monovinylarenes include, styrene, alpha-methylstyrene, 2-methylstyrene, 3-methylstyrene, 4-methylstyrene, 2-ethylstyrene, 3-ethylstyrene, 4-ethylstyrene, ~~4-n-propylstyrene~~, 4-t-butylstyrene, ~~2,4-dimethylstyrene~~, 4-cyclohexylstyrene, 4-decylstyrene, 2-ethyl-4-benzylstyrene, 4-(4-phenyl-n-butyl)styrene, 1-vinylnaphthalene, 2-vinylnaphthalene, and mixtures thereof. In one embodiment, the monovinylarene is styrene. A unit of a polymer, wherein the unit is derived from polymerization of a monovinylarene monomer, is a "monovinylarene unit."

[0013] In the polymer of the present invention, the monovinylarene-conjugated diene mixed blocks contain conjugated diene units and monovinylarene units. The monovinylarene-conjugated diene mixed blocks may be random or tapered. The mixed block is "tapered" when both (a) the mole fraction of conjugated diene units in a first section of the block is higher than the mole fraction of conjugated diene units in a second section of the block, wherein the second section of the block is closer to a given end of the block and (b) condition (a) is true for substantially all sections of the block. (Depending on the size of the sections being considered, condition (a) may not be true for all sections, but if so, will be not true at no more than about the level expected by chance).

[0014] In one embodiment, each mixed block contains conjugated diene units and monovinylarene units in a weight ratio of 0.06 to 0.28. In another embodiment, each mixed block contains conjugated diene units and monovinylarene units in a weight ratio of 0.08 to 0.26. In another embodiment, each mixed block contains conjugated diene units and monovinylarene units in a weight ratio of 0.05 to 0.09. While not wishing to be limited by theory, it is believed that having each mixed block contain the specified weight ratios of conjugated diene units and monovinylarene units provides monovinylarene-conjugated diene copolymers possessing a glass transition temperature below 100°C which are suitable for applications requiring heat shrinkability.

[0015] In one embodiment, the monovinylarene-conjugated diene block copolymer contains at least three monovinylarene-conjugated diene mixed blocks. In a further embodiment, the monovinylarene-conjugated diene block copolymer contains four or five monovinylarene-conjugated diene mixed blocks.

[0016] In one embodiment, the monovinylarene-conjugated diene block copolymer contains four consecutive monovinylarene-conjugated diene mixed blocks. In a further embodiment, the monovinylarene-conjugated diene block copolymer contains five consecutive monovinylarene-conjugated diene mixed blocks.

[0017] In addition to the plurality of mixed blocks described above, the monovinylarene-conjugated diene block copolymer can further contain blocks of monovinylarene units, conjugated diene units, random monovinylarene-conjugated diene, stepwise monovinylarene-conjugated diene, mixed monovinylarene-conjugated diene containing more conjugated diene units than a conjugated diene/monovinylarene weight ratio of 0.33, and other monomers, either alone, in copolymeric blocks, or in combination with monovinylarene units, conjugated diene units, or both.

[0018] In one embodiment, the monovinylarene-conjugated diene block copolymer further contains a proximal conjugated diene block. In this context, "proximal" refers to a position nearer the terminal end of the block copolymer than the initial end. In one embodiment, the proximal conjugated diene block contains from 5 phm conjugated diene units to 50 phm conjugated diene units, relative to the total amount of monovinylarene units and conjugated diene units in the monovinylarene-conjugated diene block copolymer. In another embodiment, the proximal conjugated diene block contains from 10 phm conjugated diene units to 35 phm conjugated diene units. In a further embodiment, the proximal conjugated diene block contains from 11 phm conjugated diene units to 25 phm conjugated diene units. While not wishing to be limited by theory, it is believed that having a proximal conjugated diene block containing the specified amount of conjugated diene units provides impact resistance to the monovinylarene-conjugated diene copolymer and blends thereof.

[0019] In another embodiment, the monovinylarene-conjugated diene block copolymer further contains a distal monovinylarene block. In this context, "distal" refers to a position nearer the initial end of the block copolymer than the terminal end. In one embodiment, the distal monovinylarene block contains from 10 phm monovinylarene units to 40 phm monovinylarene units, relative to the total amount of monovinylarene units and conjugated diene units in the monovinylarene-conjugated diene block copolymer. In a further embodiment, the distal monovinylarene block contains from 15 phm monovinylarene units to 35 phm monovinylarene units.

