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(54) **Title**: DABCO-CONTAINING COPOLYMERS

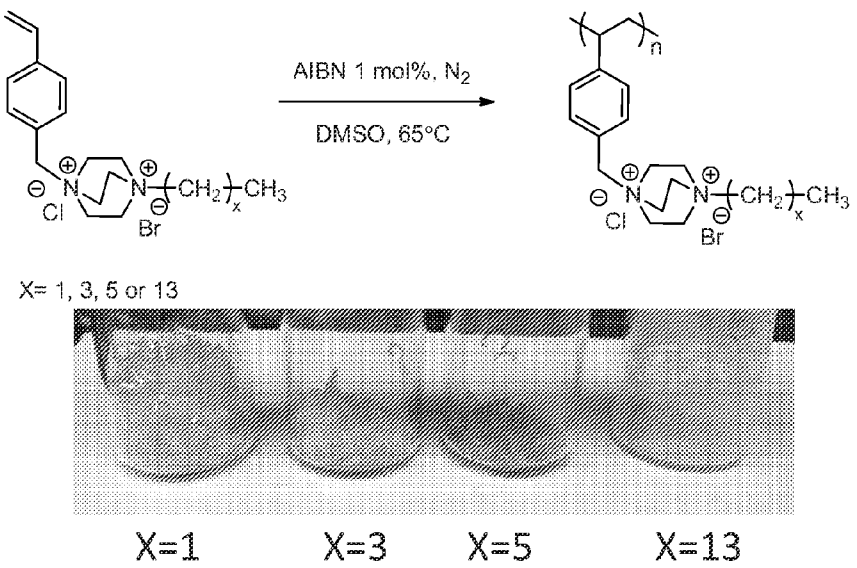

FIGURE 1

(57) **Abstract**: The present invention relates to ion-containing copolymers. In particular, the copolymers contain 1,4-diazabicyclo[2.2.2]octane (DABCO) double ammonium salt in a supramolecular network. The copolymers are useful for making, e.g., elastomeric materials, ionic adhesives, fuel cell membranes, ion-exchange membranes, gene delivery, ionic anti-microbial, anti-fouling materials, etc.

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DABCO-CONTAINING COPOLYMERS

[0001] This application claims the priority of U.S. Provisional Patent Application 61/892,514, filed October 18, 2013, which is incorporated herein by reference.

FIELD OF THE INVENTION

[0002] The present invention relates to ion-containing copolymers. In particular, the copolymers contain 1,4-diazabicyclo[2.2.2]octane (DABCO) in a supramolecular elastomeric network.

BACKGROUND OF THE INVENTION

[0003] Synthesis and characterization of ion-containing polymers are emerging research areas in both academia and industry due to the polymer's special properties and widespread applications, including adhesives, fuel cell membranes, anion exchange membranes, water filtration membranes, biosensors, gene delivery, antimicrobial materials, electromechanical devices, etc. Electrostatic interaction plays a significant role in the morphology and performance of such ion-containing polymers. One common preparation approach is to incorporate monomers bearing ionic groups during polymerization. Nafion™, for example, is a well-studied and commercialized ion-containing polymer synthesized by that method. Electrostatic interactions promote phase separation, which is attributed to self-assembly of ion aggregates into hard domains. As a result, the unique mechanical integrity and water/ion transport properties of Nafion™ film contribute to its potential as fuel cell membranes.

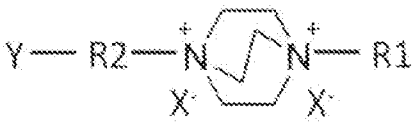
[0004] Polymerization with ion-containing monomers can produce ion-containing polymers with well-controlled polymer composition and architecture. Nexar™, for example, is a pentablock copolymer with sulfonated polystyrene as the ionic block. Its long range phase separated morphology results in advanced water permeability for water treatment applications. Common ionic groups used to produce ion-containing polymers include sulfonate, ammonium, phosphonium, imidazolium, carboxylate, phosphate, etc. Wu et. al. (Macromolecules (Washington, DC, U. S.) 2011, 44:8056) show that zwitterions promoted more well-defined microphase separation and superior elastomeric performance in a random copolymer. However, literature lacks examples of ionic monomers that contain two cations or anions.

[0005] Therefore, there remains a need for copolymers that contain monomers having two ions, which are useful, e.g., in making elastomeric materials, ionic adhesives, fuel cell membranes, ion-exchange membranes, gene delivery, ionic anti-microbial, anti-fouling materials, etc.

SUMMARY OF THE INVENTION

[0006] The present invention relates to DABCO double ammonium-containing monomers and corresponding copolymers. Copolymerization of the DABCO-containing monomer with a soft monomer provides novel ion-containing polymers which can be designed and tuned. The copolymer can be used for applications, including adhesives, fuel cells, water filtration, ion exchange membranes, ionic adhesives, anti-microbial coatings, anti-biofouling coatings, gene delivery, and sensors etc.

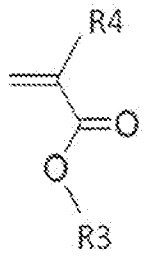
[0007] The present invention provides copolymers for making ionic thermoplastic elastomers. The copolymer contains a first comonomer and a second comonomer (the second comonomer may be a combination of different comonomers). The first comonomer has the structure of Formula I



Formula I

wherein R1 is an alkyl having 1 to 30 carbons, preferably 2-16 carbons, or alcohols, esters, or ethers thereof; R2 is an akylene having 1 to 18 carbons, preferably 1-2 carbons; Y is an acrylic, methacylic, or a styrenic group, and X^- is a halide counterion or structured counterion, such as fluoride, chloride, bromide, iodide, $^-NTf_2$, ^-OTf, $^-N(SO_2C_2F_5)_2$, $^-BF_4$, $^-PF_6$, $^-EtSO_4$, $^-PO_4Bu_2$, $^-$L-(+)-Lac, $^-HSO_4$, ^-SCN, $^-AlCl_4$, ^-OAc, and $^-MeSO_4$. Substituents other than hydrogen on the rings may be possible and may even desirable to give different effect

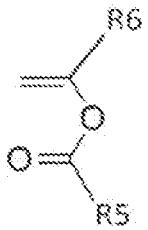
[0008] The second comonomer has the structure of Formula II or III or combinations thereof. Formula II is given as follows:



Formula II

wherein R3 is an alkyl having 1 to 16 carbons, preferably 4-8 carbons, or alcohol, esters, or ethers thereof; and R4 is hydrogen or an alkyl having 1 to 3 carbons. More preferably, R3 is a butyl. More preferably, R4 is hydrogen or methyl.

[0009] Formula III is given as follows:



Formula III

wherein R5 is an alkyl having 1 to 12 carbons, preferably 1 to 3 carbons; and R6 is hydrogen or an alkyl having 1 to 3 carbons. Preferably, R5 is a methyl. Preferably, R6 is hydrogen.

[0010] The copolymer may be a random copolymer or a block copolymer, with the random copolymer being preferred.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] Figure 1 shows (A) the synthetic scheme and (B) appearance of poly($VBDC_x$) homopolymers.

[0012] Figure 2 shows (A) the chemical structure and (B) appearance of poly($VBDC_x$-co-nBA) copolymers.

[0013] Figure 3 is a graph showing an nuclear magnetic resonance spectroscope (NMR) analysis of a poly($VBDC_x$-co-nBA) copolymer.

[0014] Figure 4 shows the dynamic mechanical analysis (DMA) plots of poly(*n*BA-*co*-$VBDC_{14}$) with 8 mol% and 20 mol% $VBDC_{14}$-BrCl.

[0015] Figure 5 shows the DMA plots of poly(*n*BA-*co*-$VBDC_{14}$) with 20 mol% $VBDC_{14}$ when the anions were BrCl, TFSI (same as NTf_2), and BF_4.

[0016] Figure 6 shows the DMA plots of poly(*n*BA-*co*-$VBDC_6$) with 12 mol% and 20 mol% $VBDC_6$-BrCl.

[0017] Figure 7 shows the DMA plots of poly(*n*BA-*co*-$VBDC_6$) with 20 mol% $VBDC_6$ when the anions were BrCl, TFSI (Tf_2N), and BF_4.

[0018] Figure 8 shows the storage and loss shear modulus pseudo-master curves of poly(*n*BA-*co*-$VBDC_{14}$) with 2 and 8 mol% $VBDC_{14}$-BrCl and poly(*n*BA-*co*-$VBDC_6$) with 1 mol% $VBDC_6$-BrCl.

[0019] Figure 9 shows the stress-strain curves of DABCO-containing copolymers.

[0020] Figure 10 shows the TGA curves of DABCO-salt containing copolymers with bromide-choride anions, double BF_4 anions, and double Tf_2N anions.

[0021] Figure 11 shows the water absorption of poly(*n*BA-*co*-$VBDC_{14}$) with bromide-choride anions and double Tf_2N anions.

[0022] Figure 12 shows the water absorption of poly(*n*BA-*co*-VBDC$_8$) with bromide-choride anions and double Tf_2N anions.

[0023] Figure 13 shows the atomic force microscopy (AFM) analysis of DABCO-salt containing copolymers.

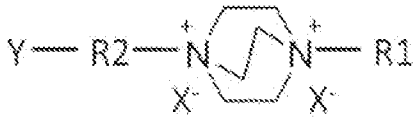
[0024] Figure 14 shows the thermal crosslinking reaction scheme of DABCO-salt containing copolymers for curable thermoset materials.

[0025] Figure 15 shows the isothermal rheology analyst to determine the gel point of DABCO-salt containing copolymers at 180 °C.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

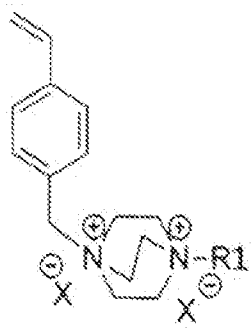
[0026] The present invention relates to copolymers having a first comonomer and a second comonomer. The first comonomer has the structure of Formula I; and the second comonomer has the structure of Formula II, III, or a combination thereof. The copolymer may be random or block copolymer. Preferably, the copolymer contains about 0.1-40 mol % of the first comonomer, more preferably about 2-10 mol %, and about 60-99.9 mol % of the second comonomer, more preferably about 90-98 mol %.

[0027] The first comonomer has the structure of Formula I



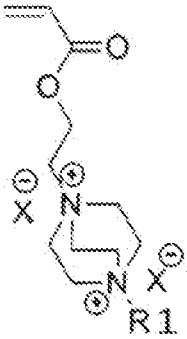
Formula I

wherein R1 is an alkyl having 1 to 30 carbons, preferably 2-16 carbons, or alcohols, esters, or ethers thereof; R2 is an akylene having 1 to 18 carbons, preferably 1-2 carbons; Y is an acrylic, methacylic, or a styrenic group; and X^- is a halide counterion or a structured counterion, such as fluoride, chloride, bromide, iodide, $^-NTf_2$, ^-OTf, $^-N(SO_2C_2F_5)_2$, $^-BF_4$, $^-PF_6$, $^-EtSO_4$, $^-PO_4Bu_2$, $^-$L-(+)-Lac, $^-HSO_4$, ^-SCN, $^-AlCl_4$, ^-OAc, $^-MeSO_4$. In preferred embodiments, R2 contains 1-2 carbons, particularly methylene or ethylene. In certain embodiments, the preferred first monomer has the structure of Formula IA, IB, or IC, or combinations thereof



Formula IA

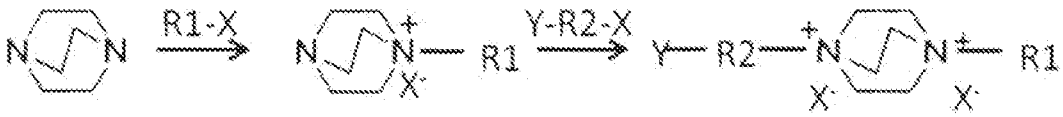
Formula IB



Formula IC

wherein R1 and X are as previously defined. Preferably, R1 includes ethyl, butyl, hexyl, octyl, decyl, dodecyl, tetradecyl, and hexadecyl. Although Formula IA shows the DABCO substituent in the para postion, it may also be located in the meta or ortho position as well.

