

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
21 February 2008 (21.02.2008)

PCT

(10) International Publication Number
WO 2008/021533 A2

(51) International Patent Classification:
C07C 211/01 (2006.01) C07C 233/01 (2006.01)
C07C 217/28 (2006.01)

(21) International Application Number:
PCT/US2007/018335

(22) International Filing Date: 17 August 2007 (17.08.2007)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/822,772 18 August 2006 (18.08.2006) US

(71) Applicant: THE GOVERNMENT OF THE UNITED STATES OF AMERICA, as represented by THE SECRETARY OF THE NAVY [US/US]; Naval Research Laboratory, 4555 Overlook Ave, SW, Code 1008.2, Washington, DC 20375 (US).

(72) Inventors: RICKS-LASKOSKI, Holly, L.; 9207 Setter Place, Springfield, VA 22153 (US). SNOW, Arthur, W.; 706 S. Pitt St., Alexandria, VA 22314 (US).

(74) Agent: KARASEK, John, J.; US Naval Research Laboratory, 4555 Overlook Ave, SW, Washington, DC 20375 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— without international search report and to be republished upon receipt of that report



WO 2008/021533 A2

(54) Title: POLYMERIZABLE SULFONATE IONIC LIQUIDS AND LIQUID POLYMERS THEREFROM AND METHODS OF MAKING SAME

(57) Abstract: Disclosed is a new ionic liquid monomer salt and methods of its synthesis and polymerization. The ionic liquid monomer salt is prepared by mixing equimolar amounts of an amine, such as tris[2-(2-methoxyethoxy)-ethyl]amine and an acid functionalized polymerizable monomer, such as 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS),- which is stirred at ambient temperature until salt formation is complete. Also disclosed is a new ionic liquid polymer salts and method for making the same. The synthesis of AMPS- ammonium salt polymer is accomplished by adding 2,2'-azobisisobutyronitrile (AIBN) to the ionic liquid monomer salt and heating the homogeneous melt at 70°C for 18 hr.

5 **POLYMERIZABLE SULFONATE IONIC LIQUIDS AND LIQUID POLYMERS**
 THEREFROM AND METHODS OF MAKING SAME

 BACKGROUND OF THE INVENTION

 Ionic liquids are salts composed of cationic and anionic components whose
structures impart a sub-room temperature melting point or glass transition to the resulting
10 material. A liquid character is associated with ions that have very weak tendencies to
coordinate toward oppositely charged ions (e.g. charge delocalized or sterically shielded), with
substituents that have weak intermolecular forces (e.g. fluorocarbons, alkanes, silicones) and
with a structural symmetry that is not conducive to efficient molecular packing. Most ionic
liquids are organic salts. The cationic component is usually organic in nature (e.g. alkyl-
15 substituted ammonium, phosphonium, imidazolium and pyridinium), and the anionic
component is most often inorganic (e.g. nitrate, sulfate, thiocyanate, halide, tetrafluoroborate,
hexafluorophosphate, etc.) but may also be organic (e.g. tosylate, alkylsulfates,
fluoroalkylsulfates, alkylcarboxylates, fluoroalkylcarboxylates, etc.). These liquid materials
have unique properties (immeasurably low volatility, non-flammability, very high polarity and
20 solvating characteristics, high ionic conductivity, and a wide electrochemical potential
window). There is currently much interest in their use as solvents for a large variety of
reactions and in sampling for chemical analysis. See Zhao et al., *J. Chem. Technol. Biotechnol.*
2005, 80, 1089 and Welton, *Chem. Rev.* 1999, 99, 2071.

 A more unique form of ionic liquid is based on a system where one of the two
25 charged components is a polymer. As such, each repeat unit incorporates the same ionic site.
There are very few reports in the literature of such systems. They are mostly based on the
imidazolium ion functionalized with a polymerizable vinyl, acrylic or styryl moiety and have
the physical form of a glass or sticky rubber. Reports include imidazolium polymers. See
Washiro, et al. *Polymer*, 2004, 45, 1577; Ding, et al., *J. Poly. Sci. Part A*, 2004, 42, 5794; Tang,
30 et al. *J. Poly. Sci. Part A*, 2005, 43, 5477; and Nakajima, et al., *Polymer*, 2005, 46, 11499 and
alkali metal sulfonate polymers, see Ogihara, et al., *Electrochim. Acta*, 2004, 49, 1797 and
Binnemans, *Chem. Rev.*, 2005, 105, 4148.. These polymers are prepared from monomers
which themselves may or may not be ionic liquids. In the case of cationic imidazolium
polymers, certain imidazolium monomer ionic liquids will yield the corresponding polymer
35 ionic liquid if appropriate substitution is made on the imidazole ring; otherwise, a glassy solid

5 is obtained. An appropriate substitution relates to the addition of a sufficient number and/or sufficient size of alkyl groups to the ring. In contrast, the anionic-form of a polymer ionic liquid has yet to be prepared directly from its analogous monomer ionic liquid. For instance, the high melting sulfonate monomer solid (usually an alkali metal salt) is first polymerized in solution followed by substitution with an appropriate cationic counter ion. Solvent removal is
10 necessary to generate the anionic polymer liquid, still retaining the alkali metal ion.

Polymerizable ionic liquids and their actuation in an electric field are a combination of material and properties with unique potential to display structural and fluid dynamics above that found for small molecule ionic liquids. Small molecule ionic liquids are generally monovalent organic salts with melting points or glass transitions below room
15 temperature. They derive their liquid character from a selection of ionic structures which have very weak tendencies to coordinate with oppositely charged ions, low intermolecular forces and low symmetry. Their properties (immeasurably low volatility, non-flammability, very high polarity and solvating characteristics, high ionic conductivity, and a wide electrochemical potential window) are of substantial interest particularly with regard to applications as green
20 solvents, analytical extraction solvents, and electrochemical supporting media. Very recently it has been reported that water immiscible ionic liquids display significant electrowetting characteristics with an interesting dependence on the size of the cationic and anionic components. See Ralston, et al., *J. Am. Chem. Soc.*, 2006, 126, 3098. Ionic liquids themselves provide an opportunity of producing a more stable actuating medium, eliminating
25 such issues as solvent evaporation and degradation due to electrolysis, typically found in aqueous based electric field induced actuators.

In an ionic liquid polymer system the cationic or anionic centers are constrained to repeat units in the polymer chain. As such, any molecular flow or diffusion requires a concerted motion of as many ionic centers as there are charged repeat units in the polymer
30 chain. When subjected to an electric field, a polymeric system may respond in an enhanced or retarded manner relative to a small molecule ionic liquid, depending on whether the covalent linkage of cationic or anionic repeat units responds as a more highly charged single molecule or whether its macromolecular size inhibits molecular motion needed for a response.

