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(54) **SULFONATED SUBSTANTIALLY RANDOM INTERPOLYMER-BASED ABSORBENT MATERIALS**

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(57) **ABSTRACT**

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The present invention pertains to absorbent polymer composition comprising A) one or more sulfonated substantially random interpolymers comprising repeating units derived from; a) ethylene and/or one or more alpha olefins; b) one or more sulfonated vinyl or vinylidene aromatic monomers; c) one or more vinyl or vinylidene aromatic monomers, or a combination of one or more vinyl or vinylidene aromatic monomers and one or more sterically hindered aliphatic or cycloaliphatic vinyl or vinylidene monomers; and optionally, B) one or more polymers other than said sulfonated substantially random interpolymer. Uses of the compositions include the preparation of absorbent foams, fibers films and membranes for the preparation of absorbent articles for personal hygiene. These include diapers, sanitary napkins adult incontinence pads, and highly absorbent wipes, and dust pickups.

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Related U.S. Application Data

(60) Provisional application No. 60/221,846, filed on Jul. 28, 2000.

**SULFONATED SUBSTANTIALLY RANDOM
INTERPOLYMER-BASED ABSORBENT
MATERIALS**

**CROSS REFERENCED TO RELATED
APPLICATIONS**

[0001] This application is a 371 of PCT/US01/23511 filed Jul. 26, 2001, which claims priority to previously filed U.S. Provisional Patent Application Serial No. 60/221,846, filed Jul. 28, 2000, both of which are incorporated by reference herein in their entirety.

**FEDERALLY SPONSORED RESEARCH
STATEMENT**

[0002] Not applicable.

REFERENCE TO MICROFICHE APPENDIX

[0003] Not applicable.

FIELD OF THE INVENTION

[0004] This present invention describes absorbent compositions comprising sulfonated substantially random interpolymers. The sulfonated substantially random interpolymers can be used either alone or as blends with other polymers, and can be in either the sulfonic acid form, or as a neutralized or partially neutralized sulfonate salt. Another feature of the present invention is a process to prepare the sulfonated substantially random interpolymers, comprising the use of a hydrocarbon swelling agent, prior to or coincident with, exposure to the sulfonating agent. The sulfonated substantially random interpolymers or blends therefrom can be used to prepare structures such as pellets, film, ribbon, sheet, strand or fiber, or closed and open cell foams, and fabricated articles therefrom.

BACKGROUND OF THE INVENTION

[0005] The generic class of substantially random α -olefin/vinyl or vinylidene aromatic monomer interpolymers, and their preparation, are known in the art, such as described in EP 416 815 A2, the entire contents of which are herein incorporated by reference. These materials offer a wide range of material structures and properties, which makes them useful for varied applications.

[0006] The structure, thermal transitions and mechanical properties of substantially random interpolymers of ethylene and styrene containing up to 50 mole percent styrene have been described (see Y. W. Cheung, M. J. Guest; *Proc. Antec '96* pages 1634-1637). These polymers were found to have glass transitions in the range -20° C. to $+35^{\circ}$ C., and show crystallinity below 25 mole percent styrene incorporation, and no measurable crystallinity above 25 mole percent styrene incorporation, that is, they are essentially amorphous. This ability to tailor the properties of the substantially random interpolymers by varying the relative amount of alpha olefin and vinyl or vinylidene aromatic monomer content provides a great deal of flexibility in tailoring their properties for a particular end use application. For example, copending U.S. application Ser. No. 09/317,389 filed on May 24, 1999 and PCT Publication WO 99/64500 (the entire contents of both of which are herein incorporated by reference) describes the use of substantially random interpolymers in formable membranes. Also, copending U.S. appli-

cation Ser. No. 08/991,036 filed on Dec. 16 1997, and PCT Publication WO 99/31176 (the entire contents of both of which are herein incorporated by reference) describes the use of substantially random interpolymers in the form of barrier membranes for retarding gas migration.

[0007] Although of utility in their own right, Industry is constantly seeking to improve the applicability of these interpolymers. There are a number of applications where the ability to absorb or transport water or ions such as protons, would be highly advantageous if combined with the flexibility of being able to tailor the product properties of the substantially random interpolymers.

[0008] In order to facilitate water migration (for water absorbent applications) or proton transfer (for electrochemical applications), polystyrene and styrenic block copolymers are often sulfonated at the aromatic ring. U.S. Pat. Nos. 5,468,574 5,468,574 and 5,679,482 (the entire contents of both of which are incorporated herein by reference) disclose ion-conducting membranes prepared from polymers composed of sulfonated hydrogenated block copolymers of styrene and butadiene.

[0009] For certain applications, it would be preferable if the sulfonated aromatic rings be randomly dispersed throughout the polymer chains and, in order to precisely tailor the resulting product properties, that the sulfonation be done in a controlled fashion such that all degrees of sulfonation can be attained including surface sulfonation, bulk sulfonation or anything in between. In contrast, quite the opposite is desirable for ionomer applications. These require both low sulfonation conversion, (i.e. <approximately 10 percent approximately 10 percent) and localized sulfonation resulting in ionic domains called clusters, which propagate physical crosslinks at low levels.

[0010] This degree of control of the amount of sulfonation, the location (surface or bulk) and control over the dispersion cannot be accomplished using block or graft styrene copolymers. Such copolymers have the aromatic rings in discrete regions or domains within the polymer chains, or as in random styrenic copolymers, a random placement of the aromatic rings which is difficult to control. In high conversion sulfonation of polystyrene (or blocky styrenic copolymers), once a phenyl group is sulfonated, it acts as a polar director toward nearest neighbor phenyl group sulfonation. This results in blocky sulfonated segments early in sulfonation and can also result in higher melt viscosities, thus slowing the overall rate of sulfonation.

[0011] The majority of such sulfonated styrenic compositions to date have been prepared either in (a) a single phase system (uncrosslinked polymer in solution) or (b) a two phase system (crosslinked beads, fiber, etc). The most common solvents/swelling agents are the halogenated hydrocarbons such as methylene chloride, ethylene dichloride, and chlorobenzene.

[0012] PCT Publication WO 99/20691 (the entire contents of which are herein incorporated by reference) discloses surface sulfonated substantially random interpolymers and articles therefrom as in the form of sheet or film, and that films and sheets made from such polymers can be used to "improve the barrier properties of articles to gases". The sulfonation of any particular phenyl group in such substantially random interpolymers has minimal directing effect on the sulfonation of other phenyl group in the interpolymer.

[0013] For substantially random interpolymers, which are uncrosslinked, we have surprisingly found that simple C₃-C₂₀ aliphatic and cycloaliphatic hydrocarbons such as hexanes, heptane, octane, cyclohexane and the like, provide rapid swelling capability without dissolution over a wide range of swelling rates. This allows for the use of sulfonation processes, which have a wide variation in residence times and thus can be either batch or continuous processes. Thus by judicious choice of process residence time and/or swelling agent one can control the degree of sulfonation of the substantially random interpolymers in a polymer (or fabricated article therefrom) such that one can achieve everything from simple surface sulfonation to almost complete bulk sulfonation.

[0014] In addition, use of the materials and processes of the present invention allows for the preparation of absorbent articles that exhibit an improved balance of wicking and absorption kinetics. This is provided by variation of both the nature of the substantially random interpolymers-based starting material (crystalline or amorphous, ionomeric or not, and degree of gel domains) as well as control of the process conditions and degree of sulfonation. Thus both variables can then be optimized to yield improvements in polymer performance and economics.

[0015] In one preferred embodiment of the present invention, such processes are applied to the manufacture of absorbent fibers comprising the sulfonated substantially random interpolymers. Existing technology for the preparation of absorbent fibers typically involves dry spinning (where a solution of polymer is spun and the solvent is evaporated is more costly). In addition, existing technology is limited to simple process control for variation in wicking/absorbent performance and the polymer composition typically has limited variability. The use of the sulfonated substantially random interpolymers-based materials for absorbent and/or superabsorbent applications represents a simple, low cost process in comparison to existing technology.

[0016] Thus the absorbent fibers of the present invention can be initially formed comprising the substantially random polymers which fibers can then be subsequently sulfonated to the required degree. Alternatively the fibers can be directly fabricated from the sulfonated substantially random interpolymers.

[0017] Similarly in the preparation of fabricated articles from the absorbent materials of the present invention, it is possible to either prepare the fabricated article from one or more sulfonated substantially random interpolymers (or blend therefrom). It is also possible to prepare the fabricated article from one or more substantially random interpolymers (or blend therefrom) with subsequent sulfonation.

[0018] In an especially preferred embodiment, the use of the materials and processes of the present invention allows the design of bicomponent/biconstituent materials comprising the sulfonated substantially random interpolymers for performance and cost optimization.

SUMMARY OF THE INVENTION

[0019] The present invention pertains to an absorbent polymer composition comprising

[0020] A) one or more sulfonated substantially random interpolymers comprising repeating units derived from;

[0021] a) ethylene and/or one or more alpha olefins;

[0022] b) one or more sulfonated vinyl or vinylidene aromatic monomers;

[0023] c) one or more vinyl or vinylidene aromatic monomers, or a combination of one or more vinyl or vinylidene aromatic monomers and one or more sterically hindered aliphatic or cycloaliphatic vinyl or vinylidene monomers; and optionally

[0024] B) one or more polymers other than said sulfonated substantially random interpolymers.

[0025] Uses of the compositions include the preparation of absorbent foams, fibers films and membranes as well as the preparation of absorbent fabricated articles for personal hygiene. These include diapers, sanitary napkins, adult incontinence pads, and highly absorbent wipes, and dust pickups.

BRIEF DESCRIPTION OF THE DRAWINGS

[0026] Not applicable.

DETAILED DESCRIPTION OF THE INVENTION

[0027] 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.

[0028] 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.

[0029] 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.

[0030] The term "hydrocarbyloxy" means a hydrocarbyl group having an oxygen linkage between it and the carbon atom to which it is attached.

[0031] 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.

[0032] The term "absorbent polymer composition" is used herein to indicate a polymer or blend of polymers able to

take up at least 5, preferably at least 50, more preferably at least 100 percent of its own weight when placed in water.

[0033] The term “superabsorbent polymer” is used herein in the conventional sense in reference to polymeric materials that imbibe fluid and thereby form a swollen hydrogel. That is, a superabsorbent polymer is a hydrogel-forming polymeric gelling agent. In particular, the polymeric gelling agent comprises a substantially water-insoluble, partially neutralized, hydrogel-forming polymer material that is typically prepared from polymerizable, unsaturated, acid-containing monomers and often grafted onto other types of polymer moieties and then slightly crosslinked with agents such as, for example, triallyl amine. See, for example, U.S. Pat. No. 5,061,259 and U.S. Pat. No. 4,654,039, the disclosures of which are incorporated herein by reference, for additional description pertaining to superabsorbent polymers. Superabsorbent polymer is referenced herein by the acronym “SAP”.

[0034] The term “absorbent fabricated article” is used herein to indicate an article such as a foam, fiber, film, membrane, or any article prepared therefrom which in turn comprises the absorbent polymer compositions of the present invention. More specifically, the term refers to devices that are placed against or in proximity to the body of the wearer to absorb and contain the various exudates discharged from the body. These exudates include, but are not limited to urine, menses, vaginal discharge, sweat and feces. The devices include, but are not limited to absorbent articles for personal hygiene such as diapers, sanitary napkins and adult incontinence pads,

[0035] The term “substantially random” (in the substantially random interpolymer comprising polymer units derived from ethylene and one or more α -olefin monomers with one or more vinyl or vinylidene aromatic monomers and/or sterically hindered aliphatic or cycloaliphatic vinyl or 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 vinyl aromatic monomer in blocks of vinyl 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.

