

**SEALS PRODUCED FROM ALPHA-OLEFIN/VINYLDENE AROMATIC
AND/OR HINDERED ALIPHATIC VINYLDENE/INTERPOLYMER BASED
MATERIALS AND SEALING SYSTEMS THEREFROM**

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In many industries, sealing systems for containers such as bottles or jars require the use of a cap or closure containing a seal or liner (such as a gasket, liner or barrier membrane) in order to effectively form a seal of the required integrity. Important for many applications is the ability of the seal to limit the permeation of
10 gases. For instance, permeation of oxygen from the outside can cause food spoilage or other adverse reactions of oxygen sensitive contents. Alternatively, in the case of, for example, carbonated beverages, diffusion of carbon dioxide out of the container contents results in loss of carbonation.

In addition, the nature of the material to be used for a given seal is often a
15 function of the pressure and temperature of the container contents and also the method by which the lid is mated with the container. For instance many containers have twist on and off lids which require that the seal material not only can tolerate a great deal of compression while maintaining its integrity, but also exhibit sufficient shape recovery.

20 Finally, the nature of the seal required for a container is often content specific, for instance some materials may not be compatible with certain medical components. In corrosive service conditions, a gasket must be impervious to the material in question, but still resilient enough to form a seal. Materials used to form seals used in the food and beverage area have similar requirements, but
25 should be acceptable for contact with the foodstuff. Furthermore, depending upon the type of food and/or liquid contents, the filling temperature might be lower or higher than room temperature, thus placing greater demands on the seal.

Seals for sealing systems have been made from a variety of structural materials, including polymers such as ethylene/vinyl acetate (EVA) and polyvinyl
30 chloride (PVC). For example, US Patent No. 4,984,703 (Burzynski) discloses plastic closures which have a sealing liner comprising a blend of ethylene/vinyl acetate and a thermoplastic elastomeric composition.

Various attempts to solve the performance requirements have also involved the use of oil additives or elastomer additives. For example, US Patent No. 5,137,164 (Bayer), the disclosure of which is incorporated herein by reference, discloses a method of lining a plastic closure with a thermoplastic. The
5 thermoplastic is a non-cross linked curable, vinyl chloride copolymer composition which has been plasticized with an epoxidized oil, an organic diglycidyl ether and a curing agent for the ether.

US Patent No. 4,807,772 (Schloss) and US Patent No. 4,846,362 (Schloss) disclose polypropylene and polyethylene closures, respectively, each having
10 removable liners made from a blend of polyethylene and a thermoplastic, elastomeric copolymer (such as a block copolymer of styrene and butadiene). The blends are said to generally include 20-50 weight percent oil.

USP 4,872,573 (Johnson et al.) discloses barrier layers for closures selected from the group consisting of ethylene/vinyl alcohol copolymers and
15 polyvinylidene chloride, especially for retarding the migration of oxygen containing gases.

US Patent No. 5,000,992 (Kelch) discloses a plastic container closure made from a coextruded multilayer foamed film. The film has at least one solid layer of a polyethylene blend and at least one foamed layer of a second polyethylene blend.

20 US Patent No. 3,786,954 (Shull) discloses laminated gaskets comprising a combination of a thick foamed polyethylene sheet material and a thin air and moisture impervious SARAN™ (trademark of and made by The Dow Chemical Company) layer adhered to the polyethylene by a low density polyethylene (LDPE) bond.

25 US Patent No. 5,104,710 (Knight) discloses improvement of gasket adhesion through use of propylene adhesion promoters. Knight also discloses a linear low density polyethylene (LLDPE) as a comparison example and shows that it has insufficient bond temperature of 200°C.

US Patent No. 4,529,740 (Trainor) discloses foamable structures made from elastomers such as styrene-butadiene block copolymers, a small amount of a salt of a sulfonated styrene polymer, and a blowing agent.

US Patent No. 4,744,478 (Hahn) discloses a molded closure comprising at least one substantially unfoamed polymer layer and an integrally molded foamed layer of the same polymer. The polymer can be an olefinic, a styrenic, polyesters, polycarbonates, or other suitable engineering resins. A preferred polymer is a copolymer of propylene and EDPM rubber.

Polyvinyl chloride (PVC) polymers have also been used extensively as food closure gaskets, but these are increasingly coming under environmental pressures. Other polymers have also been used for their softness qualities, such as ethylene/methacrylic acid or ethylene/acrylic acid copolymers, but these often times contribute negatively to taste and odor problems, for example when the polymeric gasket comes in contact with the food and certain constituents leach into the food.

High density polyethylene (HDPE) also has been disclosed as useful for forming gaskets, since the higher density polyethylene has relatively good taste and odor properties. Use of this material has not been commercially successful to date, because the polymer is too "hard" and because, by adding oil to reduce the hardness, the extractables increase, thus negating regulatory requirements for food contact. In addition, while heterogeneous linear low density polyethylene (LLDPE) has better softness properties than HDPE, neither HDPE or LLDPE adhere well to certain plastic closures (e.g., polypropylene, which is often used as a closure material, as described in USP 4,807,772) resulting in a loose polyethylene gasket.

WO 95/00599 (Shell Oil Company) discloses improved polymer compositions useful in the manufacture of closures and as liners for reclosable container closures which comprise blends of semi-crystalline poly (1-butene), ethylene-methyl acrylate, polypropylene random copolymer. Such compositions were claimed to be recyclable and did not present environmental, health and odor problems of prior art liners.

WO 88/03115 (Permian Research Corporation) teaches a molded polymeric container closure which comprises at least one substantially unfoamed polymer layer and an integrally molded foamed layer of the same polymer. These closures were claimed to provide excellent insulating properties and to be manufactured
5 more simply and economically than closures of the prior art.

WO 90/14945 (The Dow Chemical Company) disclosed coextruded multilayer foamed film for plastic container closures which films had at least one solid film layer of a first polyolefin blend containing linear low density polyethylene, low density polyethylene and optionally high density polyethylene,
10 and at least one foamed layer of a second polyolefin blend containing linear low density polyethylene, low density polyethylene and optionally ethylene vinyl acetate.

WO 95/32095 (W.R. Grace & Co.) describes heat shrinkable film and sheet materials made with an alpha olefin/vinyl aromatic copolymer such as an
15 ethylene/styrene copolymer. Also disclosed are printed film, laminates and patch bags which comprise a heat shrinkable patch adhered to a heat-shrinkable bag, or a package comprising a rigid container and a flexible lid.

However there remains a requirement for sealing systems comprising seals based on polymers which have a balance of properties including low oxygen
20 permeability, excellent tensile strain recovery and stress relaxation, low modulus/Shore A hardness, and good melt processability including melt rheology. We have now discovered that materials based on substantially random α -olefin/vinylidene aromatic and/or hindered aliphatic or cycloaliphatic vinylidene interpolymers, having a specific range of polymer units derived from
25 the vinylidene monomer, provide for improved seals for sealing systems. These materials offer a unique range of necessary attributes including, oxygen barrier performance, tensile strain recovery, stress relaxation and a range of hardness or softness, all of which depend upon the vinylidene content of the polymer or blend. We have now surprisingly found that the optimum balance of such properties are
30 exhibited in the substantially random interpolymers used to prepare the seals of

the present invention, within a relatively narrow and intermediate range of vinylidene content, and that such properties are less attractive in interpolymers having a relatively high or relatively low vinylidene content.

The seals of the present invention comprising substantially random vinylidene interpolymers or their blends demonstrate the requisite properties of an acceptable seal for a reclosable container closure. Such closures are removable from the container with satisfactory removal torque and can be removed and reclosed throughout the life of the contents of the container. The seals or liners provide for oxygen barrier, integrity and temperature stability during shipping and storage, as well as sealability even under the top load when the contents of the container are carbonated, e.g. a carbonated beverage. The seals of the present invention also show improved adhesion to steel or metal closures such as beer bottle caps which are often epoxy or acrylic coated. They also have good adhesion to closures made from non-polar substrates such as polypropylene and high density polyethylene.

The present invention discloses seals including container closure liners, gaskets and barrier membranes, comprising a polymer composition having an oxygen transmission coefficient at a temperature of 25°C of less than 300 cm³.mil/100in².day.atm., which polymer composition comprises

- (A) at least one substantially random interpolymers comprising
- (1) from 24 to 65 mol percent of polymer units derived from:
 - (a) at least one vinylidene aromatic monomer, or
 - (b) at least one hindered aliphatic or cycloaliphatic vinylidene monomer, or
 - (c) a combination of at least one aromatic vinylidene monomer and at least one hindered aliphatic or cycloaliphatic vinylidene monomer, and
 - (2) from 35 to 76 mol percent of polymer units derived from at least one C₂₋₂₀ α-olefin; or
- (B) a blend comprising

- (1) from 35 to 99 percent by weight (based on the combined weight of Components B1 and B2) of Component A; and
- (2) from 1 to 65 percent by weight (based on the combined weight of Components B1 and B2) of at least one polymer other than that of Component A; and
- (C) from 0 to 80 percent by weight (based on the combined weights of components A, B, and C) of at least one filler.

The present invention also discloses sealing systems including container closures such as bottle caps comprising these seals. The compositions used to produce the seals of the present invention exhibit a unique balance of properties including low oxygen permeability, high tensile strain recovery and stress relaxation and low Shore A hardness.

All references herein to elements or metals belonging to a certain Group refer to the Periodic Table of the Elements published and copyrighted by CRC Press, Inc., 1989. Also any reference to the Group or Groups shall be to the Group or Groups as reflected in this Periodic Table of the Elements using the IUPAC system for numbering groups.

Any numerical values recited herein include all values from the lower value to the upper value in increments of one unit provided that there is a separation of at least 2 units between any lower value and any higher value. As an example, if it is stated that the amount of a component or a value of a process variable such as, for example, temperature, pressure, time and the like is, for example, from 1 to 90, preferably from 20 to 80, more preferably from 30 to 70, it is intended that values such as 15 to 85, 22 to 68, 43 to 51, 30 to 32 etc. are expressly enumerated in this specification. For values which are less than one, one unit is considered to be 0.0001, 0.001, 0.01 or 0.1 as appropriate. These are only examples of what is specifically intended and all possible combinations of numerical values between the lowest value and the highest value enumerated are to be considered to be expressly stated in this application in a similar manner.

The term "hydrocarbyl" as employed herein means any aliphatic, cycloaliphatic, aromatic, aryl substituted aliphatic, aryl substituted cycloaliphatic, aliphatic substituted aromatic, or aliphatic substituted cycloaliphatic groups.

5 The term "hydrocarbyloxy" means a hydrocarbyl group having an oxygen linkage between it and the carbon atom to which it is attached.

The term "copolymer" as employed herein means a polymer wherein at least two different monomers are polymerized to form the copolymer.

10 The term "interpolymer" is used herein to indicate a polymer wherein at least two different monomers are polymerized to make the interpolymer. This includes copolymers, terpolymers, etc.

The term "substantially random" (in the substantially random interpolymer comprising polymer units derived from one or more α -olefin monomers with one or more vinylidene aromatic monomers and/or a hindered aliphatic or cycloaliphatic vinylidene monomers) as used herein means that the distribution of the monomers of said interpolymer can be described by the Bernoulli statistical model or by a first or second order Markovian statistical model, as described by J. C. Randall in POLYMER SEQUENCE DETERMINATION, Carbon-13 NMR Method, Academic Press New York, 1977, pp. 71-78. Preferably, substantially random interpolymers do not contain more than 15 percent of the total amount of vinylidene aromatic monomer in blocks of vinylidene aromatic monomer of more than 3 units. More preferably, the interpolymer is not characterized by a high degree of either isotacticity or syndiotacticity. This means that in the carbon-13 NMR spectrum of the substantially random interpolymer the peak areas corresponding to the main chain methylene and methine carbons representing either meso diad sequences or racemic diad sequences should not exceed 75 percent of the total peak area of the main chain methylene and methine carbons.