5 lightly crosslinked, form very easily deformed viscoelastic solids. The acid functionality is selected as one having a strong acidity and one that is readily attached to polymerizable monomers. The sulfonic acid is particularly attractive although phosphoryl or carboxylic acids could also be made to serve this function. Functionalization of an acid group onto a polymerizable monomer such as a styrene, acrylate, olefin, vinyl ether, or acrylamide results in
10 a relatively high temperature melting monomer. The 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) monomer, used in the example, has a 192 °C melting point. Other commercially available monomers appropriate for this invention would include styrene sulfonic acid and vinyl sulfonic acid. Sulfonic acid functionalized monomers are the preferred class acid functionalized monomer with the AMPS monomer being the most preferred.

15 An organic base which has a very low melting point or glass temperature is selected so that it will depress the corresponding melting point or glass transition of the salt it forms with the acid monomer to an extent that its liquid range extends well below room temperature. For example, the organic base tris[2-(2-methoxyethoxy)-ethyl]amine, there are two oxyethylene groups in each amine substituent. These substituents cause the amine to have a very low glass
20 transition, -104 °C, and it is this low glass transition that causes the salt it forms with the AMPS monomer to also to have a low glass transition, -57 °C. Other amines with similar characteristics (e.g. different numbers or mixed numbers of oxyethylene units) or with different substituents also correlating with low glass transitions (e.g. dimethylsiloxane and fluoromethylene) could work comparably. The amine base is the preferred organic base with
25 the oxyethylene functionalized tertiary amine base being the most preferred. A physical mixing of the sulfonic acid functionalized monomer with the amine base generates the ionic liquid monomer salt which is then polymerized to form the corresponding ionic liquid polymer salt. Although not required, addition of a small amount of volatile solvent will promote a more rapid dissolution of the sulfonic acid functionalized monomer in the amine base; including, but
30 not limited to methanol and ethylacetate.

A small quantity of polymerization catalyst is added to ionic liquid monomer salt to effect this transformation. The preferred catalysts are those that initiate free radical polymerization, and those that have high initiator efficiencies and solubility in the ionic liquid monomer salt are the most preferred. In cases where initiators need solubility, enhancement a
35 small quantity of volatile, readily removable solvent such as methanol or ethyl acetate can be used to disperse the initiator in the monomer melt. The quantity of catalyst and the

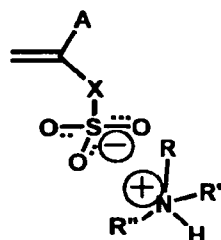
5 polymerization conditions used vary according to the specific characteristics of the catalyst and
polymer molecular weight desired. A preferred catalyst, such as 2,2'-azobisisobutyronitrile,
will typically be used in a quantity corresponding to a range of monomer:initiator ratio range
of 50:1 to 1000:1 and under of temperature and reaction conditions of 50 to 110 °C and 3 to 24
hours respectively. An important feature of the monomer salt and of the ionic liquid polymer
10 product is that they be a homogeneous melt throughout all stages of polymerization
conversion. This feature results in the polymerization approaching quantitative conversions
without an added solvent which would have to be subsequently separated. That the polymer
product is also an ionic liquid qualifies it for unique electric field driven actuations such as
physical shape changes, spreading on surfaces and droplet movement.

15 Provided are a composition of matter identified as an ionic liquid polymer salt,
composed of an organic sulfonate repeat unit and a cationic organic counter ion and a general
synthetic procedures for preparation of this class of compounds from ionic liquid monomers.
Interest in such compositions of matter is driven primarily by electric field actuations in the
form of electrowetting or Maxwell stress deformation of such materials. More specifically, an
20 ionic liquid polymer system wherein a low molecular weight counter ion promotes an ionic
liquid character in both the monomer salts and polymer salts and an observation of
electrowetting where the polymer salt displays a distinctive effect relative to that for the
monomer salt is disclosed. Disclosed is the preparation of a ionic liquid monomer salt, its
solvent-free or solvent-assisted polymerization to the corresponding ionic liquid polymer salt,
25 and an electrowetting wetting property that exceeds that of low molecular weight ionic liquids.

This new composition of mater is prepared utilizing a simple process; yet, retains
much versatility for property development. By virtue of having a large number of ionic
charges incorporated into a single polymer molecule which has liquid-like characteristics, this
material has the capability of a unique response to an applied electric field. Advantages and
30 new features reside in the accompanying properties and the applications they can support.
Compared with low molecular weight ionic liquids, this material is capable of a large and
polarity dependent response to an electric field. Applications that can take advantage of this
property are actuators. In electronics it could find application as a dielectric material in a
capacitor or perhaps as an electromigrating substance. Independent of the presence of an
35 electric field, there are surface application possibilities such as a primer to improve surface
wetting characteristics of low energy surface to accept paints and coatings of low polarity, as a

5 biocidal treatment for surfaces, and as an adsorbent for opposite charged polyelectrolytes and possibly simple ionic species in chromatography columns. In solution this material could conceivably be used as a phase transfer agent or as a sequester for ionic substances. As a precursor to a polymer with different mechanical properties than a liquid, it could be converted to an elastomer or a flexible plastic and still retain its high ionic character.

10 In one embodiment, an ionic liquid monomer salt is provided, having the general formula:



15 wherein:

A represents H or CH₃;

X represents -COY-, -*p*-C₆H₄-, -*o*-C₆H₄-, -*m*-C₆H₄-, -O-, or -CH₂-;

Y represents: -O(CH₂)_n-, where n = 1 to 4, or

-(OCH₂CH₂)_n where n = 1 to 6, or

20 -NHCH(CH₃)-, -NHC(CH₃)₂-, -N(C₁₂H₂₅)CH₂CH₂-,

-NHC(CH₃)CH₂-, or -NHCH(C₆H₅)CH₂-,

wherein each R, R', and R'' can be the same group, or R can differ from R', while R' is the same group as R'', or R, R', and R'' may be all different groups; wherein

R, R', R'' each independently represented by one of the following:

25 -H, or

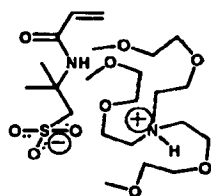
-(CH₂)_nCH₃ where n = 1 to 12, or

[-(CH₂CH₂O)_nCH₃ where n = 1 to 4, or

5 $-(\text{CH}_2)_3(\text{Si}(\text{CH}_3)_2\text{O})_n\text{CH}_3$ where $n = 1$ to 6, or

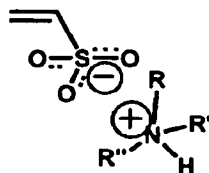
$-(\text{CF}_2)_n\text{CF}_3$, $-\text{CH}_2(\text{CF}_2)_n\text{CF}_3$ where $n = 1$ to 8.

Another embodiment of an ionic liquid monomer salt is presented, having the formula:



10

In another embodiment, an ionic liquid monomer salt is presented, having the formula:



15

wherein each R, R', and R'' can be the same group, or R can differ from R', while R' is the same group as R'', or R, R', and R'' may be all different groups; wherein

R, R', R'' each independently represented by one of the following:

-H, or

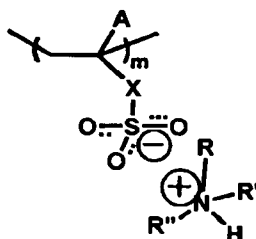
20 $-(\text{CH}_2)_n\text{CH}_3$ where $n = 1$ to 12, or

$-(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3$ where $n = 1$ to 4, or

$-(\text{CH}_2)_3(\text{Si}(\text{CH}_3)_2\text{O})_n\text{CH}_3$ where $n = 1$ to 6, or

$-(\text{CF}_2)_n\text{CF}_3$, $-\text{CH}_2(\text{CF}_2)_n\text{CF}_3$ where $n = 1$ to 8.