[0020] In one embodiment, the monovinylarene-conjugated diene copolymer is a block copolymer comprising styrene blocks and butadiene blocks (a "styrene-butadiene block copolymer"). Exemplary styrene-butadiene copolymers are commercially available under the name K-Resin® (Chevron Phillips Chemical Company, LP, The Woodlands, TX).

[0021] The monovinylarene-conjugated diene copolymer can have any proportion of monovinylarene units and conjugated diene units. In one embodiment, the monovinylarene-conjugated diene copolymer has from 50 wt%:50 wt% monovinylarene units:conjugated diene units to 90 wt%:10 wt% monovinylarene units:conjugated diene units. In one embodiment, the monovinylarene-conjugated diene copolymer has from 65 wt%:35 wt% monovinylarene units:conjugated diene units to 85 wt%:15 wt% monovinylarene units:conjugated diene units.

[0022] The monovinylarene-conjugated diene copolymer can further comprise other monomers known in the art for inclusion in monovinylarene-conjugated diene copolymers.

[0023] Generally, each block is formed by polymerizing the monomer or mixture of monomers from which the desired units of the block are derived. The polymerization process will generally be amenable to a relative lack of change in

However, more or less than stoichiometric amounts can be used for varying coupling efficiency where desired for particular products.

[0037] Following completion of the coupling reaction, if any, the polymerization reaction mixture can be treated with a terminating agent such as water, carbon dioxide, alcohol, phenols, linear saturated aliphatic mono-dicarboxylic acids, or mixtures thereof, to remove alkali metal from the block copolymer or for color control.

[0038] After termination, if any, the polymer cement (polymer in polymerization solvent) usually contains 10 to 40 weight percent solids, more usually 20 to 35 weight percent solids. The polymer cement can be flashed to evaporate a portion of the solvent so as to increase the solids content to a concentration of 50 to 99 weight percent solids, followed by vacuum oven drying, a devolatilizing extruder, a wiped film evaporator, or other methods of removing the remaining solvent.

[0039] The block copolymer can be recovered and worked into a desired shape, such as by sheet extrusion, cast film extrusion, blown film, or injection molding. The block copolymer can also contain additives such as antioxidants, anti-blocking agents, release agents, fillers, extenders, and dyes.

[0040] In an embodiment, the monovinylarene-conjugated diene copolymer further comprises a rubber modified polystyrene. An exemplary rubber modified polystyrene is a high-impact polystyrene (HIPS). A rubber modified polystyrene is a composition comprising any graft copolymer of styrene and rubber. By "graft copolymer" is meant polystyrene produced by polymerizing styrene in the presence of an unsaturated rubber wherein some amount of free radicals react with the rubber producing polystyrene chains that are covalently bonded to the rubber. During this process the rubber, grafted with polystyrene, becomes dispersed throughout the polystyrene in the form of discrete domains. In one embodiment the unsaturated rubber is polybutadiene. A suitable high-impact polystyrene is available from Chevron Phillips Chemical Company LP (The Woodlands, TX) with the designation EA8100. Generally, a composition further comprising a rubber modified polystyrene can contain from 0.1 phm rubber modified polystyrene to 5 phm rubber modified polystyrene, such as about 2 phm rubber modified polystyrene The rubber modified polystyrene may be used in some embodiments as an antiblocking agent.

[0041] In the present invention, the monovinylarene-conjugated diene block copolymer can be monomodal, that is, a population of copolymer molecules can have one peak in a histogram of the population's molecular weight distribution, or it can be polymodal, that is, have two or more peaks in a histogram of the copolymer molecules' population's molecular weight distribution. Though not to be bound by theory, the charging of multiple initiator charges will tend to yield polymer chains of different lengths and thus will tend to have different molecular weights. In addition, and again not to be bound by theory, use of a coupling agent will tend to yield coupled chains formed by coupling different numbers of chains of the same or different lengths, and thus the coupled chains will tend to have different molecular weights.

