 nm, preferably in the range of from about 50 nm to about 250 nm, and more preferably in

30 the range of from about 60 nm to about 200 nm, as measured by the smallest dimension such as perpendicular to the plane of lamellae or the diameter of spheres or cylinders. In addition, domains may have smallest dimensions that are greater than about 60 nm, greater than about 100 nm, and greater than about 150 nm. Domains may be characterized as cylinders, spheres,

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lamellae, or other morphologies known for block copolymers. The mesophase separated

polymers comprise olefin block copolymers wherein the amount of comonomer in the soft

segments as compared to that in the hard segments is such that the block copolymer

undergoes mesophase separation in the melt. The required amount of comonomer may be

5   measured in mole percent and varies with each comonomer. A calculation may be made for

any desired comonomer in order to determine the amount required to achieve mesophase

separation. The minimum level of incompatibility, expressed as χN, to achieve mesophase

separation in these polydisperse block copolymers is predicted to be $\chi N=2.0$ (I.I. Potemkin,

S.V. Panyukov, *Phys. Rev. E.* 57, 6902 (1998)). Recognizing that fluctuations usually push

10   the order-disorder transition in commercial block copolymers to slightly higher χN, a value

$\chi N=2.34$ has been used as the minimum in the calculations below. Following the approach

of D.J. Lohse, W.W. Graessley, <u>Polymer Blends Volume 1: Formulation</u>, ed. D.R. Paul, C.B.

Bucknall, 2000, χN can be converted to the product of χ/v and M/ρ where v is a reference

volume, M is the number average block molecular weight and ρ is the melt density. The melt

15   density is taken to be $0.78 g/cm^3$ and a typical value of block molecular weight is

approximately 25,500 g/mol based on a diblock at an overall molecular weight of 51,000

g/mol. χ/v for cases in which the comonomer is butene or propylene is determined using 130

°C as the temperature and then performing an interpolation or extrapolation of the data

provided in Table 8.1 in the reference by Lohse and Graessley. For each comonomer type, a

20   linear regression in mole percent comonomer was performed. For cases in which octene is

the comonomer, the same procedure was performed with the data of Reichart, G.C. et al,

Macromolecules (1998), 31, 7886. The entanglement molecular weight at 413 K (about 140

°C) in kg/mol is taken to be 1.1. Using these parameters, the minimum difference in

comonomer content is determined to be, respectively, 20.0, 30.8 or 40.7 mole percent when

25   the comonomer is octene, butene, or propylene. When the comonomer is 1-octene, the

difference in mole percent octene between the hard segment and the soft segment, Δ octene,

is greater than or equal to about 20.0 mole percent, more preferably greater than or equal to

about 22 mole percent and may also be greater than or equal to about 23 mole percent, greater

than or equal to 24 mole percent, greater than about or equal to 25 mole percent and greater

30   than about or equal to 26 mole percent. In addition, the Δ octene value may be in the range

of from about 20.0 mole percent to about 60 mole percent and more preferably in the range of

from about 22 mole percent to about 45 mole percent. When the comonomer is 1-butene, the

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difference in mole percent butene between the hard segment and the soft segment, Δ butene, is greater than or equal to about 30.8 mole percent, more preferably greater than or equal to about 33.9 mole percent and may also be greater than or equal to about 35.4 mole percent, greater than or equal to 36.9 mole percent, greater than or equal to about 38.5 mole percent

5   and greater than or equal to about 40.0. In addition, the Δ butene value may be in the range of from about 30.8 mole percent to about 80 mole percent, preferably in the range of from about 33.9 mole percent to about 60 mole percent, preferably in the range of from about 36 mole percent to about 50 mole percent and more preferably in the range of from about 37 mole percent to about 40 mole percent. When the comonomer is propylene, the difference in

10   mole percent propylene between the hard segment and the soft segment, Δ propylene, is greater than or equal to about 40.7 mole percent, greater than or equal to about 44.7 mole percent, preferably greater than or equal to about 46.8 mole percent, more preferably greater than or equal to about 48.8 mole percent and may also be greater than or equal to about 50.9 mole percent, and greater than or equal to 52.9 mole percent. In addition, the Δ propylene

15   value may be in the range of from about 40.7 mole percent to about 95 mole percent, preferably in the range of from about 44.7 mole percent to about 65 mole percent and more preferably in the range of from about 48.8 mole percent to about 60 mole percent.

[80]   The mesophase separated ethylene/α-olefin interpolymers may have characteristics of photonic crystals, periodic optical structures designed to affect the motion of photons.

20   Certain compositions of these mesophase separated ethylene/α-olefin interpolymers appear pearlescent by eye. In some instances, films of the mesophase separated ethylene/α-olefin interpolymers reflect light across a band of wavelengths in the range between about 200 nm to about 1200 nm. For example, certain films appear blue via reflected light but yellow via transmitted light. Other compositions reflect light in the ultraviolet (UV) range, from about

25   200 nm to about 400 nm, while others reflect light in the infrared (IR) range, from about 750 nm to about 1000 nm.

[81]   The ethylene/α-olefin interpolymers are characterized by an average block index, ABI, which is greater than zero and up to about 1.0 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

30   block index ("BI") for each of the polymer fractions obtained in preparative TREF (i.e., fractionation of a polymer by Temperature Rising Elution Fractionation) from 20 °C and 110 °C, with an increment of 5 °C (although other temperature increments, such as 1 °C, 2 °C, 10 °C, also can be used):

20

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

where BI_i is the block index for the ith fraction of the inventive ethylene/α-olefin interpolymer obtained in preparative TREF, and w_i is the weight percentage of the ith fraction. Similarly, the square root of the second moment about the mean, hereinafter referred to as the second

5   moment weight average block index, can be defined as follows.

$$2^{nd} \text{ moment weight average } BI = \sqrt{\frac{\sum (w_i (BI_i - ABI)^2)}{\frac{(N-1)\sum w_i}{N}}}$$

where N is defined as the number of fractions with BI_i greater than zero. Referring to Figure 9, for each polymer fraction, BI is defined by one of the two following equations (both of which give the same BI value):

10    $$BI = \frac{1/T_X - 1/T_{XO}}{1/T_A - 1/T_{AB}} \text{ or } BI = -\frac{LnP_X - LnP_{XO}}{LnP_A - LnP_{AB}}$$

where T_X is the ATREF (i.e., analytical TREF) elution temperature for the ith fraction (preferably expressed in Kelvin), P_X is the ethylene mole fraction for the ith fraction, which can be measured by NMR or IR as described below. P_{AB} is the ethylene mole fraction of the whole ethylene/α-olefin interpolymer (before fractionation), which also can be measured by

15   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 interpolymer). As an approximation or for polymers where the "hard segment" composition is unknown, the T_A and P_A values are set to those for high density polyethylene homopolymer.

[82] T_{AB} is the ATREF elution temperature for a random copolymer of the same

20   composition (having an ethylene mole fraction of P_{AB}) and molecular weight as the inventive copolymer. T_{AB} can be calculated from the mole fraction of ethylene (measured by NMR) using the following equation:

Ln P_{AB} = α/T_{AB} + β

where α and β are two constants which can be determined by a calibration using a number of

25   well characterized preparative TREF fractions of a broad composition random copolymer and/or well characterized random ethylene copolymers with narrow composition. It should be noted that α and β may vary from instrument to instrument. Moreover, one would need to create an appropriate calibration curve with the polymer composition of interest, using appropriate molecular weight ranges and comonomer type for the preparative TREF fractions

30   and/or random copolymers used to create the calibration. There is a slight molecular weight

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effect. If the calibration curve is obtained from similar molecular weight ranges, such effect would be essentially negligible. In some embodiments as illustrated in Figure 8, random ethylene copolymers and/or preparative TREF fractions of random copolymers satisfy the following relationship:

5     $\text{Ln } P = -237.83/T_{ATREF} + 0.639$.

[83]   The above calibration equation relates the mole fraction of ethylene, P, to the analytical TREF elution temperature, T_{ATREF}, for narrow composition random copolymers and/or preparative TREF fractions of broad composition random copolymers. T_{XO} is the ATREF temperature for a random copolymer of the same composition (i.e., the same

10   comonomer type and content) and the same molecular weight and having an ethylene mole fraction of P_X. T_{XO} can be calculated from $\text{Ln} P_X = \alpha/T_{XO} + \beta$ from a measured P_X mole fraction. Conversely, P_{XO} is the ethylene mole fraction for a random copolymer of the same composition (i.e., the same comonomer type and content) and the same molecular weight and having an ATREF temperature of T_X, which can be calculated from $\text{Ln } P_{XO} = \alpha/T_X + \beta$ using

15   a measured value of T_X.

[84]   Further description of the block index methodology may be found in U.S. Patent Application Publication No. 2006/0199930, published on September 7, 2006, which is herein incorporated by reference in its entirety; as well as in *Macromolecular Symposia*, Vol 257, (2007), pp 80-93 which is incorporated by reference herein in its entirety.

20   [85]   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 0.4 or from about 0.1 to about 0.3. In other embodiments, ABI is greater than about 0.4 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 about 0.6 to

25   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.

30   [86]   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 the polymer having a molecular weight distribution, M_w/M_n,

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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

5   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

10   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.

[87]   In addition to an average block index and individual fraction block indices, the ethylene/α-olefin interpolymers are characterized by one or more of the properties described

15   as follows.

[88]   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:

20    $T_m > -6553.3 + 13735(d) - 7051.7(d)^2$, and preferably

$T_m \geq -6880.9 + 14422(d) - 7404.3(d)^2$, and more preferably

$T_m \geq -7208.6 - 15109(d) - 7756.9(d)^2$.

[89]   Such melting point/density relationship is illustrated in Figure 1. Unlike the traditional random copolymers of ethylene/α-olefins whose melting points decrease with

25   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 125 °C when density ranges from 0.855 g/cc to about 0.895 g/cc. In some embodiments, the melting point of such polymers are in the range of about 110

30   °C to about 125 °C when density ranges from 0.855 g/cc to about 0.895 g/cc.

[90]   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

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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:

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

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

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

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

10   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

15   ethylene octene comparative polymers corresponds to the equation $\Delta T = -0.1299 (\Delta H) + 62.81$.

[91]   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

20   higher, preferably at least 5 percent higher, more preferably at least 10 percent higher, than that of a comparable random ethylene interpolymer fraction eluting between the same temperatures, wherein the comparable random ethylene interpolymer 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 interpolymer. Preferably, the Mw/Mn

25   of the comparable interpolymer is also within 10 percent of that of the block interpolymer and/or the comparable interpolymer has a total comonomer content within 10 weight percent of that of the block interpolymer.

[92]   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-

30   molded film of an 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); and preferably

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Re ≥1491-1629(d); and more preferably

Re ≥1501-1629(d); and even more preferably

Re ≥1511-1629(d).

[93]   Figure 3 shows the effect of density on elastic recovery for unoriented films made

5   from certain block interpolymers and traditional random copolymers. For the same density,

the block interpolymers have substantially higher elastic recoveries.

[94]   In some embodiments, the ethylene/α-olefin interpolymers have 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

10   11 cm/minute.

[95]   In other embodiments, the ethylene/α-olefin interpolymers have (1) a storage modulus

ratio, G'(25°C)/G'(100°C), of from 1 to 20, preferably from 1 to 10, more preferably from 1

to 5; 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

15   a compression set of 0 percent.

[96]   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.

20   [97]   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.

[98]   In some embodiments, the multi-block copolymers possess a PDI fitting a Schultz-

25   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

30   including terminal blocks.

[99]   In addition, the inventive block interpolymers have additional characteristics or

properties. In one aspect, the interpolymers, preferably comprising ethylene and one or more

copolymerizable comonomers in polymerized form, are characterized by multiple blocks or

25

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, characterized in that said fraction has a molar comonomer content

5   higher, preferably at least 5 percent higher, more preferably at least 10 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), 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

10   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.

[100]   Comonomer content may be measured using any suitable technique, with techniques

based on nuclear magnetic resonance ("NMR") spectroscopy preferred. Moreover, for

15   polymers or blends of polymers having relatively broad TREF curves, the polymer is first

fractionated using TREF into fractions each having an eluted 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 interpolymer.

20   [101]   In 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 (i.e., at least two 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

25   peak (but not just a molecular fraction) which elutes between 40°C and 130°C (but without

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

30   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

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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

5   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

10   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

15   determined by referencing this calibration curve using its FWHM methyl : methylene area ratio [CH_3/CH_2] of the TREF peak.

       [102]   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 a higher molar comonomer content than a corresponding

20   comparable interpolymer.

       [103]   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

25   TREF fraction being compared, measured in °C.

       [104]   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

30   is depicted by a dotted line. Also depicted are the comonomer contents for fractions of a block ethylene/1-octene interpolymer. 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 olefin block copolymer and is believed to be due to the presence

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of differentiated blocks within the polymer chains, having both crystalline and amorphous nature.

[105] Figure 5 graphically displays the TREF curve and comonomer contents of polymer fractions for Example 5 and comparative F to be discussed below. The peak eluting from

5   40°C to 130°C, preferably from 60°C to 95°C for both polymers is fractionated in 5°C increments. Actual data for three of the fractions for Example 5 are represented by triangles. The skilled artisan can appreciate that an appropriate calibration curve may be constructed for interpolymers with differing comonomer content fitted to the ATREF temperature values. Preferably, such calibration curve is obtained using comparative interpolymers of the same

10   monomers, preferably random copolymers made using a metallocene or other homogeneous catalyst composition. The olefin block copolymers are characterized by a molar comonomer content greater than the value determined from the calibration curve at the same ATREF elution temperature, preferably at least 5 percent greater, more preferably at least 10 percent greater.

15   [106] 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

20   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

25   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 Mw/Mn of the comparable interpolymer is also within 10 percent of that of the blocked interpolymer and/or the

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

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[107] 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 0.890 g/cm^3, 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

5   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.

[108] In still another aspect, the inventive polymer is an olefin interpolymer, preferably

10   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

15   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 mol percent comonomer, has a DSC melting point that corresponds to the equation:

20   Tm ≥ (-5.5926)(mol percent comonomer in the fraction) + 135.90.

[109] 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-

25   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 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:

[110]   Heat of fusion (J/gm) ≤ (3.1718)(ATREF elution temperature in Celsius) –

30   136.58,

[111] 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

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a melt enthalpy (heat of fusion) as measured by DSC, corresponding to the equation:

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

ATREF Peak Comonomer Composition Measurement by Infra-Red Detector

[112] 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/).

[113] The "composition mode" of the detector is equipped with a measurement sensor (CH_2) and composition sensor (CH_3) that are fixed narrow band infra-red filters in the region of 2800-3000 cm^{-1}. The measurement sensor detects the methylene (CH_2) carbons on the polymer (which directly relates to the polymer concentration in solution) while the composition sensor detects the methyl (CH_3) groups of the polymer. The mathematical ratio of the composition signal (CH_3) divided by the measurement signal (CH_2) is sensitive to the comonomer content of the measured polymer in solution and its response is calibrated with known ethylene alpha-olefin copolymer standards.

[114] The detector when used with an ATREF instrument provides both a concentration (CH_2) and composition (CH_3) signal response of the eluted polymer during the TREF process. A polymer specific calibration can be created by measuring the area ratio of the CH_3 to CH_2 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 CH_3 and CH_2 response (i.e. area ratio CH_3/CH_2 versus comonomer content).

[115] 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 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.

[116] 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 systems as described in the following references: Markovich, Ronald P.; Hazlitt, Lonnie G.;

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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

5   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.

[117] It should be noted that while the TREF fractions in the above description are obtained in a 5 °C increment, other temperature increments are possible. For instance, a TREF fraction

10   could be in a 4 °C increment, a 3 °C increment, a 2 °C increment, or 1 °C increment.

[118] 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 90 J/g or less; (3) an

15   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.

[119] 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.

20   Moreover, the inventive polymers possess a relatively flat storage modulus as a function of temperature in the range from 0 to 100°C (such as that illustrated in Figure 6 and Figure 24) 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

25   order of magnitude between 50 and 100°C, preferably between 0 and 100°C).

[120] 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

30   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 1g/10 minutes, 3 g/10 minutes or 5 g/10 minutes. In other embodiments, the melt index can

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be in the range of from 0.01 dg/min to 15 dg/min.

[121]   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.

5   [122]   The α-olefin content in the ethylene/α-olefin interpolymers can be about 25 mol% to about 65 mol%. When the α-olefin is octene, it is preferably present in an amount from about 25 mol% to about 40 mol%, more preferably in amount from about 28 mol % to 38 mole %. When the α-olefin is butene, it is preferably present in an amount from about 40 mol% to about 60 mol%, more preferably in an amount from about 45 mol% to about 55 mol%.

10   When the α-olefin is propylene, it is preferably present in an amount from about 45 mol% to about 60 mol%, more preferably in amount from about 47 mol% to about 57 mol%.

[123]   The process of making the polymers has been disclosed in the following patent applications and publications: 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

15   Application No. 60/662,939, filed March 17, 2005; U.S. Provisional Application No. 60/5662938, filed March 17, 2005; PCT Application No. PCT/US2005/008916, filed March 17, 2005; PCT Application No. PCT/US2005/008915, filed March 17, 2005; PCT Application No. PCT/US2005/008917, filed March 17, 2005; PCT Publication No. WO 2005/090425, published September 29, 2005; PCT Publication No. WO 2005/090426,

20   published September 29, 2005; and, PCT Publication No. WO 2005/090427, published September 29, 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:

25   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

30   (C) a chain shuttling agent.

[124]   Representative catalysts and chain shuttling agents are as follows.

[125]   **Catalyst (A1)** is [N-(2,6-di(1-methylethyl)phenyl)amido)(2-isopropylphenyl)(α-

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naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium dimethyl, prepared according to the teachings of WO 03/40195, U.S. Patents No. 6,953,764 and No. 6,960,635, and WO 04/24740.
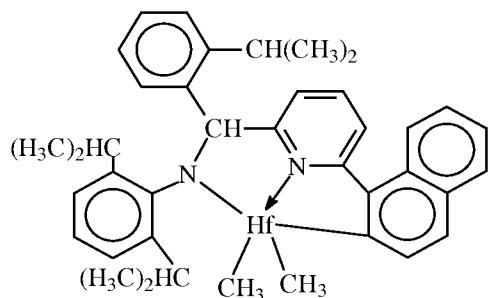
5   **[126]**   **Catalyst (A2)** is [N-(2,6-di(1-methylethyl)phenyl)amido)(2-methylphenyl)(1,2-phenylene-(6-pyridin-2-diyl)methane)]hafnium dimethyl, prepared according to the teachings of WO 03/40195, U.S. Patents No. 6,953,764 and No. 6,960,635, and WO 04/24740.
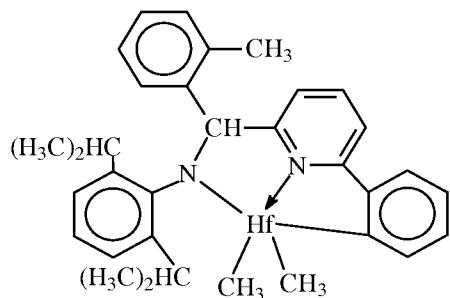
[127]   **Catalyst (A3)** is bis[N,N'''-(2,4,6-tri(methylphenyl)amido)ethylenediamine]hafnium

10   dibenzyl.

X= CH$_2$C$_6$H$_5$
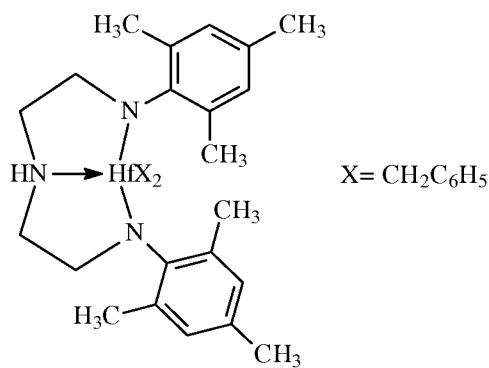
[128]   **Catalyst (A4)** is bis((2-oxoyl-3-(dibenzo-1H-pyrrole-1-yl)-5-(methyl)phenyl)-2-phenoxymethyl)cyclohexane-1,2-diyl zirconium (IV) dibenzyl, prepared substantially according to the teachings of U.S. Patent No. 6,897,276.
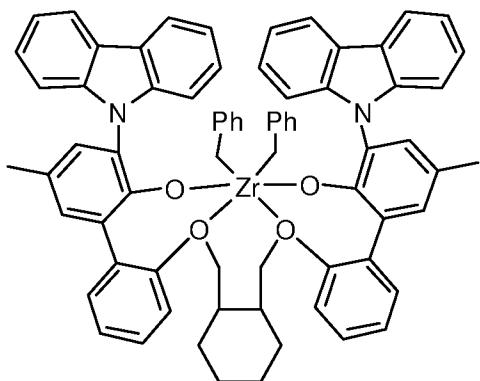
[129] **Catalyst (B1)** is 1,2-bis-(3,5-di-t-butylphenylene)(1-(N-(1-methylethyl)immino)methyl)(2-oxoyl) zirconium dibenzyl

$X = CH_2C_6H_5$
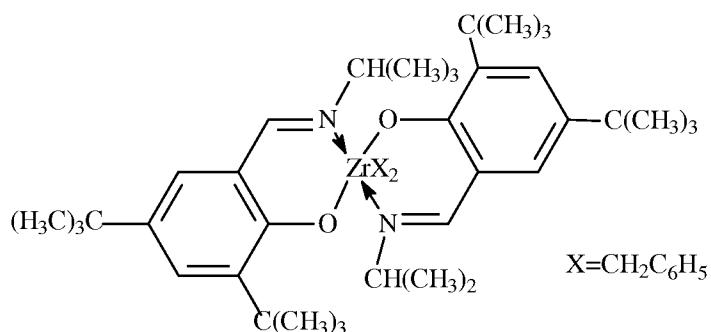
5   **[130]** **Catalyst (B2)** is 1,2-bis-(3,5-di-t-butylphenylene)(1-(N-(2-methylcyclohexyl)-immino)methyl)(2-oxoyl) zirconium dibenzyl

$X = CH_2C_6H_5$
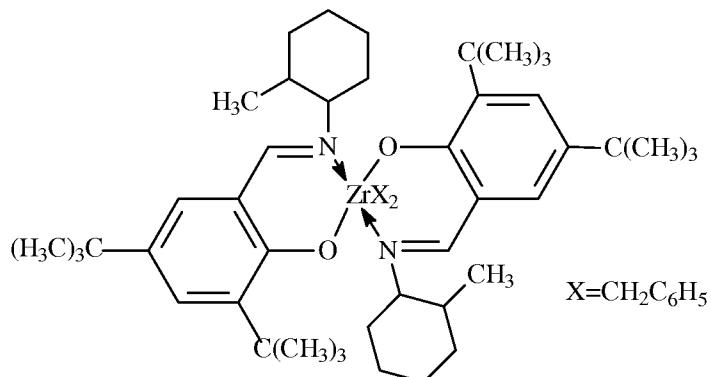
[131] **Catalyst (C1)** is (t-butylamido)dimethyl(3-N-pyrrolyl-1,2,3,3a,7a-η-inden-1-yl)silanetitanium dimethyl prepared substantially according to the techniques of U.S. Patent

10   No. 6,268,444:

34

66940 WO PCT
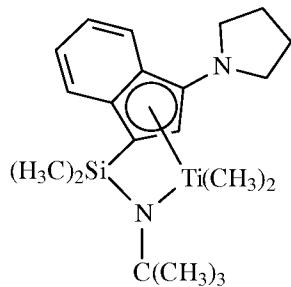
[132] **Catalyst (C2)** is (t-butylamido)di(4-methylphenyl)(2-methyl-1,2,3,3a,7a-η-inden-1-yl)silanetitanium dimethyl prepared substantially according to the teachings of U.S. Patent No. 6,825,295:
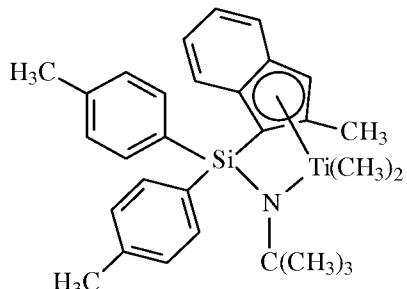
[133] **Catalyst (C3)** is (t-butylamido)di(4-methylphenyl)(2-methyl-1,2,3,3a,8a-η-s-indacen-1-yl)silanetitanium dimethyl prepared substantially according to the teachings of U.S. Patent No. 6,825,295:
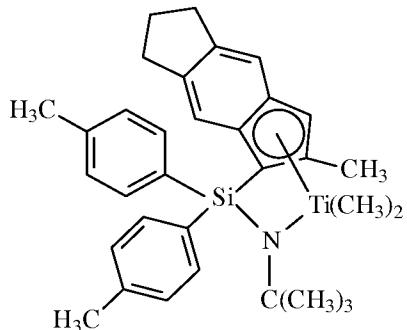
[134] **Catalyst (D1)** is bis(dimethyldisiloxane)(indene-1-yl)zirconium dichloride available from Sigma-Aldrich:

35
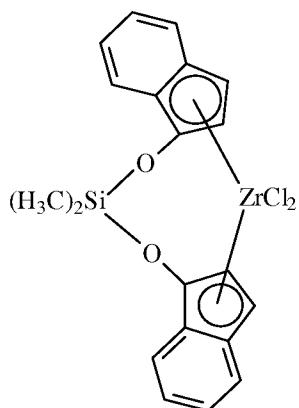
[135] Shuttling Agents The shuttling agents employed include diethylzinc, di(i-butyl)zinc, di(n-hexyl)zinc, triethylaluminum, trioctylaluminum, triethylgallium, i-butylaluminum bis(dimethyl(t-butyl)siloxane), i-butylaluminum bis(di(trimethylsilyl)amide), n-octylaluminum di(pyridine-2-methoxide), bis(n-octadecyl)i-butylaluminum, 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-butyldimethylsiloxide), ethylaluminum di(bis(trimethylsilyl)amide), ethylaluminum bis(2,3,6,7-dibenzo-1-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).

[136] Preferably, the foregoing process takes the form of a continuous solution process for forming block copolymers, especially multi-block copolymers, preferably linear multi-block copolymers of two or more monomers, more especially ethylene and a C_{3-20} olefin or cycloolefin, and most especially ethylene and a C_{4-20} 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 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.

[137] The inventive interpolymers may be differentiated from conventional, random copolymers, physical blends of polymers, and block copolymers prepared via sequential monomer addition, fluxional catalysts, anionic or cationic living polymerization techniques. In particular, compared to a random copolymer of the same monomers and monomer content, the inventive interpolymers have better (higher) heat resistance as measured by melting point,

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lower compression set, particularly at elevated temperatures, lower stress relaxation, higher

creep resistance, faster setup due to higher crystallization (solidification) temperature, and

better oil and filler acceptance.

[138] 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

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

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.

[139] 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.

[140] The ethylene/α-olefin interpolymers used in the embodiments of the invention are

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preferably interpolymers of ethylene with at least one C_3-C_{20} α-olefin. Copolymers of ethylene and a C_3-C_{20} α-olefin are especially preferred. The interpolymers may further comprise C_4-C_{18} diolefin and/or alkenylbenzene. Suitable unsaturated comonomers useful for polymerizing with ethylene include, for example, ethylenically unsaturated monomers,

5   conjugated or nonconjugated dienes, polyenes, alkenylbenzenes, etc. Examples of such comonomers include C_3-C_{20} 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

10   naphthenics (e.g., cyclopentene, cyclohexene and cyclooctene).

[141] 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.

15   Preferably, suitable olefins are C_3-C_{20} 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 C_1-C_{20} hydrocarbyl or cyclohydrocarbyl groups. Also included are mixtures of such olefins as well as mixtures of such olefins with C_4-C_{40} diolefin compounds.

20   [142] 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,

25   cyclooctene, C_4-C_{40} 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 C_4-C_{40} 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,

30   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.

[143] 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,

5   copolymers comprising ethylene, styrene and a C_3-C_{20} alpha olefin, optionally comprising a C_4-C_{20} diene, having improved properties can be prepared.

[144] 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-

10 hexadiene, 1,6-octadiene, 1,7-octadiene, 1,9-decadiene, branched chain acyclic dienes, such 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

15 tetrahydroindene, dicyclopentadiene, bicyclo-(2,2,1)-hepta-2,5-diene; alkenyl, alkylidene, 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),

20 5-ethylidene-2-norbornene (ENB), 5-vinylidene-2-norbornene (VNB), 5-methylene-2-norbornene (MNB), and dicyclopentadiene (DCPD). The especially preferred dienes are 5-ethylidene-2-norbornene (ENB) and 1,4-hexadiene (HD).

[145] One class of desirable polymers that can be made in accordance with embodiments of the invention are elastomeric interpolymers of ethylene, a C_3-C_{20} α-olefin, especially

25 propylene, and optionally one or more diene monomers. Preferred α-olefins for use in this embodiment of the present invention are designated by the formula $CH_2=CHR*$, 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

30 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

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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.

[146] Because the diene containing polymers comprise alternating segments or blocks

5   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

10   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.

[147] 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

15   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 may be copolymerized with ethylene and an optional additional comonomer to form an interpolymer of ethylene, the functional comonomer and optionally other comonomer(s).

20   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 maleic anhydride.

[148] The amount of the functional group present in the functional interpolymer can vary.

25   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

30   preferably less than about 25 weight percent.

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More on Block Index

[149]   Random copolymers satisfy the following relationship. *See* P. J. Flory, *Trans. Faraday Soc.*, **51**, 848 (1955), which is incorporated by reference herein in its entirety.

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\left(\frac{R}{\Delta H_u}\right) \ln P \qquad (1)$$

5   [150]   In Equation 1, the mole fraction of crystallizable monomers, P, is related to the melting temperature, T_m, of the copolymer and the melting temperature of the pure crystallizable homopolymer, T_m^0. The equation is similar to the relationship for the natural logarithm of the mole fraction of ethylene as a function of the reciprocal of the ATREF elution temperature (°K) as shown in Figure 7 for various homogeneously branched

10   copolymers of ethylene and olefins.

[151]   As illustrated in Figure 7, the relationship of ethylene mole fraction to ATREF peak elution temperature and DSC melting temperature for various homogeneously branched copolymers is analogous to Flory's equation. Similarly, preparative TREF fractions of nearly all random copolymers and random copolymer blends likewise fall on this line, except for

15   small molecular weight effects.

[152]   According to Flory, if P, the mole fraction of ethylene, is equal to the conditional probability that one ethylene unit will precede or follow another ethylene unit, then the polymer is random. On the other hand if the conditional probability that any 2 ethylene units occur sequentially is greater than P, then the copolymer is a block copolymer. The remaining

20   case where the conditional probability is less than P yields alternating copolymers.

