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(54) Title: POLYMERIZED IONIC LIQUID NETWORKS, METHODS OF MAKING, AND ELECTROADHESIVE MATERIALS

Polyanion
(EA-co-15Fa)

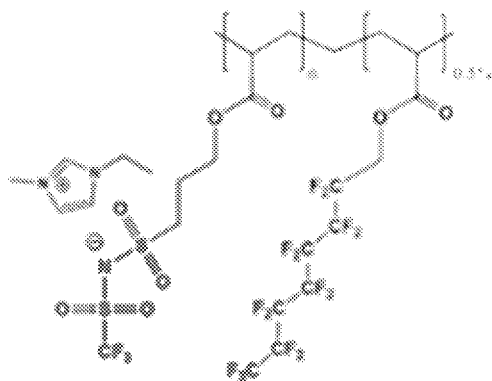


FIG. 27A

(57) Abstract: A method of synthesizing a sulfonylimide ionoelastomer by utilizing Sulfur (VI) Fluoride Exchange (SuFEx) click chemistry to produce sulfonylimide anions from sulfonyl fluoride, and crosslinking the sulfonylimide anions to form an ionoelastomeric sulfonylimide network. The sulfonylimide anions can be used to make ionoelastomeric sulfonylimide networks, either anionic or cationic, that can be used as electroadhesives.

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**POLYMERIZED IONIC LIQUID NETWORKS, METHODS OF MAKING, AND
ELECTROADHESIVE MATERIALS**

TECHNICAL FIELD

[0001] The present disclosure is directed to polymeric materials, particularly polymerized ionic liquids (PILs) having one or more loosely coordinating ions covalently linked to a polymeric backbone. The present disclosure describes a synthetic route for the production of high-purity sulfonylimide monomers using a Sulfur(VI) Fluoride Exchange (SuFEx) click reaction.

CROSS-REFERENCE

[0002] This application claims priority to U.S. provisional application 63/520,157 filed August 17, 2023 titled PENDENT SULFONYLIMIDE IONIC LIQUID MONOMERS AND IONOELASTOMERS VIA SUFEX CLICK CHEMISTRY and to U.S. provisional application 63/520,887 filed August 21, 2023 titled POLYMERIZED IONIC LIQUID NETWORKS, METHODS OF MAKING, AND ELECTROADHESIVE MATERIALS, the entire disclosures of which are incorporated herein by reference for all purposes.

BACKGROUND

[0003] Polymerized ionic liquids (PILs) having one or more loosely coordinating ions covalently linked to a polymeric backbone have gained significant attention over the last decade for their high solvent-free ionic conductivities under ambient conditions and wide electrochemical windows. These properties have enabled PILs to be used in various electronic applications ranging from energy storage devices, such as batteries and supercapacitors, to electromechanical devices such as low-voltage electroadhesives and actuators. The high degree of chemical diversity among PILs allows for applications-driven polymer design without the constraints associated with other ion-conducting polymer systems, such as the need for solvent or specific ion-backbone interactions.

[0004] However, synthetic challenges have limited the production of high-purity poly(sulfonylimide)s at scale and hindered systematic evaluation of their properties.

SUMMARY

[0005] The present disclosure describes a synthetic route for the production of high-purity sulfonylimide monomers at > 10 g scales using a Sulfur(VI) Fluoride Exchange (SuFEx) click reaction. Pendent sulfonylimide acrylate monomers with 1-ethyl-3-methylimidazolium counterions were synthesized with perfluorinated side groups of different lengths and crosslinked to form ionoelastomers. An ionoelastomer, as used herein, is a polymerized ionic liquid elastomer, or more generally, a polymerized ionic liquid network.

[0006] The resulting ionoelastomeric networks are stretchable (for example, approximate 120% strain at break), have high solvent-free ionic conductivity ($> 3.8 \times 10^{-3}$ mS/cm), and are hydrophobic with water contact angles $> 105^\circ$. The networks are suitable for electroadhesives.

[0007] In one particular implementation, this disclosure provides a method of making an ionoelastomer comprising sulfonylimide acrylate monomer, the method comprising using a Sulfur(VI) Fluoride Exchange (SuFEx) click reaction.

[0008] In another particular implementation, this disclosure provides a method of synthesizing a sulfonylimide ionoelastomer, the method including utilizing Sulfur (VI) Fluoride Exchange (SuFEx) click chemistry to produce sulfonylimide anions from sulfonylfluoride, and crosslinking the sulfonylimide anions to form an ionoelastomeric sulfonylimide network.

[0009] These and other aspects of the technology described herein will be apparent after consideration of the Detailed Description and Figures herein. It is to be understood, however, that the scope of the claimed subject matter shall be determined by the claims as issued and not by whether given subject matter addresses any or all issues noted in the Background or includes any features or aspects recited in the Summary.

BRIEF DESCRIPTION OF THE FIGURES

[0010] FIG. 1A shows a SuFEx reaction forming a sulfonylimide monomer; FIGS. 1B through 1D are chemical structures of the chemical groups of the monomer.

[0011] FIG. 2 shows the chemical structure of SuFEx click chemistry.

[0012] FIG. 3A is a chemical structure of an ionoelastomer incorporating an anionic sulfonylimide; FIGS. 3B through 3G are chemical structures of the chemical groups of the ionoelastomer.

[0013] FIG. 4A shows the chemical structure of the three ionoelastomers EA, EA-2, EA-4 studied in this work with crosslinker was removed for simplicity; FIG. 4B is a schematic representation of the molecular-scale interactions present in the anionic ionoelastomer networks describing different pendant group interactions with imidazolium counterions and themselves; FIG. 4C is a graphical representation of the transmittance of visible light through 250 μm thick ionoelastomer films; FIG. 4D is a graphical representation of AT-IR spectra of the three ionoelastomers EA, EA-2, EA-4.

[0014] FIG. 5 is a graphical representation of ^1H -NMR spectrum of EA monomer. ^1H -NMR (400 MHz, D3-AN): 8.60 (s, 1H, H2 (imidazole)), 7.46 (s, 1H, H4 (imidazole)), 7.38 (s, 1H, H5(imidazole)), 6.41-5.88 (m, 3H, $\text{CH}_2=\text{CH}-$), 4.25 (t, 2H, CO-O-CH_2-), 4.15-4.11 (m, 2H, N-CH_2-), 3.79 (s, 3H, N-CH_3), 3.18 (t, 2H, $-\text{CH}_2-\text{S}$), 2.16-2.08 (m, 2H, $\text{CO-O-CH}_2-\text{CH}_2-$), 1.49 (t, 3H, $\text{N-CH}_2-\text{CH}_3$).

[0015] FIG. 6 is a graphical representation of ^{19}F -NMR spectrum of EA monomer. ^{19}F -NMR (400 MHz, D3-AN): $\delta = -79.1$ (s, 3F)

[0016] FIG. 7 is a graphical representation of ^1H -NMR spectrum of EA-2 monomer. ^1H -NMR (400 MHz, D3-AN): 8.60 (s, 1H, H2 (imidazole)), 7.46 (s, 1H, H4 (imidazole)), 7.38 (s, 1H, H5(imidazole)), 6.41-5.88 (m, 3H, $\text{CH}_2=\text{CH}-$), 4.25 (t, 2H, CO-O-CH_2-), 4.15-4.11 (m, 2H, N-CH_2-), 3.79 (s, 3H, N-CH_3), 3.18 (t, 2H, $-\text{CH}_2-\text{S}$), 2.16-2.08 (m, 2H, $\text{CO-O-CH}_2-\text{CH}_2-$), 1.49 (t, 3H, $\text{N-CH}_2-\text{CH}_3$).

[0017] FIG. 8 is a graphical representation of ^{19}F -NMR spectrum of EA-2 monomer. ^{19}F -NMR (400 MHz, D3-AN): $\delta = -79.1$ (s, 3F), -117.8 (s, 2F).

[0018] FIG. 9 is a graphical representation of ^1H -NMR spectrum of EA-4 monomer. ^1H -NMR (400 MHz, D3-AN): 8.60 (s, 1H, H2 (imidazole)), 7.46 (s, 1H, H4 (imidazole)), 7.38 (s, 1H, H5(imidazole)), 6.41-5.88 (m, 3H, $\text{CH}_2=\text{CH}-$), 4.25 (t, 2H, CO-O-CH_2-), 4.15-4.11 (m, 2H, N-CH_2-), 3.79 (s, 3H, N-CH_3), 3.18 (t, 2H, $-\text{CH}_2-\text{S}$), 2.16-2.08 (m, 2H, $\text{CO-O-CH}_2-\text{CH}_2-$), 1.49 (t, 3H, $\text{N-CH}_2-\text{CH}_3$).

[0019] FIG. 10 is a graphical representation of ^{19}F -NMR spectrum of EA-4 monomer. ^{19}F -NMR (400 MHz, D3-AN): $\delta = -81.6$ (s, 3F), -113.5 (s, 2F), -121.8 (s, 2F), -126.6 (s, 2F).

[0020] FIG. 11 is a graphical representation of AT-IR spectra of the three ionoelastomers EA, EA-2, EA-4 from 1800 cm^{-1} to 1500 cm^{-1} .

[0021] FIG. 12 is a graphical representation of high-resolution AT-IR spectra of the three ionoelastomers EA, EA-2, EA-4 from 3200 cm^{-1} to 2900 cm^{-1} .

[0022] FIG. 13 is a graphical representation of second heating cycle DSC thermograms of the three ionoelastomers EA, EA-2, EA-4 at a temperature ramp rate of 10 K/minute.

[0023] FIG. 14 is a graphical representation of AC impedance spectroscopy of the three ionoelastomers EA, EA-2, EA-4.

[0024] FIGS. 15A and 15B are graphical representations of conductivity, where FIG. 15A shows temperature dependent conductivity of EA-x ionoelastomers as a function of inverse temperature, and FIG. 15B shows the conductivity versus inverse temperature normalized to T_g measured using DSC.

[0025] FIG. 16 is a graphical representation of wide angle X-ray scattering (WAXS) curves for the three ionoelastomers EA, EA-2, EA-4.

[0026] FIGS. 17A through 17C are graphical representations of oscillatory shear rheology measurements, FIG. 17A for EA ionoelastomer, FIG. 17B for EA-2 ionoelastomer, and FIG. 17C for EA-4 ionoelastomer.

[0027] FIGS. 18A through 18C are graphical representations for Raman spectra in the region of the SNS breathing mode, FIG. 18A for EA ionoelastomer, FIG. 18B for EA-2 ionoelastomer, and FIG. 18C for EA-4 ionoelastomer.

[0028] FIG. 19A shows photographs of static water contact angles for the three ionoelastomers EA, EA-2, EA-4; FIG. 19B is a graphical representation of static, advancing, and receding contact angles for the three ionoelastomers.

[0029] FIGS. 20A and 20B show the effects of humidity exposure. FIG. 20A is a graphical representation of AT-FTIR spectra of the exposed surface of EA-x ionoelastomers; FIG. 20B shows the weight percent of EA-x ionoelastomers as a function of exposure time.

[0030] FIG. 21 is a graphical representation of AT-FTIR spectra of the exposed surface of EA-x ionoelastomers.

[0031] FIG. 22 is a graphical representation of conductivity.

[0032] FIG. 23A provides chemical structures of additional sulfonylimide monomers; FIG. 23B provides example counter ions for the monomers of FIG. 23A, and FIG. 23C provides example crosslinkers suitable for use with the monomers of FIGS. 23A.

[0033] FIG. 24 provides chemical structures for additional monomers formed by SuFEx click chemistry.

[0034] FIG. 25 shows chemical structures of SuFEx polycondensation ionomers.

[0035] FIG. 26A is a chemical structure of an ionoelastomer incorporating a cationic sulfonylimide; FIGS. 26B through 26F are chemical structures of the chemical groups of the ionoelastomer.

[0036] FIGS. 27A and 27B are chemical structures of an example anionic and cationic ionoelastomer, respectively.

[0037] FIG. 28 is a compilation of graphical data for the ionoelastomers of FIGS. 27A and 27B.

DETAILED DESCRIPTION

[0038] As indicated above, polymerized ionic liquids (PILs) with a fixed sulfonylimide group have emerged as promising materials for energy storage applications, electromechanical devices, and gas separation membranes. However, synthetic challenges have limited the production of high-purity poly(sulfonylimide)s at scale and hindered systematic evaluation of their properties.

[0039] A wide range of approaches has been developed to synthesize diverse PILs. Particularly, PILs with pendent charges have become popular because they allow for the use of well-established polymerization chemistries, with charged functionalities added pre- or post-polymerization. The decoupling of polymer and fixed ion chemistries affords pendent PILs a high degree of customizability of backbone and IL properties while also allowing for copolymerization with various charged, uncharged, or crosslinkable species.

[0040] To date, the vast majority of pendent PILs have been polycationic, typically with a quaternized ammonium, pyridinium, pyrrolidinium, imidazolium, or phosphonium fixed ion and a bulky anionic counterion such as bis(trifluoromethane)sulfonimide (TFSI). This chemical diversity has allowed the physical properties of cationic PILs, such as hydrophilicity, modulus, and ionic conductivity, to be tuned by adjusting fixed ion chemistry. However, the choices for

polyanionic PILs are much more limited. The most readily available anionic PILs have acrylic acid or sulfonate ions covalently linked to the polymer backbone. Acrylic acid and sulfonate ions have a more localized charge than other weakly associating anions, meaning that polymers containing these species typically exhibit greater hydrophilicity, higher glass transition temperatures (T_g), and lower solvent-free ion conductivity.

[0041] Macromolecules containing covalently linked sulfonylimide anions are of particular interest as polyanionic PILs due to their more delocalized negative charge. Sulfonylimide PILs can be synthesized by converting a monomeric sulfonate ion to a sulfonylimide ion by means of a sulfonylchloride intermediate, allowing for the incorporation of sulfonylimide groups directly onto polymerizable vinyl, (meth)acrylate, and styrenic handles. This synthetic approach has been adopted more recently for single alkali-ion conducting polyelectrolytes, ion-mediated transistors, and CO₂ separations membranes. Sulfonylimide-derived PILs tend to have higher ionic conductivity values and lower glass transition temperatures than their analogous sulfonate counterparts. Moreover, their hydrophobicity makes sulfonylimide PILs relatively insensitive to changes in environmental humidity, a trait desirable for electronics used in ambient conditions. Despite their promise, the existing method to prepare such monomers requires an inert atmosphere and leads to the presence of undesired side products that limit yields and reduce monomer purities. These synthetic challenges have limited the production of poly(sulfonylimide) PILs at scale and hindered systematic evaluation of their electronic and mechanical properties.

[0042] The present disclosure provides an alternative route to synthesize these materials using Sulfur (VI) Fluoride Exchange (SuFEx) click chemistry to produce monomeric sulfonylimide anions from their parent sulfonate monomers. The sulfonylimide anions can be used to make ionoelastomeric sulfonylimide networks, either anionic or cationic, that can be used as electroadhesives.

[0043] SuFEx click chemistry is an approach for quantitative synthesis of small molecule and polymeric sulfonates and sulfonamides under moderate conditions, with high purity and yields. The approach described herein also shows lower sensitivity to air and moisture and yields highly pure ionic liquid (IL) monomers at large scales (approximately 10 g).

[0044] Pendent sulfonylimide acrylate monomers with 1-ethyl-3-methylimidazolium ([EMIM]⁺) counterion were synthesized with perfluorinated side groups of different lengths (1-4

carbons). Monomers were then photopolymerized with a small amount (2 mol%) poly(ethyleneglycol)diacrylate to produce loosely crosslinked ionoelastomer networks.

[0045] The resulting networks are stretchable (for example, approximately 120% strain at break), show high solvent-free ionic conductivity ($> 3.8 \times 10^{-3}$ mS/cm), and are hydrophobic with water contact angles $> 105^\circ$. There is a non-monotonic trend in ionic conductivity and elastic and shear moduli with respect to the glass transition temperature (T_g) of the ionoelastomer networks. Wide angle x-ray scattering (WAXS) and Raman spectroscopy reveal that short perfluorinated side groups increase counter-ion dissociation while limiting non-coulombic interactions with the polymer matrix, increasing ionic conductivity. Longer perfluorinated side chains increase ionic aggregation, resulting in a steep reduction in ionic conductivity and increase in modulus. These ionoelastomer networks can be incorporated into various low-voltage electrostatic devices, such as electrostatic clutches.

[0046] In the following description, reference is made to the accompanying drawing that forms a part hereof and in which is shown by way of illustration at least one specific implementation. The following description provides additional specific implementations. It is to be understood that other implementations are contemplated and may be made without departing from the scope or spirit of the present disclosure. The following detailed description, therefore, is not to be taken in a limiting sense. While the present disclosure is not so limited, an appreciation of various aspects of the disclosure will be gained through a discussion of the examples, including the figures, provided below. In some instances, a reference numeral may have an associated sub-label consisting of a lower-case letter to denote one of multiple similar components. When reference is made to a reference numeral without specification of a sub-label, the reference is intended to refer to all such multiple similar components.

[0047] FIG. 1A, taken together with FIGS. 1B-1D, shows the general approach to synthesizing a sulfonylimide from a sulfonylfluoride using SuFEx click chemistry. The sulfonylchloride is converted to a sulfonylfluoride (not shown), which can then be clicked onto a sulfonamide to yield an alkaline pendent sulfonylimide salt in a single step. The process does not utilize a triethylammonium sulfonylimide IL or other IL intermediate. The use of efficient SuFEx chemistry enables the synthesis of a series of pendent sulfonylimide monomers with varying perfluorinated alkyl side chain lengths with similarly high purity and yield.

[0048] R1 of the sulfonylimide is a polymerizable group, selected from those capable of undergoing chain growth polymerization such as free radical polymerization, controlled radical polymerization, or ring opening polymerization, or those capable of undergoing step-growth polymerization. Examples of suitable groups for R1 are shown in FIG. 1B.

[0049] X is a metal counter ion, counter to N⁻, and can be a Group IA or Group IIA ion. Examples of suitable metal ions are shown in FIG. 1C and include Li⁺, Na⁺, K⁺, Ca²⁺, and Mg²⁺.

[0050] R2 is a pendant group, selected from a broad class of organic substituents including aliphatic and aromatic hydrocarbons and fluorocarbons, crosslinkable or polymerizable groups, and other functional groups. Examples of suitable groups for R2 are shown in FIG. 1D.

[0051] FIG. 2 shows another, specific, example of SuFEx click chemistry to form a sulfonylimide.

[0052] The sulfonylimide from FIG. 1A and FIG. 2 can be incorporated into a network to provide an ionoelastomer. FIG. 3A shows a general structure of an anionic ionoelastomer made with a sulfonylimide synthesized via SuFEx click chemistry as per FIG. 1A.

[0053] The anionic ionoelastomer shown in FIG. 3A, having a pendant sulfonylimide prepared via SuFEx click chemistry, was synthesized by crosslinking the sulfonylimide of FIG. 1A. In FIG. 3A, R1-A-R2 represent, generally, the sulfonylimide. It is noted that R1 and R2 are not the same as R1 and R2 from FIGS. 1B and 1D, respectively; R1 and R2 for the ionoelastomer are identified in FIGS. 3B and 3E, respectively.

[0054] As indicated above, R1 is part of the sulfonylimide and is polymerizable. Examples of suitable groups for R1 are shown in FIG. 3B and include other polymerizable groups.

[0055] Examples of suitable anionic groups, as represented by A⁻ in FIG. 3A, are shown in FIG. 3C.

[0056] R2 is also a part of the sulfonylimide, selected from a broad class of organic substituents. Examples of suitable groups for R2 are shown in FIG. 3E.

[0057] Corresponding to the anion is a counter ion shown as X⁺, which can include a Group IA ion, Group IIA ion, or quaternized ammonium cations including tertiary ammonium ions, imidazolium, pyridinium, pyrrolidium, and pyrrolidinium. Examples of suitable metal counter ions are shown in FIG. 3D and can include Li⁺, Na⁺, K⁺, Ca²⁺, and Mg²⁺.

[0058] R3 can be broadly referred to as a monomer or comonomer. Examples of suitable monomers for R3 are shown in FIG. 3F, some of which are fluorinated.

[0059] R4 can be broadly referred to as a crosslinker. Examples of suitable crosslinkers for R4 are shown in FIG. 3G.

[0060] With the sulfonylimide, a family of three pendent sulfonylimide ionoelastomers with [EMIM]⁺ mobile ions were prepared, where the perfluorinated terminal portion of the pendent sulfonylimide systematically varied in length from 1 to 4 carbons. The ionoelastomers were acrylate (EA) monomers and are referred to herein as EA, EA-2 and EA-4. Although only the three ionoelastomers (having 1, 2 and 4 carbons) were produced and studied, it is to be understood that sulfonylimide EA monomers having any number of carbons can be made by the processes described herein. Together, the EA, EA-2, EA-4 and any other ionoelastomers are referred to herein as EA-x ionoelastomers.

[0061] FIG. 4A shows the chemical structure of EA, EA-2 and EA-4 with the crosslinker removed for simplicity.

[0062] FIG. 4B shows the molecular-scale interactions present in the anionic ionoelastomer networks describing different pendant group interactions with imidazolium counterions and themselves. FIG. 4C shows the transmittance of visible light through 250 μm thick ionoelastomer films. All EA-x ionoelastomers had > 90 % transmittance for essentially the entire visible spectrum. Words were easily read through the transparent ionoelastomer networks. The EA-x ionoelastomers derived from SuFEx click reaction were optically clear, a property desirable for many stretchable electronic devices such as artificial skins and flexible optoelectronic devices. Alternatively, pendent sulfonylimide polymers with monomers synthesized using the conventional method often have a hazy yellow-brown color, despite their non-polymerizable counterparts being clear slightly yellow liquids or white salts.

[0063] FIG. 4D shows the AT-IR spectra of EA-x ionoelastomers.