[0028] In an embodiment, the first comonomer may be made by two consecutive SN2 reactions depicted in Scheme 1.



DABCO Formula IV Formula I

Scheme 1

In Scheme 1, DABCO is reacted with R1-X (where R1 is as defined previously and X is a halogen, such as fluorine, chlorine, bromine, iodine) in a first solvent to form an intermediate of Formula IV. The intermediate of Formula IV is then reacted with Y-X (where Y and X are defined previously) in a second solvent to form the comonomer of Formula I. The first solvent can be, but is not limited to, ethyl acetate, hexane, cyclohexane, ether, methylene chloride, or combinations thereof. The preferred first solvent is ethyl acetate. The second solvent can be, but

is not limited to, acetonitrile, chloroform, acetone, methanol, ethanol, or combinations thereof. The preferred second solvent is acetonitrile or chloroform depending on the R1 and R2 choices. Preferably, the reactions take place at about room temperature overnight. To make the compound of Formula IA, 4-vinylbenzyl chloride is used in the reaction. Likewise, to make the compound of Formulas IB and IC, 2-chloroethyl acrylate and 2-chloroethyl methacrylate, respectively, are used.

[0029] In certain embodiments, the comonomer of Formula I produced by the method of the immediately preceeding paragraph is desired to contain structured anions, such as $^-NTf_2$, ^-OTf, $^-N(SO_2C_2F_5)_2$, $^-BF_4$, $^-PF_6$, $^-EtSO_4$, $^-PO_4Bu_2$, $^-$L-(+)-Lac, $^-HSO_4$, ^-SCN, $^-AlCl_4$, ^-OAc, $^-MeSO_4$. In that case, the comonomer of Formula I (produced in the immediately prior paragraph) may further be changed to the structured anions by anion exchange with excess lithium, sodium, or potassium salt of the structured anion.

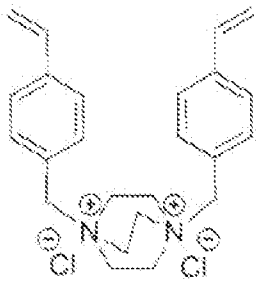
[0030] The second comonomers are well-known in the art and may be obtained using previously described methods. Indeed, the second comonomers are available commercially from many sources. For example, butyl acrylate has CAS Number 141-32-2 and is available from Dow; butyl methacrylate has CAS Number 97-88-1 and is available from Dow; 2-ethylhexyl methacrylate has CAS Number 688-84-6 and is available from Sigma Aldrich; 2-ethylhexyl acrylate has CAS Number 103-11-7 and is available from Sigma Aldrich; methyl acrylate has CAS Number 96-33-3 and is available from Dow; and methyl methacrylate has CAS Number 80-62-6 and is available from Sigma Aldrich. Specific examples of the second monomer may be, but are not limited to, acrylates or methacrylates, such as methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, isopropyl acrylate, isopropyl methacrylate, n-butyl acrylate, n-butyl methacrylate, i-butyl acrylate, i-butyl methacrylate, t-butyl acrylate, t-

butyl methacrylate, hexyl acrylate, hexyl methacrylate ethylhexyl acrylate, ethylhexyl methacrylate, 3,3 dimethylbutyl methacrylate, lauryl acrylate. The preferred second comonomers are n-butyl acrylate, n-butyl methacrylate, 2-ethylhexyl acrylate, iso-octyl acrylate, methyl acrylate, methyl methacrylate, vinyl acetate, styrene, 2-hydroxy ethyl acrylate, or combinations thereof. The most preferred second comonomer is n-butyl acrylate, ethylhexyl acrylate, or combinations thereof.

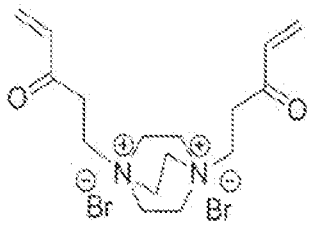
[0031] In certain embodiments of the present invention, a cross-linker may also be present to provide cross-linking of the copolymer. The cross-linker preferably has the structure of Formula V

Formula V

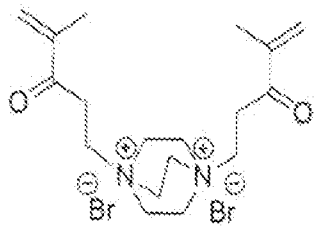
wherein each of R7 is independently an alkylene having 1 to 18 carbons, preferably 1-2 carbons; each of Y2 is an acrylile, methacylic, or a styrenic group, and X^- is as previously defined. The two R7 may be the same or different, but are preferably the same for ease of synthesis. Likewise, the two Y2 components may be the same or different, but are preferably the same. Preferably, each R7 independently contains 1-2 carbons, particularly $-CH_2-$ and $-C_2H_4-$. The preferred cross-linker has the structure of Formulas VA, VB, or VC, or combinations thereof



Formula VA



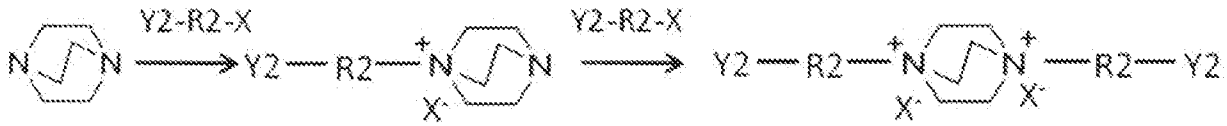
Formula VB



Formula VC

Although Formulas VA, VB, and VC show either chloride or bromide counter ions, other halides or structured anions may be substituted for the chloride or bromide shown. Preferably, the copolymer contains 1-20 mol % of the cross-linker, preferably 1-10 mol %.

[0032] The cross-linker of Formula V can be synthesized by reacting DABCO with Y2-R7-X as shown in scheme 2



Scheme 2

Scheme 2 shows a two stage reaction; however, in the case where the Y2 and R2 components on both sides of DABCO are the same, the reaction becomes a single step reacting one equivalent of DABCO with two equivalents of Y2-R7-X. The reaction preferably takes place in a solvent at about 60-70oC in the presence of a polymerization inhibitor, such as butylated hydroxytoluene (BHT) and hydroquinone. The solvent can be, but is not limited to, methanol, isopropanol, acetonitrile, or combinations thereof. For example, the compound of Formula VA can be synthesized by reacting DABCO (one equivalent) with N-4-vinylbenzyl chloride (4VBCl) (two equivalents) in BHT and methanol at reflux condition for about 14-22 hours. Compounds of Formulas VB, VC, and the like can also be similarly synthesized.

[0033] In certain embodiments, the comonomer of Formula V produced by the method of the immediately preceeding paragraph is desired to contain structured anions, such as $^-NTf_2$, ^-OTf, $^-N(SO_2C_2F_5)_2$, $^-BF_4$, $^-PF_6$, $^-EtSO_4$, $^-PO_4Bu_2$, $^-$L-(+)-Lac, $^-HSO_4$, ^-SCN, $^-AlCl_4$, ^-OAc, $^-MeSO_4$. In that case, the comonomer of Formula V (produced in the immediately prior paragraph) may further be changed to the structured anions by anion exchange with excess lithium, sodium, or potassium salt of the structured anion.

[0034] The first and second monomers are reacted to form the copolymer of the present invention. Preferably, the reaction takes place in a solvent with the presence of an initiator. In certain embodiments a cross-linker is also added to the reaction. Preferably, the reaction is carried out at 60-70°C under inert gas, such as nitrogen or argon. The solvent can be, but is not limited to, dimethyl sulfoxide (DMSO), dimethyl formamide (DMF), methanol, DMAc, toluene, THF, and ethyl acetate, or a combination thereof, with DMSO being the preferred solvent. The initiator can be, is not limited to, azobisisobutyronitrile (AIBN), 4,4'-azobis(4-cyanovaleric acid), and organic peroxides, such as di-tert-butyl peroxide and benzoyl peroxide, with AIBN being the preferred initiator.

[0035] In certain embodiments, the copolymer can be precipitated and separated from the solution. The precipitating solvents must have good solubility for the polymerization solvent and the monomers, and low solubility of the polymer product. Preferably, the copolymer is precipitated in a methanol/water mixture. The precipitated product can be dried to yield the solid copolymer.

[0036] In a preferred embodiment, the copolymer contains the comonomer of Formula IA and n-butyl acrylate. In another preferred embodiment, the copolymer contains the comonomer of Formula IA and n-butyl methacrylate.

[0037] In a further preferred embodiment, the copolymer contains the comonomer of Formula IB and n-butyl acrylate. In yet another preferred embodiment, the copolymer contains the comonomer of Formula IB and n-butyl methacrylate.

[0038] Other preferred embodiments include copolymers of Formula IC and either n-butyl acrylate or n-butyl methacrylate.

[0039] Without further description, it is believed that one of ordinary skill in the art can, using the preceding description and the following illustrative example, make and utilize the compounds of the present invention and practice the claimed methods. The following example is given to illustrate the present invention. It should be understood that the invention is not to be limited to the specific conditions or details described in the example.

Example

[0040] We describe herein for the first time the synthesis and characterization of a library of DABCO-containing monomers (Formula I) and corresponding homopolymers and copolymers. We optimized conditions to accelerate the reaction kinetics and to simplifyy the purification procedure. Monomer synthesis was time and energy efficient with a superior yield and quality. Successful homopolymerization and copolymerization with a soft monomer demonstrated the ability of our monomers to polymerize. We characterized homopolymers and copolymers to analyze their thermal, dynamic mechanical, water absorption, rheological, and morphological properties. Ultimately, our invention introduces a novel ionic group for ion-containing polymer design and provides methods for preparing and tuning polymer structure. Our DABCO-containing monomers and polymers can be used for all ionic material applications including fuel

cell, water filtration, ion exchanges membrane, ionic adhesives, anti-microbial coatings, anti-biofouling coatings, gene delivery, and sensors etc.

[0041] All DABCO salt-containing monomers' structures were confirmed through mass spectroscopy, ^{1}H NMR (nuclear magnetic resonance), and ^{13}C NMR. All DABCO salt-containing polymers investigated were characterized utilizing ^{1}H NMR, TGA (thermal gravimetric analysis), and DSC (differential scanning calorimetry).

[0042] Methods

[0043] *Synthesis of N-4VinylBenzyl-N'-alkyl DABCO ($VBDC_x$) monomers.* In a representative DABCO salt-containing monomer synthesis, DABCO (5 g, 4.5 mmol) and 1-bromoethane (3.3 mL, 4.5 mmol) were dissolved in 100 mL of ethyl acetate and stirred overnight. White suspension was suction filtered, washed with ethyl acetate, and dried in vacuo at ambient temperature. Alkylated DABCO (7.8 g, 4.4 mmol) and 4VBCl (6.8 g, 4.4 mmol) were dissolved in 100 mL acetonitrile and stirred overnight. White suspension was suction filtered, washed with acetonitrile and dried in vacuo at ambient temperature with an overall yield of 97%.

[0044] *Synthesis of DABCO Salt-Containing Homopolymers and Copolymers.* A typical conventional free radical polymerization was conducted as follows: *n*BA (2.0 g, 15.6 mmol), AIBN (2.8 mg, 0.017 mmol), $VBDC_6$ (0.669 g, 1.6 mmol) and DMSO (10.7 g) were added to a 100 ml, round-bottomed flask equipped with magnetic stirrer. The solution was purged with Ar for 20 min and stirred at 65 °C for 24 h. The resulting solution was precipitated into a MeOH-H_2O mixture. Precipitate was collected and dried in vacuo to obtain an elastic solid of 2.4 g (90% yield).

