

METHODS FOR SEPARATING SLURRY COMPONENTS

FIELD OF INVENTION

[0001] The invention relates to methods for separating slurry components. In particular, the invention relates to the concentration of polymer particles in a slurry from the polymerization of C₄-C₇ isoolefins.

BACKGROUND

[0002] Isoolefin polymers are prepared in carbocationic polymerization processes. The carbocationic polymerization of isobutylene and its copolymerization with comonomers like isoprene is mechanistically complex. See, e.g., Organic Chemistry, SIXTH EDITION, Morrison and Boyd, Prentice-Hall, 1084-1085, Englewood Cliffs, New Jersey 1992, and K. Matyjaszewski, ed, Cationic Polymerizations, Marcel Dekker, Inc., New York, 1996. The catalyst system is typically composed of two components: an initiator and a Lewis acid. Examples of Lewis acids include AlCl₃ and BF₃. Examples of initiators include Brønsted acids such as HCl, RCOOH (wherein R is an alkyl group), and H₂O. During the polymerization process, in what is generally referred to as the initiation step, isobutylene reacts with the Lewis acid/initiator pair to produce a carbenium ion. Following, additional monomer units add to the formed carbenium ion in what is generally called the propagation step. These steps typically take place in a diluent or solvent. Temperature, diluent polarity, and counterions affect the chemistry of propagation. Of these, the diluent is typically considered important.

[0003] Industry has generally accepted widespread use of a slurry polymerization process (to produce butyl rubber, polyisobutylene, etc.) in the diluent methyl chloride. Typically, the polymerization process extensively uses methyl chloride at low temperatures, generally lower than -90°C, as the diluent for the reaction mixture. Methyl chloride is employed for a variety of reasons, including that it dissolves the monomers and aluminum chloride catalyst but not

the polymer product. Methyl chloride also has suitable freezing and boiling points to permit, respectively, low temperature polymerization and effective separation from the polymer and unreacted monomers. The slurry polymerization process in methyl chloride offers a number of additional advantages in that a polymer concentration of approximately 26% to 37% by volume in the reaction mixture can be achieved, as opposed to the concentration of only about 8% to 12% in solution polymerization. An acceptable relatively low viscosity of the polymerization mass is obtained enabling the heat of polymerization to be removed more effectively by surface heat exchange. Slurry polymerization processes in methyl chloride are used in the production of high molecular weight polyisobutylene and isobutylene-isoprene butyl rubber polymers. Likewise polymerizations of isobutylene and para-methylstyrene are also conducted using methyl chloride. Similarly, star-branched butyl rubber is also produced using methyl chloride.

[0004] However, there are a number of problems associated with the polymerization in methyl chloride, for example, the tendency of the polymer particles in the reactor to agglomerate with each other and to collect on the reactor wall, heat transfer surfaces, impeller(s), and the agitator(s)/pump(s). The rate of agglomeration increases rapidly as reaction temperature rises. Agglomerated particles tend to adhere to and grow and plate-out on all surfaces they contact, such as reactor discharge lines, as well as any heat transfer equipment being used to remove the exothermic heat of polymerization, which is critical since low temperature reaction conditions must be maintained.

[0005] The commercial reactors typically used to make these rubbers are well mixed vessels of greater than 10 to 30 liters in volume with a high circulation rate provided by a pump impeller. The polymerization and the pump both generate heat and, in order to keep the slurry cold, the reaction system needs to have the ability to remove the heat. An example of such a continuous flow stirred tank reactor ("CFSTR") is found in U.S. Patent No. 5,417,930, incorporated by reference, hereinafter referred to in general as a "reactor" or "butyl reactor". In

these reactors, slurry is circulated through tubes of a heat exchanger by a pump, while boiling ethylene on the shell side provides cooling, the slurry temperature being determined by the boiling ethylene temperature, the required heat flux and the overall resistance to heat transfer. On the slurry side, the heat exchanger surfaces progressively accumulate polymer, inhibiting heat transfer, which would tend to cause the slurry temperature to rise. This often limits the practical slurry concentration that can be used in most reactors from 26 to 37 volume % relative to the total volume of the slurry, diluent, and unreacted monomers. The subject of polymer accumulation has been addressed in several patents (such as U.S. Patent No. 2,534,698, U.S. Patent No. 2,548,415, U.S. Patent No. 2,644,809). However, these patents have unsatisfactorily addressed the myriad of problems associated with polymer particle agglomeration for implementing a desired commercial process.

[0006] U.S. Patent No. 2,534,698 discloses, *inter alia*, a polymerization process comprising the steps in combination of dispersing a mixture of isobutylene and a polyolefin having 4 to 14 carbon atoms per molecule, into a body of a fluorine substituted aliphatic hydrocarbon containing material without substantial solution therein, in the proportion of from one-half part to 10 parts of fluorine substituted aliphatic hydrocarbon having from one to five carbon atoms per molecule which is liquid at the polymerization temperature and polymerizing the dispersed mixture of isobutylene and polyolefin having four to fourteen carbon atoms per molecule at temperatures between -20°C and -164°C by the application thereto a Friedel-Crafts catalyst. However, '698 teaches that the suitable fluorocarbons would result in a biphasic system with the monomer, comonomer and catalyst being substantially insoluble in the fluorocarbon making their use difficult and unsatisfactory.

[0007] U.S. Patent No. 2,548,415 discloses, *inter alia*, a continuous polymerization process for the preparation of a copolymer, the steps comprising continuously delivering to a polymerization reactors a stream consisting of a major proportion of isobutylene and a minor proportion isoprene; diluting the

mixture with from 1/2 volume to 10 volumes of ethylidene difluoride; copolymerizing the mixture of isobutylene isoprene by the continuous addition to the reaction mixture of a liquid stream of previously prepared polymerization catalyst consisting of boron trifluoride in solution in ethylidene difluoride, maintaining the temperature between -40°C and -103°C throughout the entire copolymerization reaction '415 teaches the use of boron trifluoride and its complexes as the Lewis acid catalyst and 1,1-difluoroethane as a preferred combination. This combination provides a system in which the catalyst, monomer and comonomer are all soluble and yet still affords a high degree of polymer insolubility to capture the benefits of reduced reactor fouling. However, boron trifluoride is not a preferred commercial catalyst for butyl polymers for a variety of reasons.

[0008] U.S. Patent No. 2,644,809 teaches, *inter alia*, a polymerization process comprising the steps in combination of mixing together a major proportion of a monoolefin having 4 to 8, inclusive, carbon atoms per molecule, with a minor proportion of a multiolefin having from 4 to 14, inclusive, carbon atoms per molecule, and polymerizing the resulting mixture with a dissolved Friedel-Crafts catalyst, in the presence of from 1 to 10 volumes (computed upon the mixed olefins) of a liquid selected from the group consisting of dichlorodifluoromethane, dichloromethane, trichloromonofluoromethane, dichloromonofluoromethane, dichlorotetrafluoroethane, and mixtures thereof, the monoolefin and multiolefin being dissolved in said liquid, and carrying out the polymerization at a temperature between -20°C and the freezing point of the liquid. '809 discloses the utility of chlorofluorocarbons at maintaining ideal slurry characteristics and minimizing reactor fouling, but teaches the incorporation of diolefin (i.e. isoprene) by the addition of chlorofluorocarbons (CFC). CFC's are known to be ozone-depleting chemicals. Governmental regulations, however, tightly controls the manufacture and distribution of CFC's making these materials unattractive for commercial operation.

[0009] Additionally, Thaler, W.A., Buckley, Sr., D.J., *High Molecular-Weight, High Unsaturation Copolymers of Isobutylene and Conjugated Dienes*, 49(4) Rubber Chemical Technology, 960 (1976), discloses, *inter alia*, the cationic slurry polymerization of copolymers of isobutylene with isoprene (butyl rubber) and with cyclopentadiene in heptane.

[0010] Therefore, finding alternative diluents or blends of diluents to create new polymerization systems that would reduce particle agglomeration and/or reduce the amount of chlorinated hydrocarbons such as methyl chloride is desirable. Additionally, finding new post-polymerization or "downstream" processes that would exploit such advantages such as improving productivity/efficiency and/or simplicity in downstream design is desirable.

[0011] Among such post-polymerization or "downstream" processes are methods for obtaining polymerized polymer particles, or, alternatively stated, methods for separating or concentrating slurry components such as polymer particles. A few methods have been suggested, see, for example, U.S. Patent No. 2,542,559 and RU 2 209 213 directed to polymers produced using chlorinated hydrocarbons. However, the flashing process using live steam that is traditionally used to separate the methyl chloride diluent and unreacted monomers from the polymer causes a significant energy loss. Thus, chlorinated hydrocarbons such as methyl chloride present many challenges associated with the sticky nature of the polymer particles produced using methyl chloride.

[0012] In the alternative, hydrofluorocarbons (HFC's) are of interest and are currently used as environmentally friendly refrigerants because they have a very low (even zero) ozone depletion potential. Their low ozone depletion potential is thought to be related to the lack of chlorine. The HFC's also typically have low flammability particularly as compared to hydrocarbons and chlorinated hydrocarbons.

[0013] Other background references include WO 02/34794 that discloses a free radical polymerization process using hydrofluorocarbons. Other background references include DE 100 61 727 A, WO 02/096964, WO 00/04061, U.S. Patent No. 5,624,878, U.S. Patent No. 5,527,870, and U.S. Patent No. 3,470,143.

SUMMARY OF THE INVENTION

[0014] The invention provides for methods for separating slurry components. In particular, the invention provides for the concentration of polymer particles in a slurry from the polymerization of C₄-C₇ isoolefins, producing a dilute phase of a diluent comprising one or more hydrofluorocarbon(s) (HFC) and unreacted monomer(s).

[0015] In particular, the invention provides desirable separation methods that separate polymer particles in a slurry to a more concentrated slurry and a dilute phase of diluent comprising one or more hydrofluorocarbon(s) (HFC) and unreacted monomer(s) and a low level of polymer. The dilute phase can then be recycled to the reactor feed allowing for process improvements such as refrigeration energy to be conserved and hence improving process efficiency.

[0016] In an embodiment, the invention provides for a method for separating slurry components, the method comprising obtaining a slurry comprising a diluent comprising one or more hydrofluorocarbon(s) (HFC) and applying an effective amount of force to obtain polymer particles.

[0017] In any of the previous embodiments, the force may be a gravitational force.

[0018] In the previous embodiment, the gravitational force may be 1 G.

[0019] In any of the previous embodiments, the force may be a centrifugal force.

[0020] In any of the previous embodiments, the centrifugal force may be from at least 500 G.

[0021] In any of the previous embodiments, the centrifugal force may be from at least 1,000 G.

[0022] In any of the previous embodiments, the centrifugal force may be from at least 5,000 G.

[0023] In any of the previous embodiments, the centrifugal force may be from at least 10,000 G.

[0024] In any of the previous embodiments, the force applied is provided by a hydrocyclone.

[0025] In another embodiment, the invention provides for a method for separating slurry components, the method comprising providing a first slurry comprising a diluent comprising one or more hydrofluorocarbon(s) (HFC) and passing the first slurry through a device to obtain a second slurry, to obtain polymer particles.

[0026] In the previous embodiment, the second slurry may have a slurry concentration greater than the slurry concentration of the first slurry.

[0027] In any of the previous embodiments, where applicable, the device is a filter.

[0028] In any of the previous embodiments, where applicable, the flow of the first slurry is tangential to the surface of the filter.

[0029] In any of the previous embodiments, where applicable, the filter comprises media having diameters or cross-sections greater than the diameters or cross-sections of the polymer particles.

[0030] In any of the previous embodiments, where applicable, the filter comprises media having diameters or cross-sections less than the diameters or cross-sections of from at least 40% of the polymer particles passing through the filter.

[0031] In any of the previous embodiments, where applicable, the filter comprises media having diameters or cross-sections less than the diameters or cross-sections of from at least 50% of the polymer particles passing through the filter.

[0032] In any of the previous embodiments, where applicable, the filter comprises media having diameters or cross-sections less than the diameters or cross-sections of from at least 60% of the polymer particles passing through the filter.

DETAILED DESCRIPTION

[0033] Various specific embodiments, versions and examples of the invention will now be described, including preferred embodiments and definitions that are adopted herein for purposes of understanding the claimed invention. For determining infringement, the scope of the "invention" will refer to any one or more of the appended claims, including their equivalents, and elements or limitations that are equivalent to those that are recited.

[0034] For purposes of this invention and the claims thereto the term catalyst system refers to and includes any Lewis acid(s) or other metal complex(es) used to catalyze the polymerization of the olefinic monomers of the

invention, as well as at least one initiator, and optionally other minor catalyst component(s).

[0035] In one embodiment, the invention provides a polymerization medium suitable to polymerize one or more monomer(s) to form a polymer, the polymerization medium comprising one or more Lewis acid(s), one or more initiator(s), and a diluent comprising one or more hydrofluorocarbon(s) (HFC's).

[0036] In another embodiment, the invention provides a polymerization medium suitable to polymerize one or more monomer(s) to form a polymer, the polymerization medium comprising one or more Lewis acid(s) and a diluent comprising one or more hydrofluorocarbon(s) (HFC); wherein the one or more Lewis acid(s) is not a compound represented by formula MX_3 , where M is a group 13 metal and X is a halogen.

[0037] The phrase "suitable to polymerize monomers to form a polymer" relates to the selection of polymerization conditions and components, well within the ability of those skilled in the art necessary to obtain the production of a desired polymer in light of process parameters and component properties described herein. There are numerous permutations of the polymerization process and variations in the polymerization components available to produce the desired polymer attributes. In preferred embodiments, such polymers include polyisobutylene homopolymers, isobutylene-isoprene (butyl rubber) copolymers, isobutylene and para-methylstyrene copolymers, and star-branched butyl rubber terpolymers.

