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Conventional Vulcanization

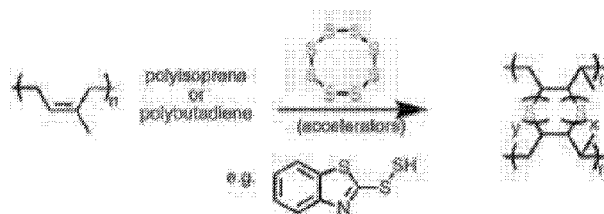


FIG. 2A

"All in One" CHIPS Vulcanization Agent

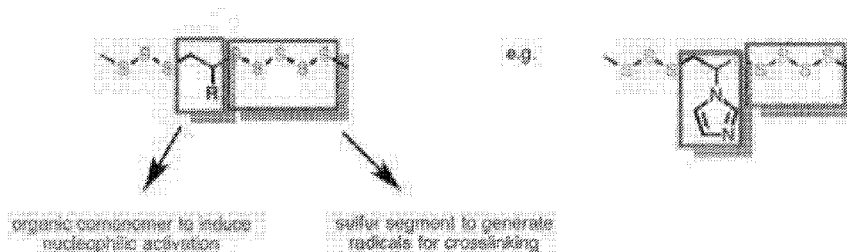


FIG. 2B

(57) Abstract: Methods of vulcanization using a high content sulfur polymer, instead of elemental sulfur, have been developed. These high sulfur content polymers are referred to as Chalcogenide Hybrid Inorganic/Organic Polymers (CHIP) materials and have good polymer compatibility in that they are soluble in a number of polymers. Furthermore, CHIP materials may have weaker bonds than the S-S bonds of elemental sulfur and thus provide for a higher crosslinking efficiency vulcanization.



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CHALCOGENIDE HYBRID INORGANIC/ORGANIC POLYMER (CHIP) MATERIALS AS IMPROVED CROSSLINKING AGENTS FOR VULCANIZATION

CROSS REFERENCE

[0001] This application claims priority to U.S. Provisional Patent Application No. 62/520,215, filed June 15, 2017, the specifications of which are incorporated herein in their entirety by reference.

FIELD OF THE INVENTION

[0002] The present invention relates to vulcanization of natural and synthetic polymers using a vulcanizing agent comprising a high sulfur content polymer or Chalcogenide Hybrid Inorganic/organic Polymer (CHIP) material.

BACKGROUND OF THE INVENTION

[0003] Vulcanization of rubber and other polymeric materials is a well-established method for enhancing physical properties by chemical crosslinking. Vulcanized materials are generally more thermally, chemically, and physically robust than their non-vulcanized analogs. These increased characteristics are attributed to the formation of carbon-sulfur bonds which allow for bridging of the polymer chains by varying numbers of sulfur atoms to form crosslinked networks.

[0004] While the practice of vulcanization has expanded to include a variety of natural and synthetic polymer substrates, limitations and drawbacks of the method have also been identified. Vulcanization of rubbers by sulfur alone is an inefficient process. The chemical reaction between sulfur and the rubber occurs mainly at the C=C double bonds and each crosslink requires 40 to 55 sulfur atoms (in the absence of an accelerator). The process of vulcanizing using only sulfur is uneconomical by today's production standards. The crosslinked materials thus produced are extremely prone to oxidative degradation and do not possess adequate mechanical properties for practical rubber applications.

[0005] These limitations have been partially overcome by use of accelerator additives in vulcanized rubber formulations. Such additives are known to increase the speed of vulcanization and to permit vulcanization to proceed at lower temperature and with greater efficiency. Despite the improvements afforded by accelerator additives, vulcanization still requires high temperatures and suffers from inefficient mixing of components due to poor incompatibility which results in incomplete curing and undesirable decomposition. Hence, there is a need for vulcanizing agents with improved polymer compatibility and lower-temperature curing.

[0006] An incredible abundance of elemental sulfur (S_8), nearly 7-million tons is generated as a waste byproduct from hydrodesulfurization of crude petroleum feedstocks, which converts alkanethiols and other (organo) sulfur compounds into S_8 . Before the invention of the inverse vulcanization process, there were only a limited number of synthetic methods available to utilize and modify elemental sulfur. Current industrial utilization of elemental sulfur is centered around sulfuric acid, agrochemicals, and vulcanization of rubber. For example, elemental sulfur is used primarily for sulfuric acid and ammonium phosphate fertilizers, where the rest of the excess sulfur is stored as megaton-sized, above ground sulfur towers.

[0007] While sulfur feedstocks are plentiful, sulfur is difficult to process. In its original form, elemental sulfur consists of a cyclic molecule having the chemical formulation S_8 . Elemental sulfur is a brittle, intractable, crystalline solid having poor solid state mechanical properties, poor solution processing characteristics, and there is a limited slate of synthetic methodologies developed for it. Hence, there is a need for the production of new materials that offers significant environmental and public health benefits to mitigate the storage of excess sulfur in powder, or brick form.

SUMMARY OF THE INVENTION

[0008] In this invention, it is surprisingly discovered that the use of a high content sulfur polymer instead of elemental sulfur as a vulcanizing agent surprisingly allows for a higher crosslinking efficiency vulcanization without the use of a separate accelerator additive. These high sulfur content polymers are referred to as Chalcogenide Hybrid Inorganic/Organic Polymers (CHIP) materials. In this invention, the CHIP materials are tuned to have good polymer compatibility or solubility in a number of polymers. Furthermore, CHIP materials may be specially selected to provide for a lower temperature vulcanization. The CHIP materials of the present invention are suitable for use as vulcanizing agents because their composition and reactivity are specially tuned via the inverse vulcanization polymerization of sulfur with functional organic comonomers. The innovative combination of appropriate comonomers improves miscibility with liquid polydienes and introduces nucleophilic groups to accelerate crosslinking.

[0009] It is an objective of the present invention to provide for compositions and methods of vulcanization using chalcogenide hybrid inorganic/organic polymers (CHIP) materials, as specified in the independent claims. Embodiments of the invention are given in the dependent claims. Embodiments of the present invention can be freely combined with each other if they are not mutually exclusive.

[0010] The unique and inventive technical features of the present invention include the use of CHIP materials as a vulcanizing agent. CHIP materials comprise one or more chalcogenic monomers at a level of at least 45 wt% of the CHIP material and one or more comonomers, at a level in the range of about 5-55 wt% of the CHIP material. In some embodiments, the one or more comonomers are co-polymerized with the chalcogenic monomers. In this invention, the physical and chemical properties of the CHIP's, such as compatibility with conventional polymers, variation of chalcogenic bonds, and crosslinking ability are optimized to allow the CHIP materials to act as superior vulcanizing agents. Without wishing to limit the invention to any theory or mechanism, it is believed that these technical features advantageously allow for vulcanization methods and compositions with better mixing and more complete and efficient crosslinking. None of the presently known prior references or work has the unique inventive technical feature of the present invention.

[0011] In one embodiment, elemental sulfur used in vulcanization is partially or completely replaced with a CHIP material or a vulcanizing agent comprising a CHIP material. The high sulfur content of the CHIP materials allows for formation of the same sulfur-bridging linkages of vulcanized polymer chains that are formed in traditional vulcanization. The chalcogen bonds in the CHIP materials may also be varied to introduce weaker bonds than those found in elemental sulfur and may result in crosslinking sulfur

vulcanization agents that are effectively more accessible for crosslinking than in other sulfur sources such as elemental sulfur. The polymeric form of the CHIP materials also circumvents the known problem of elemental sulfur's general low solubility and incompatibility with polymers.

[0012] In another embodiment, the present invention may feature a vulcanized rubber composition prepared from a latex material and a vulcanizing agent comprising a CHIP material. In some embodiments, the vulcanizing agent may vulcanize the latex material to provide a crosslinked rubber. The rubber may further comprise one or more additives. Non-limiting examples of additives include an accelerator, a peroxide, a plasticizer, an anti-ozonant, an antioxidant, a retarder, a lubricant, a filler, a colorant or a combination thereof. In yet another embodiment, the present invention may feature a method of vulcanizing a latex material to form a crosslinked rubber. In an embodiment, the method may comprise reacting said latex material with a CHIP material such that the CHIP material vulcanizes the latex material to provide said crosslinked rubber. As a non-limiting example, the method may be performed in a time of about 10 to 20 min and at a temperature of less than about 170 °C.

[0013] In some embodiments, the latex material may be natural, synthetic, or a combination thereof and may comprise a natural rubber, a polydiene, a polydiene copolymer, polybutadiene, polyisoprene, polychloroprene, a butyl rubber, a silicone rubber latex, an acrylic rubber latex or a combination thereof. In other embodiments, the chalcogenic monomers may comprise sulfur monomers derived from elemental sulfur and elemental selenium (Se_8) or be selected from a group consisting of elemental sulfur, a liquid polysulfide, an oligomer containing sulfur, and an oligomer containing sulfur and selenium units.

[0014] According to a preferred embodiment, the one or more monomers may be co-polymerized with the chalcogenic monomers via free radical polymerization, controlled radical polymerization, ring-opening polymerization, ring-opening metathesis polymerization, step-growth polymerization, or chain-growth polymerization. In further embodiments, the comonomers may be each selected from a group consisting of amine comonomers, thiol comonomers, sulfide comonomers, alkynyllyl unsaturated comonomers, epoxide comonomers, nitron comonomers, aldehyde comonomers, ketone comonomers, thiirane comonomers, ethylenically unsaturated comonomers, styrenic comonomers, vinylic comonomers, methacrylate comonomers, acrylonitrile comonomers, allylic monomers, acrylate monomers, vinylpyridine monomers, isobutylene monomers, maleimide monomers, norbornene monomers, monomers having at least one vinyl ether moiety, monomers having at least one isopropenyl moiety, monomers having at least one imidazole moiety, and monomers having at least one heterocyclic moiety.

[0015] According to another embodiment, the CHIP material may comprise chalcogenic bonds which are weaker than an S-S bond in elemental sulfur. In an embodiment, the chalcogenic bonds may break with the application of heat or a catalyst to generate one or more radical species which may react with said latex material. In some embodiments, the CHIP material may further comprise one or more second comonomers.

[0016] In one embodiment, the CHIP material may comprise one or more reactive functional groups.

These functional groups may be capable of activating one or more chalcogen bonds to accelerate vulcanization or of accelerating a breaking of one or more chalcogen bonds. In some embodiments, the functional groups may be nucleophilic functional groups. In other embodiments, the functional groups may be amine, N-heterocyclic, phosphine, or sulphide functional groups.

[0017] Any feature or combination of features described herein are included within the scope of the present invention provided that the features included in any such combination are not mutually inconsistent as will be apparent from the context, this specification, and the knowledge of one of ordinary skill in the art. Additional advantages and aspects of the present invention are apparent in the following detailed description and claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0018] The features and advantages of the present invention will become apparent from a consideration of the following detailed description presented in connection with the accompanying drawings in which:

[0019] FIG. 1A shows a non-limiting schematic of inverse vulcanization using vinylic comonomers.

[0020] FIG. 1B shows a non-limiting schematic of inverse vulcanization to form functional terpolymers.

[0021] FIG. 2A shows a reaction scheme of conventional vulcanization using elemental sulfur.

[0022] FIG. 2B shows a non-limiting example of a CHIP vulcanization agent of the present invention.

[0023] FIG. 3A shows an example reaction of liquid sulfur (left) with low molar mass polybutadiene ($M_n \sim 1500$ g/mol).

[0024] FIG. 3B shows an example reaction of poly(styrene-random-sulfur) CHIP copolymer (left) with low molar mass polybutadiene ($M_n \sim 1500$ g/mol).

[0025] FIG. 3C shows an example reaction of a CHIP copolymer from sulfur and N-vinylimidazole (left) with low molar mass polybutadiene ($M_n \sim 1500$ g/mol).

[0026] FIG. 4 shows an embodiment in which introduction of an organic comonomer unit improves miscibility of a sulfur vulcanizing agent with inexpensive vinylic, styrenic, or olefinic compounds.

[0027] FIG. 5 shows an embodiment of a vulcanizing agent with introduction of stable but weaker bonds than S-S bonds with weaker bonds than S-S bonds through a copolymer backbone (Se-S), or through a photoresponsive organic comonomer unit.

