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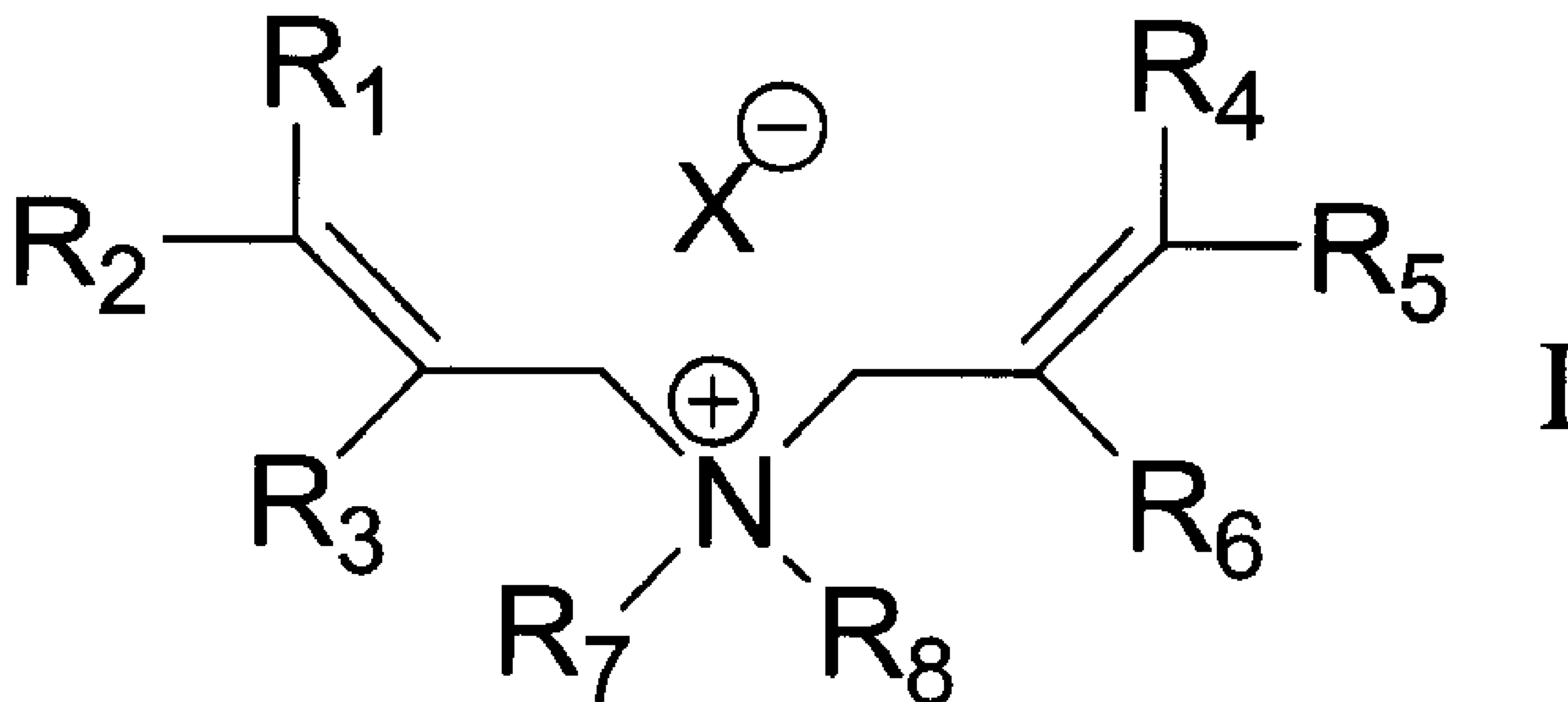
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(54) Titre : ELECTROLYTE ION-GEL POLYMERE ET COMPOSE PRECURSEUR CONNEXE

(54) Title: ION-POLYMER GEL ELECTROLYTE AND ITS PRECURSOR COMPOSITION

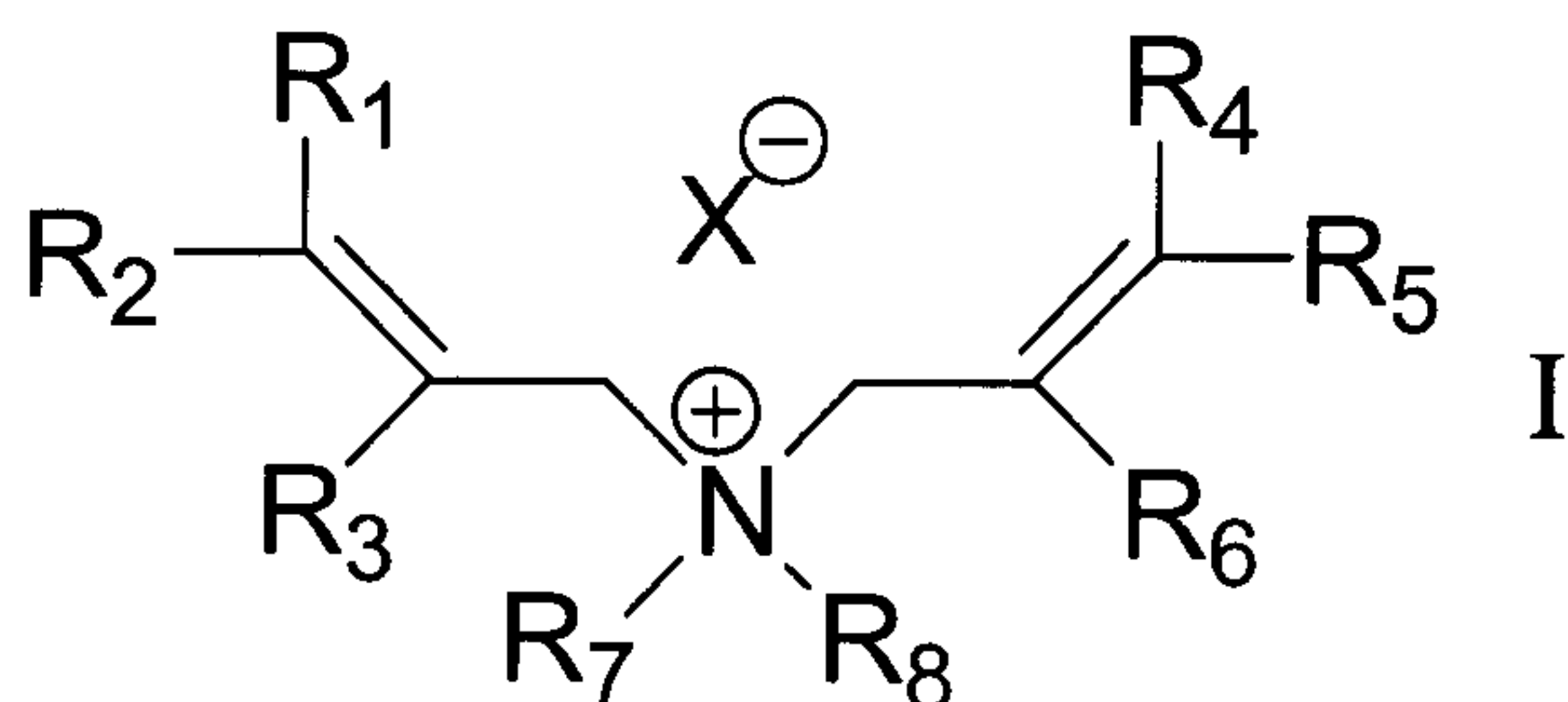


(57) Abrégé/Abstract:

A precursor composition capable to form a solid-state electrolyte having good ion conductivity and high heat-resistance, by simple curing procedure, comprising; (A) a polymerizable ion pair compound represented by formula I, (B) a cross-linker having two or more unsaturated groups co-polymerizable with the polymerizable ion pair compound (A), and (C) non-polymerizable ion pair compound. Each of R_1 , R_2 , R_3 , R_4 , R_5 and R_6 represents hydrogen atom, alkyl or aryl group having 1-12 carbon atoms; and each of R_7 and R_8 represents alkyl or aryl group having 1-12 carbon atoms. X designates either of halogen atom, $AlCl_4^-$, PF_6^- , BF_4^- , bis(oxalato)borate anion, $R_{f1}SO_3^-$, $(NC)_2N^-$, $(R_{f2}Y)_2N^-$, $(R_{f2}Y)_3C^-$, and $(R_{f2}Y)_2C-Q$, where R_{f1} designates perfluoro alkyl or aryl group having 1-8 carbon atoms; each R_{f2} designates fluorine atom, perfluoro alkyl or aryl group having 1-8 carbon atoms; Y designates $-SO_2-$ or $-PO-R_{f2}$; and Q designates $-H$ or $-CO-R_{f2}$. (see formula I)

Abstract

A precursor composition capable to form a solid-state electrolyte having good ion conductivity and high heat-resistance, by simple curing procedure, comprising; (A) a polymerizable ion pair compound represented by formula I, (B) a cross-linker having two or more unsaturated groups co-polymerizable with the polymerizable ion pair compound (A), and (C) non-polymerizable ion pair compound. Each of R_1 , R_2 , R_3 , R_4 , R_5 and R_6 represents hydrogen atom, alkyl or aryl group having 1-12 carbon atoms; and each of R_7 and R_8 represents alkyl or aryl group having 1-12 carbon atoms. X designates either of halogen atom, $AlCl_4^-$, PF_6^- , BF_4^- , bis(oxalato) borate anion, $R_{f1}SO_3^-$, $(NC)_2N^-$, $(R_{f2}Y)_2N^-$, $(R_{f2}Y)_3C^-$, and $(R_{f2}Y)_2C^-Q$, where R_{f1} designates perfluoroalkyl or aryl group having 1-8 carbon atoms; each R_{f2} designates fluorine atom, perfluoroalkyl or aryl group having 1-8 carbon atoms; Y designates $-SO_2-$ or $-PO-R_{f2}$; and Q designates $-H$ or $-CO-R_{f2}$.



Ion-polymer Gel Electrolyte and Its Precursor Composition

Field of The Invention

5 This invention relates to a polymer-gel electrolyte forming conductor for protons and ions, and to a precursor composition for producing thereof. Particularly, the invention relates to a polymer-gel electrolyte and its precursor composition that are preferably applicable to electrochemical
10 devices utilizing electrochemical reaction, such as battery, capacitor, fuel cell, solar battery and electrochemical sensor. The polymer-gel electrolyte is also applicable to solid-state catalyst for chemical reaction, and to antistatic agent or electrostatic shielding material.

15

Background Art

 In order to enhance performances or safety of lithium battery, capacitor or the like, numerous investigations has been made for utilizing gel or polymer electrolyte in place
20 of liquid-state electrolyte that has been conventionally used. As for polymer electrolytes, investigations have been made on alkylene oxides added with electrolyte salts such as lithium perchlorate, lithium methanesulfonate, and lithium bis(trifluoro methane sulfonyl imide). Nevertheless,

satisfactory ion conductivity at room temperature or at 25°C has not been achieved yet as hampered by thermo-dynamical mobility of the alkylene oxide polymer chains. Moreover, the alkylene oxide polymers are defective in thermal stability and
5 start to decompose at a temperature of 180°C or more.

Meanwhile, ionic liquid that has recently attracted attentions exhibit good ion conductivity. Nevertheless, if the ionic liquid is highly viscose, the ion conductivity deteriorates. Moreover, when the ionic liquid is converted
10 to solid state by being combined with polymer compounds, mobility of the ions is hampered by constrictions on motion of macromolecular chains; thus density of the ions and thereby the ion conductivity are further decreased. Please see JP-1998 (H10)-265673A.

15 In view of the above, it is aimed to provide precursor compositions capable to form a solid-state electrolyte having good ion conductivity and high heat-resistance by simple curing procedure such as casting into a mould or onto a surface, as well as to provide gel electrolyte obtainable from the precursor
20 compositions.

BRIEF SUMMARY OF THE INVENTION

Invention-wise precursor composition for the ion-polymer gel electrolyte is comprised of: (A) ion pair compound
25 polymerizable as to form a polymer, (B) cross-linker having

two or more unsaturated groups co-polymerizable with the ion pair compound (A), and (C) non-polymerizable ion pair compound.