5 In another embodiment, an ionic liquid polymer salt is presented, having the formula:



10 wherein $m > 1$;

A represents H or CH₃;

X represents -COY-, -*p*-C₆H₄-, -*o*-C₆H₄-, -*m*-C₆H₄-, -O-, or -CH₂-;

Y represents:

-O(CH₂)_n- where $n = 1$ to 4, or

15 -(OCH₂CH₂)_n where $n = 1$ to 6, or

-NHCH(CH₃)-, -NHC(CH₃)₂-, -N(C₁₂H₂₅)CH₂CH₂-

-NHC(CH₃)CH₂-, or -NHCH(C₆H₅)CH₂-,

wherein each R, R', and R'' can be the same group, or R can differ from R', while R' is the same group as R'', or R, R', and R'' may be all different groups; wherein

20 R, R', R'' each independently represented by one of the following:

-H, or

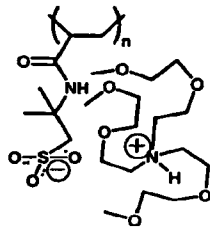
-(CH₂)_nCH₃ where $n = 1$ to 12, or

-(CH₂CH₂O)_nCH₃ where $n = 1$ to 4, or

-(CH)₃(Si(CH₃)₂O)_nCH₃ where $n = 1$ to 6, or

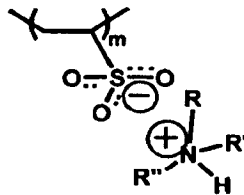
25 -(CF₂)_nCF₃, -CH₂(CF₂)_nCF₃ where $n = 1$ to 8.

5 In another embodiment, an ionic liquid polymer salt is presented, having the formula:



10

In another embodiment, an ionic liquid polymer salt is presented, having the formula:



15

wherein $m > 1$;

wherein each R, R', and R'' can be the same group, or R can differ from R', while R' is the same group as R'', or R, R', and R'' may be all different groups; wherein

20 R, R', R'' each independently represented by one of the following:

-H, or

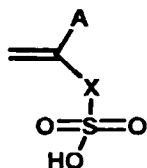
$-(\text{CH}_2)_n\text{CH}_3$ where $n = 1$ to 12,

$-(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3$ where $n = 1$ to 4,

$-(\text{CH})_3(\text{Si}(\text{CH}_3)_2\text{O})_n\text{CH}_3$ where $n = 1$ to 6,

25 $-(\text{CF}_2)_n\text{CF}_3$, $-\text{CH}_2(\text{CF}_2)_n\text{CF}_3$ where $n = 1$ to 8.

5 In another embodiment, a method for making an ionic liquid monomer salt is presented. An equimolar amount of a sulfonic acid functionalized monomer having the general formula:



10 wherein A represents H or CH₃,

X represents -COY-, -*p*-C₆H₄-, -*o*-C₆H₄-, -*m*-C₆H₄-, -O-, or -CH₂-,

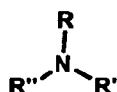
Y represents -O(CH₂)_n- where n = 1 to 4, or

- (OCH₂CH₂)_n where n = 1 to 6, or

-NHCH(CH₃)-, -NHC(CH₃)₂-, -N(C₁₂H₂₅)CH₂CH₂-,

15 -NHC(CH₃)CH₂-, or -NHCH(C₆H₅)CH₂-,

is mixed with an organic amine base having the general formula:



20 wherein each R, R', and R'' can be the same group, or R can differ from R', while R' is the same group as R'', or R, R', and R'' may be all different groups; wherein

R, R', R'' each independently represented by one of the following:

-H, or

-(CH₂)_nCH₃ where n = 1 to 12, or

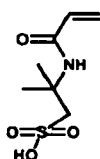
25 -(CH₂CH₂O)_nCH₃ where n = 1 to 4, or

-(CH)₃(Si(CH₃)₂O)_nCH₃ where n = 1 to 6, or

5 $-(CF_2)_nCF_3$, $-CH_2(CF_2)_nCF_3$ where $n = 1$ to 8.

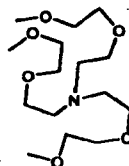
The mixture is stirred under an inert atmosphere until the sulfonic acid functionalized monomer is dissolved, wherein the dissolution completes formation of the ionic liquid monomer salt.

10 In another embodiment, a method for making an ionic liquid monomer salt is presented. An equimolar amount of a sulfonic acid functionalized monomer having the formula:



is mixed with an organic amine base having the formula:

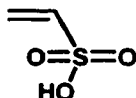
15



20

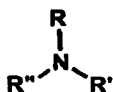
The mixture is stirred under an inert atmosphere until the sulfonic acid functionalized monomer is dissolved, wherein the dissolution completes formation of the ionic liquid monomer salt. Optionally, the ionic liquid monomer salt is in solvent methanol.

In another embodiment, a method for making an ionic liquid monomer salt is presented. An equimolar amount of a sulfonic acid functionalized monomer having the formula:



25

is mixed with the organic amine base having the general formula:



5 wherein each R, R', and R'' can be the same group, or R can differ from R', while R' is the same group as R'', or R, R', and R'' may be all different groups; wherein

R, R', R'' each independently represented by one of the following:

-H, or

-(CH₂)_nCH₃ where n = 1 to 12, or

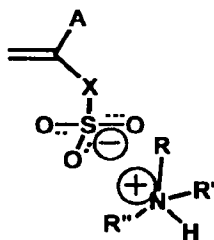
10 -(CH₂CH₂O)_nCH₃ where n = 1 to 4, or

-(CH)₃(Si(CH₃)₂O)_nCH₃ where n = 1 to 6, or

-(CF₂)_nCF₃, -CH₂(CF₂)_nCF₃ where n = 1 to 8.

15 The mixture is stirred under an inert atmosphere until said sulfonic acid functionalized monomer is dissolved, wherein the dissolution completes formation of the ionic liquid monomer salt.

