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(54) Title: COPOLYMERIC COMPOSITIONS OF TRIFLUOROSTYRENE, SUBSTITUTED TRIFLUOROSTYRENE AND SUBSTITUTED ETHYLENE, AND ION-EXCHANGE MEMBRANES FORMED THEREFROM

(57) Abstract

Polymeric compositions are derived from copolymers of substituted and unsubstituted α,β,β-trifluorostyrene, with a variety of substituted ethylene monomers. These compositions are suitable for use as membranes, particularly as ion-exchange membranes, and more particularly as solid polymer electrolytes in electrochemical applications, such as, for example, electrochemical fuel cells.

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COPOLYMERIC COMPOSITIONS OF TRIFLUOROSTYRENE, SUBSTITUTED TRIFLUOROSTYRENE AND SUBSTITUTED ETHYLENE, AND ION-EXCHANGE MEMBRANES FORMED THEREFROM

Cross-Reference To Related Applications

This application is a continuation-in-part of U.S. Patent Application Serial No. 08/442,206 filed May 16, 1995, which is a continuation of U.S. Patent Application Serial No. 08/124,924 filed September 21, 1993, now U.S. Patent No. 5,422,411 issued June 6, 1995, entitled "Trifluorostyrene And Substituted Trifluorostyrene Copolymeric Compositions And Ion-exchange Membranes Formed Therefrom". The '924 application, incorporated herein by reference in its entirety, describes polymeric compositions derived from copolymers of α,ß,ß-trifluorostyrene with a variety of substituted α,ß,ß-trifluorostyrenes. This application is also related to U.S. Patent Application Serial No. 08/480,098 filed June 6, 1995 entitled "Substituted Trifluorostyrene Compositions". The latter application, which is also incorporated herein by reference in its entirety, describes copolymers of α,ß,ß-trifluorostyrene and substituted α,ß,ß-trifluorostyrenes including sulfonyl fluoride substituted α,ß,ß-trifluorostyrene monomers that are conveniently hydrolyzed to produce polymeric compositions with ion-exchange moieties. These compositions are suitable for use as membranes, particularly as ion-exchange membranes.

Field Of The Invention

The present invention relates to substituted ethylene-trifluorostyrene based copolymeric compositions. More particularly, the present invention relates to polymeric compositions derived from copolymers of substituted and unsubstituted α,ß,ß-trifluorostyrene, with a variety of substituted ethylene monomers. These compositions are particularly suitable for use as solid polymer electrolytes in electrochemical applications, such as, for example, electrochemical fuel cells.

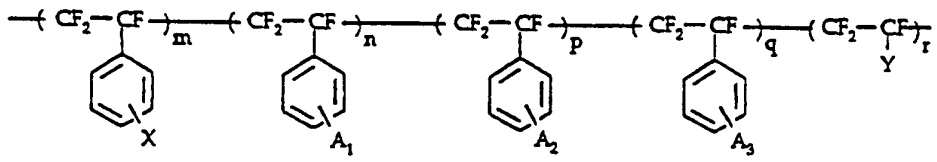
Background Of The Invention

A variety of membranes have been developed over the years for application as solid polymer electrolytes for fuel cells and other electrochemical applications. These polymers have typically been perfluorinated aliphatic compositions, such as those described in U.S. Patent Nos. 3,282,875 and 4,330,654. These compositions are very expensive membranes, and in the case of the '875 patent tend to exhibit poor fuel cell performance characteristic at high current densities. Alternatively, a series of low-cost polyaromatic-based systems have been investigated, such as those described in U.S. Patent Nos. 3,528,858 and 3,226,361. These materials suffer from poor chemical resistance and mechanical properties which tend to limit their use in fuel

cell applications. The investigation of other materials has involved the study of polymers containing the monomer unit α,ß,ß-trifluorostyrene, for example, those described in U.S. Patent No. 3,341,366 and Japanese Unexamined Patent Publication (Kokai) No. 53-26884. However, these compositions suffered from poor mechanical properties in the case of the '366 patent, and very low polymer yield in the case of the Japanese patent publication.

Summary Of The Invention

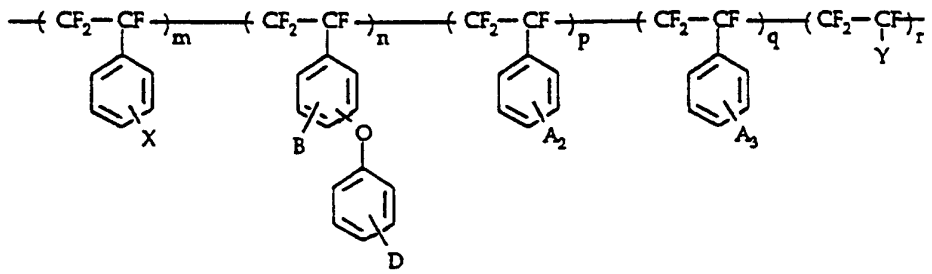
Polymeric compositions of the present invention include:



where r is an integer greater than zero, and at least one of m, n, p and q is an integer greater than zero; X is selected from the group consisting of SO_3H, PO_2H_2, PO_3H_2, $CH_2PO_3H_2$, COOH, OSO_3H, OPO_2H_2, OPO_3H_2, NR_3^+ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls) and $CH_2NR_3^+$ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls); A_1, A_2 and A_3 are selected from the group consisting of SO_2F, halogens, alkyls, perfluoroalkyls, O-R (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls), $CF=CF_2$, CN, NO_2 and OH; and Y is selected from the group consisting

of hydrogen, halogens, $C_xH_yF_z$ (where x is an integer greater than zero and y+z = 2x+1), O-R (where R is selected from the group consisting of $C_xH_yF_z$ (where x is an integer greater than zero and y+z = 2x+1) and aryls), $CF=CF_2$, CN, COOH, CO_2R^1 (where R^1 is selected from the group consisting of alkyls, perfluoroalkyls, aryls, and NR^2R^3 where R^2 and R^3 are selected from the group consisting of hydrogen, alkyls and aryls). The group from which A_1, A_2 and A_3 are selected may further consist of hydrogen provided that Y is not a fluorine, carboxylic acid or ester moiety, or provided that r and at least two of n, p and q are integers greater than zero, or provided that r and m are integers greater than zero.

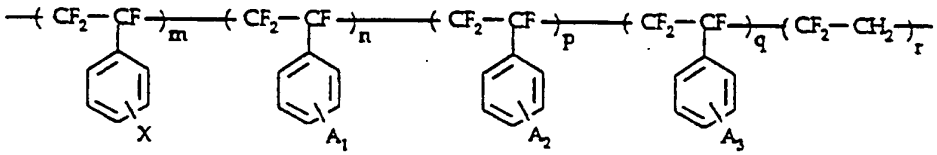
In an alternative aspect, polymeric compositions of the present invention include:



where n and r are integers greater than zero, and m, p and q are zero or an integer greater than zero; X is selected from the group consisting of SO_3H, PO_2H_2, PO_3H_2, $CH_2PO_3H_2$, COOH, OSO_3H, OPO_2H_2, OPO_3H_2, NR_3^+ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls) and $CH_2NR_3^+$ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls); B and D are selected from the group consisting of

hydrogen, SO_2F, SO_3H, PO_2H_2, PO_3H_2, $CH_2PO_3H_2$, COOH, OSO_3H, OPO_2H_2, OPO_3H_2, NR_3^+ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls) and $CH_2NR_3^+$ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls); A_2 and A_3 are selected from the group consisting of hydrogen, SO_2F, halogens, alkyls, perfluoroalkyls, O-R (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls), $CF=CF_2$, CN, NO_2, and OH; and Y is selected from the group consisting of hydrogen, halogens, $C_xH_yF_z$ (where x is an integer greater than zero and y+z = 2x+1), O-R (where R is selected from the group consisting of $C_xH_yF_z$ (where x is an integer greater than zero and y+z = 2x+1) and aryls), $CF=CF_2$, CN, COOH, CO_2R^1 (where R^1 is selected from the group consisting of alkyls, perfluoroalkyls, aryls, and NR^2R^3 where R^2 and R^3 are selected from hydrogen, alkyls and aryls).

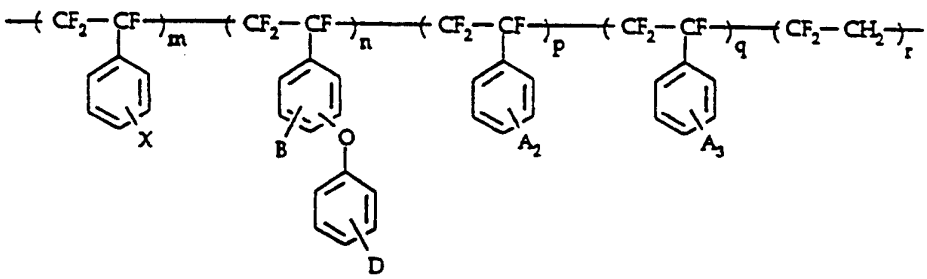
In a further alternative aspect, polymeric compositions of the present invention include:



where r is an integer greater than zero, and at least one of m, n, p and q is an integer greater than zero; X is selected from the group consisting of SO_3H, PO_2H_2, PO_3H_2, $CH_2PO_3H_2$, COOH, OSO_3H, OPO_2H_2, OPO_3H_2, NR_3^+ (where R is selected from the group

consisting of alkyls, perfluoroalkyls and aryls) and $CH_2NR_3^+$ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls); A_1, A_2 and A_3 are selected from the group consisting of hydrogen, SO_2F, halogens, alkyls, perfluoroalkyls, O-R (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls), $CF{=}CF_2$, CN, NO_2, and OH.