[0028] FIG. 6 shows an embodiment featuring installation of accelerators directly onto a sulfur vulcanizing agent that activates at elevated temperatures through an organic comonomer unit.

[0029] FIG. 7 shows a non-limiting example of polymerizations with elemental selenium.

[0030] FIG. 8 shows comparative reactions schemes for varying temperatures of polymerization of elemental sulfur and elemental selenium. Lower temperatures can lead to grey selenium cracking.

[0031] FIG. 9 shows a non-limiting example of inverse vulcanization of selenium sulfide.

[0032] FIG. 10 shows non-limiting examples of introduction of amines and N-heterocycles to CHIP materials.

[0033] FIG. 11 shows non-limiting examples of the synthesis of aniline functional polysulfides.

DESCRIPTION OF PREFERRED EMBODIMENTS

[0034] As used herein, sulfur can be provided as elemental sulfur, for example, in powdered form. Under ambient conditions, elemental sulfur primarily exists in an eight-membered ring form (S₈) which melts at temperatures in the range of 120°C -130 °C and undergoes an equilibrium ring-opening polymerization (ROP) of the S₈ monomer into a linear polysulfane with diradical chain ends. As the person of skill in the art will appreciate, while S₈ is generally the most stable, most accessible and cheapest feedstock, many other allotropes of sulfur can be used (such as other cyclic allotropes, derivable by melt-thermal processing of S₈). Any sulfur species that yield diradical or anionic polymerizing species when heated as described herein can be used in practicing the present invention.

[0035] As used herein, a "CHIP material" is a material comprising one or more chalcogenide hybrid inorganic/organic polymers. As a non-limiting example, a CHIP material may comprise a copolymer prepared by the copolymerization of one or more chalcogenide monomers with one or more comonomers.

[0036] As used herein, a "styrenic comonomer" is a monomer that has a vinyl functional group. The styrenic comonomer may comprise a styrene and at least one reactive functional group. As known to one of ordinary skill in the art, a styrene is a derivative of benzene ring that has a vinylic moiety. The sulfur diradicals can link to the vinylic moieties of the styrenic commoners to form the sulfur-styrenic polymer. In certain embodiments, the reactive functional group may be a halogen, an alkyl halide, an alkyl, an alkoxy, an amine, or a nitro functional group. Non-limiting examples of styrenic comonomers include bromostyrene, chlorostyrene, fluorostyrene, (trifluoromethyl)styrene, vinylaniline, acetoxystyrene, methoxystyrene, ethoxystyrene, methylstyrene, nitrostyrene, vinylbenzoic acid, vinylanisole, and vinylbenzyl chloride.

[0037] As used herein, the term "amine monomer" is a monomer that has an amine functional group. In one embodiment, aromatic amines and multi-functional amines may be used. Amine monomers include, but are not limited to, aromatic amines, *m*-phenylenediamine, and *p*-phenylenediamine. The various types of phenylenediamines are inexpensive reagents due to their wide-spread use in the preparation of many conventional polymers, e.g., polyureas, polyamides

[0038] As used herein, the term "thiol monomer" is a monomer that has a thiol functional group. Thiol monomers include, but are not limited to, 4,4'-thiobisbenzenethiol and the like. The term "sulfide monomers" are monomers that have sulfide functional groups.

[0039] As used herein, an alkynylly unsaturated monomer is a monomer that has an alkynylly unsaturated functional group (i.e. triple bond). The term "alkynylly unsaturated monomer" does not include compounds in which the alkynyl unsaturation is part of a long chain alkyl moiety (e.g., unsaturated fatty acids, or carboxylic salts, or esters such as oleates, and unsaturated plant oils). In one embodiment, aromatic alkynes, both internal and terminal alkynes, multi-functional alkynes may be used. Examples of alkynylly unsaturated monomers include, but are not limited to, ethynylbenzene, 1-phenylpropyne, 1,2-diphenylethyne, 1,4-diethynylbenzene, 1,4-bis(phenylethynyl) benzene, and 1,4-diphenylbuta-1,3-diyne.

[0040] As used herein, the term "nitrone monomer" is a monomer that has a nitrone groups. In one

embodiment, nitrones, dinitrones, and multi-nitrones may be used. Examples include, but are not limited to, N-benzylidene-2-methylpropan-2-amine oxide. As used herein, the term “aldehyde monomer” is a monomer that has an aldehyde functional group. In one embodiment, aldehydes, dialdehydes, and multi-aldehydes may be used. As used herein, the term “ketone monomer” is a monomer that has a ketone functional group. In one embodiment, ketones, di-ketones, and multi-ketones may be used.

[0041] As used herein, the term “epoxide monomer” is a monomer that has epoxide functional groups. Non-limiting examples of such monomers include, generally, mono- or polyoxiranylbenzenes, mono- or polyglycidylbenzenes, mono- or polyglycidyloxybenzenes, mono- or polyoxiranyl(hetero)aromatic compounds, mono- or polyglycidyl(hetero)aromatic compounds, mono- or polyglycidyloxy(hetero)aromatic compounds, diglycidyl bisphenol A ethers, mono- or polyglycidyl(cyclo)alkyl ethers, mono- or polyepoxy(cyclo)alkane compounds and oxirane-terminated oligomers. In one preferred embodiment, the epoxide monomers may be benzyl glycidyl ether and tris(4-hydroxyphenyl)methane triglycidyl ether. In certain embodiments, the epoxide monomers may include a (hetero)aromatic moiety such as, for example, a phenyl, a pyridine, a triazine, a pyrene, a naphthalene, or a polycyclic (hetero)aromatic ring system, bearing one or more epoxide groups. For example, in certain embodiments, the one or more epoxide monomers are selected from epoxy(hetero)aromatic compounds, such as styrene oxide and stilbene oxide and (hetero)aromatic glycidyl compounds, such as glycidyl phenyl ethers (e.g., resorcinol diglycidyl ether, glycidyl 2-methylphenyl ether), glycidylbenzenes (e.g., (2,3-epoxypropyl)benzene) and glycidyl heteroaromatic compounds (e.g., N-(2,3-epoxypropyl)phthalimide). In certain desirable embodiments, an epoxide monomer will have a boiling point greater than 180 °C, greater than 200 °C, or even greater than 230 °C at the pressure at which polymerization is performed (e.g., at standard pressure, or at other pressures).

[0042] As used herein, the term “thiirane monomer” is a monomer that has a thiirane functional group. Non-limiting examples of thiirane monomers include, generally, mono- or polythiiranylbenzenes, mono- or polythiiranylmethylbenzenes, mono- or polythiiranyl(hetero)aromatic compounds, mono- or polythiiranylmethyl(hetero)-aromatic compounds, dithiiranylmethyl bisphenol A ethers, mono- or polydithiiranyl (cyclo)alkyl ethers, mono- or polyepisulfide(cyclo)alkane compounds, and thiirane-terminated oligomers. In some embodiments, thiirane monomers may include a (hetero)aromatic moiety such as, for example, a phenyl, a pyridine, a triazine, a pyrene, a naphthalene, or a poly cyclic (hetero)aromatic ring system, bearing one or more thiirane groups. In certain desirable embodiments, a thiirane monomer can have a boiling point greater than 180 °C, greater than 200 °C, or even greater than 230 °C at the pressure at which polymerization is performed (e.g., at standard pressure).

[0043] As used herein, an ethylenically unsaturated monomer is a monomer that contains an ethylenically unsaturated functional group (i.e. double bond). The term “ethylenically unsaturated monomer” does not include cyclopentadienyl species such as cyclopentadiene and dicyclopentadiene. The term “ethylenically unsaturated monomer” does not include compounds in which the ethylenic unsaturation is part of a long chain alkyl moiety (e.g. unsaturated fatty acids such as oleates, and unsaturated plant oils).

[0044] Non-limiting examples of ethylenically unsaturated monomers include vinyl monomers, acryl monomers, (meth)acryl monomers, unsaturated hydrocarbon monomers, and ethylenically-terminated oligomers. Examples of such monomers include, generally, mono- or polyvinylbenzenes, mono- or polyisopropenylbenzenes, mono- or polyvinyl(hetero)aromatic compounds, mono- or polyisopropenyl(hetero)-aromatic compounds, acrylates, methacrylates, alkylene di(meth)acrylates, bisphenol A di(meth)acrylates, benzyl (meth)acrylates, phenyl(meth)acrylates, heteroaryl (meth)acrylates, terpenes (e.g., squalene) and carotene. In other embodiments, the ethylenically unsaturated monomers may include a (hetero)aromatic moiety such as, for example, phenyl, pyridine, triazine, pyrene, naphthalene, or a polycyclic (hetero)aromatic ring system, bearing one or more vinylic, acrylic or methacrylic substituents. Examples of such monomers include benzyl (meth)acrylates, phenyl (meth)acrylates, divinylbenzenes (e.g., 1,3-divinylbenzene, 1,4-divinylbenzene), isopropenylbenzene, styrenics (e.g., styrene, 4-methylstyrene, 4-chlorostyrene, 2,6-dichlorostyrene, 4-vinylbenzyl chloride), diisopropenylbenzenes (e.g., 1,3-diisopropenylbenzene), vinylpyridines (e.g., 2-vinylpyridine, 4-vinylpyridine), 2,4,6-tris((4-vinylbenzyl)thio)-1,3,5-triazine and divinylpyridines (e.g., 2,5-divinylpyridine). In certain embodiments, the ethylenically unsaturated monomers (e.g., including an aromatic moiety) bear an amino (i.e., primary or secondary) group, a phosphine group or a thiol group. One example of such a monomer is vinylbisphenylphosphine. In certain desirable embodiments, an ethylenically unsaturated monomer will have a boiling point greater than 180 °C, greater than 200 °C, or even greater than 230 °C at the pressure at which polymerization is performed (e.g., at standard pressure).

[0045] As used herein, the term “functional” in correlation with a polymer refers to functional polymers that have specified physical, chemical, biological, pharmacological, or other properties or uses that are determined by the presence of specific chemical functional groups, which are usually dissimilar to those of the backbone chain of the polymer.

[0046] As used herein, the term “chalcogenide” refers to a compound containing one or more chalcogen elements. One of ordinary skill in the art will understand that the classical chalcogen elements are sulfur, selenium and tellurium. In accordance with the present invention, the use of chalcogenide refers to compounds and/or polymers containing sulfur, selenium, or a combination thereof.

[0047] As used herein, the term “chalcogenic bond” refers to a bond to one or two chalcogen elements. Non-limiting examples include an S-S bond, a Se-Se bond, a S-Se bond, a S-C bond, a Se-C bond, a S-O bond, a Se-O bond, a S-H bond, a Se-H bond, a S-N bond or a Se-N bond.

[0048] As known to one of ordinary skill in the art, the term “isomer” refers to compounds having the same formula but differ in arrangement. For instance, isomers of cyclic selenium sulfides, such as Se_2S_6 and Se_3S_5 , can have different placements of the Se units in the ring (e.g., S-Se-Se-S or S-Se-S). Isomers of Se_2S_6 include 1,2-isomers, 1,3-isomers, 1,4-isomers, and 1,5-isomers, wherein the numbers refer to the position of the Se units in the eight-membered ring.

[0049] As used herein, the term “vulcanize” refers to a process by which one or more polymers are

chemically crosslinked by reaction with a vulcanizing agent. As used herein, the term “vulcanizing agent” refers to a compound which can be used to chemically crosslink one or more polymers, such as, for example, natural or synthetic latex.

[0050] As known to one of ordinary skill in the art, the term “latex” refers to any polymer in a water-based liquid or viscous state. As used herein, the term “latex” refers to one or more polymers which can be vulcanized.

[0051] In one embodiment, a CHIP material possessing properties allowing it to function as a vulcanizing agent may be prepared. For example, a CHIP material with enhanced polymer compatibility, reactive chalcogenic bonds, and efficient crosslinking ability may be prepared.