In another embodiment, a method for making ionic liquid polymer salts is presented. A free radical polymerization catalyst is added to an ionic liquid monomer salt having the general formula:



wherein A represents H or CH₃

X represents -COY-, -*p*-C₆H₄-, -*o*-C₆H₄-, -*m*-C₆H₄-, -O-, or -CH₂-

Y represents -O(CH₂)_n- where n = 1 to 4, or

25 -(OCH₂CH₂)_n where n = 1 to 6,

-NHCH(CH₃)-, -NHC(CH₃)₂-, -N(C₁₂H₂₅)CH₂CH₂-,

-NHC(CH₃)CH₂-, or -NHCH(C₆H₅)CH₂-,

5 wherein each R, R', and R'' can be the same group, or R can differ from R', while R' is the same group as R'', or R, R', and R'' may be all different groups; wherein

R, R', R'' each independently represented by one of the following:

-H, or

-(CH₂)_nCH₃ where n = 1 to 12, or

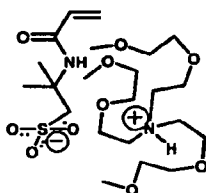
10 -(CH₂CH₂O)_nCH₃ where n = 1 to 4,

-(CH)₃(Si(CH₃)₂O)_nCH₃ where n = 1 to 6,

-(CF₂)_nCF₃, -CH₂(CF₂)_nCF₃ where n = 1 to 8

The mixture is stirred under an inert atmosphere with application catalyst-specific polymerization conditions.

15 In another embodiment, a method for making ionic liquid polymer salts is presented. A free radical polymerization catalyst is added to an ionic liquid monomer salt having the formula:

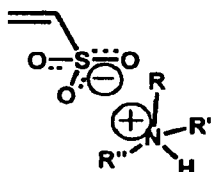


20

The mixture is stirred under an inert atmosphere with application catalyst-specific polymerization conditions. Optionally, the free radical polymerization can be conducted in solvent methanol. Preferably, the free radical polymerization catalyst is 2,2'-azobisisobutyronitrile and the monomer to free radical polymerization catalyst ratio is 100:1.

25 The inert atmosphere is preferably a nitrogen atmosphere. The catalyst-specific polymerization conditions include heating the mixture to 70 °C and stirring and heating steps are conducted for about 18 hours.

5 In another embodiment, a method for making ionic liquid polymer salts is presented. A free radical polymerization catalyst to said ionic liquid monomer salt claim 3 having the general formula:



10

wherein each R, R', and R'' can be the same group, or R can differ from R', while R' is the same group as R'', or R, R', and R'' may be all different groups; wherein

R, R', R'' each independently represented by one of the following:

-H, or

15

-(CH₂)_nCH₃ where n = 1 to 12,

-(CH₂CH₂O)_nCH₃ where n = 1 to 4,

-(CH₂)₃(Si(CH₃)₂O)_nCH₃ where n = 1 to 6,

-(CF₂)_nCF₃, -CH₂(CF₂)_nCF₃ where n = 1 to 8.

20

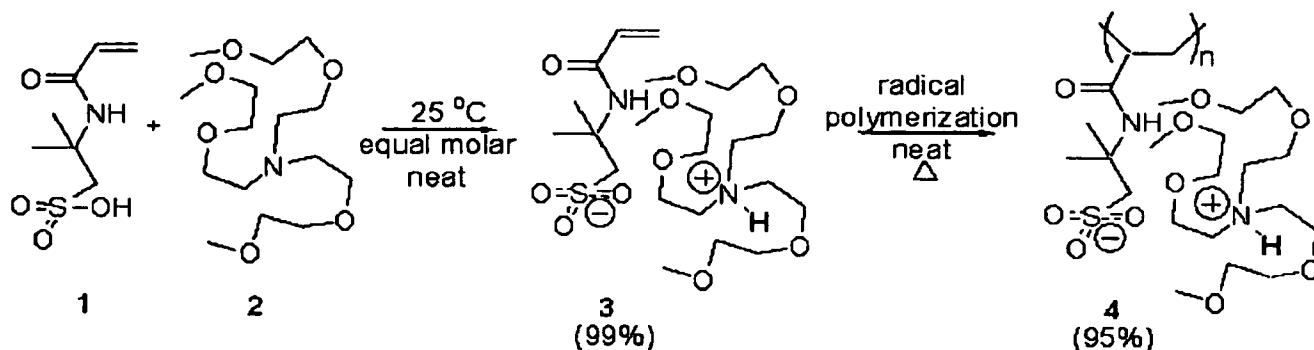
The mixture is stirred under an inert atmosphere with application catalyst-specific polymerization conditions.

25

This invention converts 1:1 mixture of a monomer having a polymerizable carbon-carbon double bond and a sulfonic acid or sulfonate group (such as 2-Acrylamido-2-methyl-1-propanesulfonic acid, AMPS, mp 192 °C) with an amine base (such as tris[2-(2-methoxyethoxy)-ethyl]amine) to an ionic liquid monomer salt that is polymerized to an ionic liquid polymer salt in the absence or presence of solvent. To convert the sulfonic acid monomer to a salt with a melting point or glass transition below room temperature, it complexed with an amine is added. This amine is functionalized with large flexible substituent structures that depress a salt solidification temperature and inhibit coordination between oppositely charged species. Typical amine substituent structures involve oxyethylene oligomers, silicone oligomers, and fluorocarbon chains.

30

5 The synthesis is a two-step procedure as depicted below using the AMPS monomer and a tertiary amine with oxyethylene appendages of seven atoms as an example. Both steps proceed in remarkably good yields. The synthesis is detailed below in Scheme 1:



Scheme 1 shows the synthesis commencing with the formation of the ammonium salt, 3. AMPS-oxyethylene ammonium salt monomer, 3, is synthesized by combining 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS), 1, with an equal molar quantity of freshly distilled tris[2-(2-methoxyethoxy)ethyl]amine, 2, under an inert atmosphere, including but not limited to nitrogen or argon. The mixture is stirred for 8 hours at ambient temperature until the AMPS crystals are completely dissolved and converted into the monomer salt, 3, a slightly yellow viscous clear liquid. With no further purification necessary, a radical initiator such as 2,2'-azobisisobutyronitrile (AIBN) is added to the reaction flask utilizing air-free handling techniques under an inert atmosphere. The reaction mixture is heated to 70° C and reacted for 18 hrs. The transparent amber ionic liquid polymer salt, 4, may be used as is or further purified to remove a small percentage (<5%) of unreacted monomer by dissolving in acetone and reprecipitating in cold diethyl ether. This precipitate is collected by cold suction filtration and upon warming, becomes a tacky transparent yellow liquid. The glass transition temperatures of the oxyethylene amine, 2, AMPS monomer salt, 3, and polymer ionic liquid, 4, are -104, -57, and -49 °C respectively. Infrared, and NMR spectral analyses are consistent with the polymer repeat unit structure. The intrinsic viscosity value of 0.3 is indicative of a low, but significant molecular weight. Electrowetting characterization displays a reversible contact angle change from 75° to 30° with an applied voltage change from 0 to 157 volts. This change is larger than that of the monomer salt or of commercial ionic liquids. Those skilled in the art would understand that other radical initiators can be used, and the time and temperature of the reaction would vary depending upon the initiator chosen.

5 The properties of this ionic liquid polymer salt can be tuned by varying the identity, size and symmetry of the substituents on the amine counter ion or by varying the structure and function of the sulfonated monomer; such that, the monomer itself could go from being a repeat unit to a branch point to a crosslink.

10 These and other features and advantages of the present invention will be presented in more detail in the following specification of the invention and the accompanying figures, which illustrate, by way of multiple examples, the principles of the invention.