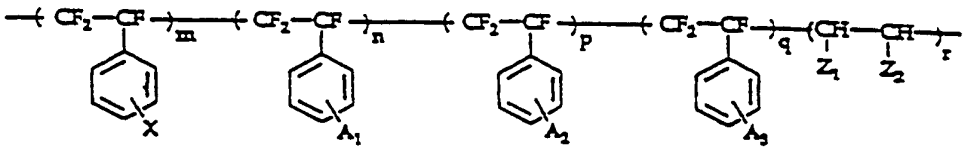
In a still further aspect, polymeric compositions of the present invention include:



where n and r are integers greater than zero, and m, p and q are zero or an integer greater than zero; X is selected from the group consisting of SO_3H, PO_2H_2, PO_3H_2, $CH_2PO_3H_2$, COOH, OSO_3H, OPO_2H_2, OPO_3H_2, NR_3^+ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls) and $CH_2NR_3^+$ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls); B and D are selected from the group consisting of hydrogen, SO_2F, SO_3H, PO_2H_2, PO_3H_2, $CH_2PO_3H_2$, COOH, OSO_3H, OPO_2H_2, OPO_3H_2, NR_3^+ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls) and $CH_2NR_3^+$ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls); A_2 and A_3 are selected from the group consisting of hydrogen, SO_2F, halogens, alkyls, perfluoroalkyls, O-R (where R is selected from the

group consisting of alkyls, perfluoroalkyls and aryls), $CF=CF_2$, CN, NO_2, and OH.

In another aspect, polymeric compositions of the present invention include:



where r is an integer greater than zero, and at least one of m, n, p and q is an integer greater than zero; X is selected from the group consisting of SO_3H, PO_2H_2, PO_3H_2, $CH_2PO_3H_2$, COOH, OSO_3H, OPO_2H_2, OPO_3H_2, NR_3^+ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls) and $CH_2NR_3^+$ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls); and A_1, A_2 and A_3 are selected from the group consisting of hydrogen, SO_2F, halogens, alkyls, perfluoroalkyls, O-R (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls), $CF=CF_2$, CN, NO_2 and OH; and Z_1 and Z_2 are selected from the group consisting of hydrogen and fluorine. Thus, in these embodiments the substituted ethylene fragment may be $-CH_2-CH_2-$, $-CH_2-CHF-$, or -CHF-CHF-.

The A_1, A_2 and A_3 substituents may be further elaborated by known techniques such as, for example, hydrolysis of the CN group to form COOH or by reduction with common reducing agents (such as, for example, Raney nickel) to form a primary amine,

thereby transforming the A_1, A_2 and A_3 substituents into ion-exchange moieties.

In any of the embodiments described above, the group from which A_1, A_2 and A_3 are selected can optionally further consist of SO_3H, PO_2H_2, PO_3H_2, $CH_2PO_3H_2$, COOH, OSO_3H, OPO_2H_2, OPO_3H_2, NR_3^+ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls) and $CH_2NR_3^+$ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls). The resulting polymeric compositions may thus comprise one or more type of ion-exchange moiety, and may also comprise both cation-exchange and anion-exchange moieties.

The substituents on the aromatic rings (A_1, A_2, A_3, X, B and D) may each be located in the ortho, meta or para positions, as indicated in the formulas wherein the chemical bond drawn for these substituents intersects the aromatic ring.

As used herein, the term "aryl" refers to a substituted or unsubstituted aromatic group.

The polymeric compositions of the present invention can also consist essentially of the above chemical units. Thus, the polymers could include amounts of other monomers such as, for example, styrene.

Crosslinking is preferably introduced into the polymeric compositions of the present invention for applications in which it is, for example, desirable to increase dimensional stability, reduce swelling, modify the mechanical properties, or control ion-exchange selectivity.

In accordance with convention in the art, the above chemical formulas for polymeric compositions

containing more than two monomers (where at least three of m, n, p, q and r are greater than zero) are intended to indicate that the monomers are present in the polymeric composition, but are not limited to the particular order in which the monomers are set forth in each general formula. For example, random linear copolymers and/or linear block copolymers formed from the indicated monomers are both contemplated.

The polymeric compositions of the present invention are suitably formed into membranes, and are preferably employed as ion-exchange membranes, most preferably as cation exchange membranes in electrochemical fuel cells.

Brief Description of the Drawing

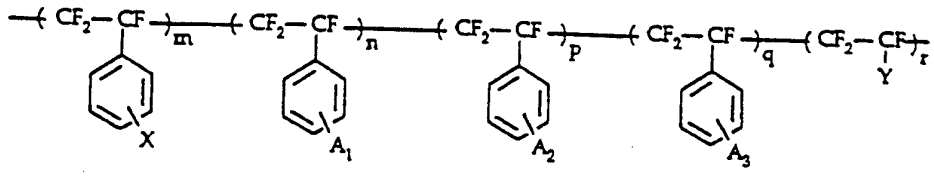
FIG. 1 is a plot of cell voltage as a function of current density (expressed in amperes per square foot or "ASF") in an electrochemical fuel cell employing, respectively, a Nafion 117 (DuPont's trade designation) cation exchange membrane, a sulfonated α,ß,ß-trifluorostyrene - tetrafluoroethylene copolymeric membrane (designated "(TFS-TFE)S05"), and a Dow experimental cation exchange membrane (designated "Dow 11").

Detailed Description Of The Preferred Embodiments

The present invention relates to polymeric compositions derived from copolymers of substituted and unsubstituted α,ß,ß-trifluorostyrene, with a variety of substituted ethylene monomers. The substituted ethylenes of the present invention include ethylene itself ($CH_2=CH_2$), and tetrafluoroethylene ($CF_2=CF_2$), as well as partially

fluorinated ethylenes such as CH_2=CHF, CHF=CHF, CF_2=CH_2, and CF_2=CHF.

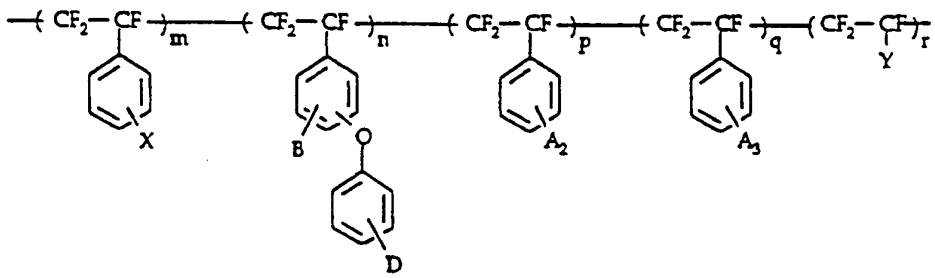
In one aspect, polymeric compositions of the present invention include:



where r is an integer greater than zero, and at least one of m, n, p and q is an integer greater than zero; X is selected from the group consisting of SO_3H, PO_2H_2, PO_3H_2, $CH_2PO_3H_2$, COOH, OSO_3H, OPO_2H_2, OPO_3H_2, NR_3^+ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls) and $CH_2NR_3^+$ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls); A_1, A_2 and A_3 are selected from the group consisting of SO_2F, halogens, alkyls, perfluoroalkyls, O-R (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls), CF=CF_2, CN, NO_2 and OH; and Y is selected from the group consisting of hydrogen, halogens, $C_xH_yF_z$ (where x is an integer greater than zero and y+z = 2x+1), O-R (where R is selected from the group consisting of $C_xH_yF_z$ (where x is an integer greater than zero and y+z = 2x+1) and aryls), CF=CF_2, CN, COOH, CO_2R^1 (where R^1 is selected from the group consisting of alkyls, perfluoroalkyls, aryls, and NR^2R^3 where R^2 and R^3 are selected from the group consisting of hydrogen, alkyls and aryls). The group from which A_1, A_2 and A_3 are selected may further consist of hydrogen

provided that Y is not a fluorine, carboxylic acid or ester moiety, or provided that r and at least two of n, p and q are integers greater than zero, or provided that r and m are integers greater than zero.