[0064] The result was optically clear liquids and had high purities from ¹H and ¹⁹F NMR, despite being synthesized under ambient conditions with non-anhydrous solvents. This was because the SO₂-F bond is less prone to reduction, and thus the SuFEx reaction can proceed quantitatively directly to the alkali salt (FIG. 2) without TEA or the triethylammonium intermediate.

[0065] The use of efficient SuFEx chemistry enables the synthesis of a series of pendent sulfonylimide monomers with varying perfluorinated alkyl side chain lengths with similarly high purity and yield (see FIGS. 5 through 10 for results for EA, EA-2 and EA-4). All EA-x monomers had a slightly yellow color, attributed to the sacrificial decomposition of the added BHT inhibitor during the workup.

[0066] Returning to FIG. 4E, the AT-IR spectra of the three ionoelastomers do not show a characteristic acrylate peak at $\approx 1630\text{ cm}^{-1}$, indicating that all residual monomer was reacted or washed out as part of the sol fraction; see also FIG. 11. High-resolution AT-IR spectra were collected for EA-x ionoelastomers in the region of C-H stretches for the imidazolium counter-ion ($2800\text{--}3500\text{ cm}^{-1}$, FIG. 12). The intensity of all imidazolium C-H stretches decreases with increasing perfluorinated side chain length, implying a decrease in ion concentration. Thus, increasing the molecular weight of monomeric units decreases the percent composition of the ionic functionality of the monomer.

[0067] All EA-x ionoelastomers have a single glass transition temperature (FIG. 13), and do not show additional transitions in the temperature range of $-80\text{ }^{\circ}\text{C}$ to $25\text{ }^{\circ}\text{C}$. Glass transition temperatures increased monotonically with increased perfluorinated side chain length (see Table 1, below). This increase is due to an increase in interaction between the perfluorinated side groups and the imidazolium counter-ion via ion-dipole interactions (FIG. 4C).

[0068] The room temperature Young's modulus (reported in Table 1, below) was nearly identical for EA (193 ± 28) and EA-2 ($175 \pm 10\text{ kPa}$), however, it was nearly 1.5 times greater for EA-4 ($264 \pm 43\text{ kPa}$). For unentangled networks well above T_g , it is expected the modulus would be inversely proportional to the average molecular weight between crosslinks. However, for linear PILs, it has been shown that ionic aggregates act as physical linkages, increasing the effective modulus.

Table 1: Physical, mechanical, and electronic properties of EA-x ionoelastomers. Error values indicate the range taken from three separate measurements.

Polymer	DSC T_g ($^{\circ}\text{C}$)	Density (g/cm^3)	σ_{DC} (22°C) (mS/cm)	Young's Modulus (kPa)	Elongation at Break (%)
EA	-26	1.41	$3.2 \pm 0.1 \times 10^{-3}$	193 ± 28	116 ± 16
EA-2	-13	1.45	$3.8 \pm 0.5 \times 10^{-3}$	175 ± 10	112 ± 8
EA-4	-6	1.44	$4.7 \pm 0.6 \times 10^{-4}$	264 ± 43	120 ± 15

[0069] To evaluate the effect of pendant structure on sulfonylimide-derived ionoelastomers, the ionic conductivity at room temperature was measured (reported in Table 1 as σ_{DC}) by means of AC impedance spectroscopy (FIG. 14). Generally for polymer electrolytes, lowering the T_g of the material tends to increase ionic conductivity by increasing segmental motion and available free volume for ion conduction. PILs are somewhat unusual in that ion motion can be decoupled from segmental dynamics, which is thought to be due to the chain packing frustration of charged pendants. Interestingly, EA-2 showed the highest room temperature (22 °C) conductivity of 3.8×10^{-3} mS/cm, despite having a higher T_g than EA ($\sigma_{DC} = 3.1 \times 10^{-3}$ mS/cm). EA-4, however, showed nearly 10x lower room temperature conductivity (4.7×10^{-4} mS/cm), which is in line with its increased T_g compared to EA and EA-2.

[0070] To better understand the molecular origins of this non-monotonic trend in conductivity with respect to the glass transition temperature, temperature-dependent conductivity measurements were done. To ensure that these samples were solvent-free, samples were dried *in vacuo* for 7 days. FIG. 15A shows the temperature dependent conductivity of EA-x ionoelastomers as a function of inverse temperature. Lines correspond to the weighted fit of the data (symbols) using EQ. 1 (below). FIG. 15B shows the conductivity versus inverse temperature normalized to T_g measured using DSC.

[0071] These conductivity results are in excellent agreement with our RT conductivity data. The data fit to the Vogel-Fulcher-Tammann (VFT) equation:

$$\sigma_{DC}(T) = \sigma_{\infty} e^{\left(\frac{-B}{T-T_0}\right)} \quad (\text{EQ. 1})$$

[0072] where $\sigma_{DC}(T)$ is the temperature-dependant DC conductivity of the material, σ_{∞} is the conductivity in the limit of infinite temperature, B is a fitting constant related to the activation energy for ion conduction and T_0 is the Vogel temperature, which is typically around 50 K below T_g . A summary of the fitted parameters can be found in Table 2.

Table 2: Fitted parameters to the VFT equation (EQ. 1) with the measured T_g from DSC for EA-x ionoelastomers

Polymer	σ_{∞} (mS/cm)	B	T_o (K)	$T_{g, DSC}$ (K)
EA	10.2	792	203	247
EA-2	20.7	838	204	260
EA-4	11.2	967	201	267

[0073] The value of T_o was determined by VFT fitting is almost constant between the three EA-x ionoelastomers, while the T_g measured by DSC tends to increase with increasing fluorinated side chain length. However, the effective T_g ($T_o + 50$ K) derived from the VFT equation has been shown to be related to conductivity relaxation, rather than segmental relaxation, which appears to be constant for EA-x ionoelastomers. This could be due to the free volume constraints from crosslinking, which should be the same for all EA-x ionoelastomers.

[0074] Conversely, at infinite temperature, in which ion conduction approaches that of an ideal electrolyte, the VFT fit indicates a much higher conductivity, σ_{∞} , for EA-2, compared to EA or EA-4. Interestingly, EA-4 also had a higher value of σ_{∞} compared to EA. This increase is attributed to an increase in the dissociation of imidazolium by the pendent fluorinated side chains. Similar trends can be seen in ammonium PILs with TFSI counterions, in which adding an additional ethylene glycol unit to the pendant structure increased the infinite temperature dielectric relaxation time scale, analogous to σ_{∞} in conductivity space. However, this does not account for the decrease in σ_{∞} between EA-2 and EA-4, despite an increase in T_g . Ion conduction is a product of both ion conduction and ion mobility. Thus, it is possible that EA-4 has a lower ion mobility than EA-2, resulting in a lower value of σ_{∞} , which could point toward an increase in aggregation or change in imidazolium coordination state for EA-4 ionoelastomers. The following sections will attempt to rationalize this non-monotonic trend in ionic conductivity by investigating polymer morphology, ionic aggregation, and ionic coordination.

[0075] To understand the underlying mechanism for the observed non-monotonic trend in ion conductivity, network morphology was investigated, using wide-angle x-ray scattering (WAXS) in the q range of $1-18 \text{ nm}^{-1}$. FIG. 16 shows wide angle X-ray scattering (WAXS) curves for EA-x ionoelastomers. Curves for EA-2 and EA-4 have been shifted vertically for clarity.

[0076] Previous studies on cationic PILs have identified three broad peaks in this range: q1 at $> 12 \text{ nm}^{-1}$, the amorphous halo, q2 generally at $> 5 \text{ nm}^{-1}$ but $< 15 \text{ nm}^{-1}$, corresponding to the average anion spacing, and q3 at $< 6 \text{ nm}^{-1}$ corresponding to the spacing between ionic aggregates.

[0077] Three distinct peaks were observed only for EA-4, which shows a clear q3 aggregation peak centered at 2.7 nm^{-1} . EA and EA-2 only show q1 and q2 as distinct peaks. The q1 and q2 peaks both shift towards lower q (larger spacing), indicating that the longer perfluorinated side chain slightly increases the available space for ion conduction between pendants. The lack of a clear q3 peak for EA and EA-2 suggests a smaller degree of aggregation and a broader range of inter-aggregate spacing compared to EA-4. The sharp decrease in ion conductivity between EA / EA-2 and EA-4 is due to this increase in ion aggregation.

[0078] To better understand the viscoelastic properties, oscillatory shear rheology measurements were conducted on EA-x ionoelastomers. FIGS. 17A through 17C show the oscillatory shear rheology measurements of EA, EA-2 and EA-4, respectively, in the frequency range of 0.5 - 50 Hz at 25 °C. Dashed red lines correspond to the frequency at which the loss modulus exceeds that of the storage modulus. In small strain frequency sweeps at 25 °C, a non-monotonic trend in plateau modulus (taken as the modulus at 0.1 Hz) exists with $\text{EA-4} > \text{EA} > \text{EA-2}$. All EA-x ionoelastomers exhibited a crossover frequency where the loss modulus (G'') becomes greater than the storage modulus (G') upon increasing frequency between the rubbery plateau at low frequencies and the glass transition at high frequencies. Similar behavior can be found in select charged and uncharged polymers as they approach T_g . The crossover reflects a broad rubbery-to-glass transition, however, this frequency may decrease with increased polymer T_g . In contrast, for EA-x ionoelastomers, a non-monotonic trend is observed in this crossover frequency, with EA-2 having the lowest crossover frequency, despite having a lower T_g than EA-4.

[0079] Alternatively, similar crossover behavior has also been found in entangled complex coacervates, with a characteristic frequency corresponding to the exchange rate between neighboring pendent ion pairs. The crossover event in the ionoelastomers can be explained in part by a similar phenomenon in which ionic aggregates, rather than ionic bonds, act similarly to physical crosslinks between chains. As aggregates break, chains are free to move past one another, resulting in G'' surpassing G' well below the frequency associated with T_g . For EA-2,

the degree of ion ionic aggregation appears to be lower, resulting in a lower terminal modulus and crossover frequency compared to EA or EA-4.

[0080] Raman spectroscopy was used to probe the local chemical environment of the sulfonylimide unit; in lithium-ion conducting poly(sulfonylimide)s this is done by analyzing the SNS breathing mode peak at 730-760 cm^{-1} . FIGS. 18A through 18C show the results of the Raman spectra in the region of the SNS breathing mode for EA (FIG. 18A), EA-2 (FIG. 18B) and EA-4 (FIG. 18C). By deconvoluting this peak, one can quantify the degree of ionic association between a counterion and sulfonylimide anion, with more upfield peaks corresponding to less coordinated binding states.

[0081] As seen in FIGS. 18A through 18C, the SNS breathing mode appears as two distinct peaks at approximately 735 cm^{-1} and approximately 753 cm^{-1} on the shoulder of a broader peak centered around approximately 710 cm^{-1} , corresponding to the C=O breathing mode of the acrylate backbone and the C-F₂ stretches for EA-2 and EA-4. These two SNS breathing mode peaks are two distinct coordination states of imidazolium with the pendent sulfonylimide ion. The most coordinated state corresponding to the peak at 753 cm^{-1} is most favored for EA-2 compared to EA or EA-4.

[0082] This coordination state is the close-ion pair between imidazolium cation and sulfonylimide anion (i.e., the most coordinated sulfonylimide ion), which is favorable for ion conduction above T_g . For RT PILs, bulky ionic molecules behave less like point charges than alkali metal ion conducting polymers, with significant non-coulombic intermolecular interactions (e.g., ion-dipole, hydrogen bonding, etc.) with other substituents. By promoting a singly coordinated state of ions in EA-2, these non-coulombic interactions are limited, while the RT IL pair retains its liquid-like ion conduction. The result is a higher RT ion conductivity and lower elastic and shear modulus for EA-2 compared to EA, despite EA-2 having a lower total ion concentration and higher T_g .

[0083] The average static contact angle of liquid water with the surface of EA-x ionoelastomers, based on measurements from the photographs of FIG. 19A, was 64°, 92°, and 105° for EA, EA-2, and EA-4 respectively, corresponding to a general decrease in surface energy and increased hydrophobicity with increasing perfluorinated side chain length. The EA ionoelastomers showed the most contact angle hysteresis with nearly a $\approx 50^\circ$ difference between advancing and receding contact angles, while EA-2 and EA-4 had less hysteresis (33° and 28°

respectively) as shown in FIG. 19B, which shows static, advancing, and receding contact angles for EA-x ionoelastomers, with error bars corresponding to the range of three separate measurements. All three materials showed advancing contact angles $> 90^\circ$, indicating that water does not wet the surface initially, but over time the wettability increases. This could be due to surface reorganization, or potentially the small amount of hydrophilic PEGDA, which could provide a route for water to permeate through the surface.

[0084] The ionoelastomers were also relatively insensitive to environmental humidity. FIG. 20A shows the AT-FTIR spectra of the exposed surface of EA-x ionoelastomers after 7 days at 75% RH. Spectra are vertically shifted for clarity. FIG. 20B shows the weight percent of EA-x ionoelastomers as a function of exposure time (days) under ambient conditions (15% RH and 23°) with inset showing the results at 75% RH. FIG. 21 also shows the AT-FTIR spectra of the exposed surface of EA-x ionoelastomers after 7 days at 15% RH. Spectra are vertically shifted for clarity.

[0085] There was no sign of water in the AT-IR spectra of all EA-x ionoelastomers after 7 days under ambient, e.g. 15% relative humidity (RH), and humid, 75% RH, conditions. Furthermore, it was found that the weight of EA-x samples was essentially constant ($< \pm 1$ wt%) over a 7-day period at 15% RH. A small increase (approximately 4 wt% and approximately 3 wt%, respectively) was observed for EA and EA-2 samples after 7 days at 75% RH, while EA-4 showed a negligible increase in weight (< 1 wt%) in the same period. This is in line with EA-4 also being the most hydrophobic of the EA-x ionoelastomers, but the difference is sufficiently small to also be due to experimental error. EA-x ionoelastomers can thus be considered non-hygroscopic under ambient and humid conditions.

[0086] The following procedures were used to prepare the above-described ionoelastomers, EA, EA-2 and EA-4.

[0087] Potassium 3-sulfopropyl acrylate (KSPA), butylated hydroxytoluene (BHT), poly(ethyleneglycol)diacrylate (PEGDA, $M_n = 250$ g/mol), phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (I-819), and all solvents were purchased from Sigma and used as received. Oxalyl chloride, sodium chloride (NaCl), potassium bifluoride (KHF_2), sodium sulfate (Na_2SO_3), potassium carbonate (K_2CO_3), and calcium carbonate (CaCO_3) were all purchased from Fisher and used as received. Trifluoromethanesulfonamide (25 g, $>98.0\%$, TCI), pentafluoroethanesulfonamide (5 g, 99.9% , Ambeed), perfluorobutanesulfonamide (25 g, 98% ,

1PlusChem), and 1-ethyl-3-methylimidazolium chloride ([EMIM][Cl], 99.5%, Iolitec Inc) were all used as received without further purification.

[0088] The following provides a general overview of synthesis of the pendent sulfonylimide monomers.

[0089] Example 1: Synthesis of 3-propylsulfonylchloride acrylate

[0090] Anhydrous dichloromethane (DCM) (120 mL) was added to a flame-dried two-opening Schlenk flask. The flask was purged with nitrogen gas (N₂). The DCM was cooled to 0 °C and a catalytic amount of dimethylformamide (DMF) (2 mL) was slowly added. Oxalyl chloride (1.3 EQ, 9.5 mL) was added dropwise to the reaction mixture at 0 °C. The reaction was then brought to room temperature and stirred for 30 minutes to allow for the formation of the chlorinating reagent. The flask was again cooled to 0 °C and KSPA (1 EQ, 20 g) was slowly added along with 100 ppm BHT (10 mg) as an inhibitor. The reaction proceeded at room temperature overnight in the dark. Water was added to the flask to quench the reaction. The DCM layer was then extracted and washed with water at least five times to remove any remaining salt and DMF. The organic layer was then washed with saturated NaCl solution (brine) two times and dried for 15 minutes with sodium sulfate. The DCM was then removed by rotary evaporation and further dried under a high vacuum for 15 minutes. The product (3-propylsulfonylchloride) acrylate was a clear, dark yellow oil, and 16.94 g was recovered (yield: 93%).

[0091] Example 2: Synthesis of 3-propylsulfonylfluoride acrylate

[0092] Conversion of (3-propylsulfonylchloride) acrylate to (3-propylsulfonylfluoride) acrylate was carried out as follows. KHF₂ (2 EQ, 12.4 g) was dissolved in water at its solubility limit (0.392 g/mL) in a plastic reaction vessel. The sulfonyl chloride was then dissolved in acetonitrile (AN) (79.5 mL) to form a 1 M solution. The AN solution was added to the KHF₂ solution, and the reaction was allowed to proceed for 4 hours at room temperature. After the reaction, DCM and water were added to the reaction flask, and the organic layer was drawn from the aqueous phase. It is important to note that HF is a byproduct of this reaction, so the separated aqueous phase was handled using plastic vessels and was immediately diluted and neutralized with calcium carbonate. The DCM phase was then washed with water five times, followed by washing with brine two times and dried for 15 minutes with sodium sulfate. The DCM was then

removed by rotary evaporation. The product (15.91 g) was a clear, light-yellow oil and slightly volatile.

[0093] Example 3: Synthesis of 1-ethyl-3-methylimidazolium 3-acryloxypropylsulfonyl(-R-[sulfonimide]) (EA-x) monomers via SuFEx click chemistry

[0094] The sulfonylfluoride monomer was used in a sulfur (VI) fluoride exchange (SuFEx) reaction to form potassium 1-[2-acryloyloxypropyl]-R-sulfonylimide followed by ion exchange to synthesize 1-ethyl-3-methylimidazolium 3-acryloxypropylsulfonyl(-R-[sulfonimide]) (EA-x, x=0, 2, 4). The following procedure was used for EA, which was also employed for all EA-x monomers. Sulfonylfluoride monomer (1.4 EQ) was dissolved in AN (non-anhydrous, 1M, 62 mL), followed by 1 EQ of trifluoromethanesulfonamide (9.3 g) and 3 EQ of potassium carbonate (25.8 g). The solution in ambient air was heated to 65 °C and refluxed overnight. After the reaction, solids were filtered, and the remaining solution was concentrated via rotary evaporation and recrystallized in DCM. The potassium salt product (19.46 g, 86% yield) was a white powder and was isolated. The quantitative conversion was determined via NMR. Next, 10 g (27.62 mmol) of the potassium salt was ion-exchanged with 1.05 EQ of [EMIM][Cl] at a concentration of 0.5 M in AN for 24 hours in the dark. BHT (10 mg) was added as an inhibitor. After ion exchange, solids were cold filtered and AN was removed by rotary evaporation. The turbid oil was redissolved in approximately 40 mL of DCM and the remaining solids were removed by centrifugation (Eppendorf-5430) at 7800 RPM for 5 minutes. The supernatant was then washed once with water and DCM was removed via rotary evaporation. The product, a viscous transparent, slightly yellow oil, was further dried under high vacuum for about 1 hour. The final product, EA monomeric IL was recovered at an 84% yield (10.06 g).

[0095] Example 4: Ionoelastomer Fabrication

[0096] Ionoelastomers as shown above in relation to FIGS. 1-2 and 3A-3G were fabricated.

[0097] The following can be considered general for all EA-x monomers. 250 mg of EA-x monomer were weighed in a glass vial and combined it with 2 mol% PEGDA crosslinker. A 100 mg/mL stock solution of photoinitiator I-819 in DCM was prepared. 0.5 mol% initiator (1 mol% for EA-4) was added and vortexed the vial until thoroughly mixed. The solution was left under vacuum overnight at 22 °C to remove excess DCM and degas the pre-polymer resin.

Molds were prepared by clamping two fluorinated glass slides together, separated by 250 μm Teflon spacers (McMaster Carr). The pre-polymer resin was then allowed to fill the molds by capillary action. Filled molds were placed under a UV curing lamp (Melodie Suzie 30 W, 365 nm) for 30 minutes. Ionoelastomers were then carefully demolded and washed with DCM for 24 hours, followed by rinsing with fresh isopropanol (IPA). Residual solvent was removed by annealing the films at 60 °C *in vacuo* for either 24 hour or 1 week. The resulting films were flexible, clear, and could readily be cut into any testing geometry.

[0098] The prepared ionoelastomers EA, EA-2, EA-4 were evaluated via multiple tests.

[0099] Spectroscopic and Thermal Characterization

[00100] ^1H -NMR and ^{19}F -NMR spectra (e.g., as in FIGS. 5 through 10) were recorded using a Bruker 400 MHz spectrometer with d_3 -acetonitrile as the solvent. Transparency measurements were performed using an Ocean Optics DH-2000-BAL UV-vis spectrometer. AT-FTIR spectra were collected using a Thermo Scientific iS50 AT-FTIR spectrometer from 540 cm^{-1} to 4000 cm^{-1} . Raman spectra were collected with a Horiba LabRAM HR Evolution Raman Spectrometer with a 532 nm excitation laser. Raman scans were collected at 50x magnification and an 1800 mm grating with a 30 s collection time per scan. For each material, 12 scans were averaged and the fluorescence signal was subtracted to yield the finished spectra. DSC thermograms were obtained using a DSC 2500 (TA Instruments) from -80 °C to 25 °C at a ramp rate of 10 °C/minute. Glass transition temperatures were determined from the 2nd heating cycle.

[00101] Mechanical Characterization

[00102] Tensile tests were conducted using a DMA 850 (TA Instruments) mechanical tester. Samples were cut into 0.5 cm x 2 cm rectangles and stretched at a strain rate of 5 %/minute at a temperature of 22 °C. Young's moduli were determined using the slope of the stress-strain curve from 1-3 % strain. Rheology measurements were conducted using ARES G2 rheometer with an 8mm Teflon probe. Rheology frequency sweeps were conducted from 0.1 Hz to 50 Hz.

[00103] Ionic Conductivity Measurements.

[00104] The ionic conductivity was measured using a Gamry 600+ potentiostat with an Instec STC200 temperature controller. The results are shown in FIG. 22.