[0038] Diluent means a diluting or dissolving agent. Diluent is specifically defined to include chemicals that can act as solvents for the Lewis Acid, other metal complexes, initiators, monomers or other additives. In the practice of the invention, the diluent does not alter the general nature of the components of the polymerization medium, i.e., the components of the catalyst system, monomers, etc. However, it is recognized that interactions between the

diluent and reactants may occur. In preferred embodiments, the diluent does not react with the catalyst system components, monomers, etc. to any appreciable extent. Additionally, the term diluent includes mixtures of at least two or more diluents.

[0039] A reactor is any container(s) in which a chemical reaction occurs.

[0040] Slurry refers to a volume of diluent comprising polymers or polymer particles that have precipitated from the diluent, monomers, and a catalyst system. The slurry concentration is the volume percent of the partially or completely precipitated polymers based on the total volume of the slurry.

[0041] As used herein, the new numbering scheme for the Periodic Table Groups are used as in CHEMICAL AND ENGINEERING NEWS, 63(5), 27 (1985).

[0042] Polymer may be used to refer to homopolymers, copolymers, interpolymers, terpolymers, etc. Likewise, a copolymer may refer to a polymer comprising at least two monomers, optionally with other monomers.

[0043] When a polymer is referred to as comprising a monomer, the monomer is present in the polymer in the polymerized form of the monomer or in the derivative form the monomer. Likewise, when catalyst components are described as comprising neutral stable forms of the components, it is well understood by one skilled in the art, that the ionic form of the component is the form that reacts with the monomers to produce polymers.

[0044] Isobutylene-based polymer refers to polymers comprising at least 80 mol % repeat units from isobutylene.

[0045] Isoolefin refers to any olefin monomer having two substitutions on the same carbon.

[0046] Multiolefin refers to any monomer having two double bonds. In a preferred embodiment, the multiolefin is any monomer comprising two conjugated double bonds such as isoprene.

[0047] Elastomer or elastomeric composition, as used herein, refers to any polymer or composition of polymers consistent with the ASTM D1566 definition. The terms may be used interchangeably with the term "rubber(s)", as used herein.

[0048] Alkyl refers to a paraffinic hydrocarbon group which may be derived from an alkane by dropping one or more hydrogens from the formula, such as, for example, a methyl group (CH_3), or an ethyl group (CH_3CH_2), etc.

[0049] Aryl refers to a hydrocarbon group that forms a ring structure characteristic of aromatic compounds such as, for example, benzene, naphthalene, phenanthrene, anthracene, etc., and typically possess alternate double bonding ("unsaturation") within its structure. An aryl group is thus a group derived from an aromatic compound by dropping one or more hydrogens from the formula such as, for example, phenyl, or C_6H_5 .

[0050] Substituted refers to the replacement of at least one hydrogen group by at least one substituent selected from, for example, halogen (chlorine, bromine, fluorine, or iodine), amino, nitro, sulfoxy (sulfonate or alkyl sulfonate), thiol, alkylthiol, and hydroxy; alkyl, straight or branched chain having 1 to 20 carbon atoms which includes methyl, ethyl, propyl, tert-butyl, isopropyl, isobutyl, etc.; alkoxy, straight or branched chain alkoxy having 1 to 20 carbon atoms, and includes, for example, methoxy, ethoxy, propoxy, isopropoxy, butoxy, isobutoxy, secondary butoxy, tertiary butoxy, pentyloxy, isopentyloxy, hexyloxy, heptyloxy, octyloxy, nonyloxy, and decyloxy; haloalkyl, which means straight or branched chain alkyl having 1 to 20 carbon atoms which is substituted by at least one halogen, and includes, for example, chloromethyl, bromomethyl, fluoromethyl, iodomethyl, 2-chloroethyl, 2-bromoethyl, 2-fluoroethyl, 3-chloropropyl, 3-bromopropyl, 3-fluoropropyl, 4-chlorobutyl, 4-fluorobutyl, dichloromethyl,

dibromomethyl, difluoromethyl, diiodomethyl, 2,2-dichloroethyl, 2,2-dibromomethyl, 2,2-difluoroethyl, 3,3-dichloropropyl, 3,3-difluoropropyl, 4,4-dichlorobutyl, 4,4-difluorobutyl, trichloromethyl, 4,4-difluorobutyl, trichloromethyl, trifluoromethyl, 2,2,2-trifluoroethyl, 2,3,3-trifluoropropyl, 1,1,2,2-tetrafluoroethyl, and 2,2,3,3-tetrafluoropropyl. Thus, for example, a "substituted styrenic unit" includes *p*-methylstyrene, *p*-ethylstyrene, etc.

[0051] In one embodiment, this invention relates to the use of hydrofluorocarbon(s) or blends of hydrofluorocarbon(s) with hydrocarbon(s) and/or chlorinated hydrocarbon(s) to produce a polymer slurry which is less prone to fouling (i.e., also observed more glass like, less sticky particles in the reaction vessel with reduced adherence to the walls of the vessel or to the stirring impeller as well as reduced particle to particle agglomeration). More particularly, this invention relates to the use of hydrofluorocarbon diluent(s) or HFC diluent blends with hydrocarbons and/or chlorinated hydrocarbon blends to polymerize and copolymerize isoolefins with dienes and/or alkylstyrenes to produce isoolefin homopolymers and copolymers with significantly reduced reactor fouling. Further, this invention relates to the use of hydrofluorocarbon diluent(s) or diluent blends with hydrocarbons and/or chlorinated hydrocarbon blends to polymerize and copolymerize isoolefins with dienes to produce isoolefin copolymers with significantly reduced reactor fouling and hence longer run life for the reactors, as compared to conventional systems.

[0052] In one embodiment, this invention relates to the discovery of new polymerization systems using diluents containing hydrofluorocarbons. These diluents effectively dissolve the selected catalyst system and monomers but are relatively poor solvents for the polymer product. Polymerization systems using these diluents are less prone to fouling due to the agglomeration of polymer particles to each other and their depositing on polymerization hardware. In addition, this invention further relates to the use of these diluents in polymerization systems for the preparation of high molecular weight polymers and copolymers at equivalent to or higher than to those polymerization

temperatures using solely chlorinated hydrocarbon diluents such as methyl chloride.

[0053] In another embodiment, this invention relates to the discovery of new polymerization systems using fluorinated aliphatic hydrocarbons capable of dissolving the catalyst system. These polymerization systems are also beneficial for isoolefin slurry polymerization and production of a polymer slurry that is less prone to fouling, while permitting dissolution of monomer, comonomer and the commercially preferred alkylaluminum halide catalysts. In addition, this invention further relates to the use of these diluents for the preparation of high molecular weight polymers and copolymers at higher polymerization temperatures as compared to polymerization systems using solely chlorinated hydrocarbon diluents such as methyl chloride.

[0054] In yet another embodiment, this invention relates to the preparation of isoolefinic homopolymers and copolymers, especially the polymerization reactions required to produce the isobutylene-isoprene form of butyl rubber and isobutylene-p-alkylstyrene copolymers. More particularly, the invention relates to a method of polymerizing and copolymerizing isoolefins in a slurry polymerization process using hydrofluorocarbon diluents or blends of hydrofluorocarbons, and chlorinated hydrocarbon diluents, like methyl chloride.

[0055] In another embodiment, the polymerization systems of the present invention provide for copolymerizing an isomonoolefin having from 4 to 7 carbon atoms and para-alkylstyrene monomers. In accordance with a preferred embodiment of the invention, the system produces copolymers containing between about 80 and 99.5 wt. % of the isoolefin such as isobutylene and between about 0.5 and 20 wt. % of the para-alkylstyrene such as para-methylstyrene. In accordance with another embodiment, however, where glassy or plastic materials are being produced as well, the copolymers are comprised between about 10 and 99.5 wt. % of the isoolefin, or isobutylene, and about 0.5 and 90 wt. % of the para-alkylstyrene, such as para-methylstyrene.

[0056] In a preferred embodiment this invention relates to a process to produce polymers of cationically polymerizable monomer(s) comprising contacting, in a reactor, the monomer(s), a Lewis acid, and an initiator, in the presence of an HFC diluent at a temperature of 0°C or lower, preferably -10°C or lower, preferably -20°C or lower, preferably -30°C or lower, preferably -40°C or lower, preferably -50°C or lower, preferably -60°C or lower, preferably -70°C or lower, preferably -80°C or lower, preferably -90°C or lower, preferably -100°C or lower, preferably from 0°C to the freezing point of the polymerization medium, such as the diluent and monomer mixture.

Monomers and Polymers

[0057] Monomers which may be polymerized by this system include any hydrocarbon monomer that is polymerizable using this invention. Preferred monomers include one or more of olefins, alpha-olefins, disubstituted olefins, isoolefins, conjugated dienes, non-conjugated dienes, styrenics and/or substituted styrenics and vinyl ethers. The styrenic may be substituted (on the ring) with an alkyl, aryl, halide or alkoxide group. Preferably, the monomer contains 2 to 20 carbon atoms, more preferably 2 to 9, even more preferably 3 to 9 carbon atoms. Examples of preferred olefins include styrene, para-alkylstyrene, para-methylstyrene, alpha-methyl styrene, divinylbenzene, diisopropenylbenzene, isobutylene, 2-methyl-1-butene, 3-methyl-1-butene, 2-methyl-2-pentene, isoprene, butadiene, 2,3-dimethyl-1,3-butadiene, β -pinene, myrcene, 6,6-dimethyl-fulvene, hexadiene, cyclopentadiene, piperylene, methyl vinyl ether, ethyl vinyl ether, and isobutyl vinyl ether and the like. Monomer may also be combinations of two or more monomers. Styrenic block copolymers may also be used a monomers. Preferred block copolymers include copolymers of styrenics, such as styrene, para-methylstyrene, alpha-methylstyrene, and C₄ to C₃₀ diolefins, such as isoprene, butadiene, and the like. Particularly preferred monomer combinations include 1) isobutylene and para-methyl styrene 2) isobutylene and isoprene, as well as homopolymers of isobutylene.

[0058] Additionally, preferred monomers include those that are cationically polymerizable as described in *Cationic Polymerization of Olefins, A Critical Inventory*, Joseph Kennedy, Wiley Interscience, New York 1975. Monomers include any monomer that is cationically polymerizable, such as those monomers that are capable of stabilizing a cation or propagating center because the monomer contains an electron donating group. For a detailed discussion of cationic catalysis please see *Cationic Polymerization of Olefins, A Critical Inventory*, Joseph Kennedy, Wiley Interscience, New York 1975.

[0059] The monomers may be present in the polymerization medium in an amount ranging from 75 wt% to 0.01 wt% in one embodiment, alternatively 60 wt% to 0.1 wt%, alternatively from 40 wt% to 0.2 wt%, alternatively 30 to 0.5 wt%, alternatively 20wt% to 0.8 wt%, alternatively and from 15 wt% to 1 wt% in another embodiment.

[0060] Preferred polymers include homopolymers of any of the monomers listed in this Section. Examples of homopolymers include polyisobutylene, polypara-methylstyrene, polyisoprene, polystyrene, polyalpha-methylstyrene, polyvinyl ethers (such as polymethylvinylether, polyethylvinylether).

[0061] Preferred polymers also include copolymers of 1) isobutylene and an alkylstyrene; and 2) isobutylene and isoprene.

[0062] In one embodiment butyl polymers are prepared by reacting a comonomer mixture, the mixture having at least (1) a C₄ to C₆ isoolefin monomer component such as isobutene with (2) a multiolefin, or conjugated diene monomer component. The isoolefin is in a range from 70 to 99.5 wt% by weight of the total comonomer mixture in one embodiment, 85 to 99.5 wt% in another embodiment. In yet another embodiment the isoolefin is in the range of 92 to 99.5 wt%. The conjugated diene component in one embodiment is present in the comonomer mixture from 30 to 0.5 wt% in one embodiment, and from 15 to 0.5 wt% in

another embodiment. In yet another embodiment, from 8 to 0.5 wt% of the comonomer mixture is conjugated diene. The C₄ to C₆ isoolefin may be one or more of isobutene, 2-methyl-1-butene, 3-methyl-1-butene, 2-methyl-2-butene, and 4-methyl-1-pentene. The multiolefin may be a C₄ to C₁₄ conjugated diene such as isoprene, butadiene, 2,3-dimethyl-1,3-butadiene, β -pinene, myrcene, 6,6-dimethyl-fulvene, hexadiene, cyclopentadiene and piperylene. One embodiment of the butyl rubber polymer of the invention is obtained by reacting 85 to 99.5 wt% of isobutylene with 15 to 0.5 wt% isoprene, or by reacting 95 to 99.5 wt% isobutylene with 5.0 wt% to 0.5 wt% isoprene in yet another embodiment. The following table illustrates how the above-referenced wt % would be expressed as mol%.

wt % IC4 ^a	mol % IC4	wt % IC5 ^b	Mol % IC5
70	73.9	.5	.4
85	87.3	5	4.2
92	93.3	8	6.7
95	95.9	15	12.7
99.5	99.6	30	26.1

a. IC4 - isobutylene

b. IC5 - isoprene

[0063] This invention further relates to terpolymers and tetrapolymers comprising any combination of the monomers listed above. Preferred terpolymers and tetrapolymers include polymers comprising isobutylene, isoprene and divinylbenzene, polymers comprising isobutylene, para-alkylstyrene (preferably paramethyl styrene) and isoprene, polymers comprising cyclopentadiene, isobutylene, and paraalkyl styrene (preferably paramethyl styrene), polymers of isobutylene cyclopentadiene and isoprene, polymers comprising cyclopentadiene,

isobutylene, and methyl cyclopentadiene, polymers comprising isobutylene, paramethylstyrene and cyclopentadiene.