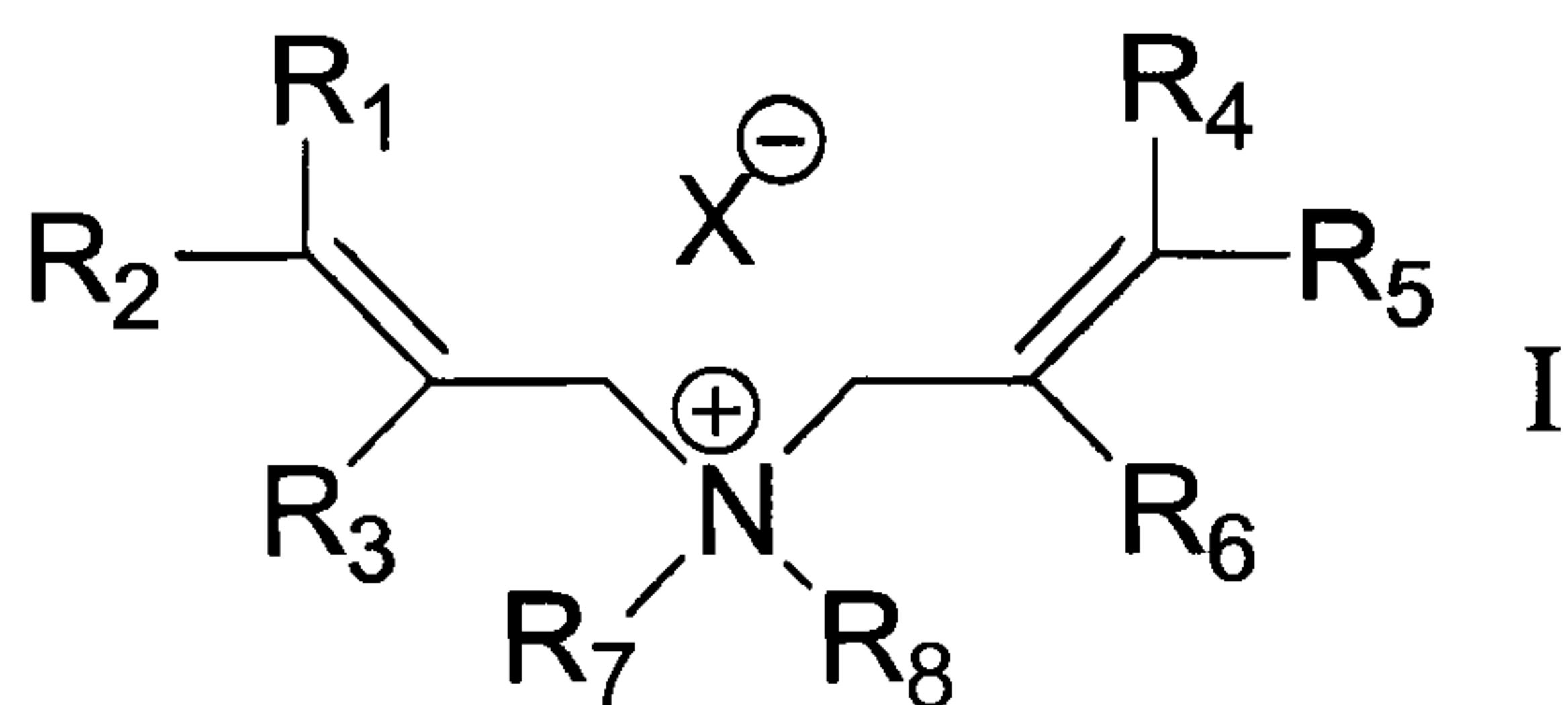
In a preferred embodiment, the precursor composition further contains polymerization initiator in a range from 0.05wt% to

5 5wt%, which is one or any combination selected from: (D) photo polymerization initiator, (E) thermal polymerization initiator, (F) redox (reduction-oxidation) polymerization initiator and the like. In a preferred embodiment the non-polymerizable ion pair compound (C) is present at no more than 95wt%.

10 By the invention-wise precursor composition, casting into a mould, impregnation, and/or casting onto a surface is easily made; and gel electrolyte having good ion conductivity is easily obtainable by a simple procedure such as ultraviolet irradiation and heating. The gel electrolyte may be placed
15 between electrodes or mixed with electrode material, and is applicable in an electrochemical device utilizing electrochemical reaction, such as battery, capacitor, fuel cell, solar battery and electrochemical sensor.

20 DETAILED DESCRIPTION OF THE INVENTION

The polymerizable ion pair compound (A) is expressed by following chemical formula I, and is exemplified by ion pairs formed of at least one selected from a group of cations listed below and at least one selected from a group of anions listed
25 below.



In above formula, each of R_1 , R_2 , R_3 , R_4 , R_5 and R_6 independently represents hydrogen atom, alkyl or aryl group having 1-12 carbon atoms; and each of R_7 and R_8 independently
 5 represents alkyl or aryl group having 1-12 carbon atoms.

Cations for (A): diallyl dimethyl ammonium, diallyl methyl-ethyl ammonium, diallyl diethyl ammonium, diallyl dipropyl ammonium, diallyl methyl-hexyl ammonium, diallyl methyl-octyl ammonium, diallyl methyl-lauryl ammonium, diallyl
 10 methyl-benzyl ammonium, allyl-methallyl dimethyl ammonium, allyl-methallyl methyl-ethyl ammonium, allyl-methallyl diethyl ammonium, allyl-methallyl dipropyl ammonium, allyl-methallyl methyl-hexyl ammonium, allyl-methallyl methyl-octyl ammonium, allyl-methallyl methyl-lauryl ammonium,
 15 dimethallyl dimethyl ammonium, dimethallyl methyl-ethyl ammonium, dimethallyl diethyl ammonium, dimethallyl dipropyl ammonium, dimethallyl methyl-hexyl ammonium, dimethallyl methyl-octyl ammonium, dimethallyl methyl-lauryl ammonium, and the like. Preferable cations among them are; diallyl dimethyl
 20 ammonium, diallyl methyl-ethyl ammonium, dimethallyl dimethyl ammonium, diallyl methyl-propyl ammonium, diallyl methyl-hexyl ammonium. Diallyl dimethyl ammonium is especially preferred

in view of production cost.

Anions for (A): Cl^- , Br^- , I^- , AlCl_4^- , PF_6^- , BF_4^- ,
 bis(oxalato) borate anion, $\text{R}_{\text{f}1}\text{SO}_3^-$, $(\text{NC})_2\text{N}^-$, $(\text{R}_{\text{f}2}\text{Y})_2\text{N}^-$, $(\text{R}_{\text{f}2}\text{Y})_3\text{C}^-$,
 and $(\text{R}_{\text{f}2}\text{Y})_2\text{C}^-\text{Q}$. $\text{R}_{\text{f}1}$ designates perfluoro alkyl or aryl group
 5 having 1-8 carbon atoms; each $\text{R}_{\text{f}2}$ designates independently
 fluorine atom, perfluoro alkyl or aryl group having 1-8 carbon
 atoms; Y designates $-\text{SO}_2-$ or $-\text{PO}-\text{R}_{\text{f}2}$; and Q designates $-\text{H}$ or
 $-\text{CO}-\text{R}_{\text{f}2}$. Preferable anion among them are $\text{R}_{\text{f}1}\text{SO}_3^-$, $(\text{NC})_2\text{N}^-$,
 $(\text{R}_{\text{f}2}\text{Y})_2\text{N}^-$, $(\text{R}_{\text{f}2}\text{Y})_3\text{C}^-$, and $(\text{R}_{\text{f}2}\text{Y})_2\text{C}^-\text{Q}$. Especially preferable
 10 anions are $(\text{CF}_3\text{SO}_2)_2\text{N}^-$, $(\text{FSO}_2)_2\text{N}^-$ and $(\text{NC})_2\text{N}^-$.