[00105] The samples were prepared by sandwiching 0.5 cm diameter circles between ITO-coated glass slides with Teflon spacers. Transparent ITO electrodes were used to ensure

conformal contact between the ionoelastomer and electrode surface, while also allowing for in-situ determination of sample area and thickness. AC potentials of 40 mV were applied in the frequency range of 1 MHz to 0.1 Hz. The conductivity was calculated using the equation below (EQ. 2):

$$\sigma_{DC} = \frac{L}{R_{DC}A} \quad (\text{EQ. 2})$$

[00106] where R_{DC} is the mid-frequency plateau of the real part of the impedance (see FIG. 22), L is the sample thickness, and A is the sample area. Temperature-dependent conductivity measurements were conducted from 60 °C to 15 °C in 5 °C increments. A 20 minute delay time was added once a steady state temperature was reached to ensure a uniform temperature profile across the thickness of the sample.

[00107] X-Ray Scattering

[00108] Wide and x-ray scattering (WAXS) was conducted using Xenox Xeus 3.0 WAXS system with a Cu Ka x-ray source. Samples were loaded in transmission under vacuum with a sample to detector distance of 43mm. Background subtracted 2D patterns were integrated azimuthally to yield 1D curves.

[00109] Contact Angle Goniometry

[00110] Water contact angles EA-x ionoelastomer films were measured using a custom-built pendant drop tensiometer and with ultra pure MiliQ water (<18.2 MΩ cm). Static contact angle measurements were taken 5 seconds after a 1 μL drop was deposited on the surface of the film. Advancing contact angle measurements were taken as the average angle as water was added to a droplet over a 2 s interval while receding contact angle measurements were taken as the average angle water was removed from a droplet over a 2 s interval. The collected images were analyzed using First Ten Angstroms contact angle software (FTA32, Portsmouth, VA) employing a sessile drop model.

[00111] Additional sulfonylimide ionoelastomers may be made. FIG. 23A provides examples of additional anionic poly(sulfonylimide) monomers made via SuFEx click chemistry, with FIG. 23B providing example counter ions (X⁺) that can be used in the monomers of FIG. 23A, and FIG. 23C providing example crosslinkers that can be used.

[00112] FIG. 24 shows additional potential monomers produced via SuFEx click chemistry. In any of these, it may be possible to introduce 30 to 100 different substituent R groups based on commercial sulfonamides for vinyl, styrenic, or (meth)acrylate backbones.

[00113] FIG. 25 shows an example of SuFEx polycondensation ionomer.

[00114] The ionoelastomers described above were anionic, based on a sulfate ion (e.g., the sulfonylimide produced above, e.g., via SuFEx click chemistry, or another sulfate ion). Cationic ionoelastomers can be prepared based on a quaternized ammonium ion.

[00115] Turning to FIG. 26A, a cationic ionoelastomer, having a pendant quaternized ammonium derivative, is shown, the ionoelastomer having been synthesized by crosslinking a pendant quaternized ammonium derivative. In FIG. 26A, R1-X represent, generally, the quaternized ammonium derivative. It is noted that R1 is not the same as R1 from FIG. 1B nor from FIG. 3B. Additionally, R3 and R4 are not necessarily the same as R3 and R4 from FIGS. 3F and 3G, respectively.

[00116] In FIG. 26A, R1 is part of the quaternized ammonium derivative and is crosslinkable with a polymerizable backbone. Examples of suitable polymers for R1 are shown in FIG. 26B and include polymerizable acrylate or methacrylate groups.

[00117] Examples of suitable cationic groups, for X⁺ of the quaternized ammonium derivative of FIG. 26A, are shown in FIG. 26C.

[00118] Corresponding to the cation is a counter ion shown as Y⁻. Examples of suitable metal counter ions are shown in FIG. 26D, all of which are fluorinated.

[00119] R3 can be broadly referred to as a monomer or comonomer. Examples of suitable monomers for R3 are shown in FIG. 26E, some of which are fluorinated.

[00120] R4 can be broadly referred to as a crosslinker. Examples of suitable crosslinkers for R4 are shown in FIG. 26F.

[00121] In addition to the sulfonylimide-based ionoelastomers described above, low surface-energy halogenated ionoelastomers can be made, the ionoelastomers being electrically conductive, thus suitable as an electroadhesive. These halogenated comonomers partitions to a surface, lower surface energy, and therefor provides an “off” electric state during adhesion. Additionally, the halogenated ionoelastomers have a high hydrophobicity, allowing for use of these ionoelastomers in humid and/or wet environments. FIGS. 27A and 27B shows two specific fluorinated ionoelastomers.

[00122] FIG. 27A shows an anionic elastomer (referred to herein as EA-co-15Fa) that can be synthesized by crosslinking a sulfonylimide formed from a sulfonylfluoride using SuFEx click chemistry along with a comonomer. In particular, FIG. 27A shows a trifluoromethanesulfonylimide acrylate (EA) monomer, with the trifluoro sulfonylimide seen at the lower left portion of the molecule as shown.

[00123] Pendant trifluoromethanesulfonylimide acrylate monomers, such as shown in FIG. 27A, can be synthesized using the SuFEx click approach of FIGS. 1A and 2. However, going directly from the sulfonylchloride to the trifluoromethanesulfonylimide monomer results in a final product with significant impurities; in one particular process, the resulting IL monomer was red-brown in color and translucent, indicative of trace impurities. It is believed there were two potential sources for these impurities. First, the sulfonylchloride group is easily reduced by nucleophiles, resulting in an unstable $R-SO_2^-$ that can undergo additional side reactions. Second, TEA is prone to oxidative decomposition with prolonged exposure to air, resulting in a yellow-to-yellow-brown impurity. Because this process is accelerated in the presence of water, the conversion of the sulfonylchloride should be conducted in air-free, extremely dry conditions in order to obtain high-purity products.

[00124] FIG. 27B shows a cationic elastomer (referred to herein as AT-co-15Fa) that can be synthesized by crosslinking a quaternized ammonium derivative with a comonomer.

[00125] FIG. 28 is a compilation of graphical data for the ionoelastomers of FIGS. 27A and 27B.

[00126] From the foregoing, it will be appreciated that specific embodiments of the invention have been described herein for purposes of illustration, but that various modifications may be made without deviating from the scope of the invention. Accordingly, the invention is not limited except as by the appended claims.

[00127] Although the technology has been described in language that is specific to certain structures and materials, it is to be understood that the invention defined in the appended claims is not necessarily limited to the specific structures and materials described. Rather, the specific aspects are described as forms of implementing the claimed invention. Because many embodiments of the invention can be practiced without departing from the spirit and scope of the invention, the invention resides in the claims hereinafter appended.

[00128] Various features and details have been provided in the multiple designs described above. It is to be understood that any features or details of one design may be utilized for any other design, unless contrary to the construction or configuration. Any variations may be made.

[00129] This disclosure describes an alternative route to synthesize poly(sulfonylimide) monomers utilizing Sulfur (VI) Fluoride Exchange (SuFEx) click chemistry. This synthetic approach can be conducted under ambient conditions and yields highly pure ionic liquid (IL) monomers at large scales (~10 g). The sulfonylimide ionoelastomers may be anionic or cationic. Anionic sulfonylimide ionoelastomers were synthesized with perfluorinated side chains of one, two, and four carbons. These ionoelastomers were stretchable ($\approx 120\%$ strain at break), showed high solvent-free ionic conductivity ($> 3.8 \times 10^{-3}$ mS/cm), and were hydrophobic with water contact angles $> 105^\circ$. The ionoelastomers can be incorporated into electroadhesives, and may be used with an electrode to instigate dimensional change in the material.

[00130] As indicated, any of the materials disclosed herein may be utilized as an electroadhesive or other electrically conductive material. For example, the materials are particularly suitable for use in batteries or other devices where a charge is present or is used to initiate a change in the material.

[00131] For example, the materials may be used as electrolytes for batteries; particular materials for electrolytes include vinyl sulfonylimides, sulfonylimide silicones, styrenic sulfonylimides, sulfonylimide block copolymers, and sulfonylimide zwitterions.

[00132] As another example, the materials may be used in low-voltage electrostatic devices, such as electrostatic clutches, actuators, and phone holders.

[00133] The coordination state of the imidazolium counterions is highly dependent on interactions with the perfluorinated side chains with shorter chains promoting cation dissociation, and longer chains causing ion aggregation. These results, however, assume equivalent contributions of backbone dynamics to the ionic conductivity of each EA-x ionoelastomer. Decoupling backbone dynamics from ion dynamics would enable more robust statements on the exact mechanism for ion conduction in EA-x ionoelastomers.

[00134] The above specification and examples provide a complete description of the structure and use of exemplary implementations of the invention. The above description provides specific implementations. It is to be understood that other implementations are contemplated and

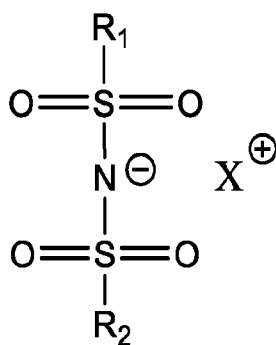
may be made without departing from the scope or spirit of the present disclosure. The above detailed description, therefore, is not to be taken in a limiting sense. While the present disclosure is not so limited, an appreciation of various aspects of the disclosure will be gained through a discussion of the examples provided.

[00135] Unless otherwise indicated, all numbers expressing feature sizes, amounts, and physical properties are to be understood as being modified by the term “about,” whether or not the term “about” is immediately present. Accordingly, unless indicated to the contrary, the numerical parameters set forth are approximations that can vary depending upon the desired properties sought to be obtained by those skilled in the art utilizing the teachings disclosed herein.

[00136] As used herein, the singular forms “a”, “an”, and “the” encompass implementations having plural referents, unless the content clearly dictates otherwise. As used in this specification and the appended claims, the term “or” is generally employed in its sense including “and/or” unless the content clearly dictates otherwise.

WHAT IS CLAIMED IS:

1. A method of synthesizing a sulfonylimide ionoelastomer, comprising:
utilizing Sulfur (VI) Fluoride Exchange (SuFEx) click chemistry to produce
sulfonylimide anions from sulfonylfluoride, and
crosslinking the sulfonylimide anions to form an ionoelastomeric sulfonylimide network.
2. The method of claim 1, wherein the sulfonylfluoride is converted from a
sulfonylchloride.
3. The method of claim 1, wherein the sulfonylimide anions are anionic.
4. An ionoelastomer material comprising a sulfonylimide anion.
5. The ionoelastomer material of claim 4, made by a SuFEx click reaction.
6. The ionoelastomer material of claim 4, having the structure



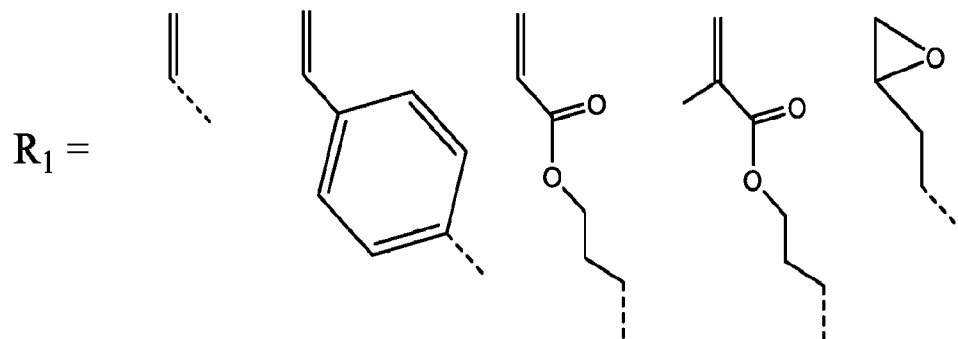
where R1 is a polymerizable group;

X⁺ is a counter ion; and

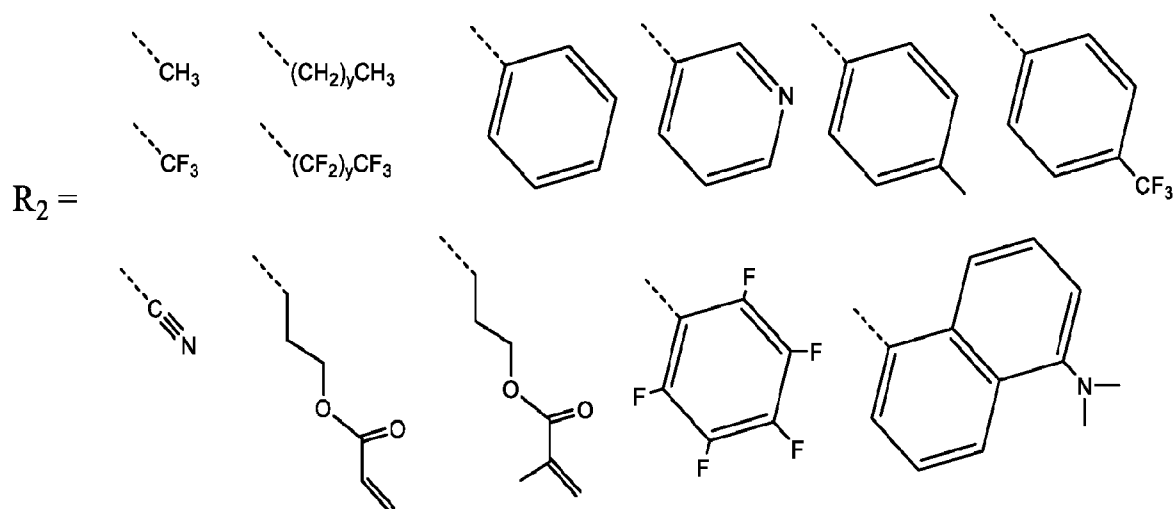
R2 is a pendant group,

7. The ionoelastomer material of claim 6, wherein X is selected from Li⁺, Na⁺, K⁺, Ca²⁺,
and Mg²⁺.

8. The ionoelastomer material of claim 6, wherein R1 is selected from:

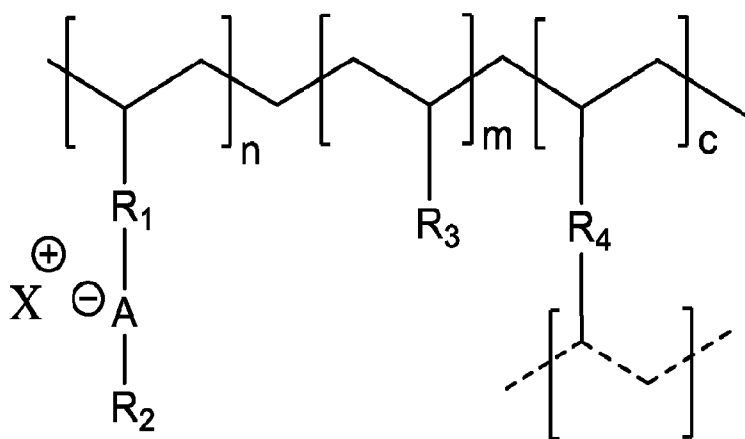


9. The ionoelastomer material of claim 6, wherein R2 is selected from:



where y=1-7.

10. An anionic ionoelastomer having the structure



where R1 is a polymeric backbone;

A⁻ is an anion;

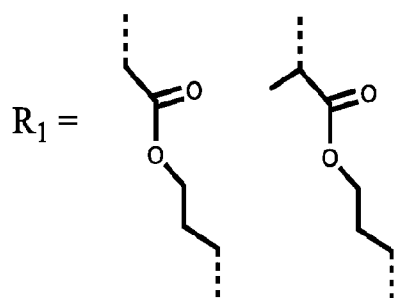
R₂ is a pendant group;

X⁺ is a counter ion;

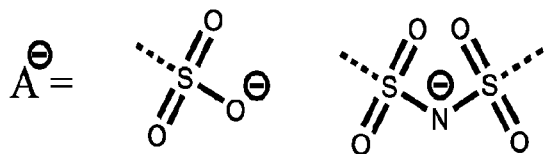
R₃ is a monomer; and

R₄ is a crosslinker.

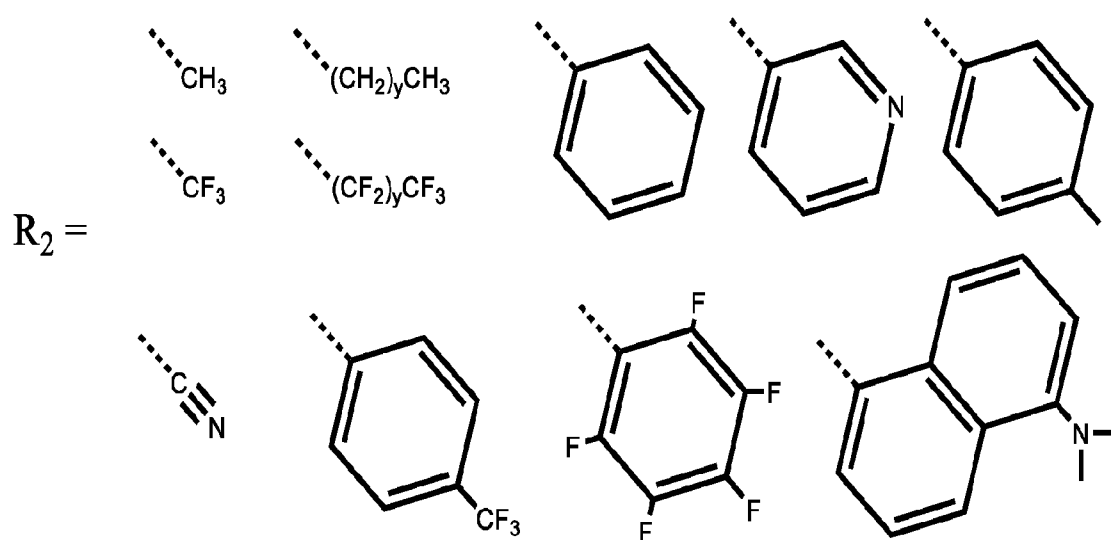
11. The anionic ionoelastomer of claim 10, wherein R₁ is selected from



12. The anionic ionoelastomer of claim 10, wherein A⁻ is selected from

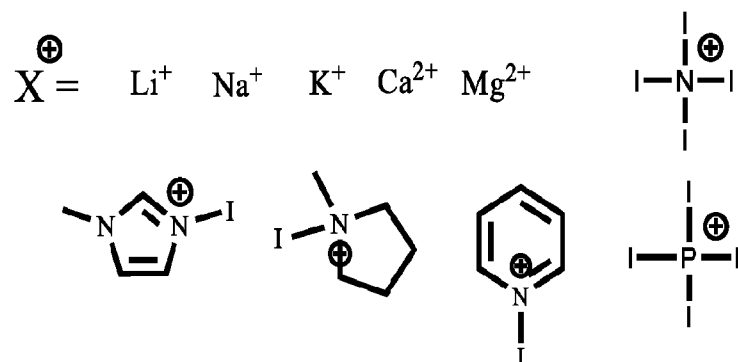


13. The anionic ionoelastomer of claim 10, wherein R₂ is selected from



where y = 1-7.