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30 The term "sealing systems" as used herein are systems for sealing containers which have a seal and a method of closure which provide containment of the container contents. Also included as sealing systems as used herein are the tamper evident sealing systems including but not limited to those used in containers

carrying, for example, prescription drug products. In a preferred embodiment, the sealing system is a reclosable plastic or metal container closure containing a seal or liner. The container could come in a variety of sizes or shapes including those containers typically referred to as bottles or jars. With reference to the preferred
5 type of container, that is, bottles, such closures are commonly referred to as "bottle caps." The sealing systems are particularly useful when made of a metal or of a plastic such as a thermoplastic polymer. Such closures typically comprise a circular base wall, a seal or liner at the lower surface of said base wall, and a peripheral skirt extending downwardly from the wall which contains some means, for
10 example, threads, designed to engage some portion, for example, complimentary threads of the container at one or more points in close proximity to the container opening, and wherein the engagement and tightening of said threads causes the seal or liner to be imposed upon the top of the container as the closure is tightened thus forming a seal.

15 The term "seal" or "liner" as used herein is the sealing system component which, on closure, is imposed on the container thus forming a seal for the container contents. Such seals include, but are not limited to, molded flanges, sealing disks, barrier membranes for retarding gas migration, (particularly oxygen, carbon dioxide and water vapor), extruded single layer and multilayer structures, films
20 supported on substrates (made from metal, plastic, foam, glass, or ceramic), closures and liners or caps for molded container closures fabricated from glass, metal or polymers (including polyethylene, polystyrene, polyethylene terephthalate (PET), or polycarbonate).

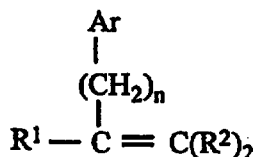
Also included as an embodiment of the seals of the present invention are
25 gaskets. Such gaskets can have many different forms, including "o-rings" and flat seals (for example, "film-like" gaskets having a thickness commensurate with the intended use). Various gasket manufacturing techniques are known including those disclosed in US Patent No. 5,215,587 (McConnelloque et al.); US Patent No. 4,085,186 (Rainer); US Patent No. 4,619,848 (Knight et al.); US Patent No. 5,104,710
30 (Knight); US Patent No. 4,981,231 (Knight); USP 4,717,034 (Mumford); US Patent

No. 3,786,954 (Shull); US Patent No. 3,779,965 (Lefforge et al.); US Patent No. 3,493,453 (Ceresa et al.); US Patent No. 3,183,144 (Caviglia); US Patent No. 3,300,072 (Caviglia); US Patent No. 4,984,703 (Burzynski); US Patent No. 3,414,938 (Caviglia); US Patent No. 4,939,859 (Bayer); US Patent No. 5,137,164 (Bayer); and US Patent
5 No. 5,000,992 (Kelch). Suitable end uses include, but are not limited to, seals for metal and plastic closures, as well as beverage cap liners, hot fill juice cap liners, polypropylene cap liners, steel or aluminum cap liners, high density polyethylene cap liners, window glass gaskets, sealed containers, closure caps, gaskets for medical devices, filter elements, pressure venting gaskets, hot melt gaskets, easy
10 twist off caps, electrochemical cell gaskets, refrigerator gaskets, galvanic cell gaskets, leak proof cell gaskets, waterproofing sheet, reusable gaskets, synthetic cork like materials, thin cell electromembrane separator, magnetic rubber materials, disc gaskets for alcoholic beverage bottle caps, freeze resistant seal rings, gaskets for plastic castings, expansion joints and waterstops, corrosion-resistant conduit
15 connectors, flexible magnetic plastics, pipe joint seals, integral weatherproof plastic lid and hinge for electrical outlets, magnetic faced foamed articles, jar rings, flexible gaskets, glass seals, tamper evident sealing liners, pressure applicators, combined bottle cap and straw structures, large condiment bottle liners, metal caps for apple sauce or salsa jars, home canning jars, and "crowns".

20 The interpolymers used to prepare the seals of the present invention include interpolymers prepared by polymerizing one or more α -olefins with one or more vinylidene aromatic monomers and/or one or more hindered aliphatic or cycloaliphatic vinylidene monomers.

Suitable α -olefins include for example, α -olefins containing from 2 to about
25 20, preferably from 2 to 12, more preferably from 2 to 8 carbon atoms. Particularly suitable are ethylene, propylene, butene-1, 4-methyl-1-pentene, hexene-1 or octene-1 or ethylene in combination with one or more of propylene, butene-1, 4-methyl-1-pentene, hexene-1 or octene-1. These α -olefins do not contain an aromatic moiety.

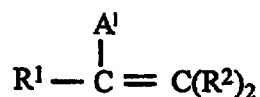
Suitable vinylidene aromatic monomers which can be employed to prepare the interpolymers include, for example, those represented by the following formula:



- 5 wherein R¹ is selected from the group of radicals consisting of hydrogen and alkyl radicals containing from 1 to 4 carbon atoms, preferably hydrogen or methyl; each R² is independently selected from the group of radicals consisting of hydrogen and alkyl radicals containing from 1 to 4 carbon atoms, preferably hydrogen or methyl; Ar is a phenyl group or a phenyl group substituted with from 1 to 5 substituents
10 selected from the group consisting of halo, C₁₋₄-alkyl, and C₁₋₄-haloalkyl; and n has a value from zero to about 4, preferably from zero to 2, most preferably zero.

Exemplary monovinylidene aromatic monomers include styrene, vinyl toluene, α-methylstyrene, t-butyl styrene, chlorostyrene, including all isomers of these compounds. Particularly suitable monomers include styrene and lower alkyl- or
15 halogen-substituted derivatives thereof. Preferred monomers include styrene, α-methyl styrene, the lower alkyl- (C₁ - C₄) or phenyl-ring substituted derivatives of styrene, such as for example, ortho-, meta-, and para-methylstyrene, the ring halogenated styrenes, para-vinyl toluene or mixtures thereof. A more preferred aromatic monovinylidene monomer is styrene.

- 20 By the term "hindered aliphatic or cycloaliphatic vinylidene compounds", it is meant addition polymerizable vinylidene monomers corresponding to the formula:



- wherein A¹ is a sterically bulky, aliphatic or cycloaliphatic substituent of up to 20
25 carbons, R¹ is selected from the group of radicals consisting of hydrogen and alkyl radicals containing from 1 to 4 carbon atoms, preferably hydrogen or methyl; each R² is independently selected from the group of radicals consisting of hydrogen and

alkyl radicals containing from 1 to about 4 carbon atoms, preferably hydrogen or methyl; or alternatively R¹ and A¹ together form a ring system.

By the term "sterically bulky" is meant that the monomer bearing this substituent is normally incapable of addition polymerization by standard Ziegler-Natta polymerization catalysts at a rate comparable with ethylene polymerizations. Preferred hindered aliphatic or cycloaliphatic vinylidene compounds are monomers in which one of the carbon atoms bearing ethylenic unsaturation is tertiary or quaternary substituted. Examples of such substituents include cyclic aliphatic groups such as cyclohexyl, cyclohexenyl, cyclooctenyl, or ring alkyl or aryl substituted derivatives thereof, and tert-butyl, norbornyl. Most preferred hindered aliphatic or cycloaliphatic vinylidene compounds are the various isomeric vinyl- ring substituted derivatives of cyclohexene and substituted cyclohexenes, and 5-ethylidene-2-norbornene. Especially suitable are 1-, 3-, and 4-vinylcyclohexene.

The substantially random interpolymers may be modified by typical grafting, hydrogenation, functionalizing, or other reactions well known to those skilled in the art. The polymers may be readily sulfonated or chlorinated to provide functionalized derivatives according to established techniques.

The substantially random interpolymers may also be modified by various cross-linking processes including, but not limited to peroxide-, silane-, sulfur-, radiation-, or azide-based cure systems. A full description of the various cross-linking technologies is described in copending U.S. Patent Application No's 08/921,641 and 08/921,642 both filed on August 27, 1997.

Dual cure systems, which use a combination of heat, moisture cure, and radiation steps, may be effectively employed. Dual cure systems are disclosed and claimed in U. S. Patent Application Serial No. 536,022, filed on September 29, 1995, in the names of K. L. Walton and S. V. Karande. For instance, it may be desirable to employ peroxide crosslinking agents in conjunction with silane crosslinking agents, peroxide crosslinking agents in conjunction with radiation, sulfur-containing crosslinking agents in conjunction with silane crosslinking agents, etc.

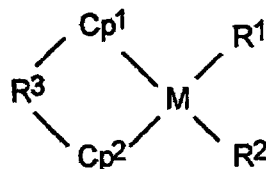
The substantially random interpolymers may also be modified by various cross-linking processes including, but not limited to the incorporation of a diene component as a termonomer in its preparation and subsequent cross linking by the aforementioned methods and further methods including vulcanization via the vinyl group using sulfur for example as the cross linking agent.

One method of preparation of the substantially random interpolymers includes polymerizing a mixture of polymerizable monomers in the presence of one or more metallocene or constrained geometry catalysts in combination with various cocatalysts.

The substantially random interpolymers can be prepared as described in US Application serial number 545,403 filed July 3, 1990 (corresponding to EP-A-0,416,815) by James C. Stevens et al. Preferred operating conditions for such polymerization reactions are pressures from atmospheric up to 3000 atmospheres and temperatures from -30°C to 200°C. Polymerizations and unreacted monomer removal at temperatures above the autopolymerization temperature of the respective monomers may result in formation of some amounts of homopolymer polymerization products resulting from free radical polymerization.

Examples of suitable catalysts and methods for preparing the substantially random interpolymers are disclosed in U.S. Application Serial No. 545,403, filed July 3, 1990 (EP-A-416,815); U.S. Application Serial No. 702,475, filed May 20, 1991 (EP-A-514,828); U.S. Application Serial No. 876,268, filed May 1, 1992, (EP-A-520,732); U.S. Application Serial No. 241,523, filed May 12, 1994; as well as U.S. Patents: 5,055,438; 5,057,475; 5,096,867; 5,064,802; 5,132,380; 5,189,192; 5,321,106; 5,347,024; 5,350,723; 5,374,696; and 5,399,635.

The substantially random α -olefin/vinylidene aromatic interpolymers can also be prepared by the methods described in JP 07/278230 employing compounds shown by the general formula



where Cp¹ and Cp² are cyclopentadienyl groups, indenyl groups, fluorenyl groups, or substituents of these, independently of each other; R¹ and R² are hydrogen atoms, halogen atoms, hydrocarbon groups with carbon numbers of 1-12, alkoxyl groups, or aryloxyl groups, independently of each other; M is a group IV metal, preferably Zr or Hf, most preferably Zr; and R³ is an alkylene group or silanediyl group used to crosslink Cp¹ and Cp²).

The substantially random α -olefin/vinylidene aromatic interpolymers can also be prepared by the methods described by John G. Bradfute et al. (W. R. Grace & Co.) in WO 95/32095; by R. B. Pannell (Exxon Chemical Patents, Inc.) in WO 94/00500; and in *Plastics Technology*, p. 25 (September 1992).

Also suitable are the substantially random interpolymers which comprise at least one α -olefin/vinyl aromatic/vinyl aromatic/ α -olefin tetrad disclosed in U. S. Application No. 08/708,809 filed September 4, 1996 by Francis J. Timmers et al.