[153]   The mole fraction of ethylene in random copolymers primarily determines a specific distribution of ethylene segments whose crystallization behavior in turn is governed by the minimum equilibrium crystal thickness at a given temperature. Therefore, the copolymer melting and TREF crystallization temperatures of the inventive block copolymers are related

25   to the magnitude of the deviation from the random relationship in Figure 8, and such deviation is a useful way to quantify how "blocky" a given TREF fraction is relative to its random equivalent copolymer (or random equivalent TREF fraction). The term "blocky" refers to the extent a particular polymer fraction or polymer comprises blocks of polymerized monomers or comonomers. There are two random equivalents, one corresponding to

30   constant temperature and one corresponding to constant mole fraction of ethylene. These form the sides of a right triangle as shown in Figure 8, which illustrates the definition of the

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block index.

[154] In Figure 8, the point (T_X, P_X) represents a preparative TREF fraction, where the ATREF elution temperature, T_X, and the NMR ethylene mole fraction, P_X, are measured values. The ethylene mole fraction of the whole polymer, P_{AB}, is also measured by NMR. The "hard segment" elution temperature and mole fraction, (T_A, P_A), can be estimated or else set to that of ethylene homopolymer for ethylene copolymers. The T_{AB} value corresponds to the calculated random copolymer equivalent ATREF elution temperature based on the measured P_{AB}. From the measured ATREF elution temperature, T_X, the corresponding random ethylene mole fraction, P_{XO}, can also be calculated. The square of the block index is defined to be the ratio of the area of the (P_X, T_X) triangle and the (T_A, P_{AB}) triangle. Since the right triangles are similar, the ratio of areas is also the squared ratio of the distances from (T_A, P_{AB}) and (T_X, P_X) to the random line. In addition, the similarity of the right triangles means the ratio of the lengths of either of the corresponding sides can be used instead of the areas.

$$BI = \frac{1/T_X - 1/T_{XO}}{1/T_A - 1/T_{AB}} \text{ or } BI = -\frac{LnP_X - LnP_{XO}}{LnP_A - LnP_{AB}}$$

[155] It should be noted that the most perfect block distribution would correspond to a whole polymer with a single eluting fraction at the point (T_A, P_{AB}), because such a polymer would preserve the ethylene segment distribution in the "hard segment", yet contain all the available octene (presumably in runs that are nearly identical to those produced by the soft segment catalyst). In most cases, the "soft segment" will not crystallize in the ATREF (or preparative TREF).

[156] Additives and adjuvants may be included in any formulation comprising the inventive polymers. Suitable additives include fillers, such as organic or inorganic particles, including clays, talc, titanium dioxide, zeolites, powdered metals, organic or inorganic fibers, including carbon fibers, silicon nitride fibers, steel wire or mesh, and nylon or polyester cording, nano-sized particles, clays, and so forth; tackifiers, oil extenders, including paraffinic or napthelenic oils; and other natural and synthetic polymers, including other polymers according to embodiments of the invention.

[157] Suitable polymers for blending with the polymers according to embodiments of the invention include thermoplastic and non-thermoplastic polymers including natural and synthetic polymers. Exemplary polymers for blending include polypropylene, (both impact modifying polypropylene, isotactic polypropylene, atactic polypropylene, and random ethylene/propylene copolymers), various types of polyethylene, including high pressure, free-

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radical LDPE, Ziegler Natta LLDPE, metallocene PE, including multiple reactor PE ("in reactor" blends of Ziegler-Natta PE and metallocene PE, such as products disclosed in U.S. Patents No. 6,545,088, 6,538,070, 6,566,446, 5,844,045, 5,869,575, and 6,448,341), ethylene-vinyl acetate (EVA), ethylene/ vinyl alcohol copolymers, polystyrene, impact modified

5   polystyrene, acrylonitrile butadiene styrene (ABS), styrene/butadiene block copolymers and hydrogenated derivatives thereof (SBS and SEBS), polyisobutylene (PIB) homopolymer, PIB-isoprene copolymer, EPDM and thermoplastic polyurethanes. Homogeneous polymers such as olefin plastomers and elastomers, ethylene and propylene-based copolymers (for example polymers available under the trade designation VERSIFY™ available from The

10   Dow Chemical Company and VISTAMAXX™ available from ExxonMobil Chemical Company) can also be useful as components in blends comprising the inventive polymers.

[158]   Additional end uses include elastic films and fibers; soft touch goods, such as tooth brush handles and appliance handles; gaskets and profiles; adhesives (including hot melt adhesives and pressure sensitive adhesives); footwear (including shoe soles and shoe liners);

15   auto interior parts and profiles; foam goods (both open and closed cell); impact modifiers for other thermoplastic polymers such as high density polyethylene, isotactic polypropylene, or other olefin polymers; coated fabrics; hoses; tubing; weather stripping; cap liners; flooring; and viscosity index modifiers, also known as pour point modifiers, for lubricants.

[159]   In some embodiments, thermoplastic compositions comprising a thermoplastic matrix

20   polymer, especially isotactic polypropylene, and an elastomeric multi-block copolymer of ethylene and a copolymerizable comonomer according to embodiments of the invention, are uniquely capable of forming core-shell type particles having hard crystalline or semi-crystalline blocks in the form of a core surrounded by soft or elastomeric blocks forming a "shell" around the occluded domains of hard polymer. These particles are formed and

25   dispersed within the matrix polymer by the forces incurred during melt compounding or blending. This highly desirable morphology is believed to result due to the unique physical properties of the multi-block copolymers which enable compatible polymer regions such as the matrix and higher comonomer content elastomeric regions of the multi-block copolymer to self-assemble in the melt due to thermodynamic forces. Shearing forces during

30   compounding are believed to produce separated regions of matrix polymer encircled by elastomer. Upon solidifying, these regions become occluded elastomer particles encased in the polymer matrix.

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[160] Particularly desirable blends are thermoplastic polyolefin blends (TPO), thermoplastic elastomer blends (TPE), thermoplastic vulcanizates (TPV) and styrenic polymer blends. TPE and TPV blends may be prepared by combining the invented multi-block polymers, including functionalized or unsaturated derivatives thereof with an optional rubber, including conventional block copolymers, especially an SBS block copolymer, and optionally a crosslinking or vulcanizing agent. TPO blends are generally prepared by blending the invented multi-block copolymers with a polyolefin, and optionally a crosslinking or vulcanizing agent. The foregoing blends may be used in forming a molded object, and optionally crosslinking the resulting molded article. A similar procedure using different components has been previously disclosed in U.S. Patent No. 6,797,779.

[161] Suitable conventional block copolymers for this application desirably possess a Mooney viscosity (ML 1+4 @ 100°C.) in the range from 10 to 135, more preferably from 25 to 100, and most preferably from 30 to 80. Suitable polyolefins especially include linear or low density polyethylene, polypropylene (including atactic, isotactic, syndiotactic and impact modified versions thereof) and poly(4-methyl-1-pentene). Suitable styrenic polymers include polystyrene, rubber modified polystyrene (HIPS), styrene/acrylonitrile copolymers (SAN), rubber modified SAN (ABS or AES) and styrene maleic anhydride copolymers.

[162] The blends may be prepared by mixing or kneading the respective components at a temperature around or above the melt point temperature of one or both of the components. For most multiblock copolymers, this temperature may be above 130° C, most generally above 145° C, and most preferably above 150° C. Typical polymer mixing or kneading equipment that is capable of reaching the desired temperatures and melt plastifying the mixture may be employed. These include mills, kneaders, extruders (both single screw and twin-screw), Banbury mixers, calenders, and the like. The sequence of mixing and method may depend on the desired final composition. A combination of Banbury batch mixers and continuous mixers may also be employed, such as a Banbury mixer followed by a mill mixer followed by an extruder. Typically, a TPE or TPV composition will have a higher loading of cross-linkable polymer (typically the conventional block copolymer containing unsaturation) compared to TPO compositions. Generally, for TPE and TPV compositions, the weight ratio of conventional block copolymer to multi-block copolymer may be from about 90:10 to 10:90, more preferably from 80:20 to 20:80, and most preferably from 75:25 to 25:75. For TPO applications, the weight ratio of multi-block copolymer to polyolefin may be from about 49:51 to about 5:95, more preferably from 35:65 to about 10:90. For modified styrenic

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polymer applications, the weight ratio of multi-block copolymer to polyolefin may also be from about 49:51 to about 5:95, more preferably from 35:65 to about 10:90. The ratios may be changed by changing the viscosity ratios of the various components. There is considerable literature illustrating techniques for changing the phase continuity by changing the viscosity

5   ratios of the constituents of a blend that a person skilled in this art may consult if necessary.

[163]   Certain compositions of the inventive block copolymers also act as plasticizers. A plasticizer is generally an organic compound incorporated into a high molecular weight polymer, such as for example a thermoplastic, to facilitate processing, increase its workability, flexibility, and/or distensibility of the polymer. Polypropylene, for example, is

10   an engineering thermoplastic that is generally stiff and even brittle below room temperature especially for highly stereoregular polypropylene.

[164]   Some embodiments of the invention provide miscible blends with polypropylene. By blending such interpolymer plasticizers with polypropylene (isotactic polypropylene, syndiotactic polypropylene and atactic polypropylene), the glass transition temperature,

15   storage modulus and viscosity of the blended polypropylene are lowered. By decreasing the transition temperature, storage modulus and viscosity, the workability, flexibility, and distensibility of polypropylene improves. As such, broadened commercial application for these new polypropylene blends in film, fibers and molded products is apparent. Furthermore, the flexibility of a product design utilizing these novel blends can be further

20   extended by taking advantage of the enhanced comonomer incorporation and tacticity control possible with metallocene and other homogeneous catalysts, both of which can reduce isotactic polypropylene crystallinity prior to blending with the inventive block interpolymer.

[165]   These plasticized polypropylene thermoplastics may be used in known applications for polypropylene compositions. These uses include, but are not limited to: hot melt

25   adhesives; pressure sensitive adhesives (as an adhesive component, particularly when the polypropylene has low levels of crystallinity, e.g., amorphous polypropylene); films (whether extrusion coatings, cast or blown; such will exhibit improved heat sealing characteristics); sheets (such as by extrusion in single or multilayer sheets where at least one layer is a plasticized polypropylene thermoplastic composition of the invention); meltblown or

30   spunbond fibers; and, as thermoplastic components in thermoformable thermoplastic olefin ("TPO") and thermoplastic elastomer ("TPE") blends where polypropylene has traditionally been demonstrated to be effective. In view of these many uses, with improved low temperature properties and increased workability, the plasticized polypropylene

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thermoplastics offer a suitable replacement in selected applications for plasticized polyvinyl chloride (PVC).

[166] The blend compositions may contain processing oils, plasticizers, and processing aids. Rubber processing oils and paraffinic, napthenic or aromatic process oils are all suitable for

5   use. Generally from about 0 to about 150 parts, more preferably about 0 to about 100 parts, and most preferably from about 0 to about 50 parts of oil per 100 parts of total polymer are employed. Higher amounts of oil may tend to improve the processing of the resulting product at the expense of some physical properties. Additional processing aids include conventional waxes, fatty acid salts, such as calcium stearate or zinc stearate, (poly)alcohols

10   including glycols, (poly)alcohol ethers, including glycol ethers, (poly)esters, including (poly)glycol esters, and metal salt-, especially Group 1 or 2 metal or zinc-, salt derivatives thereof.

[167] It is known that non-hydrogenated rubbers such as those comprising polymerized forms of butadiene or isoprene, including block copolymers (here-in-after diene rubbers),

15   have lower resistance to UV radiation, ozone, and oxidation, compared to mostly or highly saturated rubbers. In applications such as tires made from compositions containing higher concentrations of diene based rubbers, it is known to incorporate carbon black to improve rubber stability, along with anti-ozone additives and anti-oxidants. Multi-block copolymers according to the present invention possessing extremely low levels of unsaturation, find

20   particular application as a protective surface layer (coated, coextruded or laminated) or weather resistant film adhered to articles formed from conventional diene elastomer modified polymeric compositions.

[168] For conventional TPO, TPV, and TPE applications, carbon black is the additive of choice for UV absorption and stabilizing properties. Representative examples of carbon

25   blacks include ASTM N110, N121, N220, N231, N234, N242, N293, N299, S315, N326, N330, M332, N339, N343, N347, N351, N358, N375, N539, N550, N582, N630, N642, N650, N683, N754, N762, N765, N774, N787, N907, N908, N990 and N991. These carbon blacks have iodine absorptions ranging from 9 to 145 g/kg and average pore volumes ranging from 10 to 150 $cm^3/100$ g. Generally, smaller particle sized carbon blacks are employed, to

30   the extent cost considerations permit. For many such applications the present multi-block copolymers and blends thereof require little or no carbon black, thereby allowing considerable design freedom to include alternative pigments or no pigments at all. Multi-hued tires or tires matching the color of the vehicle are one possibility.

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[169] Compositions, including thermoplastic blends according to embodiments of the invention may also contain anti-ozonants or anti-oxidants that are known to a rubber chemist of ordinary skill. The anti-ozonants may be physical protectants such as waxy materials that come to the surface and protect the part from oxygen or ozone or they may be chemical

5   protectors that react with oxygen or ozone. Suitable chemical protectors include styrenated phenols, butylated octylated phenol, butylated di(dimethylbenzyl) phenol, p-phenylenediamines, butylated reaction products of p-cresol and dicyclopentadiene (DCPD), polyphenolic antioxidants, hydroquinone derivatives, quinoline, diphenylene antioxidants, thioester antioxidants, and blends thereof. Some representative trade names of such products

10 are Wingstay™ S antioxidant, Polystay™ 100 antioxidant, Polystay™ 100 AZ antioxidant, Polystay™ 200 antioxidant, Wingstay™ L antioxidant, Wingstay™ LHLS antioxidant, Wingstay™ K antioxidant, Wingstay™ 29 antioxidant, Wingstay™ SN-1 antioxidant, and Irganox™ antioxidants. In some applications, the anti-oxidants and anti-ozonants used will preferably be non-staining and non-migratory.

15 [170] For providing additional stability against UV radiation, hindered amine light stabilizers (HALS) and UV absorbers may be also used. Suitable examples include Tinuvin™ 123, Tinuvin™ 144, Tinuvin™ 622, Tinuvin™ 765, Tinuvin™ 770, and Tinuvin™ 780, available from Ciba Specialty Chemicals, and Chemisorb™ T944, available from Cytex Plastics, Houston TX, USA. A Lewis acid may be additionally included with a

20 HALS compound in order to achieve superior surface quality, as disclosed in U.S. Patent No. 6,051,681.

[171] For some compositions, additional mixing processes may be employed to pre-disperse the anti-oxidants, anti-ozonants, carbon black, UV absorbers, and/or light stabilizers to form a masterbatch, and subsequently to form polymer blends there from.

25 [172] Suitable crosslinking agents (also referred to as curing or vulcanizing agents) for use herein include sulfur based, peroxide based, or phenolic based compounds. Examples of the foregoing materials are found in the art, including in U.S. Patents No.: 3,758,643; 3,806,558; 5,051,478; 4,104,210; 4,130,535; 4,202,801; 4,271,049; 4,340,684; 4,250,273; 4,927,882; 4,311,628 and 5,248,729.

30 [173] When sulfur based curing agents are employed, accelerators and cure activators may be used as well. Accelerators are used to control the time and/or temperature required for dynamic vulcanization and to improve the properties of the resulting cross-linked article. In one embodiment, a single accelerator or primary accelerator is used. The primary

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accelerator(s) may be used in total amounts ranging from about 0.5 to about 4, preferably about 0.8 to about 1.5, phr, based on total composition weight. In another embodiment, combinations of a primary and a secondary accelerator might be used with the secondary accelerator being used in smaller amounts, such as from about 0.05 to about 3 phr, in order to

5   activate and to improve the properties of the cured article. Combinations of accelerators generally produce articles having properties that are somewhat better than those produced by use of a single accelerator. In addition, delayed action accelerators may be used which are not affected by normal processing temperatures yet produce a satisfactory cure at ordinary vulcanization temperatures. Vulcanization retarders might also be used. Suitable types of

10   accelerators that may be used in the present invention are amines, disulfides, guanidines, thioureas, thiazoles, thiurams, sulfenamides, dithiocarbamates and xanthates. Preferably, the primary accelerator is a sulfenamide. If a second accelerator is used, the secondary accelerator is preferably a guanidine, dithiocarbarnate or thiuram compound. Certain processing aids and cure activators such as stearic acid and ZnO may also be used. When

15   peroxide based curing agents are used, co-activators or coagents may be used in combination therewith. Suitable coagents include trimethylolpropane triacrylate (TMPTA), trimethylolpropane trimethacrylate (TMPTMA), triallyl cyanurate (TAC), triallyl isocyanurate (TAIC), among others. Use of peroxide crosslinkers and optional coagents used for partial or complete dynamic vulcanization are known in the art and disclosed for example

20   in the publication, "Peroxide Vulcanization of Elastomer", Vol. 74, No 3, July-August 2001.
[174] When the multi-block copolymer containing composition is at least partially crosslinked, the degree of crosslinking may be measured by dissolving the composition in a solvent for specified duration, and calculating the percent gel or unextractable component. The percent gel normally increases with increasing crosslinking levels. For cured articles

25   according to embodiments of the invention, the percent gel content is desirably in the range from 5 to 100 percent.
[175] The multi-block copolymers according to embodiments of the invention as well as blends thereof possess improved processability compared to prior art compositions, due, it is believed, to lower melt viscosity. Thus, the composition or blend demonstrates an improved

30   surface appearance, especially when formed into a molded or extruded article. At the same time, the present compositions and blends thereof uniquely possess improved melt strength properties, thereby allowing the present multi-block copolymers and blends thereof, especially TPO blends, to be usefully employed in foam and thermoforming applications

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where melt strength is currently inadequate.

[176] Thermoplastic compositions according to embodiments of the invention may also contain organic or inorganic fillers or other additives such as starch, talc, calcium carbonate, glass fibers, polymeric fibers (including nylon, rayon, cotton, polyester, and polyaramide),

5   metal fibers, flakes or particles, expandable layered silicates, phosphates or carbonates, such as clays, mica, silica, alumina, aluminosilicates or aluminophosphates, carbon whiskers, carbon fibers, nanoparticles including nanotubes, wollastonite, graphite, zeolites, and ceramics, such as silicon carbide, silicon nitride or titania. Silane based or other coupling agents may also be employed for better filler bonding.

10   [177] The thermoplastic compositions according to embodiments of the invention, including the foregoing blends, may be processed by conventional molding techniques such as injection molding, extrusion molding, thermoforming, slush molding, over molding, insert molding, blow molding, and other techniques. Films, including multi-layer films, may be produced by cast or tentering processes, including blown film processes.

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Polymer Compositions Which May Be Compatibilized

Polyolefins

[178] The polymer blends disclosed herein can comprise at least two polyoelfins, in addition to at least an ethylene/α-olefin interpolymer described above. A polyolefin is a

20   polymer derived from two or more olefins (*i.e.*, alkenes). An olefin (*i.e.*, alkene) is a hydrocarbon contains at least one carbon-carbon double bond. The olefin can be a monoene (*i.e*, an olefin having a single carbon-carbon double bond), diene (*i.e*, an olefin having two carbon-carbon double bonds), triene (*i.e*, an olefin having three carbon-carbon double bonds), tetraene (*i.e*, an olefin having four carbon-carbon double bonds), and other polyenes.   The

25   olefin or alkene, such as monoene, diene, triene, tetraene and other polyenes, can have 3 or more carbon atoms, 4 or more carbon atoms, 6 or more carbon atoms, 8 or more carbon atoms. In some embodiments, the olefin has from 3 to about 100 carbon atoms, from 4 to about 100 carbon atoms, from 6 to about 100 carbon atoms, from 8 to about 100 carbon atoms, from 3 to about 50 carbon atoms, from 3 to about 25 carbon atoms, from 4 to about 25

30   carbon atoms, from 6 to about 25 carbon atoms, from 8 to about 25 carbon atoms, or from 3 to about 10 carbon atoms. In some embodiments, the olefin is a linear or branched, cyclic or acyclic, monoene having from 2 to about 20 carbon atoms. In other embodiments, the alkene

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is a diene such as butadiene and 1,5-hexadiene. In further embodiments, at least one of the hydrogen atoms of the alkene is substituted with an alkyl or aryl. In particular embodiments, the alkene is ethylene, propylene, 1-butene, 1-hexene, 1-octene, 1-decene, 4-methyl-1-pentene, norbornene, 1-decene, butadiene, 1,5-hexadiene, styrene or a combination thereof.

[179] The amount of the polyolefins in the polymer blend can be from about 0.5 to about 99 wt%, from about 10 to about 90 wt%, from about 20 to about 80 wt%, from about 30 to about 70 wt%, from about 5 to about 50 wt%, from about 50 to about 95 wt%, from about 10 to about 50 wt%, or from about 50 to about 90 wt% of the total weight of the polymer blend. In one embodiment, the amount of the polyolefins in the polymer blend is about 50%, 60%, 70% or 80% by total weight of the polymer blend. The weight ratio of the two polyolefins can range from about 1:99 to about 99:1, preferable from about 5:95 to about 95:5, from about 10:90 to about 90:10, from about 20:80 to about 80:20, from about 30:70 to about 70:30, from about 40:60 to about 60:40, from about 45:55 to about 55:45 to about 50:50. In some embodiments, the ethylene/α-olefin block interpolymer is present in an amount in the range of from about 0.5 wt% to about 45 wt%, preferably in an amount of from about 0.5 wt% to about 10 wt%, from about 5 wt% to about 45 wt%, or from about 0.5 wt% to about 18 wt%, based on total weight of polymer.

[180] Any polyolefin known to a person of ordinary skill in the art may be used to prepare the polymer blend disclosed herein. The polyolefins can be olefin homopolymers, olefin copolymers, olefin terpolymers, olefin quaterpolymers and the like, and combinations thereof.

[181] In some embodiments, one of the at least two polyolefins is an olefin homopolymer. The olefin homopolymer can be derived from one olefin. Any olefin homopolymer known to a person of ordinary skill in the art may be used. Non-limiting examples of olefin homopolymers include polyethylene (e.g., ultralow, low, linear low, medium, high and ultrahigh density polyethylene), polypropylene, polybutylene (e.g., polybutene-1), polypentene-1, polyhexene-1, polyoctene-1, polydecene-1, poly-3-methylbutene-1, poly-4-methylpentene-1, polyisoprene, polybutadiene, poly-1,5-hexadiene.

[182] In further embodiments, the olefin homopolymer is a polypropylene. Any polypropylene known to a person of ordinary skill in the art may be used to prepare the polymer blends disclosed herein. Non-limiting examples of polypropylene include low density polypropylene (LDPP), high density polypropylene (HDPP), high melt strength polypropylene (HMS-PP), high impact polypropylene (HIPP), isotactic polypropylene (iPP),

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syndiotactic polypropylene (sPP) and the like, and combinations thereof.

[183] The amount of the polypropylene in the polymer blend can be from about 0.5 to about 99 wt%, from about 10 to about 90 wt%, from about 20 to about 80 wt%, from about 30 to about 70 wt%, from about 5 to about 50 wt%, from about 50 to about 95 wt%, from about 10 to about 50 wt%, or from about 50 to about 90 wt% of the total weight of the polymer blend. In one embodiment, the amount of the polypropylene in the polymer blend is about 50%, 60%, 70% or 80% by total weight of the polymer blend.

[184] In other embodiments, one of the at least two polyolefins is an olefin copolymer. The olefin copolymer can be derived from two different olefins. The amount of the olefin copolymer in the polymer blend can be from about 0.5 to about 99 wt%, from about 10 to about 90 wt%, from about 20 to about 80 wt%, from about 30 to about 70 wt%, from about 5 to about 50 wt%, from about 50 to about 95 wt%, from about 10 to about 50 wt%, or from about 50 to about 90 wt% of the total weight of the polymer blend. In some embodiments, the amount of the olefin copolymer in the polymer blend is about 10%, 15%, 20%, 25%, 30%, 35%, 40% or 50% of the total weight of the polymer blend.

[185] Any olefin copolymer known to a person of ordinary skill in the art may be used in the polymer blends disclosed herein. Non-limiting examples of olefin copolymers include copolymers derived from ethylene and a monoene having 3 or more carbon atoms. Non-limiting examples of the monoene having 3 or more carbon atoms include propene; butenes (*e.g.*, 1-butene, 2-butene and isobutene) and alkyl substituted butenes; pentenes (*e.g.*, 1-pentene and 2-pentene) and alkyl substituted pentenes (*e.g.*, 4-methyl-1-pentene); hexenes (*e.g.*, 1-hexene, 2-hexene and 3-hexene) and alkyl substituted hexenes; heptenes (*e.g.*, 1-heptene, 2-heptene and 3-heptene) and alkyl substituted heptenes; octenes (*e.g.*, 1-octene, 2-octene, 3-octene and 4-octene) and alkyl substituted octenes; nonenes (*e.g.*, 1-nonene, 2-nonene, 3-nonene and 4-nonene) and alkyl substituted nonenes; decenes (*e.g.*, 1-decene, 2-decene, 3-decene, 4-decene and 5-decene) and alkyl substituted decenes; dodecenes and alkyl substituted dodecenes; and butadiene. In some embodiments, the olefin copolymer is an ethylene/alpha-olefin (EAO) copolymer or ethylene/propylene copolymer (EPM). In some embodiments, the olefin copolymer is an ethylene/ /octene copolymer.

[186] In other embodiments, the olefin copolymer is derived from (i) a C_{3-20} olefin substituted with an alkyl or aryl group (*e.g.*, 4-methyl-1-pentene and styrene) and (ii) a diene (*e.g.* butadiene, 1,5-hexadiene, 1,7-octadiene and 1,9-decadiene). A non-limiting example of such olefin copolymer includes styrene-butadiene-styrene (SBS) block copolymer.

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[187]   In other embodiments, one of the at least two polyolefins is an olefin terpolymer. The olefin terpolymer can be derived from three different olefins. The amount of the olefin terpolymer in the polymer blend can be from about 0.5 to about 99 wt%, from about 10 to about 90 wt%, from about 20 to about 80 wt%, from about 30 to about 70 wt%, from about 5 to about 50 wt%, from about 50 to about 95 wt%, from about 10 to about 50 wt%, or from about 50 to about 90 wt% of the total weight of the polymer blend.

[188]   Any olefin terpolymer known to a person of ordinary skill in the art may be used in the polymer blends disclosed herein. Non-limiting examples of olefin terpolymers include terpolymers derived from (i) ethylene, (ii) a monoene having 3 or more carbon atoms, and (iii) a diene. In some embodiments, the olefin terpolymer is an ethylene/alpha-olefin/diene terpolymers (EAODM) and ethylene/propylene/diene terpolymer (EPDM).

[189]   In other embodiments, the olefin terpolymer is derived from (i) two different monoenes, and (ii) a C_{3-20} olefin substituted with an alkyl or aryl group. A non-limiting example of such olefin terpolymer includes styrene-ethylene-co-(butene)-styrene (SEBS) block copolymer.

[190]   In other embodiments, one of the at least two polyolefins can be any vulcanizable elastomer or rubber which is derived from at least an olefin, provided that the vulcanizable elastomer can be cross-linked (*i.e.*, vulcanized) by a cross-linking agent. The vulcanizable elastomer and a thermoplastic such as polypropylene together can form a TPV after cross-linking. Vulcanizable elastomers, although generally thermoplastic in the uncured state, are normally classified as thermosets because they undergo an irreversible process of thermosetting to an unprocessable state. Preferably, the vulcanized elastomer is dispersed in a matrix of the thermoplastic polymer as domains. The average domain size may range from about 0.1 micron to about 100 micron, from about 1 micron to about 50 microns; from about 1 micron to about 25 microns; from about 1 micron to about 10 microns, or from about 1 micron to about 5 microns.

[191]   Non-limiting examples of suitable vulcanizable elastomers or rubbers include ethylene/higher alpha-olefin/polyene terpolymer rubbers such as EPDM. Any such terpolymer rubber which can be completely cured (cross-linked) with a phenolic curative or other cross-linking agent is satisfactory. In some embodiments, the terpolymer rubbers can be essentially non-crystalline, rubbery terpolymer of two or more alpha-olefins, preferably copolymerized with at least one polyene (*i.e*, an alkene comprises two or more carbon-carbon double bonds), usually a non-conjugated diene. Suitable terpolymer rubbers comprise the

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products from the polymerization of monomers comprising two olefins having only one double bond, generally ethylene and propylene, and a lesser quantity of non-conjugated diene. The amount of non-conjugated diene is usually from about 2 to about 10 weight percent of the rubber. Any terpolymer rubber which has sufficient reactivity with phenolic

5   curative to completely cure is suitable. The reactivity of terpolymer rubber varies depending upon both the amount of unsaturation and the type of unsaturation present in the polymer. For example, terpolymer rubbers derived from ethylidene norbornene are more reactive toward phenolic curatives than terpolymer rubbers derived from dicyclopentadiene and terpolymer rubbers derived from 1,4-hexadiene are less reactive toward phenolic curatives

10 than terpolymer rubbers derived from dicyclopentadiene. However, the differences in reactivity can be overcome by polymerizing larger quantities of less active diene into the rubber molecule. For example, 2.5 weight percent of ethylidene norbornene or dicyclopentadiene may be sufficient to impart sufficient reactivity to the terpolymer to make it completely curable with phenolic curative comprising conventional cure activators,

15 whereas, at least 3.0 weight percent or more is required to obtain sufficient reactivity in an terpolymer rubber derived from 1,4-hexadiene. Grades of terpolymer rubbers such as EPDM rubbers suitable for embodiments of the invention are commercially available. Some of the EPDM rubbers are disclosed in Rubber World Blue Book 1975 Edition, Materials and Compounding Ingredients for Rubber, pages 406-410.

20 **[192]**   Generally, an terpolymer elastomer has an ethylene content of from about 10% to about 90% by weight, a higher alpha-olefin content of about 10% to about 80% by weight, and a polyene content of about 0.5% to about 20% by weight, all weights based on the total weight of the polymer. The higher alpha-olefin contains from about 3 to about 14 carbon atoms. Examples of these are propylene, isobutylene, 1-butene, 1-pentene, 1-octene, 2-ethyl-

25 1-hexene, 1-dodecene, and the like. The polyene can be a conjugated diene such as isoprene, butadiene, chloroprene, and the like; a nonconjugated diene; a triene, or a higher enumerated polyene. Examples of trienes are 1,4,9-decatriene, 5,8-dimethyl-1,4,9-decatriene, 4,9-dimethyl-1,4,9-decatriene, and the like. The nonconjugated dienes are more preferred. The nonconjugated dienes contain from 5 to about 25 carbon atoms. Examples are nonconjugated

30 diolefins such as 1,4-pentadiene, 1,4-hexadiene, 1,5-hexadiene, 2,5-dimethyl-1,5-hexadiene, 1,4-octadiene, and the like; cyclic dienes such as cyclopentadiene, cyclohexadiene, cyclooctadiene, dicyclopentadiene, and the like; vinyl cyclic enes such as 1-vinyl-1-cyclopentene, 1-vinyl-1-cyclohexene, and the like; alkylbicyclo nondienes such as 3-methyl-

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bicyclo (4,2,1) nona-3,7-diene, 3-ethylbicyclonondiene, and the like; indenes such as methyl tetrahydroindene and the like; alkenyl norbornenes such as 5-ethylidene-2-norbornene, 5-butylidene-2-norbornene, 2-methallyl-5-norbornene, 2-isopropenyl-5-norbornene, 5-(1,5-hexadienyl)-2-norbornene, 5-(3,7-octadieneyl)-2-norbornene, and the like; and tricyclo dienes such as 3-methyl-tricyclo-(5,2,1,0^2,6)-3,8-decadiene and the like.