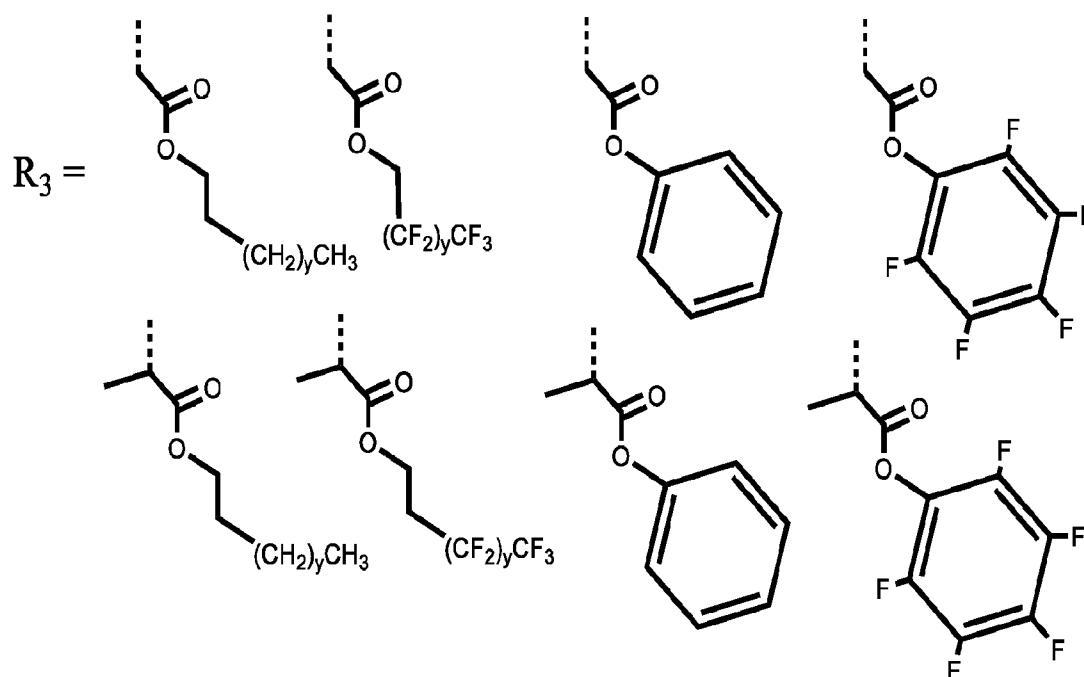
14. The anionic ionoelastomer of claim 10, wherein X^+ is selected from



where $\text{I} = \text{C}_x\text{H}_{2x+1}$

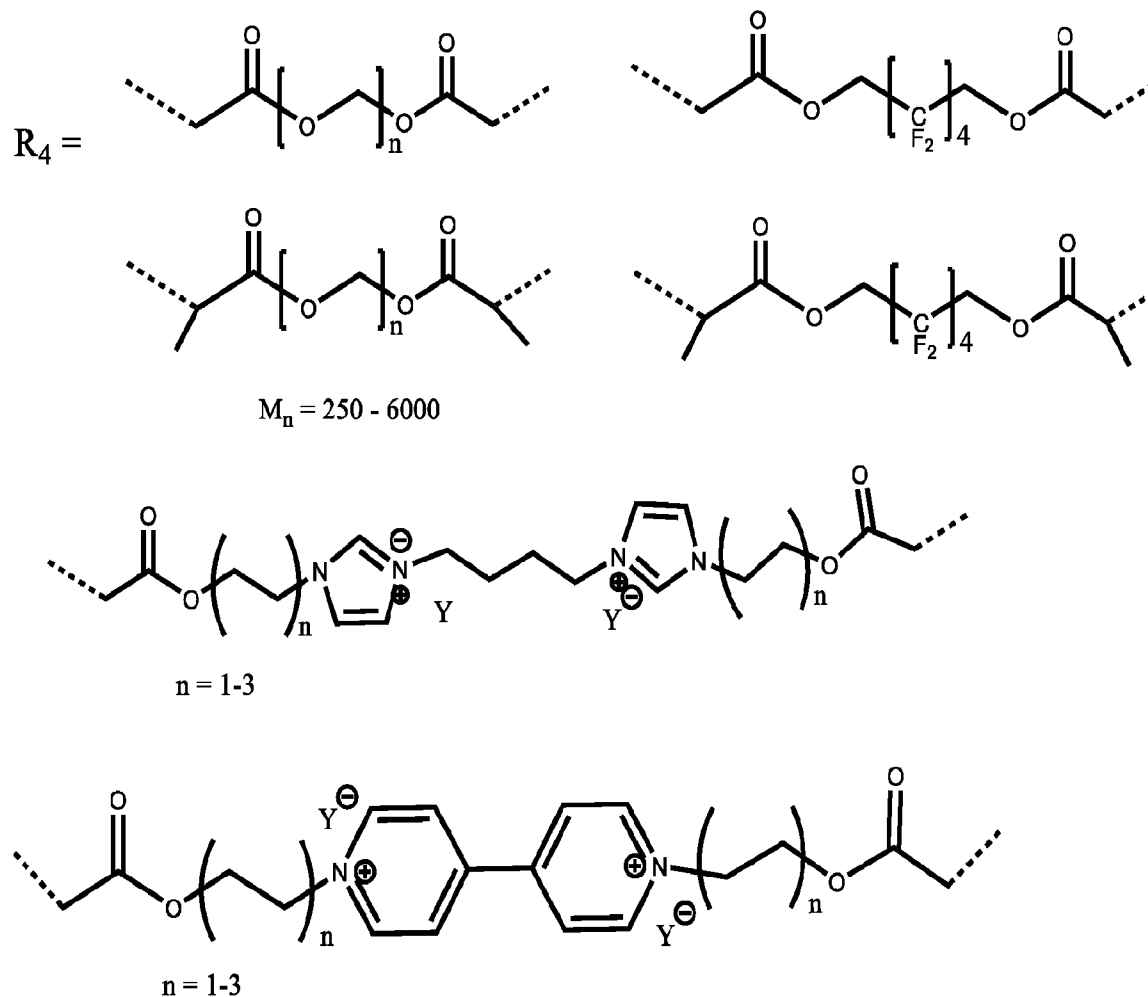
and $x = 1-12$.

15. The anionic ionoelastomer of claim 10, wherein R_3 is selected from

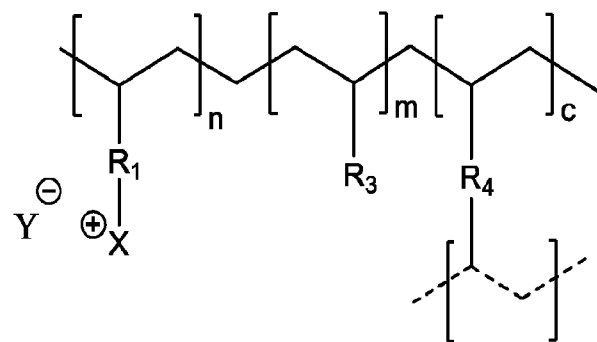


where $y = 1-7$.

16. The anionic ionoelastomer of claim 10, wherein R4 is selected from



17. A cationic ionoelastomer having the structure



where R1 is a polymeric backbone;

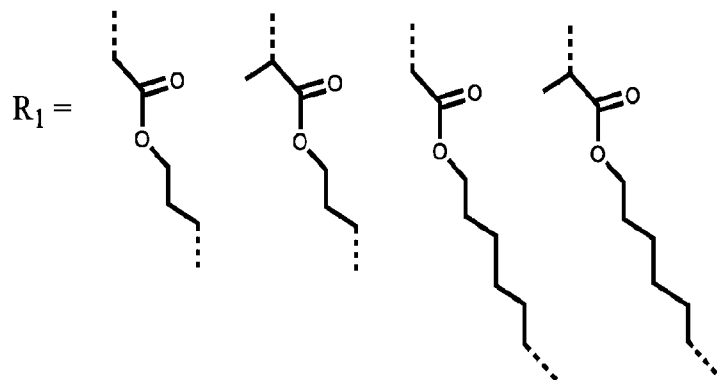
X⁺ is a cation;

Y⁻ is a counter ion;

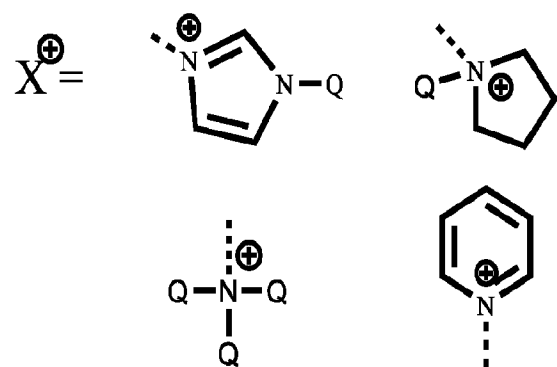
R3 is a comonomer; and

R4 is a crosslinker.

18. The cationic ionoelastomer of claim 17, wherein R1 is selected from



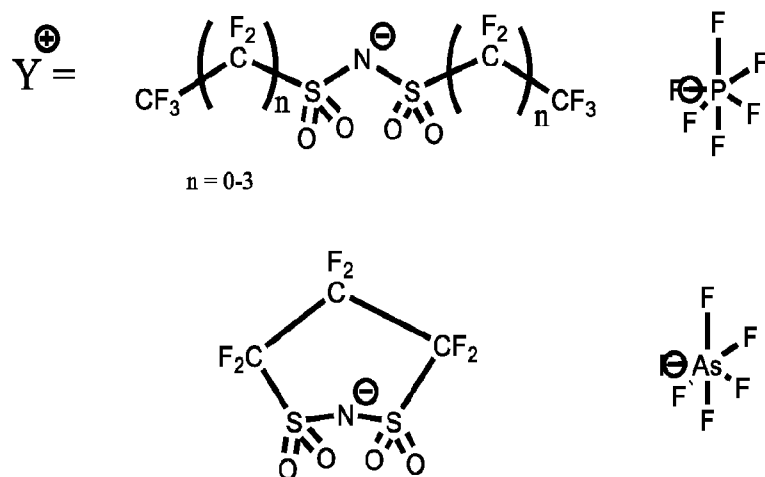
19. The cationic ionoelastomer of claim 17, wherein the X⁺ cation is selected from



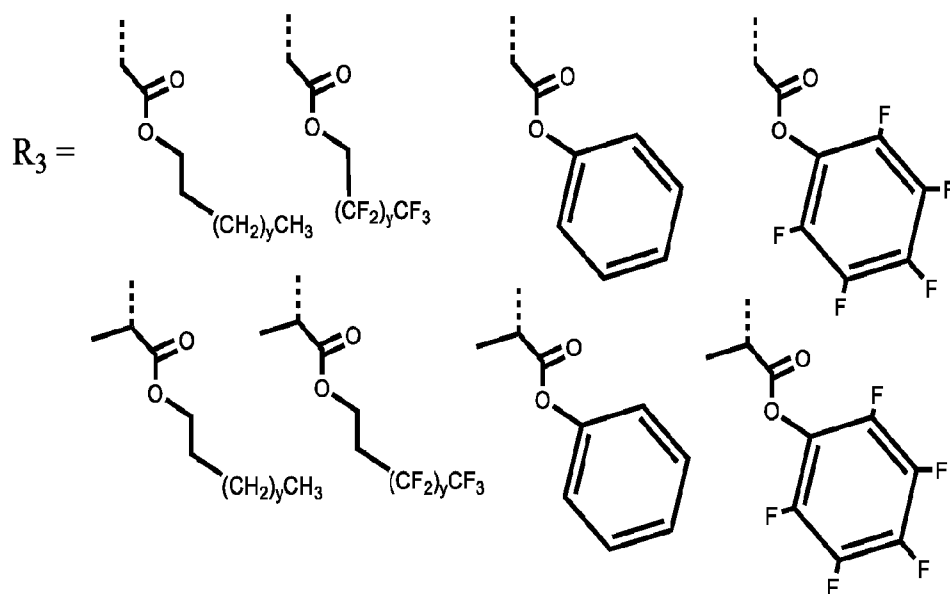
where Q = C_xH_{2x+1}

and x = 1-12.

20. The cationic ionoelastomer of claim 17, wherein the Y⁺- counter ion is selected from

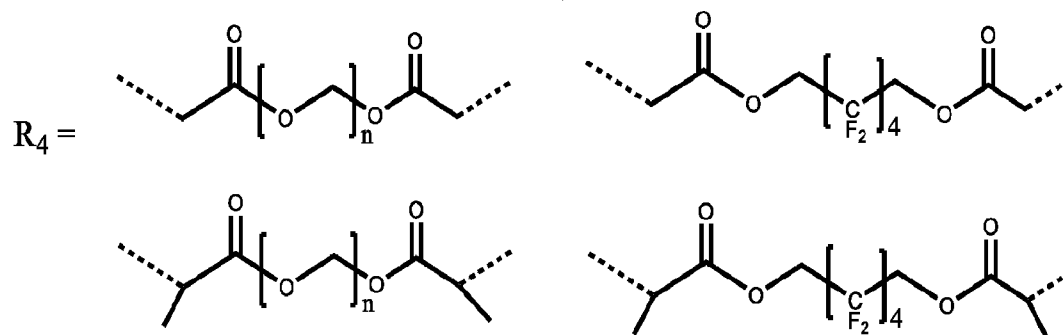


21. The cationic ionoelastomer of claim 17, wherein R₃ comonomer is selected from

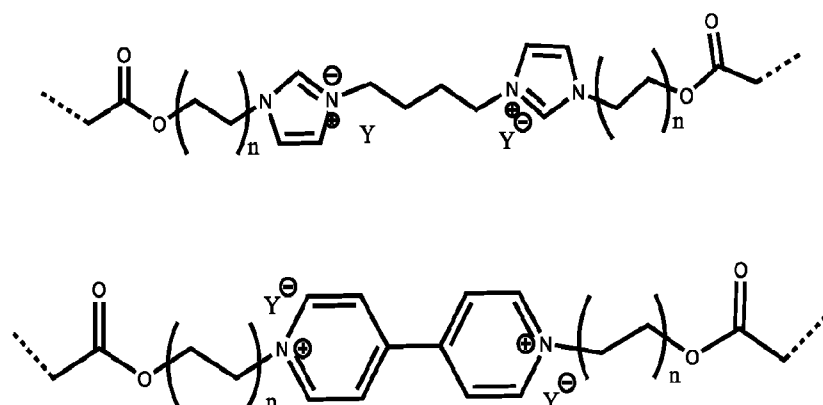


where y = 1-7.

22. The cationic ionoelastomer of claim 17, wherein R₄ is selected from

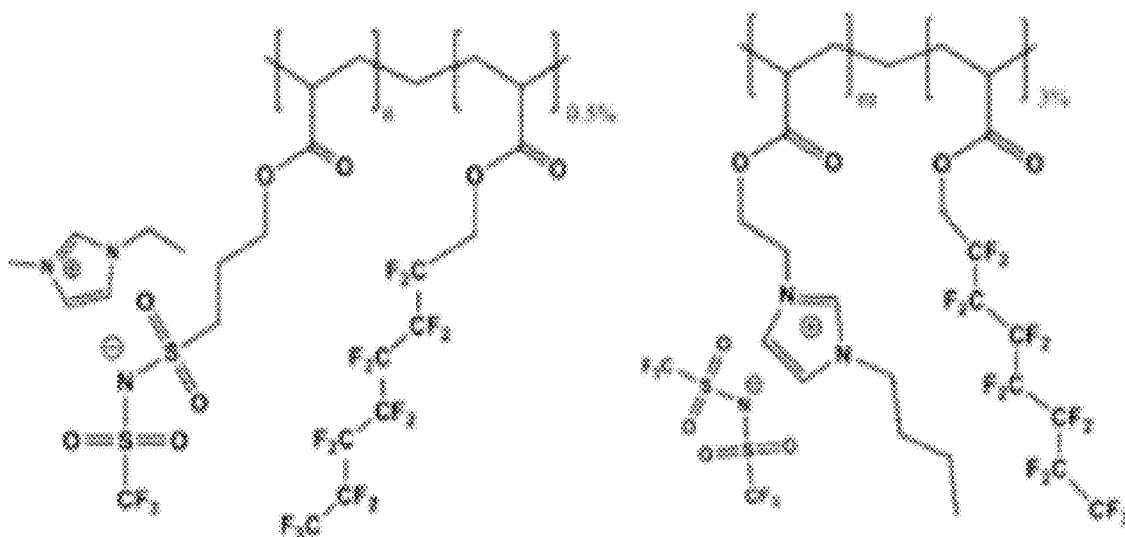


$$M_n = 250 - 6000$$



where n = 1-3.

23. An electroadhesive comprising one or both of:



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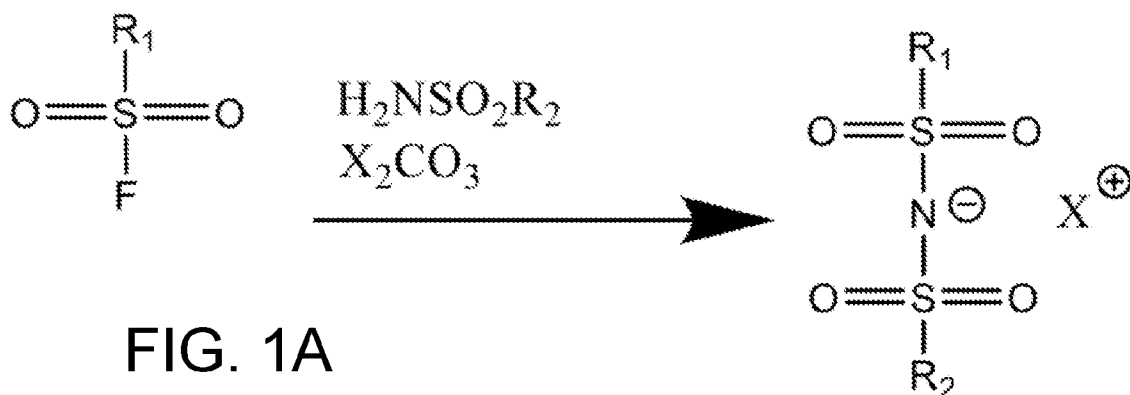


FIG. 1A

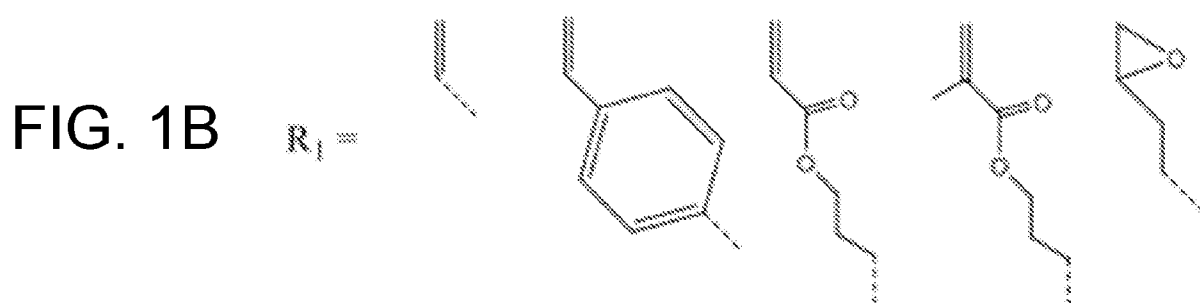


FIG. 1B

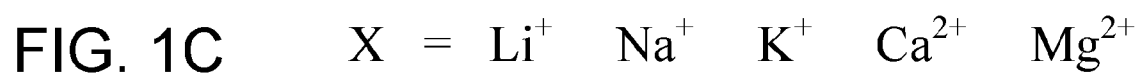


FIG. 1C

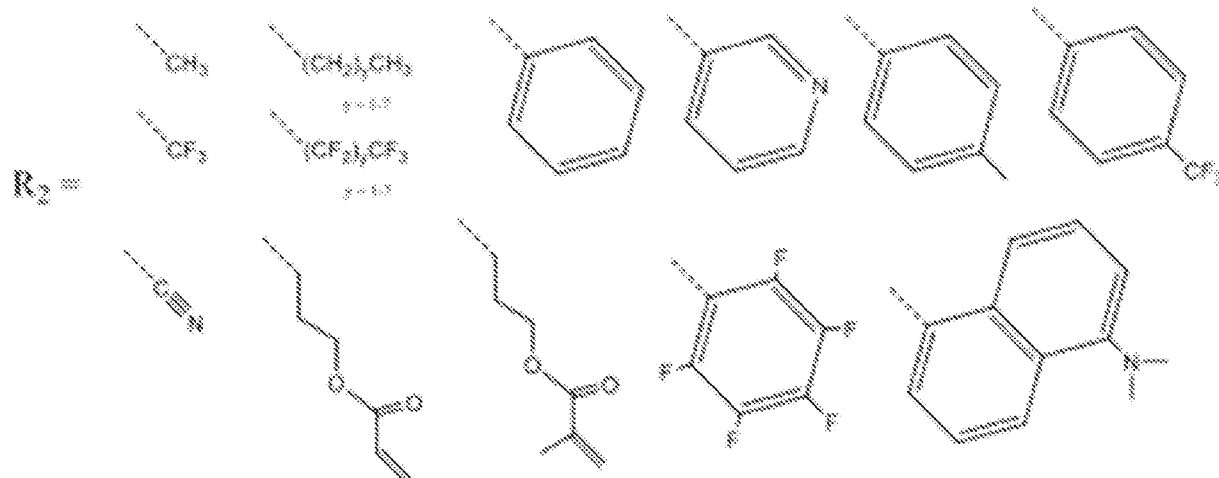


FIG. 1D

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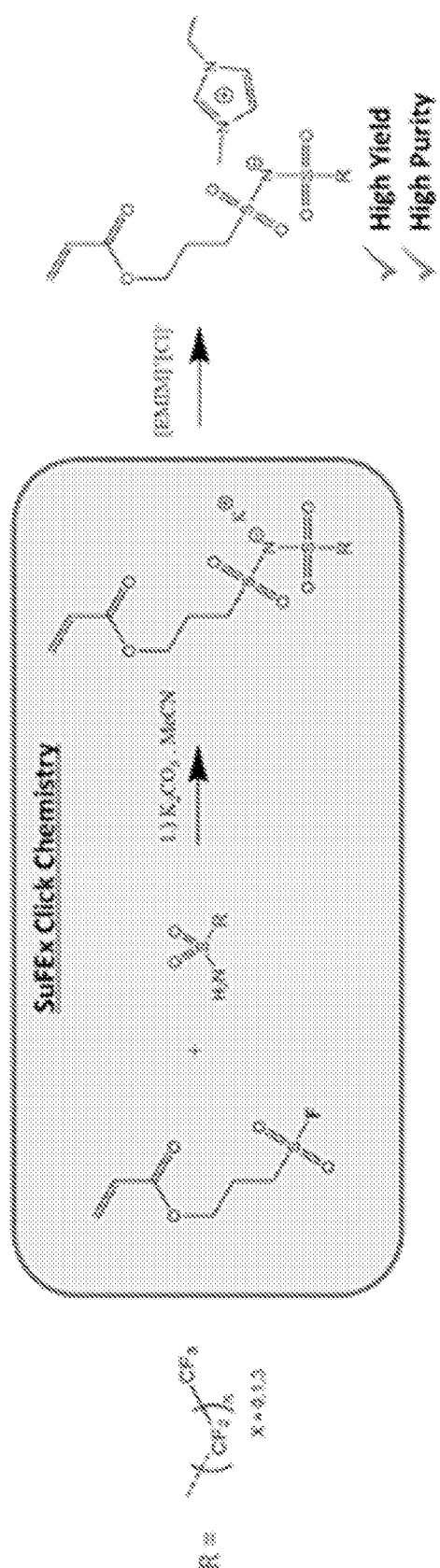


FIG. 2

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FIG. 3A

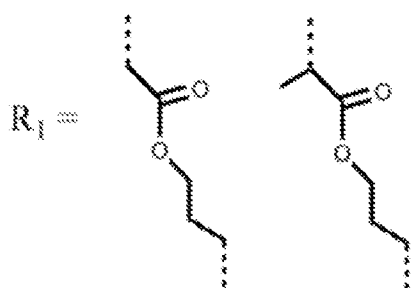
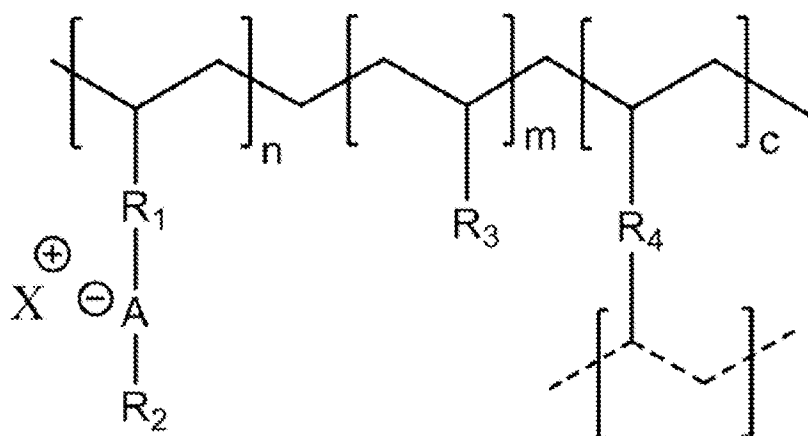