[0045] *Anion Exchange of DABCO Salt-Containining Copolymers.* A typical anion exchange experiment was conducted as follows: 0.5 g copolymer (0.45 mmol of repeat unit) was dissolved

in 5 mL methanol and added to a solution of $NaBF_4$ (0.49 g, 4.5 mmol) and 50 mL methanol dropwise slowly. A white precipitate formed and continued to stir overnight. The precipitate was decanted off solvent, washed thoroughly with deionized water and dried in vacuo. Silver nitrite solution (1 M) was used to confirm the absence of residue bromide or chloride anions.

[0046] *Analytical Methods.* ^1H NMR and ^{13}C NMR spectra spectroscopy were performed on a Varian Unity 400 at 400 MHz in deuterated DMSO. Fast atom bombardment mass spectrometry was conducted in positive ion mode on a JEOL HX110 dual focusing mass spectrometer.

[0047] Thermogravimetric analysis (TGA) was performed on a TA Instruments Q500 TGA from ambient to 600 °C at 10 °C/min. Thermal degradation temperatures (T_ds) were determined at 5% weight loss. Glass transition temperatures were measured at the midpoint of the transition in the second heating ramp.

[0048] Dynamic mechanical analysis (DMA) was conducted on a TA Instruments Q800 Dynamic Mechanical Analyzer in tension mode at a frequency of 1 Hz, an oscillatory amplitude of 15 μm, and a static force of 0.01 N. The temperature ramp was 3 °C/min.

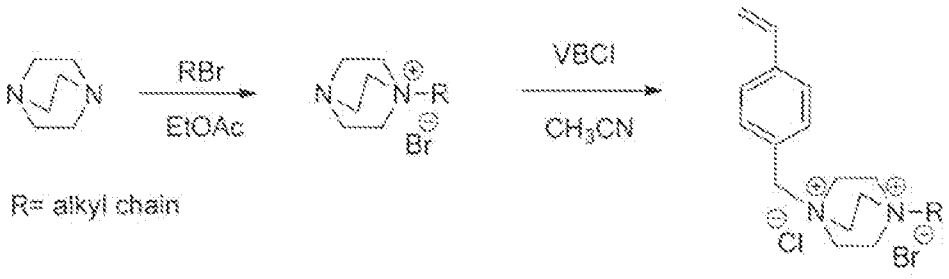
[0049] A Veeco MultiMode scanning probe microscope was used for tapping-mode atomic force microscopy (AFM) imaging. Samples were imaged around a set-point ratio of 0.7. Veeco's Nanosensor silicon tips having a spring constant of 42 N/m were utilized for imaging. Polymer films were melt pressed at 100 °C for 1 h and slowly cooled down to ambient temperature.

[0050] An Instron 4411 universal testing instrument was used to test tensile properties of the segmented copolyesters at a crosshead speed of 50 mm/min. Tensile data represent an average of five specimens. Copolymers were dissolved in dry methanol and cast into a Teflon® Petri dish, followed by slow evaporation of the solvent and drying of the film in vacuo. Discs of 8 mm

diameter were punched out for rheometry. All rheological measurements were strain-controlled at a constant nominal strain value within the linear viscoelastic range, determined with strain sweeps. The characteristic viscoelastic functions, storage modulus (G') and loss modulus (G") were measured at different temperatures and frequencies. Master curves were obtained from temperature/frequency sweep measurements using time-temperature superposition (TTS), which is described with the Williams-Landel-Ferry equation. G" curves were used as the reference curves for TTS. Rheological isothermal time sweep experiment was conducted at 180 °C to examine the crosslinking of DABCO-salt containing copolymers. A Veeco MultiMode scanning probe microscope was used for tapping-mode AFM imaging. Samples were imaged at a set-point ratio of 0.67 with a magnification of 1 μm×1 μm. Veeco's Nanosensor silicon tips having a spring constant of 42 N/m were utilized for imaging.

[0051] Results and Discussions

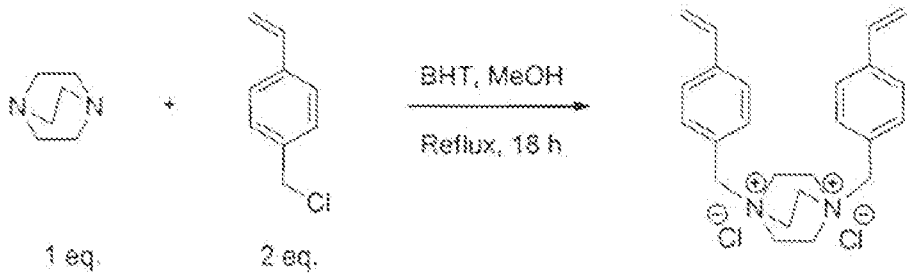
[0052] We synthesized a library of DABCO-containing styrenic, methacrylic, and acrylic monomers (Formulas IA, IB, and IC, respectively) for free radical polymerization. Two-step synthesis of these monomers followed a simple substitution mechanism. Scheme 3 shows the synthesis of a styrenic DABCO monomer as an example.



Scheme 3. Synthesis of N-4VinylBenzyl-N'-alkyl DABCO monomers

Careful solvent selections dissolved starting materials and precipitated products, which prevented byproduct formation and self-accelerate conversion. We designed the monomer

synthesis procedure to be quantitative, scalable, atom efficient, purification-free, and low-cost. Crosslinkers that contain DABCO double ammonium groups were also available when DABCO reacted with two equivalents of 4VBCl at elevated temperature (Scheme 4).

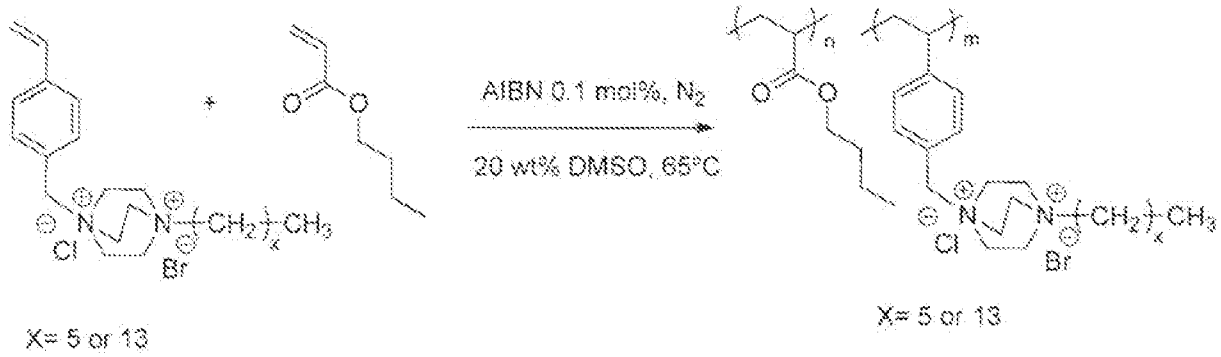


Scheme 4. Synthesis of bis(N-4VinylBenzyl)-DABCO crosslinker and structure of the acrylic and methacrylic versions

The library of DABCO-containing monomers provides various structural parameters to tune the monomer and corresponding polymer properties. These structural parameters include, but are not limited to, monomer backbone type, spacer length (for acrylics and methacrylics), alkyl tail length, counterion, and monomer functionality. They can significantly affect monomer and polymer properties, such as reactivity ratio, glass transition temperature (T_g), hydrophilicity, solubility, melting point, ionic interaction strength, and crosslinking density. We can use different monomers from the library to achieve the desired polymer performance. In addition, a wide variety of ion-containing polymers with specific performance and application may be synthesized by controlling free radical polymerization method, conditions, and comonomers.

[0053] Dialyzed homopolymers of $VBDC_x$ exhibited different color with varying alkyl chain length, suggesting potential applications as molecular probes and sensors (Figure 1). A wide variety of commercially available monomers can copolymerize with the DABCO-containing monomers. A neutral and low T_g polymer matrix is of particular interest to us for its ability to provide flexibility. Currently, we focus on the synthesis and characterization of random

copolymers of $VBDC_6/VBDC_{14}$ with *n*BA to study the effect of DABCO double ammonium groups on acrylics macroscopic performance for membrane applications (Scheme 5). Copolymers with a range of ion content were synthesized through varying ratios of the monomer feed (Table 1). Copolymers with equal or more than 9 mol% of DABCO salt were solution casted to make free standing films.



Scheme 5. Conventional free radical copolymerization of *n*BA and $VBDC_6/VBDC_{14}$.

Table 1. Feed ratio and copolymer compositions of poly(*n*BA-*co*-$VBDC_x$)

Feed ratio	mol%	($VBDC_6$:nBA)	mol%	wt%	($VBDC_{14}$:nBA)	mol%	wt%
1:30	3	1:67.3	1	5	1:53.5	2	7
1:10	9	1:7.6	12	31	1:11.1	8	28
1:5	17	1:4.1	20	45	1:4.0	20	51
1:2	33	1:1.4	42	70	1:1.6	38	72
1:0	100	1:0	100	100	1:0	100	100

[0054] DMA demonstrated the superior mechanical property of DABCO-containing copolymers in Figure 4-7. The decrease of storage modulus went through two transitions over temperature: glass transition of the acrylic matrix and dissociation of the ionic cluster phase. The

well-defined rubbery plateau region covered a range of over 100 °C. The plateau modulus and flow temperature depended on the charge density of the copolymers.

[0055] Figure 8 shows the rheology time-temperature superposition (TTS) pseudo-master curve of DABCO salt-containing acrylics shifted according to the loss modulus. Failure of TTS principle occurred in the intermediate frequency range between glass transition and ionic interaction dissociation due to the presence of two relaxation mechanisms. Fitting the shift factors around glass transition to the WLF equation $C_1^g = \frac{C_1 C_2}{C_2 + (T_g - T_r)}$ $C_2^g = C_2 + (T_g - T_r)$ yielded fractional free volume of DABCO-containing copolymers of 0.053, which is bigger compared to a neutral polymer (around 0.028) (Figure 8, Table 2). Higher temperature shift factor data fit to Arrhenius behavior and yielded a flow activation energy of 221 kJ/mol. Compared to poly*n*BA (flow activation energy of around 60 kJ/mol), DABCO-containing copolymers exhibited a significant superior thermal responsiveness. This proved its advantage of excellent melt processability. Figure 9 confirms the mechanical performance of DABCO-containing copolymers through tensile testing. Table 3 lists the Young's modulus, yield stress and strain, stress at break, and strain at break data of copolymers with different alkyl chain length and charge content. Tensile testing data demonstrated the tunable performance of DABCO salt-containing polymer through changing monomer structure and polymerization conditions.

Table 2. Glass transition temperature (T_g), flow activation energy (E_a), fraction free volume (f_g), and WLF equation constants (C_1^g, C_2^g) of poly(*n*BA-*co*-$VBDC_{14}$) and poly(*n*BA-*co*-$VBDC_6$) obtaining from fitting of the shift factor to WLF equation and Arrhenius equation

	C_1	C_2 (K)	C_1^g	C_2^g (K)	T_g (°C)	f_g	α_f (10^{-4} K^{-1})	E_a (kJ/mol)
1 mol% $VBDC_6$	3.5	99.3	10.3	34.3	-45	0.042	12.4	171
2 mol% $VBDC_{14}$	3.8	101.5	10.5	36.5	-45	0.041	11.3	155
8 mol% $VBDC_{14}$	5.3	107.5	12.0	69.5	-40	0.053	7.6	221

Table 3. Tensile testing of DABCO-containing copolymers

	Young's modulus (MPa)	**Yield stress (MPa) Yield strain (%)**	**Stress at break (MPa)**	**Strain at break (%)**
8 mol% $VBDC_{14}$	40 ± 4	4 ± 0, 25 ± 5	4.6 ± 0	284 ± 25
20 mol% $VBDC_{14}$	120 ± 10	7.5 ± 1, 16 ± 3	7.1 ± 1	122 ± 29
12 mol% $VBDC_6$	29 ± 6	2 ± 0 , 12 ± 1	4 ± 1	610 ± 39
20 mol% $VBDC_6$	78 ± 17	4 ± 1 , 9 ± 1	7 ± 1	368 ± 42

[0056] We also conducted anion-exchange experiments to study the anion effect on the DABCO-containing copolymers performance. The 5% weight loss temperature of the anion-exchanged copolymers showed an increase of about 100 °C compared to their halide analogs in Figure 10. Exchanging halide anion to BF_4^- and Tf_2N^- significantly affected the thermal stability of these copolymers due to the weaker nucleophilicity of the bulkier anion. Figures 5 and 7 reveal the effect of anion on the copolymer membrane thermal mechanical properties. The copolymer with BF_4^- had a higher rubbery plateau modulus with a higher terminal flow temperature. The copolymer with Tf_2N^- had more phase mixing behavior and a lower terminal flow temperature. We demonstrated the potential of using different anions to tune the DABCO-containing copolymer properties.