[0042] In the present invention, the monovinylarene-conjugated diene copolymer can be coupled or uncoupled, as described above.

[0043] In specific polymerization processes, typical initiator, monomer and monomer mixture charge sequences include, but are not limited, charge orders selected from the group consisting of i-C-C-i-C-B-CA, i-C-C-C-i-C-C-B-CA, i-A-C-C-C-C-B-CA, i-A-i-C-C-C-C-B-CA, i-A-i-C-C-C-C-C-CA, ~~i-A-i-C-C-C-C-C-B-CA~~, and i-A-C-C-i-C-C-B-CA, wherein i is a polymerization initiator charge, A is a monovinylarene charge, B is a conjugated diene charge, C is a monovinylarene and conjugated diene charge, and CA is a coupling agent. In a further embodiment, charge order is selected from the group consisting of i-C-C-i-C-B-CA, i-C-C-C-i-C-C-B-CA, i-A-C-C-C-C-B-CA, i-A-i-C-C-C-C-B-CA, i-A-i-C-C-C-C-C-B-CA, and i-A-C-C-i-C-C-B-CA.

[0044] In one embodiment, the conjugated diene-monovinylarene block copolymer can be formed into a film or a sheet. A typical extruded sheet can have a thickness of about 10 mils. In a further embodiment, a sheet can be stretched in at least one direction at a temperature from 50°C to 100°C, such as 90°C to form a film having a thickness of 0.5 mil to 3 mil, such as 2 mil. In this embodiment, the film formed from the conjugated diene-monovinylarene block copolymer may have a shrinkage in at least one direction of at least 40% at 100°C. In one embodiment, the film formed from the conjugated diene-monovinylarene block copolymer may have a shrinkage in at least one direction of at least 60% at 100°C, such as at least 70% at 100°C, such as from 71% to 76% at 100°C. Also, the film formed from the conjugated diene-monovinylarene block copolymer may have a haze of less than 10%. In one embodiment, the film formed from the conjugated diene-monovinylarene block copolymer may have a haze of less than 6%. Also, the film formed from the conjugated diene-monovinylarene block copolymer may have a natural shrinkage of less than 10% after 7 days. In one embodiment, the film formed from the conjugated diene-monovinylarene block copolymer may have a natural shrinkage of less than 7% after 7 days.

[0045] In another embodiment, the present invention relates to a composition containing (a) from 50 parts by weight to 95 parts by weight of a monovinylarene-conjugated diene block copolymer comprising a plurality of monovinylarene-conjugated diene mixed blocks, wherein each mixed block contains conjugated diene and monovinylarene in a weight ratio of 0.05 to 0.33; and (b) from 5 parts by weight to 50 parts by weight of polystyrene; wherein the monovinylarene-conjugated diene block copolymer and the polystyrene total 100 parts by weight.

[0046] The block copolymer can be as described above. As used herein, "polystyrene" or "PS" refers to any homopol-

monovinylarenes include, styrene, alpha-methylstyrene, 2-methylstyrene, 3-methylstyrene, 4-methylstyrene, 2-ethylstyrene, 3-ethylstyrene, 4-ethylstyrene, 4-n-propylstyrene, 4-t-butylstyrene, 2,4-dimethylstyrene, 4-cyclohexylstyrene, 4-decylstyrene, 2-ethyl-4-benzylstyrene, 4-(4-phenyl-n-butyl)styrene, 1-vinylnaphthalene, 2-vinylnaphthalene, and mixtures thereof. In one embodiment, the monovinylarene is styrene. A unit of a polymer, wherein the unit is derived from polymerization of a monovinylarene monomer, is a "monovinylarene unit."

[0013] In the polymer of the present invention, the monovinylarene-conjugated diene mixed blocks contain conjugated diene units and monovinylarene units. The monovinylarene-conjugated diene mixed blocks may be random or tapered. The mixed block is "tapered" when both (a) the mole fraction of conjugated diene units in a first section of the block is higher than the mole fraction of conjugated diene units in a second section of the block, wherein the second section of the block is closer to a given end of the block and (b) condition (a) is true for substantially all sections of the block. (Depending on the size of the sections being considered, condition (a) may not be true for all sections, but if so, will be not true at no more than about the level expected by chance).