Lewis acid

[0064] The Lewis acid (also referred to as the co-initiator or catalyst) may be any Lewis acid based on metals from Group 4, 5, 13, 14 and 15 of the Periodic Table of the Elements, including boron, aluminum, gallium, indium, titanium, zirconium, tin, vanadium, arsenic, antimony, and bismuth. One skilled in the art will recognize that some elements are better suited in the practice of the invention. In one embodiment, the metals are aluminum, boron and titanium, with aluminum being desirable. Illustrative examples include AlCl_3 , $(\text{alkyl})\text{AlCl}_2$, $(\text{C}_2\text{H}_5)_2\text{AlCl}$ and $(\text{C}_2\text{H}_5)_3\text{Al}_2\text{Cl}_3$, BF_3 , SnCl_4 , TiCl_4 .

[0065] Additionally, Lewis acids may be any of those useful in cationic polymerization of isobutylene copolymers including: aluminum trichloride, aluminum tribromide, ethylaluminum dichloride, ethylaluminum sesquichloride, diethylaluminum chloride, methylaluminum dichloride, methylaluminum sesquichloride, dimethylaluminum chloride, boron trifluoride, titanium tetrachloride, etc. with ethylaluminum dichloride and ethylaluminum sesquichloride being preferred.

[0066] Lewis acids such as methylaluminoxane (MAO) and specifically designed weakly coordinating Lewis acids such as $\text{B}(\text{C}_6\text{F}_5)_3$ are also suitable Lewis acids within the context of the invention.

[0067] As one skilled in the art will recognize the aforementioned listing of Lewis acids is not exhaustive and is provided for illustration. For a more information regarding Lewis acids in polymerization processes, see, for example, International Application Nos. PCT/US03/40903 and PCT/US03/40340.

Initiator

[0068] Initiators useful in this invention are those initiators which are capable of being complexed in a suitable diluent with the chosen Lewis acid to yield a complex which rapidly reacts with the olefin thereby forming a propagating polymer chain. Illustrative examples include Brønsted acids such as H_2O , HCl , $RCOOH$ (wherein R is an alkyl group), and alkyl halides, such as $(CH_3)_3CCl$, $C_6H_5C(CH_3)_2Cl$ and (2-Chloro-2,4,4-trimethylpentane). More recently, transition metal complexes, such as metallocenes and other such materials that can act as single site catalyst systems, such as when activated with weakly coordinating Lewis acids or Lewis acid salts have been used to initiate isobutylene polymerization.

[0069] In an embodiment, the initiator comprises one or more of a hydrogen halide, a carboxylic acid, a carboxylic acid halide, a sulfonic acid, an alcohol, a phenol, a tertiary alkyl halide, a tertiary aralkyl halide, a tertiary alkyl ester, a tertiary aralkyl ester, a tertiary alkyl ether, a tertiary aralkyl ether, alkyl halide, aryl halide, alkylaryl halide, or arylalkylacid halide.

[0070] As one skilled in the art will recognize the aforementioned listing of initiator(s) is not exhaustive and is provided for illustration. For a more information regarding initiator(s) in polymerization processes, see, for example, International Application Nos. PCT/US03/40903 and PCT/US03/40340.

Hydrofluorocarbons

[0071] Hydrofluorocarbons are preferably used as diluents in the present invention, alone or in combination with other hydrofluorocarbons or in combination with other diluents. For purposes of this invention and the claims thereto, hydrofluorocarbons ("HFC's" or "HFC") are defined to be saturated or unsaturated compounds consisting essentially of hydrogen, carbon and fluorine,

provided that at least one carbon, at least one hydrogen and at least one fluorine are present.

[0072] In certain embodiments, the diluent comprises hydrofluorocarbons represented by the formula: $C_xH_yF_z$ wherein x is an integer from 1 to 40, alternatively from 1 to 30, alternatively from 1 to 20, alternatively from 1 to 10, alternatively from 1 to 6, alternatively from 2 to 20 alternatively from 3 to 10, alternatively from 3 to 6, most preferably from 1 to 3, wherein y and z are integers and at least one.

[0073] Illustrative examples include fluoromethane; difluoromethane; trifluoromethane; fluoroethane; 1,1-difluoroethane; 1,2-difluoroethane; 1,1,1-trifluoroethane; 1,1,2-trifluoroethane; 1,1,1,2-tetrafluoroethane; 1,1,2,2-tetrafluoroethane; 1,1,1,2,2-pentafluoroethane; 1-fluoropropane; 2-fluoropropane; 1,1-difluoropropane; 1,2-difluoropropane; 1,3-difluoropropane; 2,2-difluoropropane; 1,1,1-trifluoropropane; 1,1,2-trifluoropropane; 1,1,3-trifluoropropane; 1,2,2-trifluoropropane; 1,2,3-trifluoropropane; 1,1,1,2-tetrafluoropropane; 1,1,1,3-tetrafluoropropane; 1,1,2,2-tetrafluoropropane; 1,1,2,3-tetrafluoropropane; 1,1,3,3-tetrafluoropropane; 1,2,2,3-tetrafluoropropane; 1,1,1,2,2-pentafluoropropane; 1,1,1,2,3-pentafluoropropane; 1,1,1,3,3-pentafluoropropane; 1,1,2,2,3-pentafluoropropane; 1,1,2,3,3-pentafluoropropane; 1,1,1,2,2,3-hexafluoropropane; 1,1,1,2,3,3-hexafluoropropane; 1,1,1,3,3,3-hexafluoropropane; 1,1,1,2,2,3,3-heptafluoropropane; 1,1,1,2,3,3,3-heptafluoropropane; 1-fluorobutane; 2-fluorobutane; 1,1-difluorobutane; 1,2-difluorobutane; 1,3-difluorobutane; 1,4-difluorobutane; 2,2-difluorobutane; 2,3-difluorobutane; 1,1,1-trifluorobutane; 1,1,2-trifluorobutane; 1,1,3-trifluorobutane; 1,1,4-trifluorobutane; 1,2,2-trifluorobutane; 1,2,3-trifluorobutane; 1,3,3-trifluorobutane; 2,2,3-trifluorobutane; 1,1,1,2-tetrafluorobutane; 1,1,1,3-tetrafluorobutane; 1,1,1,4-tetrafluorobutane; 1,1,2,2-tetrafluorobutane; 1,1,2,3-tetrafluorobutane; 1,1,2,4-tetrafluorobutane; 1,1,3,3-tetrafluorobutane; 1,1,3,4-tetrafluorobutane; 1,1,4,4-tetrafluorobutane; 1,2,2,3-tetrafluorobutane; 1,2,2,4-tetrafluorobutane; 1,2,3,3-tetrafluorobutane; 1,2,3,4-tetrafluorobutane; 2,2,3,3-

tetrafluorobutane; 1,1,1,2,2-pentafluorobutane; 1,1,1,2,3-pentafluorobutane;
 1,1,1,2,4-pentafluorobutane; 1,1,1,3,3-pentafluorobutane; 1,1,1,3,4-
 pentafluorobutane; 1,1,1,4,4-pentafluorobutane; 1,1,2,2,3-pentafluorobutane;
 1,1,2,2,4-pentafluorobutane; 1,1,2,3,3-pentafluorobutane; 1,1,2,4,4-
 pentafluorobutane; 1,1,3,3,4-pentafluorobutane; 1,2,2,3,3-pentafluorobutane;
 1,2,2,3,4-pentafluorobutane; 1,1,1,2,2,3-hexafluorobutane; 1,1,1,2,2,4-
 hexafluorobutane; 1,1,1,2,3,3-hexafluorobutane; 1,1,1,2,3,4-hexafluorobutane;
 1,1,1,2,4,4-hexafluorobutane; 1,1,1,3,3,4-hexafluorobutane; 1,1,1,3,4,4-
 hexafluorobutane; 1,1,1,4,4,4-hexafluorobutane; 1,1,2,2,3,3-hexafluorobutane;
 1,1,2,2,3,4-hexafluorobutane; 1,1,2,2,4,4-hexafluorobutane; 1,1,2,3,3,4-
 hexafluorobutane; 1,1,2,3,4,4-hexafluorobutane; 1,2,2,3,3,4-hexafluorobutane;
 1,1,1,2,2,3,3-heptafluorobutane; 1,1,1,2,2,4,4-heptafluorobutane; 1,1,1,2,2,3,4-
 heptafluorobutane; 1,1,1,2,3,3,4-heptafluorobutane; 1,1,1,2,3,4,4-
 heptafluorobutane; 1,1,1,2,4,4,4-heptafluorobutane; 1,1,1,3,3,4,4-
 heptafluorobutane; 1,1,1,2,2,3,3,4-octafluorobutane; 1,1,1,2,2,3,4,4-
 octafluorobutane; 1,1,1,2,3,3,4,4-octafluorobutane; 1,1,1,2,2,4,4,4-
 octafluorobutane; 1,1,1,2,3,4,4,4-octafluorobutane; 1,1,1,2,2,3,3,4,4-
 nonafluorobutane; 1,1,1,2,2,3,4,4,4-nonafluorobutane; 1-fluoro-2-methylpropane;
 1,1-difluoro-2-methylpropane; 1,3-difluoro-2-methylpropane; 1,1,1-trifluoro-2-
 methylpropane; 1,1,3-trifluoro-2-methylpropane; 1,3-difluoro-2-
 (fluoromethyl)propane; 1,1,1,3-tetrafluoro-2-methylpropane; 1,1,3,3-tetrafluoro-2-
 methylpropane; 1,1,3-trifluoro-2-(fluoromethyl)propane; 1,1,1,3,3-pentafluoro-2-
 methylpropane; 1,1,3,3-tetrafluoro-2-(fluoromethyl)propane; 1,1,1,3-tetrafluoro-2-
 (fluoromethyl)propane; fluorocyclobutane; 1,1-difluorocyclobutane; 1,2-
 difluorocyclobutane; 1,3-difluorocyclobutane; 1,1,2-trifluorocyclobutane; 1,1,3-
 trifluorocyclobutane; 1,2,3-trifluorocyclobutane; 1,1,2,2-tetrafluorocyclobutane;
 1,1,3,3-tetrafluorocyclobutane; 1,1,2,2,3-pentafluorocyclobutane; 1,1,2,3,3-
 pentafluorocyclobutane; 1,1,2,2,3,3-hexafluorocyclobutane; 1,1,2,2,3,4-
 hexafluorocyclobutane; 1,1,2,3,3,4-hexafluorocyclobutane; 1,1,2,2,3,3,4-
 heptafluorocyclobutane; and mixtures thereof and including mixtures of
 unsaturated HFC's described below. Particularly preferred HFC's include

difluoromethane, trifluoromethane, 1,1-difluoroethane, 1,1,1-trifluoroethane, fluoromethane, and 1,1,1,2-tetrafluoroethane.

[0074] Illustrative examples of unsaturated hydrofluorocarbons include vinyl fluoride; 1,1-difluoroethene; 1,2-difluoroethene; 1,1,2-trifluoroethene; 1-fluoropropene, 1,1-difluoropropene; 1,2-difluoropropene; 1,3-difluoropropene; 2,3-difluoropropene; 3,3-difluoropropene; 1,1,2-trifluoropropene; 1,1,3-trifluoropropene; 1,2,3-trifluoropropene; 1,3,3-trifluoropropene; 2,3,3-trifluoropropene; 3,3,3-trifluoropropene; 1-fluoro-1-butene; 2-fluoro-1-butene; 3-fluoro-1-butene; 4-fluoro-1-butene; 1,1-difluoro-1-butene; 1,2-difluoro-1-butene; 1,3-difluoro-1-butene; 1,4-difluoro-1-butene; 2,3-difluoro-1-butene; 2,4-difluoro-1-butene; 3,3-difluoro-1-butene; 3,4-difluoro-1-butene; 4,4-difluoro-1-butene; 1,1,2-trifluoro-1-butene; 1,1,3-trifluoro-1-butene; 1,1,4-trifluoro-1-butene; 1,2,3-trifluoro-1-butene; 1,2,4-trifluoro-1-butene; 1,3,3-trifluoro-1-butene; 1,3,4-trifluoro-1-butene; 1,4,4-trifluoro-1-butene; 2,3,3-trifluoro-1-butene; 2,3,4-trifluoro-1-butene; 2,4,4-trifluoro-1-butene; 3,3,4-trifluoro-1-butene; 3,4,4-trifluoro-1-butene; 4,4,4-trifluoro-1-butene; 1,1,2,3-tetrafluoro-1-butene; 1,1,2,4-tetrafluoro-1-butene; 1,1,3,3-tetrafluoro-1-butene; 1,1,3,4-tetrafluoro-1-butene; 1,1,4,4-tetrafluoro-1-butene; 1,2,3,3-tetrafluoro-1-butene; 1,2,3,4-tetrafluoro-1-butene; 1,2,4,4-tetrafluoro-1-butene; 1,3,3,4-tetrafluoro-1-butene; 1,3,4,4-tetrafluoro-1-butene; 1,4,4,4-tetrafluoro-1-butene; 2,3,3,4-tetrafluoro-1-butene; 2,3,4,4-tetrafluoro-1-butene; 2,4,4,4-tetrafluoro-1-butene; 3,3,4,4-tetrafluoro-1-butene; 3,4,4,4-tetrafluoro-1-butene; 1,1,2,3,3-pentafluoro-1-butene; 1,1,2,3,4-pentafluoro-1-butene; 1,1,2,4,4-pentafluoro-1-butene; 1,1,3,3,4-pentafluoro-1-butene; 1,1,3,4,4-pentafluoro-1-butene; 1,1,4,4,4-pentafluoro-1-butene; 1,2,3,3,4-pentafluoro-1-butene; 1,2,3,4,4-pentafluoro-1-butene; 1,2,4,4,4-pentafluoro-1-butene; 2,3,3,4,4-pentafluoro-1-butene; 2,3,4,4,4-pentafluoro-1-butene; 3,3,4,4,4-pentafluoro-1-butene; 1,1,2,3,3,4-hexafluoro-1-butene; 1,1,2,3,4,4-hexafluoro-1-butene; 1,1,2,4,4,4-hexafluoro-1-butene; 1,2,3,3,4,4-hexafluoro-1-butene; 1,2,3,4,4,4-hexafluoro-1-butene; 2,3,3,4,4,4-hexafluoro-1-butene; 1,1,2,3,3,4,4-heptafluoro-1-butene; 1,1,2,3,4,4,4-heptafluoro-1-butene; 1,1,3,3,4,4,4-heptafluoro-1-butene; 1,2,3,3,4,4,4-heptafluoro-1-butene; 1-fluoro-2-butene; 2-