[0036] The term “degree of sulfonation” or “percent conversion” are used interchangeably and as used herein refer to the percentage of the aromatic content of the aromatic groups in the unsulfonated substantially random interpolymer which are converted to sulfonated aromatic groups on sulfonation (on a scale of 0 to 100). It is calculated from the percent weight gain of the interpolymer on sulfonation using the following formula:

$$\text{Conversion} = \frac{(\text{percent weight gain})(MW_{\text{vas}})}{(MW_{\text{S}} - MW_{\text{vas}})(VA_{\text{f}})} \text{ where;}$$

[0037] MW_{vas} = vinyl aromatic sulfonic acid or sulfonate salt molecular weight

[0038] MW_{va} = vinyl aromatic molecular weight

[0039] VA_{f} = weight fraction of vinyl aromatic in starting substantially random interpolymer.

[0040] Thus for a substantially random interpolymer of ethylene and styrene containing 75 wt percent styrene and converted into the sodium sulfonate derivative, the calculation becomes:

$$\% \text{ Conversion} = \frac{[(\% \text{ weight gain})(104)]}{(206 - 104)(0.75)} = \frac{(\% \text{ weight gain})(1.36) \times 100}{1}$$

[0041] The term “homofil” as used herein refers to fiber which has a single polymer region or domain and does not have any other distinct polymer regions (as do bicomponent fibers), even though the polymer itself may have a plurality of phases or microphases.

[0042] The term “meltblown” is used herein in the conventional sense to refer to fibers formed by extruding the molten elastic composition through a plurality of fine, usually circular, die capillaries as molten threads or filaments into converging high velocity gas streams (e.g. air) which function to attenuate the threads or filaments to reduced diameters. Thereafter, the filaments or threads are carried by the high velocity gas streams and deposited on a collecting surface to form a web of randomly dispersed fibers with average diameters generally smaller than 10 microns.

[0043] The term “spunbond” is used herein in the conventional sense to refer to fibers formed by extruding the molten elastic composition as filaments through a plurality of fine, usually circular, die capillaries of a spinneret with the diameter of the extruded filaments then being rapidly reduced and thereafter depositing the filaments onto a collecting surface to form a web of randomly dispersed spunbond fibers with average diameters generally between about 7 and about 30 microns.

[0044] The term “nonwoven” as used herein and in the conventional sense means a web or fabric having a structure of individual fibers or threads which are randomly interlaid, but not in an identifiable manner as is the case for a knitted fabric.

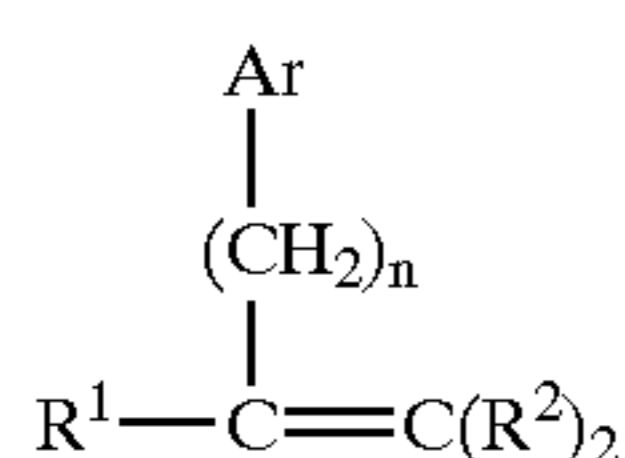
[0045] The term “conjugated” refers to fibers which have been formed from at least two polymers extruded from separate extruders but meltblown or spun together to form one fiber.

[0046] The Substantially Random Interpolymers

[0047] The interpolymers used in the present invention include the substantially random interpolymers, which are then sulfonated either prior to or after fabrication. The substantially random interpolymers are prepared by polymerizing i) ethylene and/or one or more α -olefin monomers and ii) one or more vinyl or vinylidene aromatic monomers and/or one or more sterically hindered aliphatic or cycloaliphatic vinyl or vinylidene monomers, and optionally iii) other polymerizable ethylenically unsaturated monomer(s). Suitable α -olefins include for example, α -olefins containing from 3 to about 20, preferably from 3 to about 12, more preferably from 3 to about 8 carbon atoms. Particularly suitable are ethylene, propylene, butene-1,4-methyl-1-pentene, hexene-1 or octene-1 or ethylene in combination with

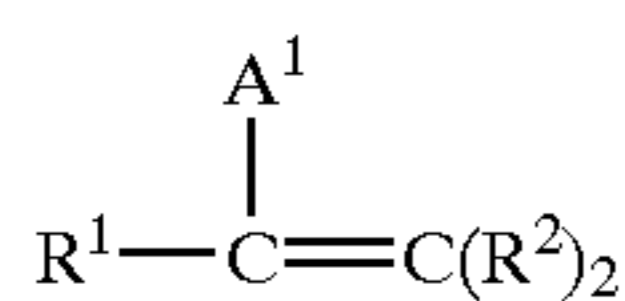
one or more of propylene, butene-1,4-methyl-1-pentene, hexene-1 or octene-1. These α -olefins do not contain an aromatic moiety.

[0048] Suitable vinyl or vinylidene aromatic monomers, which can be employed to prepare the interpolymers, include, for example, those represented by the following formula:



[0049] wherein R^1 is selected from the group of radicals consisting of hydrogen and alkyl radicals containing from 1 to about 4 carbon atoms, preferably hydrogen or methyl; each R^2 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; Ar is a phenyl group or a phenyl group substituted with from 1 to 5 substituents selected from the group consisting of halo, C_{1-4} -alkyl, and C_{1-4} -haloalkyl; and n has a value from zero to about 4, preferably from zero to 2, most preferably zero. Exemplary vinyl or vinylidene aromatic monomers include styrene, vinyl toluene, α -methylstyrene, t-butyl styrene, chlorostyrene, including all isomers of these compounds, and the like. Particularly suitable such monomers include styrene and lower alkyl- or halogen-substituted derivatives thereof. Preferred monomers include styrene, α -methyl styrene, the lower alkyl-(C_1 - C_4) 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, and the like. A more preferred aromatic vinyl monomer is styrene.

[0050] By the term "sterically hindered aliphatic or cycloaliphatic vinyl or vinylidene compounds", it is meant addition polymerizable vinyl or vinylidene monomers corresponding to the formula:



[0051] wherein A^1 is a sterically bulky, aliphatic or cycloaliphatic substituent of up to 20 carbons, R^1 is selected from the group of radicals consisting of hydrogen and alkyl radicals containing from 1 to about 4 carbon atoms, preferably hydrogen or methyl; each R^2 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 R^1 and A^1 together form a ring system. Preferred aliphatic or cycloaliphatic vinyl or 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, tert-butyl, norbornyl, and the like. Most preferred aliphatic or cycloaliphatic vinyl or 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 and 5-ethylidene-2-norbornene. Simple linear non-branched α -olefins including for example, α -olefins containing from 3 to about 20 carbon atoms such as propylene, butene-1,4-methyl-1-pentene, hexene-1 or octene-1 are not examples of sterically hindered aliphatic or cycloaliphatic vinyl or vinylidene compounds.

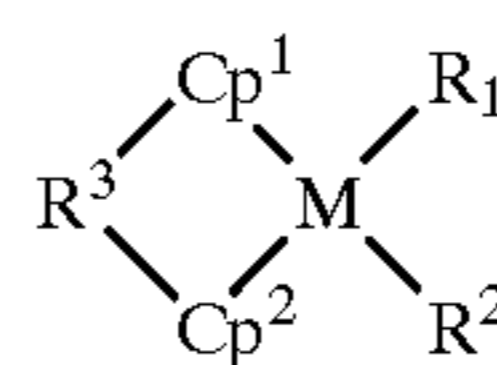
[0052] Other optional polymerizable ethylenically unsaturated monomer(s) include norbornene and C_{1-10} alkyl or C_{6-10} aryl substituted norbornenes, with an exemplary interpolymer being ethylene/styrene/norbornene.

[0053] The most preferred substantially random interpolymers are the ethylene/styrene, ethylene/propylene/styrene, ethylene/styrene/norbornene, and ethylene/propylene/styrene/norbornene interpolymers.

[0054] The substantially random interpolymers include the pseudo-random interpolymers as described in EP-A-0, 416,815 by James C. Stevens et al. and U.S. Pat. No. 5,703,187 by Francis J. Timmers, both of which are incorporated herein by reference in their entirety. The substantially random interpolymers can be prepared by polymerizing a mixture of polymerizable monomers in the presence of one or more metallocene or constrained geometry catalysts in combination with various cocatalysts. 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.

[0055] Examples of suitable catalysts and methods for preparing the substantially random interpolymers are disclosed in U.S. application Ser. No. 702,475, filed May 20, 1991 (EP-A-514,828); as well as U.S. Pat. Nos. 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; 5,399,635; 5,470,993; 5,703,187; and 5,721,185 all of which patents and applications are incorporated herein by reference.

[0056] The substantially random α -olefin/vinyl aromatic interpolymers can also be prepared by the methods described in JP 07/278230 employing compounds shown by the general formula



[0057] where Cp^1 and Cp^2 are cyclopentadienyl groups, indenyl groups, fluorenyl groups, or substituents of these, independently of each other; R^1 and R^2 are hydrogen atoms, halogen atoms, hydrocarbon groups with carbon numbers of 1-12, alkoxy groups, or aryloxy groups, independently of each other; M is a group IV metal, preferably Zr or Hf; most preferably Zr; and R^3 is an alkylene group or silanediyl group used to cross-link Cp^1 and Cp^2 .

[0058] The substantially random α -olefin/vinyl 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), all of which are incorporated herein by reference in their entirety.

[0059] 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 Ser. No. 08/708,869 filed Sep. 4, 1996 and WO 98/09999 both by Francis J. Timmers et al., the entire contents of both of which are herein incorporated by reference. These interpolymers contain additional signals in their carbon-13 NMR spectra 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.

[0060] Further preparative methods for the interpolymers used in 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 Polymer Science*, Volume 58, pages 1701-1706 [1995]) reported the use of a catalytic system based on methylalumoxane (MAO) and cyclopentadienyltitanium trichloride (CpTiCl_3) 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 $\text{MgCl}_2/\text{TiCl}_4/\text{NdCl}_3/\text{Al}(\text{iBu})_3$ 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 $\text{TiCl}_4/\text{NdCl}_3/\text{MgCl}_2/\text{Al}(\text{Et})_3$ catalyst. Sernetz and Mulhaupt, (*Macromol. Chem. Phys.*, v. 197, pp. 1071-1083, 1997) have described the influence of polymerization conditions on the copolymerization of styrene with ethylene using $\text{Me}_2\text{Si}(\text{Me}_4\text{Cp})(\text{N-tert-butyl})\text{TiCl}_2/\text{methylaluminoxane}$ Ziegler-Natta catalysts. Copolymers of ethylene and styrene produced by bridged metallocene catalysts have been described by Arai, Toshiaki and Suzuki (*Polymer Preprints, Am. Chem. Soc., Div. Polym. Chem.*) Volume 38, pages 349, 350 [1997]) and in U.S. Pat. No. 5,652,315, issued to Mitsui Toatsu Chemicals, Inc. The manufacture of α -olefin/vinyl aromatic monomer interpolymers such as propylene/styrene and butene/styrene are described in U.S. Pat. No. 5,244,996, issued to Mitsui Petrochemical Industries Ltd or U.S. Pat. No. 5,652,315 also issued to Mitsui Petrochemical Industries Ltd or as disclosed in DE 197 11 339 A1 and U.S. Pat. No. 5,883,213 to Denki Kagaku Kogyo KK. All the above methods disclosed for preparing the interpolymer component are incorporated herein by reference. Also, although of high isotacticity and therefore not "substantially random", the random copolymers of ethylene and styrene as disclosed in *Polymer Preprints*, Vol. 39, No. 1, March 1998 by Toru Aria et al. can also be employed as blend components for the foams of the present invention.