[0014] In one embodiment, each mixed block contains conjugated diene units and monovinylarene units in a weight ratio of 0.06 to 0.28. In another embodiment, each mixed block contains conjugated diene units and monovinylarene units in a weight ratio of 0.08 to 0.26. In another embodiment, each mixed block contains conjugated diene units and monovinylarene units in a weight ratio of 0.05 to 0.09. While not wishing to be limited by theory, it is believed that having each mixed block contain the specified weight ratios of conjugated diene units and monovinylarene units provides monovinylarene-conjugated diene copolymers possessing a glass transition temperature below 100°C which are suitable for applications requiring heat shrinkability.

[0015] In one embodiment, the monovinylarene-conjugated diene block copolymer contains at least three monovinylarene-conjugated diene mixed blocks. In a further embodiment, the monovinylarene-conjugated diene block copolymer contains four or five monovinylarene-conjugated diene mixed blocks.

[0016] In one embodiment, the monovinylarene-conjugated diene block copolymer contains four consecutive monovinylarene-conjugated diene mixed blocks. In a further embodiment, the monovinylarene-conjugated diene block copolymer contains five consecutive monovinylarene-conjugated diene mixed blocks.

[0017] In addition to the plurality of mixed blocks described above, the monovinylarene-conjugated diene block copolymer can further contain blocks of monovinylarene units, conjugated diene units, random monovinylarene-conjugated diene, stepwise monovinylarene-conjugated diene, mixed monovinylarene-conjugated diene containing more conjugated diene units than a conjugated diene/monovinylarene weight ratio of 0.33, and other monomers, either alone, in copolymeric blocks, or in combination with monovinylarene units, conjugated diene units, or both.

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[0019] In another embodiment, the monovinylarene-conjugated diene block copolymer further contains a distal monovinylarene block. In this context, "distal" refers to a position nearer the initial end of the block copolymer than the terminal end. In one embodiment, the distal monovinylarene block contains from 10 phm monovinylarene units to 40 phm monovinylarene units, relative to the total amount of monovinylarene units and conjugated diene units in the monovinylarene-conjugated diene block copolymer. In a further embodiment, the distal monovinylarene block contains from 15 phm monovinylarene units to 35 phm monovinylarene units.

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[0021] The monovinylarene-conjugated diene copolymer can have any proportion of monovinylarene units and conjugated diene units. In one embodiment, the monovinylarene-conjugated diene copolymer has from 50 wt%:50 wt% monovinylarene units:conjugated diene units to 90 wt%:10 wt% monovinylarene units:conjugated diene units. In one embodiment, the monovinylarene-conjugated diene copolymer has from 65 wt%:35 wt% monovinylarene units:conjugated diene units to 85 wt%:15 wt% monovinylarene units:conjugated diene units.

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However, more or less than stoichiometric amounts can be used for varying coupling efficiency where desired for particular products.

[0037] Following completion of the coupling reaction, if any, the polymerization reaction mixture can be treated with a terminating agent such as water, carbon dioxide, alcohol, phenols, linear saturated aliphatic mono-dicarboxylic acids, or mixtures thereof, to remove alkali metal from the block copolymer or for color control.

[0038] After termination, if any, the polymer cement (polymer in polymerization solvent) usually contains 10 to 40 weight percent solids, more usually 20 to 35 weight percent solids. The polymer cement can be flashed to evaporate a portion of the solvent so as to increase the solids content to a concentration of 50 to 99 weight percent solids, followed by vacuum oven drying, a devolatilizing extruder, a wiped film evaporator, or other methods of removing the remaining solvent.

[0039] The block copolymer can be recovered and worked into a desired shape, such as by sheet extrusion, cast film extrusion, blown film, or injection molding. The block copolymer can also contain additives such as antioxidants, anti-blocking agents, release agents, fillers, extenders, and dyes.