Such polymerizable ion pair compound (A), or polymerizable
 ionic liquid, presumably forms 5-member aliphatic ring ammonium
 and/or 6-member aliphatic ring ammonium as a result of
 cyclopolymerization on course of the polymerization.
 15 According to investigations made on the ionic liquid, the
 5-member and/or 6-member aliphatic ring ammonium is considered
 to be preferable. The polymerizable ion pair compound (A) is
 included in the precursor composition preferably at no less
 than 5wt%, more preferably at no less than 20wt%.

20 As for the cross-linker (B) or monomer having two or more
 unsaturated groups co-polymerizable with the ion pair compound
 (A), the unsaturated groups are preferably selected from a group
 consisting of vinyl, allyl, methallyl, acryl and methacryl
 groups; and number of the unsaturated groups is preferably two
 25 or three. The cross-linker (B) is exemplified by: ion pairs

formed of at least one selected from a group of cations listed below and at least one selected from a group of anions listed below; and/or at least one of non-ionic compounds listed below.

Cations for (B): triallyl ammine, triallyl-methyl ammonium, triallyl-ethyl ammonium, triallyl-propyl ammonium, triallyl-butyl ammonium, triallyl-hexyl ammonium, triallyl-benzyl ammonium, tetraallyl ammonium, diallyl methallyl-methyl ammonium, allyl dimethallyl-methyl ammonium and trimethallyl methyl ammonium. Preferable cations among them are; triallyl-methyl ammonium, triallyl-ethyl ammonium, triallyl-propyl ammonium, triallyl-butyl ammonium and triallyl-hexyl ammonium.

Anions for (B): Cl^- , Br^- , I^- , AlCl_4^- , PF_6^- , BF_4^- , bis(oxalato) borate anion, $\text{R}_{\text{f}1}\text{SO}_3^-$, $(\text{NC})_2\text{N}^-$, $(\text{R}_{\text{f}2}\text{Y})_2\text{N}^-$, $(\text{R}_{\text{f}2}\text{Y})_3\text{C}^-$, and $(\text{R}_{\text{f}2}\text{Y})_2\text{C}^-\text{Q}$. $\text{R}_{\text{f}1}$ designates perfluoro alkyl or aryl group having 1-8 carbon atoms; each $\text{R}_{\text{f}2}$ designates independently fluorine atom, perfluoro alkyl or aryl group having 1-8 carbon atoms; Y designates $-\text{SO}_2-$ or $-\text{PO}-\text{R}_{\text{f}2}$; and Q designates $-\text{H}$ or $-\text{CO}-\text{R}_{\text{f}2}$. Preferable anion among them are $\text{R}_{\text{f}1}\text{SO}_3^-$, $(\text{NC})_2\text{N}^-$, $(\text{R}_{\text{f}2}\text{Y})_2\text{N}^-$, $(\text{R}_{\text{f}2}\text{Y})_3\text{C}^-$, and $(\text{R}_{\text{f}2}\text{Y})_2\text{C}^-\text{Q}$. Especially preferable anions are $(\text{CF}_3\text{SO}_2)_2\text{N}^-$, $(\text{FSO}_2)_2\text{N}^-$ and $(\text{NC})_2\text{N}^-$.

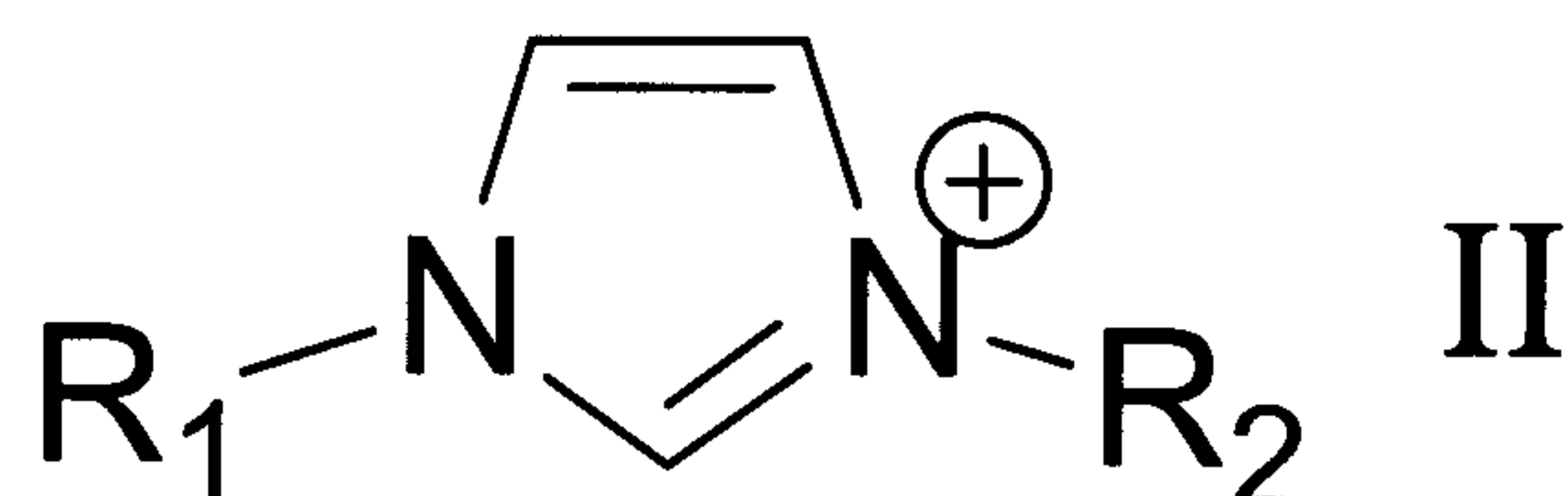
Non-ionic compounds for (B): monomers having two unsaturated groups that are poor in cyclopolymerizability, such as diallyl phthalate, diallyl terephthalate, ethylene glycol diacrylate and ethylene glycol dimethacrylate; and monomers

having three or more unsaturated groups such as triallyl isocyanurate, trimethylol propane triallyl ether and neopentyl glycol tetraallyl ether. Among them, preferable monomers are diallyl phthalate, diallyl terephthalate, triallyl isocyanurate, trimethylol propane triallyl ether. That is, compounds each having allyl groups and nitrogen atom and/or oxygen atom are preferable in view of compatibility with the other component in the composition and in view of cost efficiency. The non-ionic compound(s) as the crosslinker(s) is included in the precursor composition preferably in a range of from 1wt% to 50wt%.