FIG. 3B

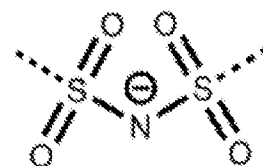
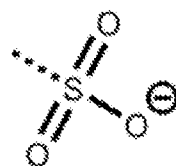


FIG. 3C

FIG. 3D

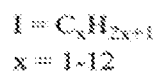
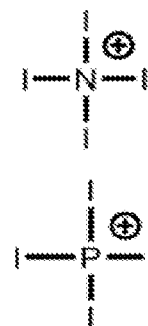
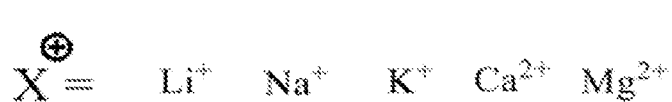
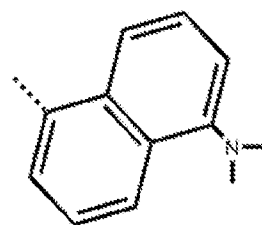
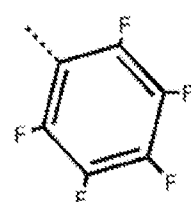
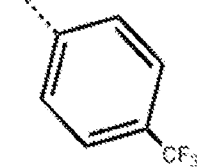
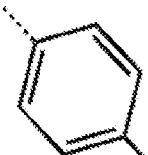
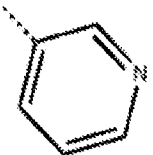
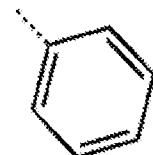
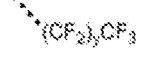
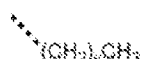


FIG. 3E



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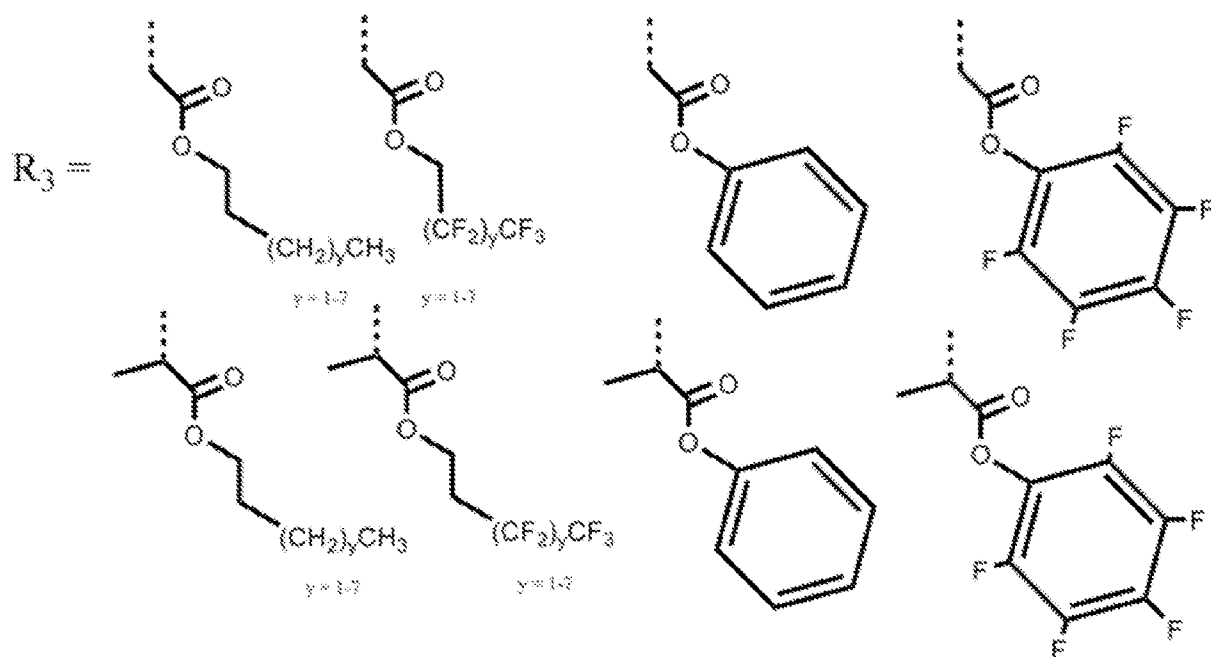


FIG. 3F

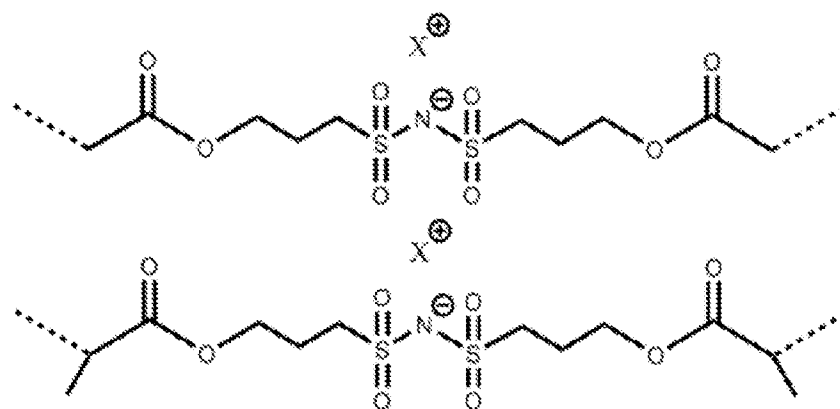
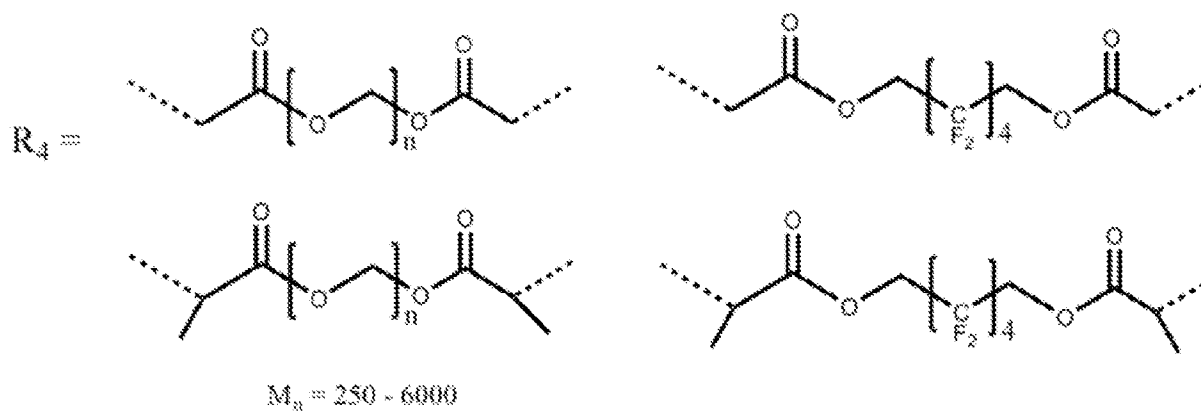


FIG. 3G

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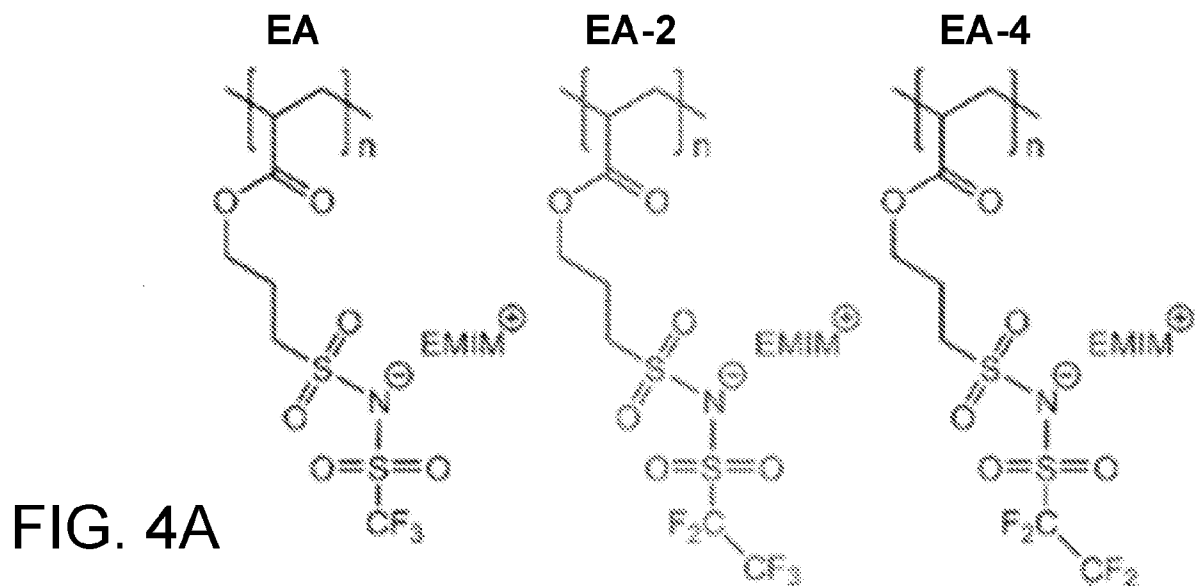


FIG. 4B

||||| Ionic
 Ion – Pendant
 --- Pendant - Pendant

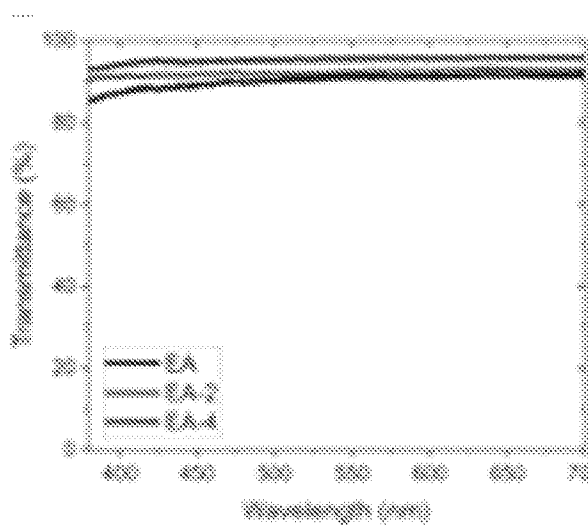
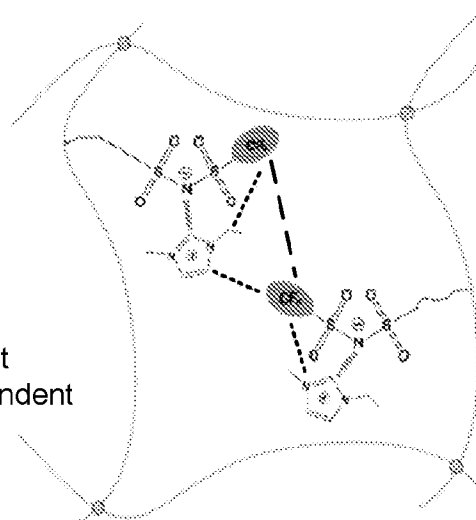


FIG. 4C

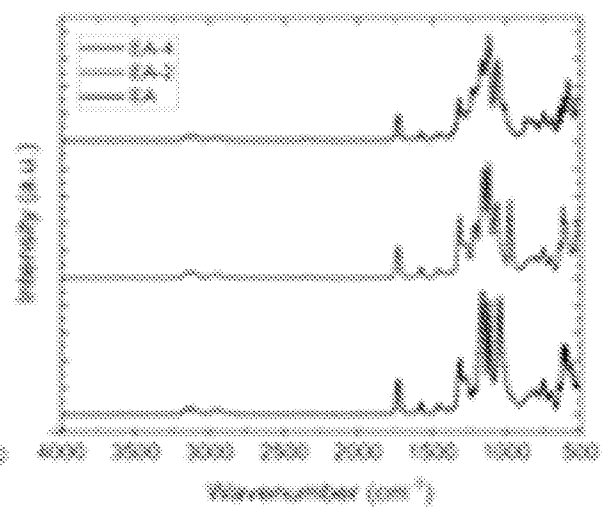


FIG. 4D

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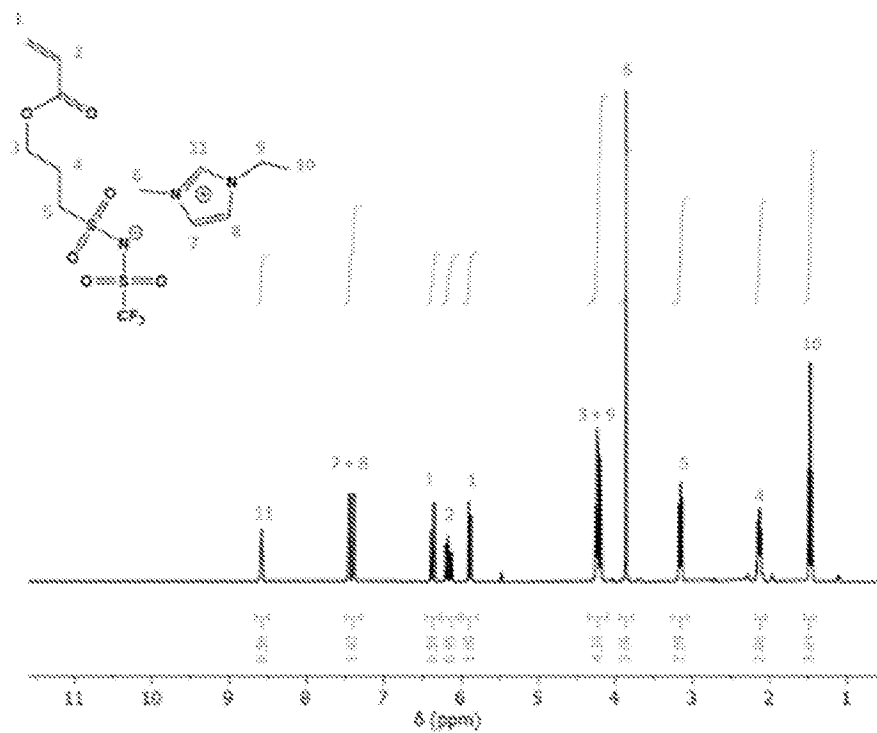


FIG. 5

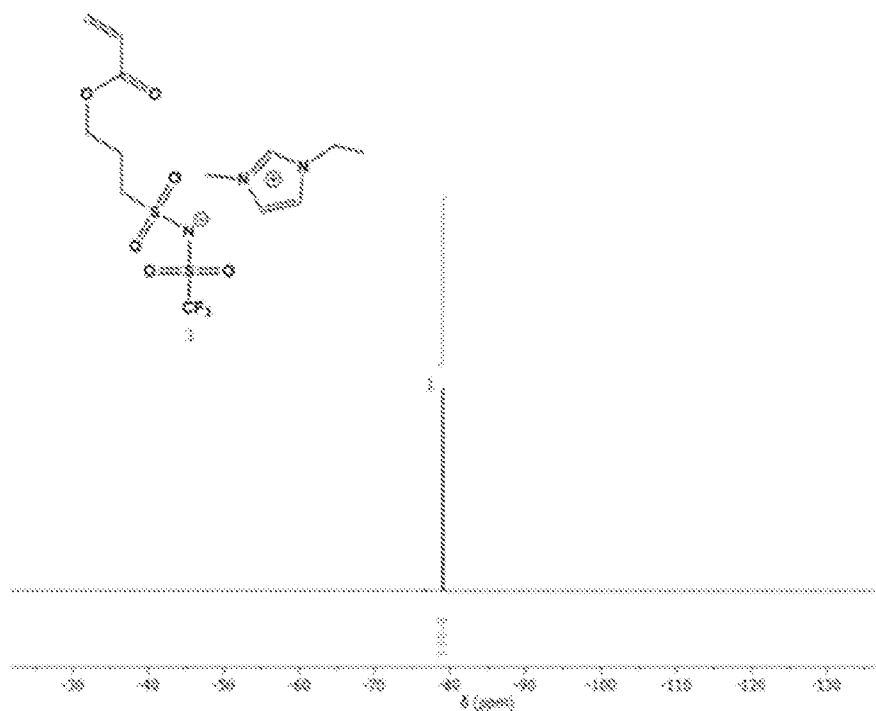


FIG. 6

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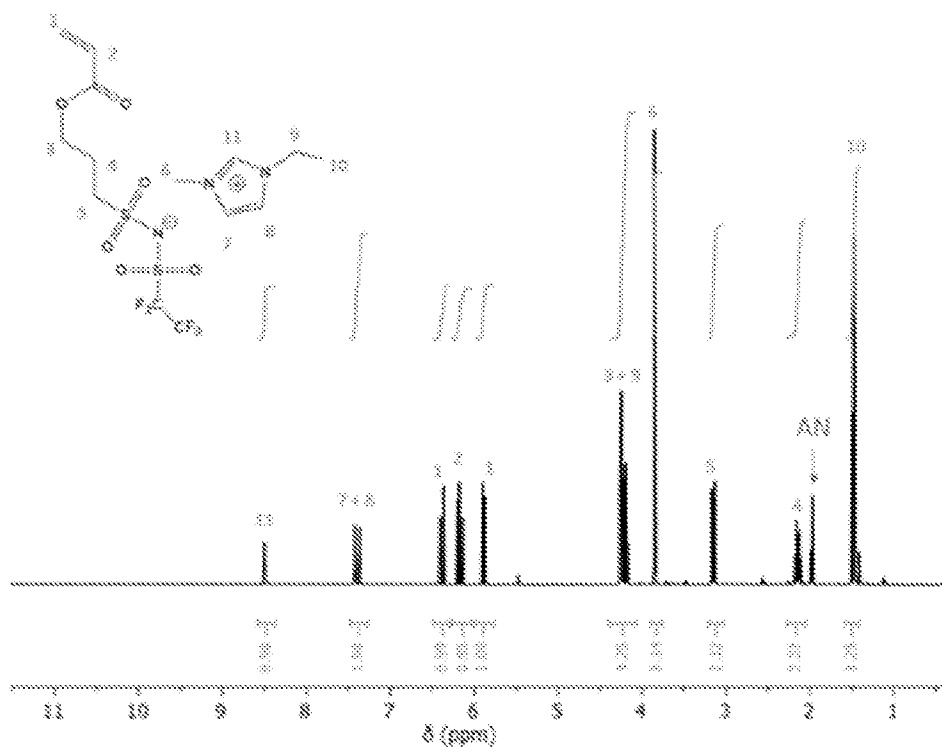


FIG. 7

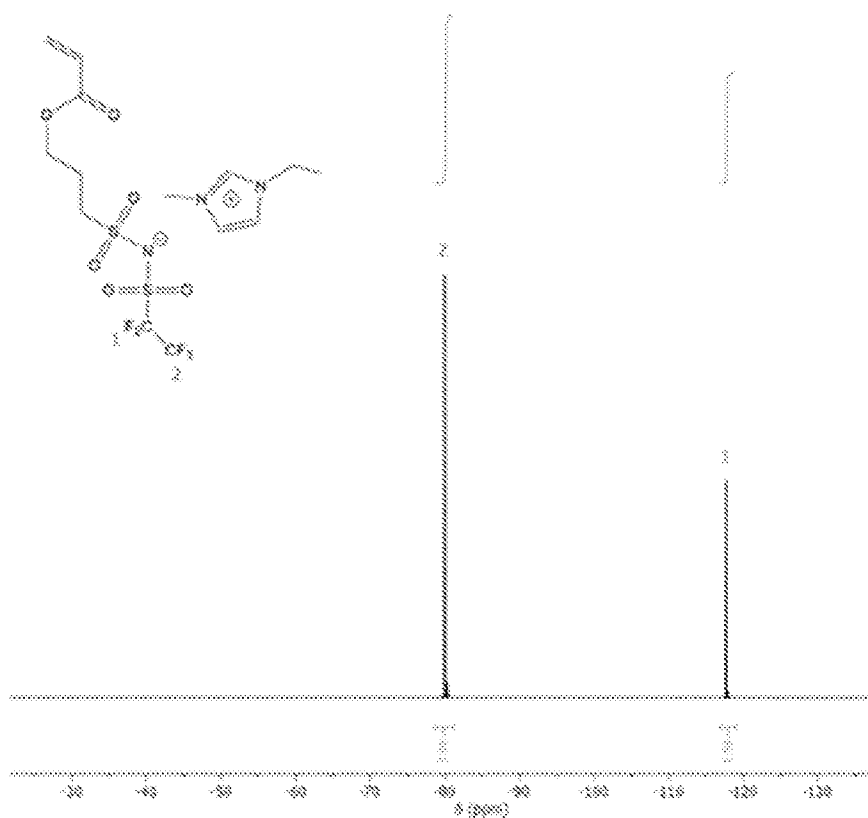


FIG. 8

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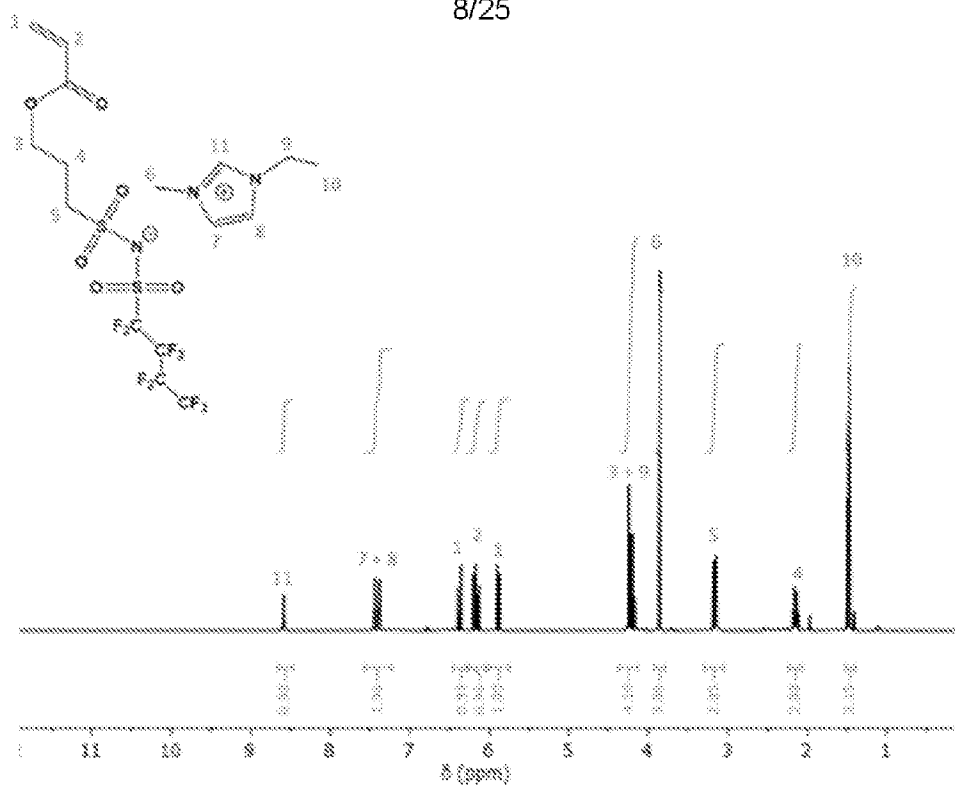