[0052] According to a preferred embodiment, the present invention may feature a vulcanizing agent comprising a CHIP material. In some embodiments, said CHIP material may comprise one or more chalcogenic monomers at a level of at least 45 wt% of the CHIP material, and one or more comonomers each having a reactive functional group, at a level in the range of about 5-55 wt% of the CHIP material, where the one or more comonomers are co-polymerized with the chalcogenic monomers. In other embodiments, said CHIP material may comprise one or more chalcogenic monomers at a level of at least 46, 47, 48, 49 or 50 wt% of the CHIP material, and one or more comonomers, at a level in the range of about 5-54, 5-53, 5-52, 5-51 or 5-50 wt% of the CHIP material. Any of the listed ranges for the chalcogenic monomers may be combined with any of the listed ranges for the comonomers.

[0053] According to some embodiments, the comonomers may be each selected from a group consisting of amine comonomers, thiol comonomers, sulfide comonomers, alkynylly unsaturated comonomers, epoxide comonomers, nitron comonomers, aldehyde comonomers, ketone comonomers, thiirane comonomers, ethylenically unsaturated comonomers, styrenic comonomers, vinylic comonomers, methacrylate comonomers, acrylonitrile comonomers, allylic monomers, acrylate monomers, vinylpyridine monomers, isobutylene monomers, maleimide monomers, norbornene monomers, monomers having at least one vinyl ether moiety, monomers having at least one isopropenyl moiety, monomers having at least one imidazole moiety, and monomers having at least one heterocyclic moiety. In further embodiments, the chalcogenic monomers may be selected from a group consisting of elemental sulfur, a liquid polysulfide, an oligomer containing sulfur, an oligomer containing sulfur and selenium units, sulfur monomers derived from elemental sulfur, and elemental selenium.

[0054] In some embodiments, the present invention may comprise methods of vulcanizing a latex material to form a crosslinked rubber. A non-limiting example is a method comprising providing said latex material, providing a CHIP material, mixing said latex material and said CHIP material, and heating the mixed latex material and CHIP material at a temperature and for a period of time sufficient to effect vulcanization of the latex material. Without wishing to limit the invention to a particular theory or mechanism, the CHIP material may vulcanize the latex material to provide said crosslinked rubber.

[0055] According to some embodiments, the latex material may be a natural or synthetic material or a

combination thereof. Non-limiting examples include a natural rubber, a polydiene, a polydiene copolymer, polybutadiene, polyisoprene, polychloroprene, a butyl rubber, a silicone rubber latex, an acrylic rubber latex, or a combination thereof.

[0056] Referring to FIG. 2B, in preferred embodiments, the CHIP material may comprise chalcogenic bonds, where said chalcogenic bonds are weaker than an S-S bond in elemental sulfur. Without wishing to limit the invention to a particular theory or mechanism, the CHIP material may comprise chalcogenic bonds that are breakable and may generate one or more radical species that can react with a latex material. For example, the radical species contains sulfur chain segment that may function as a crosslinker. In some embodiments, the chalcogenic bonds may break with the application of heat and/or catalyst or by photochemical degradation.

[0057] Referring to FIGs 1B and 2B, in other embodiments, the CHIP material may comprise functional groups that can accelerate the breaking of chalcogenic bonds. As a non-limiting example, the CHIP material may comprise an unsaturated comonomer with a functional group that can act as a vulcanization accelerator. For example, the functional group may be nucleophilic and able to activate sulfur or chalcogen bonds. As a non-limiting example, the functional group may be an amine or N-heterocyclic, phosphine, or sulphide functional group. Without wishing to limit the invention to a particular theory or mechanism, while the chalcogenic monomers are polymerized with the one or more comonomers, and in some embodiments, with additional second comonomers, a functional group of the comonomers is maintained through the polymerization reaction such that the CHIP material contains said functional group originating from the comonomers. Hence, as shown in FIG. 2B, the CHIP material contains within itself the functional group which can function as a vulcanizing accelerator by attacking and breaking the chalcogenic bonds. Unlike the conventional vulcanization, where small molecule accelerators are added into a complex vulcanization formula, the CHIP material can function as both a vulcanizing agent and a vulcanizing accelerator.

[0058] In one embodiment, the present invention may feature a curable elastomeric composition comprising a latex material and a CHIP material. Without wishing to limit the invention to a particular theory or mechanism, the CHIP material can vulcanize the latex material to provide a crosslinked rubber. In further embodiments, the curable elastic composition may comprise one or more additives. Non-limiting examples of additives include, an accelerator, a peroxide, a plasticizer, an antioxidant, a retarder, a lubricant, a filler, a colorant or a combination thereof.

[0059] In another embodiment, the present invention may feature a vulcanized rubber composition. For example, a vulcanized rubber composition may be prepared from a latex material and a vulcanizing agent which comprises a CHIP material. Without wishing to limit the invention to a particular theory or mechanism, the CHIP material can vulcanize the latex material to provide a crosslinked rubber. In further embodiments, the vulcanized rubber composition may comprise one or more additives. Non-limiting examples of additives include, an accelerator, a peroxide, a plasticizer, an anti-ozonant, an antioxidant, a retarder, a lubricant, a filler, a colorant or a combination thereof.

[0060] In another embodiment, the present invention may feature a tire having a tread comprising any of the vulcanized rubber compositions described herein. For example, the present invention may feature a tire having a tread comprising a rubber composition which has been vulcanized using a CHIP material. In other embodiments, the present invention may feature a tire having a sidewall or entire composition comprising any of the vulcanized rubber compositions described herein.

[0061] In another embodiment, the present invention may feature a rubber substrate comprising any of the vulcanized rubber compositions described herein. For example, the present invention may feature a rubber substrate comprising a rubber composition which has been vulcanized using a CHIP material. Non-limiting examples of rubber substrates include a gasket, belt, hose, mat, flooring material, weather-strip, windshield wiper, boot, automotive part, shoe material, stopper, barrier, insulator, medical device, stamp, balloon, eraser, ball, suit, glove, boat, flotation device, shock absorber, or vibration absorber.

[0062] According to some embodiments, any of the CHIP material described herein may further comprise one or more second comonomers. In some embodiments, the one or more second comonomers are selected from a group consisting of a vinyl monomer, an isopropenyl monomer, an acryl monomer, a methacryl monomer, an unsaturated hydrocarbon monomer, an epoxide monomer, a thiirane monomer, an alkynyl monomer, a diene monomer, a butadiene monomer, an isoprene monomer, a norbornene monomer, an amine monomer, a thiol monomer, a sulfide monomer, an alkynyllyl unsaturated monomer, a nitron monomer, an aldehyde monomer, a ketone monomer, an ethylenically unsaturated monomer, and a styrenic monomer. In other embodiments, the second monomers are at a level of about 2 to about 55 wt%, or about 2 to about 10 wt%, or about 10 to about 20 wt%, or about 20 to about 30 wt%, or about 30 to about 40 wt%, or about 40 to about 55 wt% of the CHIP material

[0063] In one embodiment, any one of the CHIP materials described herein may comprise one or more cyclic selenium sulfide monomers having the formula $\text{Se}_n\text{S}_{(8-n)}$, and one or more comonomers selected from a group consisting of amine comonomers, thiol comonomers, sulfide comonomers, alkynyllyl unsaturated comonomers, epoxide comonomers, nitron comonomers, aldehyde comonomers, ketone comonomers, thiirane comonomers, ethylenically unsaturated comonomers, styrenic comonomers, vinylic comonomers, methacrylate comonomers, acrylonitrile comonomers, allylic monomers, acrylate monomers, vinylpyridine monomers, isobutylene monomers, maleimide monomers, norbornene monomers, monomers having at least one vinyl ether moiety, monomers having at least one isopropenyl moiety, monomers having at least one imidazole moiety, and monomers having at least one heterocyclic moiety. In one embodiment, the comonomers are at a level in the range of about 5-55 wt% of the CHIP material. In another embodiment, the cyclic selenium sulfide monomers comprise at most about 70 wt% of selenium, and can include any isomer of the formula.

[0064] In some embodiments, n is an integer that can range from 1 to 7. For example, when $n=2$, the cyclic selenium sulfide monomers have the formula Se_2S_6 . As another example, when $n=3$, the cyclic selenium sulfide monomers have the formula Se_3S_5 . Preferably, the one or more cyclic selenium sulfide monomers can comprise all possible isomers of a specific formula. In alternative embodiments, the

selenium sulfide monomers can be of the formula Se_nS_m , wherein n ranges from 1 to 7 and m ranges from 1 to 7, wherein the selenium sulfide monomers are not necessarily cyclic. In one embodiment, assuming that $n=7$, i.e. Se_7S , then the cyclic selenium sulfide monomers may comprise at most about 70 wt% of selenium.

[0065] In some embodiments, the cyclic selenium sulfide monomers are polymerized with the one or more comonomers via free radical polymerization, controlled radical polymerization, ring-opening polymerization, ring-opening metathesis polymerization, step-growth polymerization, or chain-growth polymerization. In preferred embodiments, polymerizing the comonomers with the selenium sulfide enables at least one functional sulfur moiety of the selenium sulfide to bond with at least one functional moiety of the one or more monomers. In some embodiments, the CHIP material may further comprise one or more comonomers which react to form a terpolymer.

[0066] In one embodiment, the CHIP material may comprise one or more cyclic selenium sulfide monomers at a range of about 5 to 10 wt%, or about 10 to 20 wt%, or about 20 to 30 wt%, or about 30 to 40 wt%, or about 40 to 50 wt%, or about 50 to 60 wt%, or about 60 to 70 wt% of the CHIP material. In another embodiment, the cyclic selenium sulfide monomers may comprise selenium units of at most about 20 wt%, or at most about 30 wt%, or at most about 40 wt% or at most about 50 wt%, or at most about 60 wt%, or at most about 70 wt% of the cyclic selenium sulfur monomers. In a further embodiment, the cyclic selenium sulfide monomers comprise at most about 70 wt% of selenium. In some embodiments, the one or more comonomers are at a range of about 5 to 10 wt%, or about 10 to 20 wt%, or about 20 to 30 wt%, or about 30 to 40 wt%, or about 40 to 50 wt% of the CHIP material.

[0067] In other embodiments, the CHIP material may further comprise about 5-55 wt% of elemental sulfur (S_8). In other embodiments, the elemental sulfur can be at a range of about 5 to 10 wt%, or about 10 to 20 wt%, or about 20 to 30 wt%, or about 30 to 40 wt%, or about 40 to 55 wt% of the CHIP material.

[0068] In still other embodiments, the CHIP material may further comprise about 5-55 wt% of elemental selenium (Se_8). In further embodiments, the elemental selenium can be at a range of about 5 to 10 wt%, or about 10 to 20 wt%, or about 20 to 30 wt%, or about 30 to 40 wt%, or about 40 to 55 wt% of the CHIP material. For instance, the CHIP material may comprise 30 wt% S, 35 wt% cyclic selenium-sulfide, and 35 wt% 1,3 diisopropenyl benzene.

[0069] According to another embodiment, the CHIP material may comprise one or more sulfur monomers derived from elemental sulfur, at a level of at least 35 wt% of the CHIP material, elemental selenium (Se_8) at a level of at least 35 wt% of the CHIP material, and one or more, at a level in the range of about 5-55 wt% of the CHIP material. In yet another embodiment the comonomers may be each selected from a group consisting of amine comonomers, thiol comonomers, sulfide comonomers, alkynylly unsaturated comonomers, epoxide comonomers, nitron comonomers, aldehyde comonomers, ketone comonomers, thiirane comonomers, ethylenically unsaturated comonomers, styrenic comonomers, vinylic comonomers, methacrylate comonomers, acrylonitrile comonomers, allylic monomers, acrylate monomers, vinylpyridine

monomers, isobutylene monomers, maleimide monomers, norbornene monomers, monomers having at least one vinyl ether moiety, monomers having at least one isopropenyl moiety, monomers having at least one imidazole moiety, and monomers having at least one heterocyclic moiety.

[0070] In one embodiment, the CHIP material may comprise at least about 55 wt% sulfur monomers. In another embodiment, the CHIP material may comprise at least about 55 wt% of Se_8 . In an exemplary embodiment, the CHIP material may comprise about 35-55 wt% of sulfur monomers, about 35-55 wt% of elemental selenium, and about 15-25 wt% of the comonomers, such as diisopropenylbenzene.