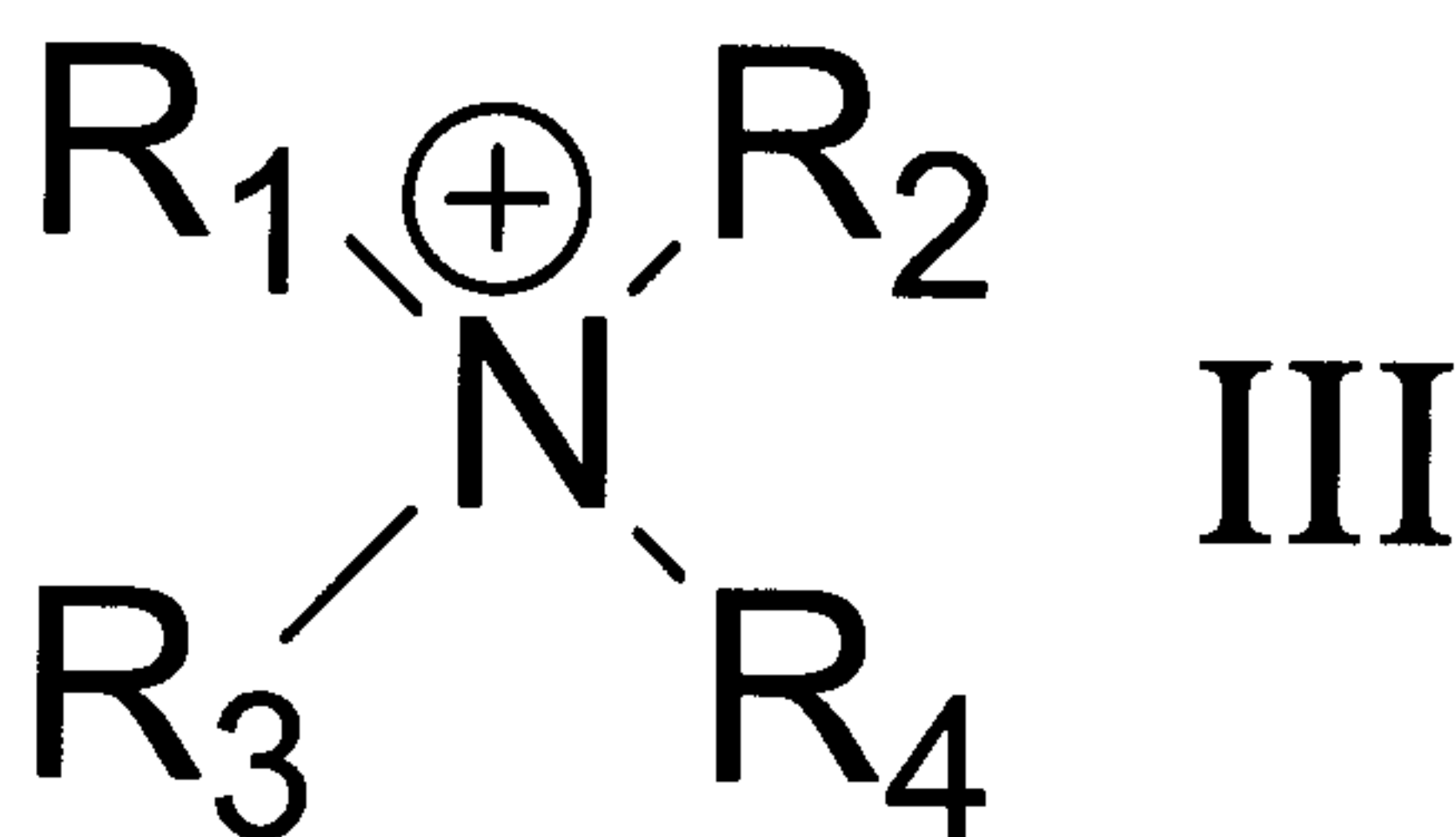
The non-polymerizable ion pair compound (C) is exemplified by ion pairs formed of at least one selected from a group of cations listed below and at least one selected from a group of anions listed below.

Cations for (C): proton, alkaline metal ions, alkaline earth metal ions, zinc ion, cadmium ion, mercury ion, and other transition metal ions; rare earth ions, diazonium ion, phosphonium ion, sulfonium ion and oxonium ion; and organic cations represented by general formula of NuR^+ , in which Nu designates ammonia, alkyl amine, pyridine, imidazole, amidine, guanidine or alkaloid, while R^+ designates alkyl or oxyalkyl group having 1-20 carbon atoms, or aryl group having 6-30 carbon atoms. More preferable cations are: lithium or sodium ions and/or imidazoliums represented by following Formula II and/or

quaternary ammonium represented by following Formula III.
 Among them, methyl ethyl imidazolium, methyl propyl imidazolium,
 methyl hexyl imidazolium, dimethyl dipropyl ammonium and
 trimethyl butyl ammonium are especially preferred in view of
 5 cost efficiency.



Each of R_1 and R_2 designates alkyl, aryl or alkoxy group
 having 1-8 carbon atoms.



10 Each of R_1 , R_2 , R_3 and R_4 designates, independently, alkyl,
 aryl or alkoxy group having 1-8 carbon atoms.

Anions for (C): Cl^- , Br^- , I^- , $AlCl_4^-$, PF_6^- , BF_4^- ,
 bis(oxalato) borate anion, $R_{f1}SO_3^-$, $(NC)_2N^-$, $(R_{f2}Y)_2N^-$, $(R_{f2}Y)_3C^-$,
 and $(R_{f2}Y)_2C^-Q$. R_{f1} designates perfluoro alkyl or aryl group
 15 having 1-8 carbon atoms; each R_{f2} designates independently
 fluorine atom, perfluoro alkyl or aryl group having 1-8 carbon
 atoms; Y designates $-SO_2-$ or $-PO-R_{f2}$; and Q designates $-H$ or
 $-CO-R_{f2}$. Preferable anion among them are $R_{f1}SO_3^-$, $(NC)_2N^-$,
 $(R_{f2}Y)_2N^-$, $(R_{f2}Y)_3C^-$, and $(R_{f2}Y)_2C^-Q$. Especially preferable

anions are $(\text{CF}_3\text{SO}_2)_2\text{N}^-$, $(\text{FSO}_2)_2\text{N}^-$ and $(\text{NC})_2\text{N}^-$. The non-polymerizable ion pair compound (C) is included in the precursor composition preferably at no more than 95wt%, and more preferably at no more than 80wt%, although content range
5 of the compound (C) is not particularly limited. If the content of the compound (C) exceeds the 95wt%, formation of a gel structure is not achievable.