[193] In some embodiments, the terpolymer rubbers contain from about 20% to about 80% by weight of ethylene, about 19% to about 70% by weight of a higher alpha-olefin, and about 1% to about 10% by weight of a nonconjugated diene. The more preferred higher alpha-olefins are propylene and 1-butene. The more preferred polyenes are ethylidene norbornene, 1,4-hexadiene, and dicyclopentadiene.

[194] In other embodiments, the terpolymer rubbers have an ethylene content of from about 50% to about 70% by weight, a propylene content of from about 20% to about 49% by weight, and a nonconjugated diene content from about 1% to about 10% by weight, all weights based upon the total weight of the polymer.

[195] Some non-limiting examples of terpolymer rubbers for use include NORDEL® IP 4770R, NORDEL® 3722 IP available from DuPont Dow Elastomers, Wilmington, DE and KELTAN® 5636A available from DSM Elastomers Americas, Addis, LA.

[196] Additional suitable elastomers are disclosed in the following U.S. Patents Nos. 4,130,535; 4,111,897; 4,311,628; 4,594,390; 4,645,793; 4,808,643; 4,894,408; 5,936,038, 5,985,970; and 6,277,916, all of which are incorporated by reference herein in their entirety.

Impact Modified Compositions

[197] The specific ethylene/α-olefin multi-block interpolymer and the amount employed as the impact modifier will vary depending, among other variables, upon the polymer to be impact modified, the application, and the desired properties. It has been found that if improved low temperature impact is desired then an ethylene/α-olefin multi-block interpolymer prepared using relatively more chain shuttling agent may be more useful. While any amount of shuttling agent may be useful, it is often preferable to prepare the interpolymer using from about 50 to about 300 ppm chain shuttling agent. While not wishing to be bound to any particular theory it is believed that this is often results in an advantageous multi-core shell morphology as described in, for example, PCT Application No. PCT/US2005/008917, filed on March 17, 2005, which claims priority to U.S. Provisional Application No. 60/553,906, filed March 17, 2004. For purposes of United States patent practice, the contents

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of said provisional and PCT application are herein incorporated by reference in their entirety.

[198] It has also been found that to a certain extent the toughening efficiency (the amount of improvement expected from a minimal amount of impact modifier) is improved as the density of the ethylene/α-olefin multi-block interpolymer is decreased. For this reason it is often desirable to employ an interpolymer with a density of from about 0.85 to about 0.89 g/cc.

[199] The amount of ethylene/α-olefin multi-block interpolymer employed will vary depending, among other variables, upon the polymer to be impact modified, the application, and the desired properties. Typically, an impact-modifying amount is employed to maintain or increase the notched Izod impact strength at 20°C at least about 5%, preferably at least about 10%, more preferably at least about 15% over a similar composition lacking ethylene/α-olefin multi-block interpolymer. If one also desires low temperature impact properties then one may employ an amount sufficient to maintain or increase the notched Izod impact strength at -20°C at least about 5%, preferably at least about 10%, more preferably at least about 15% over a similar composition lacking ethylene/α-olefin multi-block interpolymer. This amount may be the same or different than the amount employed to maintain or increase the notched Izod impact strength at 20°C.

[200] The amounts of ingredients employed will differ depending, among other things, on the desired properties and application. Often, the weight ratio of multi-block copolymer to polyolefin may be from about 49:51 to about 5:95, more preferably from 35:65 to about 10:90. Preferably, it is desirable to employ at least about 1, preferably at least about 5, more preferably at least about 10, even more preferably at least about 20 weight percent of the ethylene/α-olefin multi-block interpolymer or blend as an impact modifier. Similarly, it is desirable to employ no more than about 50, preferably no more than about 35, more preferably no more than about 25 weight percent of the ethylene/α-olefin multi-block interpolymer or blend as an impact modifier.

[201] Almost any thermoplastic polymer composition may be beneficially impact modified by the addition of one or more of the ethylene/α-olefin multi-block interpolymers discussed above. Such polymer compositions comprise thermoplastic polyurethanes (e.g., Pellathane™ or Isoplast™ made by The Dow Chemical Company), polyvinyl chlorides (PVCs), styrenics, polyolefins (including, e.g., ethylene carbon monoxide copolymers (ECO) or linear alternating ECO copolymers such as those disclosed by U.S. Ser. No. 08/009,198, filed Jan. 22, 1993 (now abandoned) in the names of John G. Hefner and Brian W. S. Kolthammer,

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entitled "Improved Catalysts For The Preparation of Linear Carbon Monoxide/Alpha Olefin Copolymers," the disclosure of which is incorporated herein by reference, and ethylene/propylene carbon monoxide polymers (EPCO)), various engineering thermoplastics (e.g., polycarbonate, thermoplastic polyester, polyamides (e.g., nylon), polyacetals, or

5   polysulfones), and mixtures thereof. Generally, the polyolefin polymers which may be most frequently used are polyethylene (e.g., high density polyethylene, such as that produced by the slurry or gas phase polymerization processes) or polypropylene or propylene based polymers.

[202]   The properties of the high density polyethylene (HDPE) useful in the present

10   invention vary depending upon the desired application. Typically, useful HDPE has a density of greater than 0.94 g/cm^3. Preferably the density is greater than 0.95 g/cm^3 but less than about 0.97 g/cm^3. The HDPE may be produced by any process including Cr and Ziegler-Natta catalyst processes. The molecular weight of the HDPE for use in the present invention varies depending upon the application but may be conveniently indicated using a melt flow

15   measurement according to ASTM D- 1238-03 Condition 190 °C/2.16 kg and Condition 190 °C/5.0 kg, which are known as I_2 and I_5, respectively. Melt flow determinations can also be performed with even higher weights, such as in accordance with ASTM D-1238, Condition 190 °C/10.0 kg and Condition 190 °C/21.6 kg, and are known as I_{10} and I_{21}, respectively. Melt flow rate is used for propylene based polymers and is inversely proportional to the

20   molecular weight of the polymer. Melt flow rate (MFR) is tested in accordance with ASTM D 1238, Condition 230C/2.16 kg (formerly Condition L). Thus, the higher the molecular weight, the lower the melt flow rate, although the relationship is not linear. The lower limits for melt index (I_2) for the HDPE useful herein varies widely depending upon the application, e.g., blow molding or injection molding,etc. but is generally at least about 0.1 grams/10

25   minutes (g/10 min), preferably about 0.5 g/10 min, especially about 1 g/10 min to a high melt index limit of about 80 g/10 min, preferably to about 25 g/10 min, and especially to about 20 g/10 min. The molecular weight of the HDPE for use in the present invention, especially for pipe applications, varies depending upon the application can also be indicated using a melt flow measurement according to ASTM D- 1238, Condition 190C/5 kg (and also known as I_5).

30   The lower limits for melt index (I_5) for the HDPE useful herein is generally about 0.1 grams/10 minutes (g/10 min), preferably about 0.2 g/10 min, to a high melt index limit of about 0.6 g/10 min. Molecular weight distribution (Mw/Mn) of the selected HDPE can be narrow or broad, e.g., Mw/Mn from about 2 to as high as about 40.

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[203] The polypropylene is generally in the isotactic form of homopolymer polypropylene, although other forms of polypropylene can also be used (e.g., syndiotactic or atactic). Polypropylene impact copolymers (e.g., those wherein a secondary copolymerization step reacting ethylene with the propylene is employed) and random copolymers (also reactor

5   modified and usually containing 1.5-7% ethylene copolymerized with the propylene), however, can also be used in the TPO formulations disclosed herein. A complete discussion of various polypropylene polymers is contained in Modern Plastics Encyclopedia/89, mid October 1988 Issue, Volume 65, Number 11, pp. 86-92, the entire disclosure of which is incorporated herein by reference. The molecular weight and hence the melt flow rate of the

10   polypropylene for use in the present invention varies depending upon the application. The melt flow rate for the polypropylene useful herein is generally from about 0.1 grams/10 minutes (g/10 min) to about 100 g/10 min, preferably from about 0.5 g/10 min to about 80 g/10 min, and especially from about 4 g/10 min to about 70 g/10 min. The propylene polymer can be a polypropylene homopolymer, or it can be a random copolymer or even an impact

15   copolymer (which already contains a rubber phase). Examples of such propylene polymers include VISTAMAX (made by Exxon Mobil), VERSIFY and INSPIRE (made by The Dow Chemical Co.).

Methods For Making Blended Compositions

20   [204] The blended compositions of the present invention are made by any convenient method, including dry blending the individual components and subsequently melt mixing, either directly in the extruder used to make the finished article (e.g., the automotive part), or by pre-melt mixing in a separate extruder (e.g., a Banbury mixer). Alternatively, the individual ingredients may be fed separately via gravimetric feeders into the compounding

25   extruder. Typically, the blends are prepared by mixing or kneading the respective components at a temperature around or above the melt point temperature of one or both of the components. For most multiblock copolymers, this temperature may be above 130° C., most generally above 145° C, and most preferably above 150° C. Typical polymer mixing or kneading equipment that is capable of reaching the desired temperatures and melt plastifying

30   the mixture may be employed. These include mills, kneaders, extruders (both single screw and twin-screw), Banbury mixers, calenders, and the like. The sequence of mixing and method may depend on the final composition. A combination of Banbury batch mixers and continuous mixers may also be employed, such as a Banbury mixer followed by a mill mixer

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followed by an extruder.

Molding Operations

[205] There are many types of molding operations which can be used to form useful

5   fabricated articles or parts from the TPO formulations disclosed herein, including various

injection molding processes (e.g., that described in Modern Plastics Encyclopedia/89, Mid

October 1988 Issue, Volume 65, Number 11, pp. 264-268, "Introduction to Injection

Molding" and on pp. 270-271, "Injection Molding Thermoplastics", the disclosures of which

are incorporated herein by reference) and blow molding processes (e.g., that described in

10   Modern Plastics Encyclopedia/89, Mid October 1988 Issue, Volume 65, Number 11, pp. 217-

218, "Extrusion-Blow Molding", the disclosure of which is incorporated herein by reference)

and profile extrusion. Some of the fabricated articles include fuel tanks, outdoor furniture,

pipes, automotive container applications, automotive bumpers, facia, wheel covers and

grilles, as well as other household and personal articles, including, for example, freezer

15   containers. Of course, one skilled in the art can also combine polymers to advantageously

use refractive index to improve, or maintain clarity of end use articles, such as freezer

containers.

Additives

20   [206] Additives such as antioxidants (e.g., hindered phenolics (e.g., Irganox^{TM} 1010),

phosphites (e.g., Irgafos^{TM} 168)), cling additives (e.g., PIB), antiblock additives, pigments,

fillers (e.g., talc, diatomaceous earth, nano-fillers, clay, metal particles, glass fibers or

particles, carbon black, other reinforcing fibers, etc.), and the like can also be included in the

TPO formulations, to the extent that they do not interfere with the enhanced formulation

25   properties discovered by Applicants.

Improved Impact Strength

[207] The compositions of the present invention have improved impact strength. Impact

strength can be measured using, for example, Notched Izod impact testing. Notched Izod

30   Impact is a single point test that measures a materials resistance to impact from a swinging

pendulum. Izod impact is defined as the kinetic energy needed to initiate fracture and

continue the fracture until the specimen is broken. Izod specimens are notched to prevent

deformation of the specimen upon impact. The testing is conducted according to ASTM D56.

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Typically, compositions of this invention maintain or increase the notched Izod impact strength at 20°C at least about 5%, preferably at least about 10%, more preferably at least about 15% over a similar composition lacking ethylene/α-olefin multi-block interpolymer. In addition, compositions of this invention often maintain or increase the notched Izod impact

5   strength at -20°C at least about 5%, preferably at least about 10%, more preferably at least about 15% over a similar composition lacking ethylene/α-olefin multi-block interpolymer. These novel impact compositions also have improved ductile-brittle transition temperature – that is, the transition from ductile to brittle failure occurs at lower temperatures, typically at least about 5C, preferably 10C, and more preferably at least 15C lower than the polymer that

10 was impact modified, and lower than an impact modified composition using a random ethylene/alpha-olefin copolymer (at about the same density and melt index as the multi-block) as the impact modifier.

EXAMPLES

15 **[208]**   The following examples are provided to illustrate the synthesis of the inventive polymers. Certain comparisons are made with some existing polymers. The examples are presented to exemplify embodiments of the invention but are not intended to limit the invention to the specific embodiments set forth. Unless indicated to the contrary, all parts and percentages are by weight. All numerical values are approximate. When numerical

20 ranges are given, it should be understood that embodiments outside the stated ranges may still fall within the scope of the invention. Specific details described in each example should not be construed as necessary features of the invention.

Testing Methods

25 **[209]**   In the examples that follow, the following analytical techniques are employed:

GPC Method for Samples 1-4 and A-C

[210]   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

30 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.

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[211] 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.

5   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) N_2. 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

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

15   **Standard CRYSTAF Method**

[212] 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 hr and stabilized at 95°C for 45 minutes. The sampling temperatures range from 95 to

20   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.

[213] The CRYSTAF peak temperature and area are identified by the peak analysis module

25   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

30   temperature limit of 0.1, and below the temperature limit of 0.3.

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

[214]   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.

[215]   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.

[216]   Calibration of the DSC is done as follows. First, a baseline is obtained by running a DSC from -90 °C without any sample in the aluminum DSC pan.   Then 7 milligrams of a fresh indium sample is analyzed by heating the sample to 180°C, cooling the sample to 140°C at a cooling rate of 10°C /min followed by keeping the sample isothermally at 140°C for 1 minute, followed by heating the sample from 140°C to 180°C at a heating rate of 10°C per minute. The heat of fusion and the onset of melting of the indium sample are determined and checked to be within 0.5°C from 156.6°C for the onset of melting and within 0.5 J/g from 28.71 J/g for the of fusion. Then deionized water is analyzed by cooling a small drop of fresh sample in the DSC pan from 25°C to -30°C at a cooling rate of 10°C per minute. The sample is kept isothermally at -30°C for 2 minutes and heat to 30°C at a heating rate of 10°C per minute. The onset of melting is determined and checked to be within 0.5°C from 0°C.

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

[217]   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

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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.

[218] 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)): $M_{polyethylene} = 0.431(M_{polystyrene})$.

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

Compression Set

[220] 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 min at 190°C, followed by 86 MPa for 2 min at 190°C, followed by cooling inside the press with cold running water at 86 MPa.

Density

[221] 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

[222] 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 according to

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ASTM D 5026-01 or equivalent technique.

Optical properties

[223]   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 min, followed by 1.3 MPa for 3 min, and then 2.6 MPa for 3

min. The film is then cooled in the press with running cold water at 1.3 MPa for 1 min. The

compression molded films are used for optical measurements, tensile behavior, recovery, and

stress relaxation.

[224]   Clarity is measured using BYK Gardner Haze-gard as specified in ASTM D 1746.

[225]   45° gloss is measured using BYK Gardner Glossmeter Microgloss 45° as specified in

ASTM D-2457

[226]   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

[227]   Stress-strain behavior in uniaxial tension is measured using ASTM D 1708

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.

[228]   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:

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

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.

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[229] 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:

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

[230] 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.

[231] 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

[232] Thermal Mechanical Analysis (Penetration Temperature) is conducted on 30 mm 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.

DMA

[233] 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.

[234] A 1.5 mm plaque is pressed and cut in a bar of dimensions 32x12 mm. The sample is clamped at both ends between fixtures separated by 10 mm (grip separation ΔL) and

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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 is sufficient and that the measurement remains in the linear regime.

[235]   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 fixtures reaches 65 mm.

Pellet Blocking Strength

[236]   Pellet blocking strength can be measured as follows: pellets (150 g) are loaded into a 2" (5 cm) diameter hollow cylinder that is made of two halves held together by a hose clamp. A 2.75 lb (1.25 kg) load is applied to the pellets in the cylinder at 45 °C for 3 days. After 3 days, the pellets loosely consolidate into a cylindrical shaped plug. The plug is removed from the form and the pellet blocking force measured by loading the cylinder of blocked pellets in compression using an Instron™ instrument to measure the compressive force needed to break the cylinder into pellets.

Melt Index

[237]   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.

ATREF

[238]   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.; Knobeloch, 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 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

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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.

5 **^{13}C NMR Analysis**

[239] The samples are prepared by adding approximately 3g of a 50/50 mixture of tetrachloroethane-d^2/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™

10 400MHz spectrometer, corresponding to a ^{13}C 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

15 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 (also known as Preparative TREF)

[240] Large-scale TREF fractionation is carried by dissolving 15-20 g of polymer in 2 liters

20 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

25 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.

[241] Approximately 2000 ml portions of eluant from the preparative TREF column are

30 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,

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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

5   weighed on an analytical balance before further testing. Additional information about hits

method is taught in Wilde, L.; Ryle, T.R.; Knobeloch, D.C.; Peat, I.R.; *Determination of*

Branching Distributions in Polyethylene and Ethylene Copolymers, J. Polym. Sci., 20, 441-

455 (1982).

10   **Melt Strength**

[242] 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

15   of accelerating nips located 100 mm below the die with an acceleration of 2.4 mm/sec^2. 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").

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Instrumented Dart Impact (IDI)

[243]   Instrumented Dart Impact (IDI) at -20 °C and -30 °C was determined

according to ASTM D3763 and is measured in inch-pounds.

25   **Test Specimen Preparation for Instrumented Dart Impact Testing**

[244] The elastomers are mixed into rigid TPO formulations. A Coperion ZSK-25 co-

rotating fully intermeshing twin screw extruder with a TPO/Talc screw design is used to

compound the materials. The twin screw extruder is operated at 500 RPM and the total

polymer feed is 50 pounds per hour. The polypropylene and other blend components are fed

30   into the extruder using individual gravimetric (loss in weight) feeders. Talc is fed with a

gravimetric feeder to a side-arm extruder that introduces it into the third zone of the extruder

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barrel. The barrel section where the side-arm extruder meets the main twin screw extruder is equipped with a talc vent to allow the large amounts of ambient air carried into the twin screw extruder to be exhausted out of the extruder. The TPO/talc screw is designed to accept large volumes of talc and then knead, mix, and compress the molten compound. Shortly

5   before the exit of the extruder, the volume in the twin screw extruder is allowed to increase to allow vacuum devolatization of the polymer. Vacuum is set at 20 inches of Hg (about 677 mbar). Test samples are injection molded utilizing a Toyo injection molder and universal insert tools that allow different insert to be utilized to make tensile dog-bones or 4 inch (about 10 cm) diameter and 0.125 inch (about .32 cm) thick instrumented dart impact test disks. For

10 the instrumented dart impact specimens, the injection rate utilized is 28 cubic centimeters per second. The melt temperature is controlled at 400 °F (about 200 °C) and the tool temperature at 100 °F (about 37 °C). All samples are conditioned in the lab at room temperature for at least seven days before testing. Ten specimens are tested per formulation.

15 **Catalysts**

[245] 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 C_{6-9} aliphatic hydrocarbons available under the trade designation Isopar E®, from ExxonMobil Chemical Company. In the event the name of a

20 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.

[246] **MMAO** refers to modified methylalumoxane, a triisobutylaluminum modified

25 methylalumoxane available commercially from Akzo-Noble Corporation.

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

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

[248] 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,

30 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-

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methylethyl)immino)methyl)(2-oxoyl) zirconium dibenzyl

[249] 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 $Zr(CH_2Ph)_4$ (500 mg, 1.1 mmol) in 50 mL toluene. The resulting dark yellow solution is stirred for 30 min. Solvent is removed under reduced pressure to yield the desired product as a reddish-brown solid.

[250] 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

[251] 2-Methylcyclohexylamine (8.44 mL, 64.0 mmol) is dissolved in methanol (90 mL), and di-t-butylsalicaldehyde (10.00 g, 42.67 mmol) is added. The reaction mixture is stirred for three hours and then cooled to -25°C for 12 hrs. 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. ^{1}H 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)
   immino)zirconium dibenzyl

[252] 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 $Zr(CH_2Ph)_4$ (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.

[253] **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(C_6F_5)$_4$], substantially as disclosed in U.S. Patent No. 5,919,9883, Ex. 2.

[254] **Cocatalyst 2** Mixed C_{14-18} alkyldimethylammonium salt of bis(tris(pentafluorophenyl)-alumane)-2-undecylimidazolide, prepared according to U.S. Patent No. 6,395,671, Ex. 16.

[255] **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-

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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-

5   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

10   **[256]** Polymerizations are conducted using a high throughput, parallel polymerization reactor (PPR) available from Symyx Technologies, Inc. and operated substantially according to U.S. 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

15   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

20   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

25   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

30   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 (*).

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[257] 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 according to embodiments of the invention are distinguishable based on branching or density.

Table 1

Ex.	Cat. (A1) (μmol)	Cat (B1) (μmol)	Cocat (μmol)	MMAO (μmol)	shuttling agent (μmol)	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] C_6 or higher chain content per 1000 carbons
[2] Bimodal molecular weight distribution

[258] It may be seen the polymers produced according to embodiments of 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.

[259] 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:

[260] The DSC curve for the polymer of Example 1 shows a 115.7°C melting point (Tm) 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 Tm and the Tcrystaf is 81.2°C.

[261] The DSC curve for the polymer of Example 2 shows a peak with a 109.7°C melting point (Tm) 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 Tm and the Tcrystaf is 63.5°C.

[262] The DSC curve for the polymer of Example 3 shows a peak with a 120.7°C melting point (Tm) 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 Tm

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and the Tcrystaf is 54.6°C.

[263] The DSC curve for the polymer of Example 4 shows a peak with a 104.5°C melting point (Tm) 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 Tm and the Tcrystaf is 74.5°C.

[264] The DSC curve for comparative A shows a 90.0°C melting point (Tm) 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 Tm and the Tcrystaf is 41.8°C.

[265] The DSC curve for comparative B shows a 129.8°C melting point (Tm) 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 Tm and the Tcrystaf is 47.4°C.

[266] The DSC curve for comparative C shows a 125.3°C melting point (Tm) 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 Tm and the Tcrystaf is 43.5°C.

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

[267] 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

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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

5   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

10   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.

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Table 2 Process details for preparation of ethylene/α-olefin block copolymers

Ex.	C_8H_{16} kg/hr	Solv. kg/hr	H_2 sccm[1]	T °C	Cat A1[2] ppm	Cat A1 Flow kg/hr	Cat B2[3] ppm	B2 Flow kg/hr	DEZ Conc %	DEZ Flow kg/hr	Cocat Conc. ppm	Cocat Flow kg/hr	$[C_2H_4]/[DEZ]$[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 cm^3/min

[2] [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)immino) 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

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Table 3 Properties of ethylene/α-olefin block copolymers

Ex.	Density (g/cm³)	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)	Tm-$T_{CRYSTAF}$ (°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	109600	53300	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	129600	28700	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

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Physical Property Testing

[268] 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,

5   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

10 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.

15   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

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[269] 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.

[270] Similarly, Table 4 shows a low (good) storage modulus ratio, G'(25°C)/G'(100°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.

[271] The data in Table 4 also demonstrate that the polymers according to embodiments 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.

[272] 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.

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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 (mm³)	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

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[273]   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 mm^3, preferably less than about 80 mm^3, and

5   especially less than about 50 mm^3. In this test, higher numbers indicate higher volume loss and consequently lower abrasion resistance.

[274]   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

10   have tear strengths no higher than 750 mJ.

[275]   Table 5 also shows that the polymers according to embodiments 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

15   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.

20   [276]   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 Haze, Clarity, and Gloss

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

[277] The haze, clarity, and gloss values reported in Table 6 are based on compression molded 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. In addition, the crystallite size may also be controlled through various processing methods and quenching conditions as well as through manipulation of the level of comonomer and hard segment content.

Extractions of Multi-Block Copolymers

[278] Extraction studies of the polymers of Examples 5, 7 and Comparative E are 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 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

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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

5 purged dry with nitrogen.

[279] 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

10 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.

[280] The polymer sample remaining in the thimble after the extractions is transferred from

15 the thimble to a weighed bottle and vacuum dried overnight at 40°C. Results are contained in Table 7.

Table 7 Results from extraction with ether and hexane

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 ^{13}C NMR

Additional Polymer Examples 19 A-I, Continuous Solution Polymerization, Catalyst

20 **A1/B2 + DEZ**

[281] **Examples 19A-I**: Continuous solution polymerizations are carried out in a computer controlled well-mixed reactor. Purified mixed alkanes solvent (Isopar™ E available from Exxon Mobil Chemical Company), 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

25 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

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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 devolatization. The solvent and unreacted monomers are removed during the devolatization process. The polymer melt is

5   pumped to a die for underwater pellet cutting.

[282] Polymer Examples 20-23 were made using similar procedures as described in the above. Process details and results are contained in Tables 8A- C. Selected polymer properties are provided in Tables 9A-B. Table 9C shows the block indices for various polymers measured and calculated according the methodology described above. For

10   calculations performed herein, T_A is 372°K, P_A is 1.

Table 8A Polymerization Conditions for Polymers 19A-J

Ex.	C₂H₄ lb/hr	C₈H₁₆ lb/hr	Solv. lb/hr	H₂ sccm[1]	T °C	Cat A1[2] Conc. ppm	Cat A1 Flow lb/hr	Cat B2[3] Conc. ppm	Cat B2 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
19A	55.29	32.03	323.03	101	120	600	0.25	200	0.42	3.0	0.70	4500	0.65	525	0.33	248
19B	53.95	28.96	325.3	577	"	"	0.25	"	0.55	3.0	0.24	"	0.63	"	0.11	90
19C	55.53	30.97	324.37	550	"	"	0.216	"	0.609	3.0	0.69	"	0.61	"	0.33	246
19D	54.83	30.58	326.33	60	"	"	0.22	"	0.63	3.0	1.39	"	0.66	"	0.66	491
19E	54.95	31.73	326.75	251	"	"	0.21	"	0.61	3.0	1.04	"	0.64	"	0.49	368
19F	50.43	34.80	330.33	124	"	"	0.20	"	0.60	3.0	0.74	"	0.52	"	0.35	257
19G	50.25	33.08	325.61	188	"	"	0.19	"	0.59	3.0	0.54	"	0.51	"	0.16	194
19H	50.15	34.87	318.17	58	"	"	0.21	"	0.66	3.0	0.70	"	0.52	"	0.70	259
19I	55.02	34.02	323.59	53	"	"	0.44	"	0.74	3.0	1.72	"	0.70	"	1.65	600

[1] standard cm³/min

[2] [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)immino) zirconium dimethyl

[4] ppm in final product calculated by mass balance

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Table 8B Additional Polymerization Conditions for Polymers 19A-J

Ex.	Poly Rate[5] lb/hr	Conv[6] wt%	Polymer wt%	$[C_2H_4]/[Zn]$[7]	$[Zn]/[C_2H_4]$ *1000[8]	Eff.[9]
19A	83.94	88.0	17.28	775	1.29	297
19B	80.72	88.1	17.2	2222	0.45	295
19C	84.13	88.9	17.16	775	1.29	293
19D	82.56	88.1	17.07	395	2.53	280
19E	84.11	88.4	17.43	513	1.95	288
19F	85.31	87.5	17.09	725	1.38	319
19G	83.72	87.5	17.34	1000	1.0	333
19H	83.21	88.0	17.46	752	1.33	312
19I	86.63	88.0	17.6	317	3.15	275

[5] polymer production rate
[6] weight percent ethylene conversion in reactor
[7] molar ratio in reactor: Zn/C_2 *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/C_2*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.
[8] molar ratio in reactor
[9] efficiency, lb polymer/lb M where lb M = lb Hf + lb Z

Table 8C Polymerization Conditions for Polymers 20-23.

						Cat A1[2]	Cat A1	Cat B2[3]	Cat B2	DEZ	DEZ	Cocat	Cocat	[C2H4]/ [Zn][4]	[Zn]/ [C2H4]* 1000[5]	Poly			
	Co.* Type	Co.*	Solv.	H2	T	Flow			Flow	Conc.	Flow	Conc.	Flow			Rate[6]	Conv[7]	Solids	
Ex.		kg/hr	kg/hr	sccm[1]	°C	ppm	kg/hr	ppm	Kg/hr	ppm Zn	kg/hr	ppm	kg/hr			kg/hr	%	%	Eff.[8]
20	Octene	1.6	11.4	104.8	119	71.7	0.059	46.4	0.055	1688	0.018	1743	0.118	9166	0.11	1.6	90	11.4	239
21	Butene	"	10.5	9.9	120	94.2	0.065	10.5	0.100	9222	0.068	1168	0.057	442	2.26	1.7	90.5	12.2	235
22	Butene	"	10.5	37.5	"	"	0.064	"	0.088	"	0.018	"	0.054	1851	0.54	1.6	90	11.9	228
23	Propylene	1.4	9.8	4.9	"	53.1	0.024	58.1	0.098	3030	0.151	429.4	0.139	1030	0.97	1.1	82.5	9.4	184

* "Co." stands for "comonomer".

1. standard cm3/min

2. [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)immino) zirconium dibenzyl

4. molar ratio in reactor; 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.

5. molar ratio in reactor

6. polymer production rate

7. percent ethylene conversion in reactor

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

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Table 9A Polymer Physical Properties

Ex.	Density (g/cc)	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 (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

Table 9B Polymer Physical Properties of Compression Molded Films

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	-

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Table 9C. Block Index for Selected Polymers

Example	Comonomer	Density (g/cc)	I_2 g/10 min.	Zn/C_2H_4*1000	Average Block Index ("BI")	
					Weight Average BI	Second Moment About the Mean Weight Average BI
F*	Octene	0.8895	0.9	0	0	0
L*	Octene	0.905	0.8	-	0	0.01
M*	Octene	0.902	1.0	-	0	0
20	Octene	0.8841	1.0	0.11	0.2	0.45
8	Octene	0.8828	0.9	0.56	0.59	0.32
19A	Octene	0.8781	0.9	1.3	0.62	0.17
5	Octene	0.8786	1.5	2.4	0.53	0.136
19B	Octene	0.8749	0.9	0.45	0.54	0.35
19I	Octene	0.8774	11.2	3.15	0.59	0.22
21	Butene	0.8795	0.9	1.89	0.65	0.22
22	Butene	0.8802	1.1	1.71	0.66	0.33
23	Propylene	0.883	1.2	0.97	0.61	0.24

1) L* is a ultra low density polyethylene made by Ziegler-Natta catalysis and available from The Dow Chemical Company under the trademark of ATTANE™ 4203.