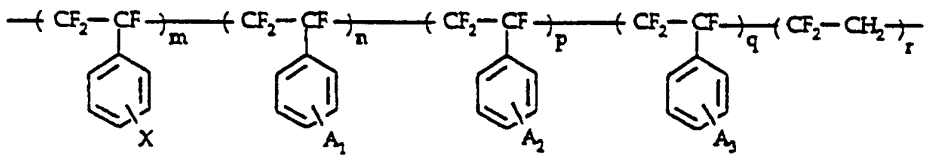
In an alternative aspect, polymeric compositions of the present invention include:



where n and r are integers greater than zero, and m, p and q are zero or an integer greater than zero; X is selected from the group consisting of SO_3H, PO_2H_2, PO_3H_2, $CH_2PO_3H_2$, COOH, OSO_3H, OPO_2H_2, OPO_3H_2, NR_3^+ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls) and $CH_2NR_3^+$ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls); B and D are selected from the group consisting of hydrogen, SO_2F, SO_3H, PO_2H_2, PO_3H_2, $CH_2PO_3H_2$, COOH, OSO_3H, OPO_2H_2, OPO_3H_2, NR_3^+ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls) and $CH_2NR_3^+$ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls); A_2 and A_3 are selected from the group consisting of hydrogen, SO_2F, halogens, alkyls, perfluoroalkyls, O-R (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls), $CF=CF_2$, CN, NO_2, and OH; and Y is selected

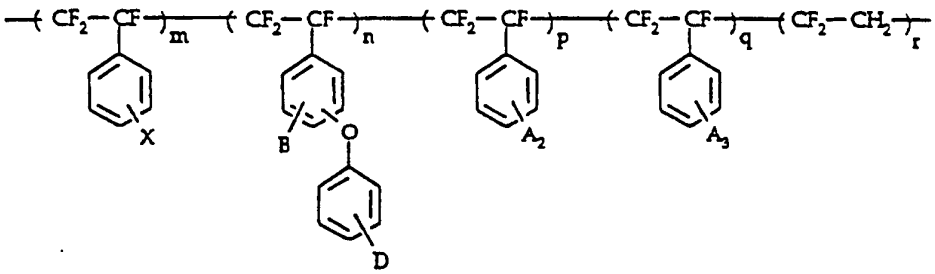
from the group consisting of hydrogen, halogens, $C_xH_yF_z$ (where x is an integer greater than zero and y+z = 2x+1), O-R (where R is selected from the group consisting of $C_xH_yF_z$ (where x is an integer greater than zero and y+z = 2x+1) and aryls), $CF=CF_2$, CN, COOH, CO_2R^1 (where R^1 is selected from the group consisting of alkyls, C_yF_{2y+1} where y is an integer greater than zero, aryls, and NR^2R^3 where R^2 and R^3 are selected from hydrogen, alkyls and aryls).

In a further alternative aspect, polymeric compositions of the present invention include:



where r is an integer greater than zero, and at least one of m, n, p and q is an integer greater than zero; X is selected from the group consisting of SO_3H, PO_2H_2, PO_3H_2, $CH_2PO_3H_2$, COOH, OSO_3H, OPO_2H_2, OPO_3H_2, NR_3^+ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls) and $CH_2NR_3^+$ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls); A_1, A_2 and A_3 are selected from the group consisting of hydrogen, SO_2F, halogens, alkyls, perfluoroalkyls, O-R (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls), $CF=CF_2$, CN, NO_2, and OH.

In a still further aspect, polymeric compositions of the present invention include:

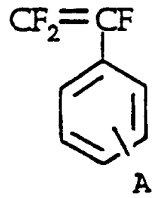


where n and r are integers greater than zero, and m, p and q are zero or an integer greater than zero; X is selected from the group consisting of SO_3H, PO_2H_2, PO_3H_2, $CH_2PO_3H_2$, COOH, OSO_3H, OPO_2H_2, OPO_3H_2, NR_3^+ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls) and $CH_2NR_3^+$ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls); B and D are selected from the group consisting of hydrogen, SO_2F, SO_3H, PO_2H_2, PO_3H_2, $CH_2PO_3H_2$, COOH, OSO_3H, OPO_2H_2, OPO_3H_2, NR_3^+ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls) and $CH_2NR_3^+$ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls); A_2 and A_3 are selected from the group consisting of hydrogen, SO_2F, halogens, alkyls, perfluoroalkyls, O-R (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls), $CF=CF_2$, CN, NO_2, and OH.

In any of the embodiments described above, the group from which A_1, A_2 and A_3 are selected can optionally further consist of SO_3H, PO_2H_2, PO_3H_2, $CH_2PO_3H_2$, COOH, OSO_3H, OPO_2H_2, OPO_3H_2, NR_3^+ (where R is selected from the group consisting of alkyls,

perfluoroalkyls and aryls) and $CH_2NR_3^+$ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls). The resulting polymeric compositions may thus comprise one or more type of ion-exchange moiety, and may also comprise both cation-exchange and anion-exchange moieties.

Polymeric compositions of the present invention can be produced by polymerization of a substituted ethylene monomer with other monomers selected from a group of substituted α,ß,ß-trifluorostyrenes having the chemical formula:



In embodiments in which the substituted ethylene monomer is tetrafluoroethylene, A is selected from the group consisting of SO_2F, halogens, alkyls, perfluoroalkyls, O-R (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls), $CF=CF_2$, CN, NO_2 and OH.

In embodiments in which the substituted ethylene is 1,1-difluoroethylene, A is selected from the group consisting of SO_2F, halogens, alkyls, perfluoroalkyls, O-R (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls), $CF=CF_2$, CN, NO_2 and OH. In an alternative embodiment in which the substituted ethylene is 1,1-difluoroethylene, the group from which A is selected further consists of hydrogen.

In a preferred method, the above monomers are mixed in an aqueous medium containing a free radical initiator and an emulsifying agent, at temperatures in the range of about 35°C - 100°C, and preferably in the range of 45°C - 65°C, for a time period of about 24 to 74 hours under an inert atmosphere. In general, the polymerization procedures and techniques employed in the preparation of polymeric compositions of the present invention are known. A suitable reference for polymerization techniques is Textbook Of Polymer Science, 3rd Edition, by F.W. Billmeyer, Jr., published by John Wiley & Sons.

In general, the monomers used in the preparation of the polymeric compositions of the present invention are commercially available or can be prepared by conventional techniques well known in the art.

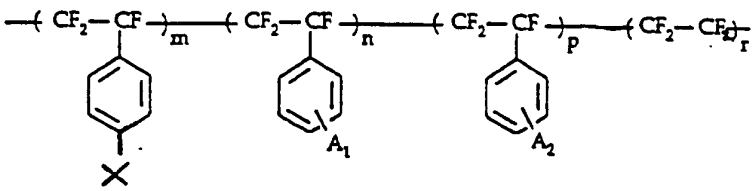
Ion-exchange moieties can be introduced into copolymers containing unsubstituted α,ß,ß-trifluorostyrene units (so-called "base copolymers") via aromatic substitution of at least a portion of those units. For example, base copolymers incorporating pendant unsubstituted phenyl rings can be sulfonated, or in accordance with a further aspect of this invention, may be phosphorylated, carboxylated, quaternary-aminoalkylated or chloromethylated, and further modified to yield $-CH_2PO_3H_2$, $-CH_2NR_3^+$ where R is an alkyl, or $-CH_2NAr_3^+$ where Ar is a substituted or unsubstituted aromatic moiety, and other substituents, to provide cation-exchange or anion-exchange moieties. Further still, the pendent phenyl moiety may contain a hydroxyl group which can be readily elaborated by

existing methods to generate $-OSO_3H$, $-OPO_2H_2$, $-OPO_2H_2$ and $-OPO_3H_2$ cationic exchange sites on the polymer.

In a typical sulfonation reaction used to produce a cationic exchange membrane, the copolymer is dissolved in an appropriate solvent and then reacted with a sulfonating reagent, such as chlorosulfonic acid or a Lewis acid-base complex of sulfur trioxide. The solvent for such a reaction can be selected from the class consisting of chlorinated aliphatic hydrocarbons, such as dichloroethane, tetrachloroethylene and chloroform. The copolymer solution is rendered completely homogeneous prior to the addition of the solution containing the sulfonating reagent. The reaction is then run within the temperature range from about 10°C up to the boiling point of the solvent, and preferably within the temperature range 18°C - 40°C. To ensure adequate functionalization of the copolymer, the reaction is allowed to continue for a period of about one to about four hours, or longer, dependent on the reaction temperature.

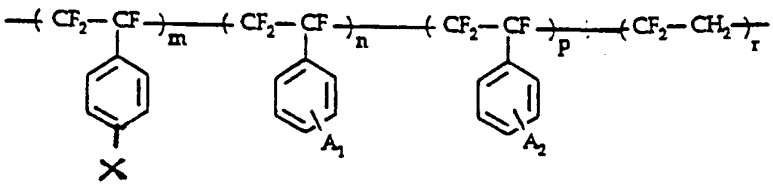
An alternative method of introducing the $-SO_3H$ cation exchange moiety is through hydrolysis of $-SO_2F$ substituents in the copolymer. In a typical hydrolysis reaction, the sulfonyl fluoride is converted to the free sulfonic acid functionality by hydrolysis in concentrated aqueous alkali metal hydroxide at elevated temperatures. This and other procedures for the hydrolysis of $-SO_2F$ to $-SO_3H$ are well-known to those skilled in the art.

Preferred polymeric compositions of the present invention include:



where m, n and r are integers greater than zero, and p is zero or an integer greater than zero; X is selected from the group consisting of SO_2F and SO_3H; A_1 and A_2 are selected from the group consisting of hydrogen, fluorine, CF_3, and para-phenoxy.

Preferred polymeric compositions of the present invention also include:



where m, n and r are integers greater than zero, and p is zero or an integer greater than zero; X is selected from the group consisting of SO_2F and SO_3H; A_1 and A_2 are selected from the group consisting of hydrogen, fluorine, CF_3, and para-phenoxy.

The substituents on the aromatic rings (A_1, A_2, A_3, X, B and D) in the embodiments described above may be located in the ortho, meta or para positions. In preferred aspects of the described embodiments, the substituents are in the meta or

para positions.

The copolymers thus prepared possess favorable properties, such as thermal stability, chemical resistance and favorable mechanical properties, such as tensile strength, compared to the homopolymeric material formed from α,ß,ß-trifluorostyrene (TFS) alone.

Crosslinking can be introduced using conventional techniques well-known to those skilled in the art, such as those employed in preparing divinylbenzene crosslinked polystyrene. Crosslinking, for example to enhance the mechanical and physical properties of the membrane material, can be introduced by reaction of appropriate groups, before or preferably after the claimed polymeric compositions are formed into membranes. Monomers with substituents on the pendant phenyl rings or on the ethylene moiety which are suitable for subsequent crosslinking can be introduced into the copolymer in controlled amounts, thereby permitting some control of the degree of crosslinking in the membrane.