15 Example: The formation of the ionic liquid monomer salt and its polymerization is depicted in Scheme 1. The polymerizable component is the 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) monomer which is a crystalline compound with a 192 °C melting point. It is converted to a liquid ammonium salt by addition of an equimolar quantity of tris[2-(2-methoxyethoxy)-ethyl]amine. This tertiary amine was selected as one that would solvate the AMPS monomer without the need of a solvent and one whose oxyethylene substituents would shield the protonated ionic center from coordinating with the sulfonated anion, thereby depressing the melting point or glass transition to a very low temperature.

20 The glass transitions of the free amine 2 (-104 °C) and of the AMPS-ammonium salt 3 (-57 °C) presented in the differential scanning calorimetry (DSC) thermogram in FIG. 1 demonstrate the remarkable capability of the oxyethylene substituted amine to extend the liquid range of a salt to low temperatures. After the liquid ammonium sulfonate monomer formation is complete, a free radical initiator (2,2'-azobisisobutyronitrile, AIBN) is added and reacted at 70 °C. The monomer conversion is 95%, and the product is a clear acetone-soluble viscous liquid. The spectroscopic characterization (IR, ¹H and ¹³C NMR) is consistent with polymer structure depicted in Scheme 1. The molecular weight is low but significant as indicated by an intrinsic viscosity measurement of 0.30 which is uncorrected for an observed polyelectrolyte coil expansion effect. The glass transition temperature of ionic liquid polymer 4 is -47 °C as depicted in the FIG. 1 thermogram. This is a remarkably modest increase from that of the unpolymerized monomer salt.

30 Electrowetting is an electrostatically driven surface effect where a liquid droplet's spreading on a hydrophobic surface is modulated by application of a voltage to the droplet and an underlying conducting substrate. A schematic of this effect is illustrated in FIG. 2. The

5 droplet rests on a very thin low-dielectric insulating film (Teflon AF) which is supported on a conducting substrate and is contacted at the top by a very fine wire contact. Application of a voltage builds up a layer of charge on both sides of the interface with the dielectric film and decreases the interfacial energy.

The observed response is a spreading of the droplet and a changing of its curvature.
 10 The dependence of the droplet's contact angle, θ , on the applied voltage, V , is described by the Young-Lippmann equation as follows (Equation 1):

$$\cos \theta = \cos \theta_0 + \frac{1}{2\gamma} CV^2 = \cos \theta_0 + \frac{\epsilon\epsilon_0}{2\gamma} V^2$$

where θ_0 is the contact angle at zero voltage, C is the capacitance per unit area, γ is
 15 the surface tension of the liquid, ϵ is the permittivity of the insulating dielectric, ϵ_0 is the electric constant and t is the thickness of the dielectric layer. Surface tension measurements of the monomer 3 and polymer 4 are 38.1 and 47.0 mJ/m² respectively. The contact angle measurements of the AMPS-ammonium salt monomer 3 and polymer 4 as a function of applied DC voltage are shown in Figure 3, and photographs of the ionic liquid polymer droplet
 20 at zero and maximum applied voltages in Figure 4 show a substantial contact angle change.

A parabolic best fit of the experimental contact angles to the voltage dependence of Equation 1 is represented by the continuous line. A parabolic best fit of the experimental contact angles to the voltage dependence of Equation 1 is represented by the continuous line in FIG. 3. Separate best fits were made for the negative and positive voltage regions of the
 25 curves. The electrowetting curve for the AMPS-ammonium sulfonate monomer, 3, is similar to those reported for small molecule ionic liquids in both magnitude and shape. No evolution of gas bubbles, discoloration, or degradation was observed between 0 and 157 V.

A monomer vs. polymer comparison of contact angle data for AMPS-ammonium salt system presents an interesting contrast. The polymer displays a larger contact angle at zero
 30 voltage; a similar magnitude of contact angle change over the voltage range; a departure from the Young-Lippmann equation at a lower voltage; and a dissymmetry between the negative and the positive voltage sections of the electrowetting curve.

5 These observed differences in electrowetting behavior correlate with the higher
surface tension of the polymer and with the polyelectrolyte molecular structure. When no
voltage is applied, the greater surface tension of the polymer is clearly consistent with the
larger contact angle observed. When a voltage is applied, an electric field is concentrated
10 across the Teflon AF interface and an ionic double layer of charge forms in the liquid at this
interface. This decreases the surface tension at the solid-liquid interface and results in
spreading of the liquid on the charged surface. A depiction is illustrated in FIG. 2. The
polymer differs from the monomer in that one of the charged components is a small cationic
molecule and the other is a large anionic polyelectrolyte. When the substrate is charged, an
15 oppositely charged component of the ionic liquid is adsorbed at the Teflon AF-ionic liquid
interface. On reversal of polarity, a grouping of small molecule ions exchanges position with
the polyelectrolyte. This disparity of molecular size correlates with the dissymmetry observed
between the positive and negative sides of the electrowetting curve in FIG. 3.

 All ¹H-NMR spectroscopy were obtained using a Bruker AC-300 spectrometer
using d6-DMSO as solvent. FTIR spectra were obtained using a Nicolet Magna-IR 750
20 spectrometer with sample supported on a NaCl plate under a nitrogen purge of 40 cm³min⁻¹.
All differential scanning calorimetric (DSC) analysis were performed on a TA Instruments
DSC Q100 Modulated thermal analyzer at a heating rate of 10 °C min⁻¹ and a nitrogen purge
of 25 cm³min⁻¹.

 Synthesis of AMPS-ammonium salt monomer. A nitrogen purged 50 ml schlenk
25 flask was charged with freshly distilled tris[2-(2-methoxyethoxy)-ethyl]amine (1.69 g, 5.24
mmol) and 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) (1.09 g, 5.24 mmol) and
stirred at ambient temperature for 8 hr or until completely dissolved. Total dissolution
completes formation of the AMPS-ammonium salt monomer as a transparent light amber oil in
a 99% yield which was used immediately without further purification.

30 Synthesis of AMPS-ammonium salt polymer. To the prepared monomer was
added 2,2'-azobisisobutyronitrile (AIBN) (6.0 mg, 0.04 mmol) under a nitrogen purge. The
reaction flask was then sealed, allowed to vent to a bubbler, and heated to 70 °C for 18 hr.
Upon cooling to ambient temperature, the transparent dark amber mixture was dissolved in
acetone (10 ml) and precipitated as white flocculants into cold diethyl ether (50 ml) (dry
35 ice/acetone bath) and quickly collected in a dry ice cooled Buchner funnel via suction

5 filtration. As the material warmed, the flocculants became a transparent amber oil which was then dried under vacuum to remove any residual solvents to yield polymer (95%).