[0061] While preparing the substantially random interpolymer, an amount of atactic vinyl aromatic homopolymer may be formed due to homopolymerization of the vinyl aromatic monomer at elevated temperatures. The presence

of vinyl aromatic homopolymer is in general not detrimental for the purposes of the present invention and can be tolerated. The vinyl aromatic homopolymer may be separated from the interpolymer, if desired, by extraction techniques such as selective precipitation from solution with a non solvent for either the interpolymer or the vinyl aromatic homopolymer. For the purpose of the present invention it is preferred that no more than 30 weight percent, preferably less than 20 weight percent based on the total weight of the interpolymers of atactic vinyl aromatic homopolymer is present.

[0062] The Sulfonated Substantially Random Interpolymers

[0063] The substantially random interpolymers can be sulfonated by any suitable means known in the art for sulfonating aromatic ring compounds including using so called "wet" (sulfuric acid, oleum, chlorosulphonic acid, SO_3 complexes) or gaseous (air sulfonation, SO_3 vapor phase sulfonation) reagents.

[0064] A preferred method involves contacting the substantially random interpolymer with a fluid phase of sulfur trioxide, present as minor composition (less than 50 percent by weight) in another carrier gas such as nitrogen or air at a temperature of from about 20° C. to about 200° C., preferably from about 50° C. to about 150° C., more preferably from about 80° C. to about 150° C. Optionally, a C_1 - C_{20} , preferably C_1 - C_{10} , more preferably C_1 - C_6 hydrocarbon swelling agent (including but not exclusively ethane, propane, butane, pentane, hexane, and cyclohexane) can be incorporated with the carrier gas or, alternatively the interpolymer can be exposed to the swelling agent prior to sulfonation.

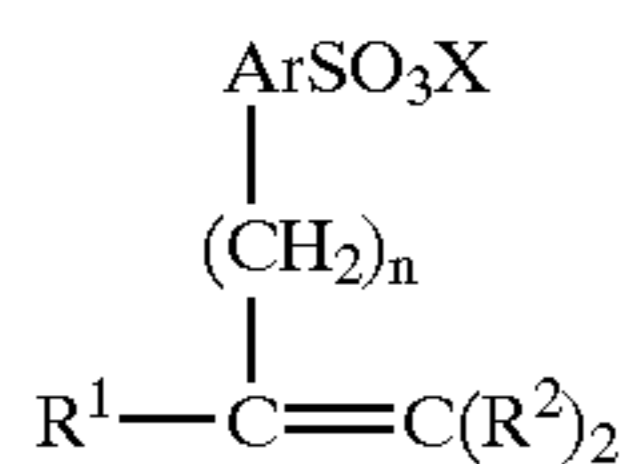
[0065] The substantially random interpolymer can also be sulfonated by contacting with a liquid phase of oleum (5-60 percent sulfur trioxide dissolved in sulfuric acid), at a temperature of from about -20° C. to about 100° C., preferably from about 0° C. to about 80° C., more preferably from about 0° C. to about 50° C. Optionally, the polymer can be exposed to a C_1 - C_{20} , preferably C_1 - C_{10} , more preferably C_1 - C_6 hydrocarbon swelling agent (including, but not exclusively, pentane, hexane, and cyclohexane) either prior to or concurrently with sulfonation.

[0066] Another suitable method is that described by Turbuk in U.S. Pat. No. 3,072,618 which is incorporated herein by reference in its entirety. The substantially random interpolymer is sulfonated by contacting with a sulfonating complex comprising the reaction product of about 2 to about 4 moles of sulfur trioxide and 1 mole of a lower trialkyl phosphate or phosphite at a temperature of from about 25° C. to about 100° C., preferably from about 50° C. to about 83° C., more preferably from about 75° C. to about 83° C. followed by recovering the resultant sulfonated polymer. Sulfur trioxide can also be supplied in the form of chlorosulfonic acid or fuming sulfuric acid. Particularly suitable trialkyl phosphates include trimethyl phosphate, triethyl phosphate, tripropyl phosphate, tributyl phosphate, trimethyl phosphite, triethyl phosphite, tripropyl phosphite, tributyl phosphate, hydrogen phosphate, diethyl hydrogen phosphate, dimethyl hydrogen phosphite, diethyl hydrogen phosphite, methyl dihydrogen phosphate, ethyl dihydrogen phosphate, methyl dihydrogen phosphite, ethyl dihydrogen phosphite, any combination thereof and the like.

[0067] Another method of sulfonation is that described by H. S. Makowski, R. D. Lundberg, and G. H. Singhal in U.S. Pat. No. 3,870,841 which is incorporated herein by reference in its entirety. In this method, a mixed anhydride is prepared by mixing sulfuric acid with acetic anhydride at a temperature of from about -70° C. to about 130° C. (preferably between -20 to about 20° C.) followed by adding this mixture to a solution of the interpolymer in a chlorinated solvent such as, for example dichloroethane, methylene chloride, chloroform, tetrachloroethane, trichloroethane or combinations thereof at a temperature of from about -20° C. to about 100° C.

[0068] The salts of the sulfonated interpolymers can be prepared by reacting with a neutralizing agent or base (ammonia, alkylamines, ammonium hydroxide, sodium hydroxide, etc.) in a solvent or as a gas phase at temperatures of from about -20° C. to about 100° C., preferably from about 40° C. to about 100° C., more preferably from about 60° C. to about 80° C. for a period of time to convert essentially all of the SO_3H groups to the neutralized salt, $-\text{SO}_3\text{Me}$ (where Me is the counterion). This time is usually from about 0.01 to about 240, preferably from about 1 to about 60, more preferably from about 5 to about 30 minutes. Me can include a group 1, 2, 7, 11 or 12 metals of the Periodic Table of Elements. The amount of the neutralizing agent employed is that which is sufficient to convert substantially all of the sulfonate groups to the neutralized salt, usually from about 1 to about 1.5, preferably from about 1 to about 1.1, more preferably about 1 mole of the neutralizing agent per mole of sulfonate group present in the interpolymer. The amount of solvent employed is that amount sufficient to create a substantially homogeneous mixture, which can range from about 5 to about 95, preferably from about 10 to about 80, more preferably from about 15 to about 75 percent by weight based on the combined weight of the mixture.

[0069] The sulfonated substantially random interpolymers comprise from about 35 to about 98.5 mol percent of polymer units derived from ethylene and/or said α -olefin which comprises at least one of propylene, 4-methyl-1-pentene, butene-1, hexene-1 or octene-1; and from about 1.5 to about 65 mol percent of polymer units derived from one or more sulfonated vinyl aromatic monomers which are mono substituted with either a sulfonic acid group or a sulfonic acid salt represented by the following formula;



[0070] wherein R^1 is selected from the group of radicals consisting of hydrogen and alkyl radicals containing from 1 to about 4 carbon atoms, each R^2 is independently selected from the group of radicals consisting of hydrogen and alkyl radicals containing from 1 to about 4 carbon atoms, Ar is a phenyl group or a phenyl group substituted with from 1 to 5 substituents selected from the group consisting of halo, C_{1-4} -alkyl, and C_{1-4} -haloalkyl; and n has a value from zero to about 4, and X is hydrogen, a group 1, 2, 7, 11 or 12 metal ion, an ammonium salt NR'_4^+ where R' is hydrogen or a

C_3 - C_{20} alkyl or a combination thereof; Preferably suitable metal salts which can be employed herein include the salts formed from group 1, 2, 7, 11 or 12 metals as well as the ammonium (NH_4^+) salts. Particularly suitable metals of group 1, 2, 7, 11, or 12 include Na, K, Li, Co, Cu, Mg, Ca, Mn, or Zn. Also suitable are the hydroxides of such metals. Particularly suitable salts and hydroxides include the hydroxides, acetates, hexanoates, and oxides of Na, Li, K, Ca, Mg, Cu, Co, Zn Al, NH_4^+ , and any combination thereof and the like. Also suitable are the hydrates of the aforementioned salts.

[0071] In the case where the sulfonation conversion is less than 100 percent, the sulfonated substantially random interpolymers would thus also comprise polymer units derived from the starting substantially random interpolymer namely ethylene and/or one or more α -olefin monomers and ii) one or more vinyl or vinylidene aromatic monomers and/or one or more sterically hindered aliphatic or cycloaliphatic vinyl or vinylidene monomers, and optionally iii) other polymerizable ethylenically unsaturated monomer(s).

[0072] Additional Blend Component(s).

[0073] The polymers used to prepare the absorbent compositions of the present invention can also comprise one or more polymers other than the sulfonated substantially random interpolymer. These additional polymers can comprise homogenous α -olefin homopolymer or interpolymers comprising polypropylene, propylene/ C_4 - C_{20} α -olefin copolymers, polyethylene, and ethylene/ C_3 - C_{20} α -olefin copolymers, the interpolymers can be either heterogeneous ethylene/ α -olefin interpolymers, preferably a heterogeneous ethylene/ C_3 - C_8 α -olefin interpolymer, most preferably a heterogeneous ethylene/octene-1 interpolymer or homogeneous ethylene/ α -olefin interpolymers, including the substantially linear ethylene/ α -olefin interpolymers, preferably a substantially linear ethylene/ α -olefin interpolymer, most preferably a substantially linear ethylene/ C_3 - C_8 α -olefin interpolymer; or a heterogeneous ethylene/ α -olefin interpolymer; or a thermoplastic olefin, preferably an ethylene/propylene rubber (EPM) or ethylene/propylene diene monomer terpolymer (EPDM) or isotactic polypropylene, most preferably isotactic polypropylene; or a styrenic block copolymer, preferably styrene-butadiene (SB), styrene-isoprene (SI), styrene-butadiene-styrene (SBS), styrene-isoprene-styrene (SIS) or styrene-ethylene/butene-styrene (SEBS) block copolymer, most preferably a styrene-butadiene-styrene (SBS) copolymer; or styrenic homopolymers or copolymers, preferably polystyrene, high impact polystyrene, polyvinyl chloride, copolymers of styrene and at least one of acrylonitrile, methacrylonitrile, maleic anhydride, or α -methyl styrene, most preferably polystyrene, or elastomers, preferably polyisoprene, polybutadiene, natural rubbers, ethylene/propylene rubbers, ethylene/propylene diene (EPDM) rubbers, styrene/butadiene rubbers, thermoplastic polyurethanes, most preferably thermoplastic polyurethanes; or engineering thermoplastics, preferably poly(methylmethacrylate) (PMMA), celluloses, nylons, poly(esters), poly(acetals); poly(amides), the poly(arylate), aromatic polyesters, poly(carbonate), poly(butylene) and polybutylene and polyethylene terephthalates, most preferably poly(methylmethacrylate) (PMMA), and poly(esters).

[0074] Especially preferred as the other polymer component is one or more existing water retentive polymers. Such

polymers can comprise nonionic polymers like polyacrylamide, polyethylene oxide, polyvinyl alcohol; anionic polymers and their neutralized salts including polyacrylic acid, graft copolymers including starch-g-polyacrylic acid, poly(vinyl alcohol-g-polyacrylic acid), hydrolyzed starch-g-poly(acrylonitrile), carboxymethylcellulose, alginic acid; cationic polymers including poly(diallyldimethylammonium chloride), polyvinylpyridine, cationic starches, and hydrolyzed chitin. These materials can be optionally crosslinked to prevent dissolution into water.

[0075] Fillers

[0076] Also included as a potential component of the polymer compositions used in the present invention are various organic and inorganic fillers, the identity of which depends upon the type of application for which the composition is to be utilized. The fillers can also be included in the sulfonated substantially random interpolymer, component, the other polymer component and/or the overall blend compositions employed in the present invention. Representative examples of such fillers include organic and inorganic fibers such as those made from asbestos, boron, graphite, ceramic, glass, metals (such as stainless steel) or polymers (such as aramid fibers) talc, carbon black, carbon fibers, calcium 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, magnesium aluminum silicate, calcium silicate, titanium dioxide, titanates, aluminum nitride, B₂O₃, nickel powder or chalk.