[0071] According to another embodiment, the CHIP material may comprise one or more sulfur monomers derived from elemental sulfur at a level of at least 35% wt of the CHIP material, and one or more comonomers, at a level in the range of about 5-45 wt% of the CHIP material. In yet another embodiment the comonomers may be each selected from a group consisting of amine comonomers, thiol comonomers, sulfide comonomers, alkynylly unsaturated comonomers, epoxide comonomers, nitron comonomers, aldehyde comonomers, ketone comonomers, thiirane comonomers, ethylenically unsaturated comonomers, styrenic comonomers, vinylic comonomers, methacrylate comonomers, acrylonitrile comonomers, allylic monomers, acrylate monomers, vinylpyridine monomers, isobutylene monomers, maleimide monomers, norbornene monomers, monomers having at least one vinyl ether moiety, monomers having at least one isopropenyl moiety, monomers having at least one imidazole moiety, and monomers having at least one heterocyclic moiety.

[0072] In some embodiments, the CHIP material comprises at least about 55 wt% sulfur monomers. In other embodiments, the one or more comonomers are at a range of about 5 to 10 wt%, or about 10 to 20 wt%, or about 20 to 30 wt%, or about 30 to 40 wt%, or about 40 to 45 wt% of the CHIP material. In still other embodiments, the CHIP material may further comprise at least about 35 wt%, or at least about 40 wt%, or at least about 55 wt% of elemental selenium.

[0073] In some embodiments, the chalcogenic monomers are polymerized with the one or more comonomers via free radical polymerization, controlled radical polymerization, ring-opening polymerization, ring-opening metathesis polymerization, step-growth polymerization, or chain-growth polymerization. In preferred embodiments, polymerizing the comonomers with the sulfur monomers enables at least one functional sulfur moiety of the sulfur monomers to bond with at least one functional moiety of the one or more monomers.

[0074] In yet other embodiments, the CHIP material may further comprise one or more termonomers. In some embodiments, the termonomers may be a vinyl monomer, an isopropenyl monomer, an acryl monomer, a methacryl monomer, an unsaturated hydrocarbon monomer, an epoxide monomer, a thiirane monomer, an alkynyl monomer, a diene monomer, a butadiene monomer, an isoprene monomer, a norbornene monomer, an amine monomer, a thiol monomer, a sulfide monomer, an alkynylly unsaturated monomer, a nitron monomer, an aldehyde monomer, a ketone monomer, an ethylenically unsaturated monomer, or a styrenic monomer. The termonomers may be present in an amount ranging from about 5

to 45 wt% of the CHIP material.

[0075] In still other embodiments, the CHIP material may further comprise one or more polyfunctional monomers, such as for example, a polyvinyl monomer, a polyisopropenyl monomer, a polyacryl monomer, a polymethacryl monomer, a polyunsaturated hydrocarbon monomer, a polyepoxide monomer, a polythiirane monomer, a polyalkynyl monomer, a polydiene monomer, a polybutadiene monomer, a polyisoprene monomer, a polynorbornene monomer, a polyamine monomer, a polythiol monomer, a polysulfide monomer, a polyalkynylly unsaturated monomer, a polynitrone monomer, a polyaldehyde monomer, a polyketone monomer, or a polyethylenically unsaturated monomer. The polyfunctional monomers may be present in an amount ranging from about 5 to 45 wt% of the CHIP material.

[0076] The CHIP material can be made, for example, by polymerization of a molten mixture of chalcogenic monomers with the comonomers. Thus, in one aspect, the invention provides a method for making the CHIP material as described above. The method includes heating a mixture of the chalcogenic monomers and the one or more monomers together at a temperature sufficient to initiate polymerization (i.e., through free radical polymerization, through anionic polymerization, or through both, depending on the monomers used). For example, elemental sulfur, elemental selenium, selenium sulfide, or combinations thereof are polymerized with the comonomers. For example, in one embodiment, the method includes heating the mixture to a temperature in the range of about 120 °C to about 230 °C, e.g., in the range of about 160 °C to about 230 °C. The person of skill in the art will select conditions that provide the desired level of polymerization. In certain embodiments, the polymerization reaction is performed under ambient pressure. However, in other embodiments, the polymerization reaction can be performed at elevated pressure (e.g., in a bomb or an autoclave). Elevated pressures can be used to polymerize more volatile monomers, so that they do not vaporize under the elevated temperature reaction conditions.

[0077] In certain embodiments, it can be desirable to use a nucleophilic viscosity modifier in liquefying the chalcogenic monomers, for example, before adding one or more of the monomers (e.g., before adding any polyfunctional monomer). For example, in certain embodiments, the chalcogenic monomers is first heated with a viscosity modifier, then the viscosity-modified chalcogenic monomers are heated with one or more monomers (e.g., with one or more polyfunctional monomers). The nucleophilic viscosity modifier can be, for example, a phosphorus nucleophile (e.g., a phosphine), a sulfur nucleophile (e.g., a thiol) or an amine nucleophile (e.g., a primary or secondary amine). When the chalcogenic monomers are heated in the absence of a nucleophilic viscosity modifier, the chalcogenic monomer rings can open to form, e.g., diradicals, which can combine to form linear chains which can provide a relatively high overall viscosity to the molten material. Nucleophilic viscosity modifiers can break these linear chains into shorter lengths, thereby lowering the overall viscosity of the molten material and making the chalcogenic monomer mixture easier to mix with other species and to stir for efficient processing. Some of the nucleophilic viscosity modifier will react to be retained as a covalently bound part of the polymer, and some will react to form separate molecular species, with the relative amounts depending on nucleophile identity and reaction conditions. While some of the nucleophilic viscosity modifier may end up as a separate molecular species from the polymer chain, as used herein, nucleophilic viscosity modifiers may become part of the polymer.

Non-limiting examples of nucleophilic viscosity modifiers include triphenylphosphine, aniline, benzenethiol, and N,N-dimethylaminopyridine. Nucleophilic viscosity modifiers can be used, for example, in an amount up to about 10 wt%, or even up to about 5 wt% of the CHIP material. When a nucleophilic viscosity modifier is used, in certain embodiments it can be used in the range of about 5 wt% to about 15 wt% of the CHIP material.

[0078] In certain embodiments, a monofunctional monomer can be used to reduce the viscosity of the CHIP material, for example, before adding other monomers (e.g., before adding any polyfunctional monomer). For example, in certain embodiments, the CHIP material is first heated with one or more monofunctional monomers. While not intending to be bound by theory, the inventors surmise that inclusion of monofunctional monomers into the polymer chains disrupts intermolecular associations and thus decreases the viscosity. The monofunctional monomer can be, for example, a mono(meth)acrylate such as benzyl methacrylate, a mono(oxirane) such as a styrene oxide or a glycidyl phenyl ether, or a mono(thiirane) such as t-butyl thiirane or phenoxyethylthiirane. A monofunctional monomer can be used to modify the viscosity of the CHIP material, for example, in an amount up to about 10 wt%, up to about 5 wt%, or even up to about 2 wt% of the CHIP material. When a monofunctional monomer is used to modify the viscosity of the CHIP material, in certain embodiments, it can be used in the range of about 0.5 wt% to about 5 wt%, or even about 0.5 wt% to about 3 wt% of the CHIP material.

[0079] Of course, viscosity modification is not required, so in other embodiments the chalcogenic monomers are heated together with the one or more monomers (and particularly with one or more polyfunctional monomers) without viscosity modification. In other embodiments, a solvent, e.g., a halobenzene such as 1,2,4-trichlorobenzene, a benzyl ether, or a phenyl ether, can be used to modify the viscosity of the materials for ease of handling. The solvent can be added, for example, to the chalcogenic monomers before reaction with a monomer in order to reduce its viscosity, or to the polymerized material in order to aid in processing into a desired form factor. A decrease in viscosity at elevated temperatures (e.g., > about 140 °C) can allow sufficient flow.

[0080] In some embodiments, any of the vulcanization methods described herein may be performed at a temperature of less than about 180 °C. In other embodiments, the vulcanization methods may be performed at a temperature of less than about 160 °C, less than about 150 °C, less than about 140 °C, less than about 130 °C, less than about 120 °C, less than about 110 °C, or less than about 100 °C.

[0081] In further embodiments, any of the vulcanization methods described herein may be performed in a time of less than about 30 min. In other embodiments, the vulcanization methods may be performed in a time of less than about 25 min, less than about 20 min, less than about 15 min, or less than about 10 min. In further embodiments, the vulcanization methods may be performed in a time ranging from about 10-15 min, or about 15-20 min, or about 20-25 min, or about 25-30 min.

[0082] As evidenced in the Examples 6 and 7, the vulcanization methods of the present invention are at least 2 times faster than conventional vulcanization. In a preferred embodiment, the vulcanization

methods of the present invention are at least 3 times faster than conventional vulcanization. In another preferred embodiment, the vulcanization methods of the present invention are at least 5 times faster than conventional vulcanization. In more preferred embodiments, the vulcanization methods of the present invention are at least 7 times faster than conventional vulcanization. For example, the conventional vulcanization method of Example 6 was completed in about 90 mins, whereas the vulcanization methods of the present invention in Example 7 was completed in just about 12 mins, which is at least a 7-fold decrease in time.

[0083] EXAMPLES

[0084] The following are non-limiting examples of the present invention, in particular, synthesis of CHIP materials and use of CHIP materials as vulcanizing agents. The examples are for illustrative purposes only and are not intended to limit the invention in any way. Equivalents or substitutes are within the scope of the invention.

[0085] EXAMPLE 1: Synthesis of poly(Sulfur-random-Styrene) or p(S-r-Sty) CHIP: Referring now to FIG. 4, to a 20 mL glass vial equipped with a magnetic stir bar, S₈ (3.50 g) was added and heated to 130 °C in a thermostatic oil bath until a clear yellow molten phase was formed. Styrene (1.50 g) was added and the reaction was stirred at 130 °C for 6 h yielding an orange fluid. The complete consumption of styrene was confirmed by ¹HNMR spectra.

[0086] EXAMPLE 2: Synthesis of p(S-r-vinylimidazole) CHIP: Sulfur (0.7 g) and vinylimidazole (0.3 g) were added to a small vial equipped with a stir bar. The vial was lowered into a thermostatic oil bath and the reaction was stirred at 130 °C for 2 h. Upon completion of the reaction a black tar-like substance was present in the vial.

[0087] EXAMPLE 3: Synthesis of p(S-r-4-vinylaniline) CHIP: Sulfur (0.25 g) was placed in a small vial equipped with a magnetic stir bar. The sulfur was melted in a thermostatic oil bath at 130 °C. Using a syringe, 4-vinylaniline (0.25 mL) was added to the molten sulfur and the reaction was stirred at 130 °C for 20 min. Upon completion of the reaction, a red glassy solid remained in the vial.

[0088] EXAMPLE 4: Synthesis of p(S-r-1,3-phenylenediamine) CHIP: Sulfur (1.0 g) and 1,3-phenylenediamine (1.0 g) were added to a vial equipped with a metal stir bar and rubber septa. Before heating the reaction, a H₂S trap composed of concentrated NaOH was prepared. A constant flow of Ar into the reaction vial and outlet into the NaOH trap ensured effective H₂S trapping. The vial was lowered into a thermostatic oil bath and allowed to react at 130 °C for 30 minutes. Upon completion of the reaction, a viscous, red liquid was present.

[0089] EXAMPLE 5: Synthesis of p(S-r-Sty-r-1,3-phenylenediamine) CHIP: P(S-r-Sty) (9.0 g, 70 wt% S) and 1,3-phenylenediamine (1.0 g) were added to a vial equipped with a metal stir bar and rubber septa. Before heating the reaction, a H₂S trap composed of concentrated NaOH was prepared. A constant flow of Ar into the reaction vial and outlet into the NaOH trap ensured effective H₂S trapping. The vial was lowered into a thermostatic oil bath and allowed to react at 130 °C for 30 minutes. Upon completion of the

reaction, a viscous, red liquid was present.

[0090] EXAMPLE 6: Vulcanization using sulfur as vulcanizing agent: Referring now to FIG. 3A, sulfur (0.2 g), polybutadiene (0.8 g, ~1,500 M_n), and pyrene (0.05 g) were added to a small vial equipped with a stir bar. The vial was lowered into a thermostatic oil bath set at 160 °C. The reaction was allowed to stir for ~90 min. until it became a black rubber.