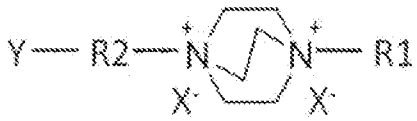
[0057] Figures 11 and 12 show the water absorption properties of DABCO-salt containing copolymers. Surface morphology analysis in Figure 13 shows the phase separation morphology of DABCO-salt copolymers. DABCO salt-containing copolymers with halide counterions have additional thermal curing capability at 170-200 °C. Figure 14 shows the reaction scheme of chemical crosslinking with the DABCO ring, providing a mechanism to convert a thermoplastic material to a thermoset material. Figure 15 shows the gel point of poly(VBDC14-co-nBA) with 0.8 mol% VBDC14-BrCl at 180 °C.

[0058] Although certain presently preferred embodiments of the invention have been specifically described herein, it will be apparent to those skilled in the art to which the invention pertains that variations and modifications of the various embodiments shown and described herein may be made without departing from the spirit and scope of the invention. Accordingly, it is intended that the invention be limited only to the extent required by the appended claims and the applicable rules of law.

What is claimed is:

1. A copolymer comprising

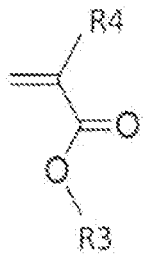
a. a first comonomer having a structure of Formula I



Formula I

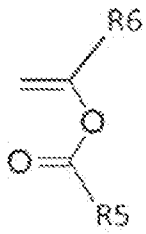
wherein R1 is an alkyl having 1 to 30 carbons, or alcohols, esters, or ethers thereof; R2 is an akylene having 1 to 18 carbons; Y is an acryloyl, methacryloyl, or a styrenic group, and X^- is a halide counterion or a structured counterion; and

b. a second comonomer having a structure of Formula II or III or combinations thereof



Formula II

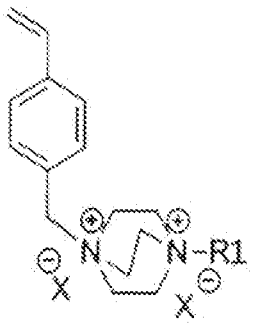
wherein R3 is an alkyl having 1 to 16 carbons or alcohol, esters, or ethers thereof; and R4 is hydrogen or an alkyl having 1 to 3 carbons;



Formula III

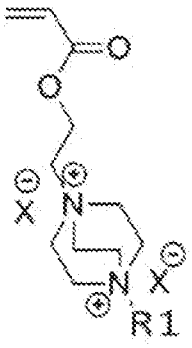
wherein R5 is an alkyl having 1 to 12 carbons; and R6 is hydrogen or an alkyl having 1 to 3 carbons.

2. The copolymer of claim 1, wherein the first monomer has the structure of Formula IA, IB, IC, or combinations thereof.



Formula IA

Formula IB



Formula IC

3. The copolymer of claim 1, wherein the second copolymer is n-butyl acrylate, n-butyl methacrylate, 2-ethylhexyl acrylate, iso-octyl acrylate, methyl acrylate, methyl methacrylate, vinyl acetate, styrene, 2-hydroxy ethyl acrylate, or combinations thereof.

4. The copolymer of claim 1, wherein the second copolymer is n-butyl acrylate, n-butyl methacrylate, or a combination thereof.

5. The copolymer of claim 1, wherein the first monomer is present at about 0.1-40 mol %.

6. The copolymer of claim 1, wherein the second comonomer is present at about 60-99.9 mol %.

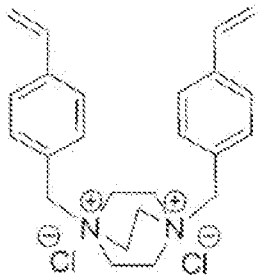
7. The copolymer of claim 1, wherein the copolymer is a random copolymer or a block copolymer.

8. The copolymer of claim 1, further comprising a cross-linker of Formula V

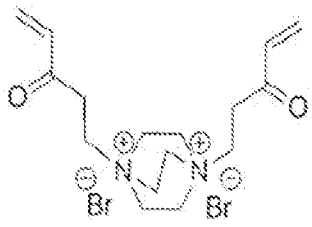
Formula V

wherein each of R7 is independently an akylene having 1 to 18 carbons; each of Y2 is an acryloyl, methacryloyl, or a styrenic group, and X^- is as previously defined.

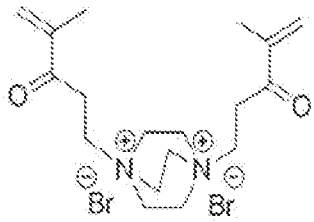
9. The copolymer of claim 8, wherein the cross-linker has the structure of Formulas VA, VB, VC, or combinations thereof



Formula VA



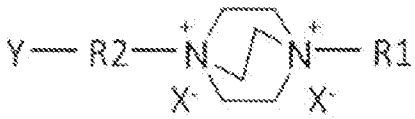
Formula VB



Formula VC

10. The copolymer of claim 8, wherein the cross-linker is present at about 1-20 mol % by weight of the total copolymer.

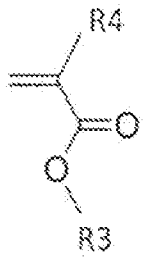
11. A method for making a copolymer comprising the step of coppolymerizing a first comonomer having a structure of Formula I



Formula I

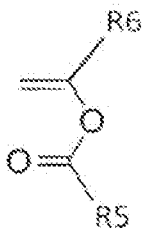
wherein R1 is an alkyl having 1 to 30 carbons, or alcohols, esters, or ethers thereof; R2 is an alkylene having 1 to 18 carbons; Y is an acrylic, methacrylic, or a styrenic group, and X^- is a halide counterion or a structured conterion; and

a second comonomer having a structure of Formula II or III or combinations thereof



Formula II

wherein R3 is an alkyl having 1 to 6 carbons or alcohol, esters, or ethers thereof; and R4 is hydrogen or an alkyl having 1 to 3 carbons;



Formula III

wherein R5 is an alkyl having 1 to 12 carbons or alcohols, esters, or ethers thereof; and R6 is hydrogen or an alkyl having 1 to 3 carbons.

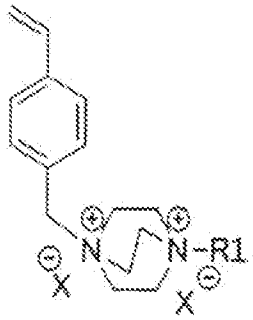
12. The method of claim 11, wherein the copolymerizing step occurs in a solvent and an initiator.

13. The method of claim 12, wherein the solvent is dimethyl sulfoxide (DMSO) dimethylformamide (DMF), methanol, dimethylacetamide (DMAc), methanol, toluene, THF, ethyl acetate, or combinations thereof.

14. The method of claim 12, wherein the initiator is azobisisobutyronitrile (AIBN), 4,4'-Azobis(4-cyanovaleric acid), organic peroxides, or combinations thereof.

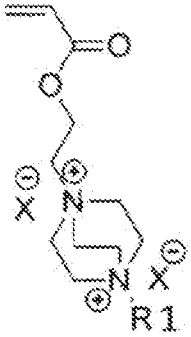
15. The method of claim 11, wherein the polymerization occurs at 60-70 °C under inert gas.

16. The method of claim 11, wherein wherein the first monomer has the structure of Formula IA, IB, IC, or combinations thereof.



Formula IA

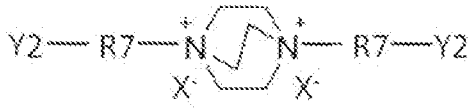
Formula IB



Formula IC

17. The method of claim 11, wherein the second copolymer is n-butyl acrylate, n-butyl methacrylate, 2-ethylhexyl acrylate, iso-octyl acrylate, methyl acrylate, methyl methacrylate, vinyl acetate, styrene, 2-hydroxy ethyl acrylate, or combinations thereof.

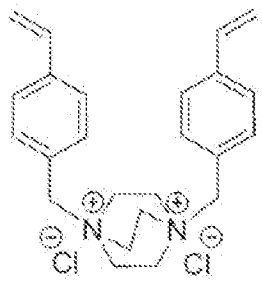
18. The method of claim 11, wherein the polymerizing step further comprises a cross-linker of Formula V



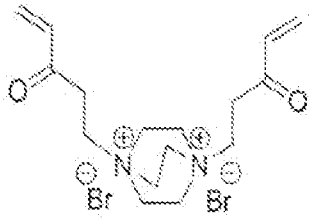
Formula V

wherein each of R7 is independently an alkylene having 1 to 18 carbons; each of Y2 is an acrylic, methacrylic, or a styrenic group, and X⁻ is as previously defined.

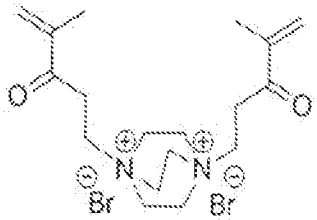
19. The method of claim 18, wherein the cross-linker has has the structure of Formulas VA, VB, VC, or combinations thereof



Formula VA



Formula VB

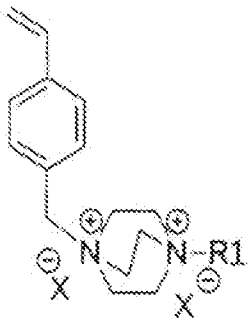


Formula VC

20. The method of claim 11, wherein the first monomer is present at about 0.1-40 mol %, and the second monomer is present at about 60-99.9 mol %.

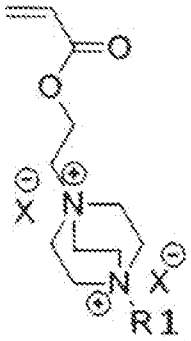
21. An adhesive comprising the copolymer of claim 1.

22. The adhesive of claim 21, wherein the first monomer has the structure of Formula IA, IB, IC, or combinations thereof.



Formula IA

Formula IB



Formula IC

23. The adhesive of claim 21, wherein the second copolymer is n-butyl acrylate, n-butyl methacrylate, 2-ethylhexyl acrylate, iso-octyl acrylate, methyl acrylate, methyl methacrylate, vinyl acetate, styrene, 2-hydroxy ethyl acrylate, or combinations thereof.

24. The adhesive of claim 21, wherein the second copolymer is n-butyl acrylate, n-butyl methacrylate, or a combination thereof.

25. The adhesive of claim 21, wherein the first monomer is present at about0.1-8 mole %.

26. The adhesive of claim 21, wherein the second comonomer is present at about 92-99.9 mole %.

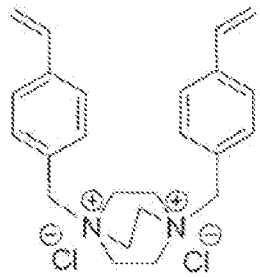
27. The adhesive of claim 21, wherein the copolymer is a random copolymer or a block copolymer.

28. The adhesive of claim 21, further comprising a cross-linker of Formula V

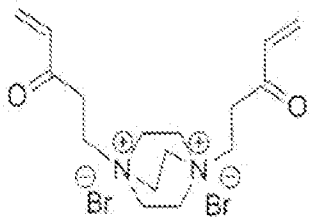
Formula V

wherein each of R7 is independently an alkylene having 1 to 18 carbons; each of Y2 is an acrylic, methacylic, or a styrenic group, and X⁻ is as previously defined.