The following examples are for purposes of illustration and are not intended to limit the invention. Examples 1 and 2 describe the synthesis of ternary and quaternary copolymers respectively, without ion-exchange moieties, wherein one of the monomers is tetrafluoroethylene. Examples 3 and 4 describe generalized procedures which may be used to prepare copolymers of the present invention. Example 3 describes a suitable method for copolymerization of monomers all of which are either liquid or solids at ambient temperature and pressure. Example 4 describes a suitable method

for copolymerization of monomers, one or more of which is gaseous at ambient temperature and pressure. Examples 5 and 6 describe the sulfonation of two base copolymers to prepare two of the claimed sulfonated copolymers.

Example 7 sets forth the results of tests performed on an ion-exchange copolymer membrane formed from a sulfonated copolymer of the present invention, in an electrochemical fuel cell.

Example 1

Emulsion copolymerization of m-trifluoromethyl-α,ß,ß-trifluorostyrene, α,ß,ß-trifluorostyrene and tetrafluoroethylene

Into a 1 L Parr® reactor under vacuum , is added (by suction) a slurry containing 350 mL of nitrogen-degassed water, dodecylamine hydrochloride (6.8 g, 27 mmol), potassium persulfate (0.52 g 1.8 mmol) and the following monomer mixture: m-trifluoromethyl-α,ß,ß-trifluorostyrene (11.3 g, 0.05 mol) and α,ß,ß-trifluorostyrene (47.4 g, 0.30 mol). The reactor is pressurized to approximately 150 psi with tetrafluoroethylene (15 g, 0.15 mol). The resultant emulsion is heated to 50 °C and kept at this temperature for approximately 72 hours. The mixture is then poured into rapidly stirring potassium hydroxide solution (8 g, 0.14 mol in 500 mL water) at 70C°. The polymer which precipitates is filtered, transferred into a Soxhlet thimble and washed by continuous extraction with refluxing methanol to afford an off-white powder; yield 46.0 g (63%), intrinsic viscosity [η] = 0.80 dL/g as determined in toluene at 30°C. ^{19}F-NMR analysis

performed on a VARIAN XL-300 NMR instrument using $CDCl_3$ as solvent is used to confirm incorporation of all three monomers.

Example 2

Emulsion copolymerization of m-trifluoromethyl-α,ß,ß-trifluorostyrene, p-sulfonyl fluoride-α,ß,ß-trifluorostyrene, α,ß,ß-trifluorostyrene and tetrafluoroethylene

Into a 1 L Parr® reactor under vacuum, is added (by suction) a slurry containing 350 mL of nitrogen-degassed water, dodecylamine hydrochloride (6.8 g, 27 mmol), potassium persulfate (0.52 g, 1.8 mol) and the following monomer mixture: m-trifluoromethyl-α,ß,ß-trifluorostyrene (6.1 g, 54 mmol), p-sulfonyl fluoride-α,ß,ß-trifluorostyrene (35 g, 0.146 mol) and α,ß,ß-trifluorostyrene (8.5 g, 54 mmol). The reactor is then pressurized to 80 psi with tetrafluoroethylene (8.1 g, 81 mol). The resultant emulsion is then heated to 50 °C and kept at this temperature for approximately 72 hours. The mixture is then poured into rapidly stirring potassium hydroxide solution (8 g, 0.14 mol in 500 mL water) at 70C°. The polymer which precipitates is filtered, transferred into a Soxhlet thimble and washed by continuous extraction with refluxing methanol to afford a yellow powder; yield 52.2 g (90%), intrinsic viscosity [η] = 1.14 dL/g as determined in toluene at 30°C. ^{19}F-NMR analysis performed on a VARIAN XL-300 NMR instrument using $CDCl_3$ as solvent is used to confirm incorporation of all four monomers.

Example 3

General Emulsion Copolymerization Procedure (for monomers which are liquid or solid at ambient temperature and pressure)

To a 12 L reaction vessel equipped with a stirrer, water-cooled condenser, heating mantle and temperature controller is added 3.2 L of water. The water is degassed with nitrogen for approximately one hour and the reaction is kept under a nitrogen atmosphere throughout. Dodecylamine hydrochloride (58 g, 0.26 mol) is added and stirred into the water. At this point the desired monomers (which may be premixed) are added to the vessel with stirring, to form an emulsion. The temperature of the emulsion is increased to 50°C and potassium persulfate (4.42 g 15 mmol) is added. The reaction is allowed to continue for approximately 72 hours. Subsequently, 2 L of water is added to dilute the emulsion, followed by a solution of potassium hydroxide (80 g, 1.43 mol) dissolved in 2 L of water. The precipitated polymer is then stirred vigorously for approximately one hour at 75°C. The mixture upon cooling is filtered, the filter cake being washed several times with fresh water. Having removed the majority of the filtrate, the cake is then transferred into a Soxhlet thimble and washed by continuous extraction with refluxing methanol to give a random, linear copolymer of the monomers introduced. The resultant product (typically an off-white powder) is sufficiently pure for further elaboration.

Example 4

General Emulsion Copolymerization Procedure (for reactions in which at least one monomer component is a gas at ambient temperature and pressure)

The reaction procedure is essentially as described in Example 3 above, with the exception that the presence of a gaseous monomer necessitates that the reaction be performed in a pressurized vessel. Thus, when for example the ethylene-based monomer is gaseous, the reaction is performed in, for example, a Parr® stainless steel reactor. The reactor is equipped with a central stirring shaft, a thermocouple and gas inlet valve, liquid inlet valve and a sampling tube. Depending on the reactivity of the gaseous monomer relative to the other monomer(s), slow addition of the more reactive monomer(s), can be achieved by fixing a pressure-controlled addition funnel to the reactor.

Example 5

Sulfonation of a α,ß,ß-Trifluorostyrene - Tetrafluoroethylene Copolymer

Chloroform (200 mL) is added to a 500 mL 3-neck flask fitted with mechanical stirrer, water-cooled condenser and thermocouple attachments. To this is added in portions 7.5 g of a copolymer-(α,ß,ß-trifluorostyrene - tetrafluoroethylene), which may be prepared according to the method described in Example 4. On obtaining a homogeneous solution, a sulfonating mixture, comprising sulfur trioxide (7.62 g, 95 mmol) and triethyl phosphate

(4.30 g, 24 mmol) in chloroform is rapidly added with vigorous stirring. The resultant mixture is stirred for a further hour at room temperature before quenching the reaction in deionized water. The precipitate is filtered, washed with deionized water, transferred into a Soxhlet thimble and washed by continuous extraction with refluxing chloroform to afford an orange solid powder; yield approximately 11 g, equivalent weight 393 g/mol, water content 184%.

Example 6

Sulfonation of a α,ß,ß-Trifluorostyrene - m-Trifluoromethyl-α,ß,ß-trifluorostyrene - Tetrafluoroethylene Copolymer

In a procedure essentially identical to that described in Example 5, 7.50 g of copolymer-(α,ß,ß-trifluorostyrene - m-trifluoromethyl-α,ß,ß-trifluorostyrene - tetrafluoroethylene), prepared according to the method described in Example 1, dissolved in 200 mL of chloroform is reacted with a sulfonating mixture, comprising sulfur trioxide (7.98 g; 0.10 mole) and triethyl phosphate (4.31 g; 0.024 mole) in chloroform. The resultant mixture is stirred for one hour at room temperature before quenching the reaction in deionized water The precipitate is filtered, washed with deionized water, transferred into a Soxhlet thimble and washed by continuous extraction with refluxing chloroform to afford an orange powder; yield approximately 10 g, equivalent weight 389 g/mol.

Example 7

An N,N-dimethylformamide solution of a sulfonated α,ß,ß-trifluorostyrene - tetrafluoroethylene copolymer (equivalent weight 393 g/mol), prepared according to the method described in Example 5, is cast onto a glass substrate using a casting knife. Controlled evaporation of the solvent under a slightly negative pressure results in formation of a membrane (thickness 0.11 mm). The membrane is bonded on opposite major surfaces to two catalyzed carbon paper electrodes at room temperature under 7,500 pounds of pressure. The membrane electrode assembly ("MEA") is tested in the Ballard Mark IV single cell fuel cell (see U.S. Patent Nos. 4,988,583; 5,108,849; 5,170,124; 5,176,966 and 5,200,278; all incorporated herein by reference in their entirety). The results for the sulfonated copolymer membrane tested (designated (TFS-TFE)S05), a DuPont Nafion 117 cation exchange membrane, and a Dow experimental cation exchange membrane (available under the trade designation XUS 13204.10), are shown in Table 1 below.

Table 1

Performance of (TFS-TFE)S05 Copolymer Membrane in a Ballard Mark IV Fuel Cell

Amps/ft^2	Cell Voltage (V)		
	BAM4G	Nafion 117	DOW
100	--	0.840	0.846
200	0.779	0.790	0.818
300	0.744	0.740	0.783
400	0.703	0.690	0.748
500	0.662	0.650	0.678
600	0.634	0.580	0.645
700	0.595	0.510	0.615
800	0.560	0.430	0.568
900	0.514	0.330	0.517
1000	0.463	0.150	0.440
1100	0.414	--	0.342

The following operating conditions applied to the fuel cell in which the membranes were tested:

Temperature = 70°C, reactant inlet pressure 24 psi for both air and H_2, reactant stoichiometries of 2.0 air and 1 to 1.15 H_2.

