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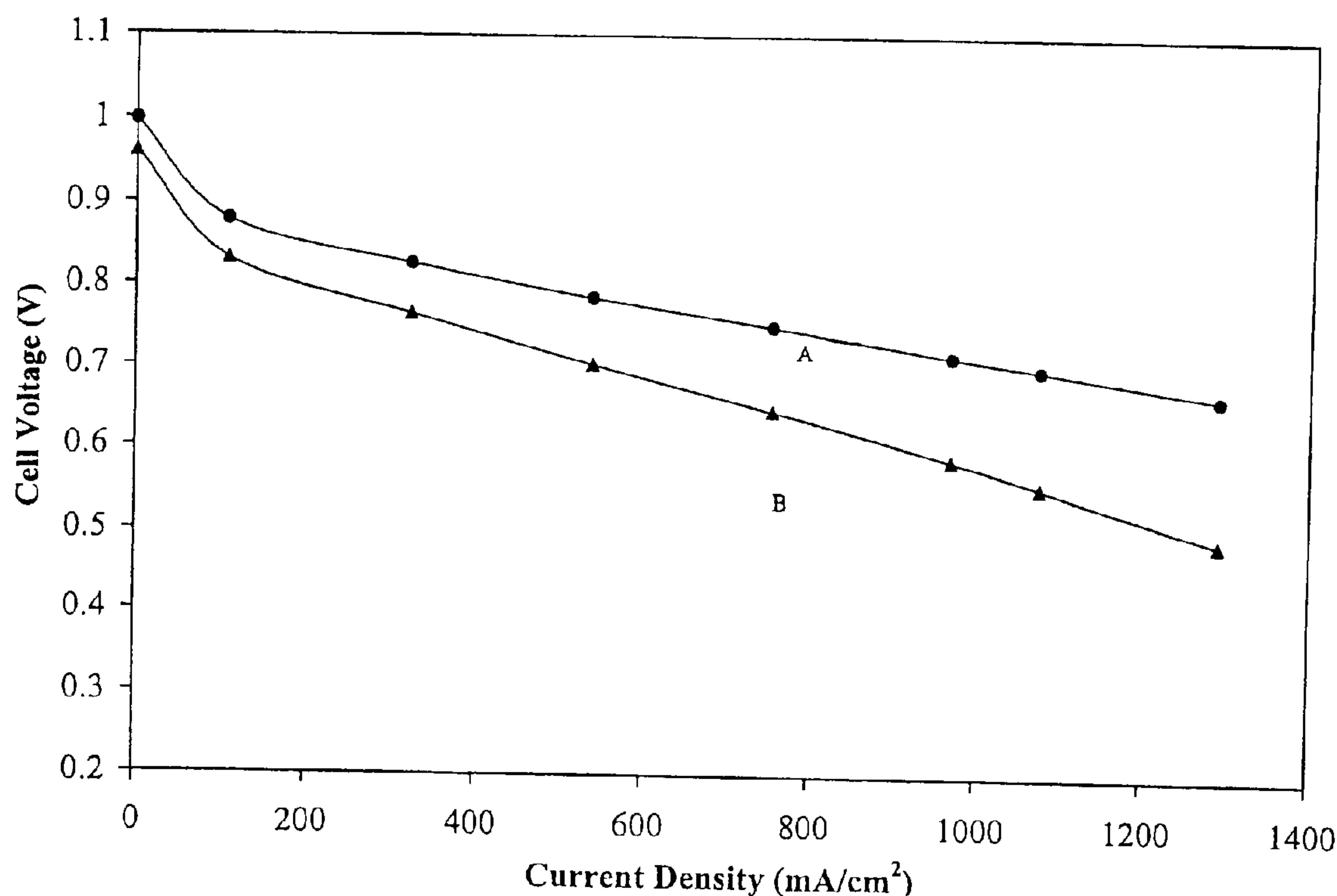
(72) Inventeurs/Inventors:
STONE, CHARLES, CA;
STECK, ALFRED E., CA;
CHOUDHURY, BISWAJIT, CA

(73) Propriétaire/Owner:
BALLARD POWER SYSTEMS INC., CA

(74) Agent: BORDEN LADNER GERVAIS LLP

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(54) Title: GRAFT POLYMERIC MEMBRANES AND ION-EXCHANGE MEMBRANES FORMED THEREFROM



(57) Abrégé/Abstract:

Graft polymeric membranes and methods for making same are provided in which one or more trifluorovinyl aromatic monomers are radiation graft polymerized to a polymeric base film. The membranes comprise a polymeric base film to which has been graft polymerized substituted α,α,β -trifluorostyrene and or α,α,β -trifluorovinyl naphthylene monomers which are activated towards graft polymerization. The membranes may be ion-exchange membranes suitable for use in electrode apparatus, including membrane electrode assemblies that may be used in, for example, fuel cells. The membranes may be crosslinked.

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(74) Agent: **DE KOCK, Elbie, R.**; Russell Reyneke, Suite 700,
Two Bentall Centre, 555 Burrard Street, Vancouver, British
Columbia V7X 1M8 (CA).

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(71) Applicant (for all designated States except US): **BALLARD POWER SYSTEMS INC.** [CA/CA]; 9000
Glenlyon Parkway, Burnaby, British Columbia V5J 5J9
(CA).

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(72) Inventors; and

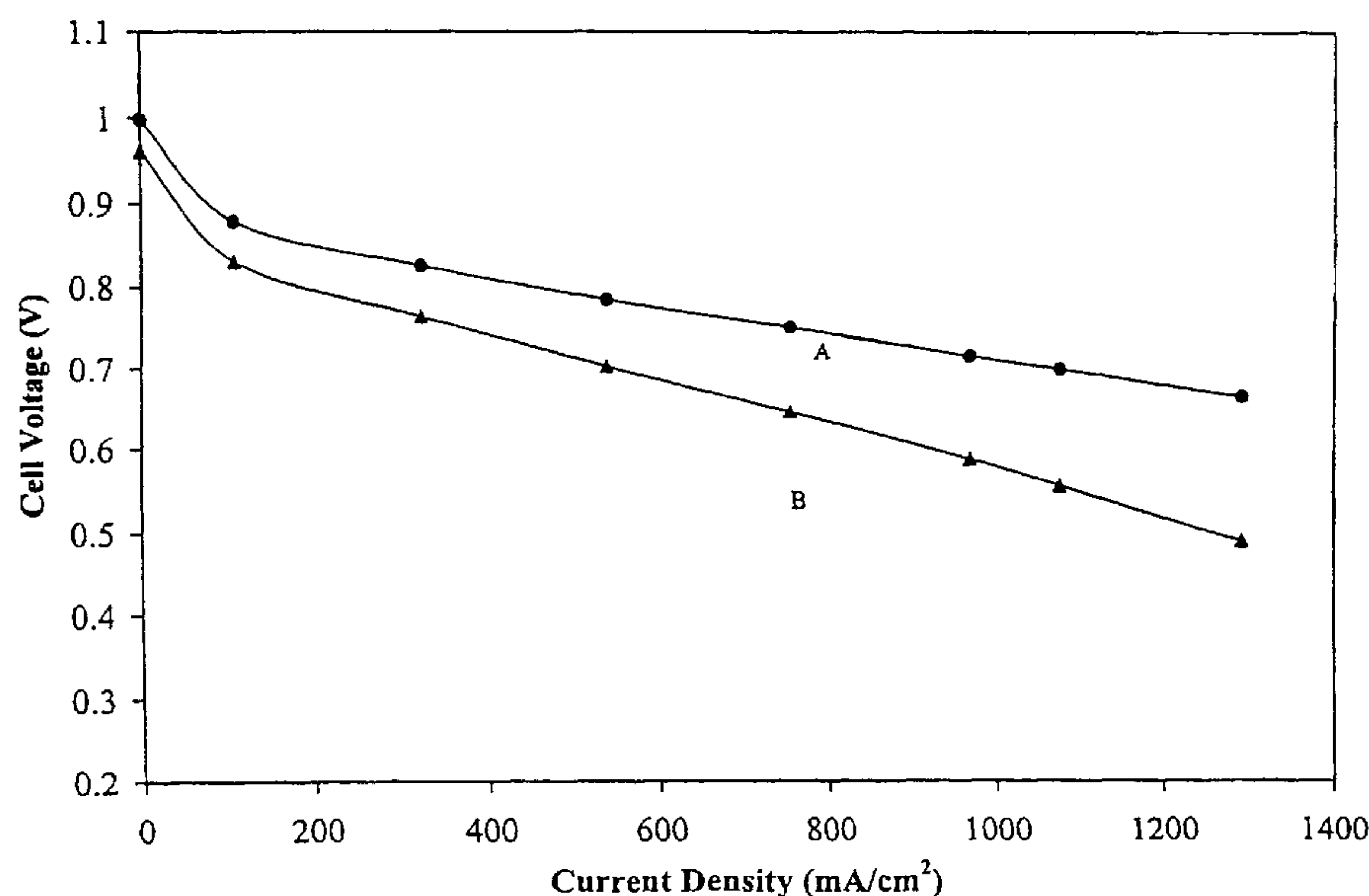
(75) Inventors/Applicants (for US only): **STONE, Charles** [CA/CA]; 4948 Edendale Lane, West Vancouver, British Columbia V7W 3H7 (CA). **STECK, Alfred, E.** [CA/CA]; 3956 Westridge Avenue, West Vancouver, British Columbia V7V 3H7 (CA).

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(54) Title: GRAFT POLYMERIC MEMBRANES AND ION-EXCHANGE MEMBRANES FORMED THEREFROM



(57) Abstract: Graft polymeric membranes and methods for making same are provided in which one or more trifluorovinyl aromatic monomers are radiation graft polymerized to a polymeric base film. The membranes comprise a polymeric base film to which has been graft polymerized substituted α,α,β -trifluorostyrene and or α,α,β -trifluorovinyl naphthylene monomers which are activated towards graft polymerization. The membranes may be ion-exchange membranes suitable for use in electrode apparatus, including membrane electrode assemblies that may be used in, for example, fuel cells. The membranes may be crosslinked.

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GRAFT POLYMERIC MEMBRANES AND
ION-EXCHANGE MEMBRANES FORMED THEREFROM

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Field Of The Invention

10 The present invention relates to graft polymeric
membranes in which one or more trifluorovinyl aromatic
monomers are radiation graft polymerized to a polymeric
base film, and methods for making same wherein the
grafted polymeric chains are modified to incorporate
15 ion-exchange groups. The resultant membranes are
useful in dialysis applications, and particularly in
electrochemical applications, for example as membrane
electrolytes in electrochemical fuel cells and
electrolyzers.

20

Background Of The Invention

 The preparation of graft polymeric membranes by
radiation grafting of a monomer to a polymeric base
25 film has been demonstrated for various combinations of
monomers and base films. The grafting of styrene to a
polymeric base film, and subsequent sulfonation of the
grafted polystyrene chains has been used to prepare
ion-exchange membranes.

30 U.S. Patent No. 4,012,303 reports the radiation
grafting of α,β,β -trifluorostyrene (TFS) to polymeric
base films using gamma ray co-irradiation, followed by
the introduction of various ion-exchange substituents
to the pendant aromatic rings of the grafted chains.
35 With co-irradiation, since the TFS monomer is
simultaneously irradiated, undesirable processes such

as monomer dimerization and/or independent homopolymerization of the monomer may occur in competition with the desired graft polymerization reaction.

5 U.S. Patent No. 4,012,303 also reports that the TFS monomer may be first sulfonated and then grafted to the base film. Thus, the introduction of ion-exchange groups into the membrane can be done as part of the grafting process, or in a second step.

10 More recently, the grafting of TFS to pre-irradiated polymeric base films, followed by the introduction of various substituents to the pendant aromatic rings of the grafted chain has been reported in U.S. Patent No. 4,605,685. Solid or porous
15 polymeric base films, such as for example polyethylene and polytetrafluoroethylene, are pre-irradiated and then contacted with TFS neat or in solution. Pre-irradiation is reportedly a more economic and efficient grafting technique, reportedly giving a percentage
20 graft of 10-50% in reaction times of 1-50 hours. Aromatic sulfonation, haloalkylation, amination, hydroxylation, carboxylation, phosphonation and phosphorylation are among the reactions subsequently
25 polymeric chains. Levels of post-sulfonation from 40% to 100% are reported.