fluoro-2-butene; 1,1-difluoro-2-butene; 1,2-difluoro-2-butene; 1,3-difluoro-2-butene; 1,4-difluoro-2-butene; 2,3-difluoro-2-butene; 1,1,1-trifluoro-2-butene; 1,1,2-trifluoro-2-butene; 1,1,3-trifluoro-2-butene; 1,1,4-trifluoro-2-butene; 1,2,3-trifluoro-2-butene; 1,2,4-trifluoro-2-butene; 1,1,1,2-tetrafluoro-2-butene; 1,1,1,3-tetrafluoro-2-butene; 1,1,1,4-tetrafluoro-2-butene; 1,1,2,3-tetrafluoro-2-butene; 1,1,2,4-tetrafluoro-2-butene; 1,2,3,4-tetrafluoro-2-butene; 1,1,1,2,3-pentafluoro-2-butene; 1,1,1,2,4-pentafluoro-2-butene; 1,1,1,3,4-pentafluoro-2-butene; 1,1,1,4,4-pentafluoro-2-butene; 1,1,2,3,4-pentafluoro-2-butene; 1,1,2,4,4-pentafluoro-2-butene; 1,1,1,2,3,4-hexafluoro-2-butene; 1,1,1,2,4,4-hexafluoro-2-butene; 1,1,1,3,4,4-hexafluoro-2-butene; 1,1,1,4,4,4-hexafluoro-2-butene; 1,1,2,3,4,4-hexafluoro-2-butene; 1,1,1,2,3,4,4-heptafluoro-2-butene; 1,1,1,2,4,4,4-heptafluoro-2-butene; and mixtures thereof and including mixtures of saturated HFC's described above.

[0075] In one embodiment, the diluent comprises non-perfluorinated compounds or the diluent is a non-perfluorinated diluent. Perfluorinated compounds being those compounds consisting of carbon and fluorine. However, in another embodiment, when the diluent comprises a blend, the blend may comprise perfluorinated compound, preferably, the catalyst, monomer, and diluent are present in a single phase or the aforementioned components are miscible with the diluent as described in further detail below. In another embodiment, the blend may also comprise chlorofluorocarbons (CFC's), or those compounds consisting of chlorine, fluorine, and carbon.

[0076] In another embodiment, when higher weight average molecular weights (Mw) (typically greater than 10,000 Mw, preferably more than 50,000 Mw, more preferably more than 100,000 Mw) are desired, suitable diluents include hydrofluorocarbons with a dielectric constant of greater than 10 at -85°C, preferably greater than 15, more preferably greater than 20, more preferably greater than 25, more preferably 40 or more. In embodiments where lower molecular weights (typically lower than 10,000 Mw, preferably less than 5,000 Mw, more preferably less than 3,000 Mw) are desired the dielectric constant may

be less than 10, or by adding larger amounts of initiator or transfer agent when the dielectric constant is above 10. The dielectric constant of the diluent ϵ_D is determined from measurements of the capacitance of a parallel-plate capacitor immersed in the diluent [measured value C_D], in a reference fluid of known dielectric constant ϵ_R [measured value C_R], and in air ($\epsilon_A=1$) [measured value C_A]. In each case the measured capacitance C_M is given by $C_M = \epsilon C_C + C_S$, where ϵ is the dielectric constant of the fluid in which the capacitor is immersed, C_C is the cell capacitance, and C_S is the stray capacitance. From these measurements ϵ_D is given by the formula $\epsilon_D = ((C_D - C_A) \epsilon_R + (C_R - C_D)) / (C_R - C_A)$. Alternatively, a purpose-built instrument such as the Brookhaven Instrument Corporation BIC-870 may be used to measure dielectric constant of diluents directly. A comparison of the dielectric constants (ϵ) of a few selected diluents at -85°C is provided below.

Diluent	ϵ at -85°C
Methyl chloride	18.34
Difluoromethane	36.29
1,1-difluoroethane	29.33
1,1,1-trifluoroethane	22.18
1,1,1,2-tetrafluoroethane	23.25
1,1,2,2-tetrafluoroethane	11.27
1,1,1,2,2-pentafluoroethane	11.83

[0077] In other embodiments, one or more HFC's are used in combination with another diluent or mixtures of diluents. Suitable additional diluents include hydrocarbons, especially hexanes and heptanes, halogenated hydrocarbons, especially chlorinated hydrocarbons and the like. Specific examples include but are not limited to propane, isobutane, pentane, methycyclopentane, isohexane, 2-methylpentane, 3-methylpentane, 2-methylbutane, 2,2-dimethylbutane, 2,3-dimethylbutane, 2-methylhexane, 3-methylhexane, 3-ethylpentane, 2,2-

dimethylpentane, 2,3-dimethylpentane, 2,4-dimethylpentane, 3,3-dimethylpentane, 2-methylheptane, 3-ethylhexane, 2,5-dimethylhexane, 2,2,4-trimethylpentane, octane, heptane, butane, ethane, methane, nonane, decane, dodecane, undecane, hexane, methyl cyclohexane, cyclopropane, cyclobutane, cyclopentane, methylcyclopentane, 1,1-dimethylcyclopentane, cis 1,2-dimethylcyclopentane, trans-1,2-dimethylcyclopentane, trans-1,3-dimethylcyclopentane, ethylcyclopentane, cyclohexane, methylcyclohexane, benzene, toluene, xylene, ortho-xylene, para-xylene, meta-xylene, and the halogenated versions of all of the above, preferably the chlorinated versions of the above, more preferably fluorinated versions of all of the above. Brominated versions of the above are also useful. Specific examples include, methyl chloride, methylene chloride, ethyl chloride, propyl chloride, butyl chloride, chloroform and the like.

[0078] In another embodiment, non-reactive olefins may be used as diluents in combination with HFC's. Examples include, but are not limited to, ethylene, propylene, and the like.

[0079] In one embodiment, the HFC is used in combination with a chlorinated hydrocarbon such as methyl chloride. Additional embodiments include using the HFC in combination with hexanes or methyl chloride and hexanes. In another embodiment the HFC's are used in combination with one or more gases inert to the polymerization such as carbon dioxide, nitrogen, hydrogen, argon, neon, helium, krypton, xenon, and/or other inert gases that are preferably liquid at entry to the reactor. Preferred gases include carbon dioxide and/or nitrogen.

[0080] In another embodiment the HFC's are used in combination with one or more nitrated alkanes, including C₁ to C₄₀ nitrated linear, cyclic or branched alkanes. Preferred nitrated alkanes include, but are not limited to, nitromethane, nitroethane, nitropropane, nitrobutane, nitropentane, nitrohexane, nitroheptane, nitrooctane, nitrodecane, nitrononane, nitrododecane, nitroundecane,

nitrocyclomethane, nitrocycloethane, nitrocyclopropane, nitrocyclobutane, nitrocyclopentane, nitrocyclohexane, nitrocycloheptane, nitrocyclooctane, nitrocyclodecane, nitrocyclononane, nitrocyclododecane, nitrocycloundecane, nitrobenzene, and the di- and tri- nitro versions of the above. A preferred embodiment is HFC's blended with nitromethane.

[0081] The HFC is typically present at 1 to 100 volume % based upon the total volume of the diluents, alternatively between 5 and 100 volume %, alternatively between 10 and 100 volume %, alternatively between 15 and 100 volume %, alternatively between 20 and 100 volume %, alternatively between 25 and 100 volume %, alternatively between 30 and 100 volume %, alternatively between 35 and 100 volume %, alternatively between 40 and 100 volume %, alternatively between 45 and 100 volume %, alternatively between 50 and 100 volume %, alternatively between 55 and 100 volume %, alternatively between 60 and 100 volume %, alternatively between 65 and 100 volume %, alternatively between 70 and 100 volume %, alternatively between 75 and 100 volume %, alternatively between 80 and 100 volume %, alternatively between 85 and 100 volume %, alternatively between 90 and 100 volume %, alternatively between 95 and 100 volume %, alternatively between 97 and 100 volume %, alternatively between 98 and 100 volume %, and alternatively between 99 and 100 volume %. In a preferred embodiment the HFC is blended with one or more chlorinated hydrocarbons. In another preferred embodiment the HFC is selected from the group consisting of difluoromethane, trifluoromethane, 1,1-difluoroethane, 1,1,1-trifluoroethane, and 1,1,1,2-tetrafluoroethane and mixtures thereof.

[0082] In another embodiment the diluent or diluent mixture is selected based upon its solubility in the polymer. Certain diluents are soluble in the polymer. Preferred diluents have little to no solubility in the polymer. Solubility in the polymer is measured by forming the polymer into a film of thickness between 50 and 100 microns, then soaking it in diluent (enough to cover the film) for 4 hours at -75°C. The film is removed from the diluent, exposed to room temperature for 90 seconds to evaporate excess diluent from the surface of the

film, and weighed. The mass uptake is defined as the percentage increase in the film weight after soaking. The diluent or diluent mixture is chosen so that the polymer has a mass uptake of less than 4 wt%, preferably less than 3 wt%, preferably less than 2 wt%, preferably less than 1 wt%, more preferably less than 0.5 wt%.

[0083] In a preferred embodiment, the diluent or diluent mixture is selected such that the difference between the measured glass transition temperature T_g of the polymer with less than 0.1 wt% of any diluent, unreacted monomers and additives is within 15°C of the T_g of the polymer measured after it has been formed into a film of thickness between 50 and 100 microns, that has been soaked in diluent (enough to cover the film) for 4 hours at -75°C . The glass transition temperature is determined by differential scanning calorimetry (DSC). Techniques are well described in the literature, for example, B. Wunderlich, "The Nature of the Glass Transition and its Determination by Thermal Analysis", in Assignment of the Glass Transition, ASTM STP 1249, R. J. Seyler, Ed., American Society for Testing and Materials, Philadelphia, 1994, pp. 17-31. The sample is prepared as described above, sealed immediately after soaking into a DSC sample pan, and maintained at a temperature below -80°C until immediately before the DSC measurement. Preferably the T_g values are within 12°C of each other, preferably within 11°C of each other, preferably within 10°C of each other, preferably within 9°C of each other, preferably within 8°C of each other, preferably within 7°C of each other, preferably within 6°C of each other, preferably within 5°C of each other, preferably within 4°C of each other, preferably within 3°C of each other, preferably within 3°C of each other, preferably within 2°C of each other, preferably within 1°C of each other.

Polymerization Process

[0084] The invention may be practiced in continuous and batch processes. Further the invention may be practiced in a plug flow reactor and/or stirred tank reactors. In particular this invention may be practiced in "butyl reactors."

Illustrative examples include any reactor selected from the group consisting of a continuous flow stirred tank reactor, a plug flow reactor, a moving belt or drum reactor, a jet or nozzle reactor, a tubular reactor, and an autorefrigerated boiling-pool reactor.

[0085] In certain embodiments, the invention is practiced using a slurry polymerization process. The polymerization processes of the invention may be a cationic polymerization process. The polymerization process of the invention may be a continuous polymerization process. The polymerization processes of the invention may be a polymerization processes for the production of C₄-C₇ isoolefin polymers such as isobutylene based polymers.

[0086] In one embodiment, the polymerization is carried out where the catalyst, monomer, and diluent are present in a single phase. Preferably, the polymerization is carried-out in a continuous polymerization process in which the catalyst, monomer(s), and diluent are present as a single phase. In slurry polymerization, the monomers, catalyst(s), and initiator(s) are all miscible in the diluent or diluent mixture, i.e., constitute a single phase, while the polymer precipitates from the diluent with good separation from the diluent. Desirably, reduced or no polymer "swelling" is exhibited as indicated by little or no T_g suppression of the polymer and/or little or no diluent mass uptake. Thus, polymerization in the diluents of the present invention provides for high polymer concentration to be handled at low viscosity with good heat transfer, reduced reactor fouling, homogeneous polymerization and/or the convenience of subsequent reactions to be run directly on the resulting polymer mixture.