[0091] EXAMPLE 7: Vulcanization using p(S-r-vinylimidazole) CHIP as vulcanizing agent: Referring now to FIG. 3C, P(S-r-vinylimidazole) (0.286 g), polybutadiene (0.714 g, ~1,500 M_n), and pyrene (0.05 g) were added to a small vial equipped with a stir bar. The vial was lowered into a thermostatic oil bath set at 160 °C. The reaction was allowed to stir for ~12 min. until it became a black rubber.

[0092] As used herein, the term “about” refers to plus or minus 10% of the referenced number.

[0093] Various modifications of the invention, in addition to those described herein, will be apparent to those skilled in the art from the foregoing description. Such modifications are also intended to fall within the scope of the appended claims. Each reference cited in the present application is incorporated herein by reference in its entirety.

[0094] Although there has been shown and described the preferred embodiment of the present invention, it will be readily apparent to those skilled in the art that modifications may be made thereto which do not exceed the scope of the appended claims. Therefore, the scope of the invention is only to be limited by the following claims. In some embodiments, the figures presented in this patent application are drawn to scale, including the angles, ratios of dimensions, etc. In some embodiments, the figures are representative only and the claims are not limited by the dimensions of the figures. In some embodiments, descriptions of the inventions described herein using the phrase “comprising” includes embodiments that could be described as “consisting of”, and as such the written description requirement for claiming one or more embodiments of the present invention using the phrase “consisting of” is met.

WHAT IS CLAIMED IS:

1. A composition comprising:
 - a. a latex material; and
 - b. a vulcanizing agent comprising a chalcogenic hybrid inorganic/organic polymer (CHIP) material, wherein the CHIP material comprises:
 - i. one or more chalcogenic monomers at a level of at least 45 wt% of the CHIP material; and
 - ii. one or more comonomers, at a level in the range of about 5-55 wt% of the CHIP material, wherein the one or more comonomers are co-polymerized with the chalcogenic monomers;wherein the vulcanizing agent vulcanizes the latex material to provide a crosslinked rubber.
2. The composition of claim 1, wherein the one or more chalcogenic monomers are at a level of at least 50 wt% of the CHIP material and the one or more comonomers are at a level in the range of about 5-50 wt% of the CHIP material.
3. The composition of claim 1 or 2, wherein the latex material is natural, synthetic, or a combination thereof.
4. The composition of any one of claim 1-3, wherein the latex material comprises a natural rubber, a polydiene, a polydiene copolymer, polybutadiene, polyisoprene, polychloroprene, a butyl rubber, a silicone rubber latex, an acrylic rubber latex or a combination thereof.
5. The composition of any one of claim 1-4, wherein the chalcogenic monomers are selected from a group consisting of elemental sulfur, a liquid polysulfide, an oligomer containing sulfur, and an oligomer containing sulfur and selenium units.
6. The composition of any one of claim 1-4, wherein the chalcogenic monomers comprises sulfur monomers derived from elemental sulfur and elemental selenium (Se_8).
7. The composition of any one of claim 1-6, wherein the one or more comonomers are each selected from a group consisting of amine comonomers, thiol comonomers, sulfide comonomers, alkynylly unsaturated comonomers, epoxide comonomers, nitrone comonomers, aldehyde comonomers, ketone comonomers, thiirane comonomers, ethylenically unsaturated comonomers, styrenic comonomers, vinylic comonomers, methacrylate comonomers, acrylonitrile comonomers, allylic monomers, acrylate monomers, vinylpyridine monomers, isobutylene monomers, maleimide monomers, norbornene monomers, monomers having at least one vinyl ether moiety, monomers having at least one isopropenyl moiety, monomers having at least one imidazole moiety, and monomers having at least one heterocyclic moiety.
8. The composition of any one of claim 1-7, wherein the one or more monomers are co-polymerized

with the chalcogenic monomers via free radical polymerization, controlled radical polymerization, ring-opening polymerization, ring-opening metathesis polymerization, step-growth polymerization, or chain-growth polymerization.

9. The composition of any one of claim 1-8, wherein the composition further comprises one or more additives, wherein the additive comprises an accelerator, a peroxide, a plasticizer, an anti-ozonant, an antioxidant, a retarder, a lubricant, a filler, a colorant or a combination thereof.
10. The composition of any one of claim 1-9, wherein the CHIP material comprises chalcogenic bonds.
11. The composition of claim 10, wherein the chalcogenic bonds are breakable to generate one or more radical species which react with said latex material.
12. The composition of claim 10 or 11, wherein the chalcogenic bonds are breakable with the application of heat or a catalyst.
13. The composition of any one of claim 1-12, wherein the CHIP material further comprises one or more second comonomers.
14. The composition of any one of claim 1-13, wherein the CHIP material comprises one or more reactive functional groups.
15. The composition of claim 14, wherein the functional groups are capable of activating one or more chalcogen bonds to accelerate vulcanization.
16. The composition of claim 14 or 15, wherein the functional groups are capable of accelerating a breaking of one or more chalcogen bonds.
17. The composition of any one of claim 14-16, wherein the functional groups are nucleophilic functional groups.
18. The composition of any one of claim 14-17, wherein the functional groups are amine, N-heterocyclic, phosphine, or sulphide functional groups.
19. A method of vulcanizing a latex material to form a crosslinked rubber, said method comprising reacting said latex material with a chalcogenic hybrid inorganic/organic polymer (CHIP) material, wherein the CHIP material comprises:
 - a. one or more chalcogenic monomers at a level of at least 45 wt% of the CHIP material; and
 - b. one or more comonomers, at a level in the range of about 5-55 wt% of the CHIP material, wherein the one or more comonomers are co-polymerized with the chalcogenic monomers;

wherein the CHIP material vulcanizes the latex material to provide said crosslinked rubber.

20. The method of claim 19, wherein the one or more chalcogenic monomers are at a level of at least 50 wt% of the CHIP material and the one or more comonomers are at a level in the range of about 5-50 wt% of the CHIP material.
21. The method of claim 19 or 20, wherein reacting the latex material with the CHIP material comprises: mixing said latex material and said CHIP material; and heating the mixed latex material and said CHIP material at a temperature and for a period of time sufficient to effect vulcanization of the latex material.
22. The method of any one of claim 19-21, wherein the latex material is natural, synthetic, or a combination thereof.
23. The method of any one of claim 19-22, wherein the latex material comprises a natural rubber, a polydiene, a polydiene copolymer, polybutadiene, polyisoprene, polychloroprene, a butyl rubber, a silicone rubber latex, an acrylic rubber latex, or a combination thereof.
24. The method of any one of claim 19-23, wherein the chalcogenic monomers are selected from a group consisting of elemental sulfur, a liquid polysulfide, an oligomer containing sulfur, and an oligomer containing sulfur and selenium units.
25. The method of any one of claim 19-24, wherein the chalcogenic monomers comprises sulfur monomers derived from elemental sulfur and elemental selenium (Se_8).
26. The method of any one of claim 19-25, wherein the one or more comonomers are each selected from a group consisting of amine comonomers, thiol comonomers, sulfide comonomers, alkynylly unsaturated comonomers, epoxide comonomers, nitron comonomers, aldehyde comonomers, ketone comonomers, thiirane comonomers, ethylenically unsaturated comonomers, styrenic comonomers, vinylic comonomers, methacrylate comonomers, acrylonitrile comonomers, allylic monomers, acrylate monomers, vinylpyridine monomers, isobutylene monomers, maleimide monomers, norbornene monomers, monomers having at least one vinyl ether moiety, monomers having at least one isopropenyl moiety, monomers having at least one imidazole moiety, and monomers having at least one heterocyclic moiety.
27. The method of any one of claim 19-26, wherein the one or more monomers are co-polymerized with the chalcogenic monomers via free radical polymerization, controlled radical polymerization, ring-opening polymerization, ring-opening metathesis polymerization, step-growth polymerization, or chain-growth polymerization.
28. The method of any one of claim 19-27, wherein the CHIP material comprises chalcogenic bonds.
29. The method of claim 28, wherein the chalcogenic bonds are breakable, wherein breaking the

chalcogenic bonds generates one or more radical species that react with said latex material.

30. The method of claim 28 or 29, wherein the chalcogenic bonds are breakable with the application of heat or a catalyst.
31. The method of any one of claim 19-30, wherein the CHIP material further comprises one or more second comonomers.
32. The method of any one of claim 19-31, wherein the CHIP material comprises one or more reactive functional groups.
33. The method of claim 32, wherein the functional groups are capable of activating one or more chalcogen bonds to accelerate vulcanization.
34. The method of claim 32 or 33, wherein the functional groups are capable of accelerating a breaking of one or more chalcogen bonds.
35. The method of any one of claim 32-34, wherein the functional groups are nucleophilic functional groups.
36. The method of any one of claim 32-35, wherein the functional groups are amine, N-heterocyclic, phosphine, or sulphide functional groups
37. The method of any one of claim 19-36, wherein the method is performed at a temperature of less than about 170 °C.
38. The method of any one of claim 19-36, wherein the method is performed in a time of about 10 to 20 min.
39. A vulcanizing agent comprising a chalcogenic hybrid inorganic/organic polymer (CHIP) material, wherein the CHIP material comprises: a. one or more chalcogenic monomers at a level of at least 45 wt% of the CHIP material; and b. one or more comonomers, at a level in the range of about 5-55 wt% of the CHIP material; wherein the one or more comonomers are co-polymerized with the chalcogenic monomers.
40. The vulcanizing agent of claim 39, wherein the one or more chalcogenic monomers are at a level of at least 50 wt% of the CHIP material and the one or more comonomers are at a level in the range of about 5-50 wt% of the CHIP material.
41. The vulcanizing agent of claim 39 or 40, wherein the chalcogenic monomers are selected from a group consisting of elemental sulfur, a liquid polysulfide, an oligomer containing sulfur, and an oligomer containing sulfur and selenium units.
42. The vulcanizing agent of any one of claim 39-41, wherein the chalcogenic monomers comprises

sulfur monomers derived from elemental sulfur and elemental selenium.

43. The vulcanizing agent of any one of claim 39-42, wherein the one or more comonomers are each selected from a group consisting of amine comonomers, thiol comonomers, sulfide comonomers, alkynylly unsaturated comonomers, epoxide comonomers, nitron comonomers, aldehyde comonomers, ketone comonomers, thiirane comonomers, ethylenically unsaturated comonomers, styrenic comonomers, vinylic comonomers, methacrylate comonomers, acrylonitrile comonomers, allylic monomers, acrylate monomers, vinylpyridine monomers, isobutylene monomers, maleimide monomers, norbornene monomers, monomers having at least one vinyl ether moiety, monomers having at least one isopropenyl moiety, monomers having at least one imidazole moiety, and monomers having at least one heterocyclic moiety.
44. The vulcanizing agent of any one of claim 39-43, wherein the one or more comonomers are copolymerized with the chalcogenic monomers via free radical polymerization, controlled radical polymerization, ring-opening polymerization, ring-opening metathesis polymerization, step-growth polymerization, or chain-growth polymerization.
45. The vulcanizing agent of any one of claim 39-44, wherein the CHIP material comprises chalcogenic bonds.
46. The vulcanizing agent of claim 45, wherein the chalcogenic bonds are breakable, wherein breaking the chalcogenic bonds generates one or more radical species react with a latex material.
47. The vulcanizing agent of claim 45 or 46, wherein the chalcogenic bonds are breakable with the application of heat or a catalyst.
48. The vulcanizing agent of any one of claim 39-47, wherein the CHIP material further comprises one or more second comonomers.
49. The vulcanizing agent of any one of claim 39-48, wherein the CHIP material comprises one or more reactive functional groups.
50. The vulcanizing agent of claim 49, wherein the functional groups are capable of activating one or more chalcogen bonds to accelerate vulcanization.
51. The vulcanizing agent of claim 49 or 50, wherein the functional groups are capable of accelerating a breaking of one or more chalcogen bonds.
52. The vulcanizing agent of any one of claim 49-51, wherein the functional groups are nucleophilic functional groups.
53. The vulcanizing agent of any one of claim 49-52, wherein the functional groups are amine, N-heterocyclic, phosphine, or sulphide functional groups.