The photo polymerization initiator (D) is exemplified by at least one selected from: 2,2-dimethoxy-2-phenyl
10 acetophenone, 1-hydroxy cyclohexyl phenyl ketone, benzophenone, 2-methyl [4-(methylthio)phenyl]-2-morpholino-1-propanone, phenyl bis(2,4,6-trimethyl benzoyl)-phosphine oxides, bis(2, 6-dimethoxy benzoyl)-2,4,4-trimethyl pentyl phosphine oxide,
15 oligo[2-hydroxy-2-methyl-1-[4-(1-methylvinyl) phenyl] propanone] and the like, while this exemplification is not meant to be limitative. Content of the photo polymerization initiator (D) in the precursor composition is preferably in a range from 0.05wt% to 5wt%. When the content is less than
20 the 0.05wt%, formation of a gel structure is not achievable; and content exceeding the 5wt% deteriorates safety and is disadvantageous in cost efficiency.

The thermal polymerization initiator (E) is exemplified by at least one selected from: methyl ethyl ketone peroxide,
25 acetyl acetone peroxide and other ketone peroxides; t-butyl

hydro peroxide and other hydro peroxides; isobutyryl peroxide and other diacyl peroxides; dicumyl peroxide, dibutyl cumyl peroxide and other dialkyl peroxides; t-butyl peroxy pivalate, t-butyl peroxy isobutylate and other alkyl peroxy esters; 5 bis(4-t-butyl cyclohexyl) peroxy dicarbonate and other peroxocarbonates and the like, while this exemplification is not meant to be limitative. Content of the thermo polymerization initiator (E) in the precursor composition is preferably in a range from 0.05wt% to 5wt%. When the content 10 is less than the 0.05wt%, formation of a gel structure is not achievable; and content exceeding the 5wt% deteriorates safety and is disadvantageous in cost efficiency.

The polymerization initiators mentioned hereto may be adopted separately one by one or in combination of two or more. 15 The precursor composition may be added with heat stabilizer, antioxidant, light stabilizer, oxidation-reduction substance, oxidizing and reducing agents, inorganic fillers or the like; and may be added with compatible solvents so far as shape of gel electrolyte product is retained after curing. The 20 precursor composition may be further added with polymerizable monomers in accordance with specific purpose such as improvements in mechanical strength or flexibility of the gel electrolyte. Such monomer able to be added is exemplified by polar monomers having one unsaturated group such as; vinyl 25 pyrrolidone, vinyl acetate, allyl acetate, vinyl formamide,

and acrylic acid esters such as hydroxyl ethyl acrylate; while these exemplification is not meant to be limitative.

Method of preparing the precursor composition is exemplified by following, while the exemplification is not meant to be limitative. A reaction vessel equipped with agitator is charged with the polymerizable ion pair compound (A) as well as the cross-linker (B) having two or more unsaturated groups co-polymerizable therewith, followed by mixing them. Then, non-polymerizable ion pair compound (C) is added to the mixture. The photo polymerization initiator (D) or the thermal polymerization initiator (E) may be further added to be dissolved if necessary or appropriate in accordance with occasion. In otherwise, the precursor composition may be prepared in following way. Methanol, ethanol, propanol, acetonitrile, or other compatible solvent is used; and the polymerizable ion pair compound (A), the cross-linker (B), the non-polymerizable ion pair compound (C) and polymerization initiator are added to the solvent one by one, or at any arbitrary time. After mixing and dissolving, the solvent is removed by vaporization. In order to improve storage stability or to prolong shelf life, the polymerization initiator may be omitted when preparing the precursor composition, and as to be added just before forming of the gel electrolyte.

The method of preparing the gel electrolyte is exemplified by followings, while the exemplification is not meant to be

limitative. The precursor composition is poured into a casting mold and then cured by UV irradiation or heating in accordance with species of the polymerization initiator. In otherwise, the precursor composition is poured or applied onto a film and then cured in same manner as above to form a film-shaped gel electrolyte. Thus obtained ion-polymer-gel electrolyte has satisfactory ion conductivity and shape retainability with no fluidity. This is presumably because the gel electrolyte ionic polymer has unfixed or movable anionic groups on an ionic polymer matrix having decently cyclized ammonium groups and has both of cation and anion components that are formed of free ion pair compound and have excellent low-temperature performance.

<Example 1>

Diallyl dimethyl ammonium- $(\text{FSO}_2)_2\text{N}^-$ (45 weight part), propyl methyl imidazolium- $(\text{FSO}_2)_2\text{N}^-$ (45 weight part), triallyl-methyl ammonium- $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ (9.5 weight part) and IrgacureTM 651 (Chiba speciality chemicals, 0.5 weight part) were mixed with each other. Thus obtained mixture was applied on a polypropylene film by thickness of 0.5mm. Then, the applied mixture was covered by a protection film formed of polypropylene, and irradiated with ultra violet light of $15\text{mW}/\text{cm}^2$ for 10 minutes, as to obtain a gel electrolyte film. Ion conductivity of the film was $10.2\text{mS}/\text{cm}$ when measured at 25°C by impedance analyzer. On thermogravimetry analysis, thermal reduction started at about

290°C.

<Example 2>

Diallyl dimethyl ammonium-(CF₃SO₂)₂N⁻ (45 weight part),
ethyl methyl imidazolium-(CF₃SO₂)₂N⁻, (45 weight part),
5 diallyl-isocyanurate (9.5 weight part) and Esacure™ KTO46
(Lamberti s.p.a., 0.5 weight part) were mixed with each other
to form a uniform mixture. Thus obtained mixture was applied
on a polypropylene film or a base, by thickness of 0.5mm. Then,
the applied mixture was covered by a protection film formed
10 of polypropylene, and irradiated with ultra violet light of
15mW/cm² for 10 minutes. A gel electrolyte film thus obtained
was homogenous, non-flowable, and self-sustainable when picked
up by forceps. The film was cut in a disk at diameter of 1cm;
and ion conductivity of thus cut film was 13.1mS/cm when measured
15 at 25°C by the impedance analyzer.