[0077] Other representative organic or inorganic, fiber or mineral, fillers include carbonates such as barium, calcium or magnesium carbonate; fluorides such as calcium or sodium aluminum fluoride; hydroxides such as aluminum hydroxide; metals such as aluminum, bronze, lead or zinc; oxides such as aluminum, antimony, magnesium or zinc oxide, or silicon or titanium dioxide; silicates such as asbestos, mica, clay (kaolin or calcined kaolin), feldspar, glass (ground or flaked glass or hollow glass spheres or microspheres or beads, whiskers or filaments), nepheline, perlite, pyrophyllite, talc or wollastonite; sulfates such as barium or calcium sulfate; metal sulfides; cellulose, in forms such as wood or shell flour; calcium terephthalate; and liquid crystals. Also included are the various classes of fillers that act as anti-microbial agents. Mixtures of more than one such filler may be used as well.

[0078] Other Additives

[0079] Additives such as antioxidants (e.g., hindered phenols such as, for example, Irganox™ 1010), phosphites (e.g., Irgafos™ 168) both trademarks of, and commercially available from, Ciba Geigy Corporation), U.V. stabilizers, cling additives (e.g., polyisobutylene), antiblock additives, colorants, pigments, and the like are optionally also included in the sulfonated substantially random interpolymer, component, the other polymer component and/or the overall blend compositions employed in the present invention, to the extent that they do not interfere with the enhanced properties discovered by Applicants.

[0080] Processing aids, which are also referred to herein as plasticizers, can also be included in the sulfonated substantially random interpolymer, component, the other polymer

component and/or the overall blend compositions employed in the present invention. These include the phthalates, such as dioctyl phthalate and diisobutyl phthalate, natural oils such as lanolin, and paraffin, naphthenic and aromatic oils obtained from petroleum refining, and liquid resins from rosin or petroleum feedstocks. Exemplary classes of oils useful as processing aids include white mineral oil (such as Kaydol™ oil (available from and a registered trademark of Witco), and Shellflex™ 371 naphthenic oil (available from and a registered trademark of Shell Oil Company). Another suitable oil is Tuflo™ oil (available from and a registered trademark of Lyondell).

[0081] Tackifiers, can also be included in the sulfonated substantially random interpolymer, component, the other polymer component and/or the overall blend compositions employed in the present invention, to alter the processing performance of a polymer and thus extend the available application temperature window of the application. A suitable tackifier may be selected on the basis of the criteria outlined by Hercules in J. Simons, *Adhesives Age*, "The HMDA Concept: A New Method for Selection of Resins", November 1996. This reference discusses the importance of the polarity and molecular weight of the resin in determining compatibility with the polymer. In the case of substantially random interpolymers of at least one α -olefin and a vinyl aromatic monomer, preferred tackifiers will have some degree of aromatic character to promote compatibility, particularly in the case of substantially random interpolymers having a high content of the vinyl aromatic monomer.

[0082] Tackifying resins can be obtained by the polymerization of petroleum and terpene feedstreams and from the derivatization of wood, gum, and tall oil rosin. Several classes of tackifiers include wood rosin, tall oil and tall oil derivatives, and cyclopentadiene derivatives, such as are described in United Kingdom patent application GB 2,032, 439A. Other classes of tackifiers include aliphatic C₅ resins, polyterpene resins, hydrogenated resins, mixed aliphatic-aromatic resins, rosin esters, natural and synthetic terpenes, terpene-phenolics, and hydrogenated rosin esters.

[0083] The additives are advantageously 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 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 desired color from the colorant or pigment. Such additives are advantageously 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. Fillers, however can be advantageously employed in amounts up to about 90 percent by weight based on the weight of the polymer or polymer blend.

[0084] The sulfonated substantially random interpolymers and blends therefrom of the present invention can be avail-

able in a wide range of structures including but not limited to, fibers, films, sheet, and foams, and fabricated articles therefrom

[0085] Preparation of Fibers Comprising the Sulfonated Substantially Random Interpolymers

[0086] In one embodiment of the present invention, the sulfonated substantially random interpolymers are used to prepare absorbent fibers. The fibers can be prepared from the sulfonated substantially random interpolymers using the methods described herein. Alternatively, the fibers can be prepared from the substantially random interpolymers and then the resulting fiber can then be sulfonated either after or during the fiber manufacturing process, using the sulfonation processes described herein. In such a post fiber sulfonation process, the nature and incorporation of the previously described swelling and sulfonation agents and reaction times can then be tailored to the particular fiber preparation.

[0087] The main advantages of the sulfonated substantially random interpolymers versus other polymers such as sulfonated polystyrene for use in fibers are the improved physical properties such as flexibility resulting from the occurrence of aromatic and ethylene and/or alpha olefin functionality in the polymer and their relative distributions. Polystyrene and sulfonated polystyrene by itself will be very brittle. In addition, the olefinic groups of the sulfonated substantially random interpolymer component provide improved compatibility with a polyolefin core fiber in bicomponent structures. In addition, the ethylene groups can provide some degree of hydrophobicity to the fiber, keeping it from dissolving even when all the aromatic rings are sulfonated.

[0088] The absorbent fibers of the present invention can be prepared using techniques well known in the art including for example, dry lay, wet lay, carding, spin bonding, ginning, and air laying processes. (See, e.g. U.S. Pat. Nos. 5,108,827, 5,487,943, 4,176,108 and 4,814,226). Nonwoven fabrics and articles can be prepared using binding techniques including, for example, hot roll, hot press, lamination, hot air bonding, calendar, spray, dip and roll transfer processes. (See, e.g., U.S. Pat. Nos. 5,824,610, 5,593,768, 5,169,580 and 5,244,695).

[0089] For the absorbent fibers of the present invention, the diameter can be widely varied. Fiber diameter can be measured and reported in a variety of fashions. Generally, fiber diameter is measured in denier per filament. Denier is a textile term that is defined as the grams of the fiber per 9000 meters of that fiber's length. Monofilament generally refers to an extruded strand having a denier per filament greater than 15, usually greater than 30. Fine denier fiber generally refers to fiber having a denier of about 15 or less. Microdenier (aka microfiber) generally refers to fiber having a diameter not greater than about 100 micrometers. The fiber denier can be adjusted to suit the capabilities of the finished article and as such, would preferably be: from about 0.5 to about 30 denier/filament for melt blown; from about 1 to about 30 denier/filament for spunbond; and from about 1 to about 20,000 denier/filament for continuous wound filament. Nonetheless, preferably, the nominal denier is greater than 37, more preferably greater than or equal to 55 and most preferably greater than or equal to 65. These preferences are due to the fact that typically durable apparel employ fibers with deniers greater than or equal to about 40.

[0090] Finishing operations can optionally be performed on the fibers of the present invention. For example, the fibers can be texturized by mechanically crimping or forming such as described in *Textile Fibers, Dyes, Finishes, and Processes: A Concise Guide*, by Howard L. Needles, Noyes Publications, 1986, pp. 17-20.

[0091] The interpolymer compositions used to make the fibers of the present invention or the fibers themselves (both prior to or post sulfonation) may also be modified by various cross-linking processes using curing methods at any stage of the fiber preparation including, but not limited to, before during, and after drawing at either elevated or ambient temperatures. Such cross-linking processes include, but are 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 Ser. Nos. 08/921,641 and 08/921,642 both filed on Aug. 27, 1997, the entire contents of both of which are herein incorporated by reference.

[0092] 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 Ser. No. 536,022, filed on Sep. 29, 1995, in the names of K. L. Walton and S. V. Karande, incorporated herein by reference. 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.

[0093] The polymer compositions 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.

[0094] The fibers of the present invention may be surface functionalized by methods including, but not limited to, chlorination using chemical treatments for permanent surfaces or incorporating a temporary coating using the various well known spin finishing processes.

[0095] The fibers comprising the sulfonated substantially random interpolymers can be essentially in the form of any fibers previously known in the art. This includes the homofil fibers including staple fibers, spunbond fibers or melt blown fibers (using, e.g., systems as disclosed in U.S. Pat. No. 4,340,563 (Appel et al.), U.S. Pat. No. 4,663,220 (Wisneski et al.), U.S. Pat. No. 4,668,566 (Braun), or U.S. Pat. No. 4,322,027 (Reba), all of which are incorporated herein by reference), and gel spun fibers (e.g., the system disclosed in U.S. Pat. No. 4,413,110 (Kavesh et al.), incorporated herein by reference). Staple fibers can be melt spun (i.e., they can be extruded into the final fiber diameter directly without additional drawing), or they can be melt spun into a higher diameter and subsequently hot or cold drawn to the desired diameter using conventional fiber drawing techniques.

[0096] The shape of the fiber is not limited. For example, typical fiber has a circular cross-sectional shape, but sometimes fibers have different shapes, such as a trilobal shape, or a flat (i.e., "ribbon" like) shape. The absorbent fibers disclosed herein, are not limited by the shape of the fiber.

[0097] The fibers comprising the sulfonated substantially random interpolymers can also be used as bonding fibers, especially where the inventive fibers have a lower melting point than the surrounding matrix fibers. In a bonding fiber application, the bonding fiber is typically blended with other matrix fibers and the entire structure is subjected to heat, where the bonding fiber melts and bonds the surrounding matrix fiber. Typical matrix fibers which benefit from use of the inventive fibers disclosed herein include, but are not limited to, poly(ethylene terephthalate) fibers, cotton fibers, nylon fibers, polypropylene fibers, heterogeneously branched polyethylene fibers, homogeneously branched ethylene polymer fibers, linear polyethylene homopolymer fibers and the like and combinations thereof. The diameter of the matrix fiber can vary depending upon the end use application.

[0098] These fibers of the present invention can comprise more than one polymer, including wettable binder fibers (U.S. Pat. No. 5,894,000); hydrophilic fibers, superabsorbent polymer fibers (U.S. Pat. Nos. 5,593,399 and 5,698,480); and the fibers listed in U.S. Pat. No. 4,176,108. The teachings of these patents, and all other patents cited herein, are hereby incorporated by reference in their entirety. Mixtures of fibers can also be employed. Examples of common materials used in the manufacture of fibers available for mixing with the fibers of the present invention include natural and synthetic materials such as, for example, polyethylene terephthalate, polyethylene, polypropylene, polyurethane, nylon, rayon, and cotton and other cellulosic materials.

[0099] In an especially preferred embodiment, the absorbent fibers comprising the sulfonated substantially random interpolymers are conjugated or bicomponent or multi-component fibers (as disclosed in U.S. Pat. Nos. 5,843,063; 5,169,580; 4,634,739; 5,921,973; 4,483,976; and 5,403,444 which are hereby incorporated by reference in their entirety). The polymer components are usually different from each other, although conjugated fibers may be mono-component fibers. The polymers are arranged in substantially constantly positioned distinct zones across the cross-section of the conjugated fibers and extend continuously along the length of the conjugated fibers. The configuration of the conjugated fibers of the present invention can be, for example, a sheath/core arrangement (wherein one polymer is surrounded by another), a side by side arrangement, a pie arrangement or an "islands-in-the-sea" arrangement. Conjugated fibers are described in U.S. Pat. No. 5,108,820 to Kaneko et al.; U.S. Pat. No. 5,336,552 to Strack et al.; and U.S. Pat. No. 5,382,400 to Pike et al., the disclosures of all of which are incorporated herein by reference. The fibers comprising the sulfonated substantially random interpolymers of the present invention can be in a conjugated configuration, for example, as a core or sheath, or both. Different sulfonated substantially random interpolymers can also be used independently as the sheath and the core in the same fiber, especially where the sheath component has a lower melting point than the core component.