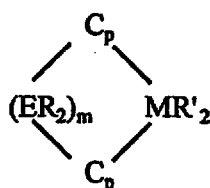
These interpolymers contain additional signals with intensities greater than three times the peak to peak noise. These signals appear in the chemical shift range 43.70-44.25 ppm and 38.0-38.5 ppm. Specifically, major peaks are observed at 44.1, 43.9 and 38.2 ppm. A proton test NMR experiment indicates that the signals in the chemical shift region 43.70-44.25 ppm are methine carbons and the signals in the region 38.0-38.5 ppm are methylene carbons.

It is believed that these new signals are due to sequences involving two head-to-tail vinyl aromatic monomer insertions preceded and followed by at least one α -olefin insertion, for example, an ethylene/styrene/styrene/ethylene tetrad wherein the styrene monomer insertions of said tetrads occur exclusively in a 1,2 (head to tail) manner. It is understood by one skilled in the art that for such tetrads involving a vinyl aromatic monomer other than styrene and an α -olefin other than ethylene that the ethylene/vinyl aromatic monomer/vinyl aromatic

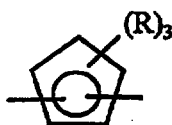
monomer/ethylene tetrad will give rise to similar carbon-¹³ NMR peaks but with slightly different chemical shifts.

These interpolymers are prepared by conducting the polymerization at temperatures of from about -30°C to about 250°C in the presence of such catalysts

5 as those represented by the formula:



wherein: each C_p is independently, each occurrence, a substituted cyclopentadienyl group π-bound to M; E is C or Si; M is a group IV metal, preferably Zr or Hf, most preferably Zr; each R is independently, each occurrence, H, hydrocarbyl, silahydrocarbyl, or hydrocarbylsilyl, containing up to about 30 preferably from 1 to about 20 more preferably from 1 to about 10 carbon or silicon atoms; each R' is independently, each occurrence, H, halo, hydrocarbyl, hydrocarbyloxy, silahydrocarbyl, hydrocarbylsilyl containing up to about 30 preferably from 1 to about 20 more preferably from 1 to about 10 carbon or silicon atoms or two R' groups together can be a C₁₋₁₀ hydrocarbyl substituted 1,3-butadiene; m is 1 or 2; and optionally, but preferably in the presence of an activating cocatalyst. particularly, suitable substituted cyclopentadienyl groups include those illustrated by the formula:



wherein each R is independently, each occurrence, H, hydrocarbyl, silahydrocarbyl, or hydrocarbylsilyl, containing up to 30 preferably from 1 to 20 more preferably from 1 to 10 carbon or silicon atoms or two R groups together form a divalent derivative of such group. Preferably, R independently each occurrence is (including where appropriate all isomers) hydrogen, methyl, ethyl, propyl, butyl,

pentyl, hexyl, benzyl, phenyl or silyl or (where appropriate) two such R groups are linked together forming a fused ring system such as indenyl, fluorenyl, tetrahydroindenyl, tetrahydrofluorenyl, or octahydrofluorenyl.

Particularly preferred catalysts include, for example, racemic-
 5 (dimethylsilanediyl)-bis-(2-methyl-4-phenylindenyl) zirconium dichloride, racemic-(dimethylsilanediyl)-bis-(2-methyl-4-phenylindenyl) zirconium 1,4-diphenyl-1,3-butadiene, racemic-(dimethylsilanediyl)-bis-(2-methyl-4-phenylindenyl) zirconium di-C₁₋₄ alkyl, racemic-(dimethylsilanediyl)-bis-(2-methyl-4-phenylindenyl) zirconium di-C₁₋₄ alkoxide, or any combination thereof.

10 It is also possible to use the following titanium-based constrained geometry catalysts, [n-(1,1-dimethylethyl)-1,1-dimethyl-1-[(1,2,3,4,5-η)-1,5,6,7-tetrahydro-s-indacen-1-yl]silanaminato(2-)-n]titanium dimethyl; (1-indenyl)(tert-butylamido)dimethyl- silane titanium dimethyl; ((3-tert-butyl)(1,2,3,4,5-η)-1-indenyl)(tert-butylamido) dimethylsilane titanium dimethyl; and ((3-iso-
 15 propyl)(1,2,3,4,5-η)-1-indenyl)(tert-butyl amido)dimethylsilane titanium dimethyl, or any combination thereof.

Further preparative methods for the interpolymers of the present invention have been described in the literature. Longo and Grassi (Makromol. Chem., Volume 191, pages 2387 to 2396 [1990]) and D'Anniello et al. (Journal of Applied
 20 Polymer Science, Volume 58, pages 1701-1706 [1995]) reported the use of a catalytic system based on methylalumoxane (MAO) and cyclopentadienyltitanium trichloride (CpTiCl₃) to prepare an ethylene-styrene copolymer. Xu and Lin (Polymer Preprints, Am. Chem. Soc., Div. Polym. Chem.) Volume 35, pages 686,687 [1994]) have reported copolymerization using a MgCl₂/TiCl₄/NdCl₃/Al(iBu)₃
 25 catalyst to give random copolymers of styrene and propylene. Lu et al (Journal of Applied Polymer Science, Volume 53, pages 1453 to 1460 [1994]) have described the copolymerization of ethylene and styrene using a TiCl₄/NdCl₃/ MgCl₂ / Al(Et)₃ catalyst. The manufacture of α-olefin/vinyl aromatic monomer interpolymers such as propylene/styrene and butene/styrene are described in US Patent No.
 30 5,244,996, issued to Mitsui Petrochemical Industries Ltd.

The interpolymers of one or more α -olefins and one or more monovinylidene aromatic monomers and/or one or more hindered aliphatic or cycloaliphatic vinylidene monomers employed in the present invention are substantially random polymers. These interpolymers usually contain from 24 to 65, preferably from 27 to 46, more preferably from 29 to 37 mole percent of at least one vinylidene aromatic monomer and/or hindered aliphatic or cycloaliphatic vinylidene monomer and from 35 to 76, preferably from 54 to 73, more preferably from 63 to 71 mole percent of at least one aliphatic α -olefin having from 2 to 20 carbon atoms.

The number average molecular weight (M_n) of the polymers and interpolymers is usually greater than 10,000, preferably from 20,000 to 1,000,000, more preferably from 50,000 to 500,000.

The interpolymers applicable to the present invention can have a melt index (I_2) of from 0.05 to 1000, preferably of from 0.1 to 500, more preferably of from 0.5 to 100g/10 min.

While preparing the substantially random interpolymers, an amount of atactic vinylidene aromatic homopolymer may be formed due to homopolymerization of the vinylidene aromatic monomer at elevated temperatures. The presence of vinylidene aromatic homopolymer is in general not detrimental for the purposes of the present invention and can be tolerated. The vinylidene aromatic homopolymer may be separated from the interpolymers, if desired, by extraction techniques such as selective precipitation from solution with a non solvent for either the interpolymers or the vinylidene aromatic homopolymer. For the purpose of the present invention it is preferred that no more than 20 weight percent, preferably less than 15 weight percent based on the total weight of the interpolymers of atactic vinylidene aromatic homopolymer is present.

The present invention also provides seals prepared from blends of the substantially random α -olefin/vinylidene interpolymers with one or more other polymer components. These other polymer components include polystyrene, high impact polystyrene, polyvinyl chloride, copolymers of styrene including

copolymers of styrene and at least one of butadiene, acrylonitrile, methacrylonitrile, maleic anhydride, or α -methyl styrene, homopolymers and copolymers of aliphatic C₂-C₂₀ α -olefins, copolymers of ethylene and vinyl acetate, chlorinated α -olefin polymers; or substantially random α -olefin/vinylidene

- 5 interpolymers having a content of less than about 24 mol percent of polymer units derived from at least one vinylidene aromatic monomer, or at least one hindered aliphatic or cycloaliphatic vinylidene monomer, or a combination of at least one aromatic vinylidene monomer and at least one hindered aliphatic or cycloaliphatic vinylidene monomer.

- 10 Also included are unsaturated block copolymers including those represented by the following formulas:

Formula I $A-B-R(-B-A)_n$ or

Formula II $A_x-(BA)_y-BA$

- wherein each A is a polymer block comprising a monovinylidene aromatic
15 monomer, preferably styrene, and each B is a polymer block comprising a conjugated diene, preferably isoprene or butadiene, and optionally a monovinylidene aromatic monomer, preferably styrene; R is the remnant of a multifunctional coupling agent; n is an integer from 1 to 5; x is zero or 1; and y is a real number from zero to 4.

- 20 The preparation of the block copolymers useful herein is not the subject of the present invention. Methods for the preparation of such block copolymers are known in the art. Suitable catalysts for the preparation of useful block copolymers with unsaturated rubber monomer units include lithium based catalysts and especially lithium-alkyls. US Patent No. 3,595,942 describes suitable methods for
25 hydrogenation of block copolymers with unsaturated rubber monomer units to form block copolymers with saturated rubber monomer units. The structure of the polymers is determined by their methods of polymerization. For example, linear polymers result by sequential introduction of the desired rubber monomer into the reaction vessel when using such initiators as lithium-alkyls or dilithiostilbene and
30 the like, or by coupling a two segment block copolymer with a difunctional

coupling agent. Branched structures, on the other hand, may be obtained by the use of suitable coupling agents having a functionality with respect to the block copolymers with unsaturated rubber monomer units of three or more. Coupling may be effected with multifunctional coupling agents such as dihaloalkanes or
5 alkenes and divinyl benzene as well as with certain polar compounds such as silicon halides, siloxanes or esters of monohydric alcohols with carboxylic acids. The presence of any coupling residues in the polymer may be ignored for an adequate description of the block copolymers forming a part of the composition of this invention.

10 Suitable block copolymers having unsaturated rubber monomer units include, but are not limited to, styrene-butadiene (SB), styrene-isoprene (SI), styrene-butadiene-styrene (SBS), styrene-isoprene-styrene (SIS), α -methylstyrene-butadiene- α -methylstyrene and α -methylstyrene-isoprene- α -methylstyrene.

15 The styrenic portion of the block copolymer is preferably a homopolymer of styrene and its analogs and homologs including α -methylstyrene and ring-substituted styrenes, particularly ring-methylated styrenes or copolymer combinations. The preferred styrenics are styrene and α -methylstyrene, and styrene is particularly preferred.

20 Block copolymers with unsaturated rubber monomer units may comprise homopolymers of butadiene or isoprene or they may comprise copolymers of one or both of these two dienes with a minor amount of styrenic monomer.

25 Preferred block copolymers with saturated rubber monomer units comprise at least one segment of a styrenic unit and at least one segment of an ethylene-butene or ethylene-propylene copolymer. Preferred examples of such block copolymers with saturated rubber monomer units include styrene/ethylene-butene copolymers, styrene/ethylene-propylene copolymers, styrene/ethylene-butene/styrene (SEBS) copolymers, styrene/ethylene-propylene/styrene (SEPS) copolymers.

30 Hydrogenation of block copolymers with unsaturated rubber monomer units is preferably effected by use of a catalyst comprising the reaction products of

an aluminum alkyl compound with nickel or cobalt carboxylates or alkoxides under such conditions as to substantially completely hydrogenate at least 80 percent of the aliphatic double bonds while hydrogenating no more than 25 percent of the styrenic aromatic double bonds. Preferred block copolymers are those where
5 at least 99 percent of the aliphatic double bonds are hydrogenated while less than 5 percent of the aromatic double bonds are hydrogenated.

The proportion of the styrenic blocks is generally between 8 and 65 percent by weight of the total weight of the block copolymer. Preferably, the block copolymers contain from 10 to 35 weight percent of styrenic block segments and
10 from 90 to 65 weight percent of rubber monomer block segments, based on the total weight of the block copolymer.

The average molecular weights of the individual blocks may vary within certain limits. In most instances, the styrenic block segments will have number average molecular weights in the range of 5,000 to 125,000, preferably from 7,000 to
15 60,000 while the rubber monomer block segments will have average molecular weights in the range of 10,000 to 300,000, preferably from 30,000 to 150,000. The total average molecular weight of the block copolymer is typically in the range of 25,000 to 250,000, preferably from 35,000 to 200,000.