2) M* is a polyethylene copolymer made by constrained geometry catalysis (i.e., single-site catalyst) and available from The Dow Chemical Company under the trademark of AFFINITY® PL1880G.

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[283] As shown in Table 9C, all the inventive polymers have a weight average block index of greater than zero, whereas the random copolymers (Polymers F*, L*, and M*) all have a block index of zero.

[284] Figure 9 shows the block index distribution for Polymer F*, Polymer 20, Polymer 8, and Polymer 5 as a function of the ATREF temperature. For Polymer F*, the block index for all the ATREF fraction is zero or substantially zero (i.e., ≤ 0.01). Polymer 20 was made with a relatively low level of the shuttling agent, diethyl zinc ("DEZ"). While the weight average block index for the whole polymer is about 0.2, the polymer includes four fractions with a block index from about 0.7 to about 0.9. For Polymers 5 and 8, their weight average block indices are not drastically different (0.52 vs. 0.59), considering the DEZ level is about a four-fold difference. Moreover, most of their fractions have a block index of about 0.6 or higher. Similar results are seen between Polymer 5 and Polymer 19B, which is illustrated in Figure 10. However, there are some notable differences in the block index for the fractions which elute from about 70 °C to about 90 °C. Polymer 19B was made with a higher level (about four fold higher) of DEZ than Polymer 5. However, Polymer 5 has more fractions that have higher block indices. This seems to suggest that there might be an optimal DEZ level for making fractions with higher block indices (i.e., greater than about 0.6).

[285] The effect of the DEZ concentration level on the average block index for some of the polymers in Table 9C is illustrated in Figure 11. The plots seem to suggest that the average block index increases with increasing DEZ initially. Once Zn/C_2H_4*1000 exceeds about 0.5, the average block index appears to level off and may even drop off if too much DEZ is used.

[286] Figure 12 is a plot of the square root of the second moment about the mean weight average block index as a function of $[Zn/C_2H_4]*1000$. It appears to decrease as DEZ increases. This would indicated that the distribution of the block indices of the fractions are becoming narrower (i.e., more homogeneous).

TREF and NMR Data

[287] Tables 10-14 list TREF, DSC, IR, and NMR data for Polymers 5, 8, 14, and 19 and various comparative polymers.

Table 10 – TREF Fractions from Ziegler-Natta LLDPE

Ex. L * - Ziegler-Natta Example (Attane™ 4203, 0.90 g/cm^3, 0.8 I$_2$)

Fractionation Temperature	ATREF T (°C)	Mol % Octene (NMR)	Tm (°C)	DeltaH melt (J/g)
35-40	49	8.0	82	84
40-45	56.5	7.0	86	97
45-50	57.5	6.6	89	101
50-55	61	6.0	92	96
55-60	63.5	5.4	95	99
60-65	67.5	4.9	98	104
65-70	72	4.3	101	112
70-75	75.5	3.7	104	112
75-80	79	3.1	107	122
80-85	83.5	2.5	112	131
85-90	90	1.7	116	154
90-95	95.5	1.1	123	160
95-100	100	0.5	128	185
100-105	101	0.2	130	195

Table 11 – TREF Fractions from Random Copolymer

5

Ex. M* - Random Copolymer Example (AFFINITY® PL1880, 0.90 g/cm^3, 1 I$_2$)

Fractionation Temperature	ATREF T (°C)	Mol % Octene (NMR)	Tm (°C)	DeltaH melt (J/g)
35-40	51.5	NM	83	102
40-45	56	7.3	87	96
45-50	61.5	6.5	90	101
50-55	63.5	5.7	93	100
55-60	66.5	5.3	95	104
60-65	69.5	4.9	97	105
65-70	72	4.4	99	111
70-75	74	4.2	101	111
75-80	76.5	3.8	106	112

Table 12 – TREF Fractions from Inventive Example 5

Inventive Example 5

Fractionation Temperature	ATREF T (°C)	Mol % Octene (NMR)	Tm (°C)	DeltaH melt (J/g)
60-65	70.5	12.6	106	45
65-70	73	12.2	108	48
70-75	77	11.7	111	51
75-80	81	10.5	113	57
80-85	84	9.8	115	68
85-90	88.5	7.0	119	83
90-95	92	5.2	123	110

Table 13 – TREF Fractions from Inventive Example 8

Inventive Example 8

Fractionation Temperature	ATREF T (°C)	Mol % Octene (NMR)	Tm (°C)	DeltaH melt (J/g)
50-55	20	16.5	98	28
55-60	57.5	16.2	104	29
60-65	61.5	16.5	106	28
65-70	65.5	16.2	109	29
70-75	70.5	15.7	112	31
75-80	73	15.5	114	32
80-85	81.5	11.6	117	37
85-90	89.5	10.7	120	58
90-95	96	4.6	126	125
95-100	96.5	1.5	129	180

Table 14 – ATREF Peak comonomer composition for random copolymers and Examples 5,8,14,19

Example	Density (g/cc)	I2	Mol % Octene (NMR)	T_ATREF (°C)	Mol % Octene TREF Peak (Infra-red)	Infra-red FWHM CH2 Area	Infra-red FWHM CH3 Area	Infra-red FWHM CH3/CH2 Area Ratio
N*	0.96	1.0	0	102	0.0	37.5	28.2	0.753
O*	0.9371	2.0	0.69	95	1.2	29.0	22.2	0.765
M*	0.9112	1.0	3.88	79	4.0	77.5	61.0	0.786
P*	0.9026	1.1	5.57	70	5.1	74.3	59.0	0.794
Q*	0.8872	0.9	9.06	57	9.2	30.9	25.5	0.824
Ex. 5	0.8786	1.5	NA	82	11.4	77.5	61.0	0.841
Ex. 8	0.8828	0.9	NA	90	12.2	34.0	28.8	0.846
Ex. 14	0.9116	2.6	NA	92	6.5	23.4	18.8	0.805
Ex. 19	0.9344	3.4	NA	97	2.8	25.3	19.7	0.777

Infra-red detector calibration: Mol % Octene = 133.38 (FWHM CH_3/CH_2 Area) – 100.8

N* is an ethylene homopolymer.

O* is an ethylene/octene copolymer available from The Dow Chemical Company under AFFINITY®
HF1030.

5   P* is an ethylene/octene copolymer available from The Dow Chemical Company under AFFINITY®
PL1880.

Q* is an ethylene/octene copolymer available from The Dow Chemical Company under AFFINITY®
VP8770.

10   **Calculation of Block Index**

[288]   With reference to Figures 7-8, the calculation of block indices is exemplified for
Polymer 5. In the calculations, the following calibration equation is used:

$$Ln\ P = -237.8341/T_{ATREF} + 0.6390$$

where P is the ethylene mole fraction, and T_{ATREF} is the ATREF elution temperature. In
15   addition, the following parameters are used:

Parameter	Value	Explanation
T_A	372.15	Analytical TREF elution temperature (°K) of hard segment
P_A	1.000	Mole fraction of ethylene of hard segment
P_{AB}	0.892	Mole fraction of ethylene of whole polymer
T_{AB}	315.722	Calculated equivalent analytical TREF elution temperature (°K) of whole polymer from whole polymer ethylene content

[289]   Table 15 gives details of the calculations for Polymer 5. The weighted average block
index, ABI, for Polymer 5, is 0.531, and the square root of sum of weighted squared
deviations about the weighted mean is 0.136. The partial sum of weights with fraction BI
20   greater than zero (see note 2 below) is 0.835.

Measurement of Weight Percent of Hard and Soft Segments

[290]   As discussed above, the block interpolymers comprise hard segments and soft
segments. The soft segments can be present in a block interpolymer from about 1 weight
25   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

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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. Conversely, the hard segments can be present in a similar range as above. The soft segment weight percentage

5   (and thus the hard segment weight percentage) can be measured by DSC or NMR.

TABLE 15 Fractional Block Index (BI) Calculations

Frac-tion #	Weight Recovered (g)	ATREF Elution Temp-erature (°K)	Mole Fraction Ethylene (NMR)	Weight Fraction Recovered	Random Equivalent ATREF Temperature from NMR Ethylene Weight Fraction (°K)	Random Equivalent mole fraction ethylene from ATREF Temperature	Fractional Block Index based on Temperature formula	Fractional Block Index based on Log_e of mole fraction formula	Weight-ed Fraction-al Block Indices	Weighted Squared Devia-tions about the Weighted Mean (Note 2)
Array Variable Name->	T_x	P_x	w_i	T_{Xo}	P_{Xo}	BI_i	BI_i	$w_i * BI_i$	$w_i * (BI_i - ABI)$
1	3.0402	(Note 1)	0.859	0.165	(Note 1)	(Note 1)	0	0	0	(Note 1)
2	1.9435	340	0.873	0.106	307	0.941	0.659	0.659	0.070	0.0017
3	0.7455	343.5	0.883	0.041	312	0.948	0.622	0.622	0.025	0.0003
4	1.0018	346	0.882	0.054	311	0.953	0.676	0.676	0.037	0.0011
5	2.3641	350	0.896	0.128	318	0.960	0.607	0.607	0.078	0.0007
6	4.1382	354	0.895	0.225	317	0.968	0.684	0.684	0.154	0.0052
7	3.5981	357	0.902	0.195	320	0.973	0.665	0.665	0.130	0.0035
8	1.2280	361.5	0.930	0.067	334	0.981	0.470	0.470	0.031	0.0003
9	0.3639	365	0.948	0.020	343	0.987	0.357	0.357	0.007	0.0006
									ABI	
	18.4233	Total Weight		1.000	Normalization check		Weighted Sums		0.531	0.0135

Note 1 : Fraction #1 does not crystallize in the analytical ATREF and is assigned $BI_i = 0$

Note 2 : The weighted squared deviations about the weighted mean use only $BI_i > 0$

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Hard Segment Weight fraction Measured by DSC

[291] For a block polymer having hard segments and soft segments, the density of the overall block polymer, $\rho_{overall}$, satisfies the following relationship:

$$\frac{1}{\rho_{overall}} = \frac{x_{hard}}{\rho_{hard}} + \frac{x_{soft}}{\rho_{soft}}$$

5 [292] where ρ_{hard}, and ρ_{soft}, are the theoretical density of the hard segments and soft segments, respectively. χ_{hard}, and χ_{soft}, are the weight fraction of the hard segments and soft segments, respectively and they add up to one. Assuming ρ_{hard} is equal to the density of ethylene homopolymer, i.e., 0.96 g/cc, and transposing the above equation, one obtains the following equation for the weight fraction of hard segments:

$$x_h = \frac{\dfrac{1}{\rho_{Overall}} - \dfrac{1}{\rho_{Soft}}}{-\dfrac{1}{\rho_{Overall}} + \dfrac{1}{0.96\,g/cc}}$$

10

[293] In the above equation, $\rho_{overall}$ can be measured from the block polymer. Therefore, if ρ_{soft} is known, the hard segment weight fraction can be calculated accordingly. Generally, the soft segment density has a linear relationship with the soft segment melting temperature, which can be measured by DSC over a certain range:

15                                 $\rho_{soft} = A*T_m + B$

[294] where A and B are constants, and T_m is the soft segment melting temperature in degrees Celsius. A and B can be determined by running DSC on various copolymers with a known density to obtain a calibration curve. It is preferable to create a soft segment calibration curve that span the range of composition (both comonomer type and content)

20 present in the block copolymer. In some embodiments, the calibration curve satisfies the following relationship:

$\rho soft = 0.00049*Tm + 0.84990$

Therefore, the above equation can be used to calculate the soft segment density if Tm in degrees Celsius is known.

25 [295] For some block copolymers, there is an identifiable peak in DSC that is associated with the melting of the soft segments. In this case, it is relatively straightforward to determine Tm for the soft segments. Once Tm in degrees Celsius is determined from DSC, the soft segment density can be calculated and thus the hard segment weight fraction.

[296] For other block copolymers, the peak associated with the melting of the soft segments is either a small hump (or bump) over the baseline or sometimes not visible as illustrated in Figure 13. This difficulty can be overcome by converting a normal DSC profile into a weighted DSC profile as shown in Figure 14. The following method is used to convert a

5 normal DSC profile to a weighted DSC profile.

[297] In DSC, the heat flow depends on the amount of the material melting at a certain temperature as well as on the temperature-dependent specific heat capacity. The temperature-dependence of the specific heat capacity in the melting regime of linear low density polyethylene leads to an increase in the heat of fusion with decreasing comonomer

10 content. That is, the heat of fusion values get progressively lower as the crystallinity is reduced with increasing comonomer content. See Wild, L. Chang, S.; Shankernarayanan, MJ. Improved method for compositional analysis of polyolefins by DSC. Polym. Prep 1990; 31: 270-1, which is incorporated by reference herein in its entirety.

[298] For a given point in the DSC curve (defined by its heat flow in watts per gram and

15 temperature in degrees Celsius), by taking the ratio of the heat of fusion expected for a linear copolymer to the temperature-dependent heat of fusion ($\Delta H(T)$), the DSC curve can be converted into a weight-dependent distribution curve.

[299] The temperature-dependent heat of fusion curve can be calculated from the summation of the integrated heat flow between two consecutive data points and then

20 represented overall by the cumulative enthalpy curve.

[300] The expected relationship between the heat of fusion for linear ethylene/octene copolymers at a given temperature is shown by the heat of fusion versus melting temperature curve. Using random ethylene/octene copolymers, one can obtain the following relationship:
Melt Enthalpy (J/g) = $0.0072 * Tm^2$ (°C) + $0.3138 * Tm$ (°C) + 8.9767

25 [301] For each integrated data point, at a given temperature, by taking a ratio of the enthalpy from the cumulative enthalpy curve to the expected heat of fusion for linear copolymers at that temperature, fractional weights can be assigned to each point of the DSC curve.

[302] It should be noted that, in the above method, the weighted DSC is calculated in the

30 range from 0 °C until the end of melting. The method is applicable to ethylene/octene copolymers but can be adapted to other polymers.

[303] Applying the above methodology to various polymers, the weight percentage of the hard segments and soft segments were calculated, which are listed in Table 16. It should be noted that sometimes it is desirable to assign 0.94 g/cc to the theoretical hard segment

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density, instead of using the density for homopolyethylene, due to the fact that the hard

segments may include a small amount of comonomers.

Table 16 Calculated Weight Percentage of Hard and Soft Segments for Various Polymers

Polymer Example No.	Overall Density	Soft Segment T_m (°C) from weighted DSC	Calculated Soft Segment Density	Calculated wt% Hard Segment	Calculated wt% Soft Segment
F*	0.8895	20.3	0.860	32%	68%
5	0.8786	13.8	0.857	23%	77%
6	0.8785	13.5	0.857	23%	77%
7	0.8825	16.5	0.858	26%	74%
8	0.8828	17.3	0.858	26%	74%
9	0.8836	17.0	0.858	27%	73%
10	0.878	15.0	0.857	22%	78%
11	0.882	16.5	0.858	25%	75%
12	0.870	19.5	0.859	12%	88%
13	0.872	23.0	0.861	12%	88%
14	0.912	21.8	0.861	54%	46%
15	0.8719	0.5	0.850	22%	78%
16	0.8758	0.3	0.850	26%	74%
18	0.9192	-	-	-	-
19	0.9344	38.0	0.869	74%	26%
17	0.8757	2.8	0.851	25%	75%
19A	0.8777	11.5	0.856	23%	77%
19B	0.8772	14.3	0.857	22%	78%

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Hard Segment Weight Percentage Measured by NMR

[304] ^{13}C NMR spectroscopy is one of a number of techniques known in the art for measuring comonomer incorporation into a polymer. An example of this technique is described for the determination of comonomer content for ethylene/α-olefin copolymers in

5   Randall (Journal of Macromolecular Science, Reviews in Macromolecular Chemistry and Physics, C29 (2 & 3), 201 - 317 (1989)), which is incorporated by reference herein in its entirety. The basic procedure for determining the comonomer content of an ethylene/olefin interpolymer involves obtaining a ^{13}C NMR spectrum under conditions where the intensity of the peaks corresponding to the different carbons in a sample is directly proportional to the

10   total number of contributing nuclei in the sample. Methods for ensuring this proportionality are known in the art and involve allowance for sufficient time for relaxation after a pulse, the use of gated-decoupling techniques, relaxation agents, and the like. The relative intensity of a peak or group of peaks is obtained in practice from its computer-generated integral. After obtaining the spectrum and integrating the peaks, those peaks associated with the comonomer

15   are assigned. This assignment can be made by reference to known spectra or literature, or by synthesis and analysis of model compounds, or by the use of isotopically labeled comonomers. The mole % comonomer can be determined by the ratio of the integrals corresponding to the number of moles of comonomer to the integrals corresponding to the number of moles of all of the monomers in the interpolymer, as described in the

20   aforementioned Randall reference.

[305]   Since the hard segment generally has less than about 2.0 wt% comonomer, its major contribution to the spectrum is only for the integral at about 30 ppm. The hard segment contribution to the peaks not at 30 ppm is assumed negligible at the start of the analysis. So for the starting point, the integrals of the peaks not at 30 ppm are assumed to come from the

25   soft segment only. These integrals are fit to a first order Markovian statistical model for copolymers using a linear least squares minimization, thus generating fitting parameters (i.e., probability of octene insertion after octene, P_{oo}, and probability of octene insertion after ethylene, P_{eo}) that are used to compute the soft segment contribution to the 30 ppm peak. The difference between the total measured 30 ppm peak integral and the computed soft segment

30   integral contribution to the 30 ppm peak is the contribution from the hard segment. Therefore, the experimental spectrum has now been deconvoluted into two integral lists describing the soft segment and hard segment, respectively. The calculation of weight percentage of the hard segment is straight forward and calculated by the ratio of the sum of

integrals for the hard segment spectrum to the sum of integrals for the overall spectrum.

[306] From the deconvoluted soft segment integral list, the comonomer composition can be calculated according to the method of Randall, for example. From the comonomer composition of the overall spectrum and the comonomer composition of the soft segment, one can use mass balance to compute the comonomer composition of the hard segment. From the comonomer composition of the hard segment, Bernoullian statistics is used to calculate the contribution of the hard segment to the integrals of non 30 ppm peaks. There is usually so little octene, typically from about 0 to about 1 mol%, in the hard segment that Bernoullian statistics is a valid and robust approximation. These contributions are then subtracted out from the experimental integrals of the non 30 ppm peaks. The resulting non 30 ppm peak integrals are then fitted to a first order Markovian statistics model for copolymers as described in the above paragraph. The iterative process is performed in the following manner: fit total non 30 ppm peaks then compute soft segment contribution to 30 ppm peak; then compute soft/hard segment split and then compute hard segment contribution to non 30 ppm peaks; then correct for hard segment contribution to non 30 ppm peaks and fit resulting non 30 ppm peaks. This is repeated until the values for soft/hard segment split converge to a minimum error function. The final comonomer compositions for each segment are reported.

[307] Validation of the measurement is accomplished through the analysis of several *in situ* polymer blends. By design of the polymerization and catalyst concentrations the expected split is compared to the measured NMR split values. The soft/hard catalyst concentration is prescribed to be 74 % / 26 %. The measured value of the soft / hard segment split is 78 % / 22 %. Table 17 shows the chemical shift assignments for ethylene octene polymers.

Table 17 Chemical Shift Assignments for Ethylene/Octene Copolymers.

41-40.6 ppm	OOOE/EOOO αα CH2
40.5-40.0 ppm	EOOE αα CH2
38.9-37.9 ppm	EOE CH
36.2 – 35.7 ppm	OOE center CH
35.6 – 34.7 ppm	OEO αγ, OOO center 6B, OOEE αδ+, OOE center 6B CH2
34.7 – 34.1 ppm	EOE αδ+ , EOE 6B CH2
33.9 – 33.5 ppm	OOO center CH
32.5 – 32.1 ppm	3B CH2
31.5 – 30.8 ppm	OEEO γγ CH2
30.8 – 30.3 ppm	OE γδ+ CH2
30.3 – 29.0 ppm	4B, EEE δ+δ+ CH2
28.0 – 26.5 ppm	OE βδ+ 5B

25.1 – 23.9 ppm	OEO ββ
23.0 – 22.6 ppm	2B
14.5 – 14.0 ppm	1B

[308]   The following experimental procedures are used. A sample is prepared by adding

0.25 g in a 10 mm NMR tube with 2.5 mL of stock solvent. The stock solvent is made by

dissolving 1 g perdeuterated 1,4-dichlorobenzene in 30 mL ortho-dichlorobenzene with 0.025

5   M chromium acetylacetonate (relaxation agent). The headspace of the tube is purged of

oxygen by displacement with pure nitrogen. The sample tube is then heated in a heating

block set at 150 °C. The sample tube is repeatedly vortexed and heated until the solution

flows consistently from top of the solution column to the bottom. The sample tube is then

left in the heat block for at least 24 hours to achieve optimum sample homogeneity.

10   [309]   The ^{13}C NMR data is collected using a Varian Inova Unity 400 MHz system with

probe temperature set at 125 °C. The center of the excitation bandwidth is set at 32.5 ppm

with spectrum width set at 250 ppm. Acquisition parameters are optimized for quantitation

including 90° pulse, inverse gated ^{1}H decoupling, 1.3 second acquisition time, 6 seconds

delay time, and 8192 scans for data averaging. The magnetic field is carefully shimmed to

15   generate a line shape of less than 1 Hz at full width half maximum for the solvent peaks prior

to data acquisition. The raw data file is processed using NUTS processing software

(available from Acorn NMR, Inc. in Livermore, CA) and a list of integrals is generated.

[310]   Inventive Polymer 19A is analyzed for the soft/hard segment split and soft/hard

comonomer composition.   The following is the list of integrals for this polymer. The NMR

20   spectrum for Polymer 19A is shown in Figure 15.

	Integral limit	Integral value
	41.0 – 40.6 ppm	1.067
	40.5 – 40.0 ppm	6.247
	38.9 – 37.9 ppm	82.343
25	36.2 – 35.7 ppm	14.775
	35.6 – 34.7 ppm	65.563
	34.7 – 34.1 ppm	215.518
	33.9 – 33.5 ppm	0.807
	32.5 – 32.1 ppm	99.612
30	31.5 – 30.8 ppm	14.691
	30.8 – 30.3 ppm	115.246
	30.3 – 29.0 ppm	1177.893
	28.0 – 26.5 ppm	258.294
	25.1 – 23.9 ppm	19.707
35	23.0 – 22.6 ppm	100
	14.5 – 14.0 ppm	99.895

[311] Using Randall's triad method, the total octene weight percentage in this sample is determined to be 34.6%. Using all the above integrals excluding the 30.3-29.0 ppm integral to fit a first order Markovian statistical model, the values for P_{oo} and P_{eo} are determined to be 0.08389 and 0.2051, respectively. Using these two parameters, the calculated integral

5   contribution from the soft segment to the 30 ppm peak is 602.586. Subtraction of 602.586 from the observed total integral for the 30 ppm peak, 1177.893, yields the contribution of the hard segment to the 30 ppm peak of 576.307. Using 576.307 as the integral for the hard segment, the weight percentage of hard segment is determined to be 26 %. Therefore the soft segment weight percentage is $100 - 26 = 74$ %. Using the above values for P_{oo} and P_{eo}, the

10   octene weight percentage of the soft segment is determined to be 47 %. Using the overall octene weight percentage and the octene weight percentage of the soft segment as well as the soft segment weight percentage, the octene weight percentage in the hard segment is calculated to be negative 2 wt%. This value is within the error of the measurement. Thus there is no need to iterate back to account for hard segment contribution to non 30 ppm peaks.

15   Table 18 summarizes the calculation results for Polymers 19A, B, F and G.

Table 18. Hard and Soft Segments Data for Polymers 19A, B, F and G

Example	wt% Soft Segment	wt% Hard Segment	wt% octene in Soft Segment
19A	74	26	47
19B	74	26	48
19F	86	14	49
19G	84	16	49

20   Additional Examples Set 1

[312] Examples 24 - 28 were prepared in a similar fashion as Examples 5-19. Table 19 shows the polymerization conditions for these examples and Table 20 shows the physical properties of these polymers.

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Table 19 – Polymerization Conditions for Examples 24 - 28

Ex.	C_8H_{16} kg/hr	Solv. kg/hr	H_2 sccm[1]	T °C	Cat Al[2] ppm	Cat Al Flow kg/hr	Cat B2[3] ppm	B2 Flow kg/hr	DEZ Conc ppm Zn	DEZ Flow kg/hr	Cocat Conc. ppm	Cocat Flow kg/hr	$[C_2H_4]$/ $[DEZ]$[4]	Poly Rate[5] kg/hr	Conv %[6]	Solids %	Eff.[7]
24	15.82	150.2	150	120	600	0.089	200	0.271	30000	0.335	4500	0.235	769	38.8	87.5	17.1	319
25	35.82	362.0	263	"	568	0.586	100	0.377	50000	0.259	5500	0.582	1377	92.7	88.1	17.7	117
26	47.77	414.4	195	"	"	0.864	"	1.111	"	0.370	"	0.968	1047	106	87.8	17.8	104
27	38.36	357.7	323	"	"	0.636	"	0.682	15000	0.891	"	0.886	1282	93	89.3	17.8	112
28	14.52	146.52	101	"	600	0.113	200	0.191	30000	0.318	4500	0.295	775	38.0	88.0	17.3	297

1. standard cm3/min
2. [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)immino) 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 20 – Polymer Properties for Examples 24 - 28

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)
24	0.865	1.1	7.5	6.8	124900	60700	2.1	27	119	88	30	89	90
25	0.875	0.5	3.7	7.3	146900	66600	2.2	51	120	101	52	68	39
26	0.866	1.0	7.3	7.3	134900	63300	2.1	22	119	98	36	83	6
27	0.877	0.5	3.9	7.2	144500	69400	2.1	48	120	99	49	71	72
28	0.878	0.9	6.4	6.9	123700	61000	2.0	56	119	97	51	67	31

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[313] Table 20 shows polymer properties for Examples 24-28, while Table 21 shows comonomer levels in the polymers as measured by ^{13}C NMR. Example 24 has a difference in octene content in the hard and soft segments, or Δ Octene, of 16.7 mol%. Examples 25 and 26 have Δ Octene = 17.5 mol%, Example 27 has Δ Octene = 18.2 mol%, and Example 28 has

5   Δ Octene = 16.2 mol%. These samples all have I_{10}/I_2 values < 7.3. The relationship between I_{10}/I_2 and Δ Octene is shown graphically in Figure 33.

Example	Overall Octene (mol %)	Octene in Soft Segment (mol %)	Octene in Hard Segment (mol %)	Δ Octene
24	15.2	17.1	0.4	16.7
25	12.3	18.0	0.5	17.5
26	15.7	18.4	0.5	17.5
27	12.83	19.1	0.9	18.2
28	11.9	16.6	0.4	16.2

Table 21 – Comonomer content

Additional Examples Set 2 – Mesophase separated polymers

10   **[314]** Examples 29 - 40 were prepared in a similar fashion as Examples 5-19. Table 22 shows the polymerization conditions for these examples and Table 23 shows the physical properties of these polymers. Some of these polymers exhibit a blueish tint via reflected light and appear yellow when viewed via transmitted light.

Table 22 – Polymerization Conditions for Examples 29-40

Ex.	C₈H₁₆ kg/hr	Solv. kg/hr	H₂ sccm[1]	T °C	Cat A1[2] ppm	Cat A1 Flow kg/hr	Cat A2[3] ppm	A2 Flow kg/hr	DEZ Conc (ppm Zn)	DEZ Flow kg/hr	Cocat Conc. ppm	Cocat Flow kg/hr	[C₂H₄]/ [DEZ][4]	Poly Rate[5] kg/hr	Conv %[6]	Solids %	Eff.[7]
29	5.21	9.53	3	120	93.2	0.111	15.9	0.119	2690	0.086	952	0.111	2113	1.6	79.6	9.6	128
30	5.24	9.89	0	"	"	0.144	"	0.152	"	0.145	"	0.150	1147	1.9	84.4	11.3	120
31	5.19	9.53	0	"	56.20	0.193	"	0.126	"	0.122	525.5	0.213	1725	1.6	79.9	9.9	127
32	5.19	9.52	8	"	93.20	0.092	"	0.097	"	0.060	951.5	0.093	2976	1.6	80.1	9.8	156
33	5.21	9.89	5	"	"	0.128	"	0.135	"	0.112	"	0.126	1385	2.0	85.3	11.7	139
34	4.62	9.89	3	"	92.90	0.183	"	0.338	"	0.101	"	0.214	1382	1.5	86.3	9.3	68
35	34.55	341.5	161	"	568	0.441	100	0.682	50000	0.518	5500	0.314	693	92	88.9	17.6	131
36	33.55	340.3	290	"	"	0.359	"	0.759	"	0.186	"	0.505	1518	92	89.3	17.4	148
37	37.55	313.8	136	"	"	0.318	"	0.814	"	0.314	"	0.482	943	89	88.0	16.8	148
38	56.1	541.6	370	"	"	0.508	"	0.590	"	0.377	5535	0.572	973	111.0	86.1	18.1	320
39	5.21	9.52	0	"	56.2	0.196	15.9	0.094	2690	0.126	526	0.203	1706	1.6	80.2	9.9	131
40	4.76	9.89	0	"	92.9	0.181	"	0.332	"	0.147	952	0.214	1042	1.6	85.6	9.7	74

1. standard cm³/min
2. [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)immino) 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

10   Table 23 – Polymer Properties for Examples 29-40

Ex.	Density (g/cm³)	I₂	I₁₀	I₁₀/I₂	Mw (g/mol)	Mn (g/mol)	Mw/Mn	Heat of Fusion (J/g)	Tₘ (°C)	T꜀ (°C)	T_CRYSTAF (°C)	Tm-T_CRYSTAF (°C)	CRYSTAF Peak Area (percent)
29	0.876	0.5	4.9	9.7	151500	70300	2.2	47	117	100	72	45	52
30	0.867	1.0	9.9	9.9	152000	56940	2.7	31	114	92	44	71	24
31	0.874	0.5	4.8	9.0	151200	68500	2.2	43	117	97	62	55	26
32	0.875	0.5	5.4	10.2	157400	69600	2.3	44	118	101	73	44	18
33	0.866	1.1	11.7	10.5	157900	61640	2.6	26	115	93	44	71	7
34	0.894	0.5	4.4	8.8	136000	66300	2.1	86	118	104	72	46	86

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35	0.889	1.1	7.8	6.9	110000	57800	1.9	70	120	102	61	59	53
36	0.888	0.9	6.7	7.7	126900	55100	2.3	69	122	104	75	47	44
37	0.884	0.9	7.3	7.9	130700	58200	2.2	62	119	102	74	45	41
38	0.872	1.0	8.9	8.5	144000	72200	2.0	36	118	96	73	46	10
39	0.871	0.7	6.0	9.1	154800	72800	2.1	47	116	97	59	57	37
40	0.888	0.6	4.9	8.4	131000	63800	2.1	75	117	101	69	48	86

Table 24 – Comonomer content for Examples 29-40

Example	Overall Octene (mol %)	Octene in Soft Segment (mol %)	Octene in Hard Segment (mol %)	Δ Octene
29	15.1	26	1.4	24.6
30	21.3	29.7	1.7	28.0
31	16.6	26.5	1.3	25.2
32	16.3	26.6	1.4	25.2
33	21.5	29.3	1.6	27.7
34	11.3	27.5	1.4	26.1
35	10.8	20.9	0.7	20.2
36	11.0	22.4	0.9	21.5
37	12.8	25.8	1.1	24.7
38	18.0	26.0	1.2	24.8
39	17.2	26.1	1.4	24.7
40	11.6	29.2	1.6	27.6

5

106

[315] One additional feature of this inventive block interpolymer is that it displayed an unusual shear thinning characteristic in the melt. At a given melt index (I_2), some embodiments of the inventive block interpolymers with high α-olefin materials have higher molecular weights and I_{10}/I_2 values than block interpolymers with lower α-olefin content.