FIG. 1 is a polarization plot of voltage as a function of current density in an electrochemical fuel cell employing, respectively, a DuPont Nafion 117 cation exchange membrane, a Dow experimental cation exchange membrane (available under the trade designation XUS 13204.10), and sulfonated α,ß,ß-trifluorostyrene - tetrafluoroethylene copolymeric membrane designated (TFS-TFE)S05 as prepared in

Example 7 above. As shown in FIG. 1, the sulfonated α,ß,ß-trifluorostyrene - tetrafluoroethylene copolymeric membrane achieved higher cell voltages than the Nafion 117 membrane at all current densities greater than 300 A/ft^2, and achieved higher cell voltages than the experimental Dow membrane at current densities greater than 900 A/ft^2.

Copolymers formed from tetrafluoroethylene, α,ß,ß-trifluorostyrene and various substituted α,ß,ß-trifluorostyrenes have been produced in yields greater than 60%.

Copolymers of the present invention have the following additional advantages:

1. Flexibility to introduce a wide variety of different ion-exchange functionalities due to the presence of the pendent aromatic groups.
2. The ability to produce a large series of polymeric materials with different equivalent weights starting from the same base copolymer; another flexibility provided by the pendent aromatic substituents.
3. Processibility, in that these copolymers are soluble in a variety of common solvents, for example, N,N-dimethylformamide, dimethyl sulfoxide and N-methylpyrrolidone.
4. The ability to introduce crosslinking, using conventional techniques, such as those employed in preparing divinylbenzene crosslinked polystyrene, to enhance physical and mechanical

properties.

5. Potentially lower cost in view of the low cost of commercially available substituted ethylene monomers.

6. Improved mechanical properties due to increased backbone flexibility and improved dimensional stability through increased overall hydrophobicity resulting from the incorporation of substituted ethylene moieties.

In addition to the utility of the sulfonated copolymeric membranes described herein as ion-exchange membranes for electrochemical fuel cells, the following further utilities are also contemplated:

1. Proton exchange membrane based water electrolysis, which involves a reverse chemical reaction to that employed in hydrogen/oxygen electrochemical fuel cells.

2. Chloralkali electrolysis, typically involving the electrolysis of a brine solution to produce chlorine and sodium hydroxide, with hydrogen as a by-product.

3. Electrode separators in conventional batteries due to the chemical inertness and high electrical conductivity of the sulfonated copolymer membranes.

4. Ion-selective electrodes, particularly those used for the potentiometric determination of a specific ion such as Ca^{2+}, Na^{+}, K^{+} and like ions. These copolymers could also be employed as the sensor material for humidity sensors, as

the electrical conductivity of an ion exchange membrane varies with humidity.

5. Ion-exchange material for separations by ion-exchange chromatography. Typical such applications are deionization and desalination of water (for example, the purification of heavy metal contaminated water), ion separations (for example, rare-earth metal ions, trans-uranium elements), and the removal of interfering ionic species.

6. Ion-exchange membranes employed in analytical preconcentration techniques (Donnan Dialysis). This technique is typically employed in analytical chemical processes to concentrate dilute ionic species to be analyzed.

7. Ion-exchange membranes in electrodialysis, in which membranes are employed to separate components of an ionic solution under the driving force of an electrical current. Electrolysis applications include the industrial-scale desalination of brackish water, preparation of boiler feed make-up and chemical process water, de-ashing of sugar solutions, deacidification of citrus juices, separation of amino acids, and the like.

8. Membranes in dialysis applications, in which solutes diffuse from one side of the membrane (the feed side) to the other side according to their concentration gradient. Separation between solutes is

obtained as a result of differences in diffusion rates across the membrane arising from differences in molecular size. Such applications include hemodialysis (artificial kidneys) and the removal of alcohol from beer.

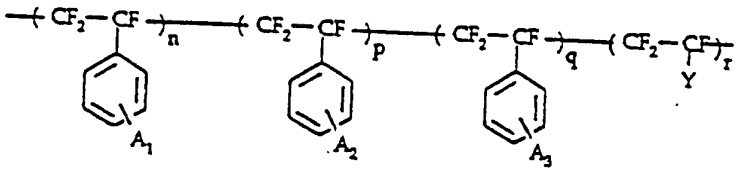
9. Membranes in gas separation (gas permeation) and pervaporation (liquid permeation) techniques.

10. Bipolar membranes employed in water splitting and subsequently in the recovery of acids and bases from waste water solutions.

While particular elements, embodiments and applications of the present invention have been shown and described, it will be understood, of course, that the invention is not limited thereto since modifications may be made by those skilled in the art, particularly in light of the foregoing teachings. It is therefore contemplated by the appended claims to cover such modifications as incorporate those features which come within the spirit and scope of the invention.

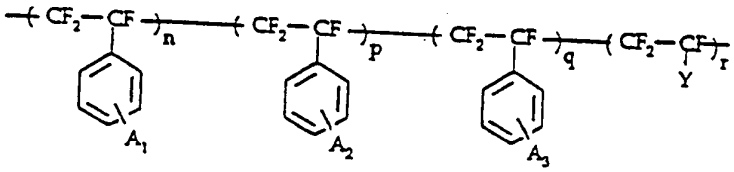
What is claimed is:

1. A polymeric composition comprising:



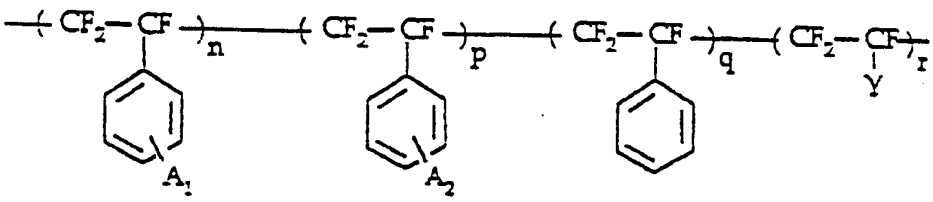
where r is an integer greater than zero, and at least one of n, p and q is an integer greater than zero; A_1, A_2 and A_3 are selected from the group consisting of SO_2F, halogens, alkyls, perfluoroalkyls, O-R (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls), $CF=CF_2$, CN, NO_2 and OH; and Y is selected from the group consisting of hydrogen, halogens, $C_xH_yF_z$ (where x is an integer greater than zero and y+z = 2x+1), O-R (where R is selected from the group consisting of $C_xH_yF_z$ (where x is an integer greater than zero and y+z = 2x+1) and aryls), $CF=CF_2$, CN, COOH, CO_2R^1 (where R^1 is selected from the group consisting of alkyls, perfluoroalkyls, aryls, and NR^2R^3 where R^2 and R^3 are selected from the group consisting of hydrogen, alkyls and aryls).

2. A polymeric composition comprising:



where r is an integer greater than zero, and at least one of n, p and q is an integer greater than zero; A_1, A_2 and A_3 are selected from the group consisting of hydrogen, SO_2F, halogens, alkyls, perfluoroalkyls, O-R (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls), $CF=CF_2$, CN, NO_2 and OH; and Y is selected from the group consisting of hydrogen, $C_xH_yF_z$ (where x is an integer greater than zero and y+z = 2x+1), O-R (where R is selected from the group consisting of $C_xH_yF_z$ (where x is an integer greater than zero and y+z = 2x+1) and aryls), $CF=CF_2$, CN, $CO_2NR^2R^3$ (where R^2 and R^3 are selected from the group consisting of hydrogen, alkyls and aryls).

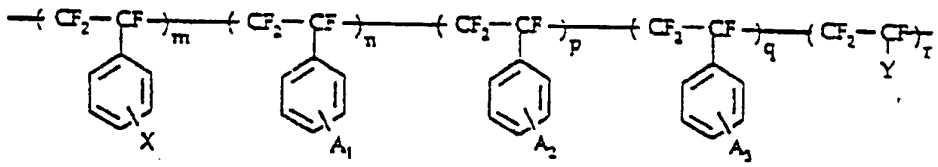
3. A polymeric composition comprising:



where n, q and r are integers greater than zero, and p is zero or an integer greater than zero; A_1 and A_2 are selected from the group consisting of SO_2F, halogens, alkyls, perfluoroalkyls, O-R (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls), $CF=CF_2$, CN, NO_2 and OH; and Y is selected from the group consisting of hydrogen, halogens, $C_xH_yF_z$ (where x is an integer greater than zero and y+z = 2x+1), O-R (where R is selected from the group consisting of $C_xH_yF_z$ (where x is an integer greater than zero and y+z = 2x+1) and aryls), $CF=CF_2$, CN, COOH, CO_2R^1 (where R^1 is

selected from the group consisting of alkyls, perfluoroalkyls, aryls and NR^2R^3 where R^2 and R^3 are selected from the group consisting of hydrogen, alkyls and aryls).