[0100] Fabrics and Fabricated Articles

[0101] Fabrics made from such novel absorbent fibers of the present invention can include both woven and nonwoven fabrics. Nonwoven fabrics can be made variously, including spunlaced (or hydrodynamically entangled) fabrics as dis-

closed in U.S. Pat. No. 3,485,706 (Evans) and U.S. Pat. No. 4,939,016 (Radwanski et al.), the disclosures of which are incorporated herein by reference; by carding and thermally bonding staple fibers; by spunbonding continuous fibers in one continuous operation; or by melt blowing fibers into fabric and subsequently calendering or thermally bonding the resultant web. These various nonwoven fabric manufacturing techniques are well known to those skilled in the art and the disclosure is not limited to any particular method. Other structures made from such fibers are also included within the scope of the invention, including e.g., blends of these novel fibers with other fibers (e.g., poly(ethylene terephthalate) (PET) or cotton or wool or polyester). For example, nonwoven fabrics of the invention may be used in filtration applications, medical applications, clean room applications, garments, barrier products, sterilization wraps, interlinings, cushioning, CSR wrap, stretchable absorbent materials, and wipes.

[0102] The absorbent articles of the present invention can be utilized in disposable products which are capable of absorbing significant quantities of body fluids, such as urine and water in body wastes. Such articles may be prepared in the form of sanitary napkins and other feminine hygiene products, disposable diapers, adult incontinence briefs, adult incontinence pads and the like.

[0103] In a preferred embodiment of the present invention the sulfonated substantially random interpolymer fibers are used in the construction of diapers, as part of the distribution, acquisition and/or surge layers and in the core. (See, e.g., U.S. Pat. Nos. 5,108,827, 5,893,063, 5,593,768, 5,646,077, and 5,244,695). Especially preferred absorbent articles of this invention are disposable diapers. Articles in the form of disposable diapers are fully described in Duncan and Baker, U.S. Pat. No. Re. 26,151, Issued Jan. 31, 1967; Duncan, U.S. Pat. No. 3,592,194, Issued Jul. 13, 1971; Duncan and Gellert, U.S. Pat. No. 3,489,148, Issued Jan. 13, 1970; and Buell, U.S. Pat. No. 3,860,003, Issued Jan. 14, 1975; which patents are incorporated herein by reference.

[0104] One means for increasing the liquid retention capabilities of such products is through the addition of superabsorbents, which are also referred to as hydrogels and hydrocolloids. This is particularly true in the case of diapers, training pants and incontinence garments. As these products have become more and more sophisticated, the manufacturers of these products have reduced the amount of wood pulp or fluff in the absorbent layers of these materials and replaced the fluff with varying amounts of superabsorbent in the form of particles. As the amount of superabsorbent has increased in these absorbent structures, a problem called gel-blocking has arisen. Early superabsorbents were made in particle form and while being capable of absorbing many times their own weight in liquid such as water and urine, would not hold their particle or generally spherical shape as they absorbed liquid. Instead, they would turn into a mushy gel which would swell, fill the voids between the wood pulp fibers and quickly turned the structure into a gelled mess. This is now referred to as gel blocking. The absorbent fibers of the present invention may be used as the sole superabsorbent core component or may be used in addition to the aforementioned core components of the prior art to facilitate liquid transport and alleviate the problem of gell blocking.

[0105] Nonwoven products prepared with the absorbent fibers of the invention may also be useful in specialty

applications such as the preparation of hygiene articles having patterned component distribution (see, e.g., U.S. Pat. Nos. 5,843,063, 5,593,399 and 5,941,862) and flushable diapers (see, e.g., U.S. Pat. No. 5,770,528).

[0106] Woven fabrics can also be made which comprise the absorbent fibers of the present invention. The various woven fabric-manufacturing techniques are well known to those skilled in the art and the disclosure is not limited to any particular method. Woven fabrics are typically stronger and more heat resistant and are thus used typically in durable, non-disposable applications as for example in the woven blends with polyester and polyester cotton blends. The woven fabrics comprising the absorbent fibers of the present invention can be used in applications including but not limited to, upholstery, athletic apparel, carpet, fabrics, bandages. In addition the fibers of the present invention can be included in the woven fabrics of the prior art (e.g. as staple fibers in existing fabrics) to promote absorbency.

[0107] The novel absorbent fibers described herein also can be used in a spunlaced (or hydrodynamically entangled) process to make novel structures. For example, U.S. Pat. No. 4,801,482 (Goggans), the disclosure of which is incorporated herein by reference, discloses a sheet which can now be made with the novel fibers/fabric described herein. Composites that utilize very high molecular weight linear polyethylene or copolymer polyethylene also benefit from the novel fibers disclosed herein. For example, for the novel fibers that have a low melting point, such that in a blend of the novel fibers and very high molecular weight polyethylene fibers (as described in U.S. Pat. No. 4,584,347 by Harpell et al., the disclosure of which is incorporated herein by reference), the lower melting fibers bond the high molecular weight polyethylene fibers without melting the high molecular weight fibers, thus preserving the high strength and integrity of the high molecular weight fiber.

[0108] Absorbent and Superabsorbent Foams

[0109] Absorbent and superabsorbent foams have attracted considerable attention as candidates for replacing multiple components of an absorbent core. They hold the potential of offering some of the same advantages sought for film or fiber forms; performing the absorbent functions of multiple components of a conventional diaper, not migrating in the product, and not creating dust. Several different approaches to superabsorbent polymer foams have been described in the patent literature. One approach seeks to embed conventional superabsorbent granules in non-superabsorbent foam. A second option is to utilize capillary suction forces, instead of or in addition to osmotic pressure, to create an absorbent material.

[0110] The incorporation of a conventional granular superabsorbent polymer into a foam structure is a relatively obvious extension of superabsorbent polymer technology. For any composite structure comprising a foam and a superabsorbent polymer to have enhanced performance, a number of technical challenges must be met. The foam must convey the fluid to the superabsorbent polymer particles rapidly and effectively. As the superabsorbent polymer swells, it must not block the passage of fluid through the foam, nor should it become detached from the foam structure.

[0111] While conventional superabsorbent polymers utilize osmotic forces to retain aqueous fluids, most other

common absorbents depend on capillary forces, or the tendency of an aqueous fluid to spread and wet a high-energy surface. Paper towels, sponges, and cellulose fluffs are examples of capillary absorbers. Recently there has been a significant amount of activity on microcellular foams as superabsorbent structures, including absorbent materials made using high internal phase-ratio emulsions (HIPES). An important aspect of these foams is that they are inherently lipophilic, requiring a post-treatment in order to absorb aqueous solutions.

[0112] In one embodiment of the present invention, the sulfonated substantially random interpolymers are used to prepare absorbent foams. The foams can be prepared from the sulfonated substantially random interpolymers using the methods described herein. Alternatively, the foams can be prepared from the substantially random interpolymers and then the resulting foams can then be sulfonated either after or during the foam manufacturing process, using the sulfonation processes described herein. In such a post foam sulfonation process, the nature and incorporation of the previously described swelling and sulfonation agents and reaction times can then be tailored to the particular foam preparation.

[0113] Foam forming steps of the process are within the skill in the art. For instance as exemplified by the excellent teachings to processes for making ethylenic polymer foam structures and processing them 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), which is incorporated here in by reference.

[0114] The absorbent foam structures of the present invention are optionally made by a conventional extrusion foaming process. The structure is advantageously prepared by heating the sulfonated substantially random interpolymer or blend to form a plasticized or melt polymer material, incorporating therein a blowing agent to form a foamable gel, and extruding the gel through a die to form the foam product. Prior to mixing with the blowing agent, the sulfonated substantially random interpolymer is heated to a temperature at or above its glass transition temperature or melting point. The blowing agent is optionally incorporated or mixed into the melt polymer material by any means known in the art such as with an extruder, mixer, blender, or the like. The blowing agent is mixed with the melt polymer material at an elevated pressure sufficient to prevent substantial expansion of the melt polymer material and to advantageously disperse the blowing agent homogeneously therein. Optionally, a nucleator is optionally blended in the melt or dry blended with the sulfonated substantially random interpolymer prior to plasticizing or melting. The foamable gel is typically cooled to a lower temperature to optimize physical characteristics of the foam structure. The gel is then extruded or conveyed through a die of desired shape to a zone of reduced or lower pressure to form the foam structure. The zone of lower pressure is at a pressure lower than that in which the foamable gel is maintained prior to extrusion through the die. The lower pressure is optionally superatmospheric or subatmospheric (vacuum) but is preferably at an atmospheric level.

[0115] In another embodiment, the resulting absorbent foam structure is optionally formed in a coalesced strand

form by extrusion of the polymer material through a multi-orifice die. The orifices are arranged so that contact between adjacent streams of the molten extrudate occurs during the foaming process and the contacting surfaces adhere to one another with sufficient adhesion to result in a unitary foam structure. The streams of molten extrudate exiting the die take the form of strands or profiles, which desirably foam, coalesce, and adhere to one another to form a unitary structure. Desirably, the coalesced individual strands or profiles should remain adhered in a unitary structure to prevent strand delamination under stresses encountered in preparing, shaping, and using the foam. Apparatuses and method for producing foam structures in coalesced strand form are seen in U.S. Pat. Nos. 3,573,152 and 4,824,720, both of which are incorporated herein by reference.

[0116] Alternatively, the resulting absorbent foam structure is conveniently formed by an accumulating extrusion process as described in U.S. Pat. No. 4,323,528, the entire contents of which are incorporated by reference herein. In another embodiment, the resulting foam structure is formed into non-crosslinked foam beads suitable for molding into articles. This process is well taught in U.S. Pat. Nos. 4,379,859 and 4,464,484, which are incorporated herein by reference.

[0117] In one modification of the uncrosslinked bead process, styrene monomer is optionally impregnated into the suspended pellets prior to their impregnation with blowing agent to form a graft interpolymer with the sulfonated substantially random interpolymer. Such a process of making such interpolymer beads is described for instance in U.S. Pat. No. 4,168,353, which is incorporated herein by reference.

[0118] The foam beads are conveniently then molded by any means within the skill in the art, such as taught for instance in U.S. Pat. Nos. 3,504,068 and 3,953,558. and C. P. Park, supra, p. 191, pp. 197-198, and pp. 227-229, the entire contents of all of which are incorporated herein by reference.

[0119] Blowing agents useful in making the absorbent foam structures of the present invention 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-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, barium azodicarboxylate, N,N'-dimethyl-N,N'-dinitrosoterephthalamide, and benzenesulfonhydrazide, 4,4-oxybenzene sulfonyl semicarbazide, and p-toluene sulfonyl semicarbazide trihydrazino triazine. Preferred blowing agents include isobutane, HFC-152a, and mixtures of the foregoing.

[0120] The absorbent foams are optionally perforated to enhance or accelerate permeation of blowing agent from the foam and air into the foam. Such perforation is within the skill in the art, for instance as taught in U.S. Pat. Nos. 5,424,016 and 5,585,058, which are incorporated herein by reference.

[0121] Various additives are optionally incorporated in the resulting foam structure such as stability control agents, nucleating agents, inorganic fillers, pigments, antioxidants, acid scavengers, ultraviolet absorbers, flame retardants, processing aids, extrusion aids, and the like.

[0122] A stability control agent is optionally added to the present foam to enhance dimensional stability. Preferred agents include amides and esters of C10-24 fatty acids. Such agents are seen in U.S. Pat. Nos. 3,644,230 and 4,214,054, which are incorporated herein by reference.

[0123] In addition, a nucleating agent is optionally 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 earth, mixtures of citric acid and sodium bicarbonate, and the like. The amount of nucleating agent employed may range from about 0.01 to about 5 parts by weight per hundred parts by weight of a polymer resin.

[0124] The resulting foam structure is optionally closed-celled or open-celled. The open cell content will range from 0 to 100 volume percent as measured according to ASTM D2856-A.

[0125] The resulting absorbent foam structure is substantially noncrosslinked or uncrosslinked, and is optionally in any physical configuration within the skill in the art, such as extruded sheet, rod, plank, and profiles.

[0126] Compositions of the Absorbent Polymers of the Present Invention

[0127] The starting material substantially random interpolymer prior to sulfonation comprise from about 0.5 to about 65, preferably from about 5 to about 65, more preferably from about 10 to about 65 mole percent of at least one vinyl or vinylidene aromatic monomer and/or aliphatic or cycloaliphatic vinyl or vinylidene monomer and from about 35 to about 99.5, preferably from about 35 to about 95, more preferably from about 35 to about 90 mole percent of ethylene and/or at least one aliphatic α -olefin having from 3 to about 20 carbon atoms.