Further, the various block copolymers suitable for use in the present
20 invention may be modified by graft incorporation of minor amounts of functional groups, such as, for example, maleic anhydride by any of the methods well known in the art.

Block copolymers useful in the present invention are commercially available, such as, for example, supplied by Shell Chemical Company under the designation
25 of KRATON™ and supplied by Dexco Polymers under the designation of VECTOR™.

The blended polymer compositions used to prepare the sealing systems of the present invention can be prepared by any convenient method, including dry blending the individual components and subsequently melt mixing or melt
30 compounding, either directly in the extruder or mill used to make the finished

article (e.g., the automotive part), or by pre-melt mixing in a separate extruder or mill (e.g., a Banbury mixer), or by solution blending, or by compression molding, or by calendering.

5 The blends used to prepare the seals of the sealing systems of the present invention comprise

(A) from 35 to 99, preferably from 40 to 97, more preferably from 40 to 95 percent of by weight based on the combined weights of Components A and B of substantially random interpolymers of one or more α -olefins and one or more monovinylidene aromatic monomers and/or one or more
10 hindered aliphatic or cycloaliphatic vinylidene monomers which comprise

a) of from 24 to 65, preferably from about 27 to about 46, more preferably from 29 to 37 mole percent of polymer units derived from at least one vinylidene aromatic monomer and/or hindered aliphatic or cycloaliphatic vinylidene monomer and
15 b) of from 35 to 76, preferably from 54 to 73, more preferably from about 63 to about 71 mole percent of polymer units derived from at least one aliphatic α -olefin having from 2 to 20 carbon atoms; and

(B) of from 65 to 1, preferably from 60 to 3, more preferably from 60 to 5
20 percent of by weight based on the combined weights of Components A and B of at least one polymer comprising polystyrene, high impact polystyrene, polyvinyl chloride, copolymers of styrene and at least one of acrylonitrile, meth-acrylonitrile, maleic anhydride, or α -methyl styrene, homopolymers and copolymers of aliphatic C_2 - C_{20} α -olefins, copolymers of ethylene and vinyl acetate, chlorinated α -
25 olefin polymers, substantially random α -olefin/vinylidene interpolymers having a content of polymer units derived from at least one vinylidene aromatic monomer, or at least one hindered aliphatic or cycloaliphatic vinylidene monomer, or a combination of at least one aromatic vinylidene monomer and at least one hindered aliphatic or cycloaliphatic vinylidene monomer of less than 24 mol percent, or
30 styrene-butadiene (SB), styrene-isoprene(SI), styrene-butadiene-styrene (SBS),

styrene-isoprene-styrene (SIS) or styrene-ethylene/butene-styrene (SEBS) block copolymers.

- Additives such as antioxidants (for example, hindered phenols such as, for example, Irganox® 1010), phosphites (for example, Irgafos® 168), u.v. stabilizers, 5
cling additives (for example, polyisobutylene), antiblock additives, colorants, pigments, fillers, and the like can also be included in the interpolymers and/or blends employed in the present invention, to the extent that they do not interfere with the enhanced properties of the sealing systems discovered by Applicants. Preferred examples of fillers are talc, carbon black, carbon fibers, calcium 10
carbonate, alumina trihydrate, glass fibers, marble dust, cement dust, clay, feldspar, silica or glass, fumed silica, alumina, magnesium oxide, magnesium hydroxide, antimony oxide, zinc oxide, barium sulfate, aluminum silicate, calcium silicate, titanium dioxide, titanates, glass microspheres or chalk. Of these fillers, barium sulfate, talc, calcium carbonate, silica/glass, glass fibers, alumina and titanium 15
dioxide, and mixtures thereof are preferred. The most preferred inorganic fillers are talc, calcium carbonate, barium sulfate, glass fibers or mixtures thereof. These fillers could be employed in amounts from 0 to 90, preferably from 0 to 80, more preferably from 0 to 70 percent by weight based on the weight of the polymer or polymer blend.
- 20 These additives are employed in functionally equivalent amounts known to those skilled in the art. For example, the amount of antioxidant employed is that amount which prevents the polymer or polymer blend from undergoing oxidation at the temperatures and environment employed during storage and ultimate use of the polymers. Such amount of antioxidants is usually in the range of from 0.01 to 25
10, preferably from 0.05 to 5, more preferably from 0.1 to 2 percent by weight based upon the weight of the polymer or polymer blend. Similarly, the amounts of any of the other enumerated additives are the functionally equivalent amounts such as the amount to render the polymer or polymer blend antiblocking, to produce the desired amount of filler loading to produce the desired result, to provide the 30
desired color from the colorant or pigment. Such additives can suitably be

employed in the range of from 0.05 to 50, preferably from 0.1 to 35, more preferably from 0.2 to 20 percent by weight based upon the weight of the polymer or polymer blend.

One type of additive found particularly useful in the polymer compositions used to prepare the seals of the present invention are lubricating agents. Such additives are better known by a variety of more common names such as slip agent or release agent which seem to depend upon the particular property modification contemplated for the additive. Illustrative lubricating agents, preferably solid lubricating agents, include organic materials such as silicones, particularly dimethylsiloxane polymers, fatty acid amides such as ethylene bis (stearamides), oleamides and erucamide; and metal salts of fatty acids such as zinc, calcium, or lead stearates. Also suitable are inorganic materials such as talc, mica, fumed silica and calcium silicate. Particularly preferred are the fatty acid amides, oleamides, and erucamide. Quantities of lubricating agent of from 0.01 to 5 percent by weight based on the total weight of the mixture are satisfactory, more preferred are quantities of from 0.05 to 4 percent by weight.

Also included in the present invention are seals prepared from the disclosed interpolymers and blend compositions which are further formulated with plasticizers, tackifiers (aliphatic, aromatic, rosin derived and their mixtures), and oils.

There are many types of molding operations which can be used to form the seals of the present invention, including, but not limited to, casting from solution, thermoforming and various injection molding processes (for example, 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") and blow molding processes (for example, that described in Modern Plastics Encyclopedia/89, Mid October 1988 Issue, Volume 65, Number 11, pp. 217-218, "Extrusion-Blow Molding") and compression molding, profile extrusion, sheet extrusion, film casting, coextrusion and multilayer extrusion, coinjection molding, lamination, and film blowing.

The seals claimed herein can also be made from extruded sheets or films prepared by conventional techniques including blown, cast or extrusion coated films, followed by stamping or cutting the sealing system from the sheet or film. Multilayer film structures are also suitable for making the seals disclosed herein, with the proviso that at least one layer comprises the substantially random interpolymer.

Foam structures comprising the substantially random interpolymers in either a cross-linked or uncross-linked form are also useful for preparing the seals of the present invention. The foamed composition can be utilized in the form of a single layer or as a layer in a multi-layer structure. Excellent teachings to processes for making ethylenic polymer foam structures and processing them are seen in C.P. Park, "Polyolefin Foam", Chapter 9, Handbook of Polymer Foams and Technology, edited by D. Klempner and K. C. Frisch, Hanser Publishers, Munich, Vienna, New York, Barcelona (1991).

Foam structures may be made by conventional extrusion foaming processes. Apparatuses and methods for producing foam structures in coalesced strand form can be found in U.S. Patent Nos. 3,573,152 and 4,824,720. The present foam structures may also be formed by an accumulating extrusion process as seen in U.S. Pat. No. 4,323,528.

The present foam structures may also be formed into foam beads suitable for molding into the seals of the present invention. This process is well taught in U.S. Pat. No. 4,379,859; U.S. Pat. No. 4,464,484; and in U.S. Pat. No. 4,168,353. The foam beads may then be molded to blocks or shaped articles by suitable molding methods known in the art. (Some of the methods are taught in U.S. Pat. Nos. 3,504,068 and 3,953,558.) Excellent teachings of the above processes and molding methods can also be found in C.P. Park, *supra*, p. 191, pp. 197-198, and pp. 227-229.

Blowing agents useful in making the present foam structures include inorganic agents, organic blowing agents and chemical blowing agents. Suitable inorganic blowing agents include carbon dioxide, nitrogen, argon, water, air, nitrogen, and helium. Organic blowing agents include aliphatic hydrocarbons

having 1-6 carbon atoms, aliphatic alcohols having 1-3 carbon atoms, and fully and partially halogenated aliphatic hydrocarbons having 1-4 carbon atoms. Aliphatic hydrocarbons include methane, ethane, propane, n-butane, isobutane, n-pentane, isopentane, neopentane, and the like. Aliphatic alcohols include methanol, ethanol, n-propanol, and isopropanol. Fully and partially halogenated aliphatic hydrocarbons include fluorocarbons, chlorocarbons, and chlorofluorocarbons. Examples of fluorocarbons include methyl fluoride, perfluoromethane, ethyl fluoride, 1,1-difluoroethane (HFC-152a), 1,1,1-trifluoroethane (HFC-143a), 1,1,1,2-tetrafluoro-ethane (HFC-134a), pentafluoroethane, difluoromethane, perfluoroethane, 2,2-difluoropropane, 1,1,1-trifluoropropane, perfluoropropane, dichloropropane, difluoropropane, perfluorobutane, perfluorocyclobutane. Partially halogenated chlorocarbons and chlorofluorocarbons for use in this invention include methyl chloride, methylene chloride, ethyl chloride, 1,1,1-trichloroethane, 1,1-dichloro-1-fluoroethane (HCFC-141b), 1-chloro-1,1-difluoroethane (HCFC-142b), 1,1-dichloro-2,2,2-trifluoroethane (HCFC-123) and 1-chloro-1,2,2,2-tetrafluoroethane (HCFC-124). Fully halogenated chlorofluorocarbons include trichloromonofluoromethane (CFC-11), dichlorodifluoromethane (CFC-12), trichlorotrifluoroethane (CFC-113), 1,1,1-trifluoroethane, pentafluoroethane, dichlorotetrafluoroethane (CFC-114), chloroheptafluoropropane, and dichlorohexafluoropropane. Chemical blowing agents include azodicarbonamide, azodiisobutyro-nitrile, benzenesulfonhydrazide, 4,4-oxybenzene sulfonyl-semicarbazide, p-toluene sulfonyl semi-carbazide, barium azodicarboxylate, N,N'-dimethyl-N,N'-dinitrosoterephthalamide, and trihydrazino triazine. Preferred blowing agents include isobutane, HFC-152a, and mixtures of the foregoing.

The amount of blowing agents incorporated into the substantially random interpolymer melt material to make a foam-forming polymer gel is from 0.2 to 5, preferably from 0.5 to 3, and most preferably from about 1 to 2.5 gram moles per kilogram of polymer.

Various additives may be incorporated in the present foam structures such as stability control agents, nucleating agents, inorganic fillers, pigments, antioxidants, acid scavengers, ultraviolet absorbers, flame retardants, processing aids, extrusion aids, and the like.

5 A stability control agent may be added to the present foam to enhance dimensional stability. Preferred agents include amides and esters of C₁₀-C₂₄ fatty acids. Such agents are seen in US Patent Nos. 3,644,230 and 4,214,054. Most preferred agents include stearyl stearamide, glycerol monostearate, glycerol monobehenate, and sorbitol monostearate. Typically, such stability control agents
10 are employed in an amount ranging from 0.1 to 10 parts per hundred parts of the polymer.

In addition, a nucleating agent may be added in order to control the size of foam cells. Preferred nucleating agents include inorganic substances such as calcium carbonate, talc, clay, titanium oxide, silica, barium sulfate, diatomaceous
15 earth, mixtures of citric acid and sodium bicarbonate, and the like. The amount of nucleating agent employed may range from 0.01 to 5 parts by weight per hundred parts by weight of a polymer resin.