FIG. 9

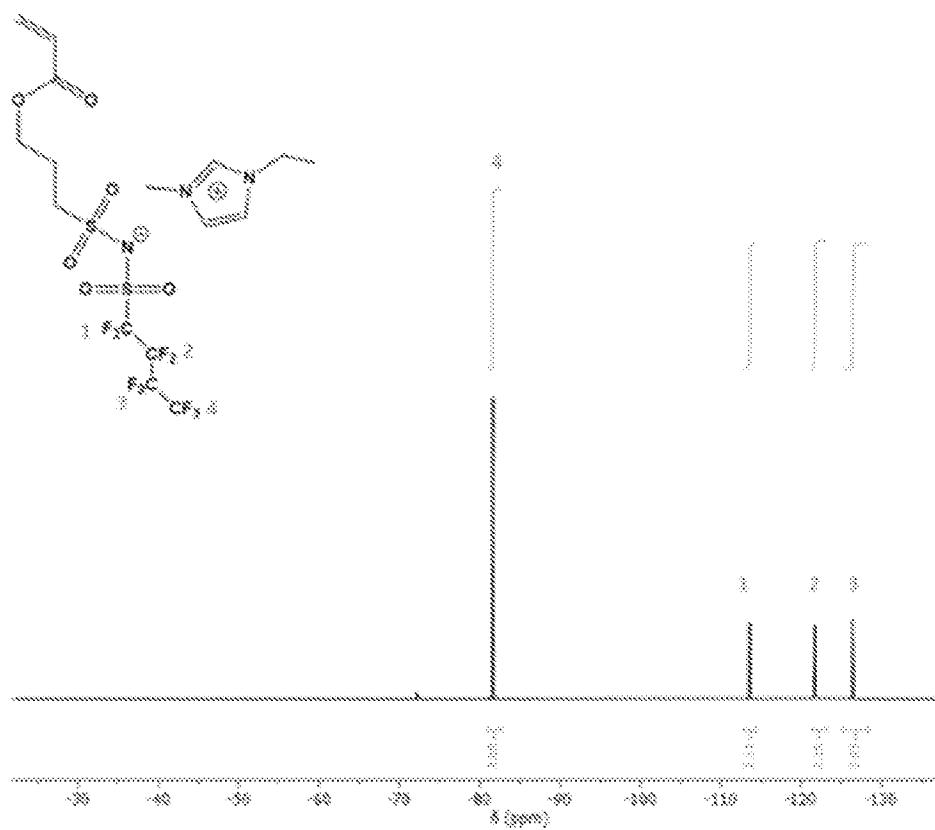


FIG. 10

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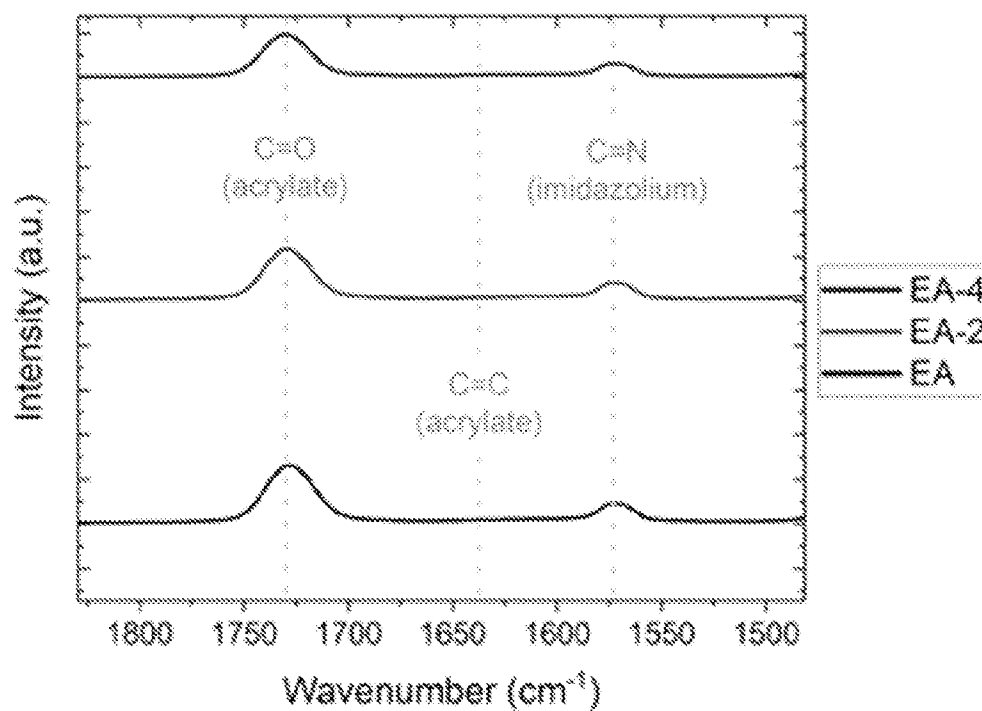


FIG. 11

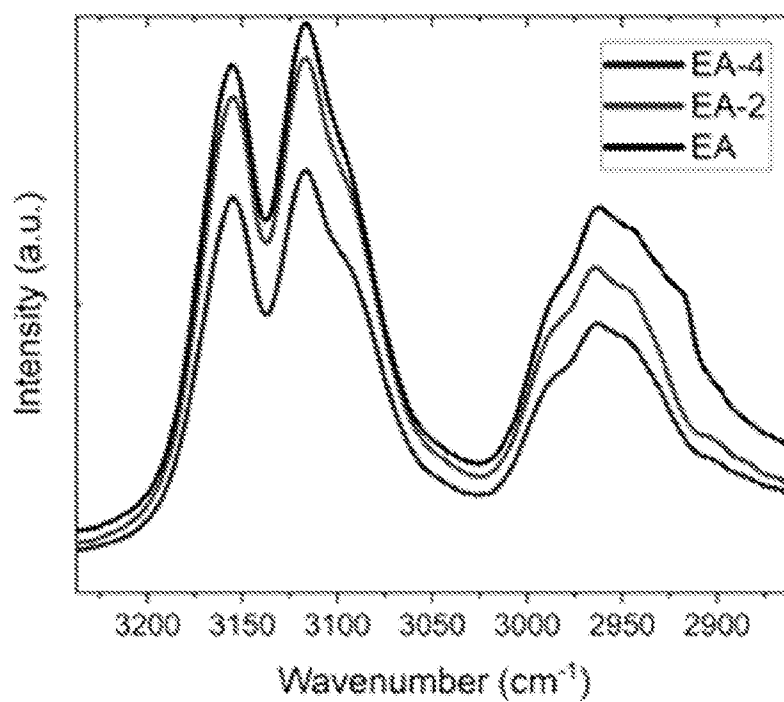


FIG. 12

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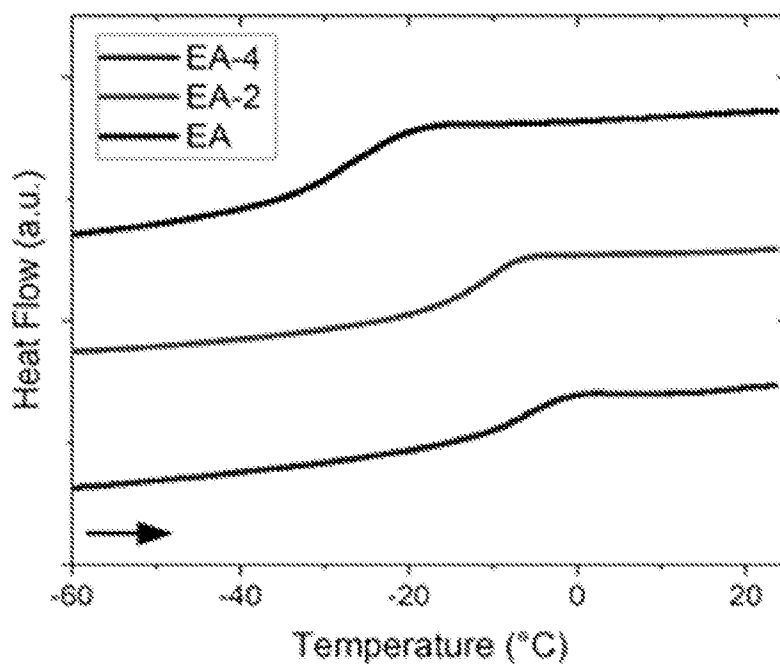


FIG. 13

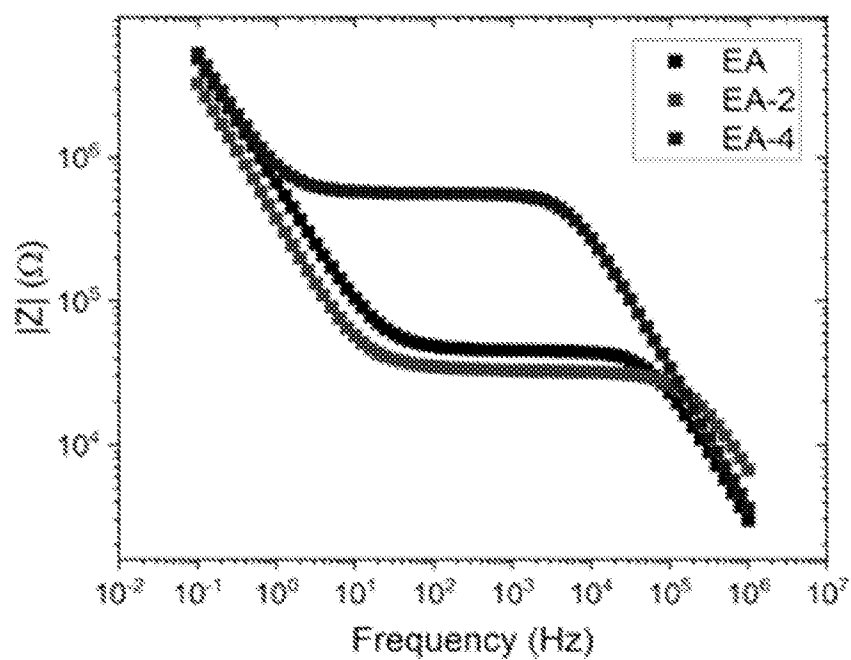


FIG. 14

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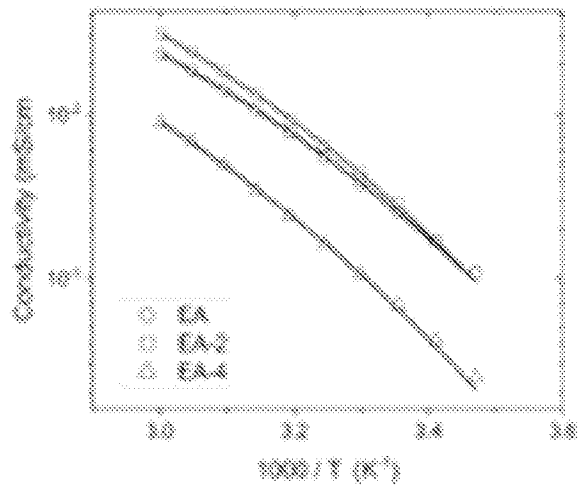


FIG. 15A

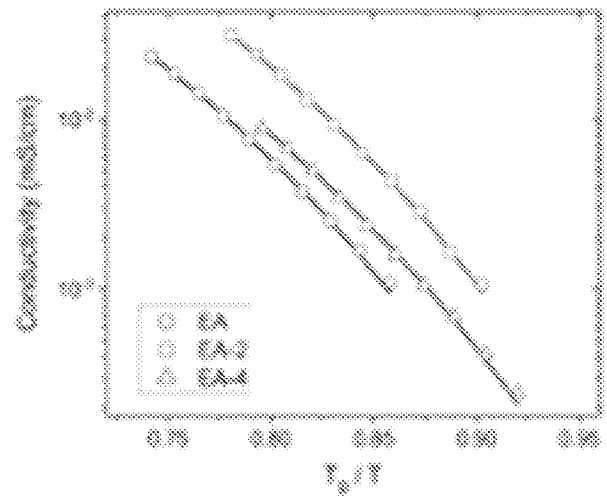


FIG. 15B

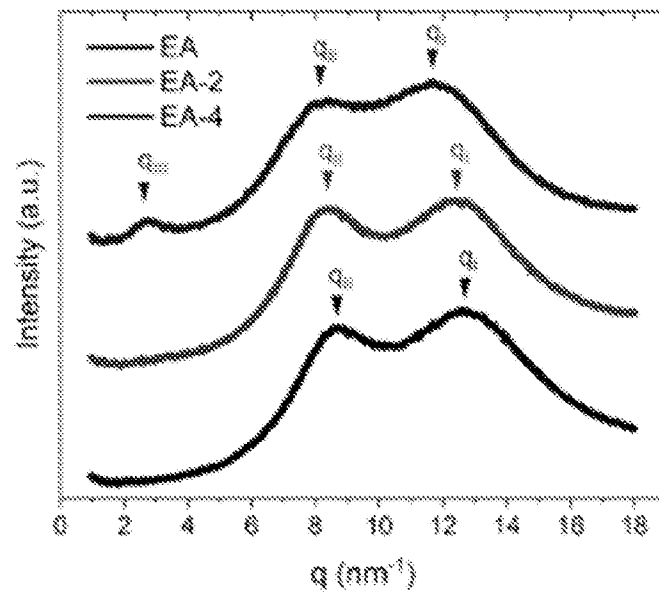


FIG. 16

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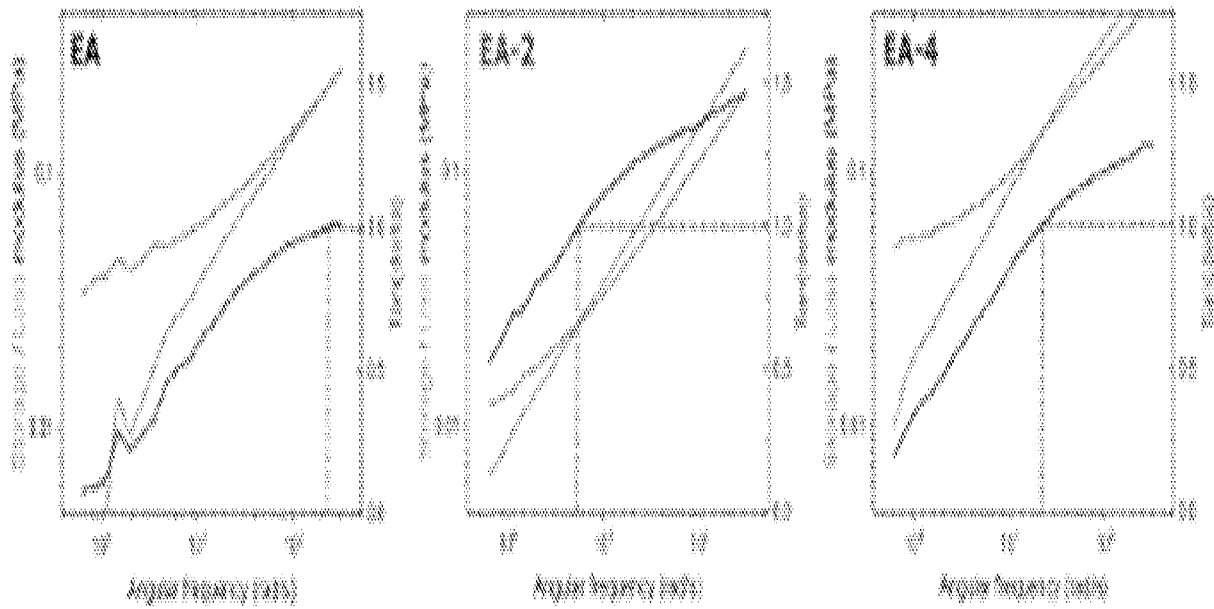


FIG. 17A

FIG. 17B

FIG. 17C

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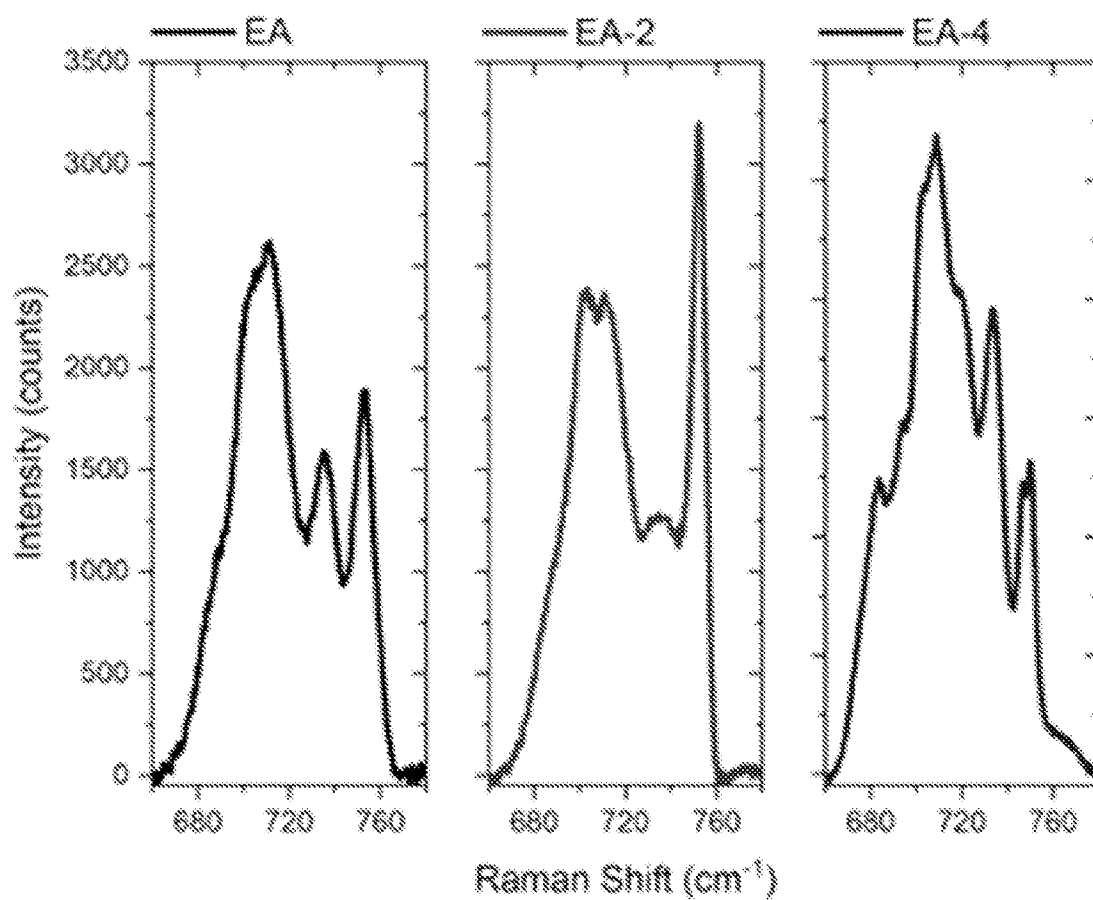