In either case the prior art TFS-based grafted membranes incorporate statistically a maximum of one functional group per monomer unit in the grafted chain.
30 Further, they typically incorporate only one type of functional group as substituents on the pendant aromatic rings in the grafted chains.

In the present invention, one or more types of substituted TFS monomers and/or substituted α, β, β -trifluorovinyl naphthylene (TFN) monomers are grafted to polymeric base films, the substituents being selected to offer particular advantages, for example:

- (a) Substituted TFS and/or TFN monomers that are activated have increased reactivity in the grafting reaction facilitating graft polymerization. By "activated" it is meant that either the percentage graft yield of the graft polymerization reaction is increased, or that the rate of the reaction is increased, in reactions employing the substituted monomers relative to reactions employing unsubstituted monomers.
- (b) Substituted TFS and/or TFN monomers in which the substituents are activating with respect to the grafting reaction, but which can be converted so as to be de-activating with respect to subsequent reactions to introduce, for example, ion-exchange functionality into the grafted chains, and thereby permit the introduction of ion-exchange groups that are more stable under certain conditions.
- (c) Substituted TFS and/or TFN monomers in which the substituents are activating with respect to the grafting reaction, but which can be converted so as to be de-activating after introduction of ion-exchange functionality into the grafted chains.
- (d) Grafted chains comprising monomer units with more than one aromatic ring permit the introduction of more than one ion-exchange group per grafted monomer unit, enabling the achievement of higher ion-exchange capacities at lower percentage grafts than in prior art grafted polymeric membranes.

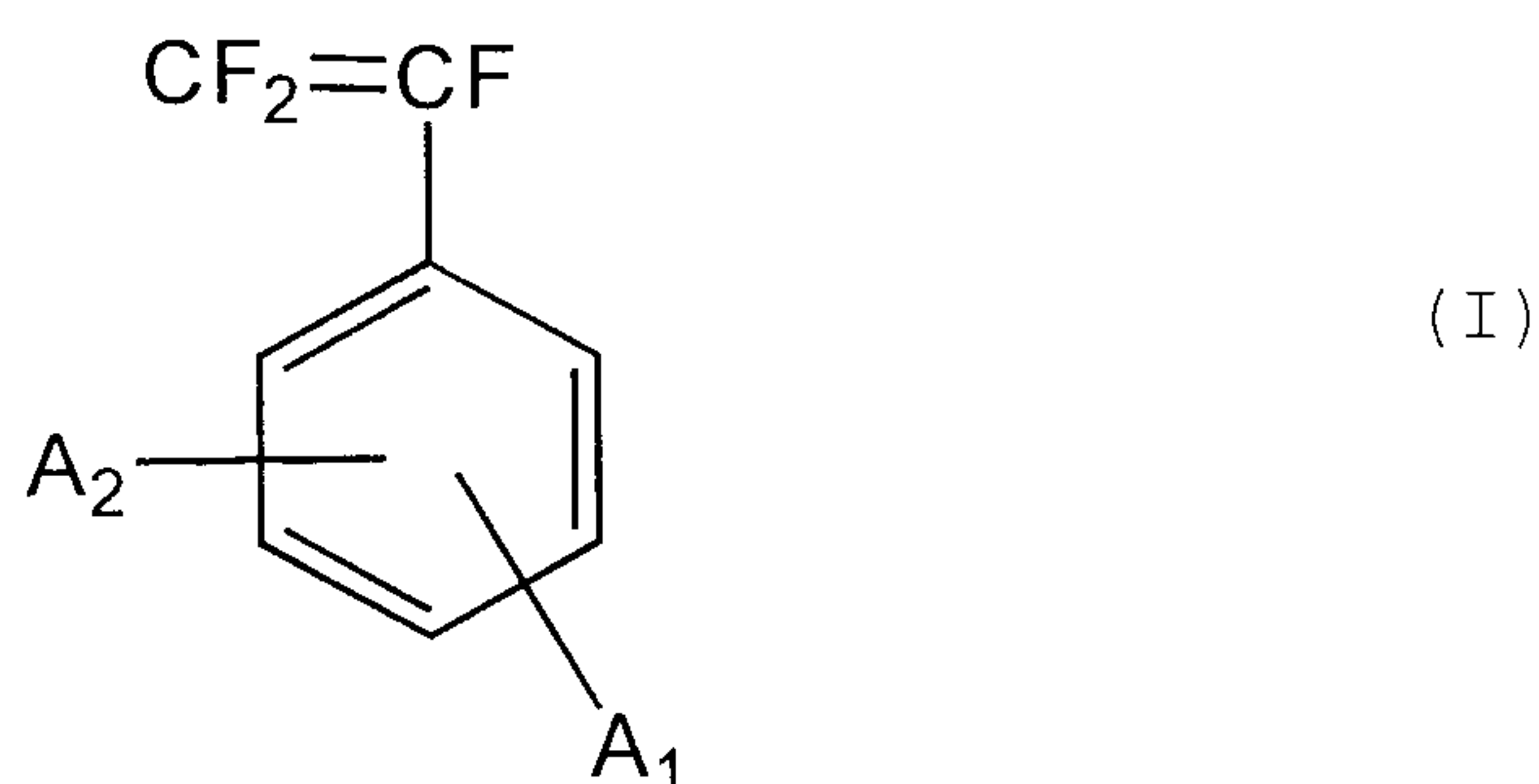
- (e) Substituted TFS and/or TFN monomers in which the substituents are precursors to ion-exchange groups may be transformed to ion-exchange groups after the grafting reaction, and can facilitate the introduction of more than one type of ion-exchange group into the grafted chains, for example, so that both cation and anion-exchange groups may be incorporated in a membrane.
- (f) Substituted TFS and/or TFN monomers in which the substituents contain functionality that can be further reacted to allow for the preparation of crosslinked graft polymeric membranes that may display, for example, greater dimensional stability under certain conditions than similar graft polymeric membranes that are not crosslinked.

Summary Of The Invention

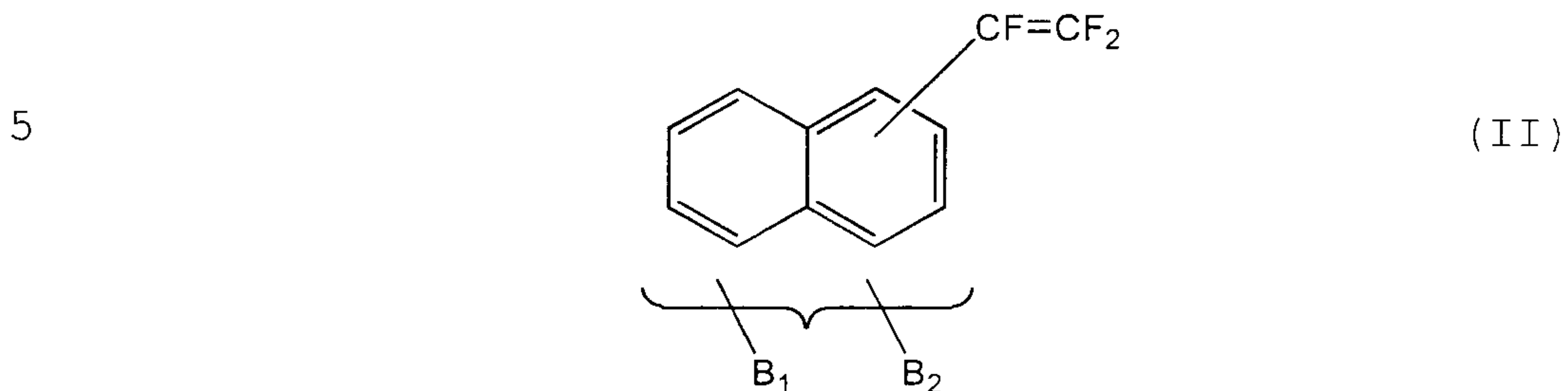
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A graft polymeric membrane is provided in which one or more types of trifluorovinyl aromatic monomers are graft polymerized to a polymeric base film. In some embodiments, the membrane comprises a polymeric base film to which has been graft polymerized a monomer (meaning at least one type of monomer) selected from the group consisting of monomers of the following formulae (I) and (II):

30



and



10 where A_1 , A_2 , and B_1 , B_2 are independently selected from the group consisting of hydrogen, lower alkyl, lower fluoroalkyl, cyclic alkyl, aryl (where aryl is other than Ph, wherein Ph is phenyl), $\text{CH}(\text{X})\text{Ph}$ (where X is selected from the group consisting of fluorine, lower

15 alkyl, lower fluoroalkyl and Ph), PRR' and $\text{P}(\text{OR})(\text{OR}')$ (where R and R' are independently selected from the group consisting of lower alkyl, cyclic alkyl and Ph, and where R and R' can be the same or different); and, wherein A_1 , A_2 , B_1 , and B_2 can be the same or different,

20 provided that in the selected monomer at least one of the substituents A_1 , A_2 , B_1 , B_2 is other than hydrogen. In other words there is at least one of the substituent on foregoing monomers used in the graft polymerization reaction. The selected substituted monomer(s) may have

25 one or two non-hydrogen substituents.

Of the listed alkyl substituents, lower alkyl and cyclic alkyl are generally preferred, with methyl (Me) being most preferred. Thus, membranes where one or both substituents on the selected monomer of formula

30 (I) or (II) are Me are particularly preferred (with para-Me being the most desirable substitution positions in formula (I)). In these embodiments the base film

preferably comprises poly(ethylene-co-tetrafluoroethylene).

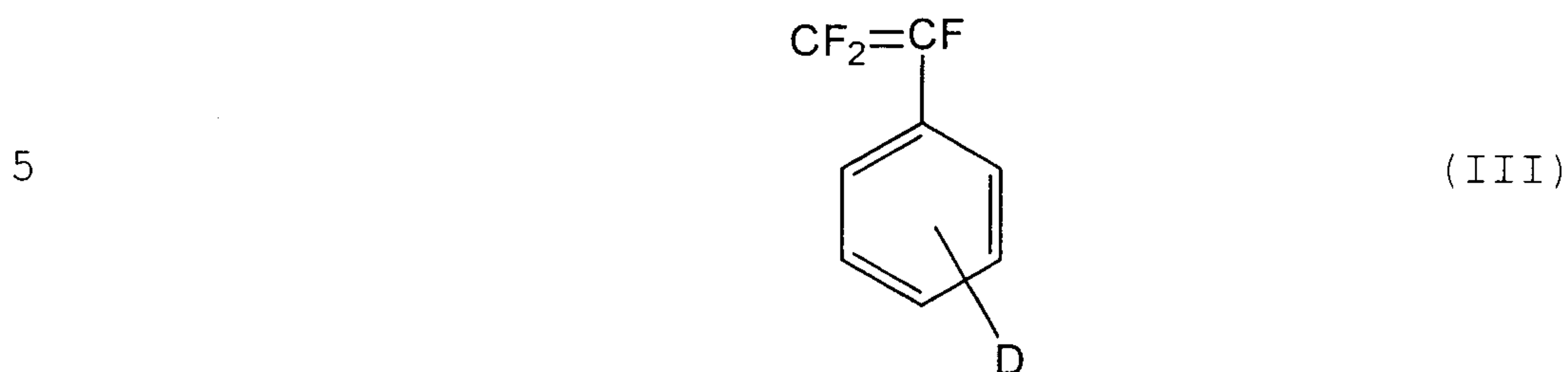
In embodiments in which a polymeric base film has been graft polymerized with a monomer of formula (I) in which A_1 is aryl (where aryl is other than Ph) and A_2 is hydrogen, the aryl is preferably a fused polycyclic aromatic with two fused rings, biphenyl, or a heteroaromatic group with at least one heteroatom which is preferably nitrogen, oxygen or sulfur. If the heteroaromatic group contains more than one heteroatom, the heteroatoms may be the same or different. If one of the heteroatoms is nitrogen it may be advantageously N-alkylated or N-benzylated for certain membrane applications. Monocyclic heteroaromatics are generally preferred over polycyclic heteroaromatics.

The above graft polymeric membrane may comprise a single monomer, whereby the grafted chains are homopolymeric, or may comprise more than one monomer such that the grafted chains are copolymeric. For example, the graft polymeric membrane may comprise more than one monomer of formula (I) having different A_1 and/or A_2 substituents, more than one monomer of formula (II) having different B_1 and/or B_2 substituents, more than one monomer of either formula (I) or formula (II) having the same substituents located at different positions, or monomers of both formula (I) and (II), such that the grafted chains are copolymeric.