Electrowetting actuation setup and experimentation. Actuation was measured using the following setup as illustrated in Figure 2: a VCA OptimaXE commercial contact angle instrument fitted with a stage was used to capture individual data points at various DC
10 voltages. An ITO coated slide, was spin-coated with Teflon AF (DuPont) at 2000 rpm for 30 seconds and heat treated in an oven at 80 °C for 18 hr which produced an insulating film with a thickness of 1.29 μm (determined by a KLA Profilometer) with an intrinsic roughness on the order of 0.5 μm . The ITO slide was coupled to an electrode in an area which was absent of Teflon AF and a Pt wire with a diameter of 0.25 mm was used as the corresponding top
15 electrode. Small aliquots of ionic liquid monomer (3) or polymer (4) (~ 50 μl) were placed onto the ITO/Teflon AF coated slide in droplet form. The Pt electrode was inserted into the droplet and snapshots were taken at ~8 V intervals from 0 to 157 V (DC) with polarities of the electrodes being reversed to obtain measurements between -157 and 0 V (DC) with respect to the ITO electrode. Contact angle software, from AST Products, Inc. VCA Version 1.90.0.9 for
20 Windows, calculated left and right advancing angles for both the AMPS oxyethylene ammonium salt monomer 3 and polymer 4, which are plotted over a voltage range in Figure 3. The voltage polarity corresponds to the ITO electrode. No discoloration, etching, or insoluble residue was resultant from these experiments involving ionic liquid 3 and 4 nor was it observed on the ITO surface itself. Once a voltage of 157 was reached (for either polarity), receding
25 contact angles were recorded as the voltage was slowly decreased back to 0.

Surface Tension Measurements: Surface tensions for both the monomer (3) and polymer (4) were measured at 23 °C by the pendant drop method using the VCA contact angle instrument and Pendant Analysis Software (Version 2.22) and found to be 38.1 and 47.0
30 mJ/m², respectively; higher than those previously reported for other ionic liquids. To further address this issue, the surface tensions of structurally relevant compounds are considered. The surface tension of the free amine (tris[2-(2-methoxyethoxy)-ethyl]amine, 2 was measured at 32.8 mJ/m² (23 °C). As a representative of a liquid organic sulfonic acid, methane sulfonic acid has a surface tension of 50.2 mJ/m² [Lange's Handbook of Chemistry, 15th Ed., J. A. Dean, 1999]. A complex formed between these two components would probably have an
35 intermediate value assuming little contribution from the ammonium sulfonate salt formation.

5 As such this ammonium-hydrogen-sulfonate ionic liquid is somewhat different from other
ionic liquids including those for which surface tensions have been reported in that significant
hydrogen bonding is incorporated into it. We would speculate that the hydrogen bonding
would elevate the surface tension. We would further speculate that transformation of the
AMPS-ammonium salt monomer 3 to polymer 4 would enhance the density of the hydrogen
10 bonding and further elevate the surface tension as observed. Hence, we speculate that a more
dense structure of the polymer and hydrogen bonding is consistent with an increased surface
tension.

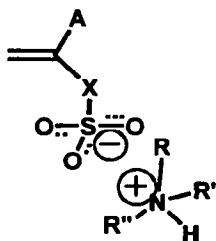
This example represents synthesis and electrowetting of individual members of
new ionic liquid monomer and polymer systems. The uniqueness of the oxyethylene amine
15 formation of the ammonium cationic species contributes to both the ionic and liquid nature of
the monomer and polymer. Even more remarkable is the ability of this polymer to maintain its
liquid nature after polymerization and wet a substrate, showing preference for one polarity
based upon the makeup of the ionic backbone of the polymer formed.

Obviously, many modifications and variations of the present invention are possible
20 in light of the above teachings. It is therefore to be understood that, within the scope of the
appended claims, the invention may be practiced otherwise than as specifically described. .

5 CLAIMS

What is claimed is:

1. An ionic liquid monomer salt having the general formula:



wherein A = H or CH₃;

X = -COY-, -*p*-C₆H₄-, -*o*-C₆H₄-, -*m*-C₆H₄-, -O-, or -CH₂-;

Y = -O(CH₂)_n- where n = 1 to 4, or

-(OCH₂CH₂)_n where n = 1 to 6, or

-NHCH(CH₃)-, -NHC(CH₃)₂-, -N(C₁₂H₂₅)CH₂CH₂-,

-NHC(CH₃)CH₂-, or -NHCH(C₆H₅)CH₂-,

wherein R = R' = R''; R ≠ R' = R''; R ≠ R' ≠ R''; and

wherein R, R', and/or R'' = -H, or

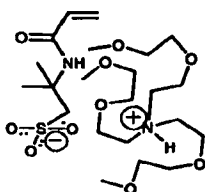
-(CH₂)_nCH₃ where n = 1 to 12, or

-(CH₂CH₂O)_nCH₃ where n = 1 to 4, or

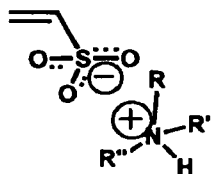
-(CH₂)₃(Si(CH₃)₂O)_nCH₃ where n = 1 to 6, or

-(CF₂)_nCF₃, -CH₂(CF₂)_nCF₃ where n = 1 to 8.

2. An ionic liquid monomer salt having the formula:



5 3. An ionic liquid monomer salt having the formula:



wherein $R = R' = R''$; $R \neq R' = R''$; $R \neq R' \neq R''$; and

10 wherein R, R', and/or R'' = -H, or

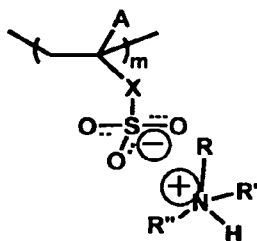
$-(\text{CH}_2)_n\text{CH}_3$ where $n = 1$ to 12, or

$-(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3$ where $n = 1$ to 4, or

$-(\text{CH}_2)_3(\text{Si}(\text{CH}_3)_2\text{O})_n\text{CH}_3$ where $n = 1$ to 6, or

$-(\text{CF}_2)_n\text{CF}_3$, $-\text{CH}_2(\text{CF}_2)_n\text{CF}_3$ where $n = 1$ to 8.

15 4. An ionic liquid polymer salt having the general formula:



wherein $m > 1$;

20 A = H or CH_3 ;

X = $-\text{COY}-$, $-p\text{-C}_6\text{H}_4-$, $-o\text{-C}_6\text{H}_4-$, $-m\text{-C}_6\text{H}_4-$, $-\text{O}-$, or $-\text{CH}_2-$;

Y = $-\text{O}(\text{CH}_2)_n-$ where $n = 1$ to 4, or

$-(\text{OCH}_2\text{CH}_2)_n$ where $n = 1$ to 6, or

$-\text{NHCH}(\text{CH}_3)-$, $-\text{NHC}(\text{CH}_3)_2-$, $-\text{N}(\text{C}_{12}\text{H}_{25})\text{CH}_2\text{CH}_2-$,

25 $-\text{NHC}(\text{CH}_3)\text{CH}_2-$, or $-\text{NHCH}(\text{C}_6\text{H}_5)\text{CH}_2-$;

5 wherein $R = R' = R''$; $R \neq R' = R''$; $R \neq R' \neq R''$; and

wherein R , R' , and/or $R'' = -H$, or

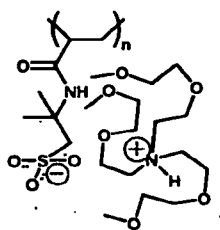
$-(CH_2)_nCH_3$ where $n = 1$ to 12 , or

$-(CH_2CH_2O)_nCH_3$ where $n = 1$ to 4 , or

$-(CH)_3(Si(CH_3)_2O)_nCH_3$ where $n = 1$ to 6 , or

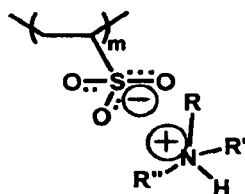
10 $-(CF_2)_nCF_3$, $-CH_2(CF_2)_nCF_3$ where $n = 1$ to 8 .