[0087] The reacted monomers within the reactor form part of a slurry. In one embodiment, the concentration of the solids in the slurry is equal to or greater than 10 vol%. In another embodiment, the concentration of solids in the slurry is present in the reactor equal to or greater than 25 vol%. In yet another embodiment, the concentration of solids in the slurry is less than or equal to 75 vol%. In yet another embodiment, the concentration of solids in slurry is present

in the reactor from 1 to 70 vol%. In yet another embodiment, the concentration of solids in slurry is present in the reactor from 5 to 70 vol%. In yet another embodiment, the concentration of solids in slurry concentration is present in the reactor from 10 to 70 vol%. In yet another embodiment, the concentration of solids in slurry concentration is present in the reactor from 15 to 70 vol%. In yet another embodiment, the concentration of solids in slurry concentration is present in the reactor from 20 to 70 vol%. In yet another embodiment, the concentration of solids in slurry concentration is present in the reactor from 25 to 70 vol%. In yet another embodiment, the concentration of solids in slurry concentration is present in the reactor from 30 to 70 vol%. In yet another embodiment, the concentration of solids in slurry concentration is present in the reactor from 40 to 70 vol%.

[0088] The order of contacting the monomer feed-stream, catalyst, initiator, and diluent may vary from one embodiment to another.

[0089] For a more information regarding polymerization processes, see, for example, International Application Nos. PCT/US03/40903 and PCT/US03/40340.

Slurry Separation

[0090] After polymerization, it is necessary to recover the polymer product or polymer particles, and recycle the diluent and unreacted monomers to the polymerization process. A slurry having large amount or made completely from methyl chloride is very slow to separate due to the sticky nature of the polymer particles, if at all, and the separation technique normally used is to flash off the diluent and monomers using live steam and hot water.

[0091] In slurry having one or more HFCs, without being bound to theory, it is believed that there is a lower level of diluent mass uptake in the polymer

particles which reduces the sticky nature of the polymer particles and allows the slurry to readily separate. Various methods and devices may be employed.

[0092] These include filters and/or separators that use the application of force to the slurry such as gravitational or centrifugal force.

[0093] In certain embodiments, the slurry is passed through a device to recover the polymer particles. In an embodiment, the slurry is passed through a filter. Such filters are commercially available and their use is well-known to one skilled in the art. In the use of conventional filters, a vacuum is generally used to suck the diluent through the septum and filter cake formed by the polymer.

[0094] In another embodiment, a Cross Flow Filter is used. Cross flow filters and cross flow electrofiltration are techniques that are particularly suitable for use with this type of slurry. In an embodiment, the flow of the slurry is tangential to surface of the filter. Cross flow filters require high shear at the filter surface in order to minimize the build of filter cake. However, for example, when butyl hydrofluorocarbon slurries are filtered, the filter cake formed can be readily reformed by back washing filter surface to remove the polymer, which will readily reform a slurry. This is not the case for methyl chloride slurries because of the sticky nature of the polymer particles in the slurry.

[0095] After concentration by the filter, the slurry can go to a vessel to flash off the remaining HFC diluent and monomers or be contacted with a solvent for the polymer to dissolve it. The diluent and monomer separated by the filter can be recycled to the reactor, thereby conserving, among other things, energy.

[0096] Such differences in diluent and polymer interactions in light of chlorinated hydrocarbons and HFCs may be due at least in part to density differences. For example, the density of the rubber phase is 61 lbs/ft³ (0.976 kg/l) at -103°F and 61.25 lbs/ft³ (0.980 kg/l) at -130°F and the diluent (R134a) is 97.91

lbs/ft³ (1.567 kg/l) at -140°F compared to methyl chloride 69.18 lbs/ft³ (1.107 kg/l) at -140°F.

[0097] Thus, methyl chloride slurries agglomerate because of the sticky nature of the polymer particles. Whereas HFC slurries do not agglomerate in this manner making the separation and concentration of polymer particles in slurries comprising one or more HFCs easier.

[0098] When filters are used to separate the polymer particles from the slurry leaving the reactor, a polymer deposit or filter cake containing residual diluent is formed. When this deposit is kept below the glass transition temperature, and because the polymer particles are not sticky, the polymer deposit can easily be broken down by minimal mechanical force and dissolved into a solvent or alternatively processed by extruders to produce a final product.

[0099] In yet other embodiments, the application of force to the slurry is employed to obtain polymer particles. The force employed may be any force suitable to separate the polymer particles from the slurry.

[00100] In an embodiment, the application of gravitation force is employed such as 1 G. For example, the slurry is transported to a settling tank whereby gravity separates the polymer particles in a phase of the slurry to form a concentration of the polymer particles. In an embodiment, the settling tank should provide for a residence time of about 15 minutes and have an upper outlet stream to remove the concentrated polymer slurry and a lower outlet stream to remove the diluent and unreacted monomers.

[00101] In another embodiment, the application of a centrifugal force to the slurry is employed. For example, centrifuges and ultra centrifuges may be used. Such devices are commercially available and should be operated as directed by the manufacturers.

[00102] In yet another embodiment, the use of a cyclone or hydrocyclone is employed. An example may be found in RU 2 209 213. In an embodiment, the polymer particles are recovered by passing the slurry from a reactor into a hydrocyclone. Two streams are formed. The underflow is a less concentrated slurry compared to the feed. The overflow is a more concentrated slurry compared to the feed. In an embodiment, the particle sizes at about above 20 μ and preferably over 30 μ are desirable to facilitate good separation of polymer particles and to recycle unreacted monomers and diluent to the polymerization process.

[00103] Without being bound to theory, it is believed that the combination of less sticky polymer particles and a larger density difference facilitates separation. This allows for several benefits. Among those, for example, are the conservation of energy such as refrigeration energy. Additionally, the diluent comprising the one or more HFCs and unreacted monomers are desirably recycled to the polymerization process.

[00104] In the aforementioned separation processes, the operational temperature may be below the glass transition temperature of the polymer, for example, -68°C for butyl rubber.

[00105] In any of the previous embodiments, the polymer particle size is from 0.1 μ to 200.0 μ , alternatively, from 20 μ to 200 μ , and alternatively, from 30 μ to 200 μ . In other embodiments, the polymer particle size is from greater than 20 μ , alternatively, from greater than 30 μ , alternatively, from greater than 40 μ , alternatively, from greater than 50 μ , alternatively, from greater than 60 μ , alternatively, from greater than 80 μ , and alternatively, from greater than 100 μ . Larger polymer particle size generally facilitates better separation of the polymer particles in the slurry.

[00106] After the polymer product is concentrated it may go to a flash or extrusion processes to remove the remaining diluent and unreacted monomers.

Alternatively, it may proceed to a process to dissolve the rubber in a diluent and then separate the remaining diluent and monomer by stripping.

INDUSTRIAL APPLICATIONS

[00107] The polymers of the invention provide chemical and physical characteristics that make them highly useful in wide variety of applications. The low degree of permeability to gases accounts for the largest uses of these polymers, namely inner tubes and tire innerliners. These same properties are also of importance in air cushions, pneumatic springs, air bellows, accumulator bags, and pharmaceutical closures. The thermal stability of the polymers of the invention make them ideal for rubber tire-curing bladders, high temperature service hoses, and conveyor belts for hot material handling.

[00108] The polymers exhibit high damping and have uniquely broad damping and shock absorption ranges in both temperature and frequency. They are useful in molded rubber parts and find wide applications in automobile suspension bumpers, auto exhaust hangers, and body mounts.

[00109] The polymers of the instant invention are also useful in tire sidewalls and tread compounds. In sidewalls, the polymer characteristics impart good ozone resistance, crack cut growth, and appearance. The polymers of the invention may also be blended. Properly formulated blends with high diene rubbers that exhibit phase co-continuity yield excellent sidewalls. Improvements in wet, snow, and ice skid resistances and in dry traction without compromises in abrasion resistance and rolling resistance for high performance tires can be accomplished by using the polymers of the instant invention.

[00110] Blends of the polymers of the invention with thermoplastic resins are used for toughening of these compounds. High-density polyethylene and isotactic polypropylene are often modified with 5 to 30 wt % of polyisobutylene. In certain applications, the instant polymers provide for a highly elastic compound

that is processable in thermoplastic molding equipment. The polymers of the instant invention may also be blended with polyamides to produce other industrial applications.

[00111] The polymers of the instant invention may also be used as adhesives, caulks, sealants, and glazing compounds. They are also useful as plasticizers in rubber formulations with butyl, SBR, and natural rubber. In linear low density polyethylene (LLDPE) blends, they induce cling to stretch-wrap films. They are also widely employed in lubricants as dispersants and in potting and electrical cable filling materials.

[00112] In certain applications, the polymers of the invention make them also useful in chewing-gum, 'as well as in medical applications such as pharmaceutical stoppers, and the arts for paint rollers.

[00113] The following examples reflect embodiments of the invention and are by no means intended to be limiting of the scope of the invention.

EXAMPLES

[00114] The polymerizations were performed in glass reaction vessels, equipped with a Teflon turbine impeller on a glass stir shaft driven by an external electrically driven stirrer. The size and design of the glass vessels is noted for each set of examples. The head of the reactor included ports for the stir shaft, thermocouple and addition of initiator/coinitiator solutions. The reactor was cooled to the desired reaction temperature by immersing the assembled reactor into a hydrocarbon bath in the dry box. The temperature of the stirred hydrocarbon bath was controlled to $\pm 2^{\circ}\text{C}$. All apparatus in liquid contact with the reaction medium were dried at 120°C and cooled in a nitrogen atmosphere before use. Isobutylene (Matheson) and methyl chloride (Air Products) were dried by passing the gas through three stainless steel columns containing barium oxide and were condensed and collected as liquids in the dry box. 1,1,1,2-

tetrafluoroethane (DuPont) and 1,1-difluoroethane (DuPont) were dried by passing the gases through stainless steel columns containing dried 3Å molecular sieves followed by condensing the materials and collecting them as liquids in the dry box. Isoprene (Aldrich) was dried over calcium hydride and distilled under Argon. The HCl (Aldrich, 99% pure) stock solution was prepared by dissolving a desirable amount of HCl gas in dry MeCl or 1,1,1,2-tetrafluoroethane to achieve 2-3 % concentration by weight. Ethylaluminum dichloride (Aldrich) was used as a 1.0 mol/L hydrocarbon solution.

[00115] The slurry copolymerizations were performed by dissolving monomer and comonomer into the liquefied methyl chloride, 1,1,1,2-tetrafluoroethane, or 1,1-difluoroethane at polymerization temperature and stirring at a pre-determined stirring speed between 800 to 1000 rpm. The use of a processor controlled electric stirring motor allowed control of the stirring speed to within 5 rpm. The initiator/coinitiator solutions were prepared in the same diluent used to prepare the monomer feed. The initiator/coinitiator solutions were prepared by adding the required amount of HCl stock solution and adding, with mixing, a 1.0 mol/L solution of the ethylaluminum dichloride. The initiator/coinitiator solutions were used immediately. The initiator/coinitiator solutions were added drop-wise to monomer feeds using a chilled glass Pasteur pipette or, optionally, a jacketed dropping funnel for examples using the 500 or 1000 ml glass reaction vessels. Catalyst solution was added to each monomer feed at a rate so as to keep the temperature of the polymerization within 3 degrees of the reported temperature. Polymerizations were continued until catalyst addition was stopped. The slurries were then manipulated as described below. Conversion is reported as weight percent of the monomers converted to polymer.

[00116] Polymer molecular weights were determined by SEC (Size Exclusion Chromatography) using a Waters Alliance 2690 separations module equipped with column heaters and a Waters 410 differential refractometer detector. Tetrahydrofuran was used as eluent (1 ml/min., 35°C) with a set of Waters Styragel HR 5µ columns of 500, 1000, 2000, 10⁴, 10⁵ and 10⁶Å pore size.

A calibration based on narrow molecular weight polyisobutylene standards (American Polymer Standards) was used to calculate molecular weights and distributions.

[00117] Polymer molecular weights can be determined on other SEC instruments using different calibration and run protocols. The methodology of SEC (also known as GPC or gel permeation chromatography) to characterize polymer molecular weights has been reviewed in many publications. One such source is the review provided by L.H. Tung in Polymer Yearbook, H.-G. Elias and R. A. Pethrick, Eds., Harwood Academic Publishers, New York, 1984, pgs. 93-100, herein incorporated by reference.

[00118] Comonomer incorporation was determined by ^1H -NMR spectrometry. NMR measurements were obtained at a field strength corresponding to 400 MHz or 500 MHz. ^1H -NMR spectra were recorded at room temperature on a Bruker Avance NMR spectrometer system using CDCl_3 solutions of the polymers. All chemical shifts were referenced to TMS.

[00119] A variety of NMR methods have been used to characterize comonomer incorporation and sequence distribution in copolymers. Many of these methods may be applicable to the polymers of this invention. A general reference which reviews the application of NMR spectrometry to the characterization of polymers is H. R. Kricheldorf in Polymer Yearbook, H.-G. Elias and R. A. Pethrick, Eds., Harwood Academic Publishers, New York, 1984, pgs. 249-257, herein incorporated by reference.

[00120] Rubber volume percents were determined by collecting and weighing a sample of the total slurry or of a separated phase. The diluent was then weathered off and the remaining rubber was dried in vacuum to determine the total weight of the rubber. These values were used to calculate the weight fraction of rubber in the collected sample. The weight fraction was converted to a

volumes using the appropriate densities at the temperature of the experiment. The density values used for the rubber were 0.976 g/cc at -75°C and 0.980 g/cc at -90°C.