In other embodiments of the present graft polymeric membrane, the membrane comprises a polymeric base film to which has been graft polymerized, with the

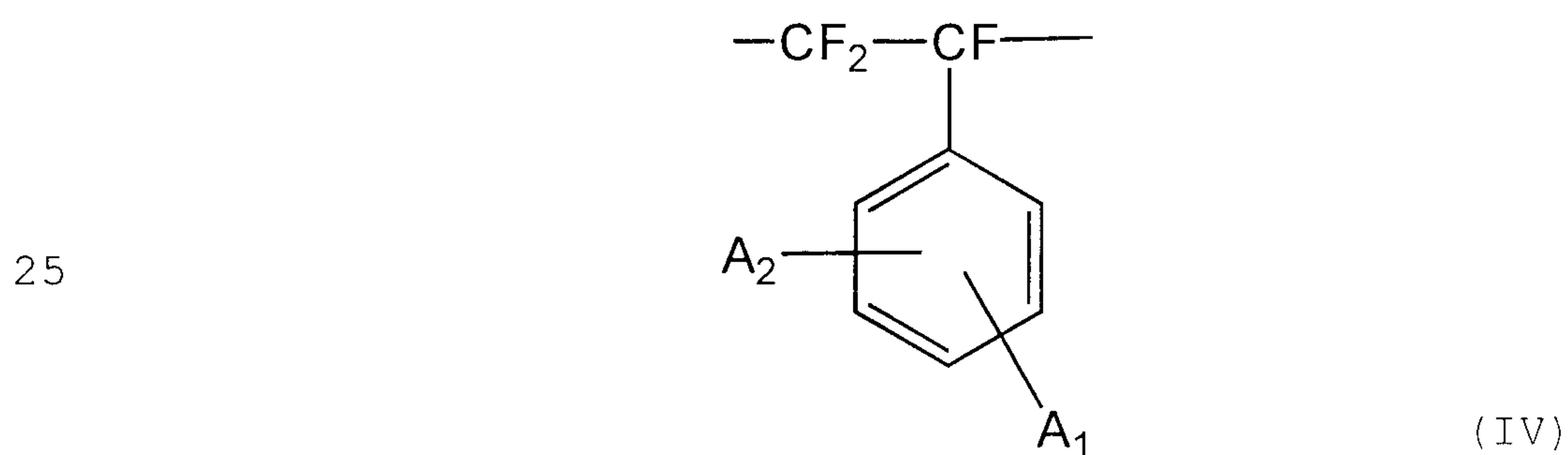
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foregoing monomers, a monomer of the following formula (III):

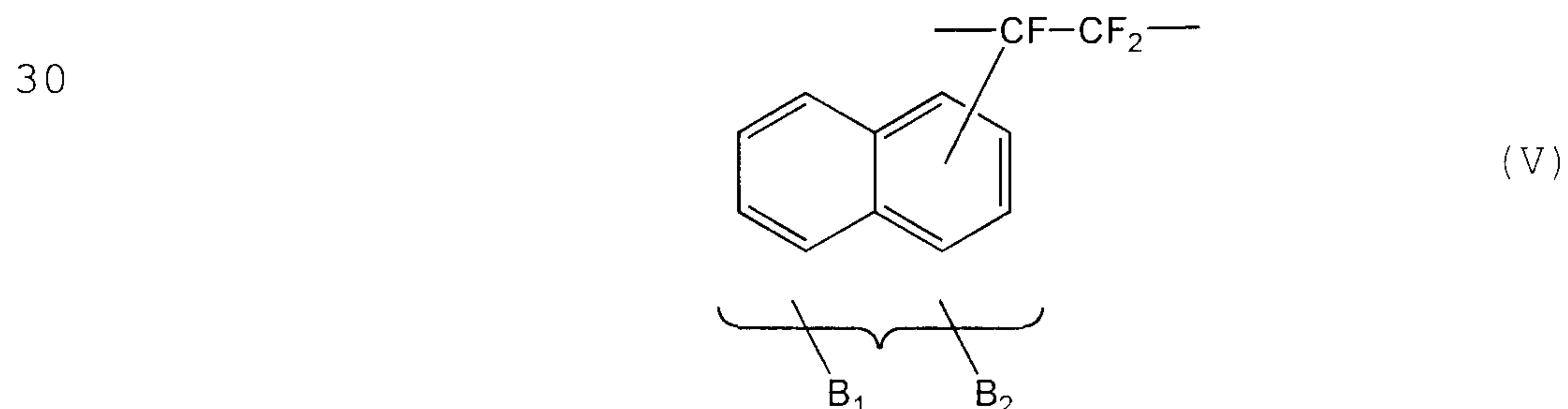


where D is selected from the group consisting of
 10 hydrogen, fluorine, CF₃, CF₂H, CF=CF₂, SO₂F and SO₃-M⁺
 where M⁺ is a suitable counterion, such as, for
 example, metal cations and quaternary ammonium ions.

Embodiments of the present graft polymeric
 membrane may comprise a polymeric base film with
 15 grafted chains comprising monomer units selected from
 the group consisting of monomer units of the following
 formulae (IV) and (V), wherein at least a portion of
 the monomer units further optionally comprise at least
 one ion-exchange substituent, in which case the
 20 membrane is an ion-exchange membrane:



and

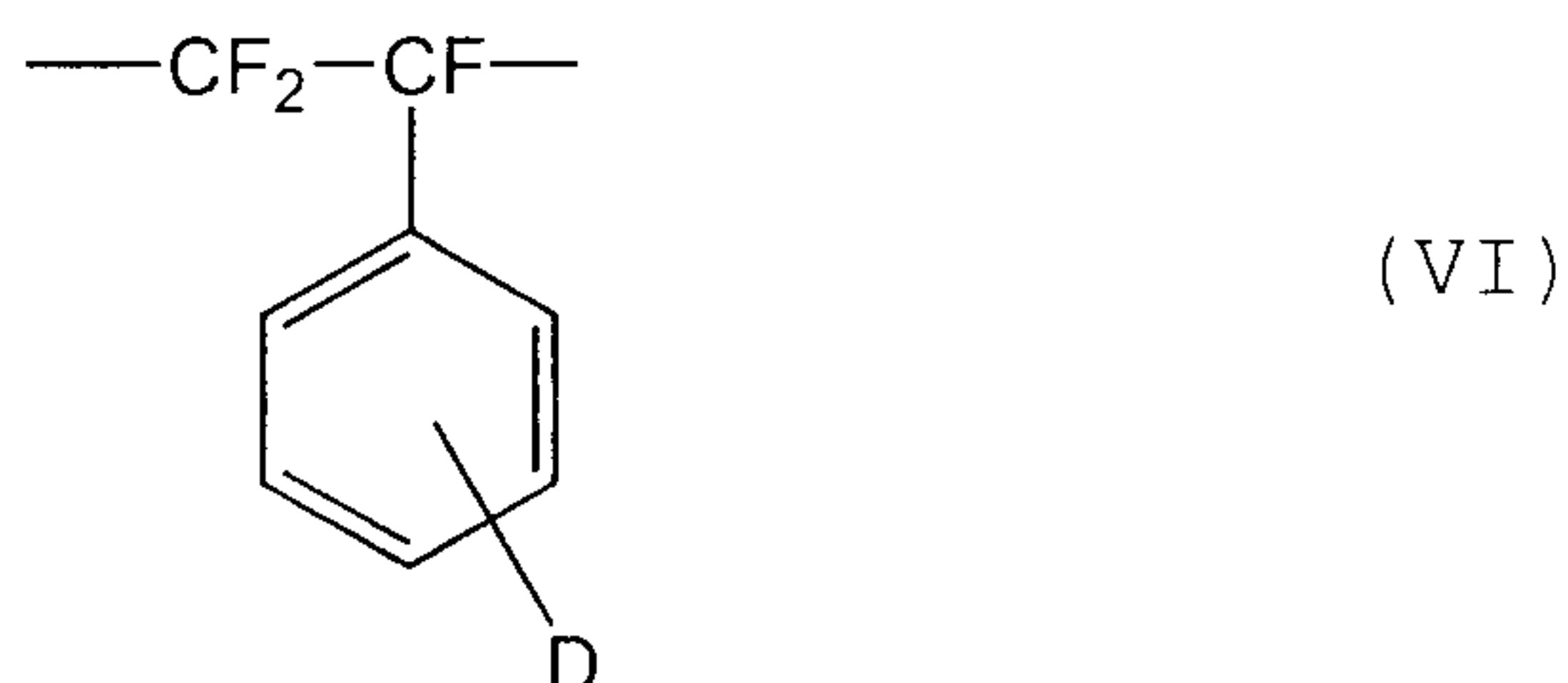


where, as before, A_1 , A_2 , and B_1 , B_2 are independently selected from the group consisting of hydrogen, lower alkyl, lower fluoroalkyl, cyclic alkyl, aryl (where aryl is other than Ph, wherein Ph is phenyl), $CH(X)Ph$ (where X is selected from the group consisting of fluorine, lower alkyl, lower fluoroalkyl and Ph), PRR' and $P(OR)(OR')$ (where R and R' are independently selected from the group consisting of lower alkyl, cyclic alkyl and Ph, and where R and R' can be the same or different); and wherein A_1 , A_2 , B_1 , and B_2 can be the same or different, provided that at least one of the substituents A_1 , A_2 is other than hydrogen. The foregoing membranes may be formed by grafting monomers to a polymeric base film, or by grafting to some other form of polymeric substrate and then forming the grafted material into a membrane. In some embodiments of the ion-exchange membranes, statistically at least 50% of the monomer units in the grafted chains have at least one ion-exchange substituent per monomer unit. In other embodiments at least a portion of the monomer units comprise more than one ion-exchange substituent, and/or portion of the grafted chains may comprise at least two different types of ion-exchange groups, which may even include both anion and cation exchange groups. The ion-exchange substituent most typically incorporated is a sulfonate or sulfonic acid group.

In preferred embodiments one or both substituents of the monomer units of formulae (IV) or (V) are $CH(X)Ph$ (where X is selected from the smaller group consisting of fluorine, Me and Ph), or Me, with para-Me being the most desirable substitution position for the Me group in units of formula (IV). In these

embodiments, again, the base film preferably comprises poly(ethylene-co-tetrafluoroethylene).

The grafted chains of ion-exchange membrane may further comprise additional monomer units, such as for example, units of formula (VI):



where D is selected from the group consisting of hydrogen, fluorine, CF_3 , CF_2H , $\text{CF}=\text{CF}_2$, SO_2F and $\text{SO}_3\text{---M}^+$ where M^+ is a suitable counterion.

The ion-exchange membrane may be substantially gas impermeable. Such gas impermeable ion-exchange membranes may be incorporated into an electrode apparatus such as, for example, a membrane electrode assembly. Electrochemical fuel cells that comprise such ion-exchange membranes are also provided. For fuel cell applications, the polymeric base film of the ion-exchange membrane is preferably less than 100 μm thick.

In the present graft polymeric membranes or ion-exchange membranes, at least a portion of the grafted chains may be crosslinked.

Other membranes may be prepared from those membranes described above by subjecting them to a reaction process selected from the group consisting of, halomethylation, sulfonation, phosphonation, amination, carboxylation, hydroxylation and nitration. These are non-limiting but preferred examples of reaction processes; other reaction processes may also be used.

Membranes so prepared may be useful ion-exchange membranes or precursors to ion-exchange membranes. Methods of preparing the present membranes and ion-exchange membranes are also contemplated and described
5 herein.

Ion-exchange membranes may be prepared by a method which comprises graft polymerizing to a polymeric base film a monomer selected from the group consisting of monomers of formulae (I) and (II) described above,
10 wherein in the selected monomer(s) at least one of the substituents A_1 , A_2 , and B_1 , B_2 is a non-hydrogen substituent which activates the monomer with respect to graft polymerization (relative to the corresponding unsubstituted monomer). The method further comprises
15 introducing a sulfonate group (or other ion-exchange group) into at least a portion of the graft polymerized monomer units and converting at least a portion of the non-hydrogen substituents to substituents which are deactivating with respect to desulfonation (relative to
20 the unsubstituted monomer unit). The conversion of the non-hydrogen substituent to a deactivating group may be performed before or after introduction of the sulfonate group into the grafted units.