There are numerous methods known to produce sealing systems or closures such as those described in US Patent 4,347,939; US Patent 4,620,426; US Patent
20 4,988,467; US Patent 4,818,577; US Patent 4,274,822; and US Patent 4,846,362.

In one embodiment, the seal or liner is incorporated in the closure for the container by preparing a film of suitable thickness as produced by extrusion, and circular disks of appropriate diameter are cut from the film and provided individually to pre-formed closures also made by conventional procedures such as
25 injection molding. The disks should be of such diameter as will snugly fit inside the skirt of the closure when placed against the internal surface of the base wall. The disks are fixed to the closure by well known methods such as through use of an adhesive or by application of heat. In a second and generally preferred embodiment, the seal or liner is extruded, cut and pressure molded inside the
30 closure.

The requirements of the closure of having a minimum threshold removal torque, retention of gases, and resealability are often met by inclusion of the sealing system or liner at the lower surface of the base wall so that the liner will be imposed upon the top of the container as the closure is tightened.

5 The seals of the present invention have an oxygen permeability of less than 300 cm³•mil/100 in²•day•atm. (1.2 cm³/cm•day•MPa), preferably less than 200 cm³•mil/100 in²•day•atm. (0.8 cm³/cm•day•MPa), more preferably less than 150 cm³•mil/100 in²•day•atm. (0.6 cm³/cm•day•MPa), usually down to a value as low as 60 cm³•mil/100 in²•day•atm. (0.2 cm³/cm•day•MPa).

10 The seals of the present invention also have a tensile strain recovery of greater than 70 percent, preferably greater than 80 percent, more preferably greater than 85 percent usually as high as 95 percent.

 The seals of the present invention also have a stress relaxation of greater than 50 percent, preferably greater than 55 percent, more preferably greater than 60
15 percent and usually as high as 85 percent.

 The seals of the present invention also have a Shore A hardness which can be less than 99, preferably lower than 90, more preferably lower than 65 and usually as low as 60.

20 EXAMPLES

 The molecular weight of the polymer compositions for use in the present invention was indicated using a melt index measurement according to ASTM D-1238, Condition 190°C/2.16 kg (formally known as "Condition (E)" and also known as I₂) was determined. Melt index is inversely proportional to the molecular
25 weight of the polymer. Thus, the higher the molecular weight, the lower the melt index, although the relationship is not linear.

 Interpolymer styrene content and atactic polystyrene concentration were determined using proton nuclear magnetic resonance (¹H N.M.R). All proton NMR samples were prepared in 1, 1, 2, 2-tetrachloroethane-d₂ (TCE-d₂). The resulting
30 solutions were 1.6 - 3.2 percent polymer by weight. Melt index (I₂) was used as a

guide for determining sample concentration. Thus when the I_2 was greater than 2, 40 mg of polymer was used; with an I_2 between 1.5 and 2, 30 mg of polymer was used; and when the I_2 was less than 1.5 g/10 minutes, 20 mg of polymer was used. The polymers were weighed directly into 5 mm sample tubes. A 0.75 mL aliquot of TCE- d_2 was added by syringe and the tube was capped with a tight-fitting polyethylene cap. The samples were heated in a water bath at 85°C to soften the polymer. To provide mixing, the capped samples were occasionally brought to reflux using a heat gun.

Proton NMR spectra were accumulated on a Varian VXR 300 with the sample probe at 80°C, and referenced to the residual protons of TCE- d_2 at 5.99 ppm. The delay times were varied between 1 second, and data was collected in triplicate on each sample. The total analysis time per sample was about 10 minutes wherein the following instrumental conditions were employed:

Varian VXR-300, standard 1H :

Sweep Width, 5000 Hz
Acquisition Time, 3.002 sec
Pulse Width, 8 μ sec
Frequency, 300 MHz
Delay, 1 sec
Transients, 16

Initially, a 1H NMR spectrum for a sample of the polystyrene, STYRONTM 680 (available from the Dow Chemical Company, Midland, MI) was acquired with a delay time of one second. The protons were "labeled": b, branch; a, alpha; o, ortho; m, meta; p, para, as shown in Figure 1.

Integrals were measured around the protons labeled in Figure 1; the 'A' designates aPS. Integral $A_{7.1}$ (aromatic, around 7.1 ppm) is believed to be the three ortho/para protons; and integral $A_{6.6}$ (aromatic, around 6.6 ppm) the two meta protons. The two aliphatic protons labeled a resonate at 1.5 ppm; and the single proton labeled b is at 1.9 ppm. The aliphatic region was integrated from about 0.8 to 2.5 ppm and is referred to as A_{al} . The theoretical ratio for $A_{7.1}$: $A_{6.6}$: A_{al} is 3: 2: 3,

or 1.5: 1: 1.5, and correlated very well with the observed ratios for the STYRON™ 680 sample for several delay times of 1 second. The ratio calculations used to check the integration and verify peak assignments were performed by dividing the appropriate integral by the integral $A_{6.6}$. Ratio A_r is $A_{7.1} / A_{6.6}$.

5 Region $A_{6.6}$ was assigned the value of 1. Ratio A_1 is integral $A_{a1} / A_{6.6}$. All spectra collected have the expected 1.5: 1: 1.5 integration ratio of ($\sigma+p$): m : ($\alpha+b$). The ratio of aromatic to aliphatic protons is 5 to 3. An aliphatic ratio of 2 to 1 is predicted based on the protons labeled a and b respectively in Figure 1. This ratio was also observed when the two aliphatic peaks were integrated separately.

10 For the ethylene/styrene interpolymers, the ^1H NMR spectra using a delay time of one second, had integrals $C_{7.1}$, $C_{6.6}$, and C_{a1} defined, such that the integration of the peak at 7.1 ppm included all the aromatic protons of the copolymer as well as the o & p protons of aPS. Likewise, integration of the aliphatic region C_{a1} in the spectrum of the interpolymers included aliphatic protons from
 15 both the aPS and the interpolymers with no clear baseline resolved signal from either polymer. The integral of the peak at 6.6 ppm $C_{6.6}$ is resolved from the other aromatic signals and it is believed to be due solely to the aPS homopolymer (probably the *meta* protons). (The peak assignment for atactic polystyrene at 6.6 ppm (integral $A_{6.6}$) was made based upon comparison to the authentic sample
 20 STYRON™ 680.) This is a reasonable assumption since, at very low levels of atactic polystyrene, only a very weak signal is observed here. Therefore, the phenyl protons of the copolymer must not contribute to this signal. With this assumption, integral $A_{6.6}$ becomes the basis for quantitatively determining the aPS content.

25 The following equations were then used to determine the degree of styrene incorporation in the ethylene/styrene interpolymers samples:

$$(C \text{ Phenyl}) = C_{7.1} + A_{7.1} - (1.5 \times A_{6.6})$$

$$(C \text{ Aliphatic}) = C_{a1} - (1.5 \times A_{6.6})$$

$$s_c = (C \text{ Phenyl}) / 5$$

$$e_c = (C \text{ Aliphatic} - (3 \times s_c)) / 4$$

30 $E = e_c / (e_c + s_c)$

$$S_c = s_c / (e_c + s_c)$$

and the following equations were used to calculate the mol percent ethylene and styrene in the interpolymers.

$$\text{Wt\%E} = \frac{E * 28}{(E * 28) + (S_c * 104)} (100)$$

5

and

$$\text{Wt\%S} = \frac{S_c * 104}{(E * 28) + (S_c * 104)} (100)$$

where s_c and e_c are styrene and ethylene proton fractions in the interpolymer, respectively, and S_c and E are mole fractions of styrene monomer and ethylene monomer in the interpolymer, respectively.

10

The weight percent of aPS in the interpolymers was then determined by the following equation:

$$\text{Wt\%aPS} = \frac{(\text{Wt\%S}) * \left(\frac{A_{6.6/2}}{s_c} \right)}{100 + \left[(\text{Wt\%S}) * \left(\frac{A_{6.6/2}}{s_c} \right) \right]} * 100$$

15

The total styrene content was also determined by quantitative Fourier Transform Infrared spectroscopy (FTIR).

Example 1

A 130 mL continuous loop reactor, consisting of two static mixers, a gear pump (1000 mL/min), inlets for liquids and gasses, a viscometer and a pair of thermocouples, was used to prepare inventive Example 1. The reactor temperature was maintained by external heating tapes. Pressure was monitored at the liquid inlet and controlled via a variable valve on the outlet. The reactor was fed with a mixture of 100 percent styrene at 12.10 mL/min, ethylene at 0.501 g/min, hydrogen

20

at 0.207 mg/min and a catalyst system composed of 0.001 M toluene solutions of tert-butylamidodimethyl (tetramethylcyclopentadienyl) silane titanium dimethyl and tris-(pentafluorophenyl) borane both at 0.20 mL/min. The reactor temperature was held at 51.3 °C and the viscosity was allowed to stabilize to approximately 9 centipoise (cP) (0.009 Pa·s). The resulting polymer solution was blended with 0.05 mL/min of a catalyst deactivator/polymer stabilizer solution (1 L of toluene, 20 g of Irganox™ 1010 and 15 mL of 2-propanol), cooled to ambient temperature and collected for 15 hours and 26 minutes. The solution was dried in a vacuum oven overnight, resulting in 1223g of a 42.1 mole percent styrene ethylene/styrene copolymer with 7.4 weight percent atactic polystyrene and having a melt index (I₂) of 0.046 g/10 min.

Examples 2 -5.

The interpolymers were prepared in a 400 gallon agitated semi-continuous batch reactor. The reaction mixture consisted of approximately 250 gallons a solvent comprising a mixture of cyclohexane (85 wt percent) and isopentane (15 wt percent), and styrene. Prior to addition, solvent, styrene and ethylene were purified to remove water and oxygen. The inhibitor in the styrene was also removed. Inerts were removed by purging the vessel with ethylene. The vessel was then pressure controlled to a set point with ethylene. Hydrogen was added to control molecular weight. The temperature in the vessel was controlled to set-point by varying the jacket water temperature on the vessel.

Prior to polymerization, the vessel was heated to the desired run temperature and the catalyst components Titanium: (N-1,1-dimethylethyl) dimethyl(1-(1,2,3,4,5-eta)-2,3,4,5-tetramethyl- 2,4-cyclopentadien-1-yl) silanaminato))(2-)N)-dimethyl, CAS# 135072-62-7; Tris (pentafluorophenyl) boron, CAS# 001109-15-5; and Modified methylaluminoxane Type 3A, CAS# 146905-79-5 were flow controlled, on a mole ratio basis of 1/3/5 respectively, combined and added to the vessel. After starting, the polymerization was allowed to proceed with ethylene supplied to the reactor as required to maintain vessel pressure. In some cases, hydrogen was added to the headspace of the reactor to maintain a mole ratio with respect to the ethylene concentration. At the end of the run, the catalyst flow was stopped, ethylene was removed from the reactor, 1000 ppm (target amount) of Irganox™ 1010 antioxidant was then added to the solution and the polymer was isolated from the solution. The resulting polymers were isolated from solution by either stripping with steam in a vessel or by use of a devolatilizing extruder. In the case of the steam stripped material, additional processing was required in extruder like equipment to reduce residual moisture and any unreacted styrene.

Comparative Experiment 1 was a substantially random ethylene styrene interpolymers prepared substantially as for Example 2 using the preparation conditions in Table 1 and having the properties summarized in Table 2.

Comparative Experiment 2 was a substantially random ethylene styrene interpolymers prepared substantially as for Example 2 using the preparation conditions in Table 1 and having the properties summarized in Table 2.