[0128] The melt index (I_2) of the starting material substantially random interpolymer prior to sulfonation is from about 0.01 to about 1000, preferably of from about 0.3 to about 30, more preferably of from about 0.5 to about 10 g/10 min.

[0129] The molecular weight distribution (M_w/M_n) of the starting material substantially random interpolymer prior to sulfonation is from about 1.5 to about 20, preferably of from about 1.8 to about 10, more preferably of from about 2 to about 5.

[0130] The density of the starting material substantially random interpolymer prior to sulfonation is greater than about 0.930, preferably from about 0.930 to about 1.045, more preferably of from about 0.930 to about 1.040, most preferably of from about 0.930 to about 1.030 g/cm³.

[0131] The degree of sulfonation of the starting material substantially random interpolymer is from about 1.5 to about 100, preferably from about 15 to about 100, more preferably from about 30 to 100 mol percent (based on the total number of aromatic rings in the initial substantially random interpolymer) of mono substituted aromatic rings substituted with a sulfonic acid group or a sulfonic acid salt.

[0132] The absorbent polymers compositions of the present invention comprise from about 10 to 100, preferably from about 20 to 100, more preferably from about 50 to 100 wt percent, (based on the combined weights of this component and the polymer component other than the sulfonated substantially random interpolymer) of one or more sulfonated substantially random interpolymers of ethylene and/or one or more α -olefins and one or more vinyl or vinylidene aromatic monomers and/or one or more sterically hindered aliphatic or cycloaliphatic vinyl or vinylidene monomers.

[0133] The sulfonated substantially random interpolymers comprise from about 35 to about 98.5, preferably from about 35 to about 85, more preferably from about 35 to about 70 mol percent of repeating units derived from ethylene and/or said ox-olefin which comprises at least one of propylene, 4-methyl-1-pentene, butene-1, hexene-1 or octene-1.

[0134] The sulfonated substantially random interpolymers comprise from about 1.5 to about 65 preferably from about 15 to about 65, more preferably from about 30 to about 65 mol percent of repeating units derived from said sulfonated vinyl or vinylidene aromatic monomers.

[0135] The sulfonated substantially random interpolymers comprise from 0 to about 63.5, preferably from 0 to about 50, more preferably from 0 to about 35 mol percent of repeating units derived from vinyl or vinylidene aromatic monomers.

[0136] The sulfonated substantially random interpolymers comprise from 0 to about 63.5, preferably from 0 to about 50, more preferably from 0 to about 35 mol percent of repeating units derived from said sterically hindered aliphatic or cycloaliphatic vinyl or vinylidene monomers.

[0137] The sulfonated substantially random interpolymers comprise from 0 to about 20 preferably, more preferably mol percent of norbornene, or a C₁₋₁₀ alkyl or C₆₋₁₀ aryl substituted norbornene.

[0138] The absorbent polymers compositions of the present invention can also comprise from 0 to about 90,

preferably from 0 to about 80, more preferably from 0 to about 50 wt percent of at least one polymer other than said sulfonated substantially random interpolymer (based on the combined weights of this component and the substantially random interpolymer).

[0139] Applications

[0140] Applications for the materials of the present invention include the various applications for membranes as described in "Membrane Technology" in The Encyclopedia of Chemical Technology, Vol 16, ppgs 135-193, (4th ed, 1995, J. Wiley and Sons Inc., NY) the entire contents of which are herein incorporated by reference.

[0141] Other applications include modification of petroleum and hydrocarbon-based materials such as oils, asphalts and bitumenous products, in which the sulfonation improves the compatibility of the polymer. Also included are reinforcement of cementitious products by the sulfonated fibers of the present invention. Films and multilayer films for food packaging, and medical applications such as medicine bags, bandages, tapes, casts and the like, as well as delivery systems for agricultural products such as herbicides, pesticides and fertilizers as well as pharmaceutical products or other pharmaceutical applications. Also included are the use of the compositions of the present invention as binders for the recovery of coal and refractory fines. Also included are applications using the materials of the present invention as solid acid catalysts including shape selective and optically active catalytic transformations. Others uses include packaging (absorbent fiber used in packaging in case of spills), food packaging, cable wrap (water block tape in cables), medical applications (bandages, surgical drapes, spill clean up), apparel (absorbent fiber for improved comfort), controlled release fiber (imbibe absorbent fiber with antimicrobial, perfume, antibiotics etc.), absorbent articles for meat trays, absorbent articles for personal hygiene such as diapers, sanitary napkins adult incontinence pads, wipes (highly absorbent wipes, dust pickup), softener (sulfonated fiber holds on to fabric softeners and slowly releases them), towels with superabsorbing power (staple fibers to be combined in cotton yarns and improved water absorption capacity of towels, even in presence of fabric softeners), and disposable high absorbing towels (staple fibers to be combined with paper/non wovens towels for disposable applications such as towels for gym clubs, hospitals, etc.)

[0142] The following examples are to illustrate this invention and do not limit it.

EXAMPLES

[0143] Test Methods.

[0144] a) Melt Flow Measurements.

[0145] Unless otherwise stated, the molecular weight of the polymer compositions for use in the present invention is conveniently 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 I_2) was determined. Melt index is inversely proportional to the molecular weight of the polymer. Thus, the higher the molecular weight, the lower the melt index, although the relationship is not linear.

[0146] b) Styrene Analyses

[0147] Interpolymer styrene content and the concentration of atactic polystyrene homopolymer impurity in the ESI interpolymers was determined using proton nuclear magnetic resonance (^1H NMR). All proton NMR samples were prepared in 1,1,2,2-tetrachloroethane- d_2 (tce- d_2). The resulting solutions contained approximately 1-3 weight percent polymer. The interpolymers were weighed directly into 5-mm sample tubes. A 0.75-ml aliquot of tce- d_2 was added by syringe and the tube sealed with a tight-fitting cap. The samples were heated at 85° C. to soften the interpolymer. To provide mixing, the capped samples were occasionally brought to reflux using a heat gun.

[0148] Proton NMR spectra were accumulated with the sample probe at 80° C., and referenced to the residual protons of tce- d_2 at 5.99 ppm. Data was collected in triplicate on each sample using the following instrumental conditions:

[0149] Sweep width, 5000 hz

[0150] Acquisition time, 3.002 sec

[0151] Pulse width, 8 μsec

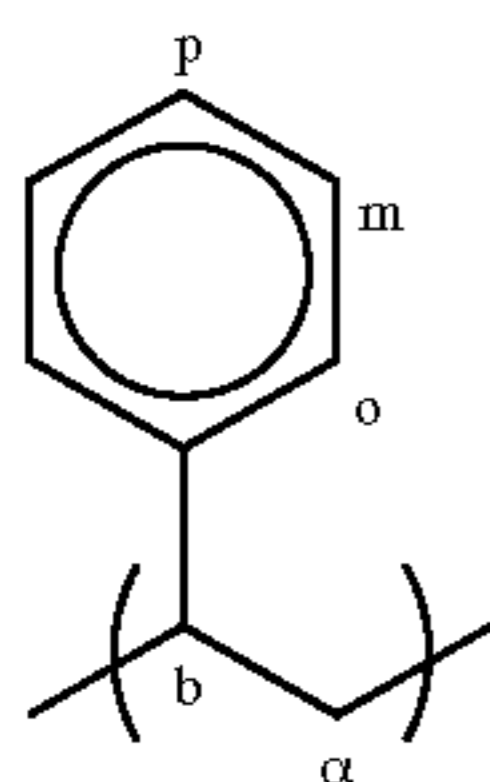
[0152] Frequency, 300 mhz

[0153] Delay, 1 sec

[0154] Transients, 16

[0155] The total analysis time per sample was about 10 minutes.

[0156] Initially, a spectrum for a sample of polystyrene (192,000 M_w) was acquired. Polystyrene has five different types of protons that are distinguishable by proton NMR. In FIG. 1, these protons are labeled b, branch; α , alpha; o, ortho; m, meta; p, para, as shown in FIG. 1. For each repeating unit in the polymer, there are one branch proton, two-alpha protons, two ortho protons, two meta protons and one para proton.



[0157] The NMR spectrum for polystyrene homopolymer includes a resonance centered around a chemical shift of about 7.1 ppm, which is believed to correspond to the three ortho and para protons. The spectrum also includes another peak centered around a chemical shift of about 6.6 ppm. That peak corresponds to the two meta protons. Other peaks at about 1.5 and 1.9 ppm correspond to the three aliphatic protons (alpha and branch).

[0158] The relative intensities of the resonances for each of these protons were determined by integration. The integral corresponding to the resonance at 7.1 ppm was designated $\text{PS}_{7.1}$ below. That corresponding to the resonance at 6.6 ppm was designated $\text{PS}_{6.6}$, and that corresponding to the

aliphatic protons (integrated from 0.8-2.5 ppm) was designated PS_{al} . The theoretical ratio for $\text{PS}_{7.1}:\text{PS}_{6.6}:\text{PS}_{\text{al}}$ is 3:2:3, or 1.5:1:1.5. For atactic polystyrene homopolymer, all spectra collected had the expected 1.5:1:1.5 integration ratio. An aliphatic ratio of 2 to 1 is predicted based on the protons labeled α and b respectively in FIG. 1. This ratio was also observed when the two aliphatic peaks were integrated separately. Further, the ratio of aromatic to aliphatic protons was measured to be 5 to 3, as predicted from theoretical considerations.

[0159] The ^1H NMR spectrum for the ESI interpolymer was then acquired. This spectrum showed resonances centered at about 7.1 ppm, 6.6 ppm and in the aliphatic region. However, the 6.6 ppm peak was relatively much weaker for the ESI interpolymer than for the polystyrene homopolymer. The relative weakness of this peak is believed to occur because the meta protons in the ESI copolymer resonate in the 7.1 ppm region. Thus, the only protons that produce the 6.6 ppm peak are meta protons associated with atactic polystyrene homopolymer that is an impurity in the ESI. The peak centered at about 7.1 ppm thus includes ortho, meta and para protons from the aromatic rings in the ESI interpolymer, as well as the ortho and para protons from the aromatic rings in the polystyrene homopolymer impurity. The peaks in the aliphatic region include resonances of aliphatic protons from both the ESI interpolymer and the polystyrene homopolymer impurity.

[0160] Again, the relative intensities of the peaks were determined by integration. The peak centered around 7.1 ppm is referred to below as $I_{7.1}$, that centered around 6.6 ppm is $I_{6.6}$ and that in the aliphatic regions is I_{al} .

[0161] $I_{7.1}$ includes a component attributable to the aromatic protons of the ESI interpolymer and a component attributable to the ortho and para protons of the aromatic rings of the polystyrene homopolymer impurity. Thus,

$$I_{7.1} = I_{c7.1} + I_{ps7.1}$$

[0162] where $I_{c7.1}$ is the intensity of the 7.1 ppm resonance attributable to the aromatic protons in the interpolymer and $I_{ps7.1}$ is the intensity of the 7.1 ppm resonance attributable to the ortho and meta protons of the polystyrene homopolymer.