Some of the membranes described above may be
25 prepared by a method comprising graft polymerizing to a polymeric base film a substituted monomer selected from the group consisting of monomers of formulae (I) and (II) described above, wherein A_1 , A_2 , and B_1 , B_2 are as described above.

30 In preferred embodiments of this method, A_1 and B_1 are independently selected from the group consisting of:

aryl (where aryl is selected from the group consisting of monocyclic heteroaromatics, fused polycyclic heteroaromatics, and heteroaromatic ring assemblies having at least one nitrogen atom); and

phosphines of the formula PRR' and phosphites of formula $P(OR)(OR')$ (where R and R' are independently selected from the group consisting of lower alkyl, cyclic alkyl and Ph, and where R and R' can be the same or different); and A_2 and B_2 are hydrogen.

The method further comprises alkylating or benzylating at least a portion of any of the nitrogen atoms of the aryl group, or the phosphorus atoms of the phosphine or phosphite.

In other embodiments where A_1 and B_1 are independently selected from the group consisting of phosphines of the formula PRR' and phosphites of formula $P(OR)(OR')$ (where R and R' are independently selected from the group consisting of lower alkyl, cyclic alkyl and Ph, and where R and R' can be the same or different), and A_2 and B_2 are hydrogen, the method may further comprise the sequential steps of introducing a nitro group into at least a portion of the monomer units of the membrane and converting at least a portion of those nitro groups to quaternary ammonium groups. This method optionally further comprises subsequently converting the phosphine or phosphite to an ion-exchange substituent.

In still another embodiment, the present method comprises graft polymerizing to a polymeric base film a monomer selected from the group consisting of monomers

of the formulae (I) and (II) described above, but where A_1 and B_1 are independently selected from the group consisting of PRR' , $P(OR)(OR')$, and SR (where R and R' are independently selected from the group consisting of lower alkyl, cyclic alkyl and Ph , and where R and R' can be the same or different), and A_2 and B_2 are the same as A_1 and B_1 respectively or hydrogen. The method comprises the steps of graft polymerizing the monomers to a polymeric base film, and oxidizing at least a portion of the PRR' , $P(OR)(OR')$, or SR groups to produce phosphine oxides, phosphones, phosphonates, sulfoxides, or sulfones. The method may further comprise introducing ion-exchange substituents into at least a portion of said monomer units, before or after the oxidation step. Where A_1 and B_1 are independently selected from the group SR (where R is selected from the group consisting of lower alkyl, cyclic alkyl and Ph), and A_2 and B_2 are the same as A_1 and B_1 respectively or hydrogen, the method optionally further comprises converting at least a portion of the SR groups to sulfonate or sulfonic acid groups.

In the above-described embodiments the substrate for the graft polymerization is preferably a polymeric base film. However, the polymeric substrate may be in other forms such as, for example, a powder or in solution, or the substrate may be an oligomer in any form. Where the substrate is not in the form of a film an additional step will be required to form the grafted material into a membrane. Where the substrate is in solution an additional solvent removal step will be required.

Brief Description Of The Drawings

FIG. 1 is a plot of cell voltage as a function of current density (expressed in mA/cm²) in an electrochemical fuel cell employing a sulfonated membrane of p-Me-TFS grafted poly(ethylene-co-tetrafluoroethylene) and operating on hydrogen-oxygen (plot A) and hydrogen-air (plot B).

FIG. 2 is a plot of cell voltage as a function of current density (expressed in mA/cm²) in an electrochemical direct methanol fuel cell employing a sulfonated membrane of p-Me-TFS grafted poly(ethylene-co-tetrafluoroethylene) operating on aqueous methanol-air.

Detailed Description Of Preferred Embodiments

As used in this description and in the appended claims, in relation to substituents of TFS and/or TFN monomers, lower alkyl means straight chain or branched C₁ - C₆ alkyl groups. Lower fluoroalkyl means partially or completely fluorinated straight or branched C₁ - C₆ saturated chains, provided that the benzylic carbon has no more than one fluorine atom attached thereto. In preferred embodiments, the lower alkyl and lower fluoroalkyl are C₁ - C₄. Other haloalkyls of the same general description may also be used in the present invention, however, fluorine is preferred due to the relative lability of chlorine, bromine and iodine to substitution, which may result in competition in other reaction processes or in undesirable side reactions. Cyclic alkyl means cyclic

alkyls having C₃ - C₇ rings. Aryl means: monocyclic aromatic rings; fused polycyclic hydrocarbons containing at least one aromatic ring (e.g., indan); fused polycyclic aromatic hydrocarbons (e.g., indene and naphthalene); aromatic ring assemblies (e.g., biphenyl); and, heteroaromatics thereof, wherein the heteroatoms are nitrogen, oxygen, or sulfur, and the heterocyclic may contain more than one heteroatom, and may also contain different species of heteroatom (e.g., indoline, pyrrole, pyridine, oxathiazine, and purine). The abbreviation Me is used to represent a methyl group, and the abbreviation Ph is used to represent a phenyl group. The formula SO₃-M⁺ represents sulfonate salts, where M⁺ may be any suitable counterion, such as, for example, metal cations and quaternary ammonium ions.

Suitable substituents for TFS and/or TFN monomers that are activating in graft polymerization reactions include, for example: lower alkyls; lower fluoroalkyls; cyclic alkyls; aryl groups; and, phosphines and phosphites. Substituents may be coupled to the aromatic rings of TFS and/or TFN monomers in any position. Meta- and para-substituted monomers are preferred, with para-substituted monomers being more preferred.

Any radiation capable of introducing sufficient concentrations of free radical sites on and within the base polymeric film may be used in the preparation of the grafted polymeric membranes described herein. For example, the irradiation may be by gamma rays, X-rays, electron beam, or high-energy UV radiation. Electron beam irradiation is generally preferable as the process times are short and thus more suited to high volume

production processes. The decay of the source and typically longer reactions times required with gamma-ray radiation tend to render it less suitable for high volume manufacturing processes.

5 The polymeric base film may be pre-irradiated prior to bringing it into contact with the monomer or monomer mixture to be grafted or the substrate and monomer(s) may be irradiated together (co-irradiation).

10 For the preparation of membranes, grafting to a polymeric base film is generally more efficient and cost-effective than grafting to a substrate in some other form such as a powder and then forming a membrane from the grafted material.

15 The preferred polymeric base film material is dependent on the application in which the grafted membrane is to be used. The base film may be a porous or dense film. Preferred substrate materials for electrochemical applications, for example, include hydrocarbons such as polyolefins, especially
20 polyethylene and polypropylene. In some applications, a perfluorinated or partially fluorinated polymeric base film may be used, for example, polytetrafluoroethylene (PTFE), poly(tetrafluoroethylene-co-hexafluoropropylene),
25 polyvinylidene fluoride, and preferably poly(ethylene-co-tetrafluoroethylene).

 In the grafting reaction, the polymeric base film is treated with the monomer(s) in the liquid phase, either as a neat liquid or in a solution.

30 Alternatively, the polymeric base film may be treated with a mixture of liquid and vapor phase monomer(s) (including aerosols), or with monomer(s) in the vapor phase only. It can be advantageous to select a solvent

that will cause the solution to penetrate the base film and cause it to swell. This facilitates grafting of the monomer(s) throughout the membrane thickness. Preferably the irradiation and grafting process is
5 carried out in an inert atmosphere.

The reaction conditions may be selected so as to introduce crosslinking between monomer units during graft polymerization or subsequent thereto. Crosslinking may be introduced into polymeric membranes
10 where it is, for example, desirable to increase dimensional stability, reduce swelling, modify chemical and/or mechanical properties, or enhance the ion-exchange efficiency. Methods of preparing crosslinked graft polymeric membranes are known in the art. For
15 example, U.S. Pat. No. 5,656,386 describes adding a crosslinking agent to vinyl monomers to be grafted to a membrane film, wherein the radiation grafting and crosslinking reactions occur simultaneously.

In the present graft polymeric membranes, the
20 constituent monomers may be selected so as to be capable of forming crosslinks without requiring the addition of a separate crosslinking agent. If crosslinking is desirable, the monomer(s) preferably contains functionality that can be crosslinked. For
25 example, monomers having a t-butyl group as a substituent would be less appropriate, since such substituents do not participate readily in crosslinking reactions. As another example, monomers having $-\text{CHF}_2$ or $-\text{CH}(\text{CF}_3)_2$ substituents are capable of forming very
30 stable crosslinks, but such monomers may be so deactivating towards polymerization that the percentage graft or rate of grafting may fall to an undesirable level. However, such monomers may be suitably used in

the grafting reaction provided they are included in the monomer mixture at a relatively low mole percentage (e.g., less than about 10 mol %).

For the preparation of grafted ion-exchange
5 membranes from substituted TFS and/or TFN monomers, substituents that are activating with respect to the polymerization reaction are typically also activating towards subsequent reactions to introduce ion-exchange groups, such as, for example, halomethylation,
10 sulfonation, phosphonation, amination, carboxylation, hydroxylation (optionally combined with subsequent phosphorylation) and nitration. Although the presence of an activating substituent may be beneficial in that it may facilitate the introduction of the ion-exchange
15 group into the monomer, where the ion-exchange group is sulfonate, for example, there may also be a disadvantage. This is because sulfonation is a macroscopically reversible process, so a substituent that is activating with respect to the introduction of
20 a sulfonate group may also make the sulfonate group less stable under certain conditions, thereby facilitating desulfonation of the monomer unit.

In some embodiments of the present membranes or method, the substituted TFS and/or TFN monomers to be
25 grafted contain a phosphine, phosphite, or thioether substituent. These substituents are activating with respect to the graft polymerization reaction. Ion-exchange groups such as, for example, sulfonate, may then be introduced into the aromatic ring of the
30 substituted TFS and/or TFN monomer units after graft polymerization. Then, following graft polymerization the phosphine, phosphite or thioether groups can be oxidized to produce phosphine oxides, phosphones,

phosphonates, sulfoxides, or sulfones. Methods suitable for such oxidations are well known to those skilled in the art. The resulting phosphine oxides, phosphones, phosphonates, sulfoxides and/or sulfones
5 are de-activating, thus making the introduced ion-exchange groups, in particular sulfonate groups, more stable under certain conditions.

In addition, these substituents may allow for the introduction of additional ion-exchange functionality
10 into the TFS and/or TFN monomer units. For example, oxidation of the phosphite substituent yields a phosphonate group, which on hydrolysis will yield a cation-exchange group. Introduction of either cation or anion-exchange groups into the substituted TFS
15 and/or TFN monomer units, followed by oxidation of phosphite and subsequent hydrolysis of the phosphonate substituent, may yield TFS and/or TFN monomer units with more than one ion-exchange group per monomer unit, on average. As another example, the phosphine or
20 phosphite substituent may be alkylated or benzylated to form an anion-exchange group. Further, employing the additional steps of nitration followed by conversion of the nitro group to an amino group, and subsequently to a quaternary ammonium salt may yield monomer units
25 having two different anion-exchange groups. As yet another example, the thioether substituent may be converted to a sulfonate group by, for example, the method described in U.S. Pat. No. 5,830,962. Again, introduction of either cation or anion-exchange groups
30 into the substituted TFS and/or TFN monomer units, followed by alkylation or benzylation of the phosphine, or conversion of thioether to sulfonate, may yield TFS and/or TFN monomer units with more than one ion-

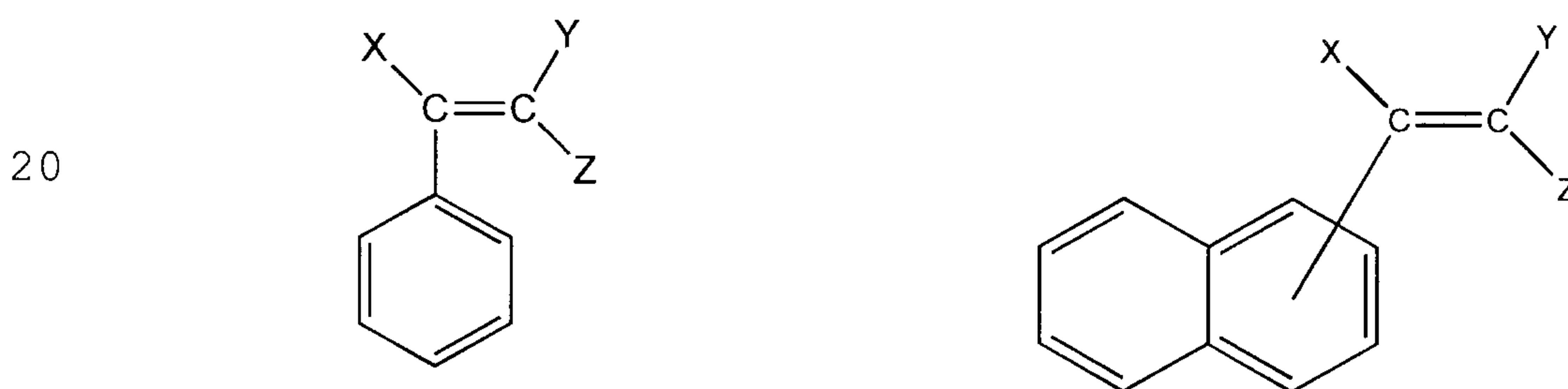
exchange group per monomer, on average, depending upon the compatibility of the chemistry involved. Thus, the present method allows for the preparation of amphoteric graft ion-exchange membranes, or graft ion-exchange
5 membranes having two different ion-exchange groups, simply by choosing the appropriate ion-exchange group to be introduced into the substituted TFS and/or TFN monomer units.