Inverse Vulcanization

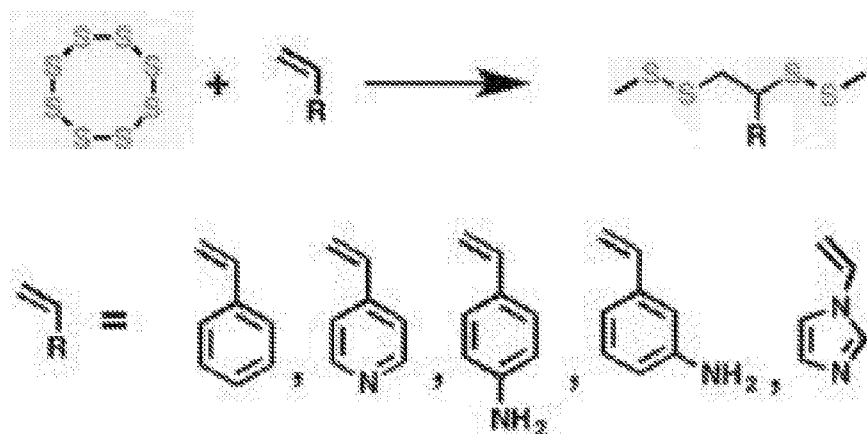


FIG. 1A

Dynamic Covalent Polymerization

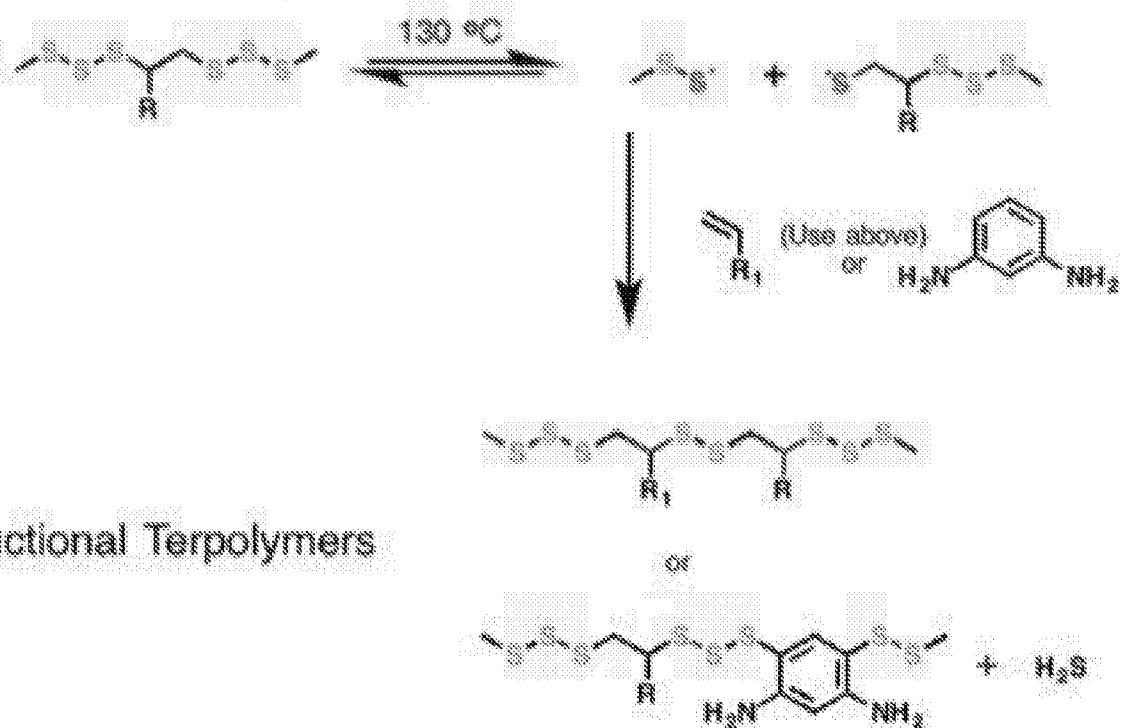


FIG. 1B

Conventional Vulcanization

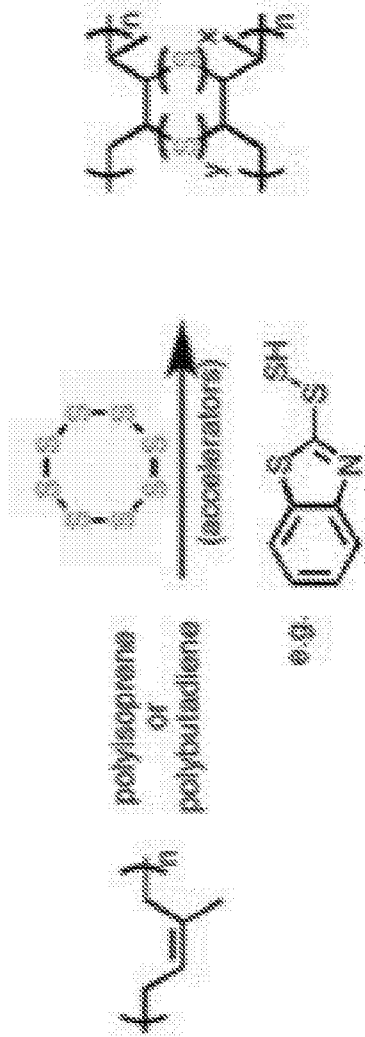


FIG. 2A

"All in One" CHIPS Vulcanization Agent

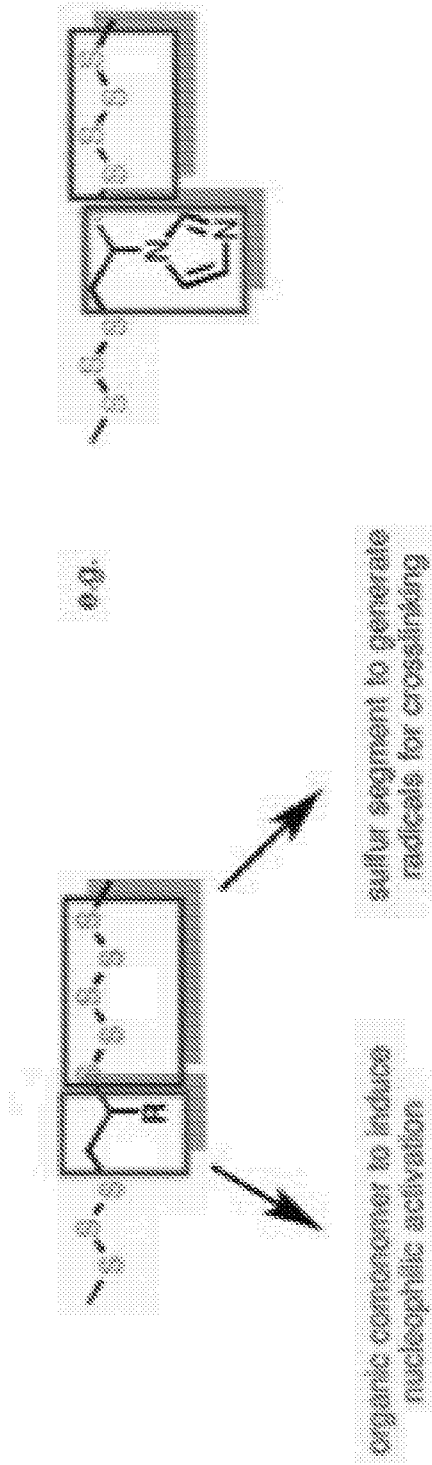
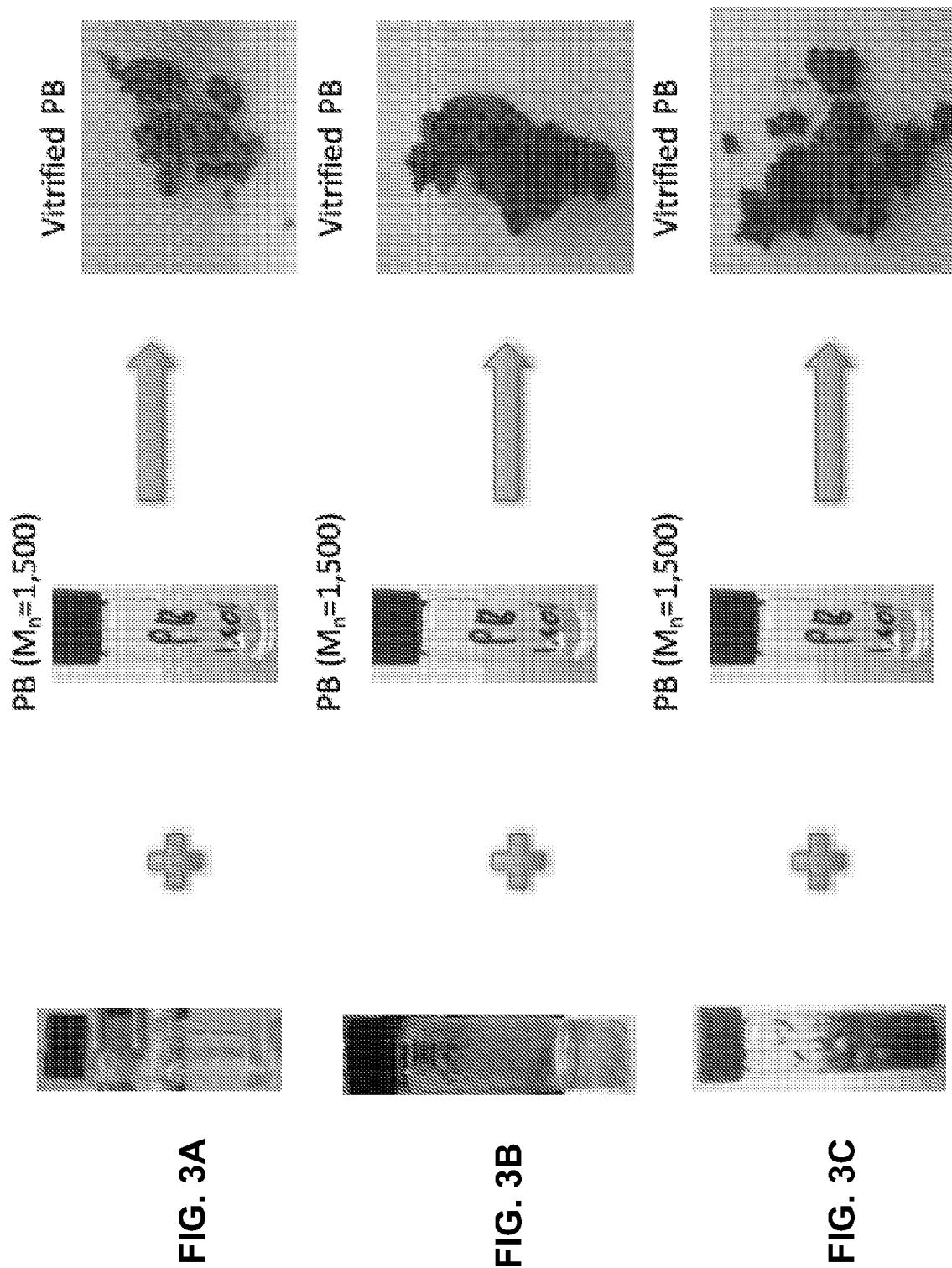