[00121] Table 1 lists the results of polymerizations conducted at -75°C in 1,1,1,2-tetrafluoroethane and 1,1-difluoroethane. Examples 1 - 5 are provided as examples of the invention. A 500 or 1000 ml glass resin kettle was used for these examples. The polymerizations for Examples 1 - 5 were conducted by combining 350 ml of 1,1,1,2-tetrafluoroethane (or 1,1-difluoroethane for Example 5), 111 ml of isobutylene and 2.8 ml of isoprene to prepare the monomer feed. The catalyst solution for Example 1 was prepared using 50 ml of 1,1,1,2-tetrafluoroethane, 222 microliters of a 1.0 mol/L ethylaluminum dichloride solution in hexane and 81 microliters of a 0.93 mol/L solution of HCl in 1,1,1,2-tetrafluoroethane. For the polymerization in Example 1, 25 ml of catalyst solution was used. The catalyst solutions for Examples 2, 3 and 4 were prepared using 50 ml of 1,1,1,2-tetrafluoroethane, 333 microliters of a 1.0 mol/L ethylaluminum dichloride solution in hexane and 125 microliters of a 1.05 mol/L solution of HCl in 1,1,1,2-tetrafluoroethane. For the polymerization in Example 2, 15 ml of catalyst solution was used. For the polymerization in Example 3, 21 ml of catalyst solution was used. For the polymerization in Example 4, 27 ml of catalyst solution was used. The catalyst solution for Example 5 was prepared using 50 ml of 1,1-difluoroethane, 333 microliters of a 1.0 mol/L ethylaluminum dichloride solution in hexane and 125 microliters of a 1.05 mol/L solution of HCl in 1,1,1,2-tetrafluoroethane. For the polymerization in Example 5, 35 ml of catalyst solution was used.

[00122] For each example, a sample of the slurry was collected immediately after the end of catalyst addition while stirring the slurry. This sample was used to determine the starting slurry volume fraction. The slurry was allowed to separate by resting for five minutes or less when 1,1,1,2-tetrafluoroethane was used as the diluent. When 1,1-difluoroethane was used as the diluent, the slurry was allowed to rest 30 minutes. The slurries separated into

an upper phase rich in rubber (noted as rubber phase in Table 1) and a lower phase poor in rubber (noted as diluent phase in Table 1). A sample of the upper phase and the lower phase was collected to determine the volume percent rubber in each phase.

Table 1

Example	Conversion (wt%)	M_w $\times 10^{-3}$	M_w/M_n	Mol% IP	Volume % Rubber		
					Starting Slurry	Rubber Phase	Diluent Phase
1	74	656	1.9	1.4	12.6	25.5	ND
2	72	765	2.2	1.7	12.8	28.1	0.5
3	47	832	2.0	1.6	7.4	22.6	0.02
4	88	481	2.3	1.8	13.9	21.2	0.4
5	84	363	1.9	1.4	15.2	24.3	0.01

ND: not determined

[00123] Table 2 lists the results of polymerizations conducted at -90 °C in methyl chloride. Examples 6 and 7 are comparative examples. A 1000 ml glass resin kettle was used for these examples. Monomer feed for Example 6 was prepared by combining 350 ml of methyl chloride, 111 ml of isobutylene and 2.8 ml of isoprene. The catalyst solution for Example 6 was prepared from 50 ml of methyl chloride, 225 microliters of a 1.05 mol/L HCl solution in 1,1,1,2-tetrafluoroethane, and 666 microliters of a 1.0 mol/L ethylaluminum dichloride solution in hexane. For the polymerization in Example 6, 20 ml of catalyst solution was used. Monomer feed for Example 7 was prepared by combining 350 ml of methyl chloride, 82 ml of isobutylene, and 2.2 ml of isoprene. The catalyst solution for Example 7 was prepared from 50 ml of methyl chloride, 180 microliters of a 1.05 mol/L HCl solution in 1,1,1,2-tetrafluoroethane and 534 microliters of a 1.0 mol/L ethylaluminum dichloride solution in hexane. For the

polymerization in Example 7, 25 ml of catalyst solution was used. Both polymerizations resulted in slurries of precipitated rubber particles suspended in the diluent.

[00124] For Examples 6 and 7, a sample of the slurry was collected immediately after the end of catalyst addition while stirring the slurry. This sample was used to determine the starting slurry volume fraction. The slurry was allowed to rest for at least 30 minutes. In the methyl chloride based slurries, a significant amount of the rubber agglomerated on standing such that typically 50 wt% of the polymer prepared would be either agglomerated or fouled at the end of this 30 minute period. The agglomerated material was physically removed from the remaining slurry in an attempt to observe the presence of a two-phase slurry system (rubber rich and rubber poor). Only in Example 6 was a second, less-dense phase observed which was not significantly different in volume fraction of rubber than the starting slurry. The total polymer collected from this phase amounted to 5.5 wt% of the total mass of rubber produced.

Table 2

Example	Conversion (wt%)	M_w $\times 10^{-3}$	M_w/M_n	Mol% IP	Volume % Rubber		
					Starting Slurry	Rubber Phase	Diluent Phase
6	81	1100	2.3	---	8.7	11.5	9.0
7	96	753	2.8	---	8.9	a	a

a: slurry separation not evident after 45 minutes

[00125] The examples in Table 3 are provided to demonstrate the reuse of the diluent/monomer blend collected by filtration of a slurry at partial conversion (Polymer 1). The reused diluent/monomer blend was used to prepare additional rubber by adding more initiator/coinitiator solution to this rubber-free diluent

(Polymer 2). Table 3 lists the results of polymerizations conducted at -95°C in 1,1-difluoroethane (152a) (Examples 8 and 9). Examples 8, 9 are examples of the current invention. Example 10 is a comparative example prepared in methyl chloride (CH₃Cl) at -95°C.

[00126] For Examples 8, 9 and 10, a monomer solution was prepared by dissolving 5.6 ml of isobutylene (collected at -95°C) and 0.3 ml of isoprene into 30 ml of cold diluent in a 100 ml glass cylindrical flask. Separately, a catalyst solution was prepared in 35 ml of diluent by adding 0.111 ml of a 0.93 mol/L stock solution of hydrogen chloride (HCl) in 1,1,1,2-tetrafluoroethane and 310 microliters of a 1.0 mol/L ethylaluminum dichloride solution in hexane. The resulting catalyst solution was used immediately. Catalyst solution was added while mechanically stirring the monomer solution. The amount of catalyst solution added to the freshly prepared monomer solution is indicated in Table 3. The monomers and diluent were removed from the polymer by suction filtration through a 2 micron stainless steel frit and collected in a chilled receiving vessel. Polymer was separated and could be re-slurried with fresh diluent when either 1,1-difluoroethane or 1,1,1,2-tetrafluoroethane was used as the diluent demonstrating the stability of the rubber particles. The separated polymer was collected and dried. The data pertaining to this polymer is listed in Table 3 as polymer 1. Polymer separation was incomplete when the diluent was methyl chloride. The polymer prepared in methyl chloride could not be re-slurried as the rubber particles agglomerated when diluent was filtered off.

[00127] In Example 8, the monomers left in the filtered diluent were then polymerized by the addition of initiator and then catalyst. To the filtered reactor fluid, 15.9 microliters of a 0.93 mol/L stock solution of hydrogen chloride solution in 1,1,1,2-tetrafluoroethane was added without formation of polymer. This addition was followed by the drop-wise addition of 1 ml 1,1-difluoroethane containing 3.2 microliters of a 0.93 mol/L HCl solution in 1,1,1,2-tetrafluoroethane and 8.9 microliters of a 1.0 mol/L ethylaluminum dichloride solution in hexane. This last addition resulted in the formation of polymer 2.

[00128] In example 9, 2 ml of an HCl solution, prepared from 5 ml of 1,1-difluoroethane and 15.9 microliters of a 0.93 mol/L HCl solution in 1,1,1,2-tetrafluoroethane, was added without formation of polymer. This addition was followed by the drop-wise addition of 1 ml of an ethylaluminum dichloride solution prepared from 5 ml of 1,1-difluoroethane and 44.3 microliters of a 1.0 mol/L ethylaluminum dichloride solution in hexane. This last addition resulted in formation of polymer 2.

[00129] In example 10, the slurry prepared in methyl chloride, could not be effectively filtered to provide enough diluent blend for the second polymerization test. Example 10 is a comparative example.

Table 3^a

Example	Catalyst Volume (ml)	Conversion (wt%)	Polymer 1		Conversion (wt%)	Polymer 2	
			M_w $\times 10^{-3}$	M_w/M_n		M_w $\times 10^{-3}$	M_w/M_n
8	1.5	27	830	2.3	23	159	2.3
9	2.0	24	815	2.3	24	363	2.0
10	4.2	55	567	3.8	b	b	b

- a: Conversion is reported on the basis of the total monomers added at the beginning of the experiment. The total conversion for the entire polymerization is the sum of the conversions for each example.
- b: Not enough diluent could be collected for generation of Polymer 2

[00130] The examples in the preceding tables show that the separation of slurries formed in diluents comprising hydrofluorocarbons occurs faster than slurries formed in methyl chloride diluents. Polymer particles formed in diluents comprising hydrofluorocarbons absorb less of the diluent and are less sticky. Additionally, the density difference between rubber and R134a is greater than the density difference between rubber and methyl chloride. This increased density difference coupled with the less sticky nature of the polymer particles facilitates separation of the solid and liquid phases. This allows surprisingly faster separation of the polymer and diluent by a number of techniques herein. Such results can not be achieved with methyl chloride slurries.

[00131] All patents and patent applications, test procedures (such as ASTM methods), and other documents cited herein are fully incorporated by reference *to the extent such disclosure is not inconsistent with this invention* and for all jurisdictions in which such incorporation is permitted.

[00132] When numerical lower limits and numerical upper limits are listed herein, ranges from any lower limit to any upper limit are contemplated.

[00133] While the illustrative embodiments of the invention have been described with particularity, it will be understood that various other modifications will be apparent to and can be readily made by those skilled in the art without departing from the spirit and scope of the invention. Accordingly, it is not intended that the scope of the claims appended hereto be limited to the examples and descriptions set forth herein but rather that the claims be construed as encompassing all the features of patentable novelty which reside in the present invention, including all features which would be treated as equivalents thereof by those skilled in the art to which the invention pertains.

CLAIMS

WHAT IS CLAIMED IS:

1. A method for separating slurry components, the method comprising obtaining a slurry comprising a diluent comprising one or more hydrofluorocarbon(s) (HFC) and applying an effective amount of force to the slurry to obtain polymer particles.
2. The method of claim 1, wherein the force is a gravitational force.
3. The method of claim 2, wherein the gravitational force is 1 G.
4. The method of claim 1, wherein the force is a centrifugal force.
5. The method of claim 4, wherein the centrifugal force is from at least 500 G.
6. The method of claim 4, wherein the centrifugal force is from at least 1,000 G.
7. The method of claim 4, wherein the centrifugal force is from at least 5,000 G.
8. The method of claim 4, wherein the centrifugal force is from at least 10,000 G.
9. The method of claim 1, wherein the force applied is provided by a hydrocyclone.
10. The method of any of the preceding claims, wherein the polymer particles have a diluent mass uptake of less than 4 wt%.

11. The method of any of the preceding claims, wherein the polymer particles have a diluent mass uptake of less than 3 wt%.
12. The method of any of the preceding claims, wherein the polymer particles have a diluent mass uptake of less than 2 wt%.
13. The method of any of the preceding claims, wherein the polymer particles have a diluent mass uptake of less than 1 wt%.
14. The method of any of the preceding claims, wherein the polymer particles have a diluent mass uptake of less than 0.5 wt%.
15. The method of any of the preceding claims, wherein the one or more hydrofluorocarbon(s) is represented by the formula: $C_xH_yF_z$ wherein x is an integer from 1 to 40 and y and z are integers of one or more.
16. The method of claim 15, wherein x is from 1 to 10.
17. The method of claim 15, wherein x is from 1 to 6.
18. The method of claim 15, wherein x is from 1 to 3.
19. The method of any of the preceding claims, wherein the one or more hydrofluorocarbon(s) is independently selected from the group consisting of fluoromethane; difluoromethane; trifluoromethane; fluoroethane; 1,1-difluoroethane; 1,2-difluoroethane; 1,1,1-trifluoroethane; 1,1,2-trifluoroethane; 1,1,1,2-tetrafluoroethane; 1,1,2,2-tetrafluoroethane; 1,1,1,2,2-pentafluoroethane; 1-fluoropropane; 2-fluoropropane; 1,1-difluoropropane; 1,2-difluoropropane; 1,3-difluoropropane; 2,2-difluoropropane; 1,1,1-trifluoropropane; 1,1,2-trifluoropropane; 1,1,3-trifluoropropane; 1,2,2-trifluoropropane; 1,2,3-trifluoropropane; 1,1,1,2-