In another embodiment of the present membranes and
10 method, the substituted TFS and/or TFN monomers to be grafted contain a heteroaromatic substituent containing at least one nitrogen heteroatom. These substituents are also activating with respect to the graft polymerization reaction. Following graft
15 polymerization, the heteroaromatic substituents can be N-alkylated or N-benzylated, forming anion-exchange sites in the grafted chains. Optionally, cation-exchange groups may also be introduced, either before or preferably after N-alkylation or N-benylation,
20 resulting in amphoteric ion-exchange membranes.

In any of the foregoing embodiments of the present membranes and method, sulfonate ion-exchange groups can be introduced to the monomer units in the grafted chains. For example, the membrane, preferably swollen
25 with an appropriate solvent to facilitate sulfonation throughout its thickness, can be reacted with a solution of sulfur trioxide, or with sulfur trioxide vapor alone (or indeed an aerosol mist of sulfur trioxide). Other sulfonation reagents can be used, as
30 will be familiar to those skilled in the art, such as oleum and chlorosulfonic acid, for example.

While the foregoing methods have been described in relation to substituted TFS and/or TFN monomers, it

will be readily apparent to those skilled in the art that the foregoing methods are readily adaptable to other monomers. It is anticipated that other vinyl monomers containing an aromatic ring may be suitably adaptable to the disclosed methods. For example, in the preparation of graft membranes employing styrenic monomers, it would still be advantageous to employ substituents that are activating with respect to the graft polymerization reaction, but which can be converted to de-activating substituents in subsequent reactions where it is desirable to introduce, for example, ion-exchange groups that may, by this process, be more stable under certain conditions. In addition to styrenic monomers, it is expected that the foregoing methods will be adaptable to substituted and unsubstituted monomers of the following basic structures:



25 where X can be H, F or Me and
if X = F, then Y = Z = H, or one of Y, Z is H and the other is F,
if X = H, then Y = Z = H, or one of Y, Z is H and the other is F, and
30 if X = Me, then Y = Z = H.

The following examples are for purposes of illustration and are not intended to limit the invention.

EXAMPLE 1

Grafting of para-methyl- α,β,β -trifluorostyrene (p-Me-TFS) to

5 **poly(ethylene-co-tetrafluoroethylene) (Tefzel®) Film**

A 2 mil (approx. 50 μm) thick, 7 inch $\times$ 7 inch (18 cm $\times$ 18 cm) piece of poly(ethylene-co-tetrafluoroethylene) (Tefzel®) film was irradiated with a dose of 20 Mrad
10 using a high energy electron beam (60 kW) radiation source, in an inert atmosphere. The irradiated base film was kept at -30 °C in an inert atmosphere prior to use. The irradiated membrane was then exposed to neat, degassed p-Me-TFS in an inert atmosphere at 80 °C for
15 24 hours. The p-Me-TFS grafted film was removed, washed with toluene and dried at 60 °C. The percentage graft was 79%. In these Examples, the percentage graft is the increase in weight of the film after the grafting reaction compared to the weight of the film
20 before the grafting reaction.

EXAMPLE 2

Grafting of para-methyl- α,β,β -trifluorostyrene (p-Me-TFS) to

25

poly(ethylene-co-tetrafluoroethylene) (Tefzel®) Film

A 2 mil (approx. 50 μm) thick, 15 inch $\times$ 15 inch (38 cm $\times$ 38 cm) piece of poly (ethylene-co-
30 tetrafluoroethylene) (Tefzel®) film was irradiated with a dose of 20 Mrad using a high energy electron beam (60 kW) radiation source, in an inert atmosphere. The irradiated base film was stored at -30 °C in an inert atmosphere prior to use. The irradiated membrane was

then exposed to neat, degassed p-Me-TFS in an inert atmosphere at 70 °C for 3 hours. The p-Me-TFS grafted film was removed, washed with toluene and dried at 60 °C. The percentage graft was 67%.

5

EXAMPLE 3

Grafting of para-methyl- α,β,β -trifluorostyrene (p-Me-TFS) to poly(ethylene-co-tetrafluoroethylene) (Tefzel®)

10 **Film and Sulfonation of the Grafted Membrane**

a) A 2 mil (approx. 50 μ m) thick, 7 inch x 7 inch (18 cm x 18 cm) piece of poly(ethylene-co-tetrafluoroethylene) (Tefzel®) film was irradiated with
15 a dose of 10 Mrad using a high energy electron beam (60 kW) radiation source, in an inert atmosphere. The irradiated base film was kept at -30 °C in an inert atmosphere prior to use. It was then exposed to neat, degassed, p-Me-TFS in an inert atmosphere at 50 °C for
20 60 hours. The p-Me-TFS grafted film was removed, washed with toluene and dried at 60 °C. The percentage graft was 49%.

b) A sulfonating solution was prepared by careful
25 addition of 30 g of liquid sulfur trioxide to 70 g of 1,1,2,2-tetrachloroethane. The grafted membrane was sulfonated by immersion in the above-mentioned sulfonating solution for 2 hours at 70 °C. The resultant ion-exchange membrane was washed with water
30 and dried at 60 °C. The equivalent weight of the sulfonated membrane was 660 g/mol, with a water content of 26% at room temperature.

EXAMPLE 4**Grafting of para-methyl- α,β,β -trifluorostyrene (p-Me-TFS) to poly(ethylene-co-tetrafluoroethylene) (Tefzel®) Film and Sulfonation of the Grafted Membrane**

5

a) A 2 mil (approx. 50 μm) thick, 7 inch x 7 inch (18 cm x 18 cm) piece of poly(ethylene-co-tetrafluoroethylene) (Tefzel®) film was grafted with para-methyl- α,β,β -trifluorostyrene similarly as in
10 Example 3, using a 5 Mrad irradiation dose. The percentage graft was 35%.

b) The grafted film was sulfonated according to the procedure described in step (b) of Example 3. The equivalent weight of the sulfonated membrane was 821
15 g/mol, with a water content of 18% at room temperature.

EXAMPLE 5**Use of Sulfonated p-Me-TFS grafted poly(ethylene-co-tetrafluoroethylene) Membrane as an Ion-exchange
20 Membrane in a Fuel Cell**

The membrane prepared as described in Example 3 was bonded to two catalyzed carbon fiber paper
25 electrodes to form a membrane electrode assembly having a total platinum catalyst loading of 1 mg/cm². The membrane electrode assembly was tested in a Ballard Mark IV single cell fuel cell. The following operating conditions were used:

30

Temperature: 80 °C

Reactant inlet pressure:

24

3.02 bara for oxidant and fuel

Reactant stoichiometries:

2.0 oxidant and 1.5 hydrogen.

FIG. 1 shows polarization plots of voltage as a function of current density for the sulfonated grafted membrane employed in a membrane electrode assembly in the electrochemical fuel cell operating on hydrogen-oxygen (plot A) and hydrogen-air (plot B).

EXAMPLE 6

Use of Sulfonated p-Me-TFS grafted poly(ethylene-co-tetrafluoroethylene) Membrane as an Ion-exchange Membrane in a Fuel Cell

The membrane prepared as described in Example 4 was bonded to two catalyzed carbon fiber paper electrodes to form a membrane electrode assembly having a total platinum catalyst loading of 8 mg/cm². The membrane electrode assembly was tested in a Ballard Mark IV single cell direct methanol fuel cell. The following operating conditions were used:

Temperature: 110 °C

Fuel: 0.4 M methanol solution (in water)

Reactant inlet pressure: 3.02 bara for oxidant and fuel

Reactant stoichiometries: 2.0 oxidant and 3.0 methanol.

FIG. 2 shows polarization plots of voltage as a function of current density for the sulfonated grafted membrane employed in a membrane electrode assembly in

the electrochemical fuel cell operating on methanol-air.

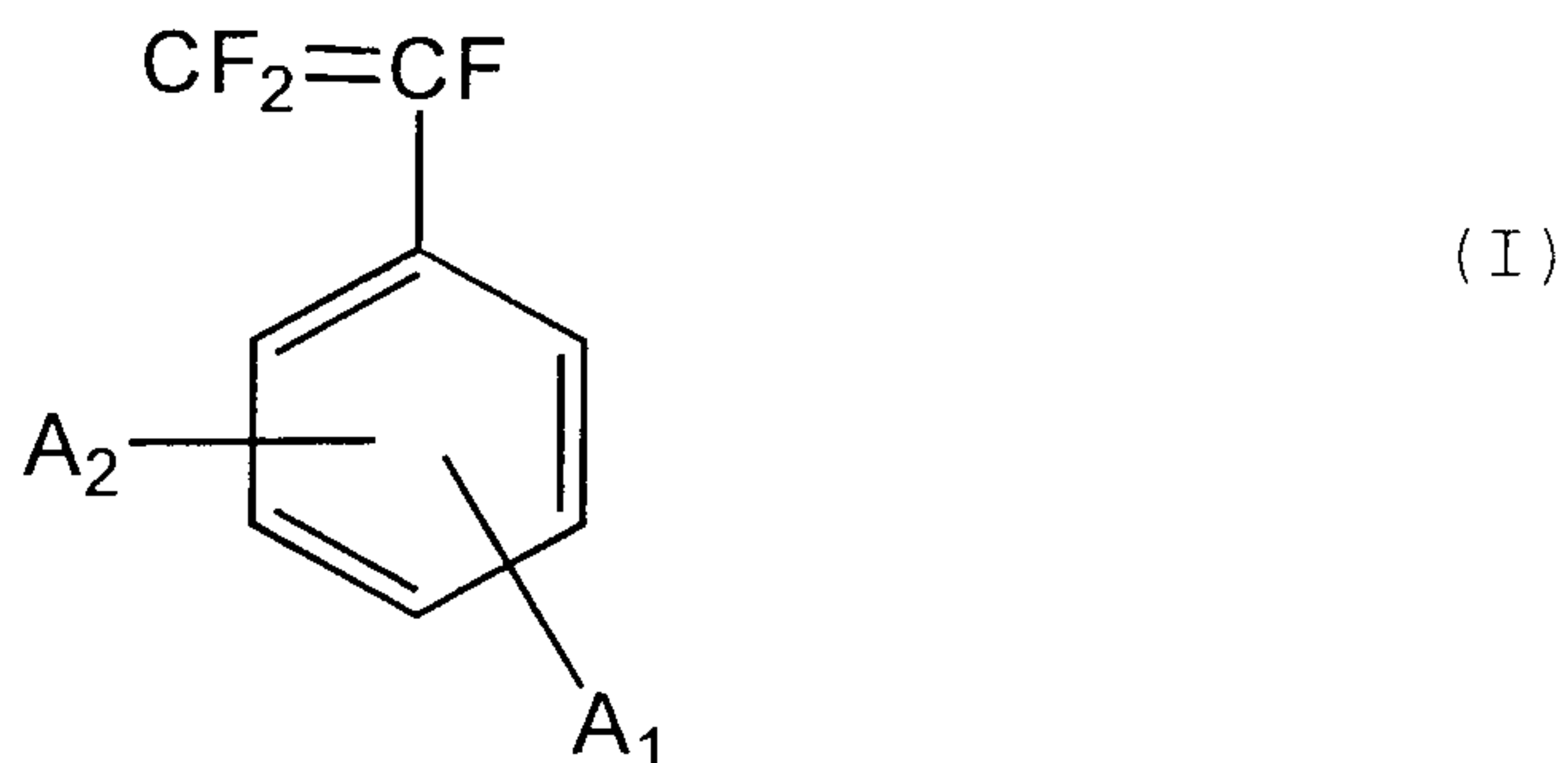
In addition to the utility of the grafted membranes described herein in ion exchange membranes for electrochemical fuel cells, it is contemplated that such membranes will also have utility in the following applications:

1. as membranes in filtration and ultrafiltration applications;
- 10 2. as proton exchange membranes in water electrolysis, which involves a reverse chemical reaction to that employed in hydrogen/oxygen electrochemical fuel cells;
3. as membranes in chloralkali electrolysis, which typically involves the electrolysis of a brine solution to produce chlorine and sodium hydroxide, with hydrogen as a by-product;
- 15 4. as electrode separators in conventional batteries, provided the membrane has the requisite chemical inertness and high electrical conductivity;
- 20 5. as ion-selective electrodes, particularly those used for the potentiometric determination of a specific ion such as Ca^{2+} , Na^{+} , K^{+} and like ions;
- 25 6. as sensor materials for humidity sensors based on ion exchange membranes, as the electrical conductivity of an ion exchange membrane varies with humidity;
- 30 7. as ion exchange membranes for separations by ion exchange chromatography - typical such applications are deionization and desalination of water, ion separations, removal of interfering ionic species, and separation and purification of biomolecules;

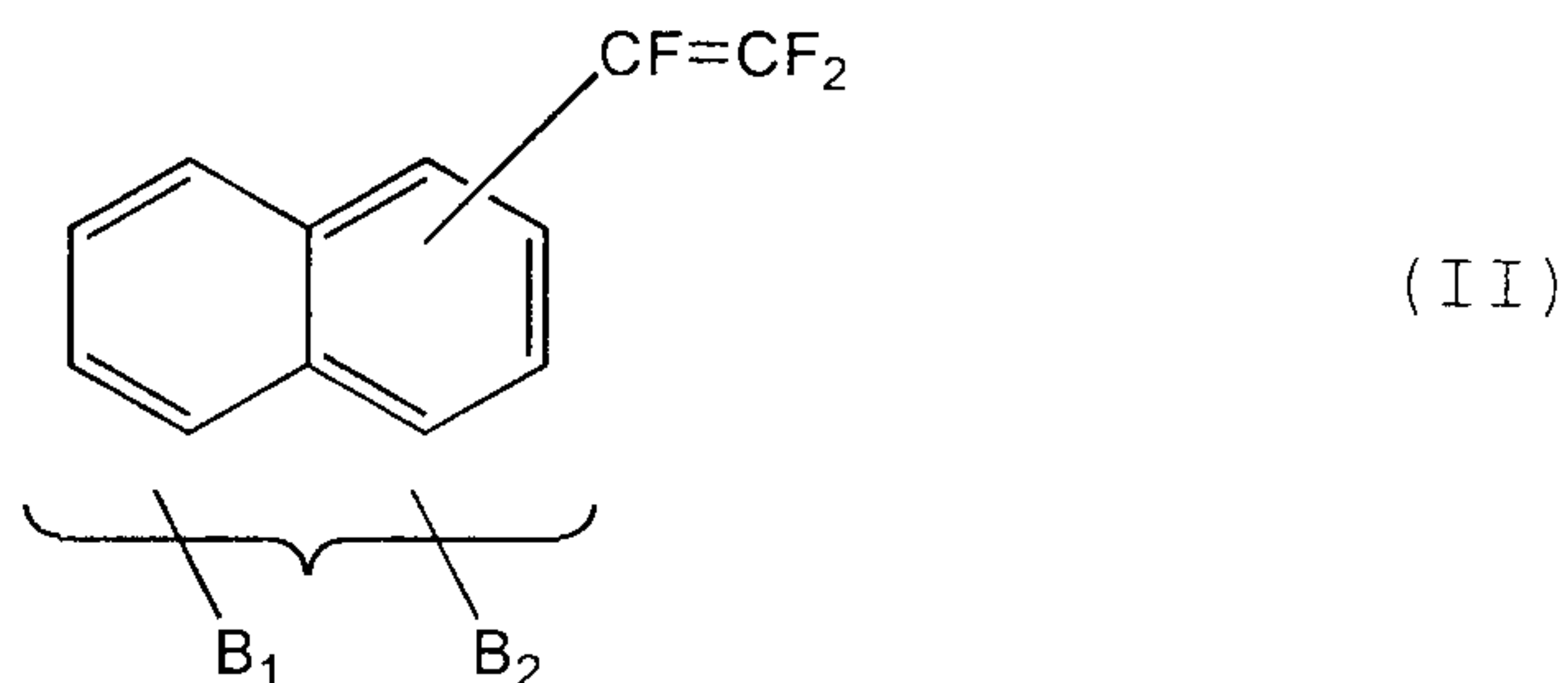
8. as ion exchange membranes employed in analytical pre-concentration techniques (e.g., Donnan Dialysis);
9. as ion exchange membranes in electrodialysis, in
5 which membranes are employed to separate components of an ionic solution under the driving force of an electrical current - industrial applications include desalination of brackish water, preparation of boiler feed make-up and chemical process
10 water, de-ashing of sugar solutions, deacidification of citrus juices, separation of amino acids, and the like;
10. as membranes in dialysis applications, in which solutes diffuse from one side of the membrane
15 (the feed side) to the other side according to their concentration gradient - applications include haemodialysis and the removal of alcohol from beer;
11. as membranes in gas separation (gas permeation) and
20 pervaporation (liquid permeation) techniques; and
12. as bipolar membranes employed in water splitting and subsequently in the recovery of acids and bases from waste water solutions.

What is claimed is:

1. A membrane comprising a polymeric base film to which has been graft polymerized a monomer selected from the group consisting of monomers of formula (I)



and formula (II)



where A_1 , A_2 , and B_1 , B_2 are independently selected from the group consisting of:

hydrogen, lower alkyl, lower fluoroalkyl, cyclic alkyl,

aryl (where aryl is other than Ph),

$\text{CH}(\text{X})\text{Ph}$, where X is selected from the group consisting of fluorine, lower alkyl, lower fluoroalkyl and Ph,

PRR' and $\text{P}(\text{OR})(\text{OR}')$, where R and R' are independently selected from the group consisting

of lower alkyl, cyclic alkyl and Ph, and where R and R' can be the same or different, and

wherein A_1 , A_2 , B_1 , and B_2 can be the same or different, provided that in each monomer, at least one of the substituents A_1 , A_2 , B_1 , B_2 is other than hydrogen.

2. A membrane according to claim 1 comprising a polymeric base film to which has been graft polymerized a monomer of formula (I), wherein A_1 is other than hydrogen, and A_2 is hydrogen.
3. A membrane according to claim 1 comprising a polymeric base film to which has been graft polymerized a monomer of formula (I), wherein A_1 and A_2 are other than hydrogen.
4. A membrane according to claim 1 comprising a polymeric base film to which has been graft polymerized a monomer of formula (II) wherein B_1 is other than hydrogen, and B_2 is hydrogen.
5. A membrane according to claim 1 comprising a polymeric base film to which has been graft polymerized a monomer of formula (II), wherein B_1 and B_2 are other than hydrogen.
6. A membrane according to claim 1 comprising a polymeric base film to which has been graft polymerized a monomer of formula (I) wherein A_1 is selected from the group consisting of lower alkyl and cyclic alkyl, and A_2 is the same as A_1 or

hydrogen.

7. A membrane according to claim 1 comprising a
polymeric base film to which has been graft
5 polymerized a monomer of formula (II) wherein B_1
is selected from the group consisting of lower
alkyl and cyclic alkyl, and B_2 is the same as B_1
or hydrogen.
- 10 8. A membrane according to claim 1 comprising a
polymeric base film to which has been graft
polymerized a monomer of formula (I) wherein A_1 is
selected from the group consisting of aryl groups,
and wherein A_2 is hydrogen.
- 15 9. A membrane according to claim 8, wherein said aryl
group is a fused polycyclic aromatic with two
fused rings.
- 20 10. A membrane according to claim 8, wherein said aryl
group is biphenyl.
11. A membrane according to claim 8, wherein said aryl
group is a heteroaromatic group.
- 25 12. A membrane according to claim 11, wherein said
aryl group is a heteroaromatic group containing at
least one heteroatom, wherein said at least one
heteroatom is selected from the group consisting
30 of nitrogen, oxygen and sulfur.
13. A membrane according to claim 12, wherein said
heteroaromatic group contains at least two of said

heteroatoms, and said heteroatoms can be the same or different.

14. A membrane according to claim 12, wherein at least one of said heteroatoms is nitrogen which is N-alkylated or N-benzylated.
15. A membrane according to claim 12, wherein said heteroaromatic group is monocyclic.
16. A membrane according to claim 1 comprising a polymeric base film to which has been graft polymerized a monomer of formula (I) wherein A_1 is selected from the group consisting of PRR' and $P(OR)(OR')$, where R and R' are independently selected from the group consisting of lower alkyl, cyclic alkyl and Ph, and where R and R' can be the same or different, and wherein A_2 is hydrogen.
17. A membrane according to claim 1 comprising a polymeric base film to which has been graft polymerized a monomer of formula (I) wherein A_1 is selected from the group consisting of Me and $CH(X)Ph$, where X is selected from the group consisting of fluorine, Me, and Ph, and A_2 is the same as A_1 or hydrogen.
18. A membrane according to claim 1 comprising a polymeric base film to which has been graft polymerized a monomer of formula (II) wherein B_1 is selected from the group consisting of Me and $CH(X)Ph$, where X is selected from the group consisting of fluorine, Me and Ph, and B_2 is

hydrogen.

19. A membrane according to claim 1 comprising a
polymeric base film to which has been graft
5 polymerized a monomer of formula (I) wherein A_1 is
Me and A_2 is Me or hydrogen.
20. A membrane according to claim 1 comprising a
polymeric base film to which has been graft
10 polymerized a monomer of formula (II) wherein B_1
is Me and B_2 is Me or hydrogen.
21. A membrane according to claim 1 comprising a
polymeric base film to which has been graft
15 polymerized a monomer of formula (I) wherein A_1 is
para-Me, A_2 is hydrogen, and said base film
comprises poly(ethylene-co-tetrafluoroethylene).
22. A membrane according to claim 1 comprising a
20 polymeric base film to which has been graft
polymerized a monomer of formula (II) wherein B_1
is Me, B_2 is hydrogen, and said base film
comprises poly(ethylene-co-tetrafluoroethylene).
- 25 23. A membrane according to claim 1 comprising a
polymeric base film to which has been graft
polymerized one monomer selected from the group
consisting of said monomers of formula (I) and
formula (II), whereby the grafted chains are
30 homopolymeric.
24. A membrane according to claim 1 comprising a
polymeric base film to which has been graft

polymerized more than one monomer selected from the group consisting of said monomers of formula (I) and formula (II), whereby said grafted chains are copolymeric.

5

25. A membrane according to claim 1 comprising a polymeric base film to which has been graft polymerized more than one monomer of formula (I), whereby the grafted chains are copolymeric.