Comparative Experiment 3 was an ethylene/1-octene copolymer having a density of 0.87 g/cm³ and a melt index (I₂) of 1.00 g/10 min available from DuPont Dow Elastomers under the trade name ENGAGE™ EG8100.

Comparative Experiment 4 was a hydrogenated SEBS styrene block copolymer available from Shell Chemical under the trade name KRATON™ G.

Comparative Experiment 5 was an oriented polystyrene film available from the Dow Chemical Company under the trade name TRICITE™.

Table 1

Example	Solvent loaded		Styrene loaded		Pressure		Temp.	Total H ₂ Added	Run Time
	lbs	kg	lbs	kg	Psig	kPa	°C	grams	Hours
Ex 2	839	381	659	299	70	483	60	22	5.2
Ex 3	252	114	1320	599	42	290	60	0	2.8
Ex 4	839	381	659	299	70	483	60	35	5.6
Ex 5	252	114	1320	599	40	276	60	23	6.5
Comp Ex 1	1196	542	225	102	70	483	60	7.5	6.1
Comp Ex 2	839	381	661	300	105	724	60	53.1	4.8

Table 2

Example	I ₂ g/10 min.	Mol percent Styrene in Interpolymer	Talc Level Weight Percent	Isolation Method
Example 2	0.87	30.3	0	Steam. Stripping.
Example 3	0.18	43.6	<2.5	Steam. Stripping.
Example 4	0.49	28.8	0	Steam. Stripping.
Example 5	1.8	41.8	<2.0	Steam. Stripping.
Comp Ex 1	0.03	9.2	0	Extruder
Comp Ex 2	2.6	17.1	0	Extruder

Examples 6 - 8

Examples 6 - 8 are substantially random ethylene/styrene interpolymers
 5 which were prepared using the following catalyst and polymerization procedures.

Catalyst A, (dimethyl[N-(1,1-dimethylethyl)-1,1-dimethyl-1-[(1,2,3,4,5-h)-
 1,5,6,7-tetrahydro-3-phenyl-s-indacen-1-yl]silanaminato(2-)-N]-titanium), was
 prepared as follows. First, 3,5,6,7-Tetrahydro-s-Hydrindacen-1(2H)-one was
 prepared as follows. Indan (94.00 g, 0.7954 moles) and 3-chloropropionyl chloride
 10 (100.99 g, 0.7954 moles) were stirred in CH₂Cl₂ (300 mL) at 0°C as AlCl₃ (130.00 g,
 0.9750 moles) was added slowly under a nitrogen flow. The mixture was then
 allowed to stir at room temperature for 2 hours. The volatiles were then removed.
 The mixture was then cooled to 0°C and concentrated H₂SO₄ (500 mL) slowly
 added. The forming solid had to be frequently broken up with a spatula as stirring
 15 was lost early in this step. The mixture was then left under nitrogen overnight at
 room temperature. The mixture was then heated until the temperature readings
 reached 90°C. These conditions were maintained for a 2 hour period of time during
 which a spatula was periodically used to stir the mixture. After the reaction period
 crushed ice was placed in the mixture and moved around. The mixture was then
 20 transferred to a beaker and washed intermittently with H₂O and diethylether and
 then the fractions filtered and combined. The mixture was washed with H₂O (2 x
 200 mL). The organic layer was then separated and the volatiles removed. The

desired product was then isolated via recrystallization from hexane at 0°C as pale yellow crystals (22.36 g, 16.3 percent yield).

¹H NMR (CDCl₃) provided: δ2.04-2.19 (m, 2 H), 2.65 (t, ³J_{HH}=5.7 Hz, 2 H), 2.84-3.0 (m, 4 H), 3.03 (t, ³J_{HH}=5.5 Hz, 2 H), 7.26 (s, 1 H), 7.53 (s, 1 H).

5 ¹³C NMR (CDCl₃) provided: δ25.71, 26.01, 32.19, 33.24, 36.93, 118.90, 122.16, 135.88, 144.06, 152.89, 154.36, 206.50.

GC-MS: Calculated for C₁₂H₁₂O 172.09, found 172.05.

1,2,3,5-Tetrahydro-7-phenyl-s-indacen was prepared as follows. 3,5,6,7-Tetrahydro-s-Hydrindacen-1(2H)-one (12.00 g, 0.06967 moles) was stirred in
10 diethylether (200 mL) at 0°C as PhMgBr (0.105 moles, 35.00 mL of 3.0 M solution in diethylether) was added slowly. This mixture was then allowed to stir overnight at room temperature. After the reaction period, the mixture was quenched by pouring the mixture over ice. The mixture was then acidified (pH=1) with HCl and stirred vigorously for 2 hours. The organic layer was then separated and washed
15 with H₂O (2 x 100 mL) and then dried over MgSO₄. Filtration followed by the removal of the volatiles resulted in the isolation of the desired product as a dark oil (14.68 g, 90.3 percent yield).

¹H NMR (CDCl₃) provided: δ2.0-2.2 (m, 2 H), 2.8-3.1 (m, 4 H), 6.54 (s, 1H), 7.2-7.6 (m, 7 H).

20 GC-MS: Calculated for C₁₈H₁₆ 232.13, found 232.05.

1,2,3,5-Tetrahydro-7-phenyl-s-indacene dilithium salt was prepared as follows. 1,2,3,5-Tetrahydro-7-phenyl-s-indacen (14.68 g, 0.06291 moles) was stirred in hexane (150 mL) as nBuLi (0.080 moles, 40.00 mL of 2.0 M solution in cyclohexane) was slowly added. This mixture was then allowed to stir overnight.
25 After the reaction period, the solid was collected via suction filtration as a yellow solid which was washed with hexane, dried under vacuum, and used without further purification or analysis (12.2075 g, 81.1 percent yield).

Another catalyst component, Chlorodimethyl(1,5,6,7-tetrahydro-3-phenyl-s-indacen-1-yl)silane, was prepared as follows. 1,2,3,5-Tetrahydro-7-phenyl-s-

indacene, dilithium salt (12.2075 g, 0.05102 moles) in THF (50 mL) was added dropwise to a solution of Me_2SiCl_2 (19.5010 g, 0.1511 moles) in THF (100 mL) at 0°C . This mixture was then allowed to stir at room temperature overnight. After the reaction period, the volatiles were removed and the residue extracted and filtered using hexane. The removal of the hexane resulted in the isolation of the desired product as a yellow oil (15.1492 g, 91.1 percent yield).

^1H NMR (CDCl_3) provided: δ 0.33 (s, 3 H), 0.38 (s, 3 H), 2.20 (p, $^3\text{J}_{\text{HH}}=7.5$ Hz, 2 H), 2.9-3.1 (m, 4 H), 3.84 (s, 1 H), 6.69 (d, $^3\text{J}_{\text{HH}}=2.8$ Hz, 1 H), 7.3-7.6 (m, 7 H), 7.68 (d, $^3\text{J}_{\text{HH}}=7.4$ Hz, 2 H).

^{13}C NMR (CDCl_3) provided: δ 0.24, 0.38, 26.28, 33.05, 33.18, 46.13, 116.42, 119.71, 127.51, 128.33, 128.64, 129.56, 136.51, 141.31, 141.86, 142.17, 142.41, 144.62.

GC-MS: Calculated for $\text{C}_{20}\text{H}_{21}\text{ClSi}$ 324.11, found 324.05.

N-(1,1-Dimethylethyl)-1,1-dimethyl-1-(1,5,6,7-tetrahydro-3-phenyl-s-indacen-1-yl)silanamine was prepared as follows. Chlorodimethyl(1,5,6,7-tetrahydro-3-phenyl-s-indacen-1-yl)silane (10.8277 g, 0.03322 moles) was stirred in hexane (150 mL) as NEt_3 (3.5123 g, 0.03471 moles) and *t*-butylamine (2.6074 g, 0.03565 moles) were added. This mixture was allowed to stir for 24 hours. After the reaction period, the mixture was filtered and the volatiles removed resulting in the isolation of the desired product as a thick red-yellow oil (10.6551 g, 88.7 percent yield).

^1H NMR (CDCl_3) provided: δ 0.02 (s, 3 H), 0.04 (s, 3 H), 1.27 (s, 9 H), 2.16 (p, $^3\text{J}_{\text{HH}}=7.2$ Hz, 2 H), 2.9-3.0 (m, 4 H), 3.68 (s, 1 H), 6.69 (s, 1 H), 7.3-7.5 (m, 4 H), 7.63 (d, $^3\text{J}_{\text{HH}}=7.4$ Hz, 2 H).

^{13}C NMR (CDCl_3) provided: δ -0.32, -0.09, 26.28, 33.39, 34.11, 46.46, 47.54, 49.81, 115.80, 119.30, 126.92, 127.89, 128.46, 132.99, 137.30, 140.20, 140.81, 141.64, 142.08, 144.83.

N-(1,1-Dimethylethyl)-1,1-dimethyl-1-(1,5,6,7-tetrahydro-3-phenyl-s-indacen-1-yl)silanamine dilithium salt was prepared as follows. N-(1,1-Dimethylethyl)-1,1-dimethyl-1-(1,5,6,7-tetrahydro-3-phenyl-s-indacen-1-

yl)silanamine (10.6551 g, 0.02947 moles) was stirred in hexane (100 mL) as nBuLi (0.070 moles, 35.00 mL of 2.0 M solution in cyclohexane) was added slowly. This mixture was then allowed to stir overnight during which time no salts precipitated out of the dark red solution. After the reaction period, the volatiles were removed and the residue quickly washed with hexane (2 x 50 mL). The dark red residue was then pumped dry and used without further purification or analysis (9.6517 g, 87.7 percent yield).

Dichloro[N-(1,1-dimethylethyl)-1,1-dimethyl-1-[(1,2,3,4,5-h)-1,5,6,7-tetrahydro-3-phenyl-s-indacen-1-yl]silanaminato(2-)-N]titanium was prepared as follow. N-(1,1-Dimethylethyl)-1,1-dimethyl-1-(1,5,6,7-tetrahydro-3-phenyl-s-indacen-1-yl)silanamine, dilithium salt (4.5355 g, 0.01214 moles) in THF (50 mL) was added dropwise to a slurry of $\text{TiCl}_3(\text{THF})_3$ (4.5005 g, 0.01214 moles) in THF (100 mL). This mixture was allowed to stir for 2 hours. PbCl_2 (1.7136 g, 0.006162 moles) was then added and the mixture allowed to stir for an additional hour. After the reaction period, the volatiles were removed and the residue extracted and filtered using toluene. Removal of the toluene resulted in the isolation of a dark residue. This residue was then slurried in hexane and cooled to 0°C. The desired product was then isolated via filtration as a red-brown crystalline solid (2.5280 g, 43.5 percent yield).

^1H NMR (CDCl_3) provided: δ 0.71 (s, 3 H), 0.97 (s, 3 H), 1.37 (s, 9 H), 2.0-2.2 (m, 2 H), 2.9-3.2 (m, 4 H), 6.62 (s, 1 H), 7.35-7.45 (m, 1 H), 7.50 (t, $^3J_{\text{HH}}=7.8$ Hz, 2 H), 7.57 (s, 1 H), 7.70 (d, $^3J_{\text{HH}}=7.1$ Hz, 2 H), 7.78 (s, 1 H).

^1H NMR (C_6D_6) provided: δ 0.44 (s, 3 H), 0.68 (s, 3 H), 1.35 (s, 9 H), 1.6-1.9 (m, 2 H), 2.5-3.9 (m, 4 H), 6.65 (s, 1 H), 7.1-7.2 (m, 1 H), 7.24 (t, $^3J_{\text{HH}}=7.1$ Hz, 2 H), 7.61 (s, 1 H), 7.69 (s, 1 H), 7.77-7.8 (m, 2 H).