[0163] From theoretical considerations, as confirmed by the ^1H NMR spectrum of the polystyrene homopolymer, the intensity of the 7.1 ppm resonance attributable to the polystyrene homopolymer impurity ($I_{ps7.1}$), equals 1.5 times the intensity of the 6.6 ppm resonance. This provides a basis for determining $I_{c7.1}$ from measured values, as follows:

$$I_{c7.1} = I_{7.1} - 1.5(I_{6.6}).$$

[0164] Similarly, I_{al} can be resolved into resonances attributable to the ESI and the polystyrene homopolymer impurity using the relationship

$$I_{\text{al}} = I_{\text{cal}} + I_{\text{psal}}$$

[0165] wherein I_{cal} is the intensity attributable to the aliphatic protons on the interpolymer and I_{psal} is the intensity attributable to the aliphatic protons of the polystyrene homopolymer impurity. Again, it is known from theoretical considerations and the spectrum from the atactic polystyrene homopolymer that I_{psal} will equal 1.5 times $I_{6.6}$. Thus the following relationship provides a basis for determining I_{cal} from measured values:

$$I_{\text{cal}} = I_{\text{al}} - 1.5(I_{6.6}).$$

[0166] The mole percent ethylene and styrene in the interpolymer are then calculated as follows:

$$\begin{aligned} s_c &= I_{c7.1}/5 \\ e_c &= (I_{cal} - (3 \times s_c))/4 \\ E &= e_c / (s_c + e_c), \text{ and} \\ S &= s_c / (s_c + e_c), \end{aligned}$$

[0167] wherein E and S are the mole fractions of copolymerized ethylene and styrene, respectively, contained in the interpolymer.

[0168] Weight percent ethylene and styrene were calculated using the equations:

$$\begin{aligned} \text{Wt \% } E &= \frac{100\% * 28 E}{(28 E + 104 S)} \quad \text{and} \\ \text{Wt \% } S &= \frac{100\% * 104 S}{(28 E + 104 S)}. \end{aligned}$$

[0169] The weight percent of polystyrene homopolymer impurity in the ESI sample was then determined by the following equation:

$$\text{Wt \% } PS = \frac{100\% * \text{Wt \% } S * (I_{6.6}/2S)}{100 - [\text{Wt \% } S * (I_{6.6}/2S)]}$$

[0170] The total styrene content was also determined by quantitative Fourier transform infrared spectroscopy (FTIR).

[0171] Polymer Components Used in the Examples

[0172] PP1 is INSPIRE™ H700-12 polypropylene (a trademark of and available from The Dow Chemical Company) having a melt index (ASTM D-1238, Condition 230° C./2.16 kg) of 12 g/10 min

[0173] Preparation of the Ethylene/Styrene Interpolymer, ESI 2.

[0174] Preparation of Catalyst B; (1H-cyclopenta[1]phenanthrene-2-yl)dimethyl(t-butylamido)-silanetitanium 1,4-diphenylbutadiene).

[0175] 1) Preparation of lithium 1H-cyclopenta[1]phenanthrene-2-yl

[0176] To a 250 ml round bottom flask containing 1.42 g (0.00657 mole) of 1H-cyclopenta[1]phenanthrene and 120 ml of benzene was added dropwise, 4.2 ml of a 1.60 M solution of n-BuLi in mixed hexanes. The solution was allowed to stir overnight. The lithium salt was isolated by filtration, washing twice with 25 ml benzene and drying under vacuum. Isolated yield was 1.426 g (97.7 percent). 1H NMR analysis indicated the predominant isomer was substituted at the 2 position.

[0177] 2) Preparation of (1H-cyclopenta[1]phenanthrene-2-yl)dimethylchlorosilane

[0178] To a 500 ml round bottom flask containing 4.16 g (0.0322 mole) of dimethyldichlorosilane (Me₂SiCl₂) and 250 ml of tetrahydrofuran (THF) was added dropwise a solution of 1.45 g (0.0064 mole) of lithium 1H-cyclopenta

[1]phenanthrene-2-yl in THF. The solution was stirred for approximately 16 hours, after which the solvent was removed under reduced pressure, leaving an oily solid which was extracted with toluene, filtered through diatomaceous earth filter aid (Celite™), washed twice with toluene and dried under reduced pressure. Isolated yield was 1.98 g (99.5 percent).

[0179] 3) Preparation of (1H-cyclopenta[1]phenanthrene-2-yl)dimethyl(t-butyl amino)silane

[0180] To a 500 ml round bottom flask containing 1.98 g (0.0064 mole) of (1H-cyclopenta[1]phenanthrene-2-yl)dimethylchlorosilane and 250 ml of hexane was added 2.00 ml (0.0160 mole) of t-butylamine. The reaction mixture was allowed to stir for several days, then filtered using diatomaceous earth filter aid (Celite™), washed twice with hexane. The product was isolated by removing residual solvent under reduced pressure. The isolated yield was 1.98 g (88.9 percent).

[0181] 4) Preparation of dilithio (1H-cyclopenta[1]phenanthrene-2-yl)dimethyl(t-butylamido)silane

[0182] To a 250 ml round bottom flask containing 1.03 g (0.0030 mole) of (1H-cyclopenta[1]phenanthrene-2-yl)dimethyl(t-butylamino)silane and 120 ml of benzene was added dropwise 3.90 ml of a solution of 1.6 M n-BuLi in mixed hexanes. The reaction mixture was stirred for approximately 16 hours. The product was isolated by filtration, washed twice with benzene and dried under reduced pressure. Isolated yield was 1.08 g (100 percent).

[0183] 5) Preparation of (1H-cyclopenta[1]phenanthrene-2-yl)dimethyl(t-butylamido)silanetitanium dichloride

[0184] To a 250 ml round bottom flask containing 1.17 g (0.0030 mole) of TiCl₃·3THF and about 120 ml of THF was added at a fast drip rate about 50 ml of a THF solution of 1.08 g of dilithio (1H-cyclopenta[1]phenanthrene-2-yl)dimethyl(t-butylamido)silane. The mixture was stirred at about 20° C. for 1.5 h at which time 0.55 gm (0.002 mole) of solid PbCl₂ was added. After stirring for an additional 1.5 h the THF was removed under vacuum and the residue was extracted with toluene, filtered and dried under reduced pressure to give an orange solid. Yield was 1.31 g (93.5 percent).

[0185] 6) Preparation of (1H-cyclopenta[1]phenanthrene-2-yl)dimethyl(t-butylamido)silanetitanium 1,4-diphenylbutadiene

[0186] To a slurry of (1H-cyclopenta[1]phenanthrene-2-yl)dimethyl(t-butylamido) silanetitanium dichloride (3.48 g, 0.0075 mole) and 1.551 gm (0.0075 mole) of 1,4-diphenylbutadiene in about 80 ml of toluene at 70° C. was added 9.9 ml of a 1.6 M solution of n-BuLi (0.0150 mole). The solution immediately darkened. The temperature was increased to bring the mixture to reflux and the mixture was maintained at that temperature for 2 hrs. The mixture was cooled to about -20° C. and the volatiles were removed under reduced pressure. The residue was slurried in 60 ml of mixed hexanes at about 20° C. for approximately 16 hours. The mixture was cooled to about -25° C. for about 1 hour. The solids were collected on a glass frit by vacuum filtration and dried under reduced pressure. The dried solid was placed in a glass fiber thimble and solid extracted continuously with hexanes using a Soxhlet extractor. After 6 hours

a crystalline solid was observed in the boiling pot. The mixture was cooled to about -20°C ., isolated by filtration from the cold mixture and dried under reduced pressure to give 1.62 g of a dark crystalline solid. The filtrate was discarded. The solids in the extractor were stirred and the extraction continued with an additional quantity of mixed hexanes to give an additional 0.46 g of the desired product as a dark crystalline solid.

[0187] Polymerization

[0188] ESI #'s 1-2 were prepared in a continuously operating loop reactor (36.8 gal). An Ingersoll-Dresser twin screw pump provided the mixing. The reactor ran liquid full at 475 psig (3,275 kPa) with a residence time of approximately 25 minutes. Raw materials and catalyst/cocatalyst flows were fed into the suction of the twin screw pump through injectors and Kenics static mixers. The twin screw pump discharged into a 2 inch diameter line which supplied two Chemineer-Kenics 10-68 Type BEM Multi-Tube heat exchangers in series. The tubes of these exchangers contained twisted tapes to increase heat transfer. Upon exiting the last exchanger, loop flow returned through the injectors and static mixers to the suction of the pump. Heat transfer oil was circulated through the exchangers' jacket to control the loop temperature probe located just prior to the first exchanger. The exit stream of the loop reactor was taken off between the two exchangers. The flow and solution density of the exit stream was measured by a Micro-Motion™ mass flow meter.

[0189] Solvent feed to the reactor was supplied by two different sources. A fresh stream of toluene from an 8480-S-E Pulsafeeder™ diaphragm pump with rates measured by a Micro-Motion™ mass flow meter was used to provide flush flow for the reactor seals (20 lb/hr (9.1 kg/hr)). Recycle solvent was mixed with uninhibited styrene monomer on the suction side of five 8480-5-E Pulsafeeder™ diaphragm pumps in parallel. These five Pulsafeeder™ pumps supplied solvent and styrene to the reactor at 650 psig (4,583 kPa). Fresh styrene flow was measured by a Micro-Motion™ mass flow meter, and total recycle solvent/styrene flow was measured by a separate Micro-Motion™ mass flow meter. Ethylene was supplied to the reactor at 687 psig (4,838 kPa). The ethylene stream was measured by a Micro-Motion™ mass flow meter. A Brooks flow meter/controller was used to deliver hydrogen into the ethylene stream at the outlet of the ethylene control valve.

[0190] The ethylene/hydrogen mixture combined with the solvent/styrene stream at ambient temperature. The tempera-

ture of the entire feed stream as it entered the reactor loop was lowered to 2°C . by an exchanger with -10°C . glycol on the jacket. Preparation of the three catalyst components took place in three separate tanks. Fresh solvent and concentrated catalyst/cocatalyst premix were added and mixed into their respective run tanks and fed into the reactor via variable speed 680-S-AEN7 Pulsafeeder™ diaphragm pumps. As previously explained, the three component catalyst system entered the reactor loop through an injector and static mixer into the suction side of the twin screw pump. The raw material feed stream was also fed into the reactor loop through an injector and static mixer downstream of the catalyst injection point but upstream of the twin screw pump suction.

[0191] Polymerization was stopped with the addition of catalyst kill (water mixed with solvent) into the reactor product line after the Micro-Motion™ mass flow meter measuring the solution density. 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 the solvent removal flash. This flash occurred as the effluent exited the post reactor heater and the pressure was dropped from 475 psig (3,275 kPa) down to 450 mmHg (60 kPa) of absolute pressure at the reactor pressure control valve.

[0192] This flashed polymer entered the first of two hot oil jacketed devolatilizers. The volatiles flashing from the first devolatilizer were condensed with a glycol jacketed exchanger, passed through the suction of a vacuum pump, and were discharged to the solvent and styrene/ethylene separation vessel. Solvent and styrene were removed from the bottom of this vessel as recycle solvent while ethylene exhausted from the top. The ethylene stream was measured with a Micro-Motion™ mass flow meter. The measurement of vented ethylene plus a calculation of the dissolved gases in the solvent/styrene stream were used to calculate the ethylene conversion. The polymer and remaining solvent separated in the devolatilizer was pumped with a gear pump to a second devolatilizer. The pressure in the second devolatilizer was operated at 5 mmHg (0.7 kPa) absolute pressure to flash the remaining solvent. This solvent was condensed in a glycol heat exchanger, pumped through another vacuum pump, and exported to a waste tank for disposal. The dry polymer (<1000 ppm total volatiles) was pumped with a gear pump to an underwater pelletizer with 6-hole die, pelletized, spin-dried, and collected in 1000 lb boxes.

TABLE 1

ESI #	Preparation Conditions for ESI 2*									
	Reactor Temp ° C.	Solvent Flow lb/hr	Ethylene Flow lb/hr	Hydrogen Flow sccm	Styrene Flow lb/hr	Ethylene Conversion percent	B/Ti Ratio	MMAO ^c / TI Ratio	Co-Catalyst	Co-Catalyst
ESI 2	58	308	34	0	263	97.9	4.0	8.0	A	B

^aCatalyst A is ;(1H-cyclopenta[1]phenanthrene-2-yl)dimethyl(t-butylamido)-silanetitanium 1,4-diphenylbutadiene)

^bCocatalyst B is tris(pentafluorophenyl)borane, (CAS#001109-15-5),.