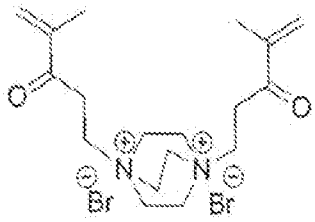
29. The adhesive of claim 28, wherein the cross-linker has the structure of Formulas VA, VB, VC, or combinations thereof



Formula VA



Formula VB



Formula VC

30. The adhesive of claim 28, wherein the cross-linker is present at about 0.1-3 mol %.

31. An elastomer comprising the copolymer of claim 1.

32. The elastomer of claim 31, wherein the first comonomer has the structure of Formula IA, IB, IC, or combinations thereof.

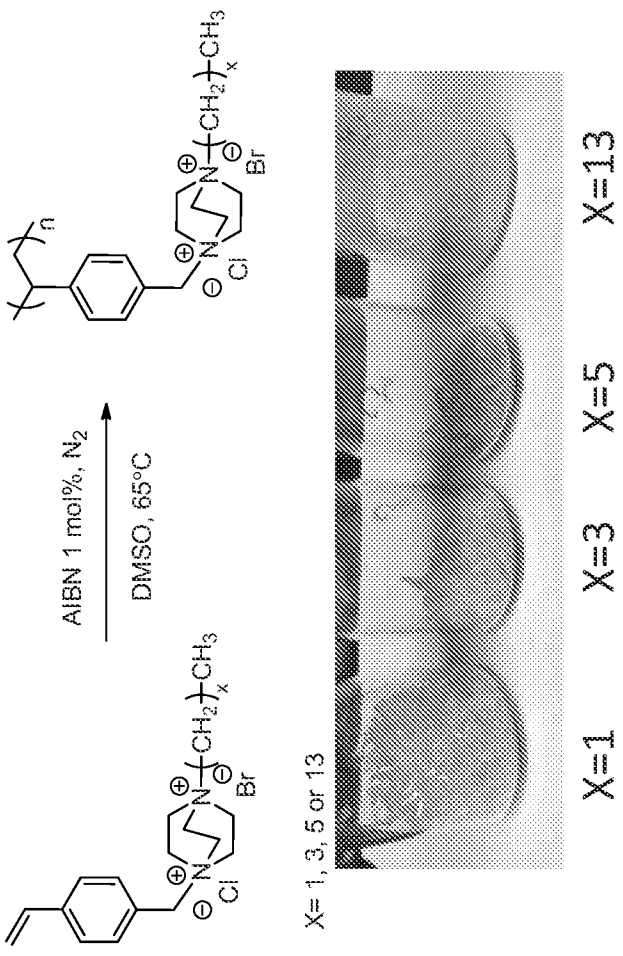
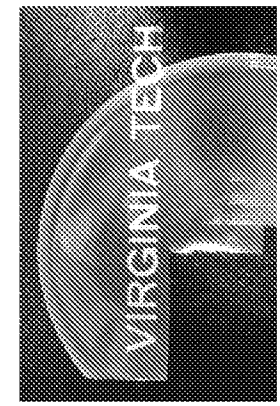


FIGURE 1



VBDC$_{14}$ 20 mol%

VBDC$_6$ 20 mol%

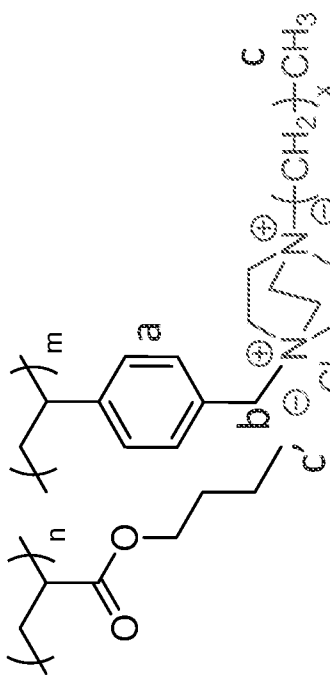


FIGURE 2

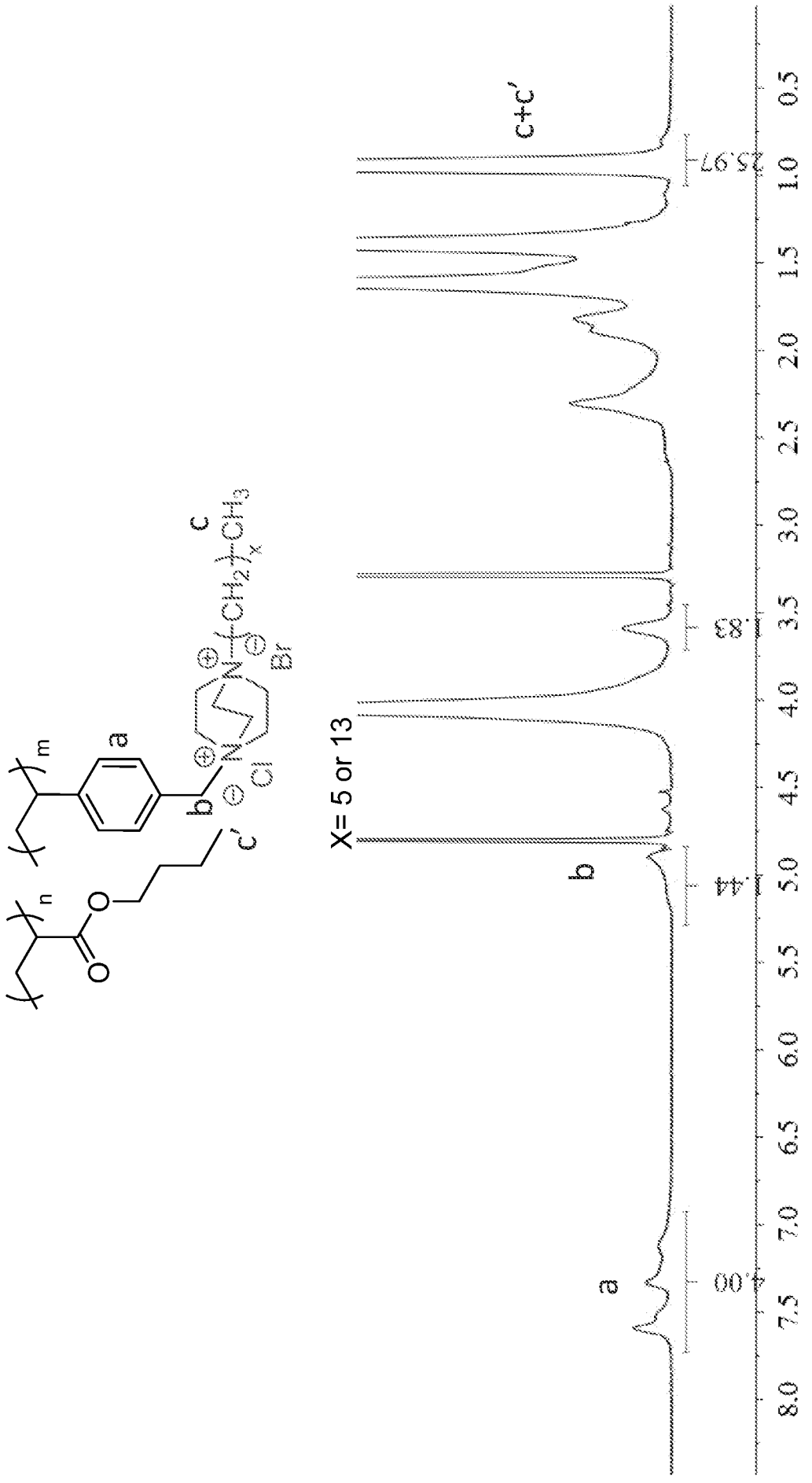

X= 5 or 13
a
b
c+c'
00
44
83
25.97
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
m
n
O
O
a
b
c'
c
Cl
Br
x

FIGURE 3

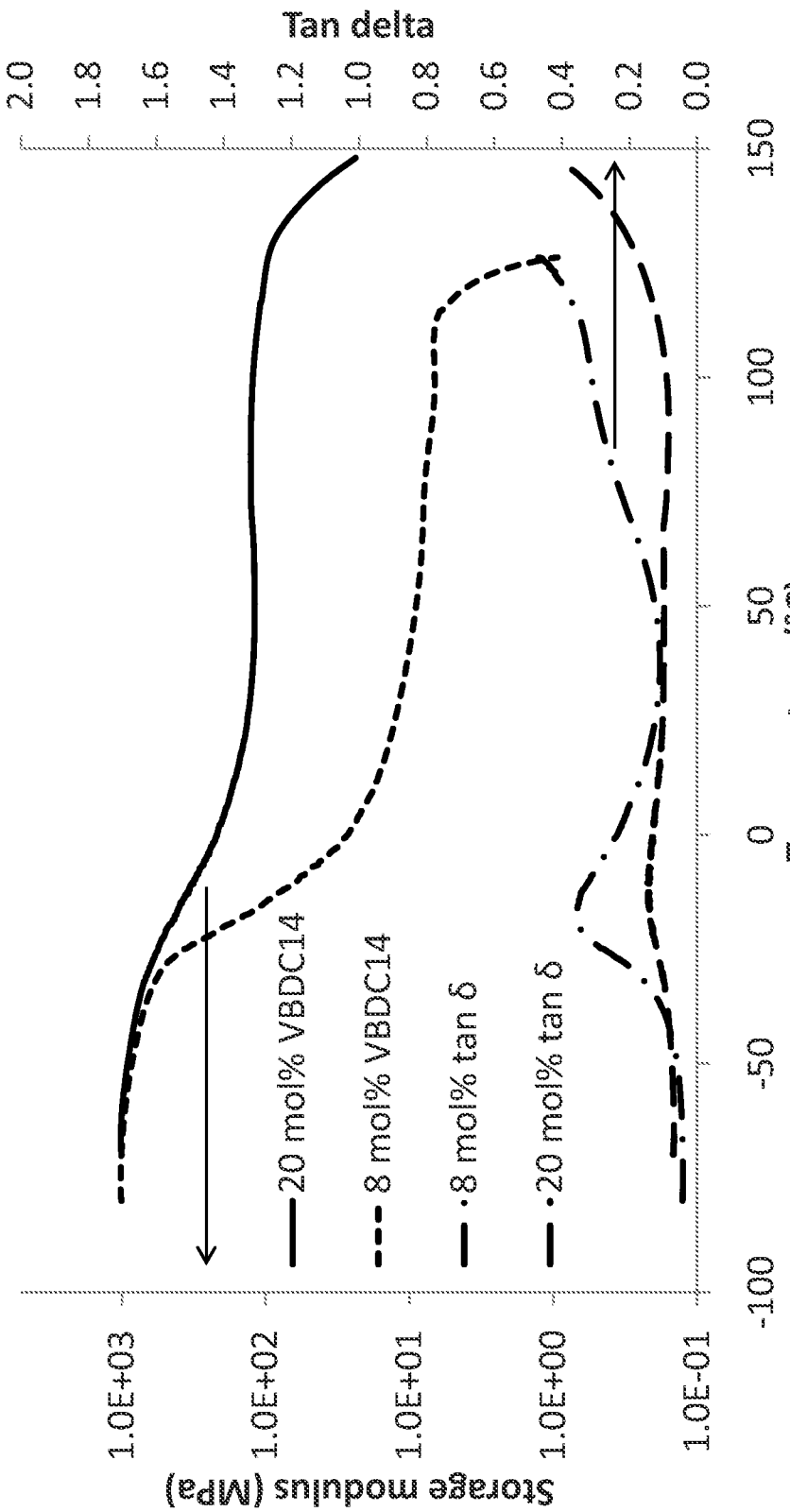

Tan delta
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
150
100
50
0
-50
-100
Temperature (°C)
1.0E+03
1.0E+02
1.0E+01
1.0E+00
1.0E-01
Storage modulus (MPa)
20 mol% VBDC14
8 mol% VBDC14
8 mol% tan δ
20 mol% tan δ