^{13}C NMR (CDCl_3) provided: δ 1.29, 3.89, 26.47, 32.62, 32.84, 32.92, 63.16, 98.25, 118.70, 121.75, 125.62, 128.46, 128.55, 128.79, 129.01, 134.11, 134.53, 136.04, 146.15, 148.93.

¹³C NMR (C₆D₆) provided: δ 0.90, 3.57, 26.46, 32.56, 32.78, 62.88, 98.14, 119.19, 121.97, 125.84, 127.15, 128.83, 129.03, 129.55, 134.57, 135.04, 136.41, 136.51, 147.24, 148.96.

Dimethyl[N-(1,1-dimethylethyl)-1,1-dimethyl-1-[(1,2,3,4,5-h)-1,5,6,7-tetrahydro-3-phenyl-s-indacen-1-yl]silanaminato(2-)-N]titanium was prepared as follows. Dichloro[N-(1,1-dimethylethyl)-1,1-dimethyl-1-[(1,2,3,4,5-h)-1,5,6,7-tetrahydro-3-phenyl-s-indacen-1-yl]silanaminato(2-)-N]titanium (0.4970 g, 0.001039 moles) was stirred in diethylether (50 mL) as MeMgBr (0.0021 moles, 0.70 mL of 3.0 M solution in diethylether) was added slowly. This mixture was then stirred for 1 hour. After the reaction period, the volatiles were removed and the residue extracted and filtered using hexane. Removal of the hexane resulted in the isolation of the desired product as a golden yellow solid (0.4546 g, 66.7 percent yield).

¹H NMR (C₆D₆) provided: δ 0.071 (s, 3 H), 0.49 (s, 3 H), 0.70 (s, 3 H), 0.73 (s, 3 H), 1.49 (s, 9 H), 1.7-1.8 (m, 2 H), 2.5-2.8 (m, 4 H), 6.41 (s, 1 H), 7.29 (t, ³J_{HH}=7.4 Hz, 2 H), 7.48 (s, 1 H), 7.72 (d, ³J_{HH}=7.4 Hz, 2 H), 7.92 (s, 1 H).

¹³C NMR (C₆D₆) provided: δ 2.19, 4.61, 27.12, 32.86, 33.00, 34.73, 58.68, 58.82, 118.62, 121.98, 124.26, 127.32, 128.63, 128.98, 131.23, 134.39, 136.38, 143.19, 144.85.

Examples 6 - 8 were prepared in a 6 gallon (22.7 L), oil jacketed, autoclave continuously stirred tank reactor (CSTR). A magnetically coupled agitator with Lightning A-320 impellers provided the mixing. The reactor ran liquid full at 475 psig (3,275 kPa). Process flow was in at the bottom and out of the top. A heat transfer oil was circulated through the jacket of the reactor to remove some of the heat of reaction. At the exit of the reactor was a micromotion flow meter that measured flow and solution density. All lines on the exit of the reactor were traced with 50 psi (344.7 kPa) steam and insulated.

Toluene solvent was supplied to the reactor at 30 psig (207 kPa). The feed to the reactor was measured by a Micro-Motion mass flow meter. A variable speed diaphragm pump controlled the feed rate. At the discharge of the solvent pump, a

side stream was taken to provide flush flows for the catalyst injection line (1 lb/hr (0.45 kg/hr)) and the reactor agitator (0.75 lb/hr (0.34 kg/hr)). These flows were measured by differential pressure flow meters and controlled by manual adjustment of micro-flow needle valves. Uninhibited styrene monomer was

5 supplied to the reactor at 30 psig (207 kPa). The feed to the reactor was measured by a Micro-Motion mass flow meter. A variable speed diaphragm pump controlled the feed rate. The styrene stream was mixed with the remaining solvent stream. Ethylene was supplied to the reactor at 600 psig (4,137 kPa). The ethylene stream was measured by a Micro-Motion mass flow meter just prior to the flow control

10 valve. A Brooks flow meter/controller was used to deliver hydrogen into the ethylene stream at the outlet of the ethylene control valve. The ethylene/hydrogen mixture combined with the solvent/styrene stream at ambient temperature. The temperature of the solvent/monomer as it entered the reactor was dropped to approximately 5 °C by an exchanger with approximately 5°C glycol on the jacket.

15 This stream entered the bottom of the reactor. The three component catalyst system and its solvent flush also entered the reactor at the bottom but through a different inlet than the monomer stream. Preparation of the catalyst components took place in an inert atmosphere glove box. The diluted components were put in nitrogen padded cylinders and charged to the catalyst run tanks in the process

20 area. From these run tanks, the catalyst was pressured up with piston pumps and the flow was measured with Micro-Motion mass flow meters. These streams combined with each other and the catalyst flush solvent just prior to entry through a single injection line into the reactor.

Polymerization was stopped with the addition of catalyst kill (water mixed with solvent) into the reactor product line after the micromotion flow meter

25 measuring the solution density. Other polymer additives can be added with the catalyst kill. A static mixer in the line provided dispersion of the catalyst kill and additives in the reactor effluent stream. This stream next entered post reactor heaters that provided additional energy for solvent removal flash. This flash

30 occurred as the effluent exited the post reactor heater and the pressure was

dropped from 475 psig (3,275 kPa) down to approximately 250 mm of pressure absolute at the reactor pressure control valve. This flashed polymer entered a hot oil jacketed devolatilizer. Approximately 85 percent of the volatiles by weight were removed from the polymer in the devolatilizer. The volatiles exited the top of the devolatilizer. The stream was condensed with a glycol jacketed exchanger and entered the suction of a vacuum pump and was discharged to a glycol jacket solvent and styrene/ethylene separation vessel. Solvent and styrene were removed from the bottom of the vessel and ethylene from the top. The ethylene stream was measured with a Micro-Motion mass flow meter and analyzed for composition. The measurement of vented ethylene plus a calculation of the dissolved gasses in the solvent/styrene stream were used to calculate the ethylene conversion. The polymer separated in the devolatilizer was pumped out with a gear pump to a ZSK-30 twin-screw devolatilizing vacuum extruder. The dry polymer exited the extruder as a single strand. This strand was cooled as it was pulled through a water bath. The excess water was blown from the strand with air and the strand was chopped into pellets with a strand chopper.

The various catalysts, co-catalysts and process conditions used to prepare the various individual ethylene styrene interpolymers of Examples 6 - 8 are summarized in Table 3.

Table 3

Example	Ex 6	Ex 7	Ex 8
Reactor Temp, °C	83.2	81.4	79.8
Solvent Flow, lb/hr (kg/hr)	37.0 (16.8)	37.0 (16.8)	41.0 (18.6)
Ethylene Flow, lb/hr (kg/hr)	1.9 (0.9)	1.9 (0.9)	2.2 (1.0)
Hydrogen Flow, lb/hr (kg/hr)	1.3 (0.6)	10 (4.5)	20 (9.1)
Styrene Flow, lb/hr (kg/hr)	7.1 (3.2)	7.0 (3.2)	21.0 (9.5)
Percent C ₂ H ₄ Conversion	97.0	96.4	97.4
Co-Catalyst	FAB ^b	FAB ^b	FAB ^b
B/Ti Ratio	3.5	3.5	3.5
MMAO ^c /Ti Ratio	3.5	3.5	6.0

a The catalyst was dimethyl[N-(1,1-dimethylethyl)-1,1-dimethyl-1-[(1,2,3,4,5-h)-1,5,6,7-tetrahydro-3-phenyl-s-indacen-1-yl]silanaminato(2-)-N]-titanium.

b FAB is tris(pentafluorophenyl)borane.

c a modified methylaluminoxane commercially available from Akzo Nobel as MMAO-3A.

For oxygen permeability measurements, samples were melted at 190°C for 3 minutes and compression molded at 190°C under 20,000 lb (9072 kg) of pressure for another 2 minutes. Subsequently, the molten materials were quenched in a press equilibrated at room temperature.

- 5 The oxygen permeability of the resulting films was measured in accordance with ASTM D 3985-95 using moist test gases at 25°C on an OXTRAN 2/20 system. Oxygen concentration was 21 percent. Data was corrected to 100 percent oxygen concentration. These data are summarized in Table 4. The results demonstrated that the lowest oxygen permeability values occur at intermediate styrene contents
- 10 in the interpolymers as opposed to either low or high styrene contents.

Table 4

Example	Styrene (mol percent)	O ₂ Transmission (cc. mil/100 in ² .day.atm O ₂) (cm ³ /cm ² ·day·MPa)
Example 1	42.1	125* (0.49)
Example 2	30.3	90.3 (0.35)
Example 3	43.6	72* (0.28)
Comp. Experiment 1	9.2	498 (1.93)
Comp. Experiment 2	17.1	520 (2.02)
Comp. Experiment 3	0	2412 (9.37)
Comp. Experiment 4	N/A	3340 (12.98)
Comp. Experiment 5	100	306 (1.19)

* average of 2 numbers.

- 15 The tensile strain recovery for the samples was determined as follows. The samples were prepared using ASTM 1708 and deformed in an Instron 1145 tensile machine at a strain rate of 100 percent/min. until rupture. After 24 hours, the distance between marked regions on the sample was determined and compared to

the distance between the same regions prior to deformation. This difference was expressed as a percent and taken as the tensile strain recovery. These data are summarized in Table 5.

Tensile stress relaxation was determined as follows. Uniaxial tensile stress relaxation was evaluated using an Instron 1145 tensile machine. Compression molded film (~ 20 mil (0.51 mm) thick) with a 10 mil (0.25 mm) gauge length was deformed to a strain level of 50 percent at a strain rate of 20 min^{-1} . The force required to maintain 50 percent elongation was monitored for 10 min. The magnitude of the stress relaxation was defined as S_r , the percentage = $(f_i - f_f / f_i) \times 100$ where f_i is the initial force and f_f is the final force. These data are summarized in Table 5.

Shore A hardness was measured at 23°C following ASTM-D240. These data are summarized in Table 5.

The results in Table 5 demonstrate that optimum values of tensile strain recovery and stress relaxation occur over a specific range of interpolymer styrene content (around 30 mol percent). These data also demonstrate that the Shore A hardness of the material also varied with interpolymer styrene content.

We claim:

1. A seal comprising a polymer composition having an oxygen transmission coefficient at a temperature of 25°C of less than 300 cm³•mil/100 in²•day•atm. (1.2 cm³/cm•day•MPa), wherein the polymer composition comprises:

A) at least one substantially random interpolymer comprising;

(1) from 24 to 65 mol percent of polymer units derived from;

(i) at least one vinylidene aromatic monomer, or

(ii) at least one hindered aliphatic or cycloaliphatic vinylidene monomer, or

(iii) a combination of at least one aromatic vinylidene monomer and at least one hindered aliphatic or cycloaliphatic vinylidene monomer, and

(2) from 35 to 76 mol percent of polymer units derived from at least one C₂₋₂₀ α-olefin; or

B) a blend comprising

(1) from 35 to 99 percent by weight (based on the combined weight of Components B1 and B2) of Component A; and

(2) from 1 to 65 percent by weight (based on the combined weight of Components B1 and B2) of at least one polymer other than that of Component A; and

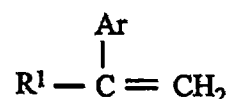
C) from 0 to 90 percent by weight (based on the combined weights of components A, B, and C) of at least one filler.