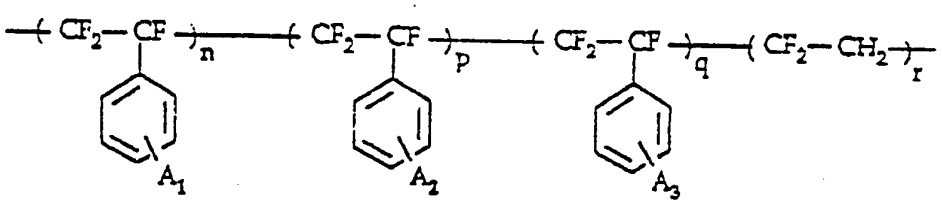
4. A polymeric composition comprising:



where m and r are integers greater than zero, and n, p and q are zero or an integer greater than zero; X is selected from the group consisting of SO_3H, PO_2H_2, PO_3H_2, $CH_2PO_3H_2$, COOH, OSO_3H, OPO_2H_2, OPO_3H_2, NR_3^+ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls) and $CH_2NR_3^+$ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls); A_1, A_2 and A_3 are selected from the group consisting of hydrogen, SO_2F, halogens, alkyls, perfluoroalkyls, O-R (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls), $CF=CF_2$, CN, NO_2, and OH; and Y is selected from the group consisting of hydrogen, halogens, $C_xH_yF_z$ (where x is an integer greater than zero and y+z = 2x+1), O-R (where R is selected from the group consisting of $C_xH_yF_z$ (where x is an integer greater than zero and y+z = 2x+1) and aryls), $CF=CF_2$, CN, COOH, CO_2R^1 (where R^1 is selected from the group consisting of alkyls, perfluoroalkyls, aryls, and NR^2R^3 where R^2 and R^3 are selected from the group consisting of hydrogen, alkyls and aryls).

5. The polymeric composition of claim 4 wherein the group from which A_1, A_2 and A_3 are selected further consists of SO_3H, PO_2H_2, PO_3H_2, $CH_2PO_3H_2$, COOH, OSO_3H, OPO_2H_2, OPO_3H_2, NR_3^+ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls) and $CH_2NR_3^+$ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls), and at least one of A_1, A_2 and A_3 is selected from the group consisting of SO_3H, PO_2H_2, PO_3H_2, $CH_2PO_3H_2$, COOH, OSO_3H, OPO_2H_2, OPO_3H_2, NR_3^+ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls) and $CH_2NR_3^+$ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls).

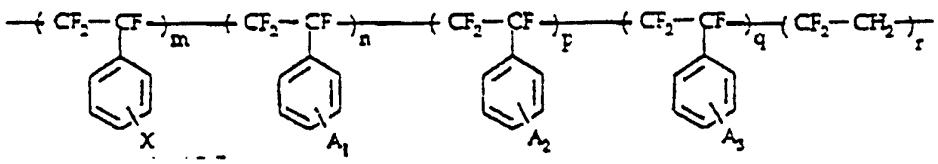
6. A polymeric composition comprising:



where r is an integer greater than zero, and at least one of n, p and q is an integer greater than zero; A_1, A_2 and A_3 are selected from the group consisting of SO_2F, halogens, alkyls, perfluoroalkyls, O-R (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls), $CF{=}CF_2$, CN, NO_2 and OH.

7. The polymeric composition of claim 6 wherein the group from which A_1, A_2 and A_3 are selected further consists of hydrogen.

8. A polymeric composition comprising:

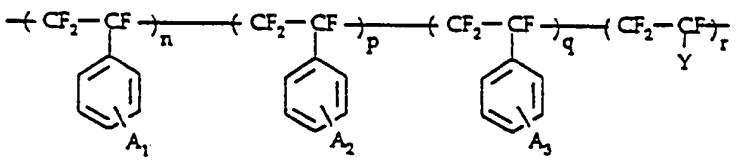


where m and r are integers greater than zero, and n, p and q are zero or an integer greater than zero; X is selected from the group consisting of SO_3H, PO_2H_2, PO_3H_2, $CH_2PO_3H_2$, COOH, OSO_3H, OPO_2H_2, OPO_3H_2, NR_3^+ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls) and $CH_2NR_3^+$ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls); and A_1, A_2 and A_3 are selected from the group consisting of hydrogen, SO_2F, halogens, alkyls, perfluoroalkyls, O-R (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls), $CF=CF_2$, CN, NO_2, and OH.

9. The polymeric composition of claim 8 wherein the group from which A_1, A_2 and A_3 are selected further consists of SO_3H, PO_2H_2, PO_3H_2, $CH_2PO_3H_2$, COOH, OSO_3H, OPO_2H_2, OPO_3H_2, NR_3^+ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls) and $CH_2NR_3^+$ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls), and at least one of A_1, A_2 and A_3 is selected from the group consisting of SO_3H, PO_2H_2, PO_3H_2, $CH_2PO_3H_2$, COOH, OSO_3H, OPO_2H_2, OPO_3H_2, NR_3^+ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls)

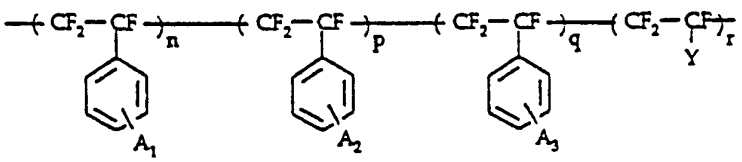
and $CH_2NR_3^+$ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls).

10. A polymeric composition consisting essentially of:



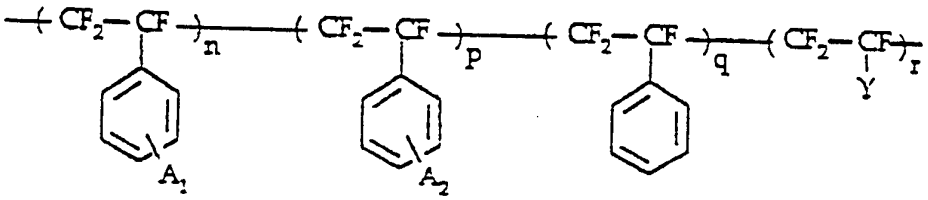
where r is an integer greater than zero, and at least one of n, p and q is an integer greater than zero; A_1, A_2 and A_3 are selected from the group consisting of SO_2F, halogens, alkyls, perfluoroalkyls, O-R (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls), $CF=CF_2$, CN, NO_2 and OH; and Y is selected from the group consisting of hydrogen, halogens, $C_xH_yF_z$ (where x is an integer greater than zero and y+z = 2x+1), O-R (where R is selected from the group consisting of $C_xH_yF_z$ (where x is an integer greater than zero and y+z = 2x+1) and aryls), $CF=CF_2$, CN, COOH, CO_2R^1 (where R^1 is selected from the group consisting of alkyls, perfluoroalkyls, aryls, and NR^2R^3 where R^2 and R^3 are selected from the group consisting of hydrogen, alkyls and aryls).

11. A polymeric composition consisting essentially of:



where r is an integer greater than zero, and at least one of n, p and q is an integer greater than zero; A_1, A_2 and A_3 are selected from the group consisting of hydrogen, SO_2F, halogens, alkyls, perfluoroalkyls, O-R (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls), $CF=CF_2$, CN, NO_2 and OH; and Y is selected from the group consisting of hydrogen, $C_xH_yF_z$ (where x is an integer greater than zero and y+z = 2x+1), O-R (where R is selected from the group consisting of $C_xH_yF_z$ (where x is an integer greater than zero and y+z = 2x+1) and aryls), $CF=CF_2$, CN, $CO_2NR^2R^3$ (where R^2 and R^3 are selected from the group consisting of hydrogen, alkyls and aryls).

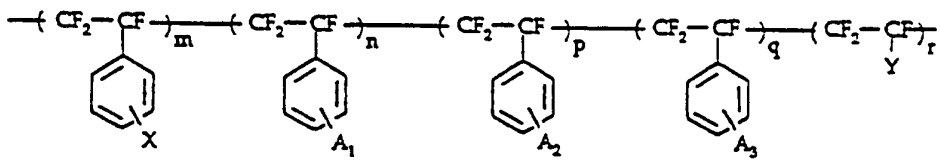
12. A polymeric composition consisting essentially of:



where at n, q and r are integers greater than zero, and p is zero or an integer greater than zero; A_1 and A_2 are selected from the group consisting of SO_2F, halogens, alkyls, perfluoroalkyls, O-R (where R is selected from the group consisting of alkyls,

perfluoroalkyls and aryls), $CF=CF_2$, CN, NO_2 and OH; and Y is selected from the group consisting of hydrogen, halogens, $C_xH_yF_z$ (where x is an integer greater than zero and y+z = 2x+1), O-R (where R is selected from the group consisting of $C_xH_yF_z$ (where x is an integer greater than zero and y+z = 2x+1) and aryls), $CF=CF_2$, CN, COOH, CO_2R^1 (where R^1 is selected from the group consisting of alkyls, perfluoroalkyls, aryls and NR^2R^3 where R^2 and R^3 are selected from the group consisting of hydrogen, alkyls and aryls).

13. A polymeric composition consisting essentially of:

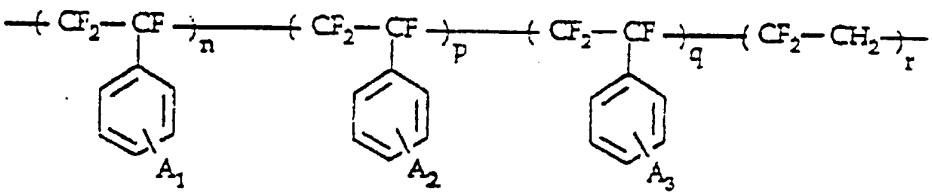


where m and r are integers greater than zero, and n, p and q are zero or an integer greater than zero; X is selected from the group consisting of SO_3H, PO_2H_2, PO_3H_2, $CH_2PO_3H_2$, COOH, OSO_3H, OPO_2H_2, OPO_3H_2, NR_3^+ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls) and $CH_2NR_3^+$ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls); A_1, A_2 and A_3 are selected from the group consisting of hydrogen, SO_2F, halogens, alkyls, perfluoroalkyls, O-R (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls), $CF=CF_2$, CN, NO_2, and OH; and Y is selected from the group consisting of hydrogen, halogens,

$C_xH_yF_z$ (where x is an integer greater than zero and y+z = 2x+1), O-R (where R is selected from the group consisting of $C_xH_yF_z$ (where x is an integer greater than zero and y+z = 2x+1) and aryls), $CF=CF_2$, CN, COOH, CO_2R^1 (where R^1 is selected from the group consisting of alkyls, perfluoroalkyls, aryls, and NR^2R^3 where R^2 and R^3 are selected from the group consisting of hydrogen, alkyls and aryls).