FIGURE 4

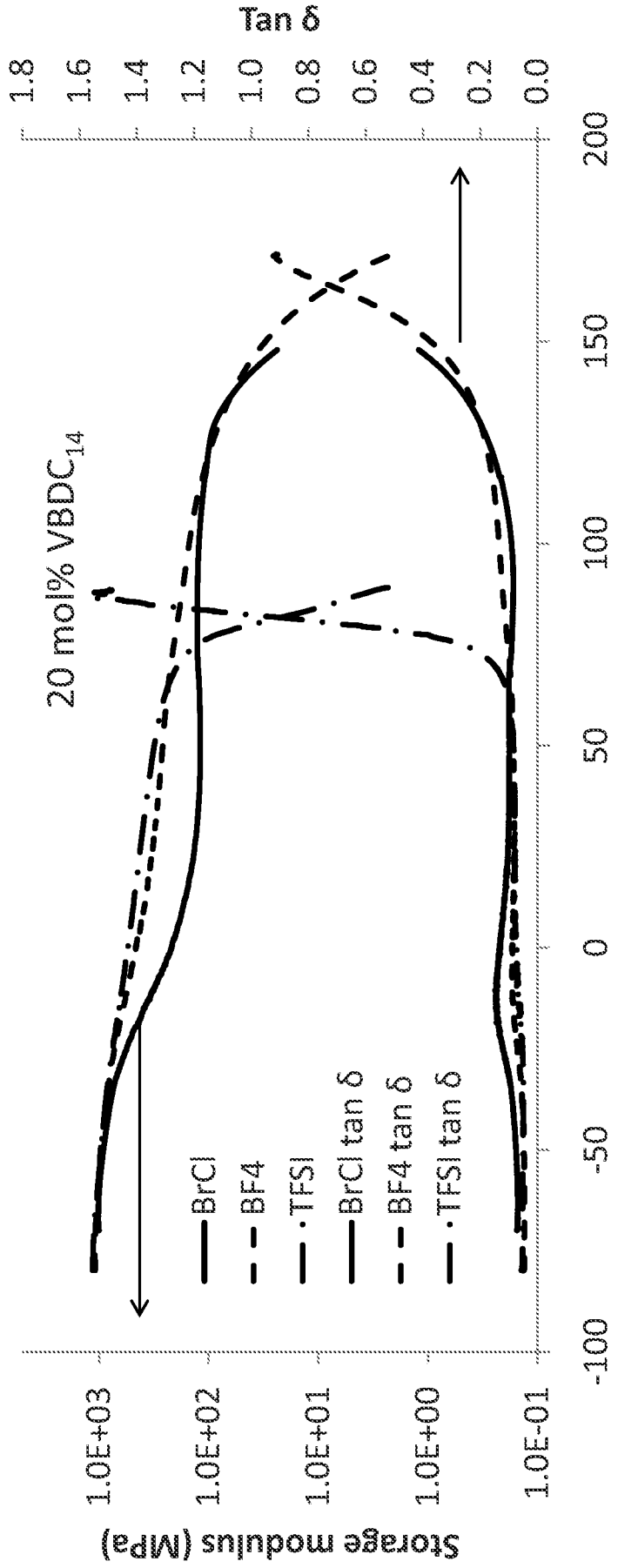

Tan δ
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
200
150
100
50
0
-50
-100
Temperature (°C)
20 mol% VBDC14
BrCl
BF4
TFSI
BrCl tan δ
BF4 tan δ
TFSI tan δ
1.0E+03
1.0E+02
1.0E+01
1.0E+00
1.0E-01
Storage modulus (MPa)

FIGURE 5

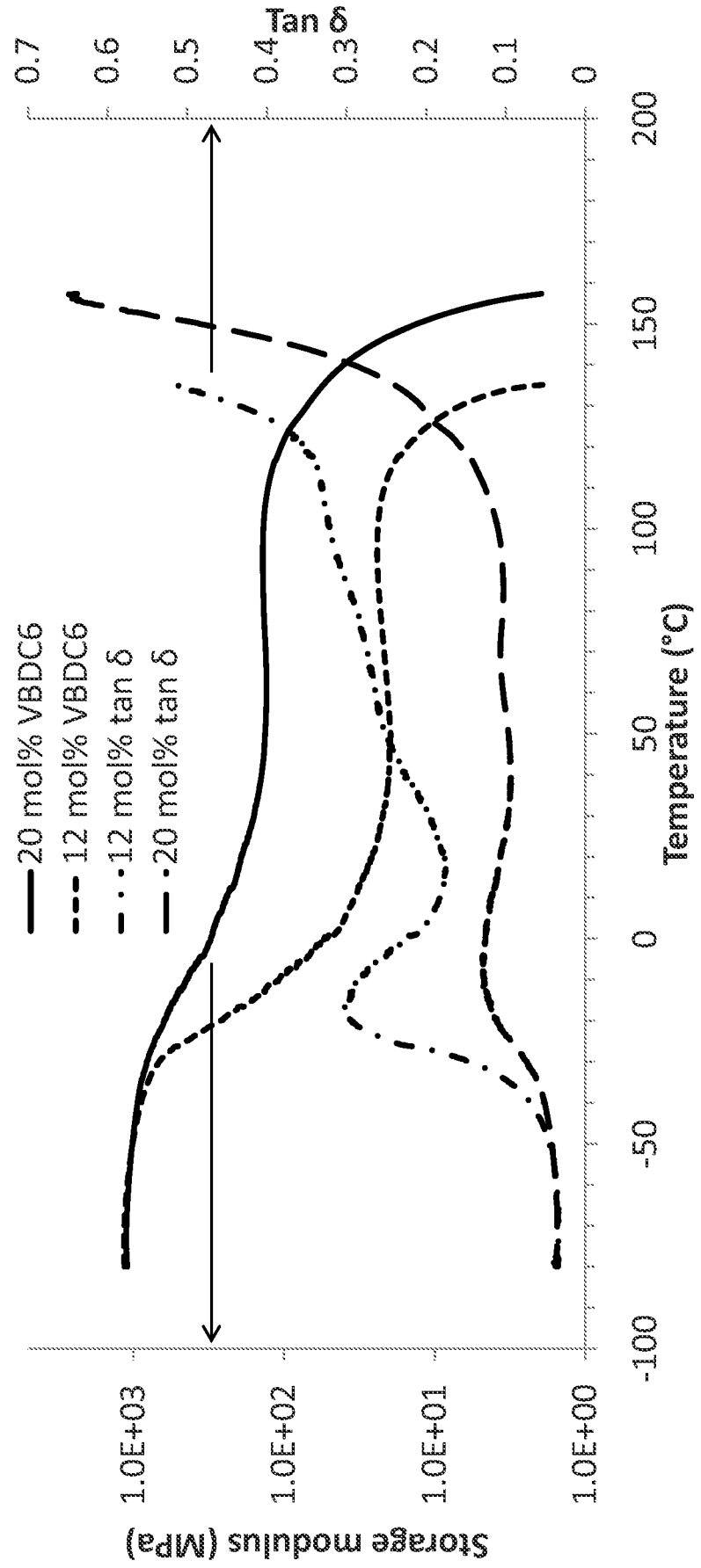

Tan δ
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
200
150
100
50
0
-50
-100
Temperature (°C)
20 mol% VBDC6
12 mol% VBDC6
12 mol% tan δ
20 mol% tan δ
1.0E+03
1.0E+02
1.0E+01
1.0E+00
Storage modulus (MPa)

FIGURE 6

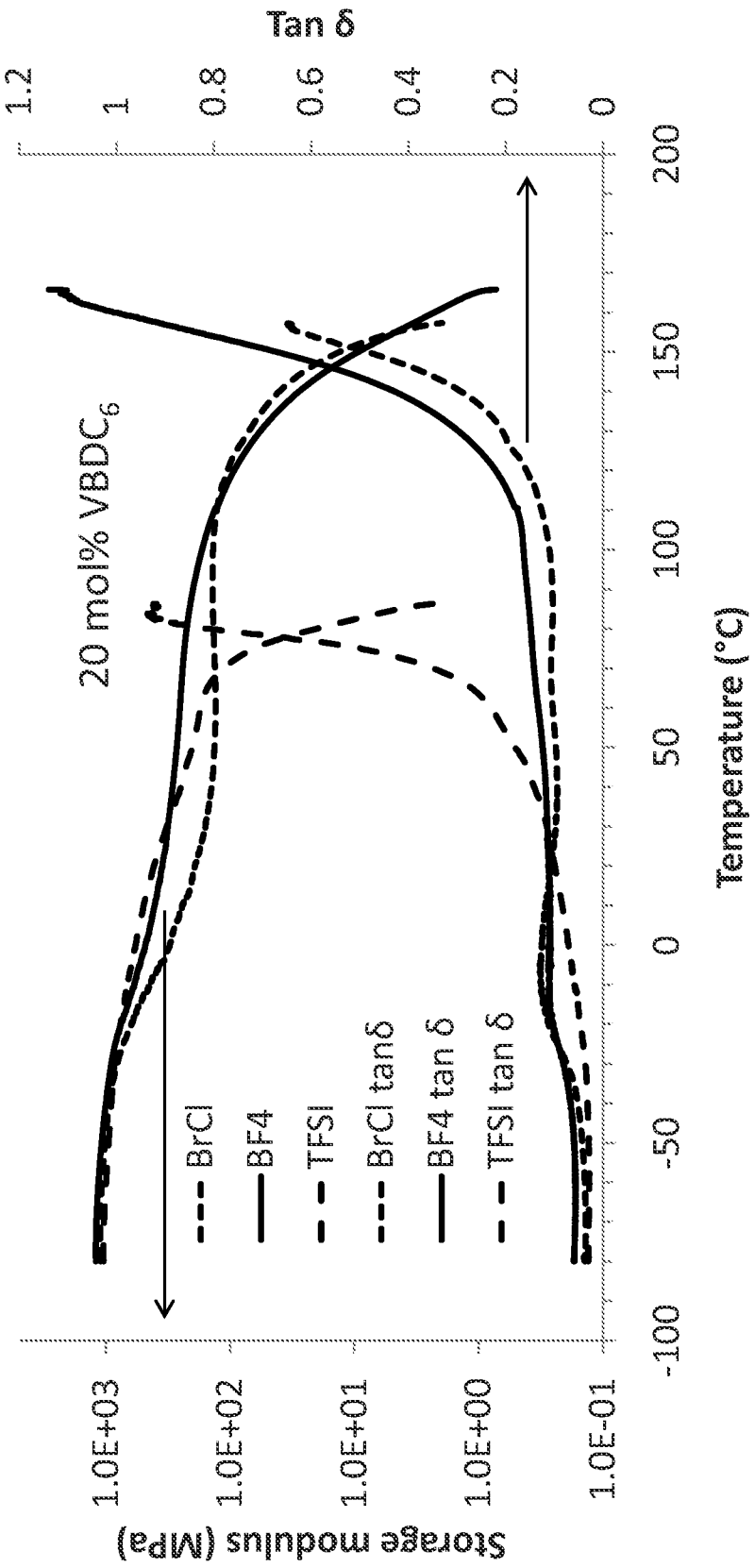

Tan δ
1.2
1
0.8
0.6
0.4
0.2
0
20 mol% VBDC6
BrCl
BF4
TFSI
BrCl tanδ
BF4 tan δ
TFSI tan δ
Storage modulus (MPa)
1.0E+03
1.0E+02
1.0E+01
1.0E+00
1.0E-01
-100
-50
0
50
100
150
200
Temperature (°C)