10

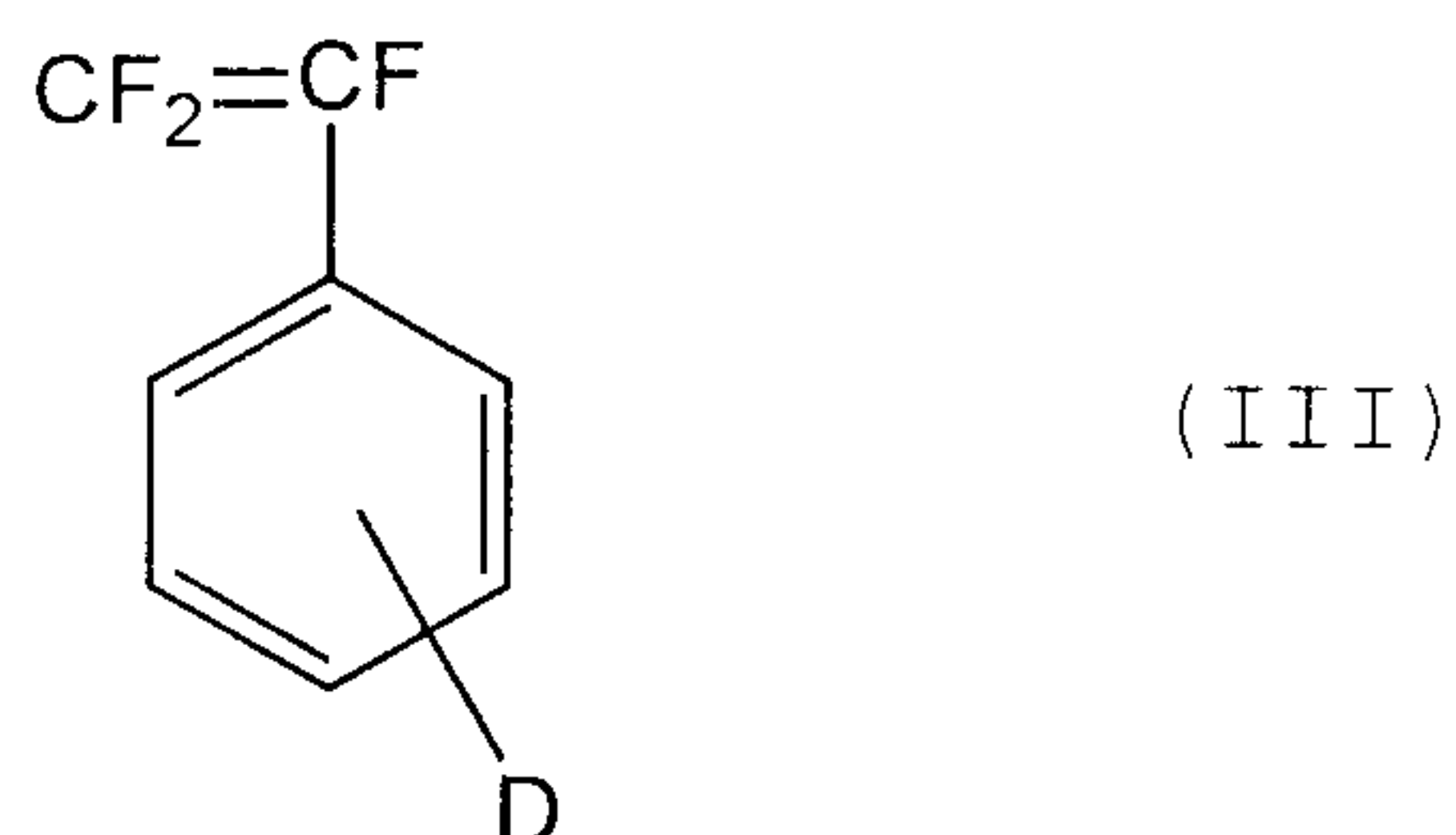
26. A membrane according to claim 1 comprising a polymeric base film to which has been graft polymerized more than one monomer of formula (II), whereby the grafted chains are copolymeric.

15

27. A membrane according to claim 1 comprising a polymeric base film to which has been graft polymerized a monomer of formula (III) in addition to said monomers selected from the group consisting of monomers of formula (I) and formula (II):

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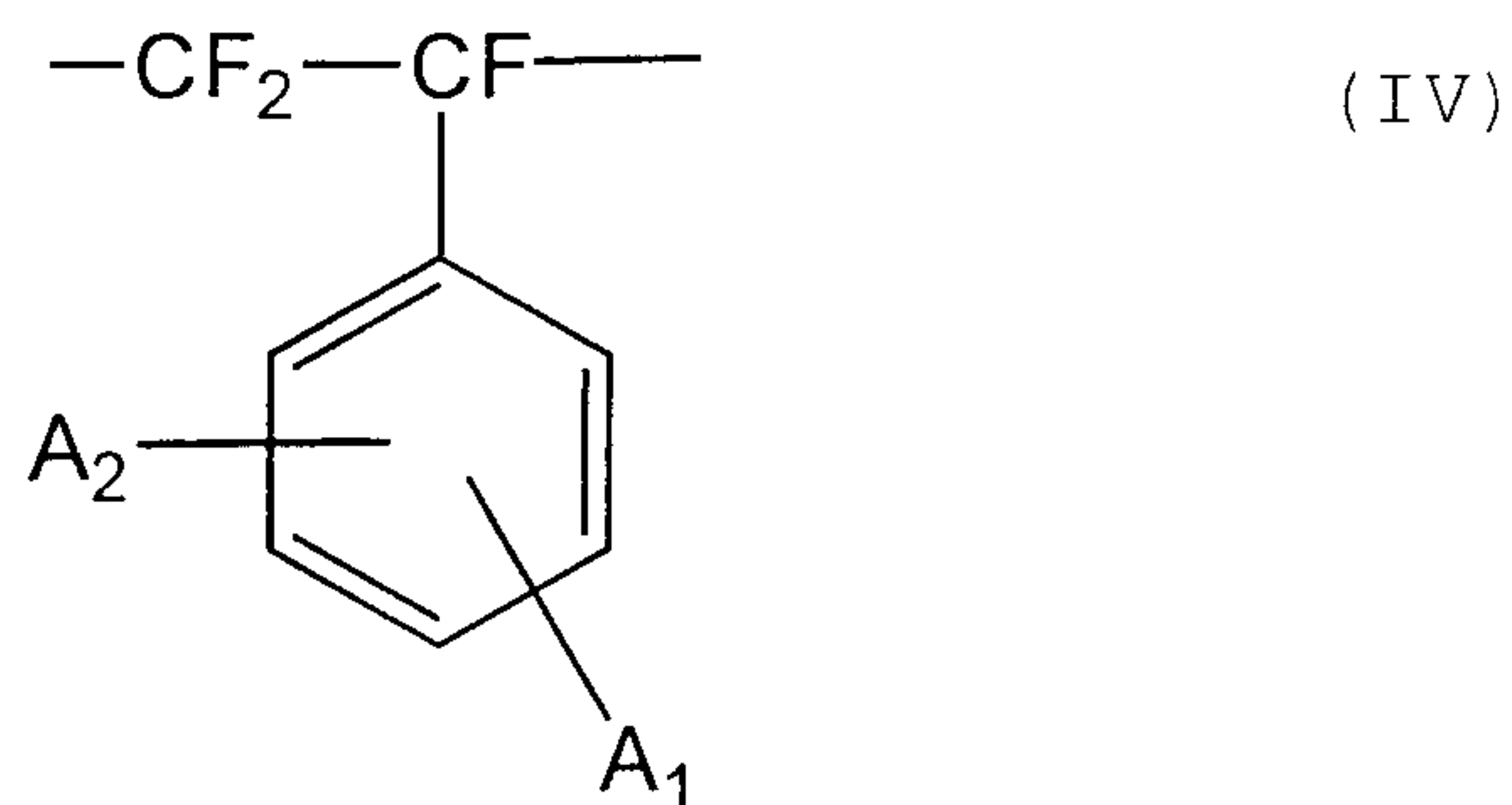
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where D is selected from the group consisting of hydrogen, fluorine, CF_3 , CF_2H , $\text{CF}=\text{CF}_2$, SO_2F and SO_3-M^+ where M^+ is a suitable counterion.

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28. A membrane comprising a polymeric base film with grafted chains comprising monomer units selected from the group consisting of monomer units of formula (IV)

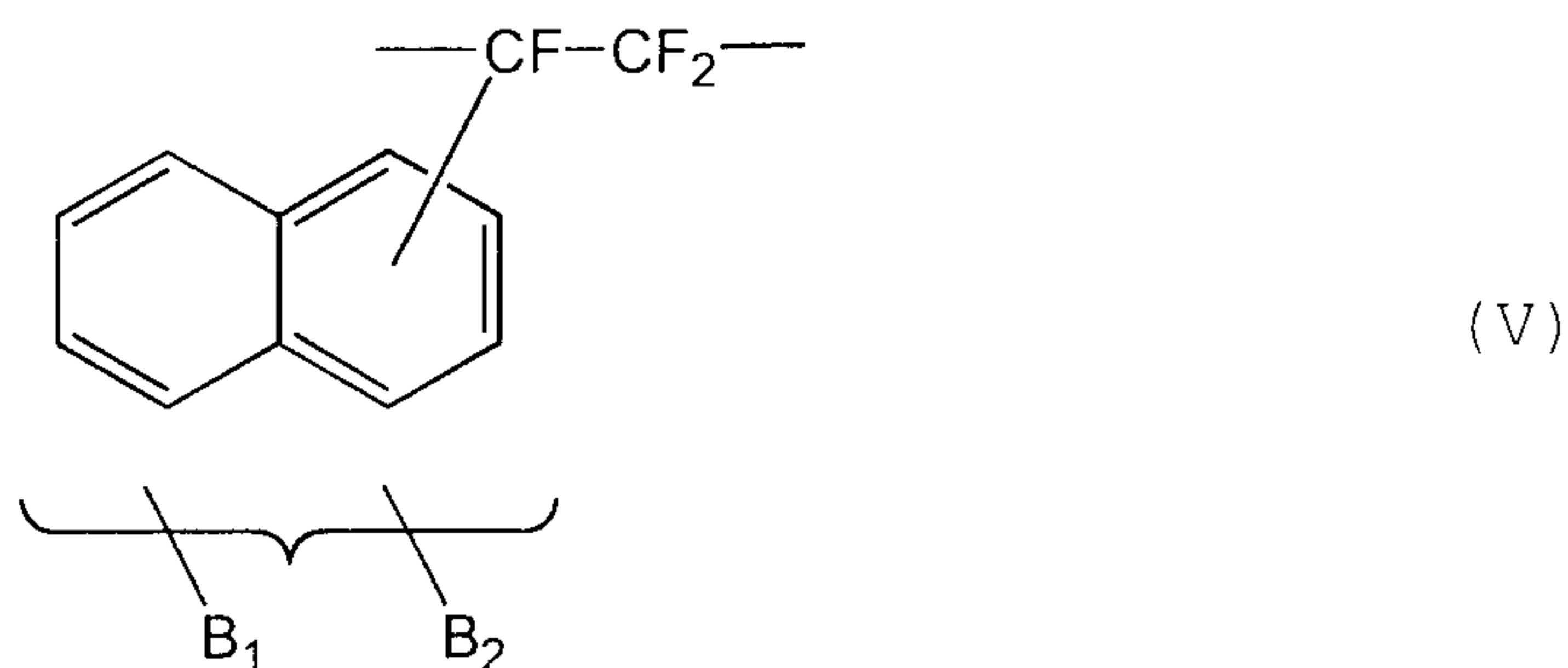
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10

and formula (V)

15



20

where A_1 , A_2 , and B_1 , B_2 are independently selected from the group consisting of:

hydrogen, lower alkyl, lower fluoroalkyl, cyclic alkyl,

25

aryl (where aryl is other than Ph),

$\text{CH}(\text{X})\text{Ph}$, where X is selected from the group consisting of fluorine, lower alkyl, lower fluoroalkyl and Ph,

30

PRR' and $\text{P}(\text{OR})(\text{OR}')$ where R and R' are independently selected from the group consisting of lower alkyl, cyclic alkyl and Ph, and where R and R' can be the same or different,

34

and wherein A_1 , A_2 , B_1 , and B_2 can be the same or different, provided that in each of said monomer units at least one of the substituents A_1 , A_2 , B_1 , B_2 is other than hydrogen.