14. The polymeric composition of claim 13 wherein the group from which A_1, A_2 and A_3 are selected further consists of SO_3H, PO_2H_2, PO_3H_2, $CH_2PO_3H_2$, COOH, OSO_3H, OPO_2H_2, OPO_3H_2, NR_3^+ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls) and $CH_2NR_3^+$ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls), and at least one of A_1, A_2 and A_3 is selected from the group consisting of SO_3H, PO_2H_2, PO_3H_2, $CH_2PO_3H_2$, COOH, OSO_3H, OPO_2H_2, OPO_3H_2, NR_3^+ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls) and $CH_2NR_3^+$ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls).

15. A polymeric composition consisting essentially of:

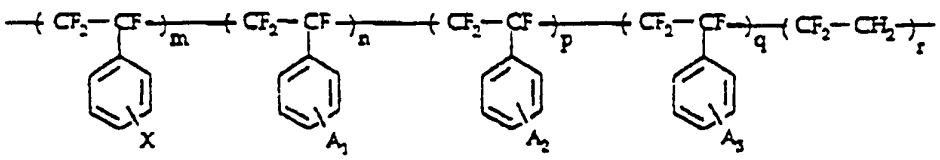


where r is an integer greater than zero, and at

least one of n, p and q is an integer greater than zero; A_1, A_2 and A_3 are selected from the group consisting of SO_2F, halogens, alkyls, perfluoroalkyls, O-R (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls), $CF=CF_2$, CN, NO_2 and OH.

16. The polymeric composition of claim 15 wherein the group from which A_1, A_2 and A_3 are selected further consists of hydrogen.

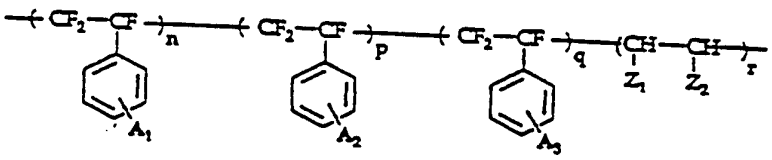
17. A polymeric composition consisting essentially of:



where m and r are integers greater than zero, and n, p and q are zero or an integer greater than zero; X is selected from the group consisting of SO_3H, PO_2H_2, PO_3H_2, $CH_2PO_3H_2$, COOH, OSO_3H, OPO_2H_2, OPO_3H_2, NR_3^+ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls) and $CH_2NR_3^+$ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls); and A_1, A_2 and A_3 are selected from the group consisting of hydrogen, SO_2F, halogens, alkyls, perfluoroalkyls, O-R (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls), $CF=CF_2$, CN, NO_2, and OH.

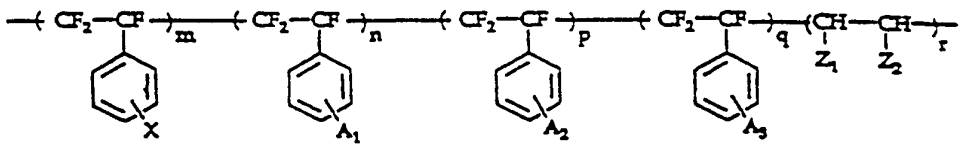
18. The polymeric composition of claim 17 wherein the group from which A_1, A_2 and A_3 are selected further consists of SO_3H, PO_2H_2, PO_3H_2, $CH_2PO_3H_2$, COOH, OSO_3H, OPO_2H_2, OPO_3H_2, NR_3^+ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls) and $CH_2NR_3^+$ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls), and at least one of A_1, A_2 and A_3 is selected from the group consisting of SO_3H, PO_2H_2, PO_3H_2, $CH_2PO_3H_2$, COOH, OSO_3H, OPO_2H_2, OPO_3H_2, NR_3^+ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls) and $CH_2NR_3^+$ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls).

19. A polymeric composition comprising:



where r is an integer greater than zero, and at least one of n, p and q is an integer greater than zero; A_1, A_2 and A_3 are selected from the group consisting of hydrogen, SO_2F, halogens, alkyls, perfluoroalkyls, O-R (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls), $CF=CF_2$, CN, NO_2 and OH; and Z_1 and Z_2 are selected from the group consisting of hydrogen and fluorine.

20. A polymeric composition comprising:

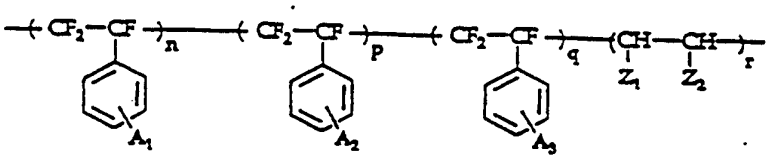


where m and r are integers greater than zero, and n, p and q are zero or an integer greater than zero; X is selected from the group consisting of SO_3H, PO_2H_2, PO_3H_2, $CH_2PO_3H_2$, COOH, OSO_3H, OPO_2H_2, OPO_3H_2, NR_3^+ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls) and $CH_2NR_3^+$ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls); and A_1, A_2 and A_3 are selected from the group consisting of hydrogen, SO_2F, halogens, alkyls, perfluoroalkyls, O-R (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls), $CF=CF_2$, CN, NO_2 and OH; and Z_1 and Z_2 are selected from the group consisting of hydrogen and fluorine.

21. The polymeric composition of claim 20 wherein the group from which A_1, A_2 and A_3 are selected further consists of SO_3H, PO_2H_2, PO_3H_2, $CH_2PO_3H_2$, COOH, OSO_3H, OPO_2H_2, OPO_3H_2, NR_3^+ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls) and $CH_2NR_3^+$ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls), and at least one of A_1, A_2 and A_3 is selected from the group consisting of SO_3H, PO_2H_2, PO_3H_2, $CH_2PO_3H_2$, COOH, OSO_3H, OPO_2H_2, OPO_3H_2, NR_3^+ (where R is selected from the group

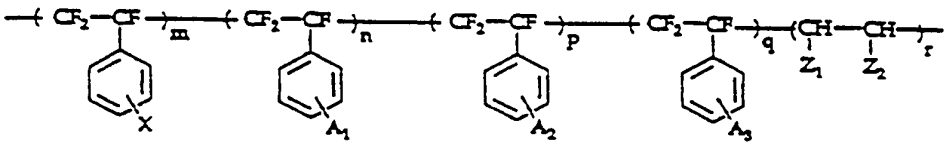
consisting of alkyls, perfluoroalkyls and aryls) and $CH_2NR_3^+$ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls).

22. A polymeric composition consisting essentially of:



where r is an integer greater than zero, and at least one of n, p and q is an integer greater than zero; A_1, A_2 and A_3 are selected from the group consisting of hydrogen, SO_2F, halogens, alkyls, perfluoroalkyls, O-R (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls), $CF=CF_2$, CN, NO_2 and OH; and Z_1 and Z_2 are selected from the group consisting of hydrogen and fluorine.

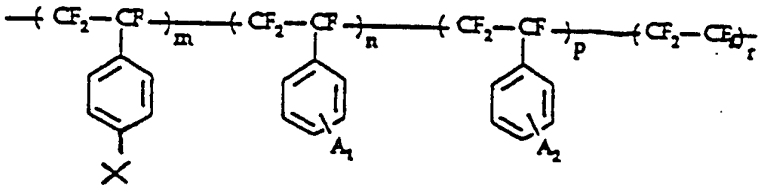
23. A polymeric composition consisting essentially of:



where m and r are integers greater than zero, and n, p and q are zero or an integer greater than zero; X is selected from the group consisting of SO_3H, PO_2H_2, PO_3H_2, $CH_2PO_3H_2$, COOH, OSO_3H, OPO_2H_2, OPO_3H_2, NR_3^+ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls) and $CH_2NR_3^+$ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls); and A_1, A_2 and A_3 are selected from the group consisting of hydrogen, SO_2F, halogens, alkyls, perfluoroalkyls, O-R (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls), $CF=CF_2$, CN, NO_2 and OH; and Z_1 and Z_2 are selected from the group consisting of hydrogen and fluorine.

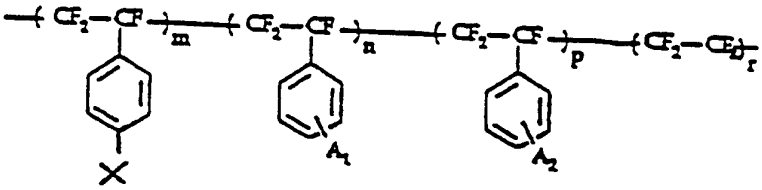
24. The polymeric composition of claim 23 wherein the group from which A_1, A_2 and A_3 are selected further consists of SO_3H, PO_2H_2, PO_3H_2, $CH_2PO_3H_2$, COOH, OSO_3H, OPO_2H_2, OPO_3H_2, NR_3^+ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls) and $CH_2NR_3^+$ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls), and at least one of A_1, A_2 and A_3 is selected from the group consisting of SO_3H, PO_2H_2, PO_3H_2, $CH_2PO_3H_2$, COOH, OSO_3H, OPO_2H_2, OPO_3H_2, NR_3^+ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls) and $CH_2NR_3^+$ (where R is selected from the group consisting of alkyls, perfluoroalkyls and aryls).