FIGURE 7

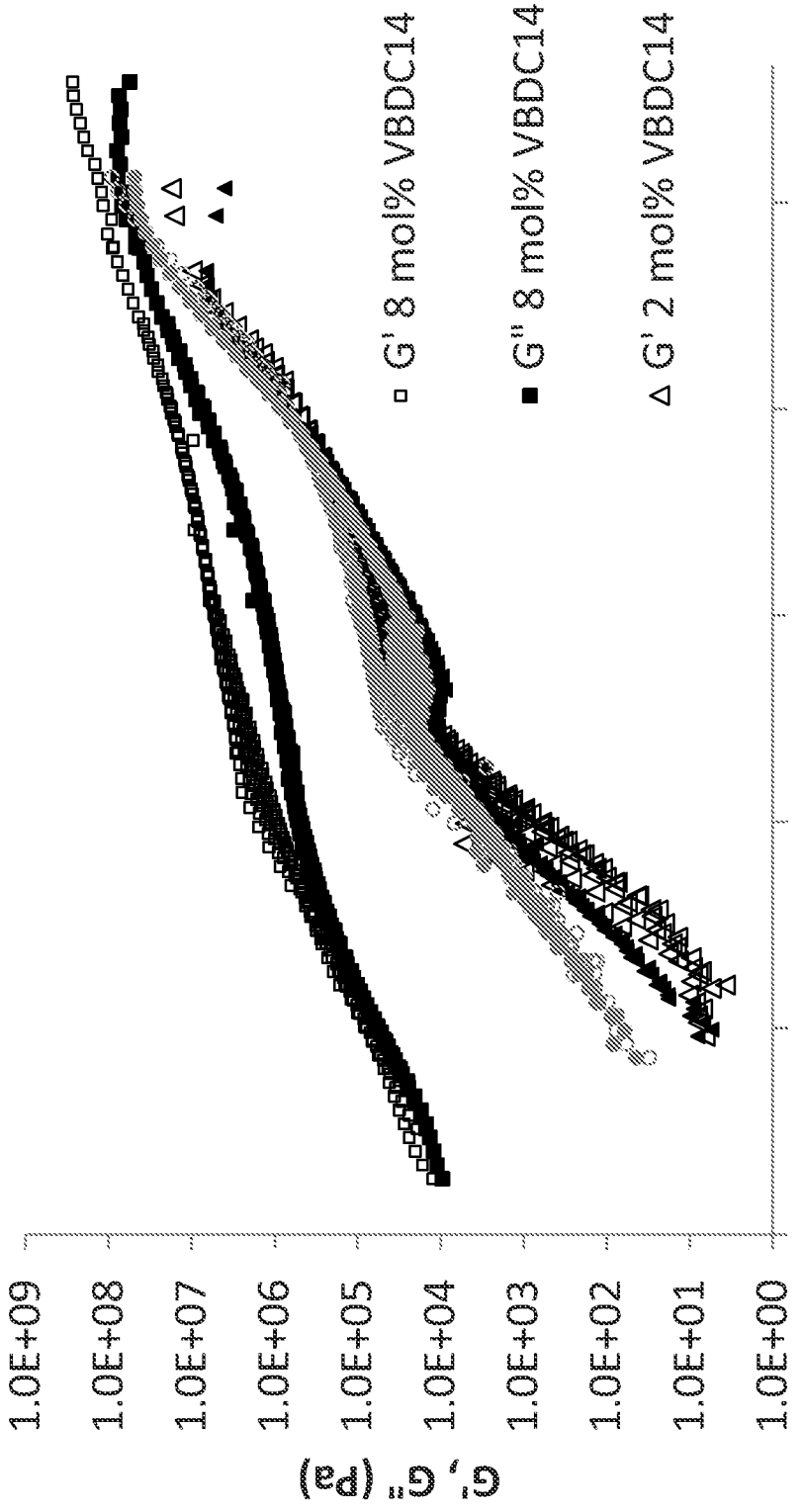

G' 8 mol% VBDC14
G'' 8 mol% VBDC14
G' 2 mol% VBDC14
G', G'' (Pa)
1.0E+09
1.0E+08
1.0E+07
1.0E+06
1.0E+05
1.0E+04
1.0E+03
1.0E+02
1.0E+01
1.0E+00
1.0E-08
1.0E-05
1.0E-02
1.0E+01
1.0E+04
1.0E+07
$a_T\omega$ (rad/s)

FIGURE 8

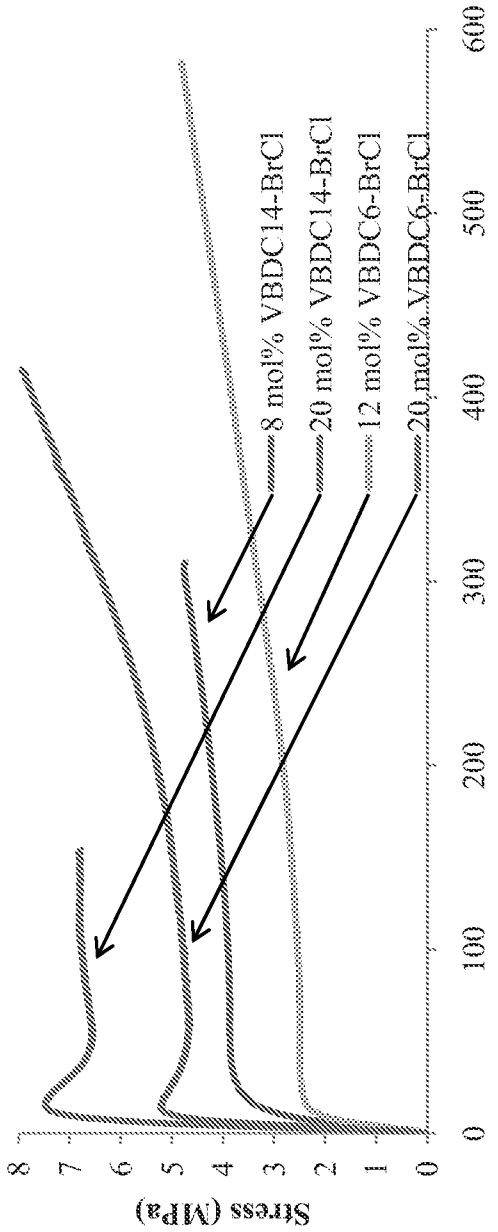

Stress (MPa)
0
1
2
3
4
5
6
7
8
0
100
200
300
400
500
600
Strain (%)
8 mol% VBDC14-BrCl
20 mol% VBDC14-BrCl
12 mol% VBDC6-BrCl
20 mol% VBDC6-BrCl

FIGURE 9

T_d (°C) C_{14}	BrCl	BF_4	TF_2N
20 mol%	197	286	266

T_d (°C) C_6	BrCl	BF_4	TF_2N
20 mol%	203	293	276

FIGURE 10

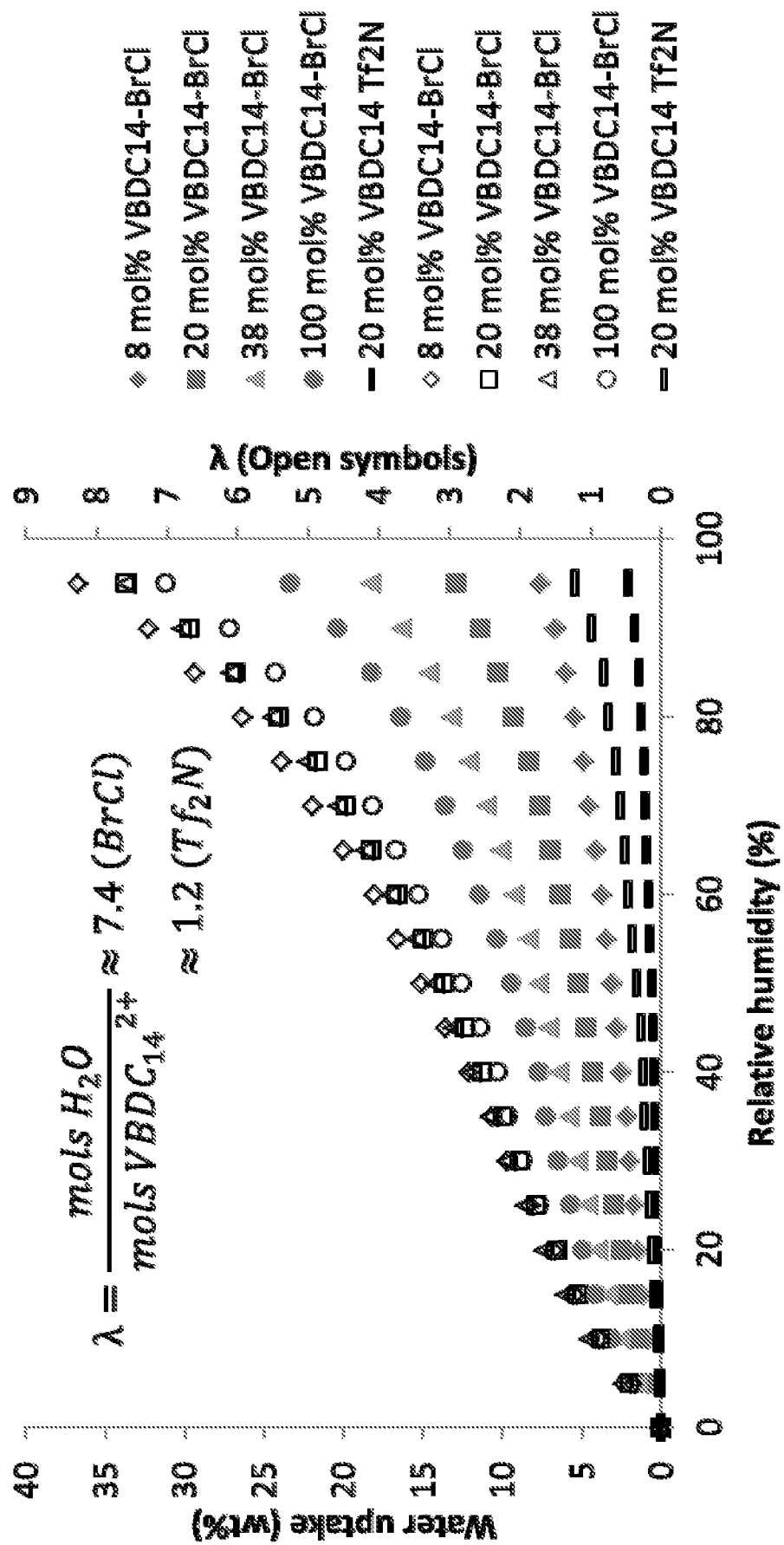

8 mol% VBDC14-BrCl
20 mol% VBDC14-BrCl
38 mol% VBDC14-BrCl
100 mol% VBDC14-BrCl
20 mol% VBDC14 Tf2N
8 mol% VBDC14-BrCl
20 mol% VBDC14-BrCl
38 mol% VBDC14-BrCl
100 mol% VBDC14-BrCl
20 mol% VBDC14 Tf2N
λ (Open symbols)
Water uptake (wt%)
Relative humidity (%)
$\lambda = \frac{mols\ H_2O}{mols\ VBDC_{14}^{2+}}$
≈ 7,4 (BrCl)
≈ 1,2 (Tf2N)