5   Examples 24-28 have Δ Octene < 18.5 mol% and I_{10}/I_2 < 7.3. As seen in Table 24, Examples 29-40 all have Δ Octene > 18.5 mol%. Example 35 has Δ Octene = 20.2 and I_{10}/I_2 = 6.9, but the rest of the examples (Examples 29-34, 36-40) have $I_{10}/I_2 \geq$ 7.7. This higher I_{10}/I_2 may be used to distinguish these examples from examples with Δ Octene < 18.5 mol%. Differences in I_{10}/I_2 and Δ Octene for the samples is shown graphically in Figure 33. The higher I_{10}/I_2

10   values indicate that the polymer under high shear stresses flows more readily than a block interpolymer with low octene content. This enhanced flow may be useful for the coating of pressure sensitive adhesives, for example, which requires easy flow; it may also allow the use of higher molecular weight polymers in adhesive formulations which may result in improved creep resistance and holding power.

15

Microscopy Studies

Preparation of Compression Molded Samples

[316] About 40 g of the polymer was compression molded into a 2 inch x 2 inch x 0.06 inch plaque between Mylar sheets sandwiched between metal platens in a Carver compression

20   molding machine for 3 minutes at 190°C, 2 kpsi pressure for 3 minutes, 190°C, 20 kpsi pressure for 3 minutes, then cooling at 15°C, 20 kpsi for 3 minutes.

Preparation of Examples 32-34 for AFM Study

[317] Examples 32-34 were studied using tapping mode Atomic Force Microscopy (AFM). Compression molded samples were first polished using an ultramicrotome (Reichert-Jung

25   Ultracut E) at -120° C perpendicular to the plaques near the center of the core area. A thin section was placed on a mica surface for AFM imaging using a DI NanoScope IV, MultiMode AFM operating in Tapping Mode with phase detection. The tip was tuned to a voltage of 3V and the tapping ratio was 0.76 - 0.83. Nano-sensor tips were used with tip parameters of: L = 235µm, tip ratio = 5-10 nm, Spring constant = 37-55 N/m, F_0=159-164

30   kHz.

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[318]   Figures 16-18 show images of Examples 32-34 taken via AFM at approximately
3,000X magnification. These images show mesophase morphology similar to SBC
morphology except for the size range of the observed domains; the domains are much larger
than those of a monodisperse block copolymer with similar molecular weight. An example
of an SBC polymer (28 wt% styrene, 83 mol% "butene" in the B-block, M_n = 64,000 g/mol)
at approximately 30,000X magnification is shown in Figure 20.

Preparation of Example 34 for TEM Study

[319]   Example 34 was studied using transmission electron microscopy (TEM). The
compression molded sheets were trimmed so that sections could be collected between the
skin and core. The trimmed sheets were cryopolished prior to staining by removing sections
from the blocks at -60 °C to prevent smearing of the elastomer phases. The cryo-polished
blocks were stained with the vapor phase of a 2% aqueous ruthenium tetraoxide solution for 3
hrs at ambient temperature. The staining solution was prepared by weighing 0.2 gm of
ruthenium (III) chloride hydrate ($RuCl_3$ x H_2O) into a glass bottle with a screw lid and adding
10 mL of 5.25% aqueous sodium hypochlorite to the jar. The samples were placed in the
glass jar using a glass slide having double sided tape. The slide was placed in the bottle in
order to suspend the blocks about 1 inch above the staining solution. Sections of
approximately 100 nanometers in thickness were collected at ambient temperature using a
diamond knife on a Leica EM UC6 microtome and placed on 400 mesh virgin TEM grids for
observation.

[320]   Images were collected on a JEOL JEM-1230 operated at 100 kV accelerating voltage
and collected on a Gatan-791 and 794 digital cameras. The images were post processed using
Adobe Photoshop 7.0. Figure 19 shows a TEM micrograph of Example 34 at approximately
30,000X magnification.

Preparation of Examples 29, 30, 32, and 33-40 for Reflectance Spectroscopy Study

[321]   The reflectance spectra of Examples 29, 30, 32, and 33-40 were collected with a
Labsphere™ (model 60MM RSA ASSY) integrating sphere. Spectralon™ diffuse
reflectance standards were first mounted on both sample and reference ports of integrating
sphere and the baseline correction was performed for the spectral range from 200- 1200 nm.
The slit width and spectral resolution were 2 nm and the spectrum was acquired with 1

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nm/point. The Spectralon[TM] standard was then removed from the sample port and the film sample mounted in the sample port at a 90 degree incidence angle to the sample beam. No backing material was used and the film itself provided the only means of light reflectance.

[322]   Figures 29, 30 and 31 show the reflectance spectra of compression molded films of

5   Examples 35 thru 38, Examples 29, 30, 32 and 33 and Examples 34, 39 and 40 respectively. A compression molded film of AFFINITY® PL1280G (available from The Dow Chemical Company)) is also provided in each Figure for comparison. In contrast to the reflectance spectra of the film of the AFFINITY® material, which exhibits little or no reflection across the measured range of wavelengths, each of the Example films exhibit a peak reflectance

10   between 12 and 45% reflectivity. Figure 32 shows the reflectance spectra for Examples 25 and 26 which are not mesophase separated, which exhibit peak reflectances of less than about 12%.

Physical properties of Examples 26, 27, and 30 - 32.

15   [323]   The data presented in Table 25 demonstrates that at the same density, the mesophase separated materials have a lower Shore A and 100% secant modulus than the samples with lower values of Δ octene. This same data is presented graphically in Figure 21 which shows Shore A vs. density for Examples 26, 27, 30 and 31 and Figure 22 which shows 100% Modulus vs. density for these same Examples. This shows that ethylene/α-olefin block

20   copolymer-based materials may be made having a lower modulus or Shore A at a given density. When compared at the same Shore A (Ex 26 and Ex 31), the mesophase separated material has a significantly lower 70°C ASTM compression set compared to the non-mesophase separated material (35% versus 64%). Figure 23 shows 70 °C compression set vs. Shore A for these Examples as well as Ex 27 and 30. The mesophase separated examples

25   show comparable permanent set as the non-phase separated materials at about the same density when stretched to 300% strain.

30

Table 25

Example	Density (g/cm^3)	Shore A Hardness (0.5 sc)	100% Secant Modulus (MPa)	Compression set (70 °C)	300% Permanent Set (%)
26	0.866	61	1.5	64	36
27	0.877	75	2.4	39	44
30	0.867	46	0.8	46	41
31	0.874	61	1.5	35	43

[324] The dynamic mechanical relaxation responses as a function of temperature are presented as Tan δ curves in Figures 25 and 26 for Examples 26 and 30 and Examples 27 and 31, respectively. The glass transition, T_g, from the Tan δ curve and intensity of the peak are tabulated in Table 26. At similar density, the mesophase separated materials exhibit T_g's that are approximately 7°C lower than non-mesophase separated materials. A lower Tg offers the advantage of lower useful temperature range when used as an impact modifier.

Table 26

Example	Density (g/cm^3)	Tg (°C)	Max tan δ
26	0.866	-48	0.44
27	0.877	-45	0.45
30	0.867	-55	0.86
31	0.874	-52	0.55

[325] Figure 24 shows that the mesophase separated materials exhibit a similarly flat storage modulus as exhibited by the non-mesophase separated materials.

Blends with Oil and Polypropylene

[326] Blend formulations using inventive Ex. 29 and Comp. Ex. 25 with oil and polypropylene are listed in Table 27 together with Shore A and 70 °C compression set results. As also observed in Ex. 30 and Ex. 31, the inventive Ex 29 has lower Shore A than non-mesophase separated material at similar density. The lower Shore A is also observed in blends with the inventive example. This means that one can achieve softer blends using the mesophase separated material. Figure 27 shows 70 °C Compression Set vs Shore A for Blends 3, 4, 7 and 8. It is observed that blends with mesophase separated material result in a lower 70 °C Compression Set at a similar Shore A. In formulated soft compounds, one can achieve softer materials with lower compression set when using the inventive polymer.

Table 27

Example	wt.% Ex. 25 polymer	Wt. % Ex. 29 polymer	wt.% oil[1]	wt.% hPP[2]	Density (g/cc)	Shore A Hardness (5 sec)	Compression set (70°C)
Ex. 25	100	0	0	0	0.875	75	45
Ex. 29	0	100	0	0	0.876	61	35
Blend 1	35	0	50	15		53	64
Blend 2	28	0	60	12		31	60
Blend 3	0	35	50	15		31	54
Blend 4	0	28	60	12		19	53

1 Chevron ParaLux 6001R Oil (Chevron U.S.A. Inc.)
2 Polypropylene H314-02Z (The Dow Chemical Company)

Block Index for Example 34

[327] The weighted average block index, ABI, for Example 34, is 0.75, and the square root of sum of weighted squared deviations about the weighted mean is 1.12 (Table 28).

Table 28

Inventive Example 34

Fractionation Temperature	Wt Fraction Recovered	ATREF T (°C)	Mol % Octene (NMR)	Tm (°C)	DeltaH melt (J/g)	Fractional Block Index
20	0.0387	20	25.4	115.1	5.4	0
20-60	0.0154	53.5	22.4	115.3	22.7	1.38
60-65	0.0126	63	20.8	105.2	32.4	1.39
65-70	0.0111	69.5	19.2	109.5	42.6	1.33
70-75	0.0199	75	18.3	112.3	48.5	1.33
75-80	0.0497	80.5	16.1	114.3	58.3	1.19
80-85	0.2059	87	12.4	114.7	72.4	0.93
85-90	0.4877	90	8.3	116.9	97.4	0.59
90-95	0.1585	93	4.4	120.0	127.2	0.28
			Weight Average Block Index			0.75
	Square root of sum of weighted squared deviations about the weighted mean					1.12

[328] Figure 34 graphically shows that the heat of fusion (determined by DSC) of ATREF fractions of Example 34 are significantly lower than those of ATREF fractions of random ethylene octene copolymers (ATTANE® 4203, 0.90 g/cm^3, 0.8 I_2 and AFFINITY® PL1880, 0.90 g/cm^3, 1 I_2 – each available from The Dow Chemical Company). Specifically, the block interpolymer has molecular fractions which elute between 40 °C and 130 °C, when fractionated using TREF increments, that are 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: Heat of fusion (J/gm) $\leq$

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(3.1718)(ATREF elution temperature in Celsius) – 136.58, while 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: Heat of fusion (J/gm) $\leq$ (1.1312)(ATREF elution temperature in Celsius) + 22.97.

5   **[329]** Figure 35 graphically shows that the melting points of ATREF fractions of Example 34 are significantly higher than those from ATREF fractions of random ethylene octene copolymers (ATTANE® 4203, 0.90 g/cm^3, 0.8 I_2 and AFFINITY® PL1880, 0.90 g/cm^3, 1 I_2 – each available from The Dow Chemical Company) that are fit to a line representing (-5.5926 (mol % comonomer of the ATREF fraction) + 135.90 (solid line).

10   Additional Examples Set 3 – Impact Modification of Polypropylene

[330] Examples 41 - 50 are prepared in a process similar to that of Examples 5-19 above.

Table 29

Example	Co-monomer	Density (g/cc)	MI	Mw	Mn	Mw / Mn
41	octene	0.867	0.3	179800	76330	2.4
42	octene	0.863	0.4	188300	62780	3.0
43	octene	0.867	0.4	182800	81120	2.3
44	octene	0.860	0.3	254100	87550	2.9
45	octene	0.863	0.3	223900	77940	2.9
46	octene	0.862	0.2	273600	97460	2.8
47	octene	0.858	0.3	278800	75790	3.7
48	octene	0.864	0.3	233600	87040	2.7
49	butene	0.865	0.8	127700	53010	2.4
50	octene	0.863	0.5	179700	71620	2.5

Table 30 – Process conditions for Examples 41-50 performed at T = 120 °C[1]

Ex.	C_2H_4 Conc g/L	Comon Conc g/L	Solv. kg/hr	H_2 Sccm[2]	Cat Al[3] ppm	Cat Al Flow kg/hr	[A1]/ ([A1]+[B2]) Catalyst ratio[4]	Zn in poly ppm	[DEZ]/ [C2H4] *1000[5]	Poly Rate[6] kg/hr	Residence time (min)	Eff.[7]
41	7.5	83.1	215	0	206	1.1	0.76	141	0.26	67	21.9	131
42	6.8	94.0	215	0	222	1.0	0.80	125	0.26	68	22.0	145
43	7.6	92.5	232	0	200	1.2	0.74	142	0.28	77	20.2	146
44	7.6	120	166	0	200	0.71	0.74	71	0.17	52	28.5	166
45	7.5	121	199	0	180	1.1	0.69	102	0.22	63	23.7	148
46	7.2	120	199	0	182	1.1	0.69	74	0.16	64	23.7	145
47	7.4	146	166	0	277	0.52	0.80	62	0.17	55	28.3	173
48	7.2	144	183	0	245	0.68	0.68	87	0.20	59	25.8	162
49	6.9	70.0	213	0	332	1.0	0.93	229	0.38	70	21.9	95
50[8]	7.2	115	256	45	169	0.74	0.88	103	0.23	65	33.9	233

1. Unless noted, polymerizations employed a molar ratio of cocatalyst to total catalyst of 1.5 molar equivalents and a ratio of DEZ to MMAO of 100 to 6.
2. standard cm3/min
3. [N-(2,6-di(1-methylethyl)phenyl)amido)(2-isopropylphenyl)(α-naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium dimethyl
4. bis-(1-(2-methylcyclohexyl)ethyl)(2-oxoyl-3,5-di(t-butyl)phenyl)immino) zirconium dibenzyl
5. molar ratio in reactor
6. polymer production rate
7. efficiency, kg polymer/g M where g M = g Hf + g Zr
8. Polymerization employed a molar ratio of cocatalyst to total catalyst of 1.2 molar equivalents and a ratio of DEZ to MMAO of 100 to 8.

Table 31 – Polymer properties for Examples 41 - 50

Ex.	Tc (°C)	Tm (°C)	Tg (°C)	Heat of Fusion (J/g)	Cryst %	Total Co-monomer Mol%	Soft Segment, Co-monomer Mol%	Hard Segment, Co-Monomer Mol%	Wt % Soft Segment
41	87.6	117	-66.3	29	10	18.0	22.6	1.13	84
42	82.1	116	-67.1	21	7	20.6	25.0	1.28	87
43	89.5	116	-66.9	30	10	18.7	24.2	1.23	83
44	75.5	114	-68.8	15	5	25.5	30.8	1.68	90
45	76.9	114	-68.4	23	8	22.7	29.7	1.6	85
46	75.9	114	-68.5	21	7	22.9	30.0	1.62	85
47	74.1	112	-68.8	11	4	29.8	34.9	2.0	92
48	77.0	113	-68.7	24	8	24.3	34.0	1.93	82
49	76.0	115	-67.5	13	4	25.0	35.7	2.06	85
50	90.2	119	-65.8	31	10	20.0	23.9	1.2	88

[331] The TPO formulations, and their instrumented dart impact results, are shown in the table below. The weight percents for the polymers were adjusted so that the polymer weight ratios remained 70/30 weight percent polypropylene/impact modifier. D221 is a polypropylene homopolymer available from The Dow Chemical Company with an MFR of 35 and a density of 0.900 g/cc. Jetfill 700C is a compacted high purity North American talc

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with a median particle size of 1.5 micron. The Irganox B-225 is a 1/1 blend of a phenolic primary antioxidant and a phosphate secondary antioxidant.

Table 32 – Elastomer/polypropylene Formulations

Component	F1	F2	F3	F4	CF-1	CF-2	F5	F6	F7	F8	CF-3	F9	CF-4
D221	56	56	56	56	56	56	56	56	56	56	56	56	56
41	24												
42		24											
43			24										
44				24									
45							24						
46								24					
47									24				
48										24			
49												24	
R*					24	24					24		24
JetFil 700C	20	20	20	20	20	20	20	20	20	20	20	20	20
Irganox B225	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
TOTAL	100.2	100.2	100.2	100.2	100.2	100.2	100.2	100.2	100.2	100.2	100.2	100.2	100.2

*Comparative Example R is a random ethylene/octene copolymer with a density of 0.863 and a melt index of 0.5 commercially available as ENGAGE™ 8180 from The Dow Chemical Company

Table 33 – Instrumented Dart Impact Testing at -20 °C and -30 °C

	F1	F2	F3	F4	CF-1	CF-2	F5	F6	F7	F8	CF-3	F9	CF-4
Avg. IDI (in-lbs) -20 °C	363	332	364	370	319	309	333	347	335	323	277	321	338
% Ductile at -20 °C	80	50	80	70	20	10	80	70	70	70	0	80	10
Avg. IDI (in-lbs) -30 °C	332	329	387	350	297	317	334	330	340	363	273	340	261
% Ductile at -30 °C	20	20	10	40	0	0	40	50	30	0	0	20	0
Flex Mod., MPa	2087	2104	2094	1980	2216	2140	1913	1943	1634	1772	2099	1925	2077

Addition to Polypropylene Impact Copolymer

[332] The polypropylene impact copolymer is polypropylene C700-35N, available from The Dow Chemical Company. This polypropylene has a density of about 0.9 g/cc, a melt flow rate (230°C) of about 35 dg/min and a flexural modulus of about 1520 MPa, as measured according to ASTM D790A. The C700-35N is compounded with the elastomers, talc, and antioxidant described previously, using the compounding method described previously. The

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ingredients used and their levels are shown in Table 38.

Table 38 Formulations Using Polypropylene Impact Copolymer

Formulation #	F10	CF-5
Ingredient	**Parts**	**Parts**
C700-35N	62.3	62.3
R	0	17.7
Ex. 50	17.7	0
JetFil 700C	20	20
Irganox B225	0.2	0.2

[333] The compounds are injection molded into test specimens under the conditions

described previously. Flexural modulus and instrumented dart impact testing are performed

as described previously.   Notched Izod impact is tested according to ISO 180.

[334] The physical property results of these two compounds are shown in Table 39. As can

be seen, the inventive elastomer imparts much higher instrumented dart impact ductility at

both test temperatures. It also imparts significantly higher Izod impact energy at -10°C with

little change to the compound modulus.

Table 39 Physical Property Test Results, Formulations F10 and CF-5

Formulation		F10	CF-5
	Unit	Value	Value
Flex Modulus, avg	MPa	1730	1777
Instrumented Dart Impact	Unit	Value	Value
Temperature	°C	-30	-30
% Ductile		50	0
Total energy, avg	inch-lbs	336	325
Temperature	°C	-20	-20
% Ductile		90	70
Total energy, avg	inch-lbs	341	348
Izod impact, -10 °C	kJ/m2	27.3	10.8

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Additional Examples Set 4 – OBC as minor component for improved impact modification

Table 40. Polymerization Conditions for Examples S and 51, T=120 °C, DEZ conc. (ppm Zn) = 3016

Ex.	C$_8$H$_{16}$ kg/hr	Solv. kg/hr	H$_2$ sccm[1]	Cat A[2] ppm	Cat A Flow g/hr	Cat B[3] ppm	Cat B Flow g/hr	DEZ Flow g/hr	Cocat Conc. ppm	Cocat Flow g/hr	[DEZ]/ [C$_2$H$_4$] *1000[4]	Poly Rate[5] kg/hr	Conv %[6]	Eff.[7]
S*	10.5	20.3	5.0	129	83	16	110	79	1413	76	0.61	1.94	85	146
51	10.6	20.4	4.8	"	80	"	70	55	"	68	0.40	2.06	82	143

* Comparative, not an example of the invention
1. standard cm^3/min
2. [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)immino) 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 41. Polymer Properties for Comparative Examples R and S and Example 51

Ex.	Density (g/cm^3)	I$_2$	I$_{10}$	I$_{10}$/I$_2$	Mw (g/mol)	Mn (g/mol)	Mw/ Mn	T$_c$ (°C)	T$_m$ (°C)	T$_g$ (°C)	Heat of Fusion (J/g)	Zn (ppm)
R*	0.863	0.5	na	na	182500	93600	1.9	na	50.0	-55.0	39.8	0
S	0.873	1.0	10.4	10.0	126700	57130	2.2	98.8	117	-67.6	46.4	170
51	0.868	0.7	8.4	11.5	160800	62260	2.6	91.5	115	-68.2	26.8	130

*Comparative Example R is a random ethylene/octene copolymer with a density of 0.863 and a melt index of 0.5 commercially available as ENGAGE™ 8180 from The Dow Chemical Company

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[335]   The OBC's are characterized for molecular weight, melt index, and composition; the

results are summarized in Table 41 and Table 42. The melt index is measured according to

ASTM D1238.

[336]   The results of the Inventive and Comparative Polymer Sample characterization are

5   shown in Table 42.

Table 42 – Comonomer content for Comparative Example R and S and Example 51 as

determined by ^{13}C NMR

Example	Overall Octene (mol %)	Octene in Soft Segment (mol %)	Soft Segment (wt %)	Octene in Hard Segment (mol %)	HS (wt %)	Δ Octene
R*	12.5[1]	12.5[1]	100	na	na	na
S	18.5	29.9	73	1.6	27	28.3
51	24.3	32.3	84	1.8	16	30.5

*Comparative Example R is a random ethylene/octene copolymer with a density of 0.863 and a melt
index of 0.5 commercially available as ENGAGE™ 8180 from The Dow Chemical Company
10   1. Determined by FT-IR

[337]   The TPO formulations and their instrumented dart impact results are shown in Table

43. The weight percents for the polymers are adjusted so that the polymer volume ratios

remain 65/35 polypropylene/impact modifier. The polypropylene used was D221 as above.

15   The Jetfill 700C is a compacted, fine particle talc. The Irganox B-225 is a 1/1 blend of a

phenolic primary antioxidant and a phosphate secondary antioxidant.

Table 43. TPO Formulations

Formulation #	CF-6	CF-7	F11
Ingredient	**Parts**	**Parts**	**Parts**
PP (D221)	56	56	56
R	24	20	20
S		4	
51			4
JetFil 700C	20	20	20
Irganox B225	0.2	0.2	0.2

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Table 44 Physical Property Test Results, Formulations CF-6, CF-7 and F11

Formulation		CF-6	CF-7	F11
	Unit	Value	Value	Value
Flex Modulus, avg	MPa	2190	2076	2055
Instrumented Dart Impact	Unit	Value	Value	Value
Temperature	°C	-30	-30	-30
% Ductile		40	50	90
Total energy, avg	inch-lbs	326	331	352

[338] Formulation F11, containing Example 51, yields high levels of ductile impact failure
5   at -30 °C without sacrificing flexural modulus performance. Comparative Formulations CF-6
and CF-7 do not exhibit fully ductile impact performance at -30 °C.

[339] Not wishing to be bound by any particular theory, it is believed that the improved
results in using F11 result from improved compatibilization between the polypropylene and
component R.

10   Additional Examples Set 5 – Examples 52-56

[340] Examples 52-56 were prepared in a process similar to that of Examples 5-19 above.
Tables 45 and 46 show physical properties of these polymers. Properties were determined in
similar fashion to Examples 41-51 above.

15   Table 45

Example	Density (g/cc)	MI @ 190°C (g/10min)	Mw	Mn	Mw / Mn
52	0.8628	5.36	102,600	37,970	2.7
53	0.8655	0.427	179,600	69,740	2.58
54	0.8679	0.578	162,800	76,160	2.14
55	0.8683	4.46	108,800	45,610	2.39
56	0.8698	0.52	177,200	76,640	2.31

Table 46

Example	Tc °C	Tm °C	Tg °C	Heat of Fusion (J/gr)	Crystal. wt%	Total Co-monomer Mole %	Soft Segment, Mole %	Hard Segment, Mole %	Wt % Soft Segment
52	96.02	120	-66.4	25.49	9	20.83	27.1	1.42	84
53	89.96	119	-66.7	41.64	14	20.32	27.5	1.45	82
54	92.26	116	-56.5	31.04	11	19.53	26.5	1.38	81
55	95.28	119	-66.9	35.36	12.19	20	27.7	1.46	81
56	90.82	117	-66.2	31.37	10.82	19.68	27.4	1.44	80

[341]   TPO formulations F12-F16 are made with 20.7 parts each of Examples 52-56
respectively; and, formulations CF8 and CF9 are made with Comparative R and Comparative
T, respectively. Each is compounded into 59.3 parts ProFax Ultra SG853 (LyondellBasell
Polyolefins). Each formulation also contains 20 parts JetFil 700C talc and 0.2 parts of
Irganox B225. Compounds were formulated as described above. Four inch diameter, 0.125
inch thick injection molded specimens were used to test for instrumented dart impact. Ten
specimens were tested per formulation at 6.7m/sec. The physical testing results are shown in
Table 47. Comparative T is a random ethylene/octene copolymer with a density of 0.87 g/cc
and a Melt Index of 5, available as ENGAGE™ 8200 from The Dow Chemical Company.

Table 47

Formulation	CF8	CF9	F12	F13	F14	F15	F16
Chord Mod avg	1620.0	1582.0	1544.0	1591.0	1589.0	1506.0	1653.0
MFR	17.0	27.7	30.2	18.8	18.1	29.3	19.3
Peak energy avg (-20C)	242.7	251.0	255.3	248.0	257.2	259.3	261.8
Peak energy avg (-30C)	261.4	234.2	255.3	240.7	268.5	248.6	258.7
Total energy avg (-20C)	366.8	385.0	326.9	342.1	326.8	321.4	328.7
Total energy avg (-30C)	334.9	329.2	309.8	338.3	349.9	325.9	365.5
% Ductile at -20C	100%	100%	90%	90%	90%	100%	80%
% Ductile at -30C	47%	33%	80%	73%	73%	80%	70%
ISOEnergy avg (32F); kJ/m2	54.9	46.6	47.9	55.5	54.0	46.5	50.8
ISOEnergy avg (14F); kJ/m2	47.5	35.6	39.1	42.8	44.7	37.8	40.2
ISOEnergy avg (-4F); kJ/m2	23.4	9.7	12.3	19.4	17.9	11.0	13.6
ISOEnergy avg (-22); kJ/m2	11.0	6.3	7.8	10.0	9.7	8.2	10.0

[342]   Figure 36 shows the morphology of F15 on the left as compared to that of CF9, which
is shown on the right. As may be observed, the elastomer particles in CF9 are more
elongated whereas those of F15 are more rounded particles which is preferred for impact
modification purposes.

[343]   As demonstrated above, embodiments of the invention provide a new class of
ethylene and α-olefin block interpolymers. The block interpolymers are characterized by an

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average block index of greater than zero, preferably greater than 0.2. Due to the block structures, the block interpolymers have a unique combination of properties or characteristics not seen for other ethylene/α-olefin copolymers. Moreover, the block interpolymers comprise various fractions with different block indices. The distribution of such block

5   indices has an impact on the overall physical properties of the block interpolymers. It is possible to change the distribution of the block indices by adjusting the polymerization conditions, thereby affording the abilities to tailor the desired polymers. Such block interpolymers have many end-use applications. For example, the block interpolymers can be used to make polymer blends, fibers, films, molded articles, lubricants, base oils, etc. Other

10   advantages and characteristics are apparent to those skilled in the art.

[344]   While the invention has been described with respect to a limited number of embodiments, the specific features of one embodiment should not be attributed to other embodiments of the invention. No single embodiment is representative of all aspects of the invention. In some embodiments, the compositions or methods may include numerous

15   compounds or steps not mentioned herein. In other embodiments, the compositions or methods do not include, or are substantially free of, any compounds or steps not enumerated herein. Variations and modifications from the described embodiments exist. The method of making the resins is described as comprising a number of acts or steps. These steps or acts may be practiced in any sequence or order unless otherwise indicated. Finally, any number

20   disclosed herein should be construed to mean approximate, regardless of whether the word "about" or "approximately" is used in describing the number. The appended claims intend to cover all those modifications and variations as falling within the scope of the invention.

<u>What is claimed is:</u>

1.   A composition comprising:

A)   a thermoplastic polymer composition, and

B)   an impact modifying amount of an ethylene/α-olefin block interpolymer, wherein the ethylene/α-olefin block interpolymer comprises hard blocks and soft blocks, wherein the ethylene/α-olefin block interpolymer is characterized by a molecular weight distribution, M_w/M_n, in the range of from about 1.4 to about 2.8 and:

        (a)   has 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:

$$T_m > -6553.3 + 13735(d) - 7051.7(d)^2, \text{ or}$$

        (b)   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:

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

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

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

        (c)   is characterized by 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:

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

        (d)   has 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

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index, density, and molar comonomer content (based on the whole polymer) within 10

percent of that of the ethylene/α-olefin interpolymer; or

(e)   has a storage modulus at 25°C, G'(25°C), and a storage modulus at 100°C, G'(100°C),

wherein the ratio of G'(25°C) to G'(100°C) is in the range of about 1:1 to about 9:1; or

5   (f)   is characterized by an average block index greater than zero and up to about 1.0; and,

wherein the ethylene/α-olefin block interpolymer is mesophase separated.

2.   The composition of Claim 1, wherein the value for χN for the ethylene/α-olefin block

interpolymer, where N is the number average block length, is in the range of from

about 2 to about 20, preferably in the range of from about 2.5 to about 15 and more

10   preferably in the range of from about 3 to about 10.

3.   A composition comprising:

A)   a thermoplastic polymer composition, and

B)   an impact modifying amount of an ethylene/α-olefin block interpolymer having hard

blocks and soft blocks wherein the copolymer is characterized by an average molecular

15   weight of greater than 40,000 g/mol, a molecular weight distribution, Mw/Mn, in the range of

from about 1.4 to about 2.8, and a difference in mole percent α-olefin content between the

soft block and the hard block of greater than about 18.5 mole percent.

4.   The composition of Claim 1 or Claim 3 wherein the ethylene/α-olefin block copolymer

comprises domains wherein the domains have a smallest dimension in the range of from

20   about 40 nm to about 300 nm.

5.   The composition of Claim 4 wherein the α-olefin of the ethylene/α-olefin block

copolymer is octene and the difference in mole percent α-olefin content between the

soft block and the hard block is greater than about 20.0 mole percent.

6.   The composition of Claim 4 wherein the α-olefin of the ethylene/α-olefin block

25   copolymer is butene and the difference in mole percent α-olefin content between the

soft block and the hard block is greater than about 30.8 mole percent.