FIG. 2B



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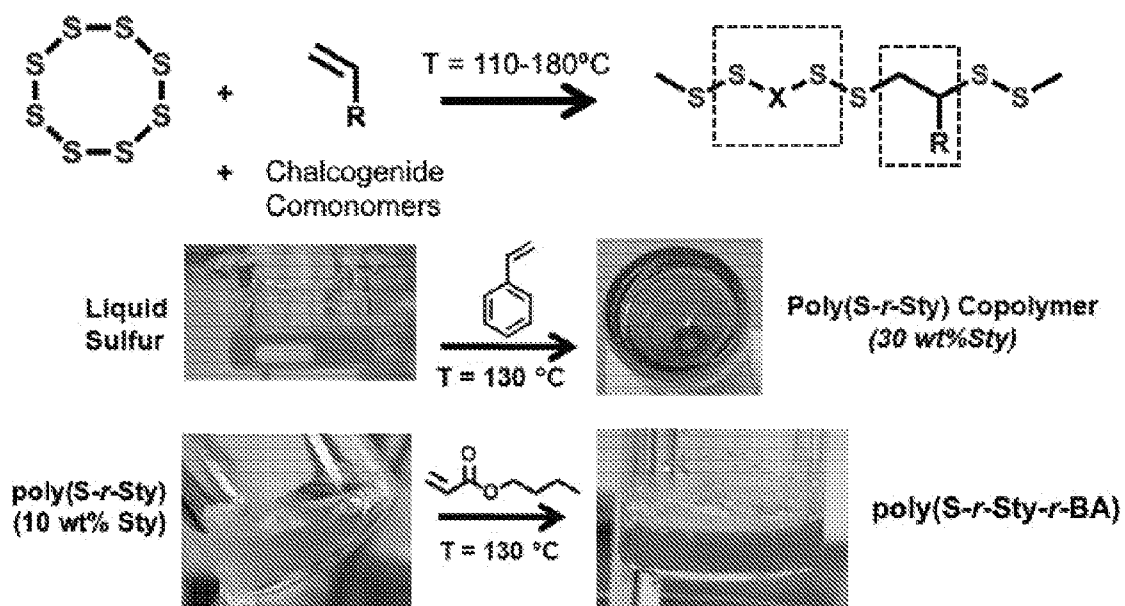


FIG. 4

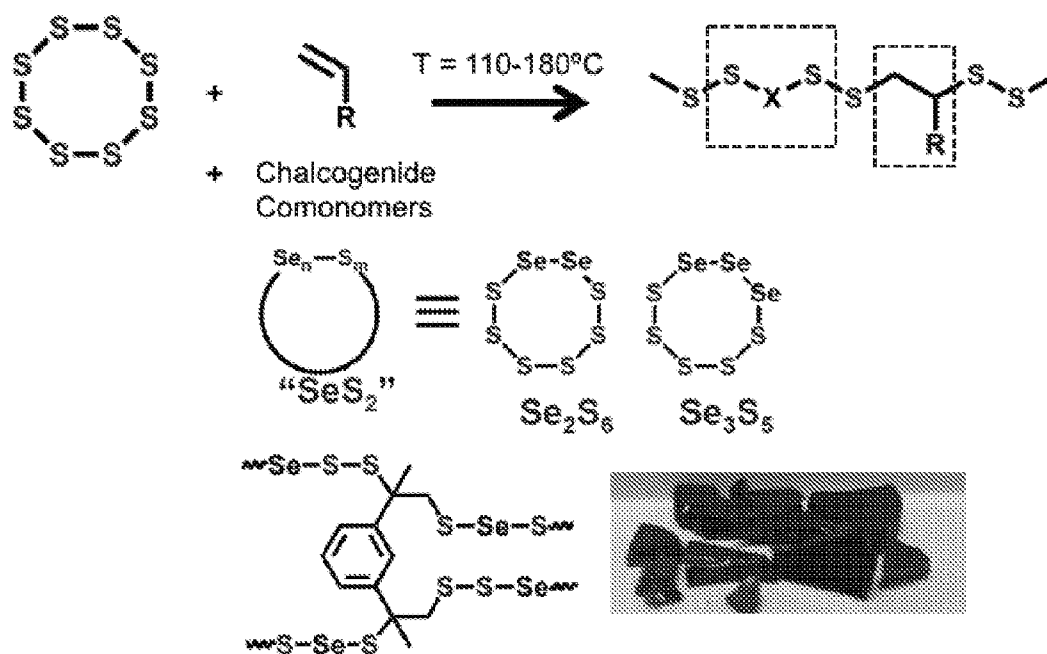


FIG. 5

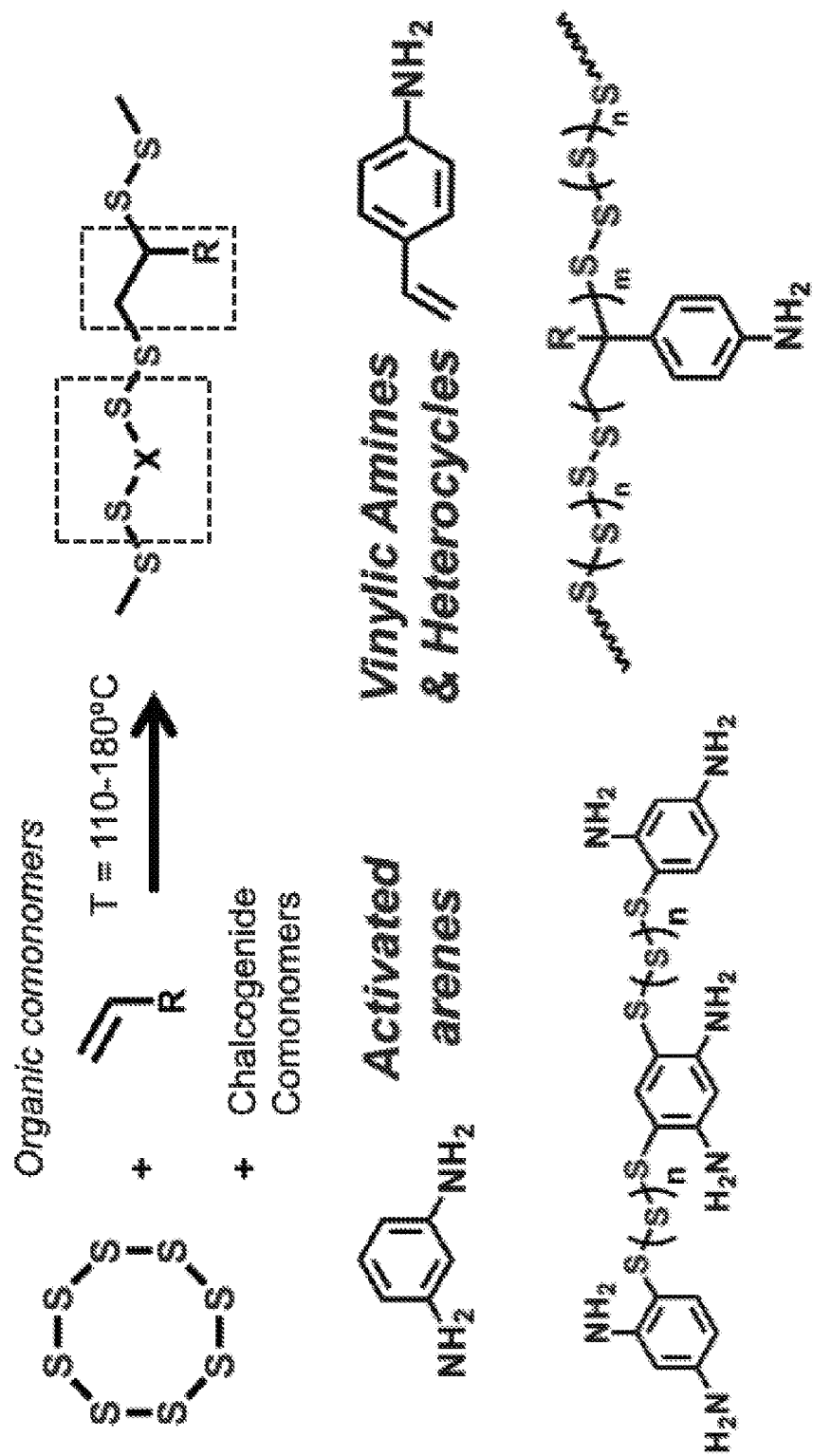


FIG. 6

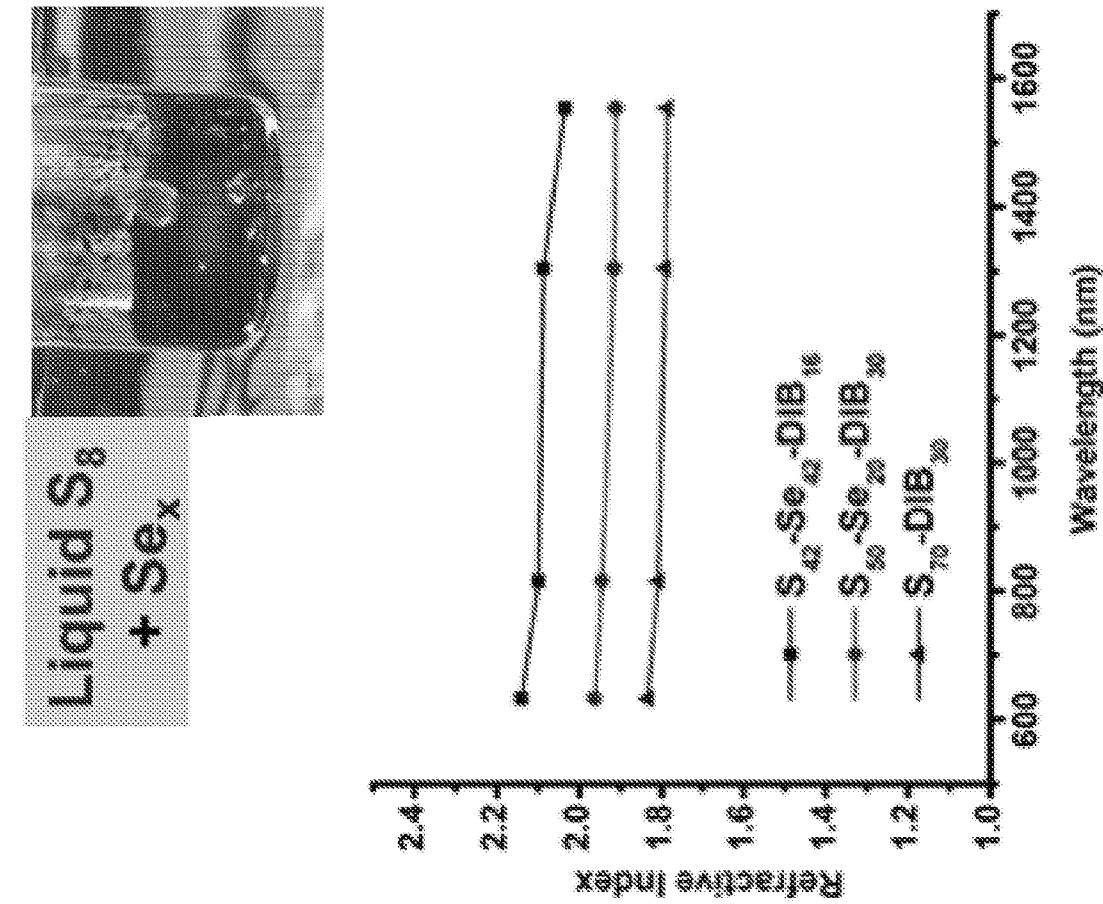
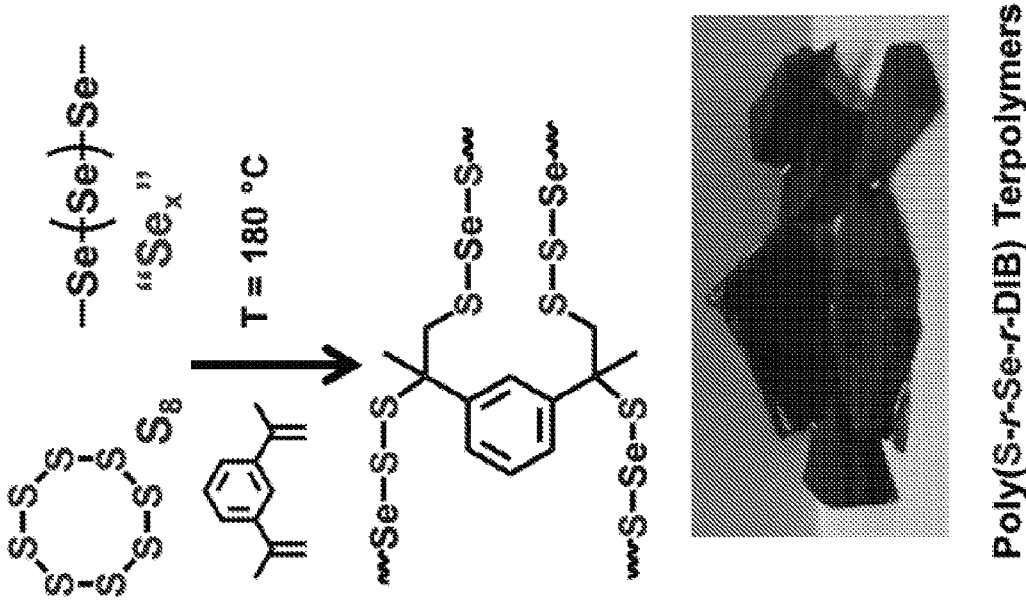