<Example 3>

Diallyl dimethyl ammonium-(CF₃SO₂)₂N⁻ (76 weight part),
ethyl propyl imidazolium-(CF₃SO₂)₂N⁻, (18 weight part),
diallyl-phthalate (5 weight part) and Esacure KTO46 (Lamberti
20 s.p.a., 1 weight part) were mixed with each other to form a
uniform mixture. Thus obtained mixture was applied on a
polypropylene film or a base, by thickness of 0.5mm. Then,
the applied mixture was covered by a protection film formed
of polypropylene, and irradiated with ultra violet light of

15mW/cm² for 10 minutes. A gel electrolyte film thus obtained was homogenous, non-flowable, and self-sustainable when picked up by forceps. The film was cut in a disk at diameter of 1cm; and ion conductivity of thus cut film was 4.6mS/cm when measured
5 at 25°C by the impedance analyzer.

<Example 4>

A reaction vessel equipped with an agitator is charged with acetonitrile (200 weight part) and then Li-(CF₃SO₂)₂N⁻ (17 weight part) is added and dissolved in the acetonitrile.
10 Diallyl dimethyl ammonium-(CF₃SO₂)₂N⁻ (45 weight part), ethyl methyl imidazolium-(CF₃SO₂)₂N⁻, (25 weight part), triallyl isocyanurate (5 weight part) and Esacure KTO46 (Lambert s.p.a., 1 weight part) were further admixed to form a uniform solution. From thus obtained mixture solution, the acetonitrile or solvent
15 was removed by heating at 60°C under vacuuming, as to form a precursor composition. Thus obtained precursor composition was applied on a polypropylene film or a base, by thickness of 0.5mm. Then, the applied mixture was covered by a protection film formed of polypropylene, and irradiated with ultra violet
20 light of 15mW/cm² for 10 minutes. A gel electrolyte film thus obtained was homogenous, non-flowable, and self-sustainable when picked up by forceps. The film was cut in a disk at diameter of 1cm; and ion conductivity of thus cut film was 8.1mS/cm when measured at 25°C by the impedance analyzer.
25 <Example 5>

Diallyl dimethyl ammonium- $(\text{NC})_2\text{N}^-$ (25 weight part), trimethyl butyl ammonium- $(\text{NC})_2\text{N}^-$, (50 weight part), triallyl isocyanurate (24 weight part) and PerkadoxTM 16 (Kayaku Akzo Corporation, 1 weight part) were uniformly mixed with each other. Thus obtained mixture was poured into a glass vial having a diameter of 3cm; and, an electrode for measuring conductivity was immersed in the mixture. Then, the mixture was heated at 70°C for 2 hours, as to obtain a gel electrolyte. Ion conductivity of the gel electrolyte was 10.5mS/cm when measured at 25°C by the impedance analyzer.

<Comparative Example 1>

Diallyl dimethyl ammonium- $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ (50 weight part), ethyl methyl imidazolium- $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ (49 weight part) and Esacure KT046 (Lamberti s.p.a., 1 weight part) were mixed with each other to form a uniform mixture. Thus obtained mixture was applied on a polypropylene film or a base, by thickness of 0.5mm. Then, the applied mixture was covered by a protection film formed of polypropylene, and irradiated with ultra violet light of 15mW/cm² for 10 minutes. Cured product was homogeneous and non-flowable, but a paste form; thus self-sustainable gel electrolyte film was not achieved. Meanwhile, ion conductivity of the paste was 15.1mS/cm when measured at 25°C by the impedance analyzer.

<Comparative Example 2>

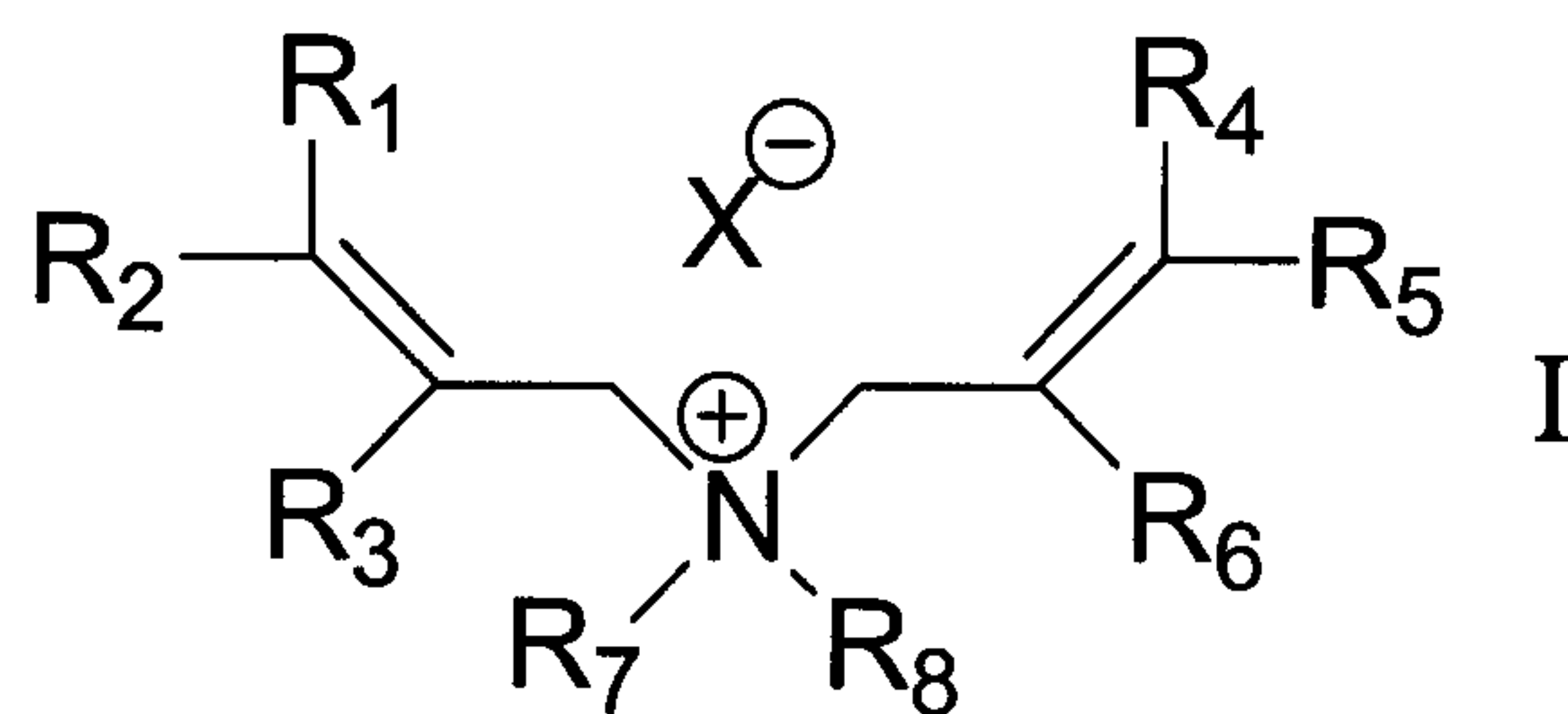
Diallyl dimethyl ammonium- $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ (4 weight part), ethylmethylimidazolium- $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ (95 weight part), triallyl isocyanurate (0.5 weight part) and Esacure KTO46 (Lamberti s.p.a., 0.5 weight part) were mixed with each other to form
5 a uniform mixture. Thus obtained mixture was applied on a polypropylene film or a base, by thickness of 0.5mm. Then, the applied mixture was covered by a protection film formed of polypropylene, and irradiated with ultra violet light of $15\text{mW}/\text{cm}^2$ for 10 minutes. Product was remained to be liquid;
10 thus a gel electrolyte film was not achieved.