FIG. 18A

FIG. 18B

FIG. 18C

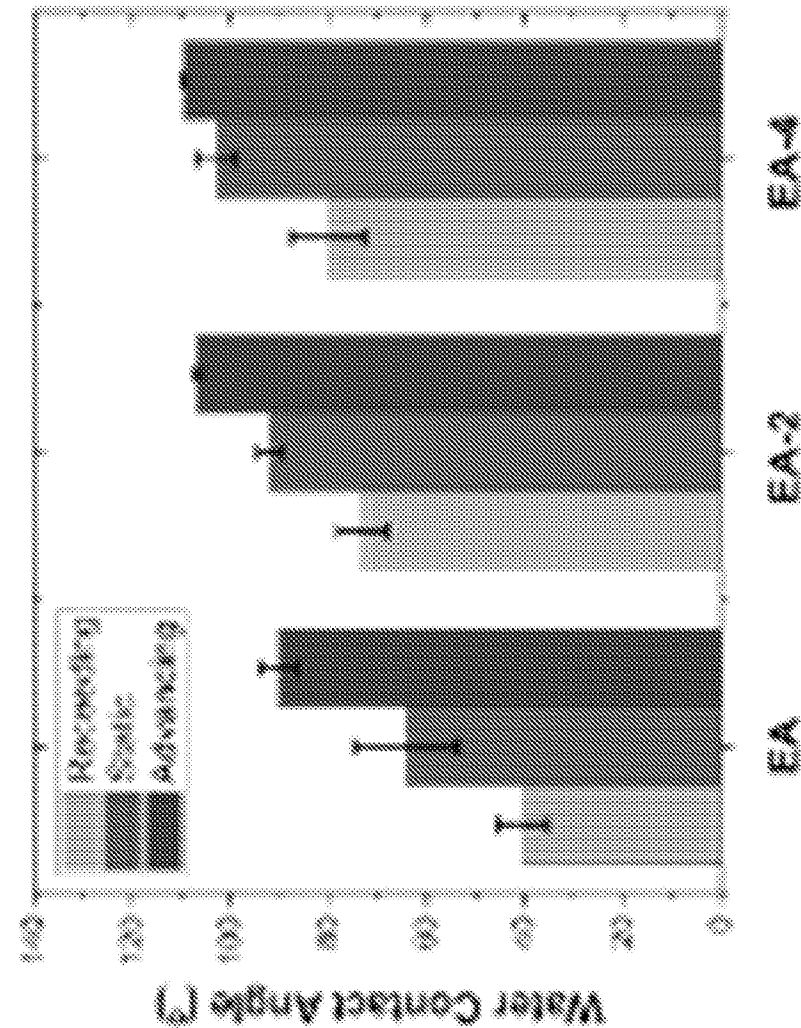


FIG. 19B

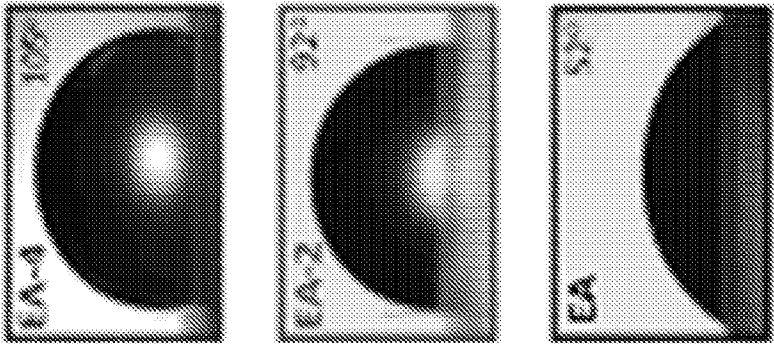


FIG. 19A

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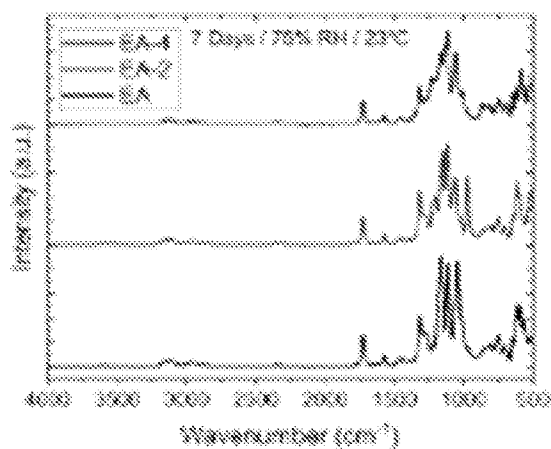


FIG. 20A

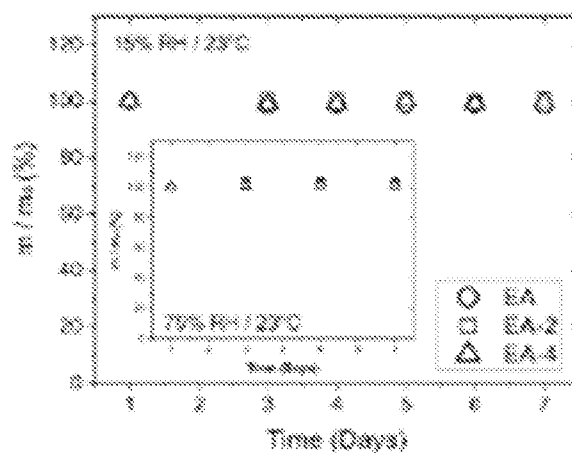


FIG. 20B

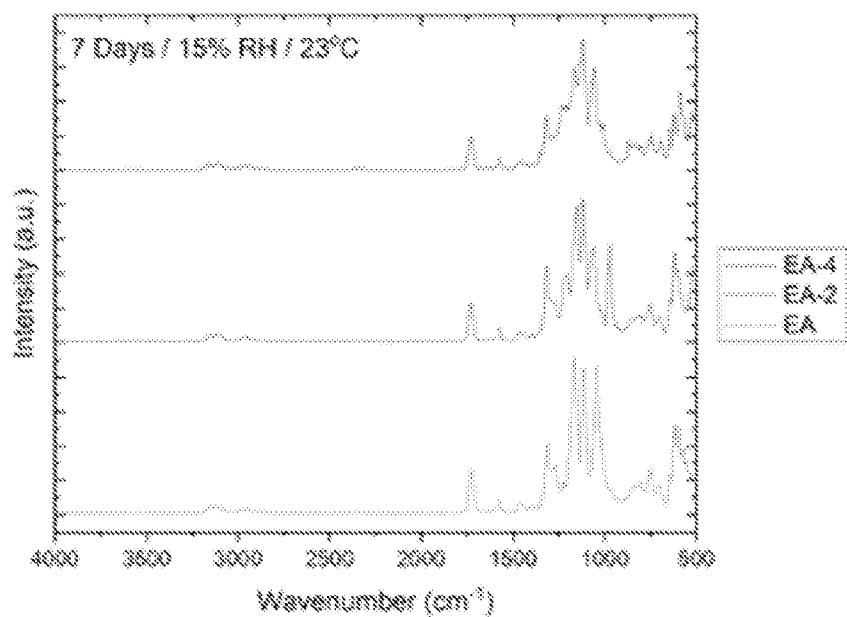


FIG. 21

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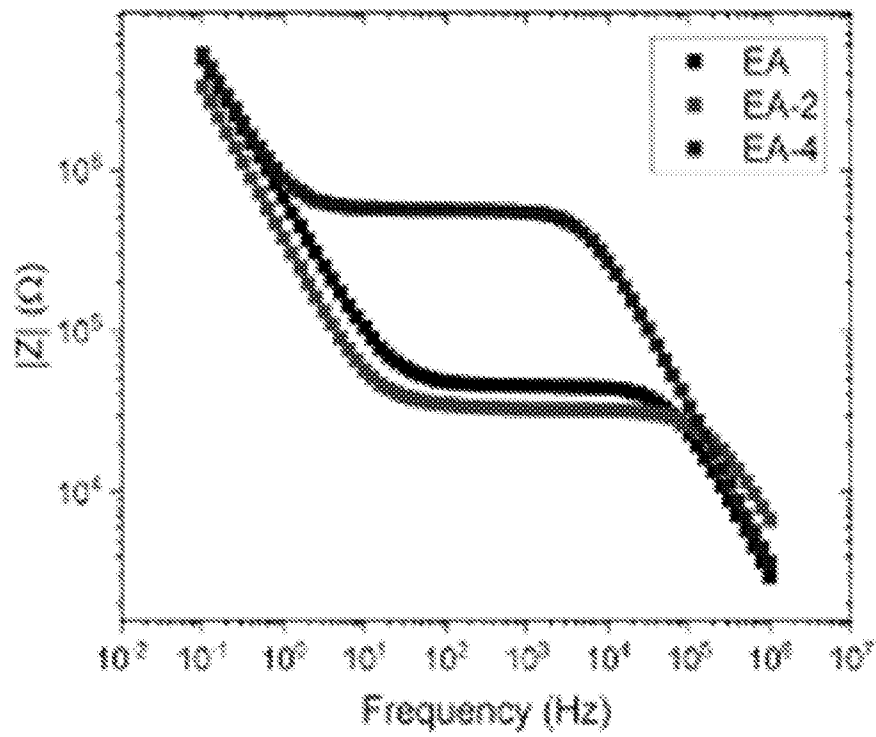


FIG. 22

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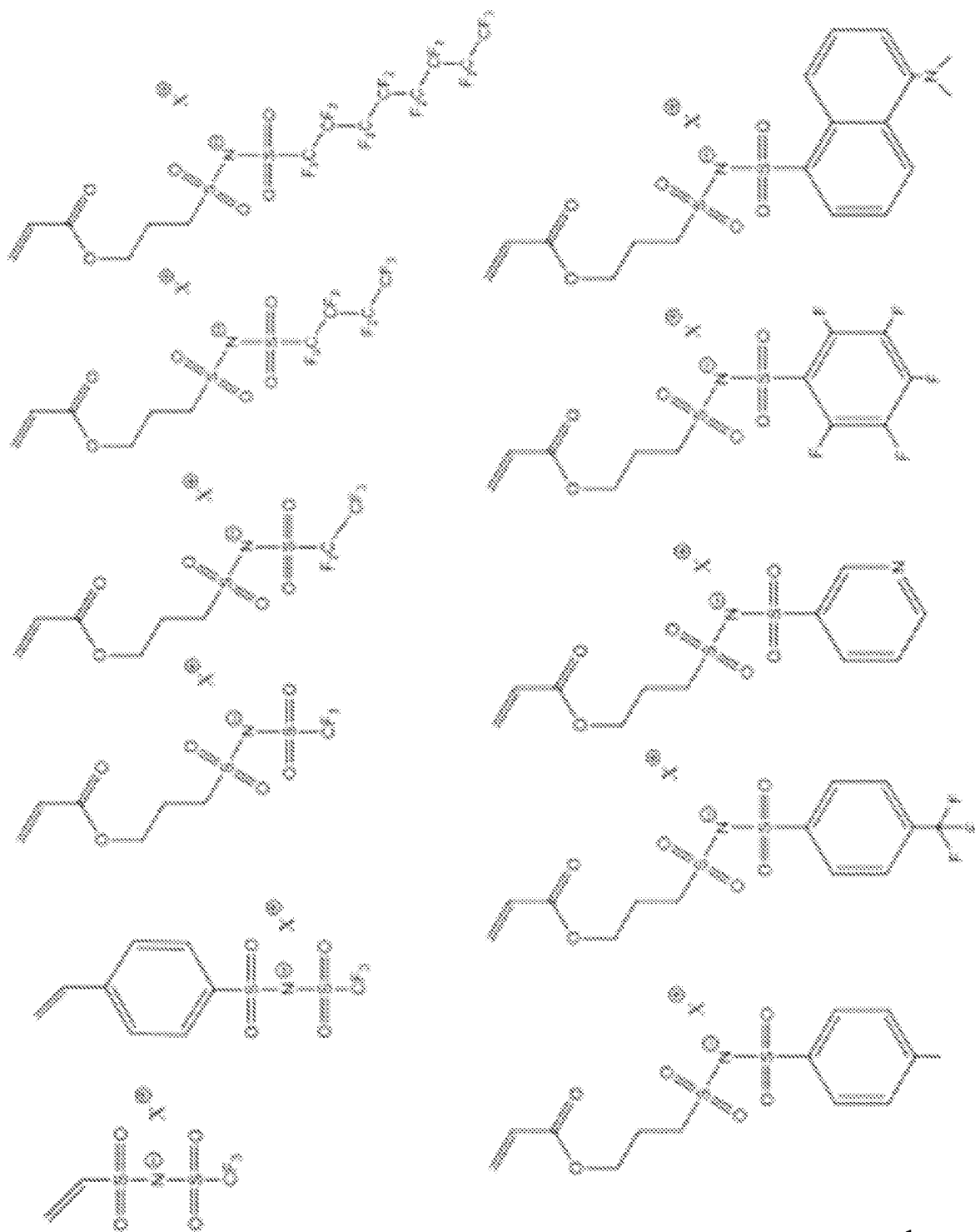


FIG. 23A

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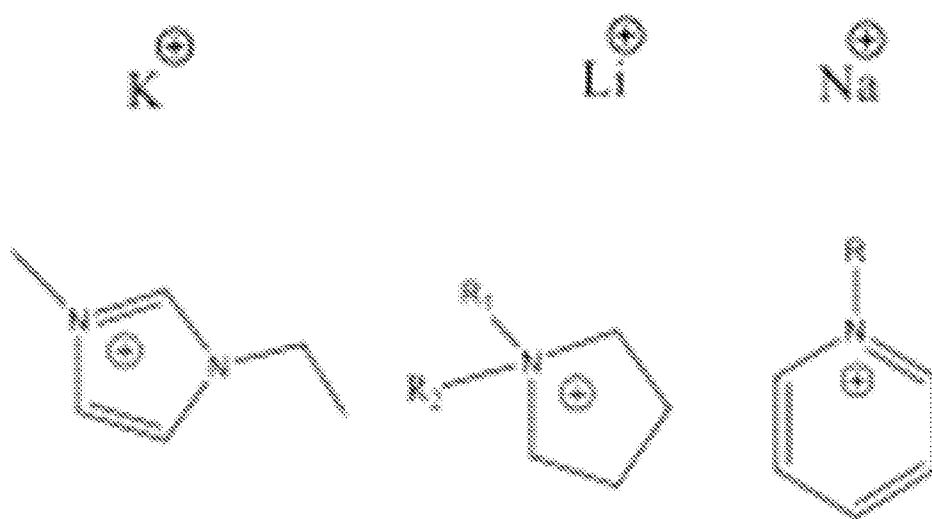


FIG. 23B

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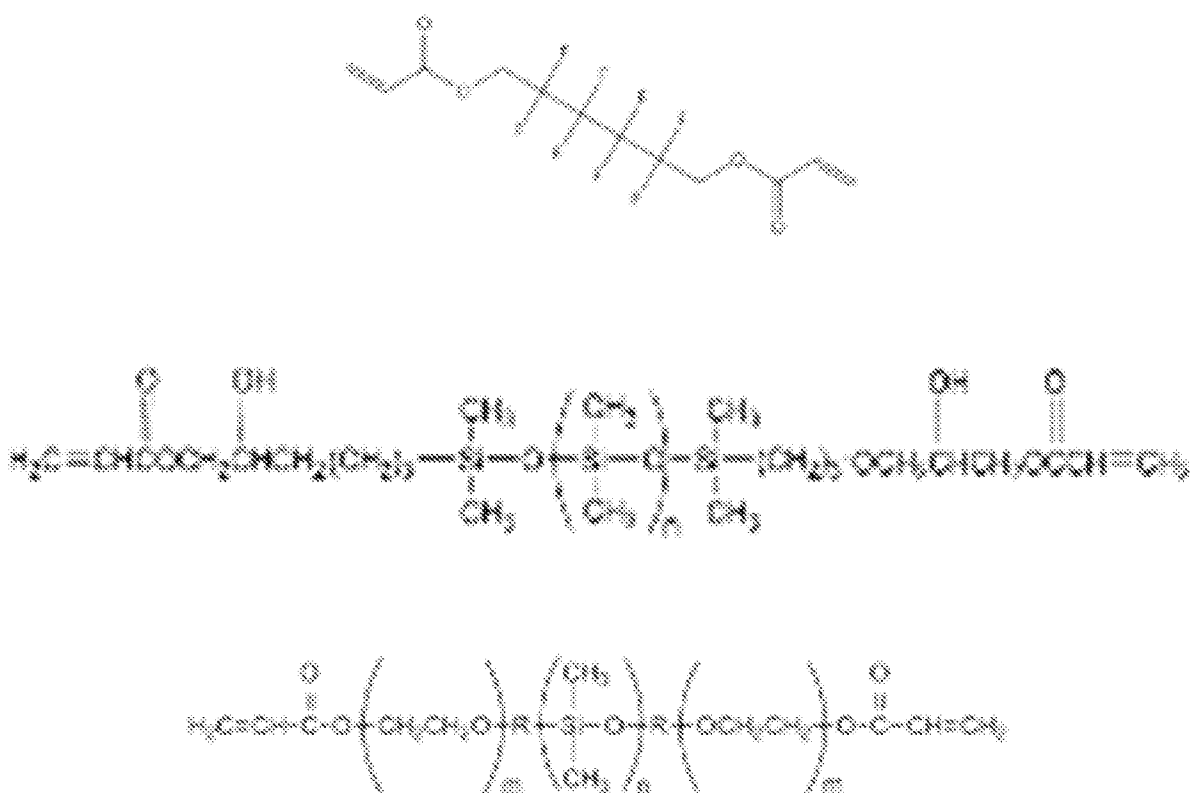


FIG. 23C

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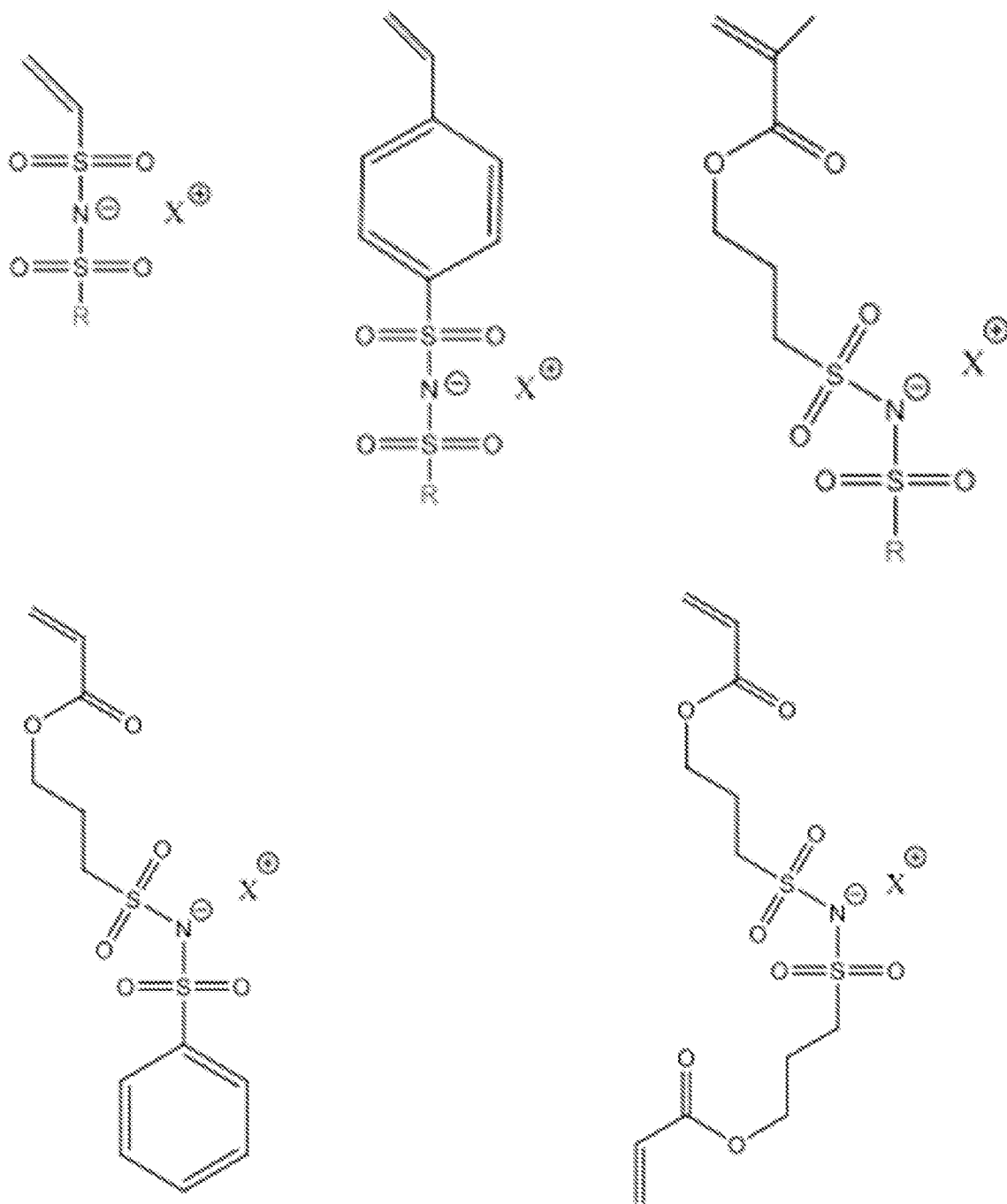