7.   The composition of Claim 4 wherein the α-olefin of the ethylene/α-olefin block

copolymer is propylene and the difference in mole percent α-olefin content between the

soft block and the hard block is greater than about 40.7 mole percent.

30   8.   The composition of Claim 1 or Claim 3, wherein the ethylene content of the ethylene/α-

olefin block copolymer is greater than about 50 mole percent.

9.   The composition of Claim 1 or Claim 3, wherein the hard segments of the ethylene/α-

olefin block copolymer are present in an amount of from about 10 wt% to about 40

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wt%.

10. The composition of Claim 1 or Claim 3, wherein the soft segments of the ethylene/α-olefin block copolymer comprise less than 90% of ethylene by weight.

11. The composition of Claim 1 or Claim 3, wherein the block copolymer displays a reflection spectrum that reaches a value of at least 12 percent within the region of infrared, visible or ultraviolet light.

12. A composition comprising:

A)   a thermoplastic polymer composition, and

B)   an impact modifying amount of an ethylene/α-olefin block interpolymer comprising hard blocks and soft blocks, wherein the ethylene/α-olefin block interpolymer is characterized by a molecular weight distribution, M_w/M_n, in the range of from about 1.4 to about 2.8 and:

(a)   has 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:

$$T_m > -6553.3 + 13735(d) - 7051.7(d)^2, \text{ or}$$

(b)   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:

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

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

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

(c)   is characterized by 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:

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

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(d)   has 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

(e)   has a storage modulus at 25°C, G'(25°C), and a storage modulus at 100°C, G'(100°C), wherein the ratio of G'(25°C) to G'(100°C) is in the range of about 1:1 to about 9:1; or

(f)   is characterized by an average block index greater than zero and up to about 1.0; and,

(g)   is characterized by $I_{10}/I_2 > 8$.

13. The composition of Claim 1, Claim 3 or Claim 12 wherein the ethylene/α-olefin block interpolymer is present in an amount in the range of from about 5 wt% to about 45 wt% based on the total weight of the composition.
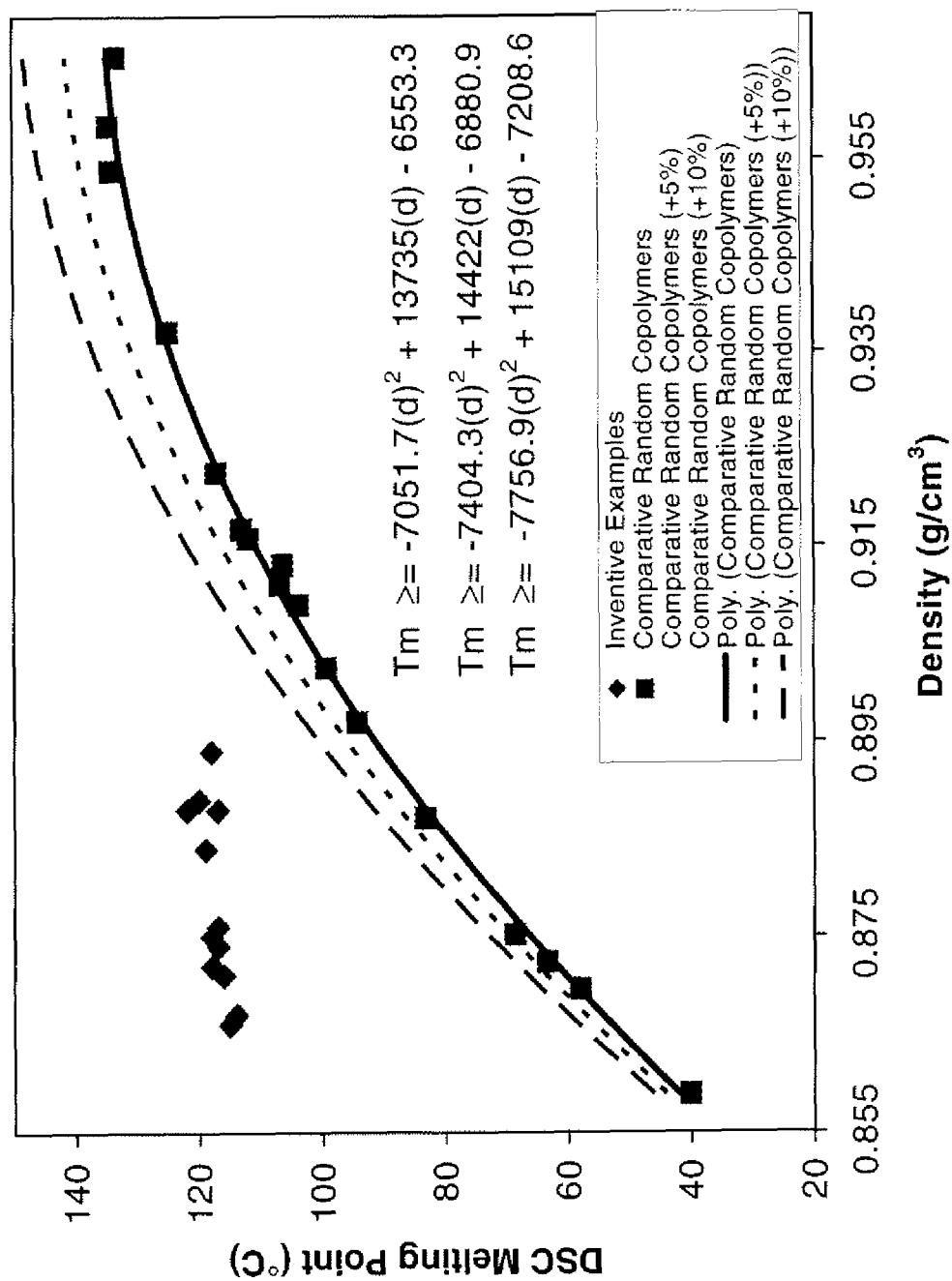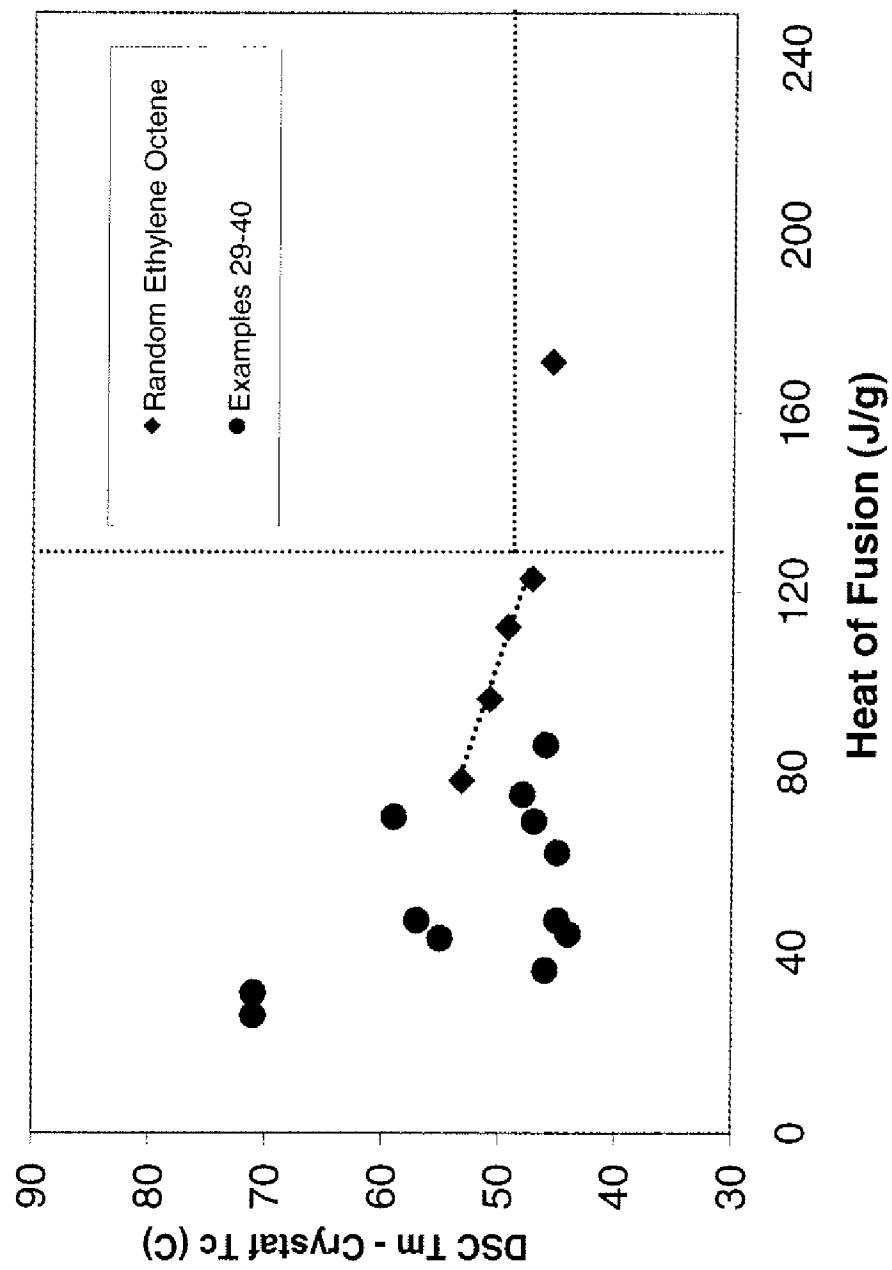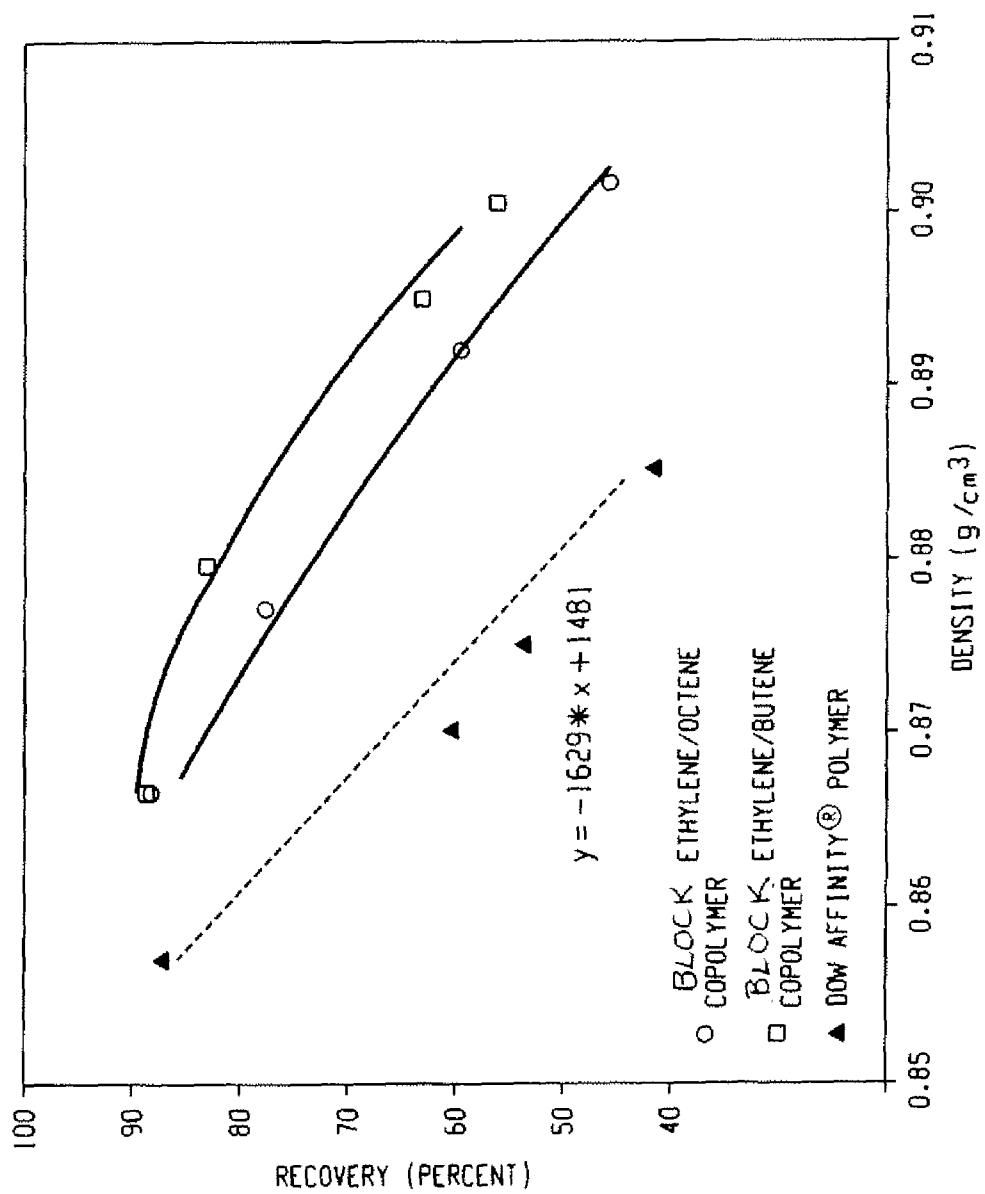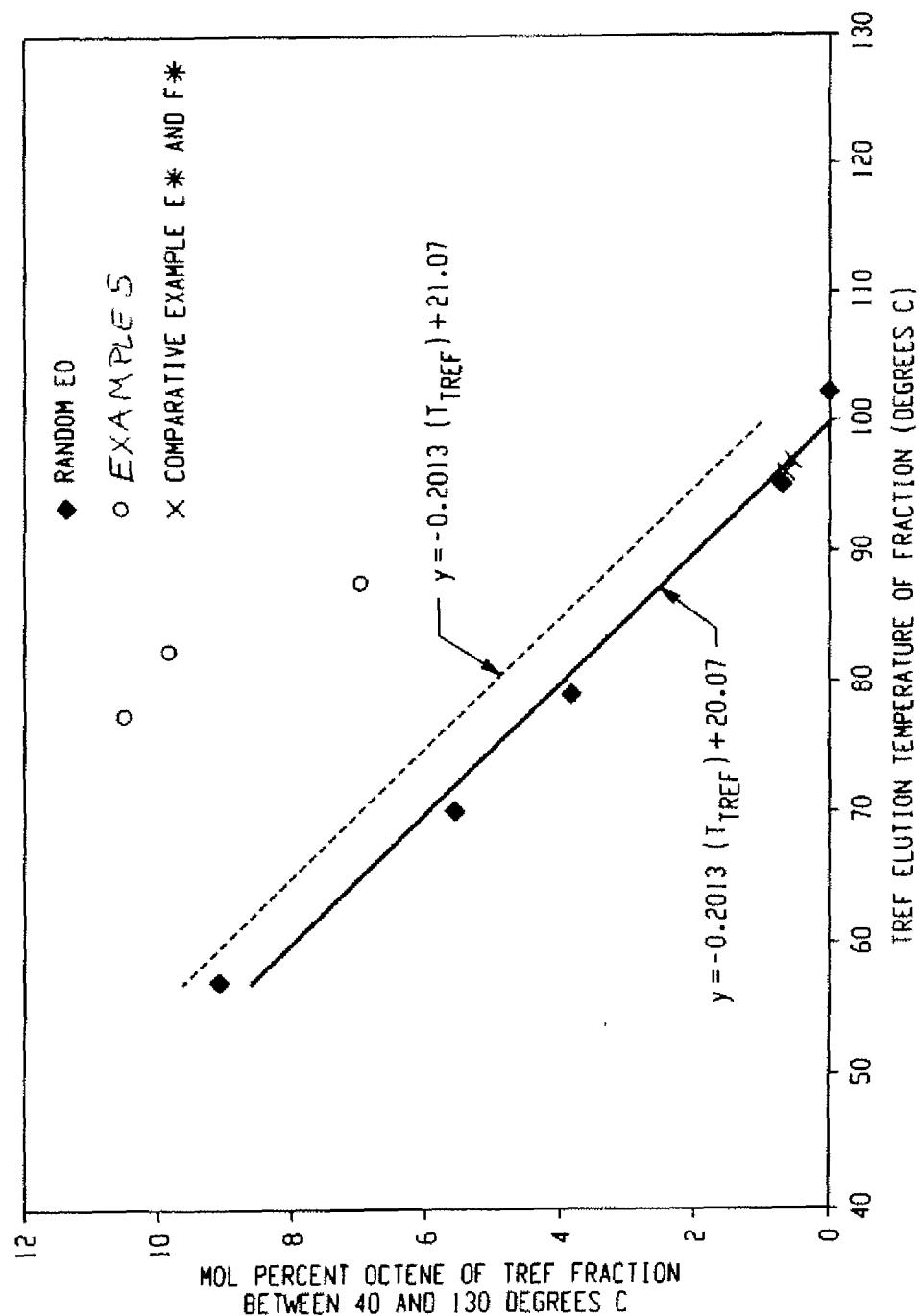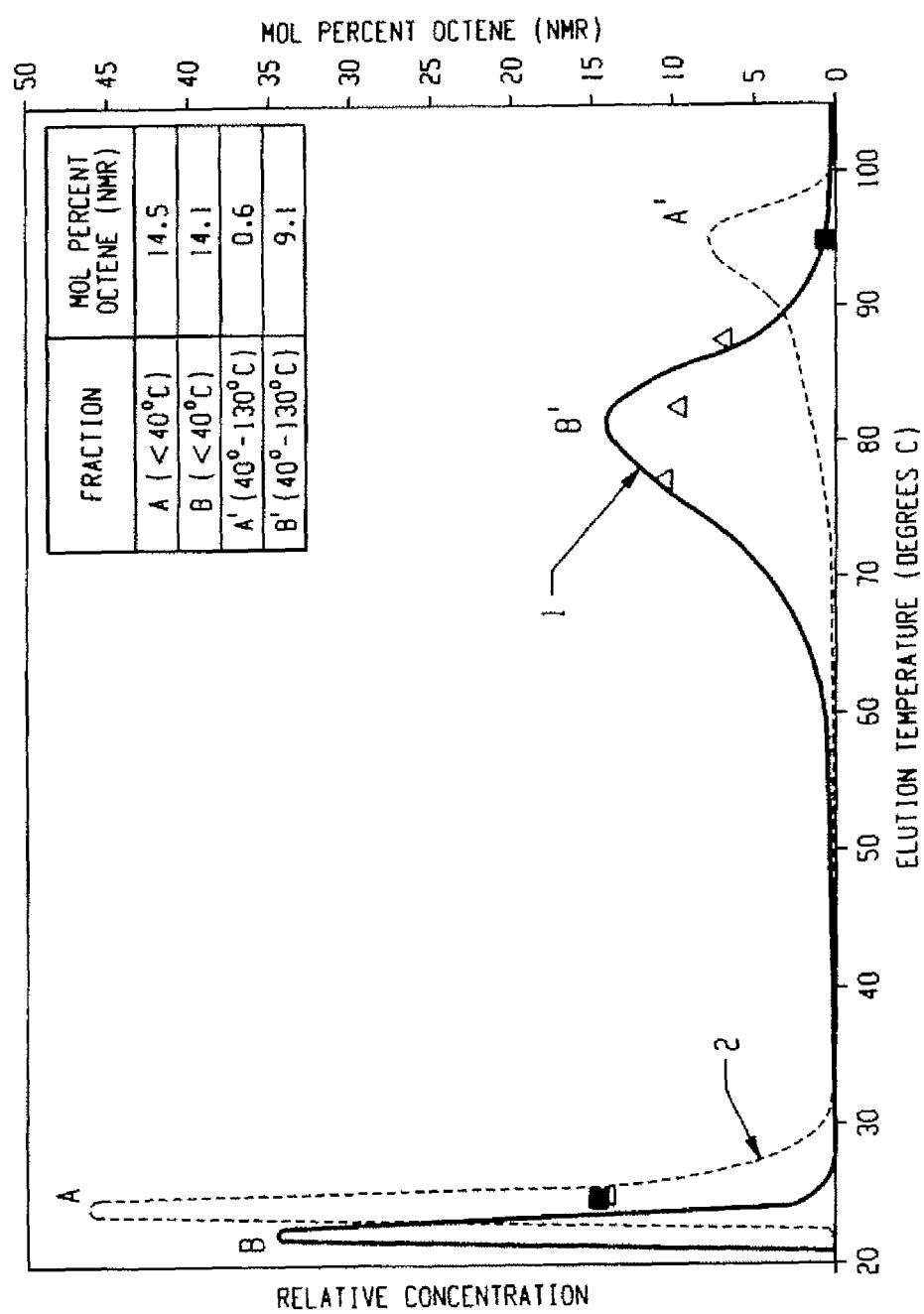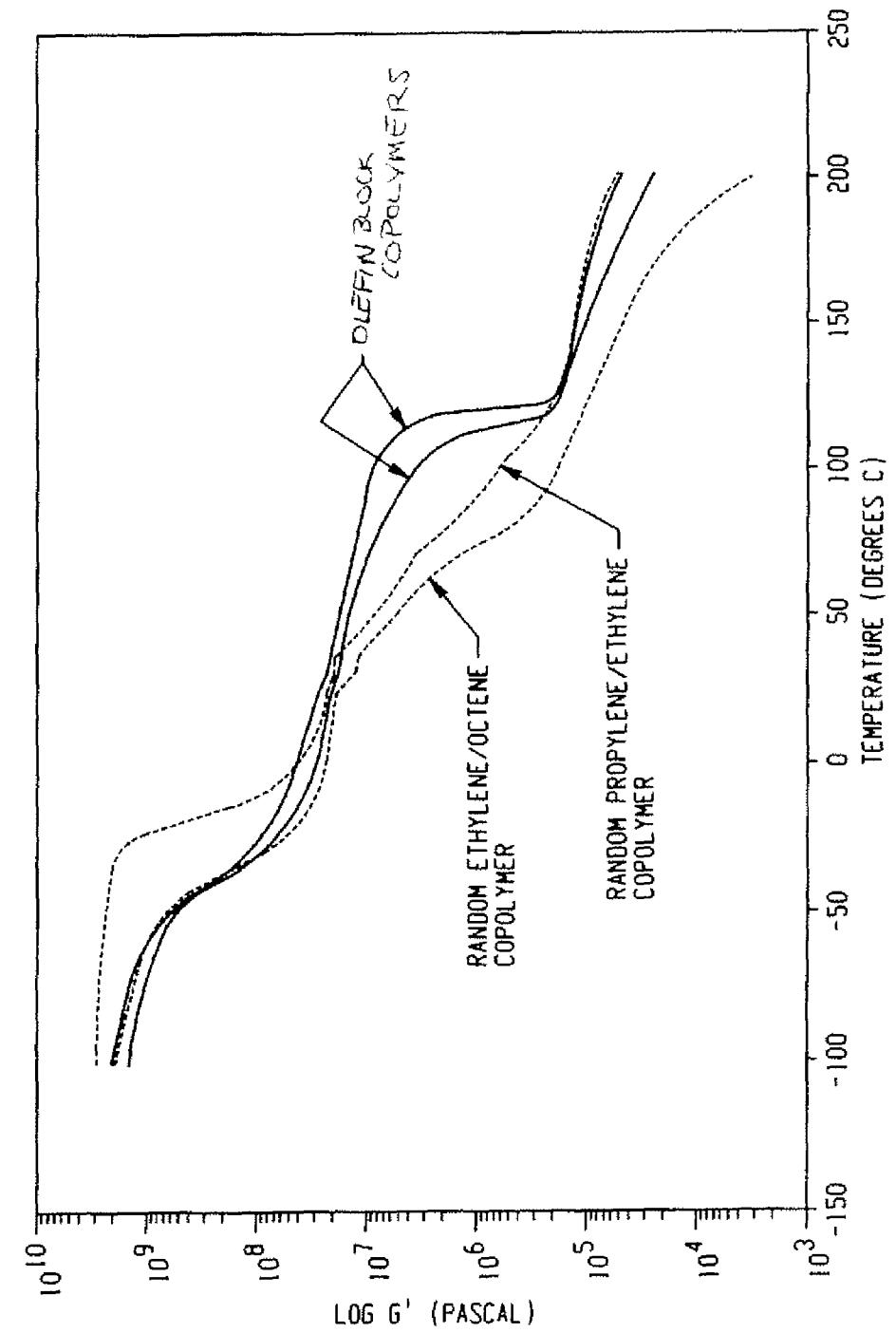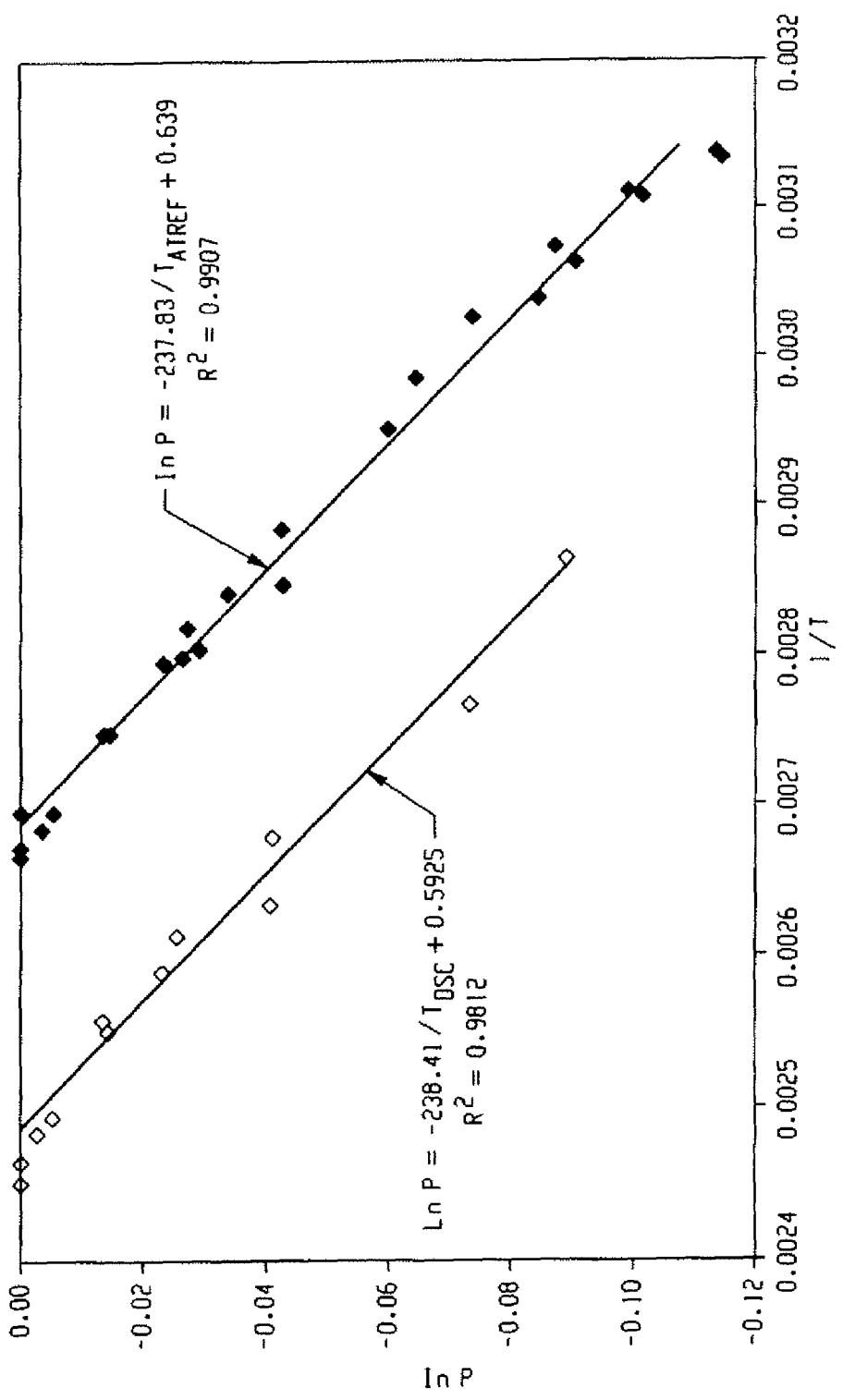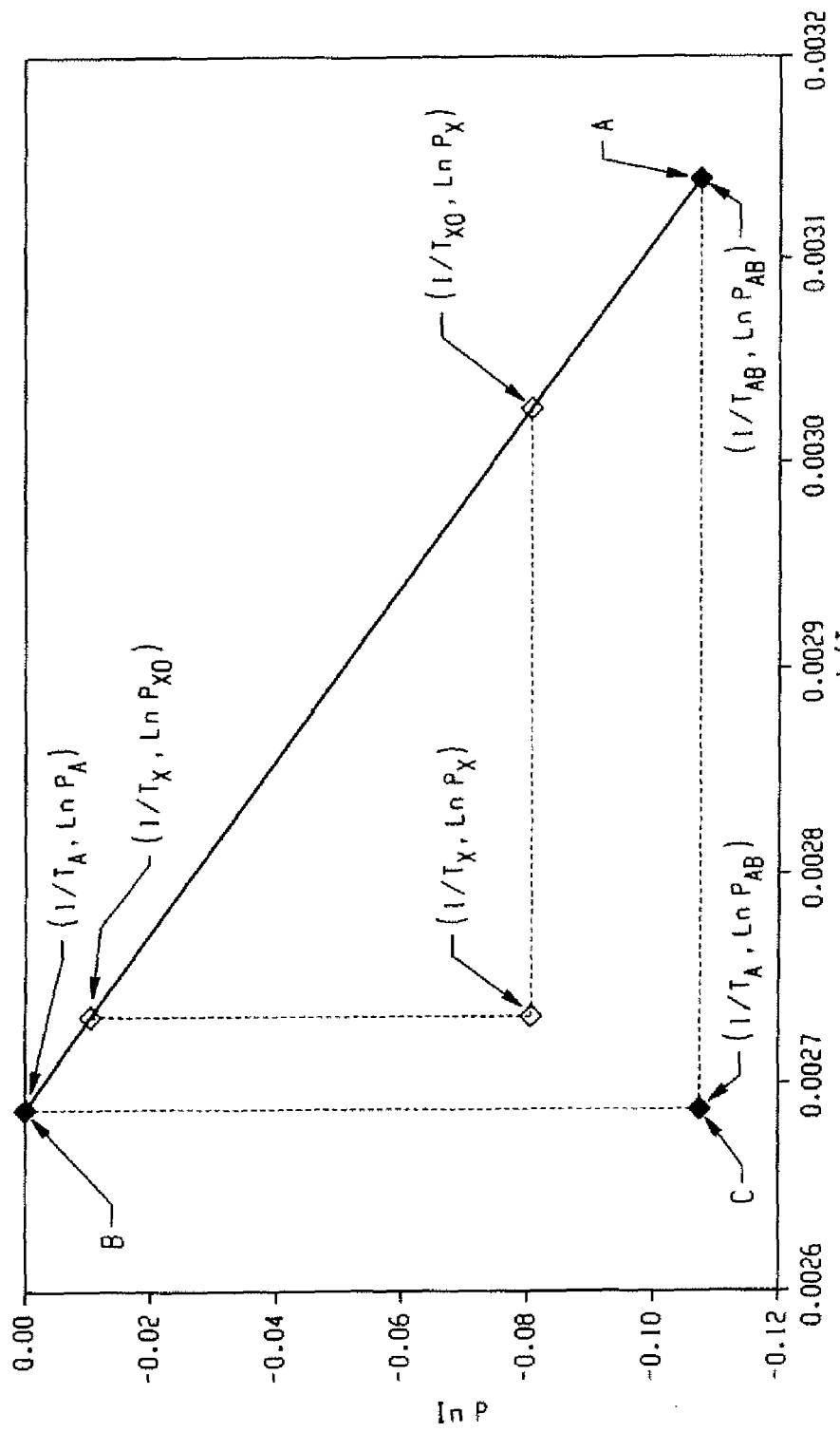
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Fig. 1