^ca modified methylaluminumoxane commercially available from Akzo Nobel as MMAO-3A (CAS# 146905-79-5)

[0193]

TABLE 2

Properties of ESI #'s 1 and 2				
ESI #	Copolymer Styrene (wt percent)	Copolymer Styrene (mol percent)	Atactic Polystyrene (wt percent)	I ₂ (g/10 min)
ESI 1	75	45	N/A	1.0
ESI 2	77	48	8.4	1.1

[0194] As a preliminary to sulfonation, a series of experiments were performed in order to determine which solvents swell the substantially random interpolymers, and over what time period, a sample of ESI 1 extruded film (5 mil thick) were cut into 25 mm diameter disks. Individual disks were weighed to the nearest milligram and exposed to an excess of liquid solvent (cyclohexane, hexane, Isopar™ C, and Isopar™ M, the latter two both products and registered trademarks of Exxon Chemical) in small glass culture dishes. At various time intervals, the disks were removed with tweezers, dabbed to remove surface bulk solvent with an absorbent wiper, and weighed. The percent weight increase from solvent absorption was calculated and plotted versus time (Table 1). From these data it is clear that cyclohexane causes a rapid swelling of the polymer composition, followed by hexane, Isopar™ C and Isopar™ M. This allows tailoring of the swelling agent to the residence time of the sulfonation process, and allows sulfonation in either a continuous (low residence time therefore requires rapid swelling) or batch (longer residence time, slower swelling processes available) process.

Example 1a, b, and c

[0195] Disks (5 mil thick; 25 mm diameter) prepared from extruded film of ESI 1 were placed in 4 ounce glass vials followed by 25 ml of swelling solvents (hexanes, Isopar C, Isopar M). The disks were allowed to swell for 15 minutes; followed by addition of an equivalent volume of 30 percent oleum. The oleum formed a separate lower phase to the swelling solvent; the disk remained at the interface between the two fluids. After 5 minutes, the disks were removed with tweezers from the vial and immersed into 1 Normal aqueous sodium hydroxide in a beaker. Immediate, significant expansion (1.25-1.75× original diameter) of the disk resulted with voids observed in the core of the disk. The samples soaked in the caustic solution for 10 minutes followed by soaking in deionized water for 10 minutes. The disks were then placed in small glass petri dishes and dried at ambient temperature for 15 hours, followed by weighing.

[0196] Excess deionized water was added to the dried sulfonated disks in the petri dishes (total-immersion) for 30 minutes, followed by placing each swollen disk between several plies of absorbent towels and pressure from two fingers (approximately one kilogram) applied to the disks. This surface water removal process was repeated with fresh towels until no transfer of water was observed on the towels (2-3×). The samples were weighed and percent increase in water weight determined (Table 3).

TABLE 3

Percent Increase in Water Weight		
Example No.	Solvent	Percent Water Gain
1a	Hexanes	40
1b	Isopar C	182
1c	Isopar M	26

Example 2a, b, c

[0197] Using procedure as described in Example 1, three ESI 1 disks (Examples 2 a,b,c) were exposed to 15 minutes of hexane solvent followed by 5, 10, and 15 minutes of 30 percent oleum exposure, respectively. After neutralization and drying, the weight gain was 7, 18, and 24 percent, respectively. Using procedure as described in Example 1, sulfonated disks (Exs 2a,b,c), after water exposure gained 109, 143, and 231 percent weight, respectively. The percent weight increase from sulfonation/neutralization versus water uptake is shown in Table 4.

TABLE 4

Percent Weight Increase From Sulfonation/Neutralization Versus Water Uptake			
Example	percent weight gain	percent conversion ^a	Mol percent sulfonated styrene content
2a	7	10	4.5
2b	18	24	10.8
2c	24	33	15.0

^apercent conversion = the percentage of the aromatic content of the aromatic groups converted to sulfonated aromatic, on a scale of 0 to 100. Thus; percent Conversion = [(percent weight gain)(MWs)]/[MW_{sss} - MWs)(Sf)] × 100/1; where MW_{sss} = sodium styrene sulfonate molecular weight, MWs = styrene molecular weight, Sf = weight fraction of styrene in ESI

Example 3a, b, and c

[0198] A round bicomponent fiber (1000 Denier; 72 monofilaments; tenacity=2.5 g/denier) was prepared by coextruding 30 wt percent polypropylene (PP1) as the core; and 70 wt percent ESI 2 as the shell. The fibers were fabricated using two 1.25 inch diameter extruders which fed two gear pumps each pumping at a rate of 6 cm³/rev. The gear pumps pushed the material through a spin pack containing a filter and a multiple hole spinneret. The spin head temperature was typically from about 285° C., and varied depending upon the melting point and degradation temperature of the polymer components being spun. Generally the higher the molecular weight of the polymers, the higher the melt temperature. Quench air (about 10° C.) was used to help the melt spun fibers cool. The quench air was located just below the spinneret and blows air perpendicularly across the length of the fibers as they are extruded. The fibers were collected on a series of godet rolls to produce the yarn. The first godet located about 2.5 meters below the spinneret die and having a diameter of about 6 inches (15.24 cm).

[0199] The fiber was tested on an Instron tensile testing device equipped with a small plastic jaw on the cross-head (the jaw has a weight of about six gms) and a 500 gram load cell. The jaws are set 1 inch (2.54 cm) apart. The cross head

speed is set at 5 inches/minute (12.7 cm/minute). A single fiber is loaded into the Instron jaws for testing. The fiber is then stretched to 100 percent of strain (i.e., it is stretched another 1 inch), where the tenacity is recorded. The fiber is allowed to return to the original Instron setting (where the jaws are again 1 inch apart) and the fiber is again pulled. At the point where the fiber begins to provide stress resistance, the strain is recorded and the percent permanent set is calculated. Thus, a fiber pulled for the second time which did not provide stress resistance (i.e., pull a load) until it had traveled 0.1 inches (0.25 cm) would have a percent permanent set is of 10 percent, i.e., the percent of strain at which the fiber begins to provide stress resistance. The numerical difference between the percent permanent set and 100 percent is known as the percent elastic recovery. Thus, a fiber having a permanent set of 10 percent will have a 90 percent elastic recovery. After recording percent permanent set, the fiber is pulled to 100 percent strain and the tenacity recorded. The fiber pulling process is repeated several times, with the percent permanent set recorded each time and the 100 percent strain tenacity recorded as well. Finally, the fiber is pulled to its breaking point and the ultimate breaking tenacity and elongation recorded.

[0200] The tow was cut into 1.5-2.5 cm lengths, then placed in a Waring Blender, combined with water (ca 500 grams water/100 grams chopped tow) and stirred at high speed for 2 minutes. The fibrillated chopped tow was then dried in a forced air oven overnight at 50° C. Fibrillated chopped tow was placed into three 6 inch long by 1 inch diameter open cylinder made from coarse stainless screen material. The screens were then sequentially (as defined below) immersed in a series of beakers containing excess hexane swelling agent, 30 percent oleum, 100 percent sulfuric acid, 50 percent sulfuric acid, 1 normal aqueous sodium hydroxide for the indicated times.

[0201] All samples were then filtered on a coarse glass filter and washed with excess deionized water, followed by drying overnight at 50° C. in a forced air oven to constant weight. The samples were then evaluated for moisture gain using the procedure as described in Example 2. The sulfonation times and moisture gain data are summarized in Table 5.

TABLE 5

Sulfonation Times and Moisture Gain Data						
Example	Hexane (sec)	30 percent oleum (sec)	100 percent Sulfuric Acid (sec)	50 percent Sulfuric Acid (sec)	Aq. NaOH (min)	Moisture Gain (percent)
3a	0	30	30	30	2	90
3b	0	60	30	30	2	150
3c	20	20	30	30	2	520

What is claimed is:

1. A bicomponent fiber comprising an inner core and an outer sheath; wherein said inner core or said outer core sheath can comprises one or more sulfonated substantially random interpolymers wherein said bicomponent fiber can absorb at least 50% of the total weight of the sulfonated substantially random interpolymers of water.

2. A bicomponent fiber comprising an inner core and an outer sheath of claim 2 wherein;

(A) said inner core comprises from 25 to 80 wt percent (based on the total fiber weight) of one or more propylene homopolymers or copolymers; and

(B) said outer sheath comprises from 20 to 75 wt percent (based on the total fiber weight) of a composition comprising

1) from 10 to 100 wt percent of one or more sulfonated substantially random interpolymers comprising units derived from;

a) from 35 to 98.5 mol percent ethylene and/or one or more alpha olefins;

b) from 1.5 to 65 mol percent of one or more sulfonated vinyl aromatic monomers which are mono substituted with either a sulfonic acid group or a sulfonic acid salt;

c) from 0 to 63.5 mol percent of one or more vinyl aromatic monomers; and

2) from 0 to 90 wt percent of one or more polymers other than said sulfonated substantially random interpolymers,

wherein said bicomponent fiber is able to absorb at least 50% of the total sulfonated substantially random interpolymers of the outer sheath weight of water.

3. A bicomponent fiber of claim 2 wherein;

A) said inner core comprises from 25 to 80 wt percent (based on the total fiber weight) of one or more propylene homopolymers or copolymers; and

B) said outer sheath comprises from 20 to 75 wt percent (based on the total fiber weight) of a composition comprising

1) from 10 to 50 wt percent of one or more sulfonated substantially random interpolymers comprising units derived from;

a) from 35 to 98.5 mol percent ethylene and/or one or more alpha olefins;

b) from 1.5 to 65 mol percent of one or more sulfonated vinyl aromatic monomers which are mono substituted with either a sulfonic acid group or a sulfonic acid salt;

c) from 0 to 63.5 mol percent of one or more vinyl aromatic monomers; and

2) from 50 to 90 wt percent of one or more polymers other than said sulfonated substantially random interpolymer.

4. The bicomponent fiber of claim claims 1-3, wherein the sheath has a higher softening and melting point than the core material.

5. The bicomponent fiber of claim claims 1-3, wherein the sheath material has a lower softening and melting point than the core material.

6. An absorbent fabricated article comprising

1) one or more sulfonated substantially random interpolymers comprising units derived from;

a) from 35 to 98.5 mol percent ethylene and/or one or more alpha olefins;

b) from 1.5 to 65 mol percent of one or more sulfonated vinyl aromatic monomers;

c) from 0 to 63.5 mol percent of one or more vinyl aromatic monomers; and

2) one or more other polymers,

wherein said absorbent fabricated article is able to absorb at least 50% of the total polymer weight of water.

7. The absorbent fabricated article of claim 6 is in the form of a diaper, sanitary napkins or an adult incontinence article.

8. The absorbent fabricated article of claim 7, wherein the article comprises at least one acquisition distribution layer, a binder material or a plurality of binder fibers, an absorbent core material, or a topsheet/backsheet.

9. The absorbent fabricated article of claim 8, wherein the absorbent core material comprises multilobal shaped fibers to provide wicking.

10. The absorbent fabricated article of claim 8, wherein the acquisition distribution layer comprises a foam material or nonwoven material.

11. The absorbent fabricated article of claim 8, wherein the acquisition distribution layer comprises a foam material and a nonwoven material.

12. The absorbent fabricated article of claim claims 10 and 11, wherein the nonwoven material comprises carded, air laid, or wet laid structures from staple fibers.

13. The absorbent fabricated article of claim claims 10 and 11, wherein the nonwoven material comprises curly, self crimping, bicomponent, multicomponent, tip trilobal, bonded multiconstituent, microfiber, capillary or hollow fibers.

14. The absorbent fabricated article of claim claims 10 and 11, wherein the nonwoven material comprises surface treated fibers.

15. The absorbent fabricated article of claim 14, wherein the surface treated fibers are prepared by a surface treatment which includes plasma, corona, sulfonation or azide treatment.

16. A method of absorbing an aqueous liquid comprising the steps of:

placing the fabricated article of claim 6 in contact with an aqueous liquid.

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