2. The seal of Claim 1 having an oxygen transmission coefficient at a temperature of 25°C of less than 200 cm³•mil/100 in²•day•atm. (0.8 cm³/cm•day•MPa), and a tensile strain recovery, for a sample strained at a strain



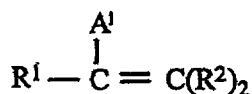
rate of 100 percent/minute, of greater than 70 percent, and wherein the polymer composition comprises:

- A) at least one substantially random interpolymer comprising
- 5 (1) from 27 to 46 mol percent of polymer units derived from
- (i) said vinylidene aromatic monomer represented by the following formula:



10 wherein R¹ is selected from the group of radicals consisting of hydrogen and alkyl radicals containing three carbons or less, and Ar is a phenyl group or a phenyl group substituted with from 1 to 5 substituents selected from the group consisting of halo, C₁₋₄-alkyl, and C₁₋₄-haloalkyl; or

- 15 (ii) said hindered aliphatic or cycloaliphatic vinylidene monomer is represented by the following general formula;



20 wherein A¹ is a sterically bulky, aliphatic or cycloaliphatic substituent of up to 20 carbons, R¹ is selected from the group of radicals consisting of hydrogen and alkyl radicals containing from 1 to 4 carbon atoms, preferably hydrogen or methyl; each R² is independently selected from the group of radicals consisting of hydrogen and alkyl radicals containing

25 from 1 to 4 carbon atoms, preferably hydrogen or methyl; or alternatively R¹ and A¹ together form a ring system; and

- (2) from 54 to 73 mol percent of polymer units derived from said α -olefin which comprises ethylene, or ethylene and at least one of propylene, 4-methyl-1-pentene, butene-1, hexene-1 or octene-1; or

5

B) said blend Component B, comprises

- (1) from 40 to 97 percent by weight (based on the combined weight of Components B1 and B2) of Component A; and
- (2) from 60 to 3 weight percent (based on the combined weights of Components B1 and B2) of said polymer other than that of Component A which comprises one or more of polystyrene, high impact polystyrene, polyvinyl chloride, copolymers of styrene and at least one of acrylonitrile, meth-acrylonitrile, maleic anhydride, or α -methyl styrene, homopolymers and copolymers of aliphatic C_2 - C_{20} α -olefins, copolymers of ethylene and vinyl acetate, chlorinated α -olefin polymers, styrene-butadiene (SB), styrene-isoprene(SI), styrene-butadiene-styrene (SBS), styrene-isoprene-styrene (SIS), styrene-ethylene/butene-styrene (SEBS) block copolymers; or substantially random α -olefin/vinylidene interpolymers having a content of polymer units derived from at least one vinylidene aromatic monomer, or at least one hindered aliphatic or cycloaliphatic vinylidene monomer, or a combination of at least one aromatic vinylidene monomer and at least one hindered aliphatic or cycloaliphatic vinylidene monomer of less than 24 mol percent; and

10

15

20

25

- C) said filler, Component C, is present in an amount from 0 to 80 percent by weight (based on the combined weights of components A, B, and C) and comprises talc, calcium carbonate, alumina trihydrate, carbon

30



black, glass fibers, clay, feldspar, silica or glass, fumed silica, alumina, magnesium oxide, magnesium hydroxide, antimony oxide, zinc oxide, barium sulfate, aluminum silicate, calcium silicate, titanium dioxide, glass microspheres, chalk and any combination thereof.

5

3. The seal of Claim 1 having an oxygen transmission coefficient at a temperature of 25°C of less than 150 cm³•mil/100 in²•day•atm. (0.6 cm³/cm•day•MPa), and a tensile strain recovery for a sample strained at a strain rate of 100 percent/minute of greater than 85 percent; and wherein said polymer composition comprises:

10

- A) at least one substantially random interpolymer comprising
- (1) from 29 to 37 mol percent of polymer units derived from;
- i) said vinylidene aromatic monomer which comprises
- 15 styrene, α -methyl styrene, ortho-, meta-, and para-methylstyrene, and the ring halogenated styrenes, or
- ii) said hindered aliphatic or cycloaliphatic vinylidene monomers which comprises 5-ethylidene-2-norbornene or 1-vinylcyclo-hexene, 3-vinylcyclohexene, and 4-
- 20 vinylcyclohexene;
- (2) from 63 to 71 mol percent of polymer units derived from said α -olefin, which comprises ethylene, or ethylene and at least one of propylene, 4-methyl-1-pentene, butene-1, hexene-1 or octene-1; or
- 25
- B) said blend Component B, comprises
- (1) from 40 to 95 percent by weight (based on the combined weight of Components B1 and B2) of Component A; and



(2) from 60 to 5 weight percent (based on the combined weights of Components B1 and B2) of said polymer other than that of Component A which comprises one or more of polystyrene, high impact polystyrene, polyvinyl chloride, homopolymers and copolymers of aliphatic C₂-C₂₀ α -olefins, copolymers of ethylene and vinyl acetate, styrene-butadiene (SB), styrene-isoprene(SI), styrene-butadiene-styrene (SBS), styrene-isoprene-styrene (SIS) block copolymers, or substantially random α -olefin/vinylidene interpolymers having a content of polymer units derived from at least one vinylidene aromatic monomer, or at least one hindered aliphatic or cycloaliphatic vinylidene monomer, or a combination of at least one aromatic vinylidene monomer and at least one hindered aliphatic or cycloaliphatic vinylidene monomer of less than 24 mol percent; and

C) said filler, Component C is present in an amount from 0 to 70 percent by weight (based on the combined weights of components A, B, and C) and comprises talc, calcium carbonate, alumina trihydrate, barium sulfate, titanium dioxide, or any combination thereof.

4. The seal of Claim 3 wherein said polymer composition comprises 100 weight percent of said substantially random interpolymers, and wherein Component A1 is styrene, and Component A2 is ethylene.

5. The seal of Claim 3 wherein said polymer composition comprises 100 percent of said substantially random interpolymers, and wherein Component A1 is styrene and Component A2 is an interpolymers of ethylene and at least one of propylene, 4-methyl-1-pentene, butene-1, hexene-1 or octene-1.



* C L N S *

6. The seal of Claim 1 wherein said substantially random interpolymer is crosslinked.

7. The seal of Claim 1 in the form of a gasket, a container closure liner,
5 or a barrier membrane.

8. A sealing system comprising the seal of Claim 1.

9. The sealing system of Claim 8 in the form of a container closure.

10

10. A plastic container closure comprising:

- (a) a plastic base wall; and
- (b) a sealing liner wherein said liner is extruded, cut and compression molded inside the interior of said base wall (a),
15 which liner comprises the seal of Claim 1.

11. A metal container closure comprising:

- (a) a metal base wall; and
- (b) a sealing liner wherein said liner is extruded, cut and
20 compression molded inside the interior of said base wall (a),
which liner comprises the seal of Claim 1.

20

12. The plastic container closure of Claim 10 wherein said sealing liner is
a foam.

25

13. The metal container closure of Claim 11 wherein said sealing liner is a
foam.

14. The plastic container closure of Claim 10 wherein said sealing liner is
30 extruded as a sheet and wherein circular discs are cut from said sheet thereby



providing preformed closures for subsequent adhesion or heat fixation to the interior of said basewall (a).

15. The metal container closure of Claim 11, wherein said sealing liner is
5 extruded as a sheet and wherein circular discs are cut from said sheet thereby providing preformed closures for subsequent adhesion or heat fixation to the interior of said basewall (a).

16. The plastic container closure of Claim 14, wherein said sealing liner is
10 a foam.

17. The metal container closure of Claim 15, wherein said sealing liner is a foam.

18. A bottle cap molded from thermoplastic resin, said bottle cap
15 comprising a sealing layer adapted to provide a sealing engagement when said bottle cap is applied to a bottle, said sealing layer comprising a polymer composition having an oxygen transmission coefficient at a temperature of 25°C of less than 200 cm³•mil/100 in²•day•atm. (0.8 cm³/cm•day•MPa) and a tensile strain
20 recovery, for a sample strained at a strain rate of 100 percent/minute, of greater than 70 percent, and wherein said polymer composition comprises:

- A) at least one substantially random interpolymer comprising
- (1) from 27 to 46 mol percent of polymer units derived from
- 25 (a) at least one vinylidene aromatic monomer, or
- (b) at least one hindered aliphatic or cycloaliphatic vinylidene monomer, or
- (c) a combination of at least one aromatic vinylidene monomer and at least one hindered aliphatic or
- 30 cycloaliphatic vinylidene monomer, and



- (2) from 54 to 73 mol percent of polymer units derived from at least one C_{2-20} α -olefin; or

B) a blend comprising

- (1) from 35 to 99 percent by weight (based on the combined weight of Components B1 and B2) of Component A; and
(2) from 1 to 65 percent by weight (based on the combined weight of Components B1 and B2) of at least one polymer other than that of Component A; and

- C) from 0 to 80 percent by weight based on the combined weights of components A, B, and C of at least one filler.

19. A bottle cap molded from metal, said bottle cap comprising a sealing layer adapted to provide a sealing engagement when said bottle cap is applied to a bottle, said sealing layer comprising a polymer composition having an oxygen transmission coefficient at a temperature of 25°C of less than 200 $cm^3 \cdot mil / 100 in^2 \cdot day \cdot atm.$ ($0.8 cm^3 / cm \cdot day \cdot MPa$) and a tensile strain recovery, for a sample strained at a strain rate of 100 percent/minute, of greater than 70 percent, and wherein said polymer composition comprises:

A) at least one substantially random interpolymers comprising

- (1) from 27 to 46 mol percent of polymer units derived from
(a) at least one vinylidene aromatic monomer, or
(b) at least one hindered aliphatic or cycloaliphatic vinylidene monomer, or
(c) a combination of at least one aromatic vinylidene monomer and at least one hindered aliphatic or cycloaliphatic vinylidene monomer, and
(2) from 54 to 73 mol percent of polymer units derived from at least one C_{2-20} α -olefin; or



- B) a blend comprising
- (1) from 35 to 99 percent by weight (based on the combined weight of Components B1 and B2) of Component A; and
- 5 (2) from 1 to 65 percent by weight (based on the combined weight of Components B1 and B2) of at least one polymer other than that of Component A; and
- C) from 0 to 80 percent by weight based on the combined weights of
- 10 Components A, B, and C of at least one filler.
20. The seal of Claim 1 in the form of a film.
21. The seal of Claim 1 in the form of a foam.
- 15 22. The seal of Claim 21, wherein said foam comprises a crosslinked substantially random interpolymer.
23. A multilayer film comprising at least two layers wherein at least one
- 20 of said layers comprises a polymer composition having an oxygen transmission coefficient at a temperature of 25°C of less than $300 \text{ cm}^3 \cdot \text{mil} / 100 \text{ in}^2 \cdot \text{day} \cdot \text{atm}$. ($1.2 \text{ cm}^3 / \text{cm} \cdot \text{day} \cdot \text{MPa}$) which polymer composition comprises:
- A) at least one substantially random interpolymer comprising
- 25 (1) from 24 to 65 mol percent of polymer units derived from
- (a) at least one vinylidene aromatic monomer, or
- (b) at least one hindered aliphatic or cycloaliphatic vinylidene monomer, or



- 5 (c) a combination of at least one aromatic vinylidene monomer and at least one hindered aliphatic or cycloaliphatic vinylidene monomer, and
- (2) from 35 to 76 mol percent of polymer units derived from at least one C₂₋₂₀ α -olefin; or
- 10 B) a blend comprising
- (1) from 35 to 99 percent by weight (based on the combined weight of Components B1 and B2) of Component A and
- 10 (2) from 1 to 65 percent by weight (based on the combined weight of Components B1 and B2) of at least one polymer other than that of Component A; and
- 15 C) from 0 to 80 percent by weight based on the combined weights of components A, B, and C of at least one filler;

and wherein at least one other layer comprises a polymer composition other than that of Component A or B.

- 20 24. The bottle cap of Claim 18 wherein said sealing layer comprises the multilayer film of Claim 23.
- 25 25. The bottle cap of Claim 19 wherein said sealing layer comprises the multilayer film of Claim 23.
26. A sealing system comprising the seal of Claim 6.
27. A sealing system comprising the seal of Claim 22.