[0040] In an embodiment, the monovinylarene-conjugated diene copolymer further comprises a rubber modified polystyrene. An exemplary rubber modified polystyrene is a high-impact polystyrene (HIPS). A rubber modified polystyrene is a composition comprising any graft copolymer of styrene and rubber. By "graft copolymer" is meant polystyrene produced by polymerizing styrene in the presence of an unsaturated rubber wherein some amount of free radicals react with the rubber producing polystyrene chains that are covalently bonded to the rubber. During this process the rubber, grafted with polystyrene, becomes dispersed throughout the polystyrene in the form of discrete domains. In one embodiment the unsaturated rubber is polybutadiene. A suitable high-impact polystyrene is available from Chevron Phillips Chemical Company LP (The Woodlands, TX) with the designation EA8100. Generally, a composition further comprising a rubber modified polystyrene can contain from 0.1 phm rubber modified polystyrene to 5 phm rubber modified polystyrene, such as about 2 phm rubber modified polystyrene The rubber modified polystyrene may be used in some embodiments as an antiblocking agent.

[0041] In the present invention, the monovinylarene-conjugated diene block copolymer can be monomodal, that is, a population of copolymer molecules can have one peak in a histogram of the population's molecular weight distribution, or it can be polymodal, that is, have two or more peaks in a histogram of the copolymer molecules' population's molecular weight distribution. Though not to be bound by theory, the charging of multiple initiator charges will tend to yield polymer chains of different lengths and thus will tend to have different molecular weights. In addition, and again not to be bound by theory, use of a coupling agent will tend to yield coupled chains formed by coupling different numbers of chains of the same or different lengths, and thus the coupled chains will tend to have different molecular weights.

[0042] In the present invention, the monovinylarene-conjugated diene copolymer can be coupled or uncoupled, as described above.

[0043] In specific polymerization processes, typical initiator, monomer and monomer mixture charge sequences include, but are not limited, charge orders selected from the group consisting of i-C-C-i-C-B-CA, i-C-C-C-i-C-C-B-CA, i-A-C-C-C-C-B-CA, i-A-i-C-C-C-C-B-CA, i-A-i-C-C-C-C-CA, i-A-i-C-C-C-C-C-B-CA, and i-A-C-C-i-C-C-B-CA, wherein i is a polymerization initiator charge, A is a monovinylarene charge, B is a conjugated diene charge, C is a monovinylarene and conjugated diene charge, and CA is a coupling agent. In a further embodiment, charge order is selected from the group consisting of i-C-C-i-C-B-CA, i-C-C-C-i-C-C-B-CA, i-A-C-C-C-C-B-CA, i-A-i-C-C-C-C-B-CA, i-A-i-C-C-C-C-C-B-CA, and i-A-C-C-i-C-C-B-CA.

[0044] In one embodiment, the conjugated diene-monovinylarene block copolymer can be formed into a film or a sheet. A typical extruded sheet can have a thickness of about 10 mils. In a further embodiment, a sheet can be stretched in at least one direction at a temperature from 50°C to 100°C, such as 90°C to form a film having a thickness of 0.5 mil to 3 mil, such as 2 mil. In this embodiment, the film formed from the conjugated diene-monovinylarene block copolymer may have a shrinkage in at least one direction of at least 40% at 100°C. In one embodiment, the film formed from the conjugated diene-monovinylarene block copolymer may have a shrinkage in at least one direction of at least 60% at 100°C, such as at least 70% at 100°C, such as from 71% to 76% at 100°C. Also, the film formed from the conjugated diene-monovinylarene block copolymer may have a haze of less than 10%. In one embodiment, the film formed from the conjugated diene-monovinylarene block copolymer may have a haze of less than 6%. Also, the film formed from the conjugated diene-monovinylarene block copolymer may have a natural shrinkage of less than 10% after 7 days. In one embodiment, the film formed from the conjugated diene-monovinylarene block copolymer may have a natural shrinkage of less than 7% after 7 days.

[0045] In another embodiment, the present invention relates to a composition containing (a) from 50 parts by weight to 95 parts by weight of a monovinylarene-conjugated diene block copolymer comprising a plurality of monovinylarene-conjugated diene mixed blocks, wherein each mixed block contains conjugated diene and monovinylarene in a weight ratio of 0.05 to 0.33; and (b) from 5 parts by weight to 50 parts by weight of polystyrene; wherein the monovinylarene-conjugated diene block copolymer and the polystyrene total 100 parts by weight.

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