Claims:

1. A precursor composition for an ion-polymer gel electrolyte comprising: (A) a polymerizable ion pair compound, (B) a cross-linker having two or more unsaturated groups co-polymerizable with the polymerizable ion pair compound (A), (C) non-polymerizable ion pair compound at no more than 95wt%, and a polymerization initiator in a range from 0.05wt% to 5wt%, which is (D) photo polymerization initiator and/or (E) thermal polymerization initiator.

10

2. The precursor composition according to claim 1, the polymerizable ion pair compound (A) being a monomer represented by following general formula I



Each of R_1 , R_2 , R_3 , R_4 , R_5 and R_6 independently represents hydrogen atom, alkyl or aryl group having 1-12 carbon atoms; and each of R_7 and R_8 independently represents alkyl or aryl group having 1-12 carbon atoms; X designates either of halogen atom, AlCl_4^- , PF_6^- , BF_4^- , bis(oxalato) borate anion, $\text{R}_{\text{f}1}\text{SO}_3^-$, $(\text{NC})_2\text{N}^-$, $(\text{R}_{\text{f}2}\text{Y})_2\text{N}^-$, $(\text{R}_{\text{f}2}\text{Y})_3\text{C}^-$ and $(\text{R}_{\text{f}2}\text{Y})_2\text{C}^-Q$, where $\text{R}_{\text{f}1}$ designates perfluoro alkyl or aryl group having 1-8 carbon atoms; each

20

R_{f2} designates independently fluorine atom, perfluoro alkyl or aryl group having 1-8 carbon atoms; Y designates $-SO_2-$ or $-PO-R_{f2}$; and Q designates $-H$ or $-CO-R_{f2}$.

5 3. The precursor composition according to claim 1 or 2, the non-polymerizable ion pair compound (C) being formed of a cation group selected from a group consisting of: proton, alkaline metal ions, alkaline earth metal ions, zinc ion, cadmium ion, mercury ion, rare earth ions, diazonium ion, phosphonium
10 ion, sulfonium ion and oxonium ion; and organic cations represented by general formula of NuR^+ , in which Nu designates ammonia, alkyl amine, pyridine, imidazole, amidine, or guanidine, while R^+ designates alkyl or oxyalkyl group having 1-20 carbon atoms, or aryl group having 6-30 carbon atoms.

15

4. The precursor composition according to claim 2 or 3, wherein each of R_1 , R_2 , R_4 and R_5 in the general formula I represents hydrogen atom; and each of R_3 and R_6 independently represents hydrogen atom or methyl group.

20

5. The precursor composition according to claim 4, wherein the polymerizable ion pair compound (A) is formed of:

cation group species selected from the group consisting of diallyl dimethyl ammonium, diallyl methyl-ethyl ammonium,
25 dimethallyl dimethyl ammonium, diallyl methyl-propyl ammonium

and diallyl methyl-hexyl ammonium; and

anion group species selected from the group consisting of $R_{f1}SO_3^-$, $(NC)_2N^-$, $(R_{f2}Y)_2N^-$, $(R_{f2}Y)_3C^-$, and $(R_{f2}Y)_2C^-Q$ where R_{f1} designates perfluoro alkyl or aryl group having 1-8 carbon atoms; each R_{f2} designates independently fluorine atom, perfluoro alkyl or aryl group having 1-8 carbon atoms; Y designates $-SO_2-$ or $-PO-R_{f2}$; and Q designates $-H$ or $-CO-R_{f2}$.

6. The precursor composition according to claim 5, wherein the polymerizable ion pair compound (A) is formed of anion group selected from the group consisting of $(CF_3SO_2)_2N^-$, $(FSO_2)_2N^-$ and $(NC)_2N^-$.

7. The precursor composition according to claim 4, wherein the cross-linker (B) is ion pair compound formed of:

cation group species selected from the group consisting of triallyl-methyl ammonium, triallyl-ethyl ammonium, triallyl-propyl ammonium, triallyl-butyl ammonium and triallyl-hexyl ammonium; and

anion group species selected from the group consisting of $R_{f1}SO_3^-$, $(NC)_2N^-$, $(R_{f2}Y)_2N^-$, $(R_{f2}Y)_3C^-$, and $(R_{f2}Y)_2C^-Q$ where R_{f1} designates perfluoro alkyl or aryl group having 1-8 carbon atoms; each R_{f2} designates independently fluorine atom, perfluoro alkyl or aryl group having 1-8 carbon atoms; Y

designates $-\text{SO}_2-$ or $-\text{PO-R}_{\text{f}2}$; and Q designates $-\text{H}$ or $-\text{CO-R}_{\text{f}2}$;
or

non-ionic compound selected from the group consisting
of diallyl phthalate, diallyl terephthalate, triallyl
5 isocyanurate and trimethylol propane triallyl ether.

8. The precursor composition according to claim 7, wherein
the cross-linker (B) is ion pair compound formed of:

cation group species selected from the group consisting
10 of triallyl-methyl ammonium, triallyl-ethyl ammonium,
triallyl-propyl ammonium, triallyl-butyl ammonium and
triallyl-hexyl ammonium; and

anion group species selected from the group consisting
of $(\text{CF}_3\text{SO}_2)_2\text{N}^-$, $(\text{FSO}_2)_2\text{N}^-$ and $(\text{NC})_2\text{N}^-$; or

15 non-ionic compound selected from the group consisting
of diallyl phthalate, diallyl terephthalate, triallyl
isocyanurate and trimethylol propane triallyl ether.

9. An ion-polymer gel electrolyte formed by curing the
20 precursor composition according to any one of the claims 1-8.