25. A polymeric composition comprising:



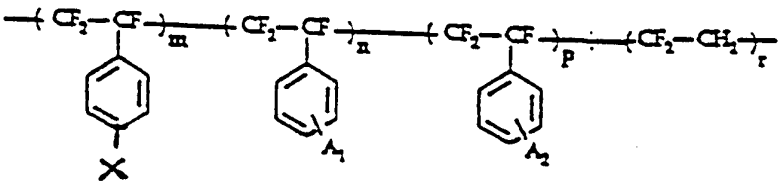
where m, n and r are integers greater than zero, and p is zero or an integer greater than zero: X is selected from the group consisting of SO_2F and SO_3H; A_1 and A_2 are selected from the group consisting of hydrogen, fluorine, CF_3, and para-phenoxy.

26. A polymeric composition consisting essentially of:



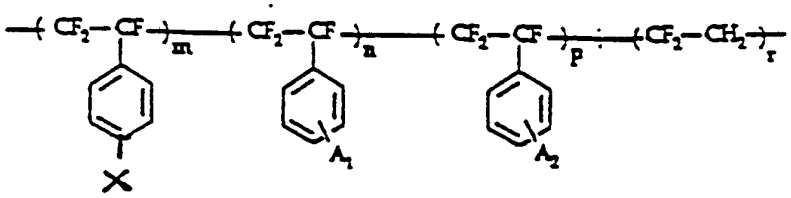
where m, n and r are integers greater than zero, and p is zero or an integer greater than zero: X is selected from the group consisting of SO_2F and SO_3H; A_1 and A_2 are selected from the group consisting of hydrogen, fluorine, CF_3, and para-phenoxy.

27. A polymeric composition comprising:



where m, n and r are integers greater than zero, and p is zero or an integer greater than zero: X is selected from the group consisting of SO_2F and SO_3H; A_1 and A_2 are selected from the group consisting of hydrogen, fluorine, CF_3, and para-phenoxy.

28. A polymeric composition consisting essentially of:



where m, n and r are integers greater than zero, and p is zero or an integer greater than zero: X is selected from the group consisting of SO_2F and SO_3H; A_1 and A_2 are selected from the group consisting of hydrogen, fluorine, CF_3, and para-phenoxy.

29. The polymeric composition of any of claims 1-28 wherein the composition is at least partially crosslinked.

30. A polymeric membrane comprising the polymeric composition of any of claims 1-29.

31. A polymeric membrane consisting essentially of the polymeric composition of any of claims 1-29.

32. An electrochemical fuel cell comprising the polymeric membrane of claim 30 wherein said polymeric membrane is an ion exchange membrane.

33. An electrochemical fuel cell comprising the polymeric membrane of claim 31 wherein said polymeric membrane is an ion exchange membrane.

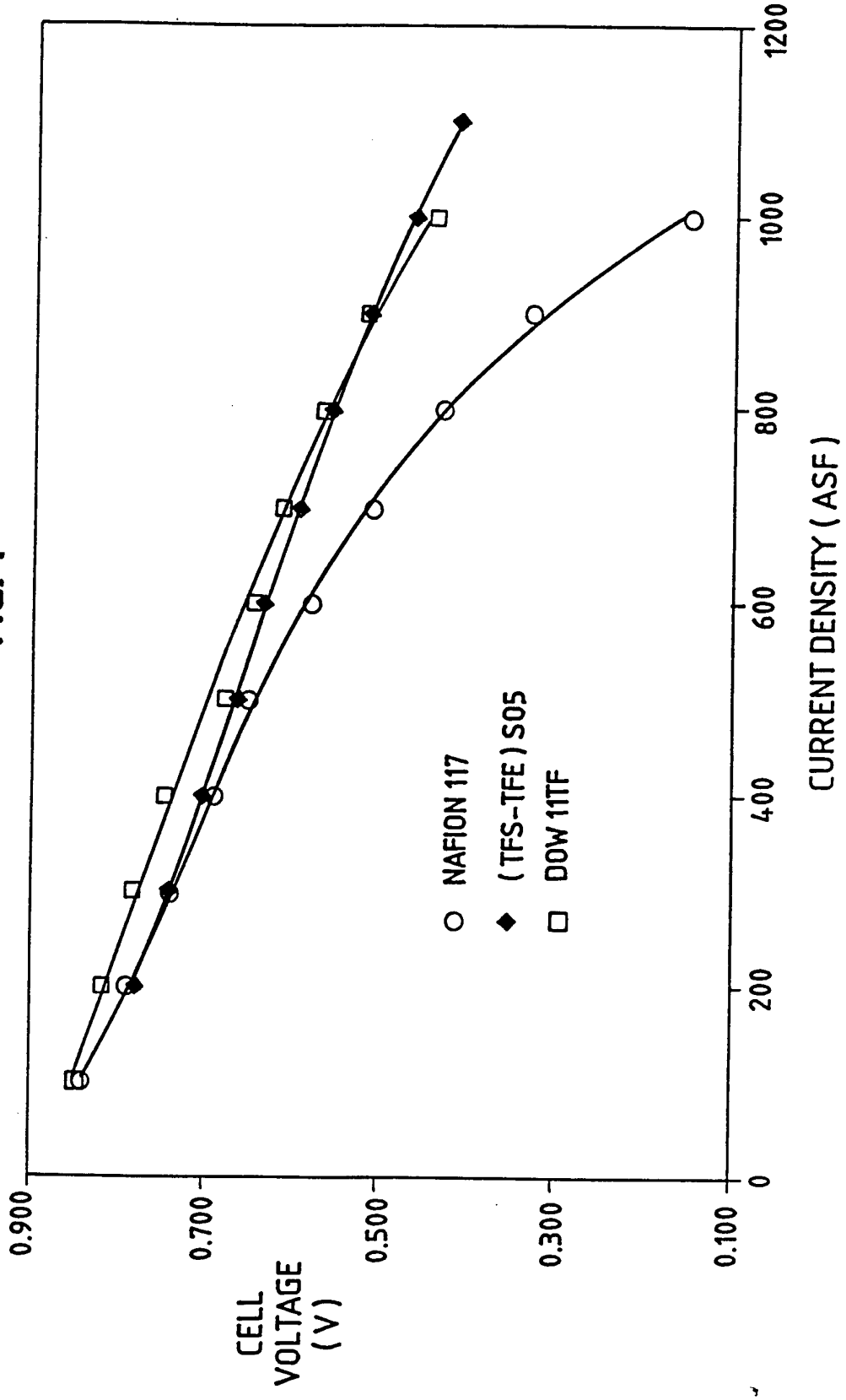

0.900
0.700
0.500
0.300
0.100
CELL VOLTAGE (V)
0
200
400
600
800
1000
1200
CURRENT DENSITY (ASF)
NAFION 117
(TFS-TFE) S05
DOW 11TF

FIG. 1

INTERNATIONAL SEARCH REPORT

International Application No
PCT/CA 96/00369

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08F8/00 C08F212/14

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08F

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO,A,95 08581 (BALLARD POWER SYSTEMS INC.) 30 March 1995 cited in the application see page 4, line 10 - page 5, line 19 see page 18, line 16 - page 20, line 25; claims 1-18 ---	1-3, 10-12, 29-33
A	FR,A,2 096 180 (DUNLOP HOLDINGS LTD.) 11 February 1972 see claims 1-26 ---	1
A	US,A,4 126 588 (HIROSHI UKIHASHI) 21 November 1978 see claims 1-13 ---	1
	-/--	

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

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

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

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

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

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

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

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

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

"&" document member of the same patent family

1

Date of the actual completion of the international search	Date of mailing of the international search report
18 September 1996	- 3. 10. 96
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Permentier, W

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Interna' ıl Application No
PCT/CA 96/00369

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,3 442 825 (R. B. HODGDON) 6 May 1969 cited in the application see column 3, line 62 - column 4, line 22 see column 4, line 64 - column 5, line 15; claims 1-6 -----	1,29-33

1

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

.rmation on patent family members

Interna al Application No
PCT/CA 96/00369

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
WO-A-9508581	30-03-95	US-A-	5422411	06-06-95
		AU-A-	7649294	10-04-95
		CA-A-	2171298	30-03-95
		EP-A-	0720628	10-07-96
		US-A-	5498639	12-03-96
FR-A-2096180	11-02-72	GB-A-	1352138	08-05-74
US-A-4126588	21-11-78	JP-C-	1226180	31-08-84
		JP-A-	52116790	30-09-77
		JP-B-	58000895	08-01-83
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		JP-A-	52084191	13-07-77
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		FR-A-	2337162	29-07-77
		GB-A-	1531068	01-11-78
US-A-3442825	06-05-69	BE-A-	668486	16-12-65
		CH-A-	463462	
		DE-A-	1570681	12-03-70
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		GB-A-	1096879	
		NL-A-	6510859	21-02-66
		SE-B-	337921	23-08-71
		US-A-	3341366	12-09-67