tetrafluoropropane; 1,1,1,3-tetrafluoropropane; 1,1,2,2-tetrafluoropropane;
 1,1,2,3-tetrafluoropropane; 1,1,3,3-tetrafluoropropane; 1,2,2,3-
 tetrafluoropropane; 1,1,1,2,2-pentafluoropropane; 1,1,1,2,3-
 pentafluoropropane; 1,1,1,3,3-pentafluoropropane; 1,1,2,2,3-
 pentafluoropropane; 1,1,2,3,3-pentafluoropropane; 1,1,1,2,2,3-
 hexafluoropropane; 1,1,1,2,3,3-hexafluoropropane; 1,1,1,3,3,3-
 hexafluoropropane; 1,1,1,2,2,3,3-heptafluoropropane; 1,1,1,2,3,3,3-
 heptafluoropropane; 1-fluorobutane; 2-fluorobutane; 1,1-difluorobutane;
 1,2-difluorobutane; 1,3-difluorobutane; 1,4-difluorobutane; 2,2-
 difluorobutane; 2,3-difluorobutane; 1,1,1-trifluorobutane; 1,1,2-
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 trifluorobutane; 1,2,3-trifluorobutane; 1,3,3-trifluorobutane; 2,2,3-
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 1,1,1,4-tetrafluorobutane; 1,1,2,2-tetrafluorobutane; 1,1,2,3-
 tetrafluorobutane; 1,1,2,4-tetrafluorobutane; 1,1,3,3-tetrafluorobutane;
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 1,2,3,4-tetrafluorobutane; 2,2,3,3-tetrafluorobutane; 1,1,1,2,2-
 pentafluorobutane; 1,1,1,2,3-pentafluorobutane; 1,1,1,2,4-
 pentafluorobutane; 1,1,1,3,3-pentafluorobutane; 1,1,1,3,4-
 pentafluorobutane; 1,1,1,4,4-pentafluorobutane; 1,1,2,2,3-
 pentafluorobutane; 1,1,2,2,4-pentafluorobutane; 1,1,2,3,3-
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 hexafluorobutane; 1,1,2,3,4,4-hexafluorobutane; 1,2,2,3,3,4-
 hexafluorobutane; 1,1,1,2,2,3,3-heptafluorobutane; 1,1,1,2,2,4,4-

heptafluorobutane; 1,1,1,2,2,3,4-heptafluorobutane; 1,1,1,2,3,3,4-heptafluorobutane; 1,1,1,2,3,4,4-heptafluorobutane; 1,1,1,2,4,4,4-heptafluorobutane; 1,1,1,3,3,4,4-heptafluorobutane; 1,1,1,2,2,3,3,4-octafluorobutane; 1,1,1,2,2,3,4,4-octafluorobutane; 1,1,1,2,3,3,4,4-octafluorobutane; 1,1,1,2,2,4,4,4-octafluorobutane; 1,1,1,2,3,4,4,4-octafluorobutane; 1,1,1,2,2,3,3,4,4-nonafluorobutane; 1,1,1,2,2,3,4,4,4-nonafluorobutane; 1-fluoro-2-methylpropane; 1,1-difluoro-2-methylpropane; 1,3-difluoro-2-methylpropane; 1,1,1-trifluoro-2-methylpropane; 1,1,3-trifluoro-2-methylpropane; 1,3-difluoro-2-(fluoromethyl)propane; 1,1,1,3-tetrafluoro-2-methylpropane; 1,1,3,3-tetrafluoro-2-methylpropane; 1,1,3-trifluoro-2-(fluoromethyl)propane; 1,1,1,3,3-pentafluoro-2-methylpropane; 1,1,3,3-tetrafluoro-2-(fluoromethyl)propane; 1,1,1,3-tetrafluoro-2-(fluoromethyl)propane; fluorocyclobutane; 1,1-difluorocyclobutane; 1,2-difluorocyclobutane; 1,3-difluorocyclobutane; 1,1,2-trifluorocyclobutane; 1,1,3-trifluorocyclobutane; 1,2,3-trifluorocyclobutane; 1,1,2,2-tetrafluorocyclobutane; 1,1,3,3-tetrafluorocyclobutane; 1,1,2,2,3-pentafluorocyclobutane; 1,1,2,3,3-pentafluorocyclobutane; 1,1,2,2,3,3-hexafluorocyclobutane; 1,1,2,2,3,4-hexafluorocyclobutane; 1,1,2,3,3,4-hexafluorocyclobutane; 1,1,2,2,3,3,4-heptafluorocyclobutane; vinyl fluoride; 1,1-difluoroethene; 1,2-difluoroethene; 1,1,2-trifluoroethene; 1-fluoropropene, 1,1-difluoropropene; 1,2-difluoropropene; 1,3-difluoropropene; 2,3-difluoropropene; 3,3-difluoropropene; 1,1,2-trifluoropropene; 1,1,3-trifluoropropene; 1,2,3-trifluoropropene; 1,3,3-trifluoropropene; 2,3,3-trifluoropropene; 3,3,3-trifluoropropene; 1-fluoro-1-butene; 2-fluoro-1-butene; 3-fluoro-1-butene; 4-fluoro-1-butene; 1,1-difluoro-1-butene; 1,2-difluoro-1-butene; 1,3-difluoropropene; 1,4-difluoro-1-butene; 2,3-difluoro-1-butene; 2,4-difluoro-1-butene; 3,3-difluoro-1-butene; 3,4-difluoro-1-butene; 4,4-difluoro-1-butene; 1,1,2-trifluoro-1-butene; 1,1,3-trifluoro-1-butene; 1,1,4-trifluoro-1-butene; 1,2,3-trifluoro-1-butene; 1,2,4-trifluoro-1-butene; 1,3,3-trifluoro-1-butene; 1,3,4-trifluoro-1-butene; 1,4,4-trifluoro-1-butene; 2,3,3-trifluoro-1-butene; 2,3,4-

trifluoro-1-butene; 2,4,4-trifluoro-1-butene; 3,3,4-trifluoro-1-butene; 3,4,4-trifluoro-1-butene; 4,4,4-trifluoro-1-butene; 1,1,2,3-tetrafluoro-1-butene; 1,1,2,4-tetrafluoro-1-butene; 1,1,3,3-tetrafluoro-1-butene; 1,1,3,4-tetrafluoro-1-butene; 1,1,4,4-tetrafluoro-1-butene; 1,2,3,3-tetrafluoro-1-butene; 1,2,3,4-tetrafluoro-1-butene; 1,2,4,4-tetrafluoro-1-butene; 1,3,3,4-tetrafluoro-1-butene; 1,3,4,4-tetrafluoro-1-butene; 1,4,4,4-tetrafluoro-1-butene; 2,3,3,4-tetrafluoro-1-butene; 2,3,4,4-tetrafluoro-1-butene; 2,4,4,4-tetrafluoro-1-butene; 3,3,4,4-tetrafluoro-1-butene; 3,4,4,4-tetrafluoro-1-butene; 1,1,2,3,3-pentafluoro-1-butene; 1,1,2,3,4-pentafluoro-1-butene; 1,1,2,4,4-pentafluoro-1-butene; 1,1,3,3,4-pentafluoro-1-butene; 1,1,3,4,4-pentafluoro-1-butene; 1,1,4,4,4-pentafluoro-1-butene; 1,2,3,3,4-pentafluoro-1-butene; 1,2,3,4,4-pentafluoro-1-butene; 1,2,4,4,4-pentafluoro-1-butene; 2,3,3,4,4-pentafluoro-1-butene; 2,3,4,4,4-pentafluoro-1-butene; 3,3,4,4,4-pentafluoro-1-butene; 1,1,2,3,3,4-hexafluoro-1-butene; 1,1,2,3,4,4-hexafluoro-1-butene; 1,1,2,4,4,4-hexafluoro-1-butene; 1,2,3,3,4,4-hexafluoro-1-butene; 1,2,3,4,4,4-hexafluoro-1-butene; 2,3,3,4,4,4-hexafluoro-1-butene; 1,1,2,3,3,4,4-heptafluoro-1-butene; 1,1,2,3,4,4,4-heptafluoro-1-butene; 1,1,3,3,4,4,4-heptafluoro-1-butene; 1,2,3,3,4,4,4-heptafluoro-1-butene; 1-fluoro-2-butene; 2-fluoro-2-butene; 1,1-difluoro-2-butene; 1,2-difluoro-2-butene; 1,3-difluoro-2-butene; 1,4-difluoro-2-butene; 2,3-difluoro-2-butene; 1,1,1-trifluoro-2-butene; 1,1,2-trifluoro-2-butene; 1,1,3-trifluoro-2-butene; 1,1,4-trifluoro-2-butene; 1,2,3-trifluoro-2-butene; 1,2,4-trifluoro-2-butene; 1,1,1,2-tetrafluoro-2-butene; 1,1,1,3-tetrafluoro-2-butene; 1,1,1,4-tetrafluoro-2-butene; 1,1,2,3-tetrafluoro-2-butene; 1,1,2,4-tetrafluoro-2-butene; 1,2,3,4-tetrafluoro-2-butene; 1,1,1,2,3-pentafluoro-2-butene; 1,1,1,2,4-pentafluoro-2-butene; 1,1,1,3,4-pentafluoro-2-butene; 1,1,1,4,4-pentafluoro-2-butene; 1,1,2,3,4-pentafluoro-2-butene; 1,1,2,4,4-pentafluoro-2-butene; 1,1,1,2,3,4-hexafluoro-2-butene; 1,1,1,2,4,4-hexafluoro-2-butene; 1,1,1,3,4,4-hexafluoro-2-butene; 1,1,1,4,4,4-hexafluoro-2-butene; 1,1,2,3,4,4-hexafluoro-2-butene; 1,1,1,2,3,4,4-

heptafluoro-2-butene; 1,1,1,2,4,4,4-heptafluoro-2-butene; and mixtures thereof.

20. The method of any of the preceding claims, wherein the one or more hydrofluorocarbon(s) is independently selected from the group consisting of fluoromethane, difluoromethane, trifluoromethane, 1,1-difluoroethane, 1,1,1-trifluoroethane, 1,1,1,2-tetrafluoroethane, and mixtures thereof.
21. The method of any of the preceding claims, wherein the diluent comprises from 15 to 100 volume % HFC based upon the total volume of the diluent.
22. The method of any of the preceding claims, wherein the diluent comprises from 20 to 100 volume % HFC based upon the total volume of the diluent.
23. The method of any of the preceding claims, wherein the diluent comprises from 25 to 100 volume % HFC based upon the total volume of the diluent.
24. The method of any of the preceding claims, wherein the diluent further comprises a hydrocarbon, a non-reactive olefin, and/or an inert gas.
25. The method of claim 24, wherein the hydrocarbon is a halogenated hydrocarbon other than an HFC.
26. The method of claim 25, wherein the halogenated hydrocarbon is methyl chloride.
27. The method of any of the preceding claims, wherein the polymer particles are polymerized by a continuous process.
28. The method of any of the preceding claims, wherein the polymer particles are polymerized by a cationic polymerization process.

29. The method of any of the preceding claims, wherein the polymer particles are less dense than the diluent.
30. The method of any of the preceding claims, wherein the polymer particles comprise isobutylene based polymers.
31. The method of claim 30, wherein the isobutylene based polymers are copolymers of isobutylene and isoprene.
32. The method of claim 30, wherein the isobutylene based polymers are copolymers of isobutylene and an alkylstyrene, preferably methylstyrene, more preferably *paramethylstyrene*.
33. The method of claim 30, wherein the isobutylene based polymers are homopolymers of isobutylene.
34. The method of any of the preceding claims, wherein the polymer particles are from at least 30 μ .
35. The method of any of the preceding claims, wherein the polymer particles are from at least 40 μ .
36. The method of any of claims 1-33, wherein the polymer particles are from 0.1 μ to 200.0 μ .
37. The method of any of claims 1-33, wherein the polymer particles are from 30 μ to 200 μ .
38. A method for separating slurry components, the method comprising providing a first slurry comprising a diluent comprising one or more hydrofluorocarbon(s) (HFC) and passing the first slurry through a device to obtain a second slurry, to obtain polymer particles.

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Replacement Sheet.

39. The method of claim 38, wherein the second slurry has a slurry concentration greater than the slurry concentration of the first slurry.
40. The method of claim 38 or 39, wherein the device is a filter.
41. The method of claim 40, wherein the flow of the first slurry is tangential to the surface of the filter.
42. The method of claim 40, wherein the filter comprises media having diameters or cross-sections less than the diameters or cross-sections of the polymer particles.
43. The method of claim 40, wherein the filter comprises media having diameters or cross-sections less than the diameters or cross-sections of from at least 40% of the polymer particles passing through the filter.
44. The method of claim 40, wherein the filter comprises media having diameters or cross-sections less than the diameters or cross-sections of from at least 50% of the polymer particles passing through the filter.
45. The method of claim 40, wherein the filter comprises media having diameters or cross-sections less than the diameters or cross-sections of from at least 60% of the polymer particles passing through the filter.
46. The method of any of claims 38-45, wherein the polymer particles have a diluent mass uptake of less than 4 wt%.
47. The method of any of claims 38-45, wherein the polymer particles have a diluent mass uptake of less than 3 wt%.