5. An ionic liquid polymer salt having the formula:



15

6. An ionic liquid polymer salt having the formula:



20 wherein $m > 1$;

wherein $R = R' = R''$; $R \neq R' = R''$; $R \neq R' \neq R''$; and

wherein R , R' , and/or $R'' = -H$, or

$-(CH_2)_nCH_3$ where $n = 1$ to 12 , or

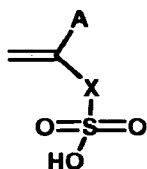
$-(CH_2CH_2O)_nCH_3$ where $n = 1$ to 4 , or

25 $-(CH)_3(Si(CH_3)_2O)_nCH_3$ where $n = 1$ to 6 , or

5 $-(CF_2)_nCF_3, -CH_2(CF_2)_nCF_3$ where $n = 1$ to 8 .

7. A method for making an ionic liquid monomer salt comprising:

mixing an equimolar amount of a sulfonic acid functionalized monomer having the general formula:



wherein $A = H$ or CH_3 ;

$X = -COY-, -p-C_6H_4-, -o-C_6H_4-, -m-C_6H_4-, -O-,$ or $-CH_2-$;

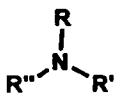
$Y = -O(CH_2)_n-$ where $n = 1$ to 4 , or

15 $-(OCH_2CH_2)_n$ where $n = 1$ to 6 , or

$-NHCH(CH_3)-, -NHC(CH_3)_2-, -N(C_{12}H_{25})CH_2CH_2-,$

$-NHC(CH_3)CH_2-,$ or $-NHCH(C_6H_5)CH_2-$;

with an organic amine base having the general formula:



wherein $R = R' = R''; R \neq R' = R''; R \neq R' \neq R'';$

wherein $R, R',$ and/or $R'' = -H,$ or

$-(CH_2)_nCH_3$ where $n = 1$ to $12,$ or

$-(CH_2CH_2O)_nCH_3$ where $n = 1$ to $4,$ or

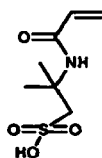
25 $-(CH)_3(Si(CH_3)_2O)_nCH_3$ where $n = 1$ to $6,$ or

5 $-(CF_2)_nCF_3$, $-CH_2(CF_2)_nCF_3$ where $n = 1$ to 8 ; and

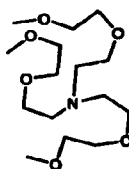
stirring said mixture under an inert atmosphere until said sulfonic acid functionalized monomer is dissolved, wherein the dissolution completes formation of the ionic liquid monomer salt.

8. A method for making an ionic liquid monomer salt comprising:

10 mixing an equimolar amount of a sulfonic acid functionalized monomer having the formula:



with an organic amine base having the formula:



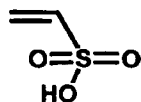
15 ; and

stirring said mixture under an inert atmosphere until said sulfonic acid functionalized monomer is dissolved, wherein the dissolution completes formation of the ionic liquid monomer salt.

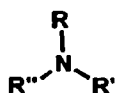
20 9. The method of claim 8 wherein said ionic liquid monomer salt is in solvent methanol.

10. A method for making an ionic liquid monomer salt comprising:

mixing an equimolar amount of a sulfonic acid functionalized monomer having the formula:



25 with the organic amine base having the general formula:



5 wherein $R = R' = R''$; $R \neq R' = R''$; $R \neq R' \neq R''$;

wherein R , R' , and/or $R'' = -H$, or

$-(CH_2)_nCH_3$ where $n = 1$ to 12 , or

$-(CH_2CH_2O)_nCH_3$ where $n = 1$ to 4 , or

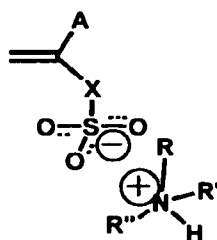
$-(CH)_3(Si(CH_3)_2O)_nCH_3$ where $n = 1$ to 6 , or

10 $-(CF_2)_nCF_3$, $-CH_2(CF_2)_nCF_3$ where $n = 1$ to 8 ; and

stirring said mixture under an inert atmosphere until said sulfonic acid functionalized monomer is dissolved, wherein the dissolution completes formation of the ionic liquid monomer salt.

15 11. A method for making an ionic liquid polymer salt comprising:

providing the ionic liquid monomer salt of claim 1 having the general formula:



20

wherein $A = H$ or CH_3 ;

$X = -COY-$, $-p-C_6H_4-$, $-o-C_6H_4-$, $-m-C_6H_4-$, $-O-$, or $-CH_2-$;

$Y = -O(CH_2)_n-$ where $n = 1$ to 4 , or

$-(OCH_2CH_2)_n$ where $n = 1$ to 6 , or

25 $-NHCH(CH_3)-$, $-NHC(CH_3)_2-$, $-N(C_{12}H_{25})CH_2CH_2-$,

5 $\text{-NHC(CH}_3\text{)CH}_2\text{-}$, or $\text{-NHCH(C}_6\text{H}_5\text{)CH}_2\text{-}$;

wherein $\text{R} = \text{R}' = \text{R}''$; $\text{R} \neq \text{R}' = \text{R}''$; $\text{R} \neq \text{R}' \neq \text{R}''$;

wherein R , R' , and/or $\text{R}'' = \text{-H}$, or

$\text{-(CH}_2\text{)}_n\text{CH}_3$ where $n = 1$ to 12 , or

$\text{-(CH}_2\text{CH}_2\text{O)}_n\text{CH}_3$ where $n = 1$ to 4 , or

10 $\text{-(CH)}_3\text{(Si(CH}_3\text{)}_2\text{O)}_n\text{CH}_3$ where $n = 1$ to 6 , or

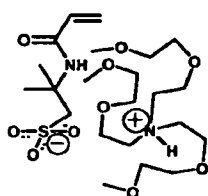
$\text{-(CF}_2\text{)}_n\text{CF}_3$, $\text{-CH}_2\text{(CF}_2\text{)}_n\text{CF}_3$ where $n = 1$ to 8 ;

adding a free radical polymerization catalyst to said ionic liquid monomer salt; and

15 stirring said mixture under an inert atmosphere with application catalyst-specific polymerization conditions.

12. A method for making an ionic liquid polymer salt comprising:

providing the ionic liquid monomer salt claim 2 having the formula:

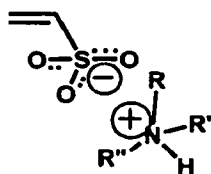


adding a free radical polymerization catalyst to said ionic liquid monomer salt;

stirring said mixture under an inert atmosphere with application catalyst-specific free radical polymerization conditions.