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Fig. 2

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Fig. 3

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Fig. 4

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Fig. 5

| FRACTION	MOL PERCENT OCTENE (NMR)
A (<40°C)	14.5
B (<40°C)	14.1
A' (40°–130°C)	0.6
B' (40°–130°C)	9.1

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Fig. 6

$$\ln P = -237.83 / T_{ATREF} + 0.639$$
$$R^2 = 0.9907$$

$$\ln P = -238.41 / T_{DSC} + 0.5925$$
$$R^2 = 0.9812$$

Fig. 7

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Fig. 8

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Fig. 9

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Fig. 10

Fig. 11

Fig. 12

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Fig. 13

Fig. 14

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Fig. 15

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Fig. 16

0   10.0 μm

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Fig. 17

0   10.0 µm

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Fig. 18

0   10.0 μm
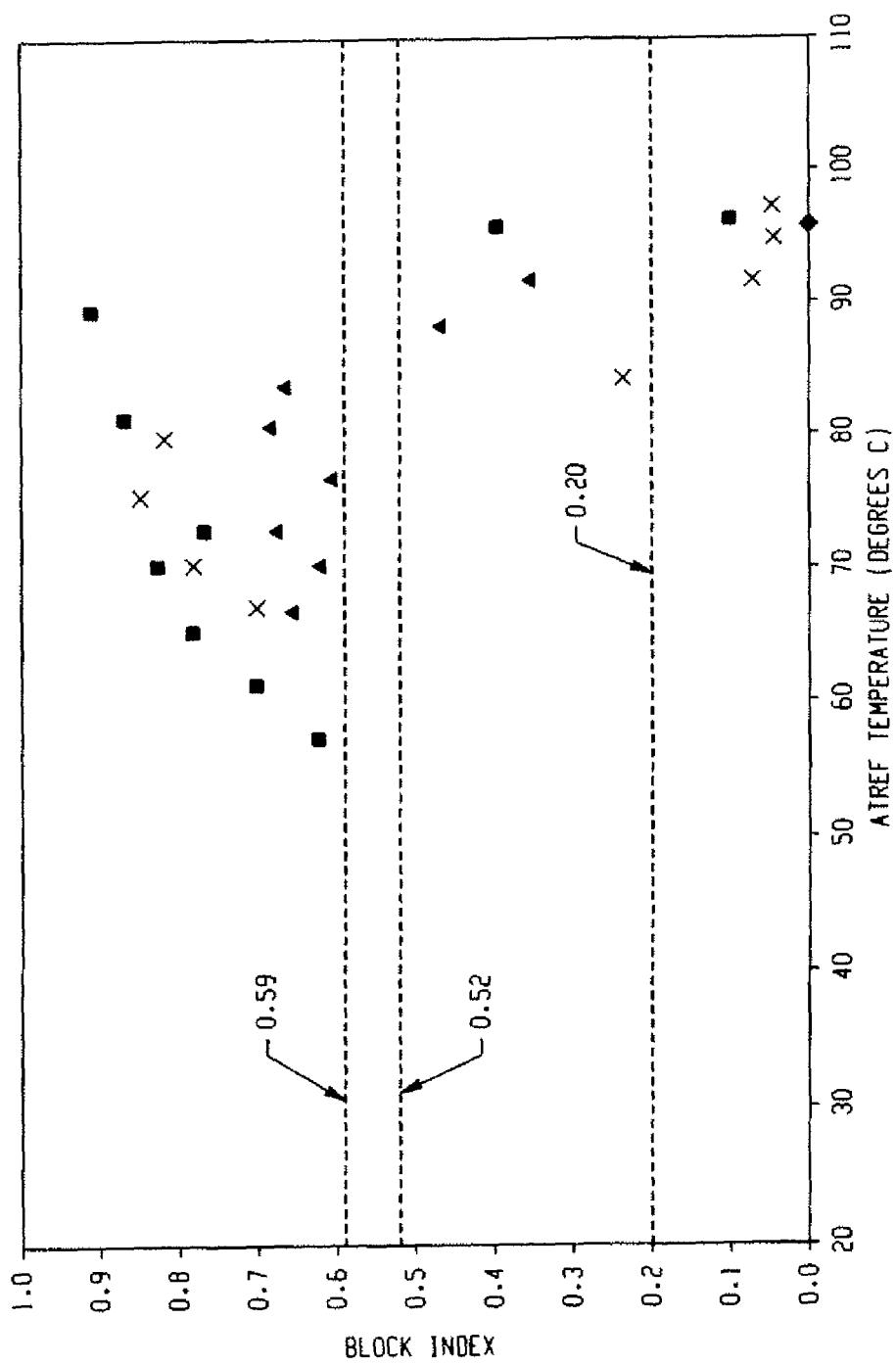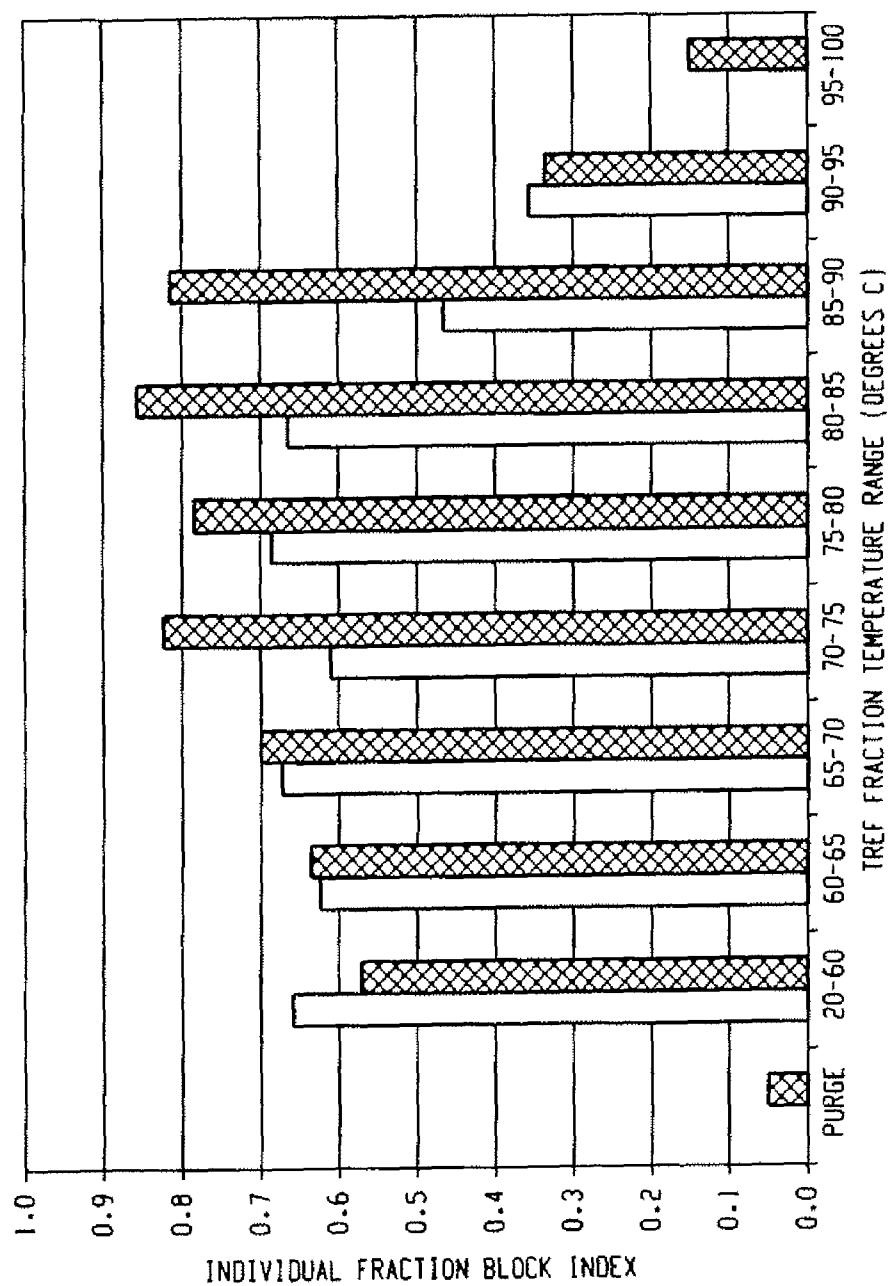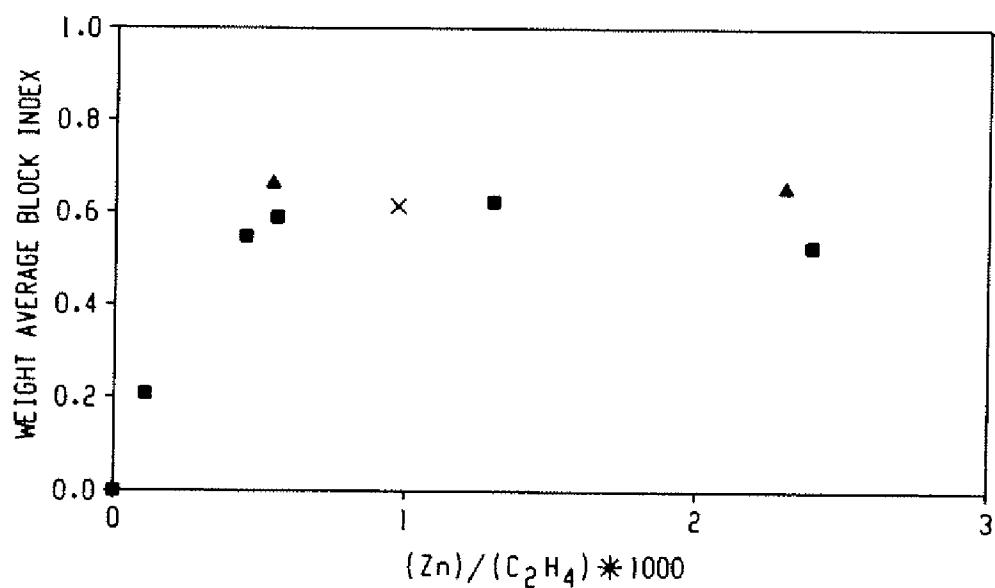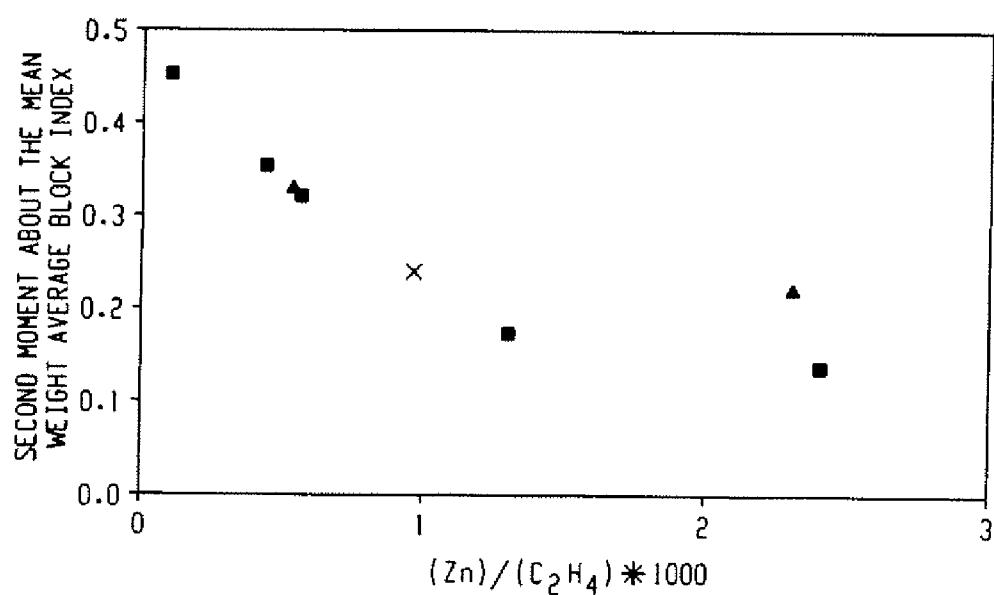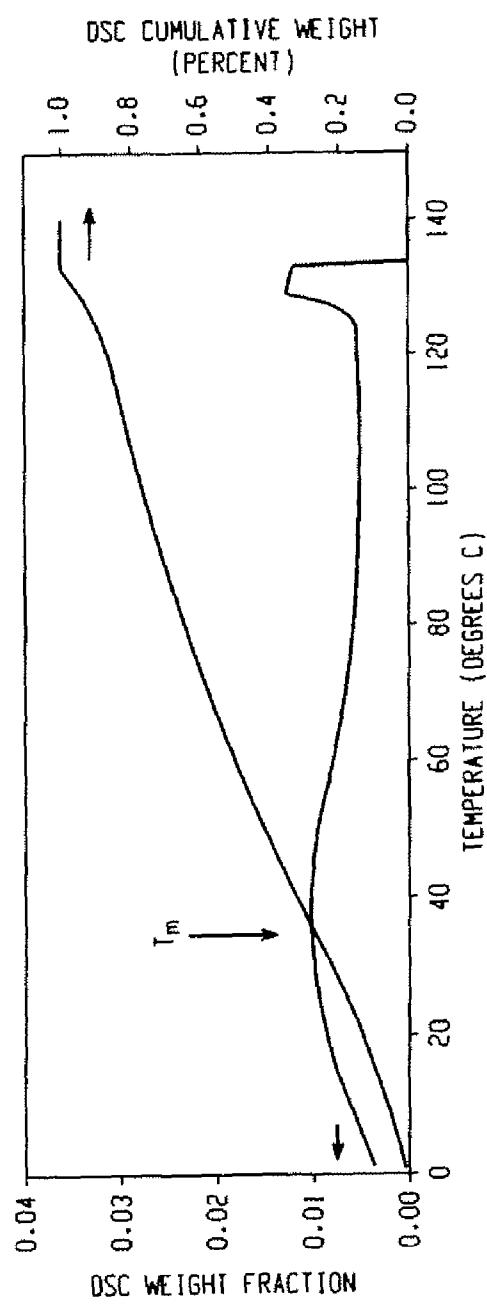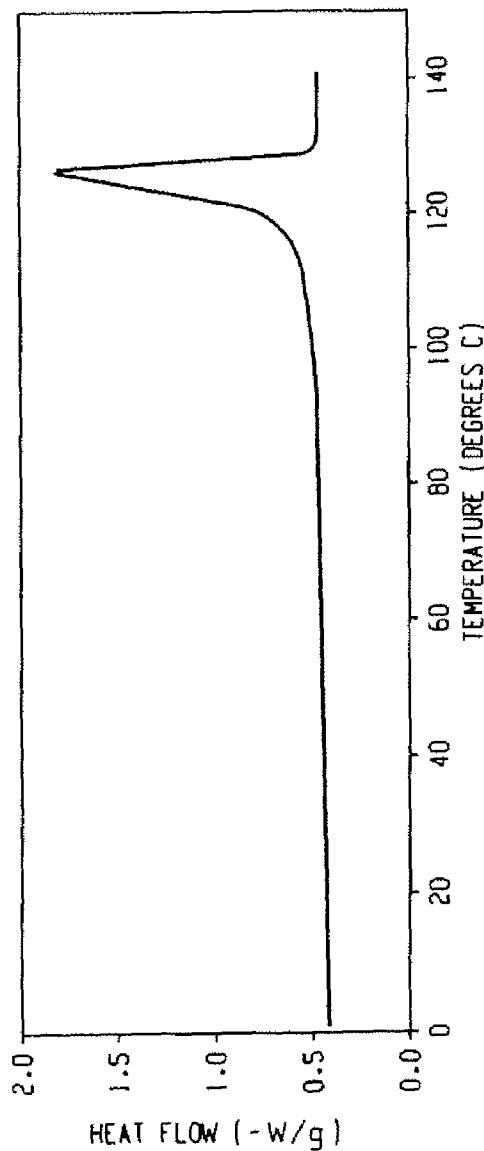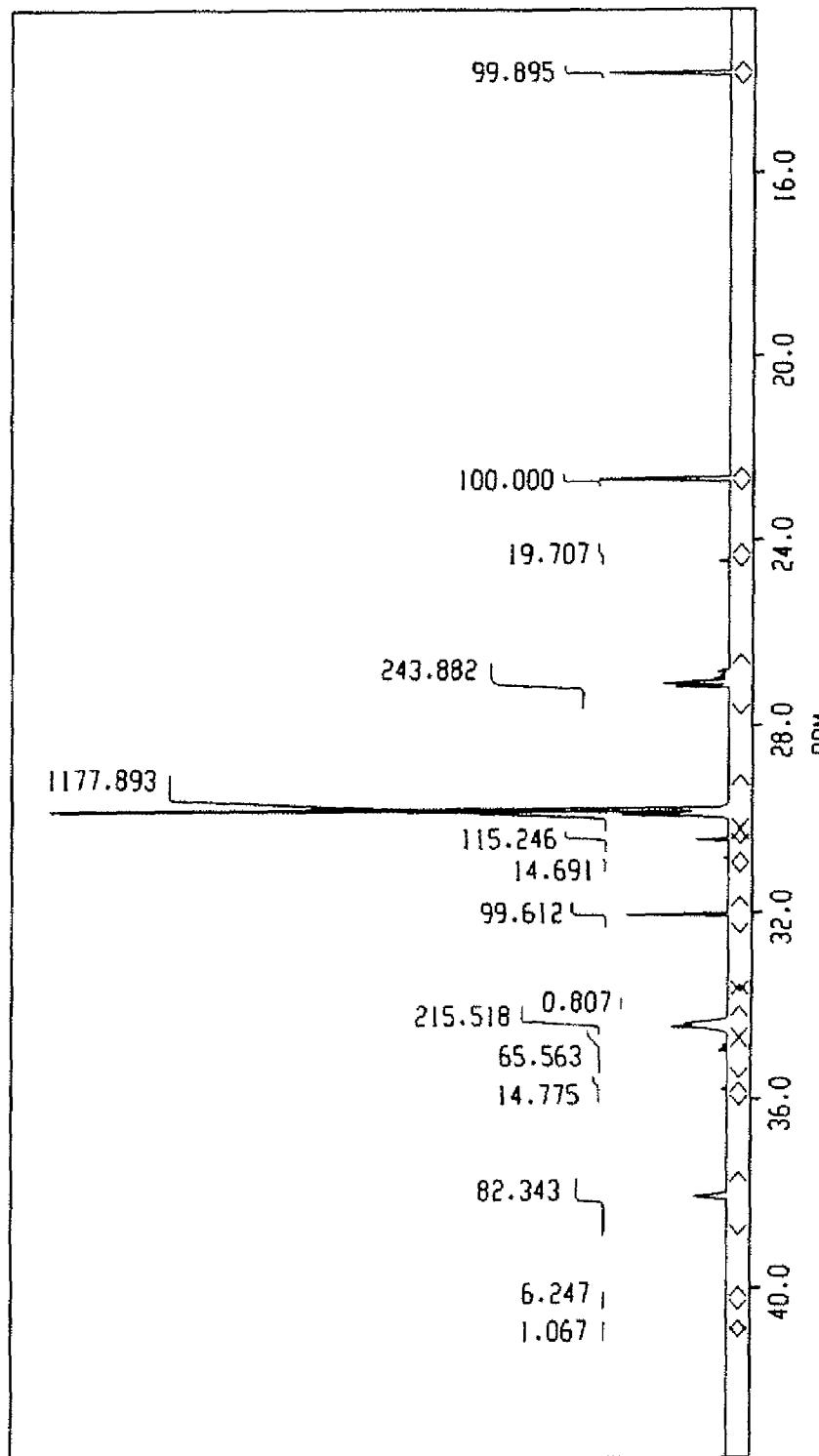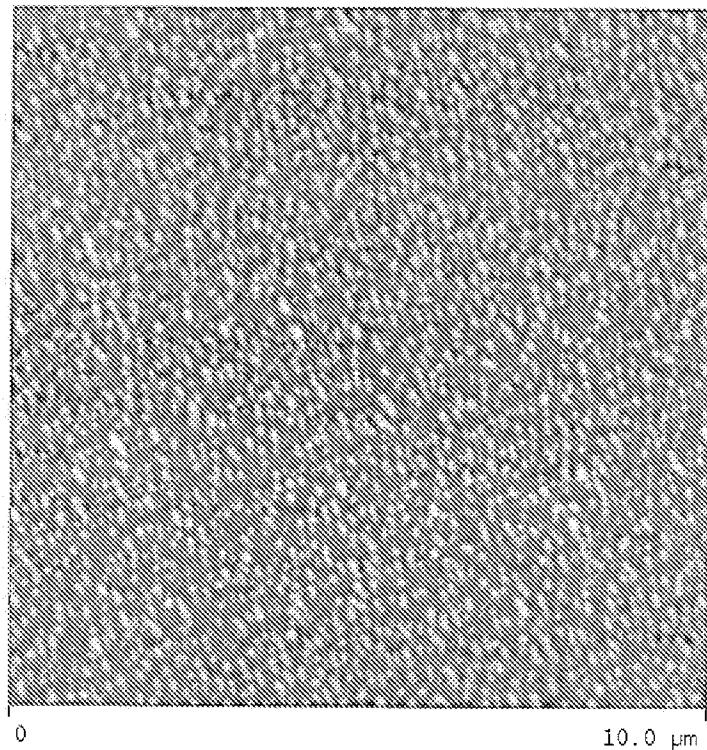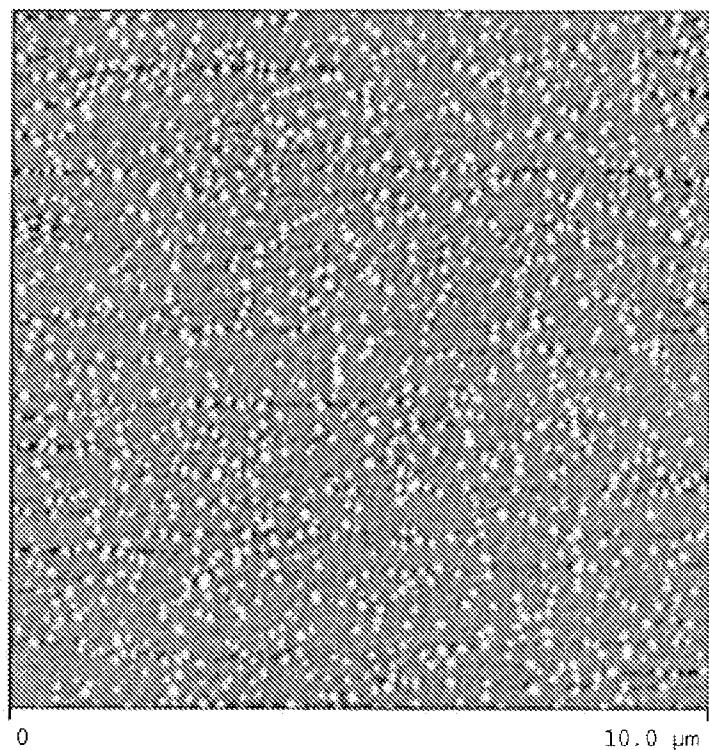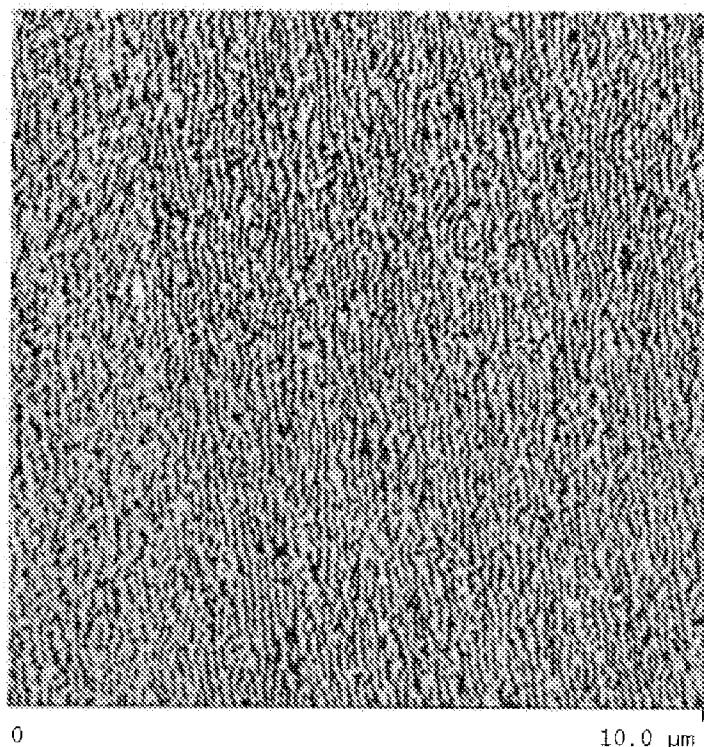
66940