48. The method of any of claims 38-45, wherein the polymer particles have a diluent mass uptake of less than 2 wt%.
49. The method of any of claims 38-45, wherein the polymer particles have a diluent mass uptake of less than 1 wt%.
50. The method of any of claims 38-45, wherein the polymer particles have a diluent mass uptake of less than 0.5 wt%.
51. The method of any of claims 38-50, wherein the one or more hydrofluorocarbon(s) is represented by the formula: $C_xH_yF_z$ wherein x is an integer from 1 to 40 and y and z are integers of one or more.
52. The method of claim 51, wherein x is from 1 to 10.
53. The method of claim 51, wherein x is from 1 to 6.
54. The method of claim 51, wherein x is from 1 to 3.
55. The method of any of claims 38-54, wherein the one or more hydrofluorocarbon(s) is independently selected from the group consisting of fluoromethane; difluoromethane; trifluoromethane; fluoroethane; 1,1-difluoroethane; 1,2-difluoroethane; 1,1,1-trifluoroethane; 1,1,2-trifluoroethane; 1,1,1,2-tetrafluoroethane; 1,1,2,2-tetrafluoroethane; 1,1,1,2,2-pentafluoroethane; 1-fluoropropane; 2-fluoropropane; 1,1-difluoropropane; 1,2-difluoropropane; 1,3-difluoropropane; 2,2-difluoropropane; 1,1,1-trifluoropropane; 1,1,2-trifluoropropane; 1,1,3-trifluoropropane; 1,2,2-trifluoropropane; 1,2,3-trifluoropropane; 1,1,1,2-tetrafluoropropane; 1,1,1,3-tetrafluoropropane; 1,1,2,2-tetrafluoropropane; 1,1,2,3-tetrafluoropropane; 1,1,3,3-tetrafluoropropane; 1,2,2,3-tetrafluoropropane; 1,1,1,2,2-pentafluoropropane; 1,1,1,2,3-pentafluoropropane; 1,1,1,3,3-pentafluoropropane; 1,1,2,2,3-

pentafluoropropane;	1,1,2,3,3-pentafluoropropane;	1,1,1,2,2,3-
hexafluoropropane;	1,1,1,2,3,3-hexafluoropropane;	1,1,1,3,3,3-
hexafluoropropane;	1,1,1,2,2,3,3-heptafluoropropane;	1,1,1,2,3,3,3-
heptafluoropropane;	1-fluorobutane;	2-fluorobutane;
	1,1-difluorobutane;	
1,2-difluorobutane;	1,3-difluorobutane;	1,4-difluorobutane;
2,2-	difluorobutane;	2,3-difluorobutane;
	1,1,1-trifluorobutane;	1,1,2-
trifluorobutane;	1,1,3-trifluorobutane;	1,1,4-trifluorobutane;
1,2,2-	trifluorobutane;	1,2,3-trifluorobutane;
	1,3,3-trifluorobutane;	2,2,3-
trifluorobutane;	1,1,1,2-tetrafluorobutane;	1,1,1,3-tetrafluorobutane;
1,1,1,4-tetrafluorobutane;	1,1,2,2-tetrafluorobutane;	1,1,2,3-
tetrafluorobutane;	1,1,2,4-tetrafluorobutane;	1,1,3,3-tetrafluorobutane;
1,1,3,4-tetrafluorobutane;	1,1,4,4-tetrafluorobutane;	1,2,2,3-
tetrafluorobutane;	1,2,2,4-tetrafluorobutane;	1,2,3,3-tetrafluorobutane;
1,2,3,4-tetrafluorobutane;	2,2,3,3-tetrafluorobutane;	1,1,1,2,2-
pentafluorobutane;	1,1,1,2,3-pentafluorobutane;	1,1,1,2,4-
pentafluorobutane;	1,1,1,3,3-pentafluorobutane;	1,1,1,3,4-
pentafluorobutane;	1,1,1,4,4-pentafluorobutane;	1,1,2,2,3-
pentafluorobutane;	1,1,2,2,4-pentafluorobutane;	1,1,2,3,3-
pentafluorobutane;	1,1,2,4,4-pentafluorobutane;	1,1,3,3,4-
pentafluorobutane;	1,2,2,3,3-pentafluorobutane;	1,2,2,3,4-
pentafluorobutane;	1,1,1,2,2,3-hexafluorobutane;	1,1,1,2,2,4-
hexafluorobutane;	1,1,1,2,3,3-hexafluorobutane;	1,1,1,2,3,4-
hexafluorobutane;	1,1,1,2,4,4-hexafluorobutane;	1,1,1,3,3,4-
hexafluorobutane;	1,1,1,3,4,4-hexafluorobutane;	1,1,1,4,4,4-
hexafluorobutane;	1,1,2,2,3,3-hexafluorobutane;	1,1,2,2,3,4-
hexafluorobutane;	1,1,2,2,4,4-hexafluorobutane;	1,1,2,3,3,4-
hexafluorobutane;	1,1,2,3,4,4-hexafluorobutane;	1,2,2,3,3,4-
hexafluorobutane;	1,1,1,2,2,3,3-heptafluorobutane;	1,1,1,2,2,4,4-
heptafluorobutane;	1,1,1,2,2,3,4-heptafluorobutane;	1,1,1,2,3,3,4-
heptafluorobutane;	1,1,1,2,3,4,4-heptafluorobutane;	1,1,1,2,4,4,4-
heptafluorobutane;	1,1,1,3,3,4,4-heptafluorobutane;	1,1,1,2,2,3,3,4-
octafluorobutane;	1,1,1,2,2,3,4,4-octafluorobutane;	1,1,1,2,3,3,4,4-

octafluorobutane; 1,1,1,2,2,4,4,4-octafluorobutane; 1,1,1,2,3,4,4,4-octafluorobutane; 1,1,1,2,2,3,3,4,4-nonafluorobutane; 1,1,1,2,2,3,4,4,4-nonafluorobutane; 1-fluoro-2-methylpropane; 1,1-difluoro-2-methylpropane; 1,3-difluoro-2-methylpropane; 1,1,1-trifluoro-2-methylpropane; 1,1,3-trifluoro-2-methylpropane; 1,3-difluoro-2-(fluoromethyl)propane; 1,1,1,3-tetrafluoro-2-methylpropane; 1,1,3,3-tetrafluoro-2-methylpropane; 1,1,3-trifluoro-2-(fluoromethyl)propane; 1,1,1,3,3-pentafluoro-2-methylpropane; 1,1,3,3-tetrafluoro-2-(fluoromethyl)propane; 1,1,1,3-tetrafluoro-2-(fluoromethyl)propane; fluorocyclobutane; 1,1-difluorocyclobutane; 1,2-difluorocyclobutane; 1,3-difluorocyclobutane; 1,1,2-trifluorocyclobutane; 1,1,3-trifluorocyclobutane; 1,2,3-trifluorocyclobutane; 1,1,2,2-tetrafluorocyclobutane; 1,1,3,3-tetrafluorocyclobutane; 1,1,2,2,3-pentafluorocyclobutane; 1,1,2,3,3-pentafluorocyclobutane; 1,1,2,2,3,3-hexafluorocyclobutane; 1,1,2,2,3,4-hexafluorocyclobutane; 1,1,2,3,3,4-hexafluorocyclobutane; 1,1,2,2,3,3,4-heptafluorocyclobutane; vinyl fluoride; 1,1-difluoroethene; 1,2-difluoroethene; 1,1,2-trifluoroethene; 1-fluoropropene, 1,1-difluoropropene; 1,2-difluoropropene; 1,3-difluoropropene; 2,3-difluoropropene; 3,3-difluoropropene; 1,1,2-trifluoropropene; 1,1,3-trifluoropropene; 1,2,3-trifluoropropene; 1,3,3-trifluoropropene; 2,3,3-trifluoropropene; 3,3,3-trifluoropropene; 1-fluoro-1-butene; 2-fluoro-1-butene; 3-fluoro-1-butene; 4-fluoro-1-butene; 1,1-difluoro-1-butene; 1,2-difluoro-1-butene; 1,3-difluoropropene; 1,4-difluoro-1-butene; 2,3-difluoro-1-butene; 2,4-difluoro-1-butene; 3,3-difluoro-1-butene; 3,4-difluoro-1-butene; 4,4-difluoro-1-butene; 1,1,2-trifluoro-1-butene; 1,1,3-trifluoro-1-butene; 1,1,4-trifluoro-1-butene; 1,2,3-trifluoro-1-butene; 1,2,4-trifluoro-1-butene; 1,3,3-trifluoro-1-butene; 1,3,4-trifluoro-1-butene; 1,4,4-trifluoro-1-butene; 2,3,3-trifluoro-1-butene; 2,3,4-trifluoro-1-butene; 2,4,4-trifluoro-1-butene; 3,3,4-trifluoro-1-butene; 3,4,4-trifluoro-1-butene; 4,4,4-trifluoro-1-butene; 1,1,2,3-tetrafluoro-1-butene; 1,1,2,4-tetrafluoro-1-butene; 1,1,3,3-tetrafluoro-1-butene; 1,1,3,4-tetrafluoro-1-butene; 1,1,4,4-tetrafluoro-1-butene; 1,2,3,3-tetrafluoro-1-

butene; 1,2,3,4-tetrafluoro-1-butene; 1,2,4,4-tetrafluoro-1-butene; 1,3,3,4-tetrafluoro-1-butene; 1,3,4,4-tetrafluoro-1-butene; 1,4,4,4-tetrafluoro-1-butene; 2,3,3,4-tetrafluoro-1-butene; 2,3,4,4-tetrafluoro-1-butene; 2,4,4,4-tetrafluoro-1-butene; 3,3,4,4-tetrafluoro-1-butene; 3,4,4,4-tetrafluoro-1-butene; 1,1,2,3,3-pentafluoro-1-butene; 1,1,2,3,4-pentafluoro-1-butene; 1,1,2,4,4-pentafluoro-1-butene; 1,1,3,3,4-pentafluoro-1-butene; 1,1,3,4,4-pentafluoro-1-butene; 1,1,4,4,4-pentafluoro-1-butene; 1,2,3,3,4-pentafluoro-1-butene; 1,2,3,4,4-pentafluoro-1-butene; 1,2,4,4,4-pentafluoro-1-butene; 2,3,3,4,4-pentafluoro-1-butene; 2,3,4,4,4-pentafluoro-1-butene; 3,3,4,4,4-pentafluoro-1-butene; 1,1,2,3,3,4-hexafluoro-1-butene; 1,1,2,3,4,4-hexafluoro-1-butene; 1,1,2,4,4,4-hexafluoro-1-butene; 1,2,3,3,4,4-hexafluoro-1-butene; 1,2,3,4,4,4-hexafluoro-1-butene; 2,3,3,4,4,4-hexafluoro-1-butene; 1,1,2,3,3,4,4-heptafluoro-1-butene; 1,1,2,3,4,4,4-heptafluoro-1-butene; 1,1,3,3,4,4,4-heptafluoro-1-butene; 1,2,3,3,4,4,4-heptafluoro-1-butene; 1-fluoro-2-butene; 2-fluoro-2-butene; 1,1-difluoro-2-butene; 1,2-difluoro-2-butene; 1,3-difluoro-2-butene; 1,4-difluoro-2-butene; 2,3-difluoro-2-butene; 1,1,1-trifluoro-2-butene; 1,1,2-trifluoro-2-butene; 1,1,3-trifluoro-2-butene; 1,1,4-trifluoro-2-butene; 1,2,3-trifluoro-2-butene; 1,2,4-trifluoro-2-butene; 1,1,1,2-tetrafluoro-2-butene; 1,1,1,3-tetrafluoro-2-butene; 1,1,1,4-tetrafluoro-2-butene; 1,1,2,3-tetrafluoro-2-butene; 1,1,2,4-tetrafluoro-2-butene; 1,2,3,4-tetrafluoro-2-butene; 1,1,1,2,3-pentafluoro-2-butene; 1,1,1,2,4-pentafluoro-2-butene; 1,1,1,3,4-pentafluoro-2-butene; 1,1,1,4,4-pentafluoro-2-butene; 1,1,2,3,4-pentafluoro-2-butene; 1,1,2,4,4-pentafluoro-2-butene; 1,1,1,2,3,4-hexafluoro-2-butene; 1,1,1,2,4,4-hexafluoro-2-butene; 1,1,1,3,4,4-hexafluoro-2-butene; 1,1,1,4,4,4-hexafluoro-2-butene; 1,1,2,3,4,4-hexafluoro-2-butene; 1,1,1,2,3,4,4-heptafluoro-2-butene; 1,1,1,2,4,4,4-heptafluoro-2-butene; and mixtures thereof.

56. The method of any of claims 38-54, wherein the one or more hydrofluorocarbon(s) is independently selected from the group consisting

of fluoromethane, difluoromethane, trifluoromethane, 1,1-difluoroethane, 1,1,1-trifluoroethane, 1,1,1,2-tetrafluoroethane, and mixtures thereof.

57. The method of any of claims 38-56, wherein the diluent comprises from 15 to 100 volume % HFC based upon the total volume of the diluent.
58. The method of any of claims 38-56, wherein the diluent comprises from 20 to 100 volume % HFC based upon the total volume of the diluent.
59. The method of any of claims 38-56, wherein the diluent comprises from 25 to 100 volume % HFC based upon the total volume of the diluent.
60. The method of any of claims 38-59, wherein the diluent further comprises a hydrocarbon, a non-reactive olefin, and/or an inert gas.
61. The method of claim 60, wherein the hydrocarbon is a halogenated hydrocarbon other than an HFC.
62. The method of claim 61, wherein the halogenated hydrocarbon is methyl chloride.
63. The method of any of claims 38-62, wherein the polymer particles are polymerized by a continuous process.
64. The method of any of claims 38-63, wherein the polymer particles are polymerized by a cationic polymerization process.
65. The method of any of claims 38-64, wherein the polymer particles are less dense than the diluent.
66. The method of any of claims 38-65, wherein the polymer particles comprise isobutylene based polymers.

67. The method of claim 66, wherein the isobutylene based polymers are copolymers of isobutylene and isoprene.
68. The method of claim 66, wherein the isobutylene based polymers are copolymers of isobutylene and an alkylstyrene, preferably methylstyrene, more preferably *paramethylstyrene*.
69. The method of claim 66, wherein the isobutylene based polymers are homopolymers of isobutylene.
70. The method of any of claims 38-69, wherein the polymer particles are from at least 30 μ .
71. The method of any of claims 38-69, wherein the polymer particles are from at least 40 μ .
72. The method of any of claims 38-69, wherein the polymer particles are from 0.1 μ to 200.0 μ .
73. The method of any of claims 38-69, wherein the polymer particles are from 30 μ to 200 μ .