FIG. 7



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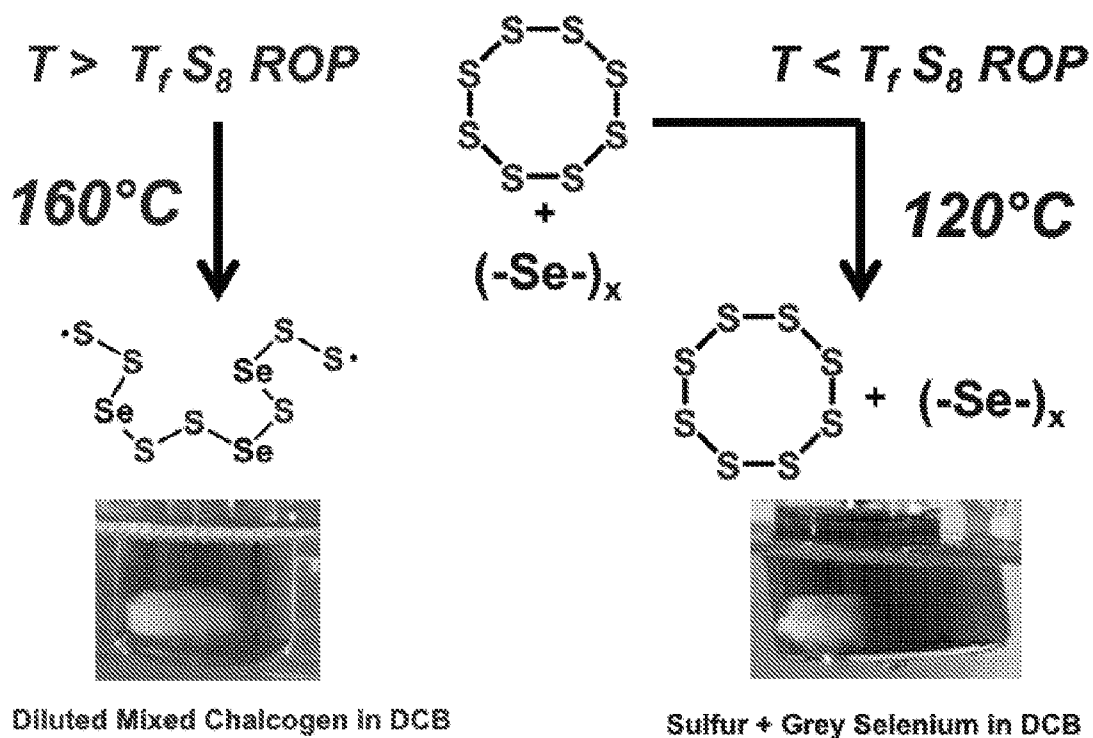


FIG. 8

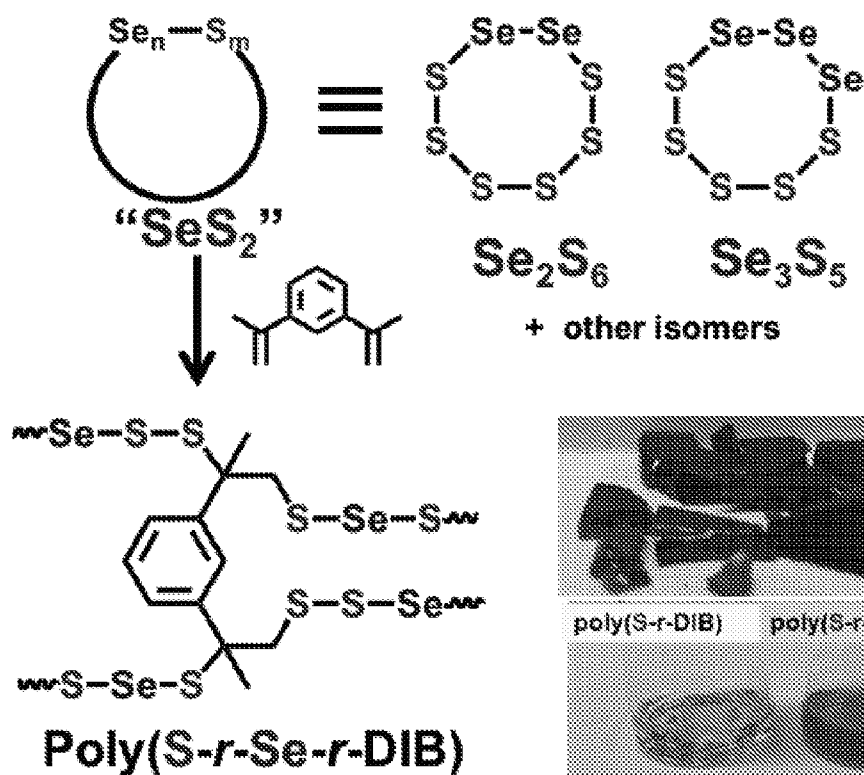
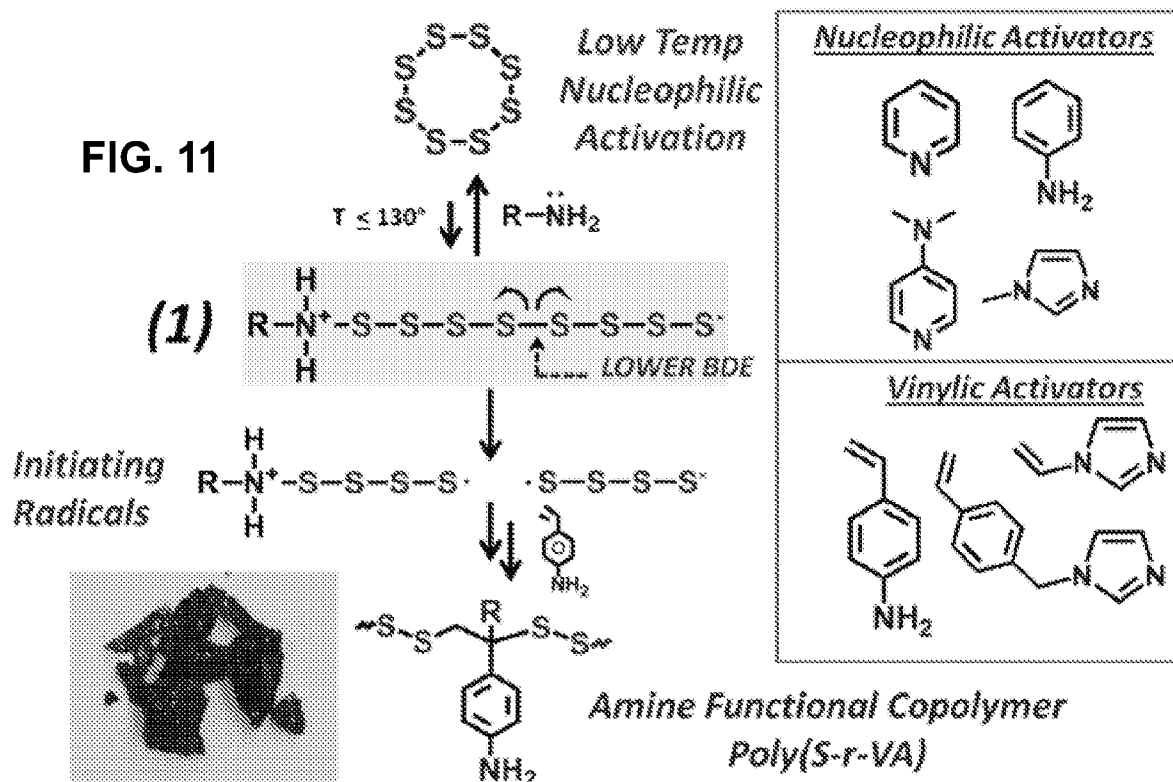
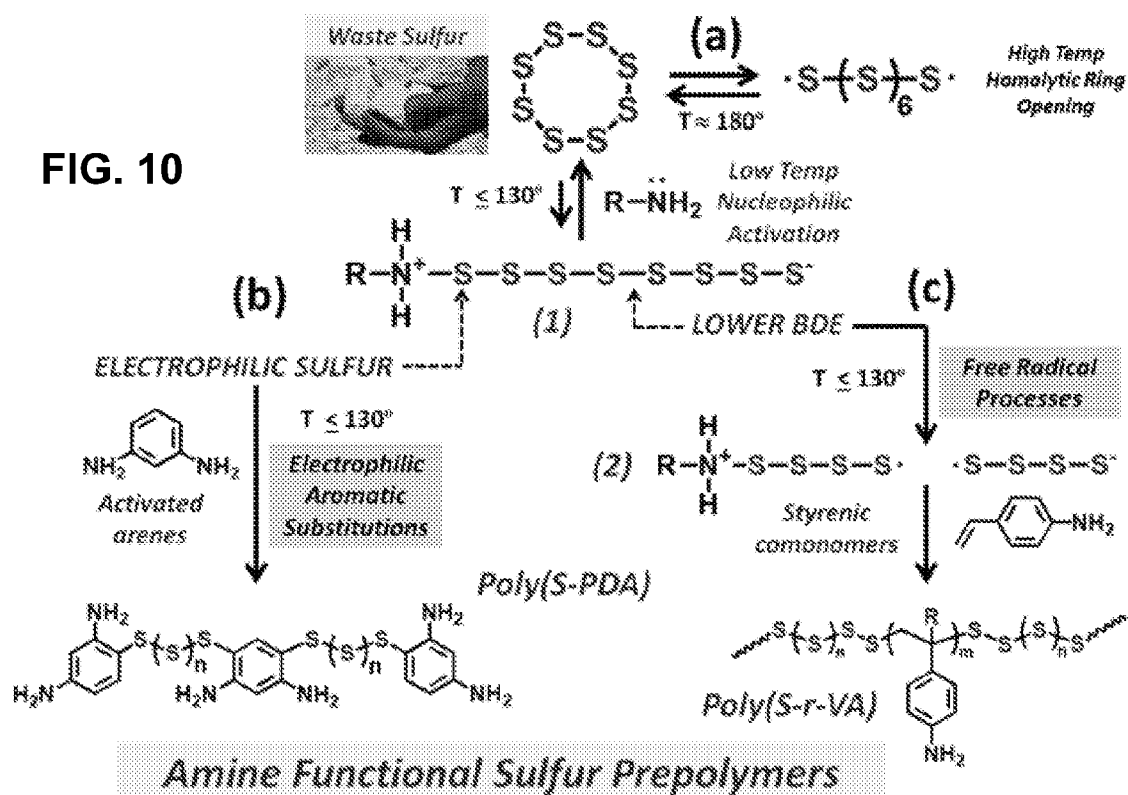


FIG. 9



INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2018/037598

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C08L 21/02; C08K 5/00; C08L 21/00 (2018.01)

CPC - C08K 5/0025; C08K 5/00; C08L 21/00; C08L 21/02 (2018.08)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

See Search History document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2,989,513 A (HENDRY et al) 20 June 1961 (20.06.1961) entire document	1-3, 19-21, 39-41
A	US 4,752,507 A (JOHANSSON et al) 21 June 1988 (21.06.1988) entire document	1-3, 19-21, 39-41
A	US 3,563,962 A (MIRVISS) 16 February 1971 (16.02.1971) entire document	1-3, 19-21, 39-41

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

13 August 2018

Date of mailing of the international search report

29 AUG 2018

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2018/037598

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 4-18, 22-38, 42-53
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.