Fig. 19

66940

Fig. 20

Phase 40.00 °

0　　　　　　　　　　　　　　　　　　　　　　1.00 µm
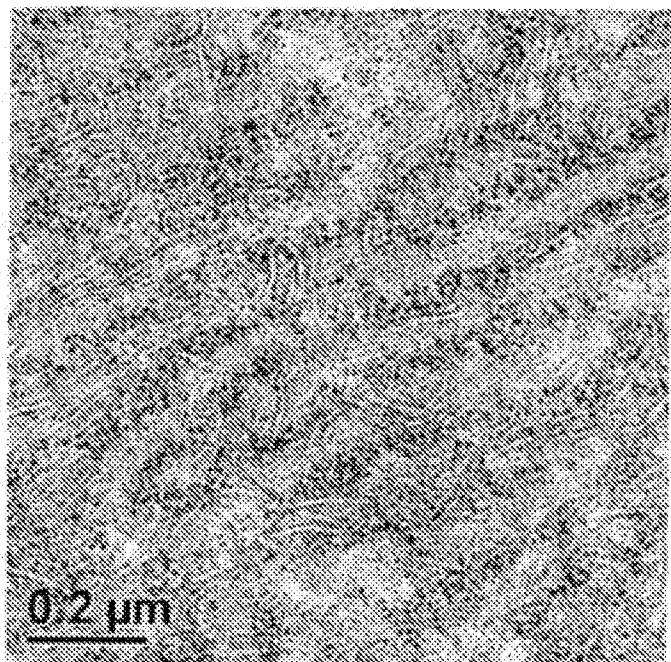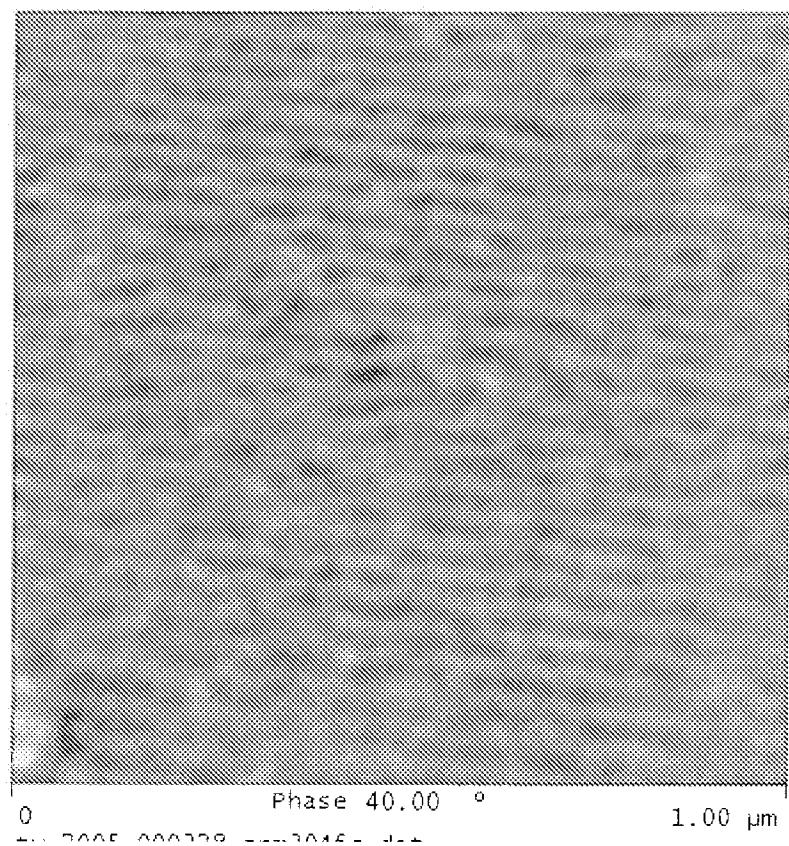
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Fig. 21
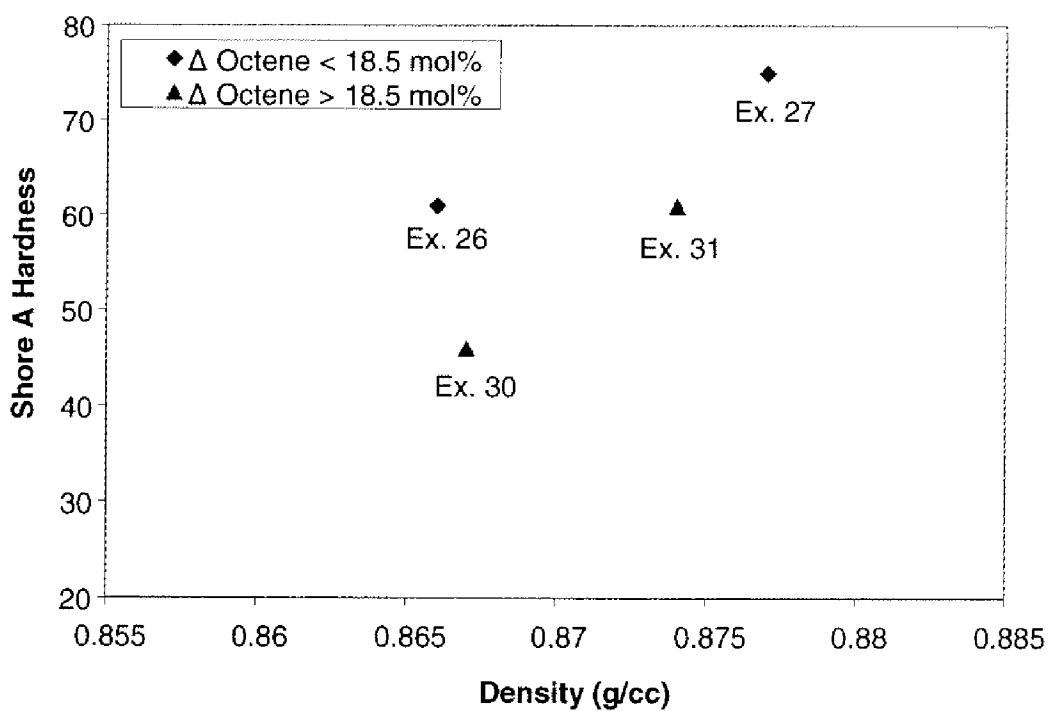
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Fig. 22
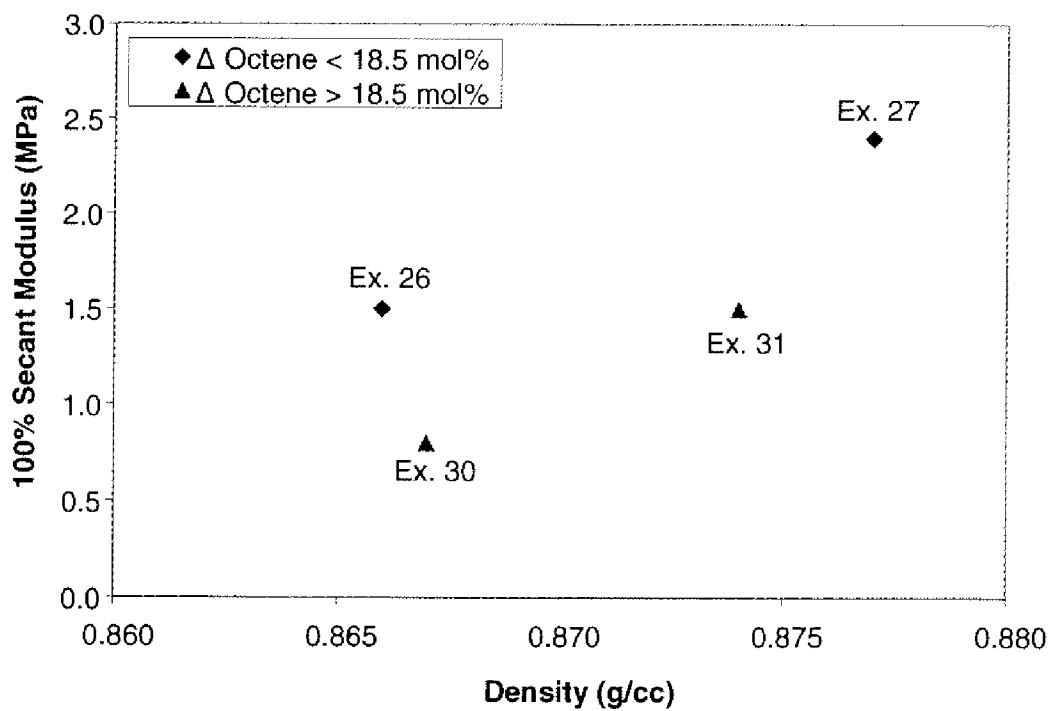
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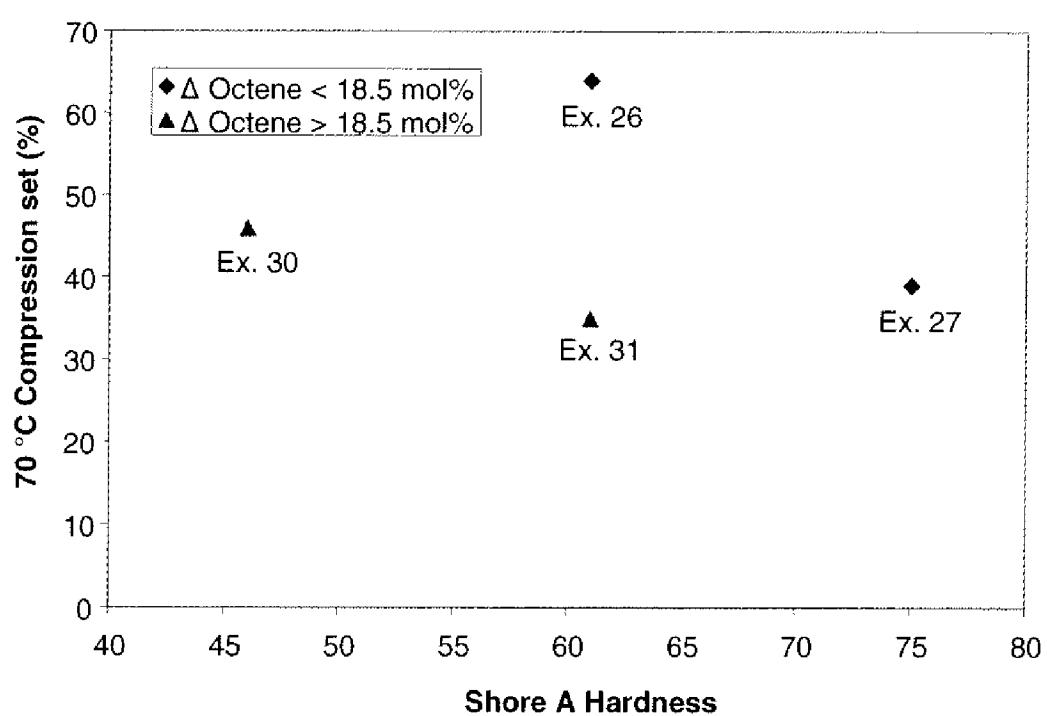
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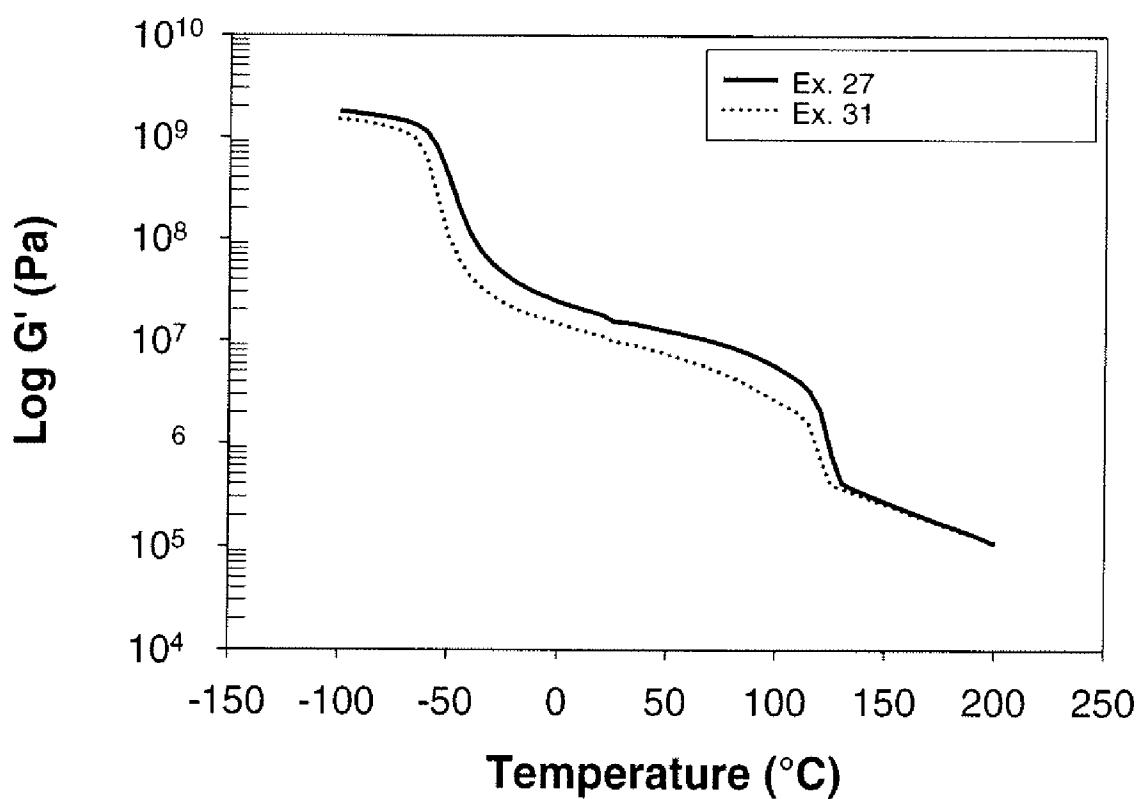
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Fig. 25
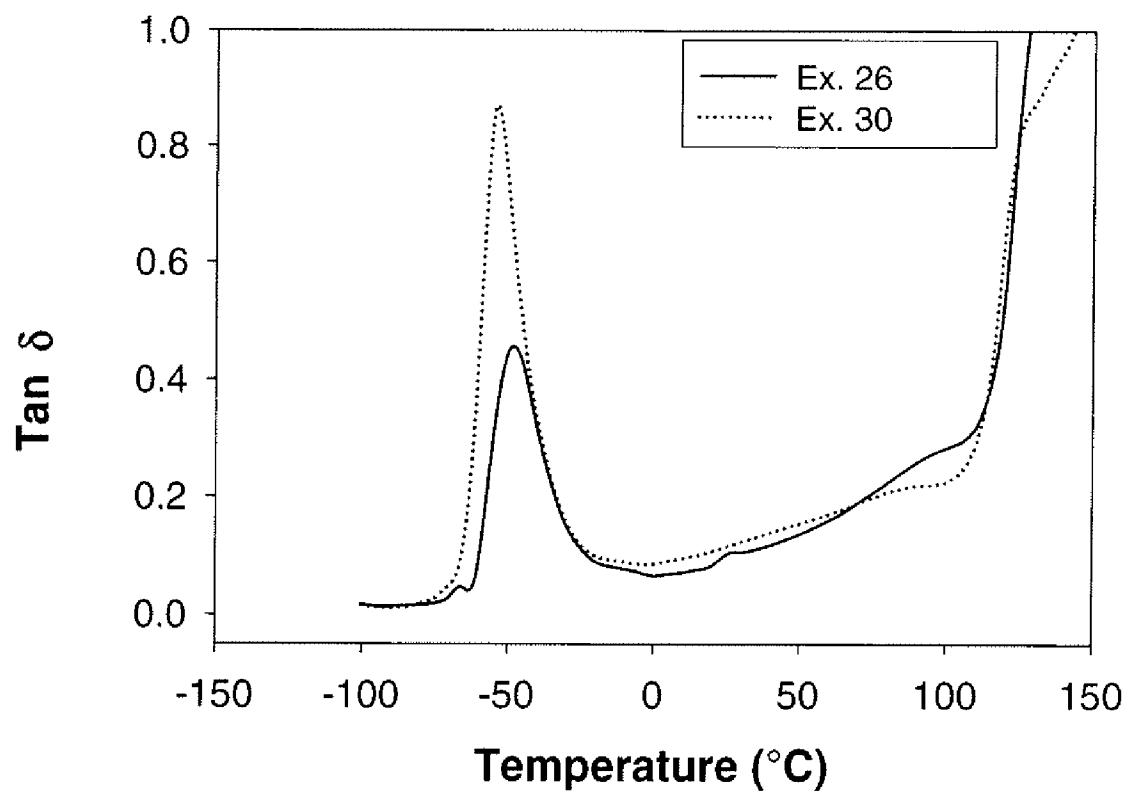
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Fig. 26
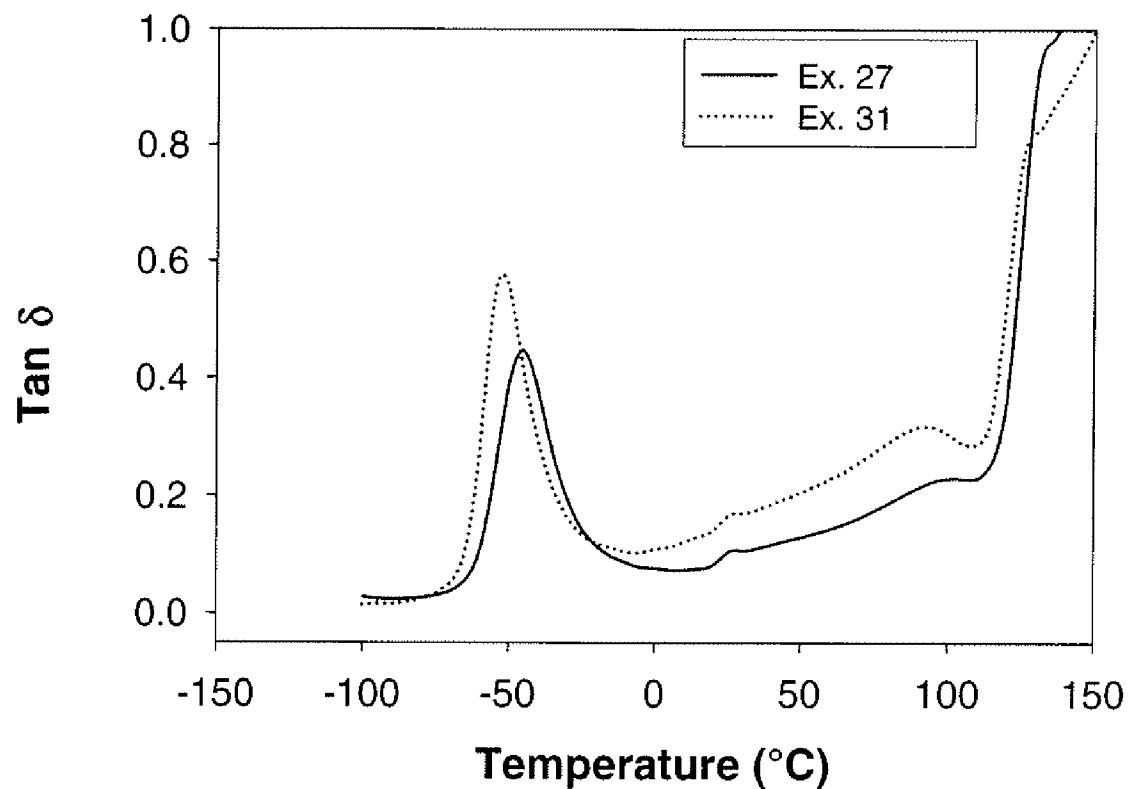
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Fig. 27
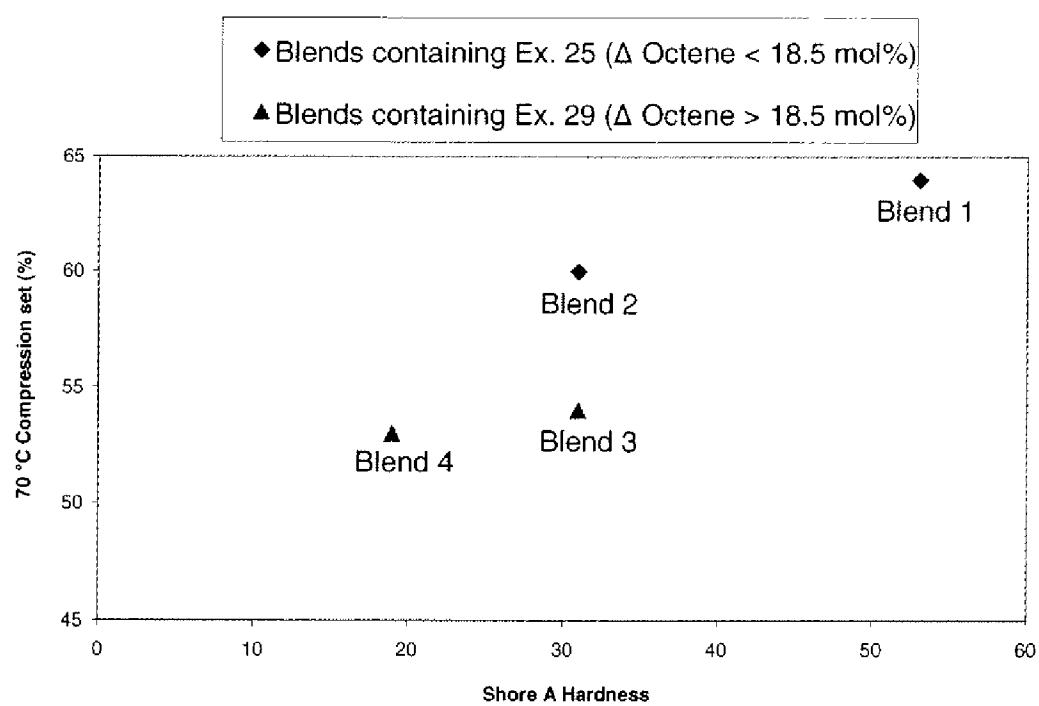
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Fig. 28
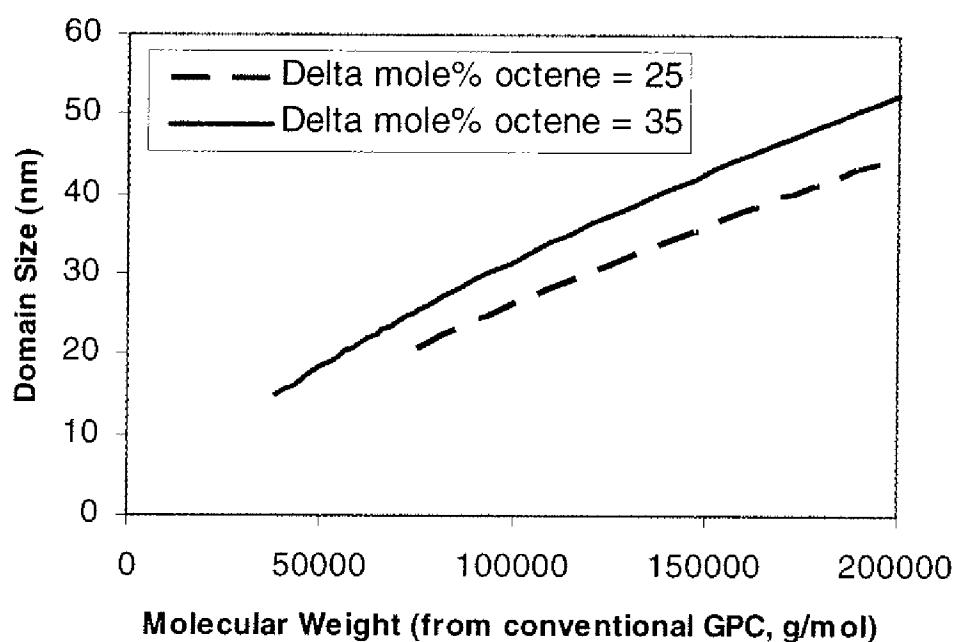
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Fig. 29
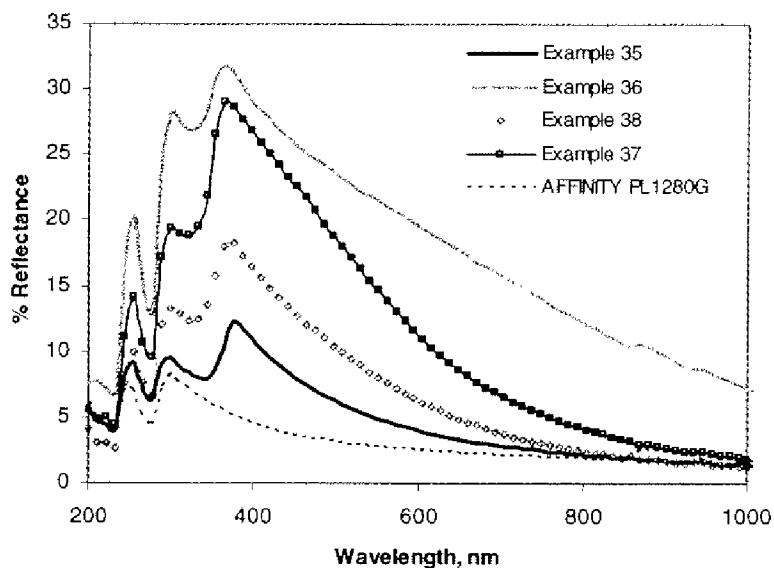
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Fig. 30
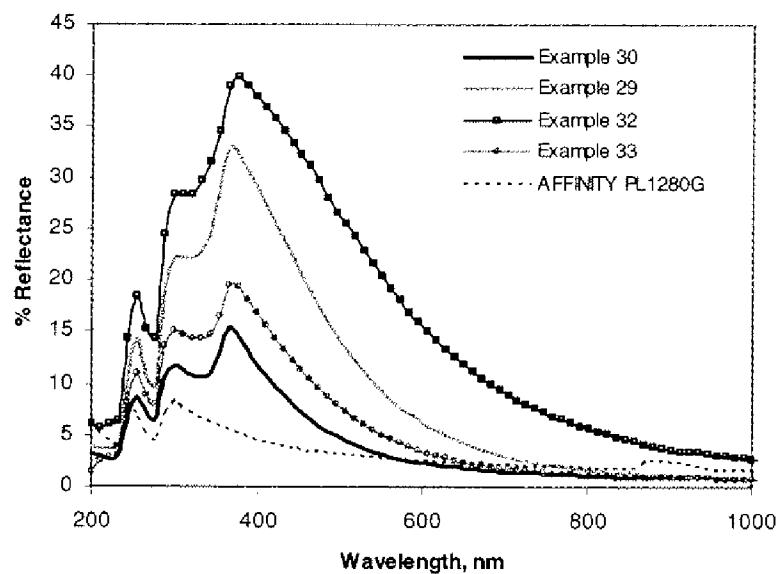
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Fig. 31
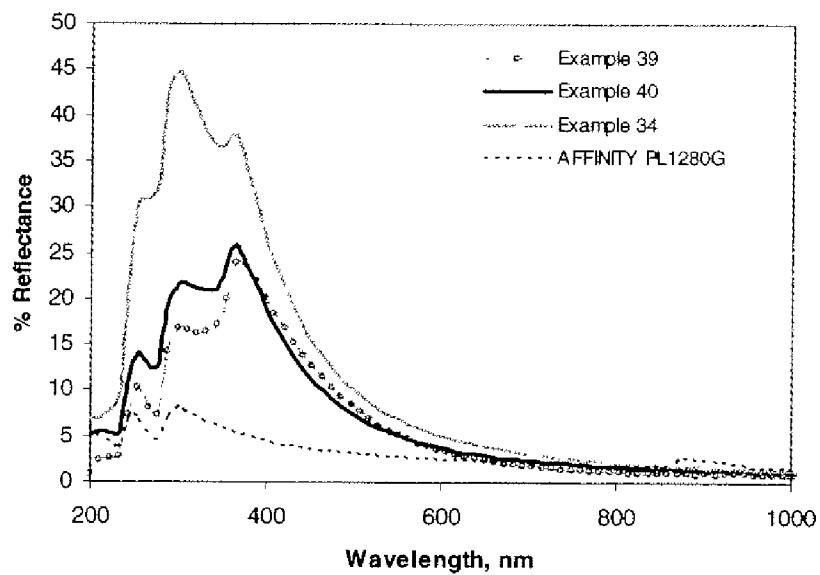
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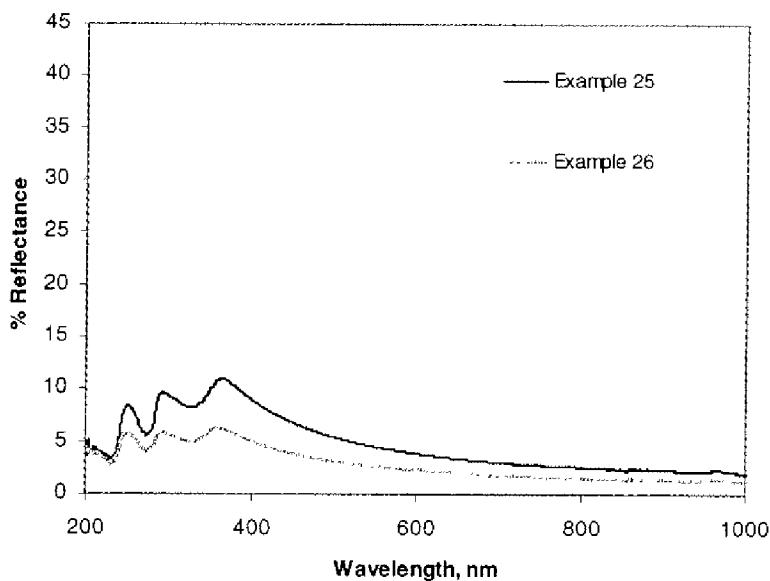
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Fig. 33
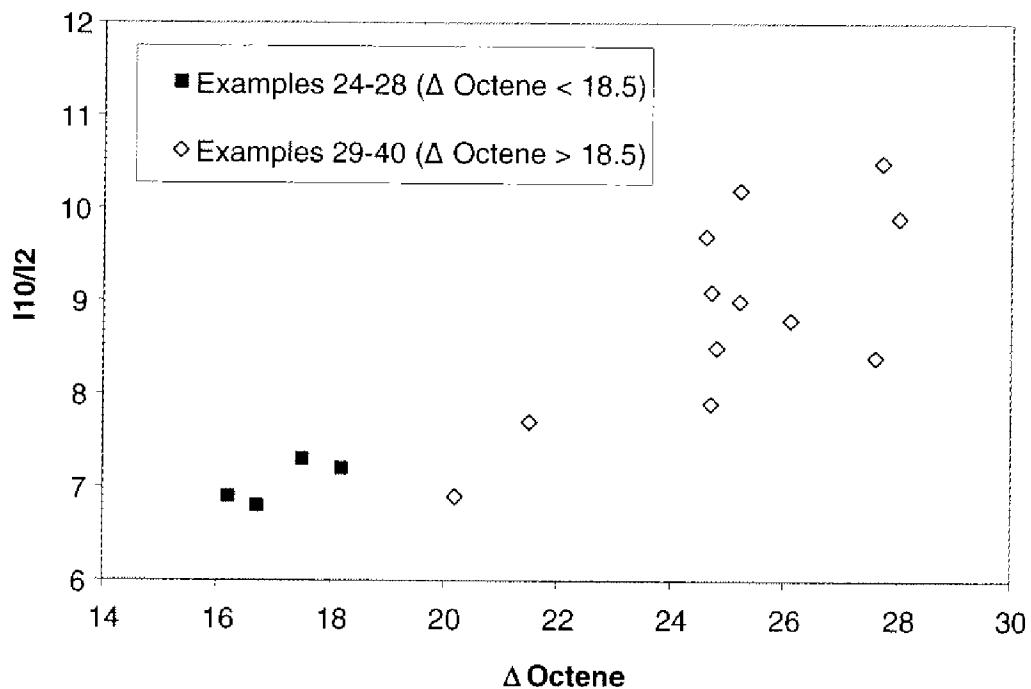
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Figure 34
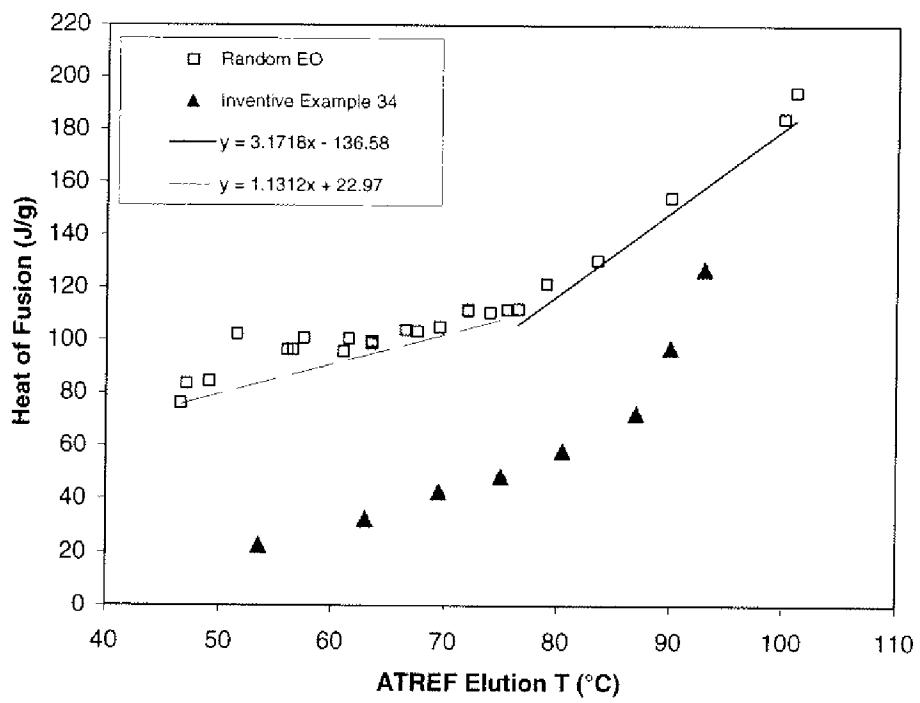
Figure 35
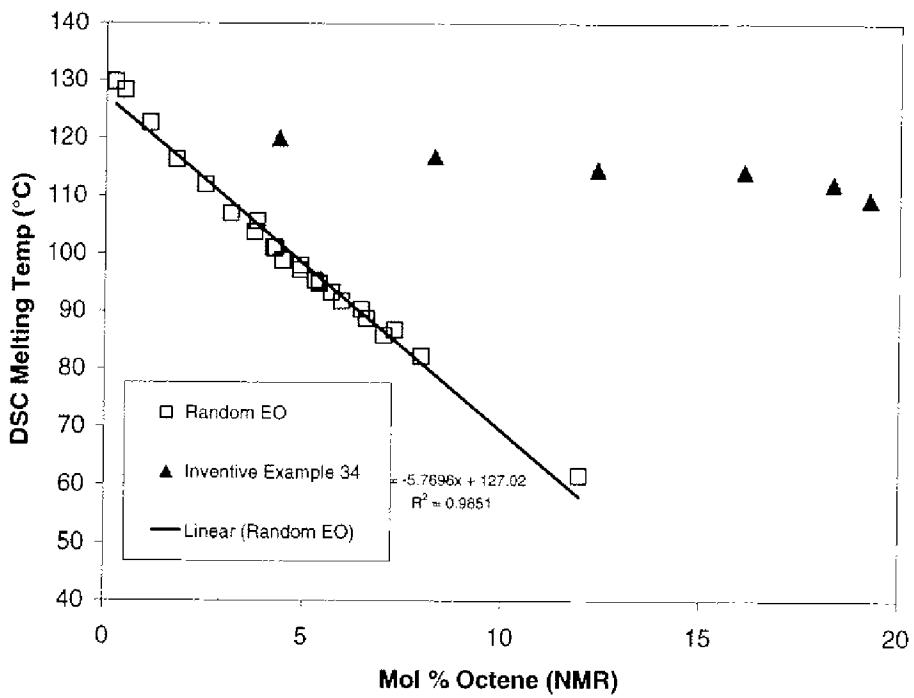
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