FIGURE 11

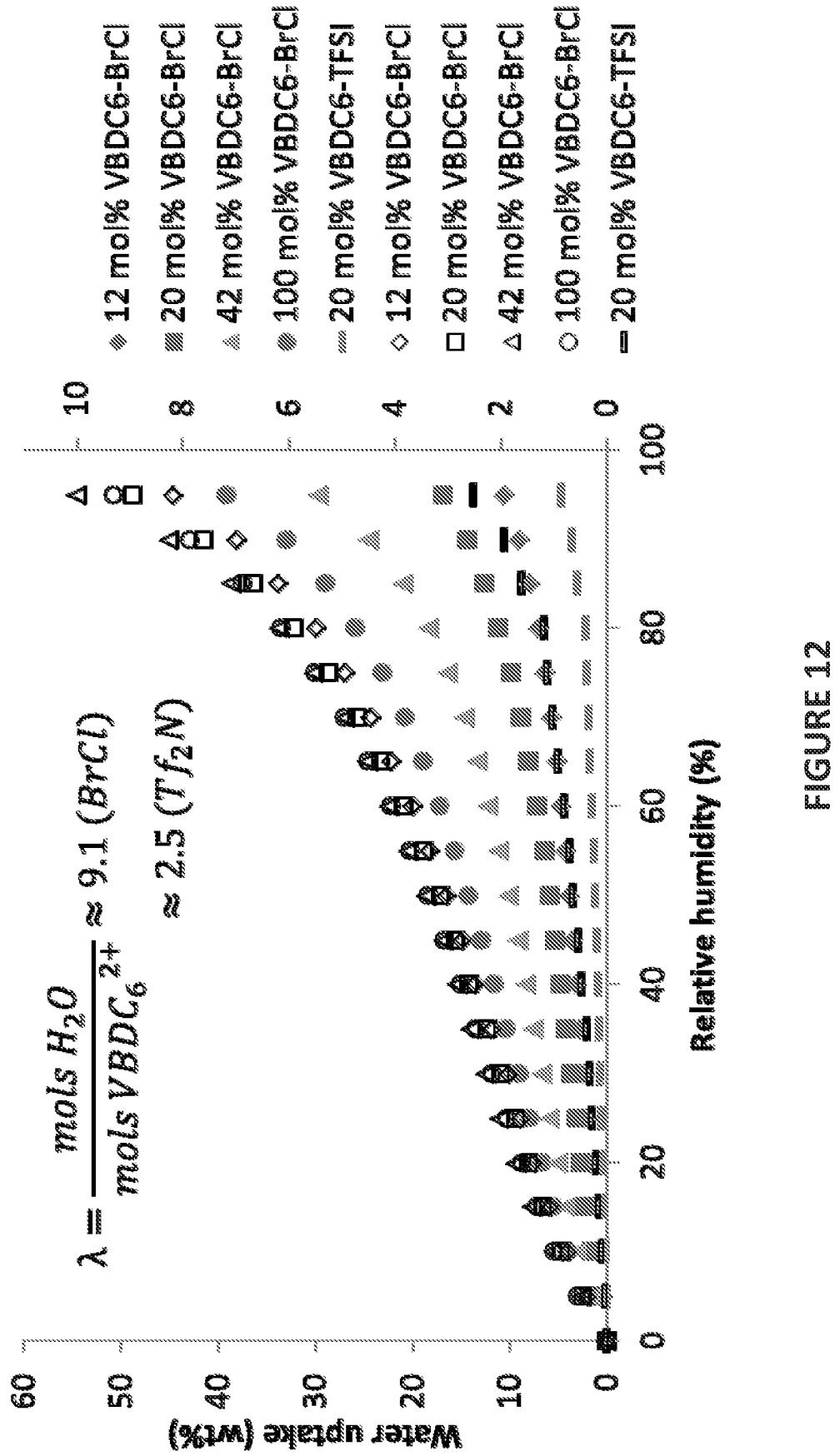
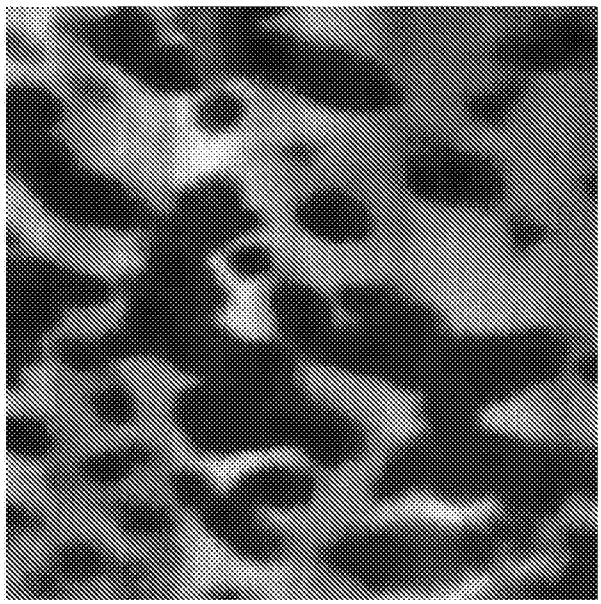
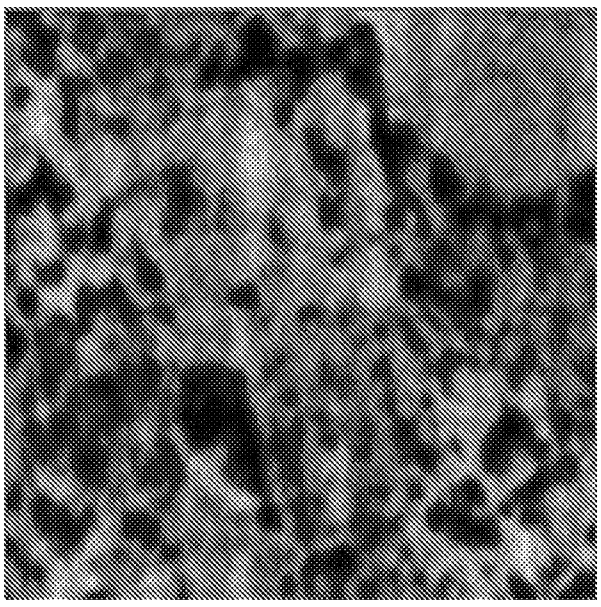

Water uptake (wt%)
Relative humidity (%)
$\lambda = \frac{mols\ H_2O}{mols\ VBDC_6^{2+}} \approx 9.1\ (BrCl)$
$\approx 2.5\ (Tf_2N)$
12 mol% VBDC6-BrCl
20 mol% VBDC6-BrCl
42 mol% VBDC6-BrCl
100 mol% VBDC6-BrCl
20 mol% VBDC6-TFSI
12 mol% VBDC6-BrCl
20 mol% VBDC6-BrCl
42 mol% VBDC6-BrCl
100 mol% VBDC6-BrCl
20 mol% VBDC6-TFSI

FIGURE 12



20 mol% VBDC$_6$-BrCl



20 mol% VBDC$_{14}$-BrCl

FIGURE 13

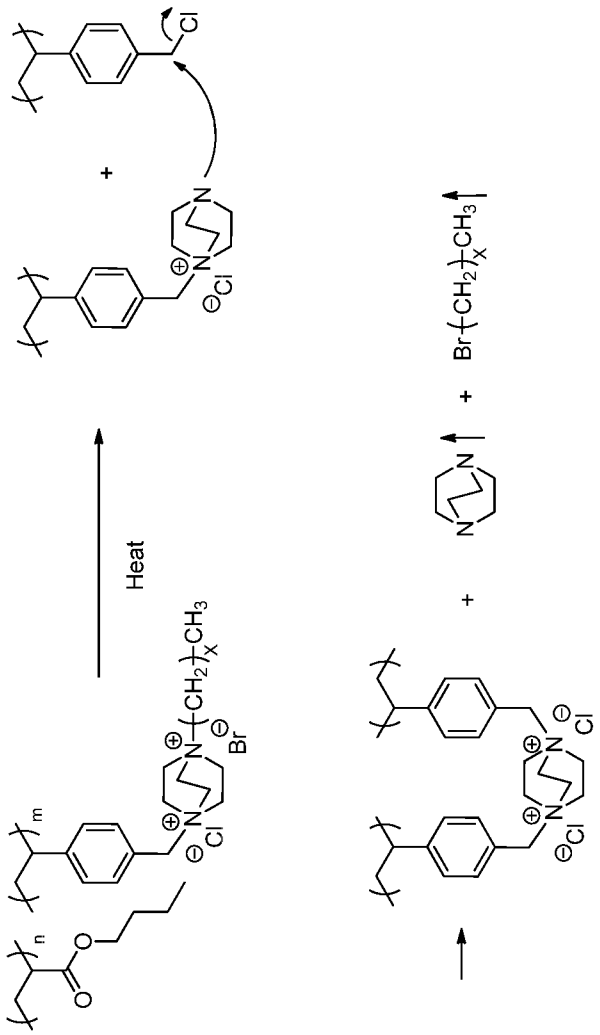


FIGURE 14

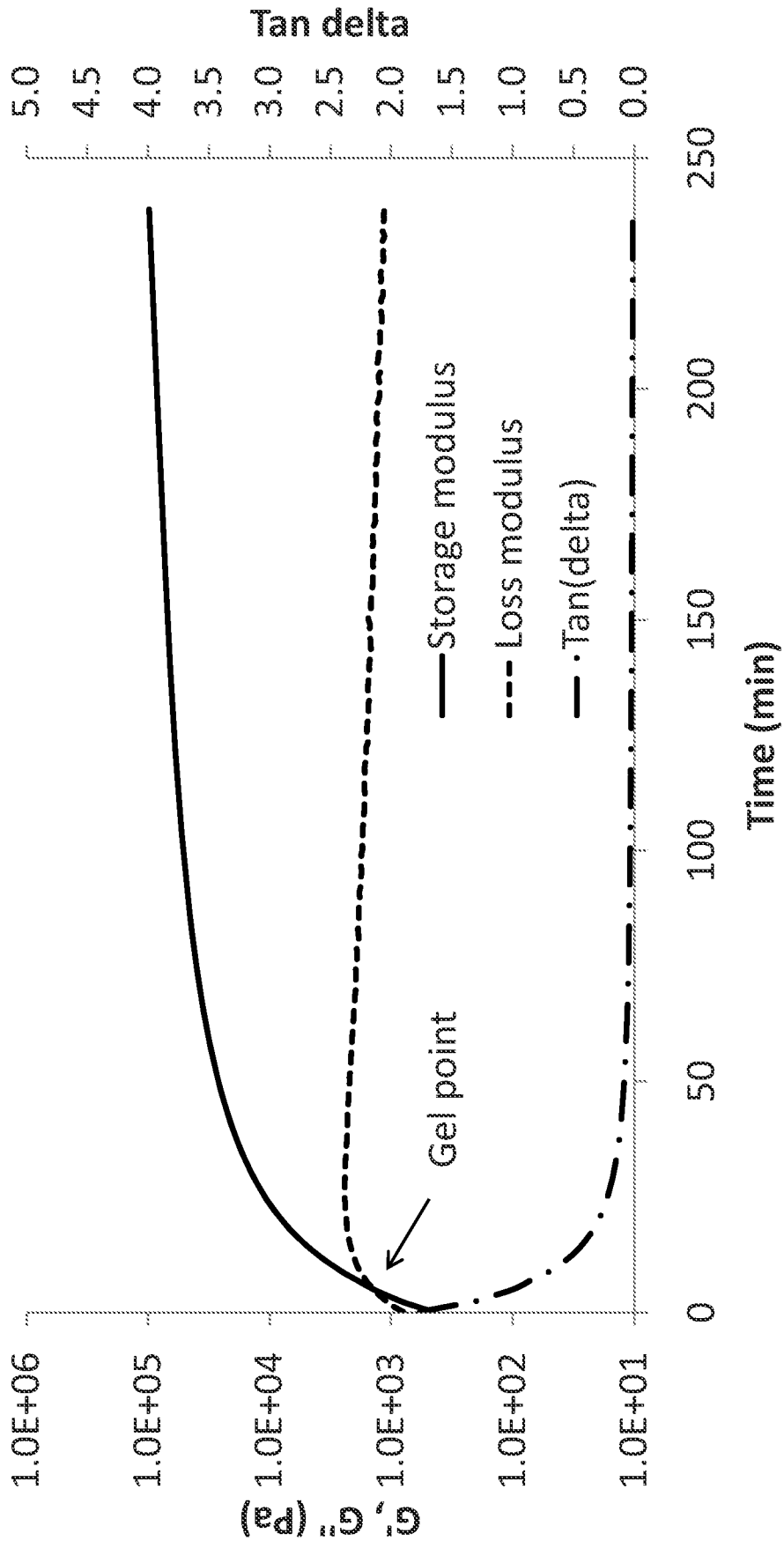

Tan delta
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Storage modulus
Loss modulus
Tan(delta)
Gel point
Time (min)
0
50
100
150
200
250
1.0E+06
1.0E+05
1.0E+04
1.0E+03
1.0E+02
1.0E+01
G', G'' (Pa)

FIGURE 15