FIG. 24

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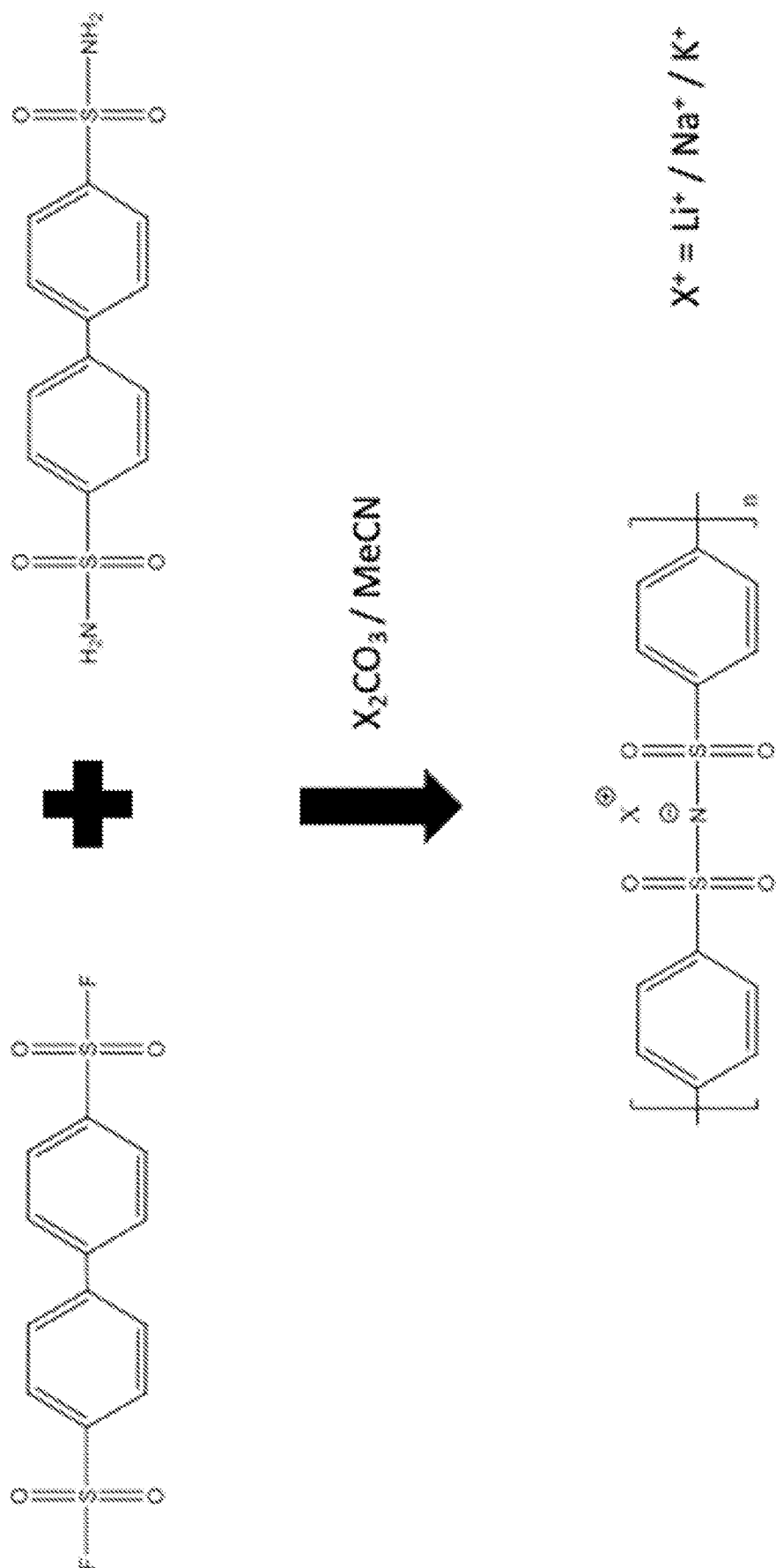


FIG. 25

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FIG. 26A

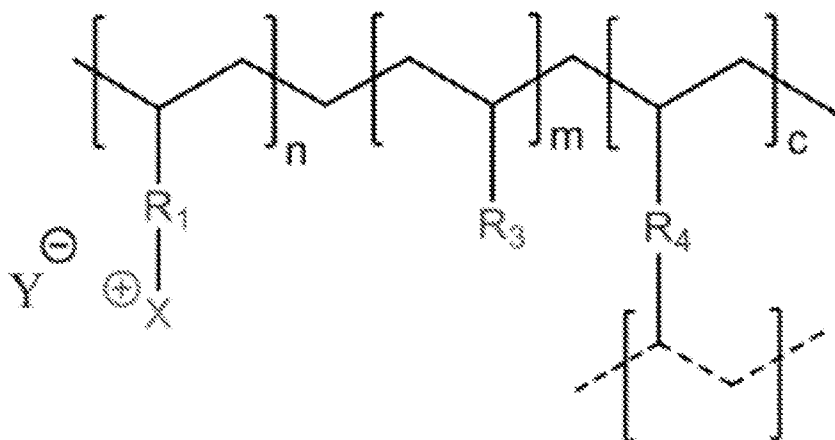


FIG. 26B

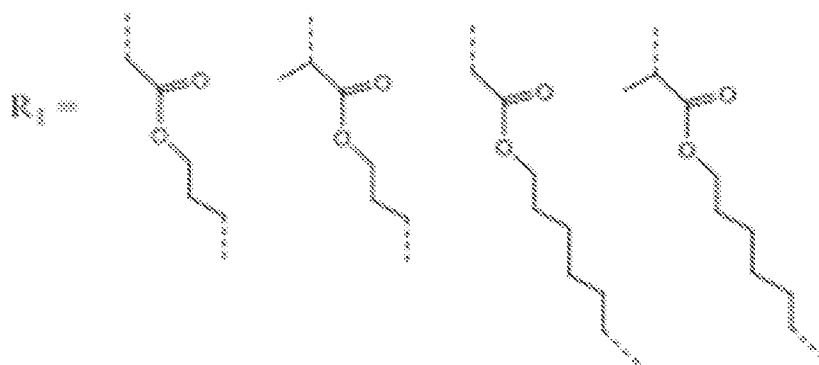


FIG. 26C

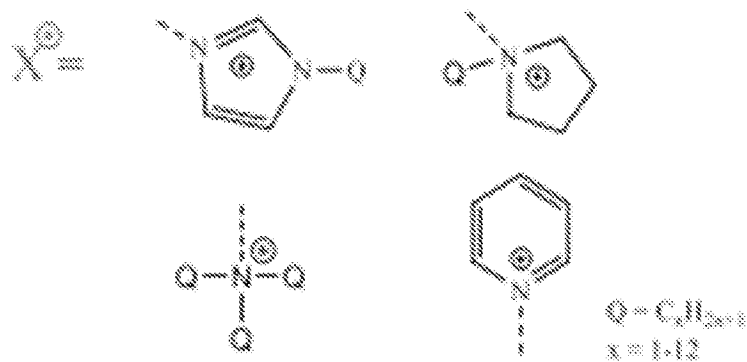
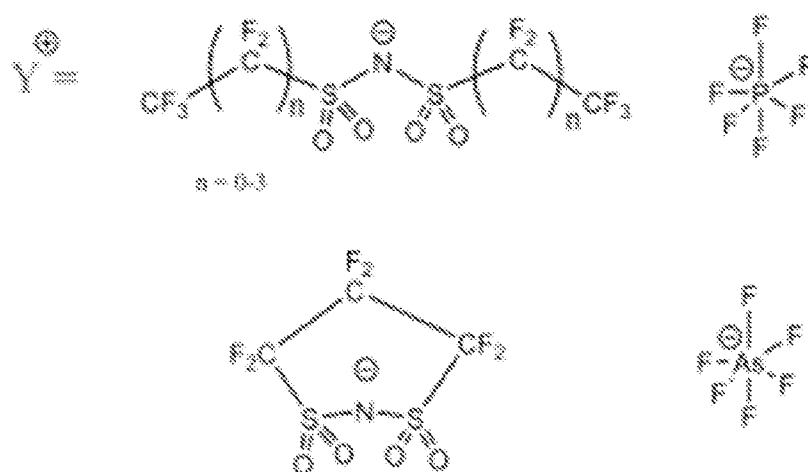


FIG. 26D



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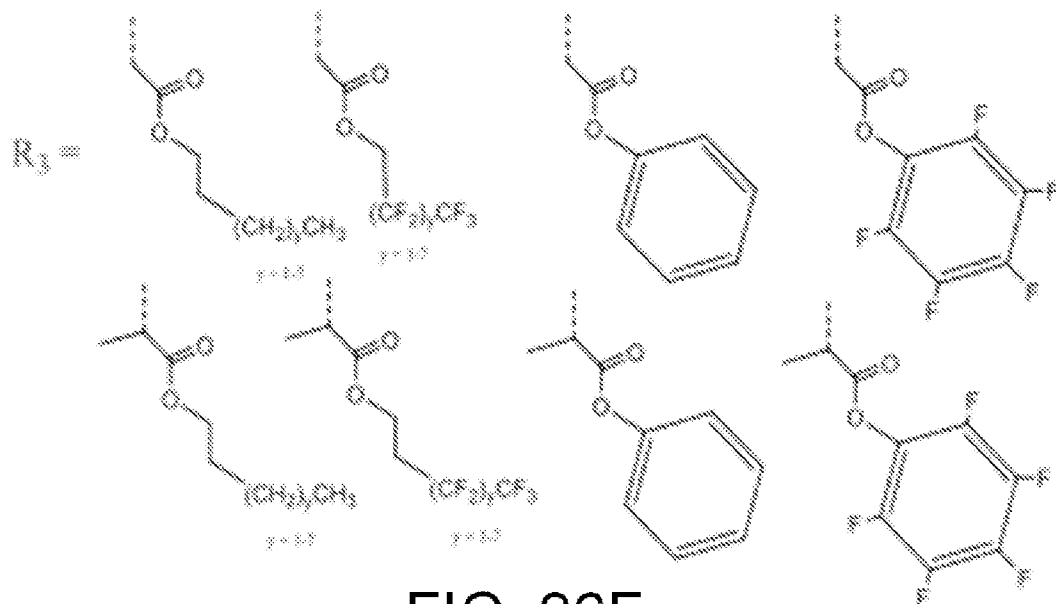


FIG. 26F

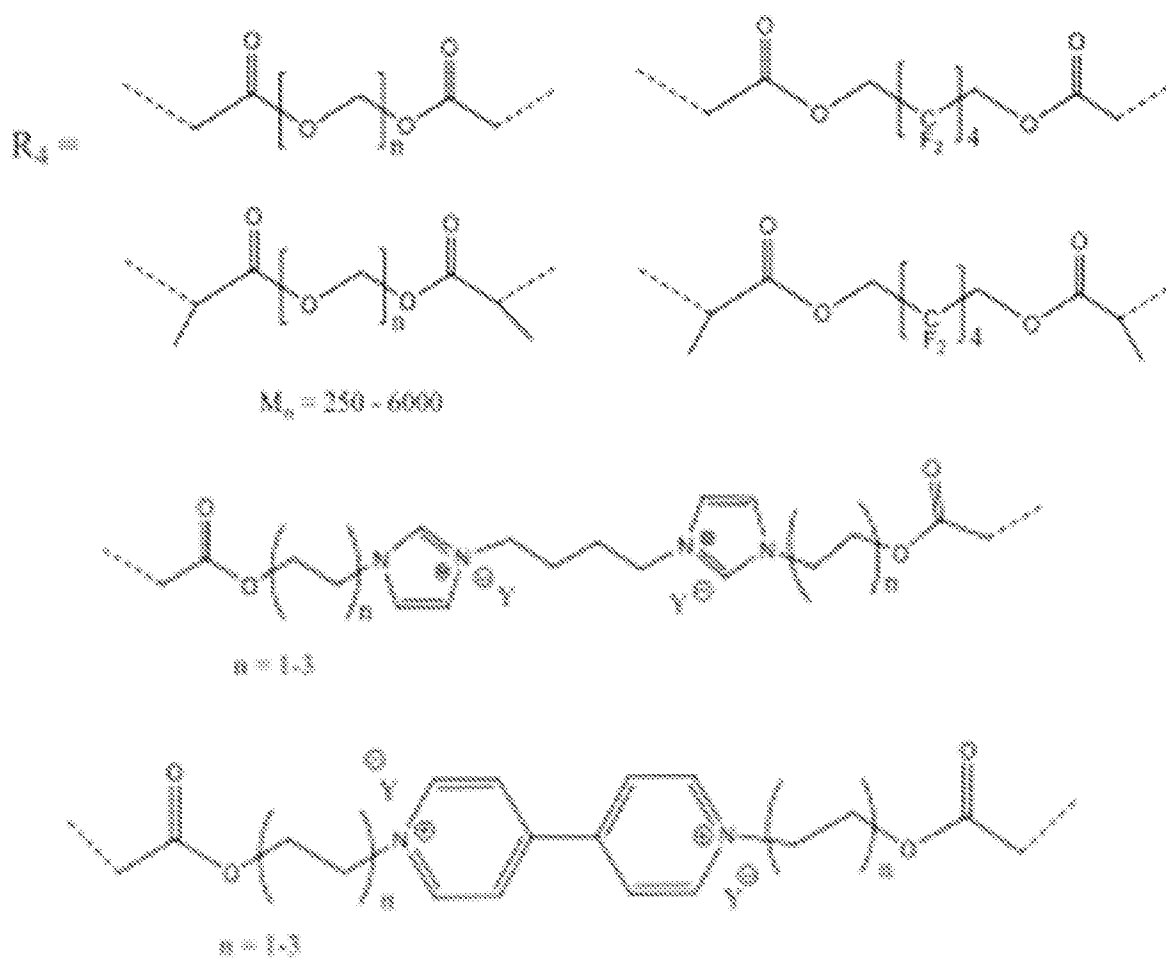


FIG. 26G

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Polyanion
(EA-co-15Fa)

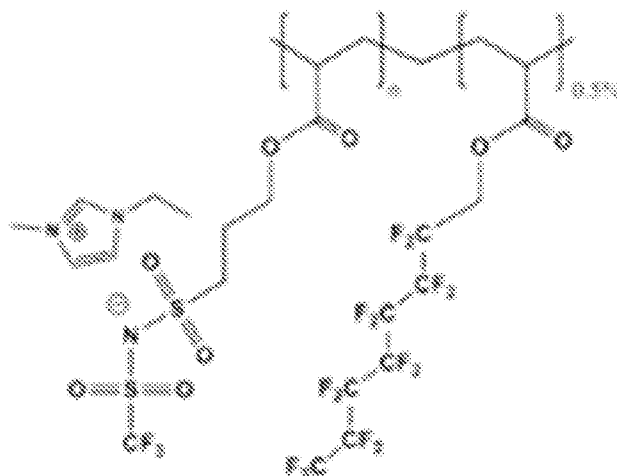


FIG. 27A

Polycation
(AT-co-15Fa)

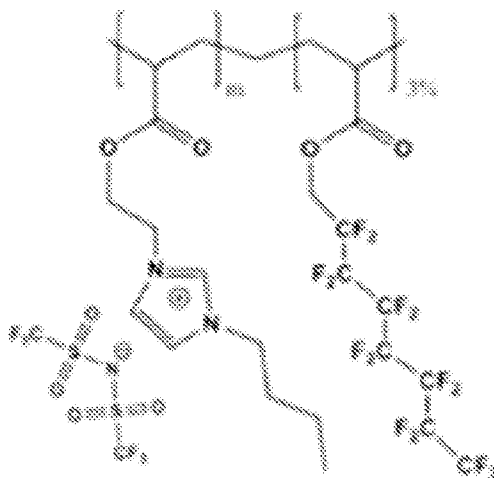


FIG. 27B

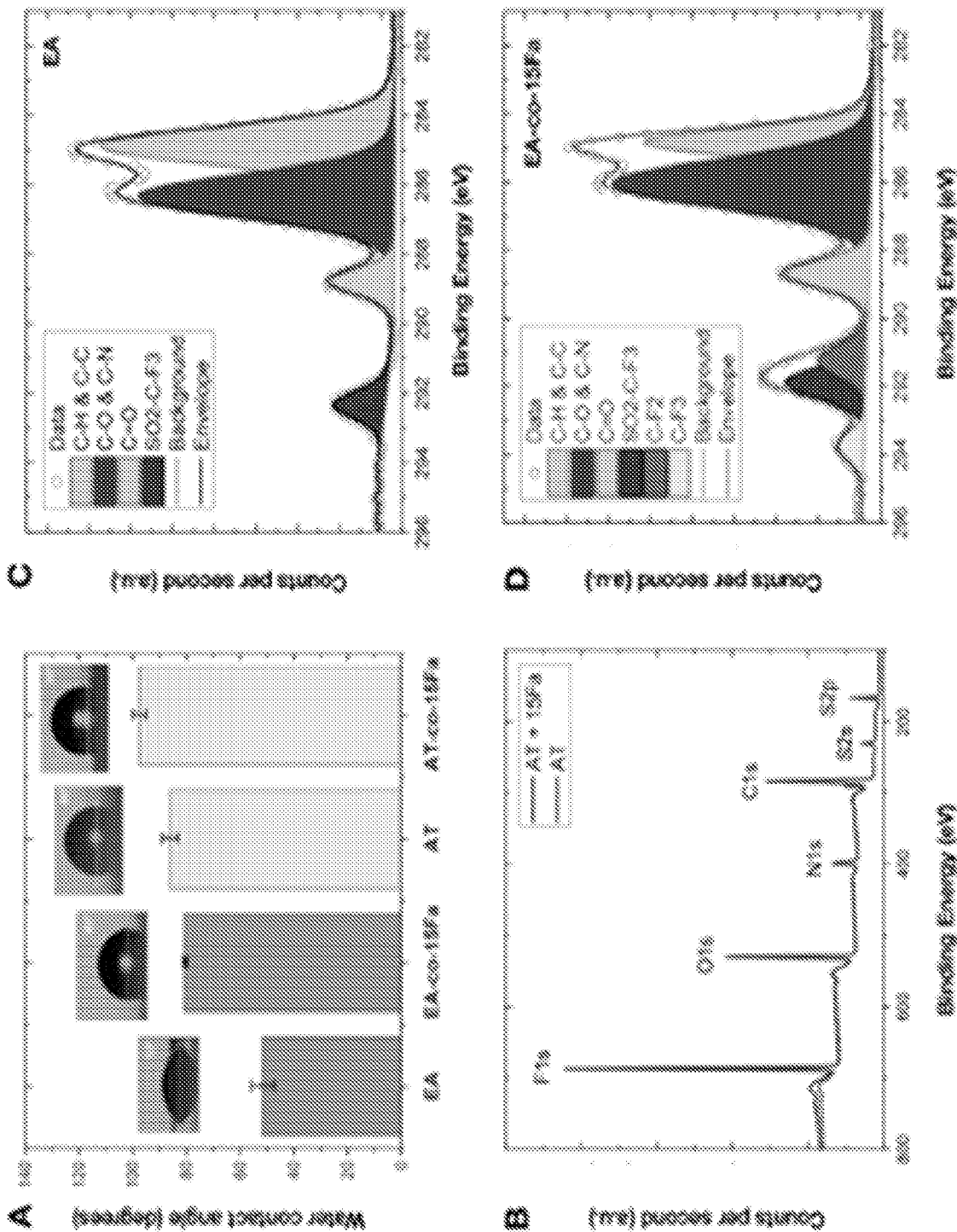


FIG. 28

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2024/042718

A. CLASSIFICATION OF SUBJECT MATTERIPC: **H01B 1/12** (2023.01); **H01M 8/1032** (2023.01); **H01M 8/103** (2023.01); **H01M 8/1072** (2023.01); **C09J 133/24** (2023.01)CPC: **H01B 1/122**; **H01M 8/1032**; **H01M 8/103**; **H01M 8/1072**; **C09J 133/24**

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

See Search History Document

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.
A	WO 2023/076344 A1 (META PLATFORMS TECHNOLOGIES, LLC) 04 May 2023 (04.05.2023) entire document	1-3
A	US 2022/0396672 A1 (KOREA UNIVERSITY RESEARCH AND BUSINESS FOUNDATION ET AL.) 15 December 2022 (15.12.2022) entire document	1-3
A	US 2022/0131186 A1 (FORD GLOBAL TECHNOLOGIES, LLC) 28 April 2022 (28.04.2022) entire document	1-3
X	Thomas et al. "Predicting the Electrical, Mechanical, and Geometric Contributions to Soft Electroadhesives through Fracture Mechanics" ACS Applied Materials & Interfaces. 14 June 2023 vol 15, pg. 30956-30963 pg. 30957, Figure 1, pg. 30958, right col, para 3, pg. 30962, left col, para 2, 4, Thomas-SI, pg. 2, para 3, Figure S1	1-3



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

"D" document cited by the applicant in the international application

"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

12 December 2024 (12.12.2024)

Date of mailing of the international search report

27 December 2024 (27.12.2024)

Name and mailing address of the ISA/US

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Authorized officer

KARI RODRIQUEZ

Facsimile No. 571-273-8300

Telephone No. PCT Help Desk: 571-272-4300

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:

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1.

Group I: Claims 1-3, directed to method of synthesizing a sulfonylimide ionoelastomer utilizing Sulfur (VI) Fluoride Exchange (SuFEx) click chemistry.

Group II: Claims 4-9, directed to an ionoelastomer material comprising a sulfonylimide anion.

Group III: Claims 10-16, directed to an anionic ionoelastomer having the structure listed.

Group IV: Claims 17-22, directed to a cationic ionoelastomer having the structure listed.

Group V: Claim 23, directed to an electroadhesive comprising one or both of structures listed.

The group of inventions listed above do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

Special Technical Features:

Group I includes the technical feature of a method of synthesizing a sulfonylimide ionoelastomer utilizing Sulfur (VI) Fluoride Exchange (SuFEx) click chemistry, which is not required by any other invention of Group II-V.

Group II includes the technical feature of an ionoelastomer material comprising a sulfonylimide anion, which is not required by any other invention of Group III-V.

Group III includes the technical feature of an anionic ionoelastomer having the structure listed, which is not required by any other invention of Group I-II or IV-V.

Group IV includes the technical feature of a cationic ionoelastomer having the structure listed, which is not required by any other invention of Group I-III or V.

Group V includes the technical feature of an electroadhesive comprising one or both of structures listed, which is not required by any other invention of Group I-IV.

Common Technical Features:

The inventions of Groups I-III share the technical feature of an ionoelastomer material comprising a sulfonylimide anion.

The inventions of Groups I-IV share the technical feature of an ionoelastomer material.

The inventions of Groups I, II and V share the technical feature of a material comprising a sulfonylimide anion.

These shared technical features, however, do not provide a contribution over the prior art, as being anticipated by WO 2023/076344 A1 to META PLATFORMS TECHNOLOGIES, LLC (hereinafter Meta). Meta discloses an ionoelastomer material comprising a sulfonylimide anion (para [0006]: ionoelastomer membrane comprises a crosslinked network of poly [1-(2- acryloyloxyethyl)-3-buthylimidazolium]bis(trifluoromethane) sulfonimide (AT)).

As said compound was known in the art, these cannot be considered special technical features that would otherwise unify the inventions of Groups I-V. The inventions of Group I-V thus lack unity under PCT Rule 13.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2024/042718

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

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.: **1-3**

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.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	Lee et al. "Pendent Sulfonylimide Ionic Liquid Monomers and Ionoelastomers via SuFEx Click Chemistry" Chemistry of Materials. 29 November 2023 vol 35, pg. 10030-10040 entire document	1-3