25 13. The method of claim 12 wherein said free radical polymerization is conducted in solvent methanol.

- 5 14. The method of claim 12 wherein said free radical polymerization catalyst is 2,2'-azobisisobutyronitrile.
15. The method of claim 12 wherein said monomer and said free radical polymerization catalyst has a ratio of 100:1.
- 10 16. The method of claim 12 wherein said inert atmosphere is a nitrogen atmosphere.
17. The method of claim 12 wherein said catalyst-specific polymerization conditions is heating said mixture to about 70 °C.
18. The method of claim 17 wherein said stirring and heating is conducted for about 18 hours.
- 15 19. A method for making an ionic liquid polymer salt comprising:
 providing the ionic liquid monomer salt claim 3 having the general formula:



20 wherein $R = R' = R''$; $R \neq R' = R''$; $R \neq R' \neq R''$;

 wherein R, R', and/or R'' = -H, or

$-(\text{CH}_2)_n\text{CH}_3$ where $n = 1$ to 12, or

$-(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3$ where $n = 1$ to 4, or

$-(\text{CH})_3(\text{Si}(\text{CH}_3)_2\text{O})_n\text{CH}_3$ where $n = 1$ to 6, or

25 $-(\text{CF}_2)_n\text{CF}_3$, $-\text{CH}_2(\text{CF}_2)_n\text{CF}_3$ where $n = 1$ to 8;

 adding a free radical polymerization catalyst to said ionic liquid monomer salt;

- 5 **stirring said mixture under an inert atmosphere with application
catalyst-specific polymerization conditions.**

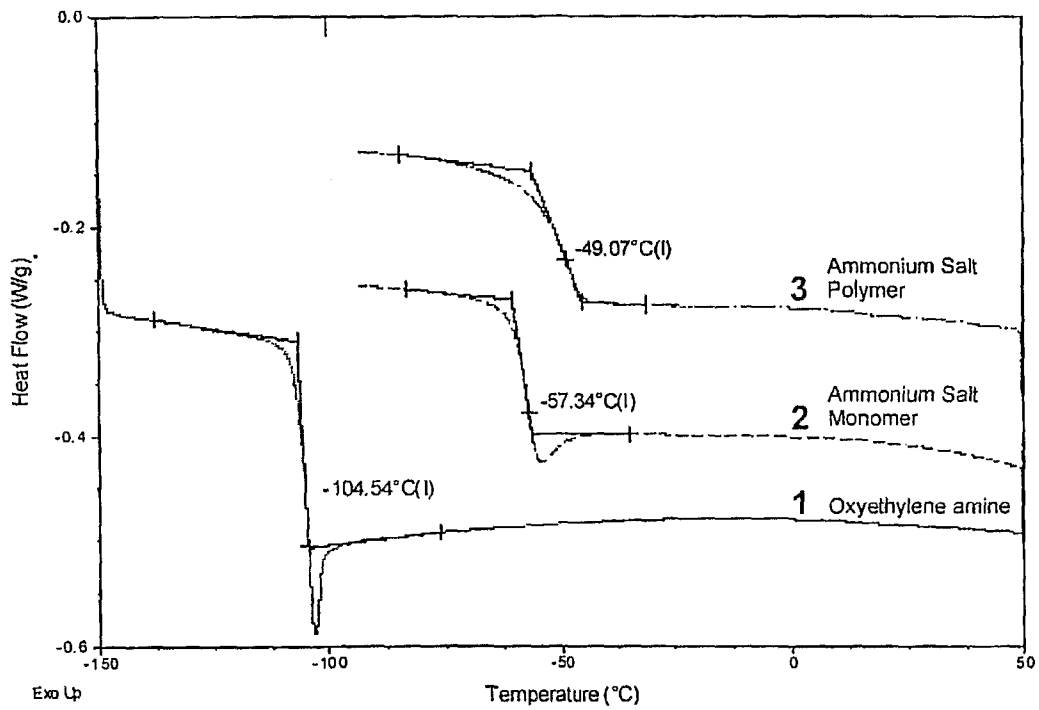


FIG. 1

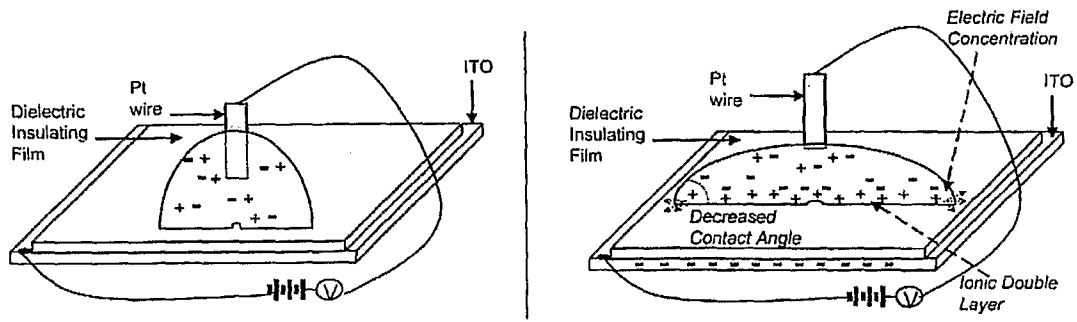


FIG. 2

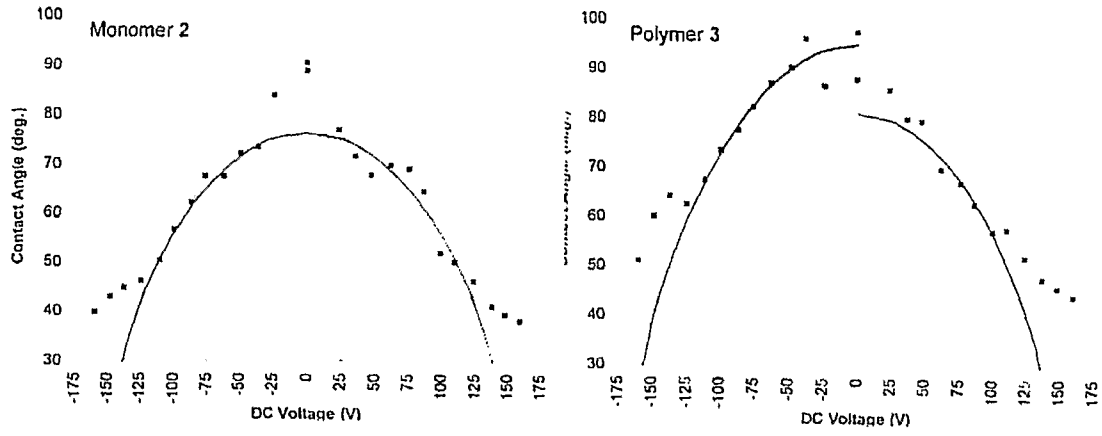


FIG. 3



FIG. 4