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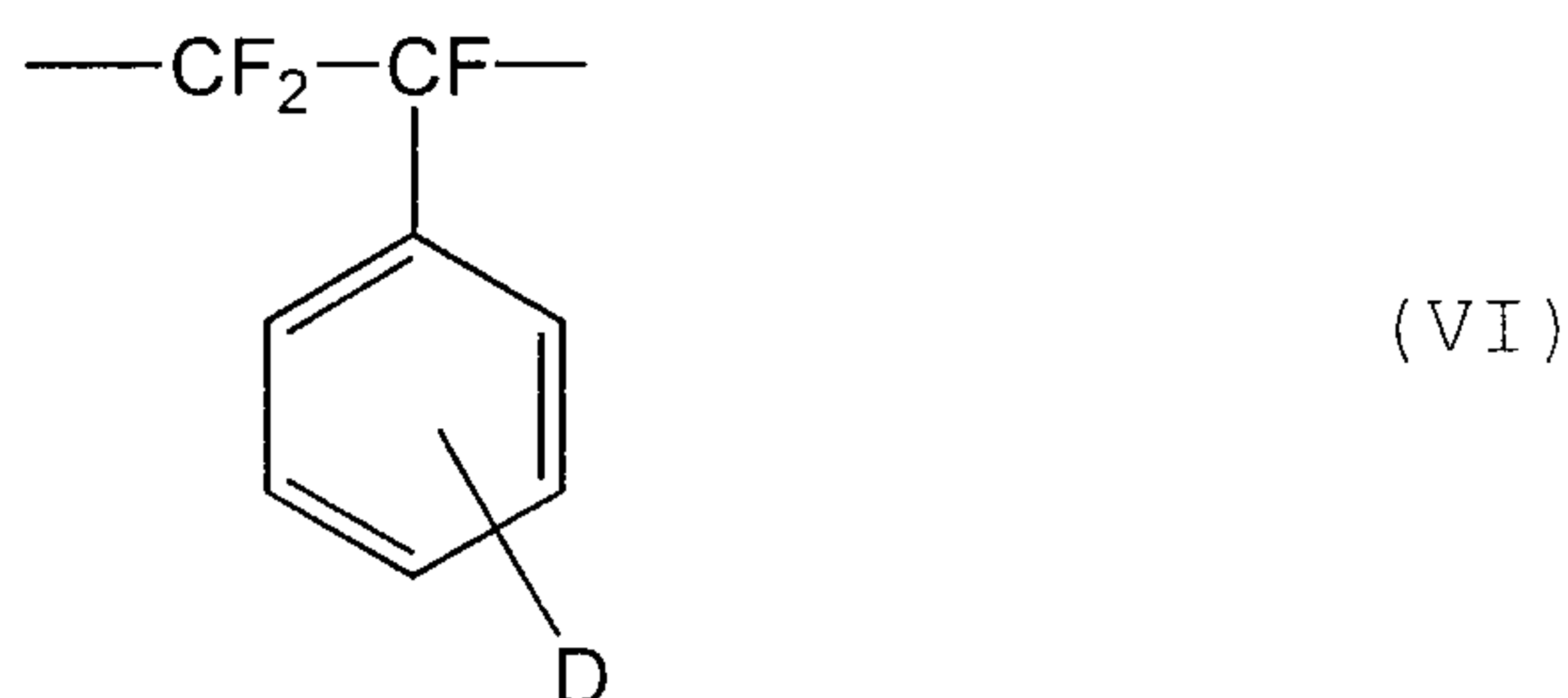
29. A membrane according to any of claims 1, 19-22, 27 or 28 wherein at least a portion of the grafted chains are crosslinked.

10 30. A membrane according to claim 28 wherein at least a portion of said monomer units further comprise at least one ion-exchange substituent, whereby said membrane is an ion-exchange membrane.

15 31. An ion-exchange membrane according to claim 30 wherein said at least one ion-exchange substituent is a sulfonate or sulfonic acid substituent.

20 32. An ion-exchange membrane according to claim 30 comprising a polymeric base film with grafted chains further comprising monomer units of formula (VI) in addition to said monomer units selected from the group consisting of monomer units of formula (IV) and formula (V):

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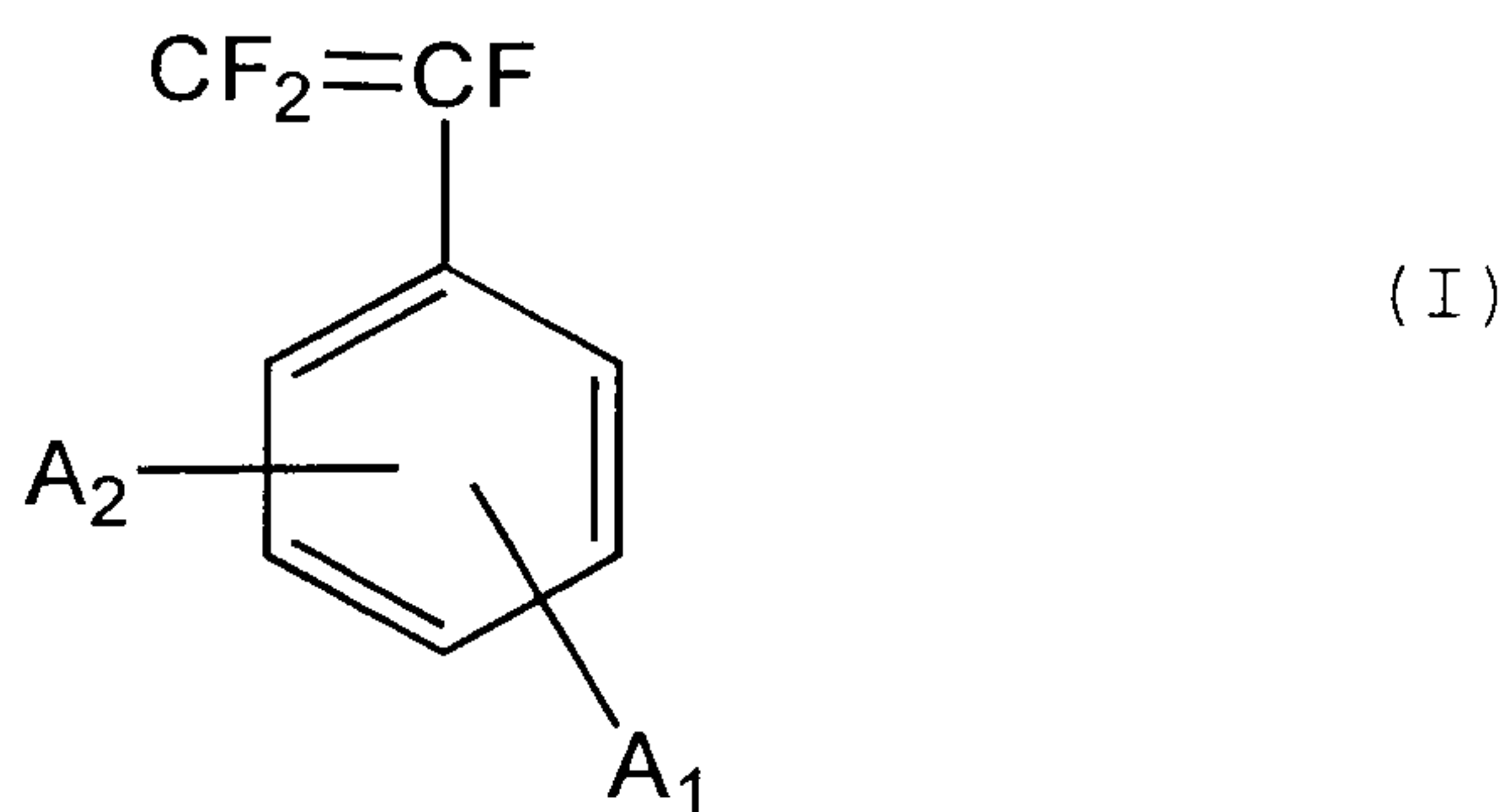
where D is selected from the group consisting of hydrogen, fluorine, CF_3 , CF_2H , $\text{CF}=\text{CF}_2$, SO_2F and $\text{SO}_3\text{---M}^+$ wherein M^+ is a suitable counterion.

33. An ion-exchange membrane according to claim 30 wherein at least a portion of said monomer units comprise at least two ion-exchange substituents.
- 5 34. An ion-exchange membrane according to claim 30 wherein at least 50% of said monomer units in said grafted chains have at least one ion-exchange substituent per monomer unit.
- 10 35. An ion-exchange membrane according to claim 30 wherein said grafted chains comprise at least two different types of ion-exchange groups.
- 15 36. An ion-exchange membrane according to claim 30 wherein said grafted chains comprise an anion-exchange group and a cation-exchange group.
- 20 37. An ion-exchange membrane according to any of claims 30 and 32 wherein at least a portion of the grafted chains are crosslinked.
- 25 38. An ion-exchange membrane according to claim 30 wherein said ion-exchange membrane is substantially gas impermeable.
39. An ion-exchange membrane according to claim 31 wherein said ion-exchange membrane is substantially gas impermeable.
- 30 40. An ion-exchange membrane according to claim 30 wherein said monomer units are of formula (IV).

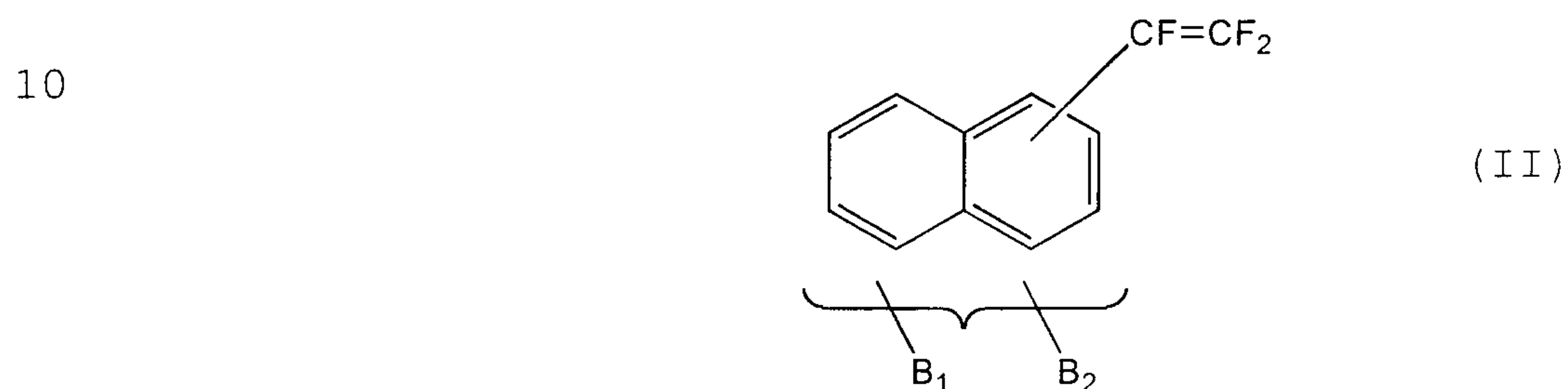
41. An ion-exchange membrane according to claim 40
wherein A_1 is selected from the group consisting
of Me and $CH(X)Ph$, where X is selected from the
group consisting of fluorine, Me and Ph, and A_2 is
the same as A_1 or hydrogen.
42. An ion-exchange membrane according to claim 40
wherein A_1 is Me and A_2 is Me or hydrogen.
43. An ion-exchange membrane according to claim 40
wherein A_1 is para-Me, A_2 is hydrogen, said base
film comprises poly(ethylene-co-
tetrafluoroethylene), and said at least one ion-
exchange substituent is a sulfonate or sulfonic
acid group.
44. An ion-exchange membrane according to claim 30
wherein said monomer units are of formula (V).
45. An ion-exchange membrane according to claim 44
wherein B_1 is selected from the group consisting
of Me and $CH(X)Ph$, where X is selected from the
group consisting of fluorine, Me and Ph, and B_2 is
hydrogen.
46. An ion-exchange membrane according to claim
44 wherein B_1 is Me and B_2 is Me or hydrogen.
47. An ion-exchange membrane according to claim 44
wherein B_1 is Me, B_2 is hydrogen, said base film
comprises poly(ethylene-co-tetrafluoroethylene),
and said at least one ion-exchange substituent is
a sulfonate or sulfonic acid group.

48. An electrode apparatus comprising an ion-exchange membrane of claim 38.
49. An electrode apparatus comprising an ion-exchange
5 membrane of claim 39.
50. A membrane electrode assembly comprising an ion-exchange membrane of claim 38.
- 10 51. A membrane electrode assembly comprising an ion-exchange membrane of claim 39.
52. An electrochemical fuel cell comprising an ion-exchange membrane of claim 38.
- 15 53. An electrochemical fuel cell comprising an ion-exchange membrane of claim 39.
54. An electrochemical fuel cell according to any of
20 claims 52 and 53 wherein said polymeric base film is less than 100 μm thick.
55. A membrane prepared by subjecting a membrane of claim 1 to a reaction process selected from the
25 group consisting of halomethylation, sulfonation, phosphonation, amination, carboxylation, hydroxylation and nitration.
56. A method of preparing a membrane, said method
30 comprising graft polymerizing to a polymeric base film a monomer selected from the group consisting of monomers of formula (I)

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and formula (II)



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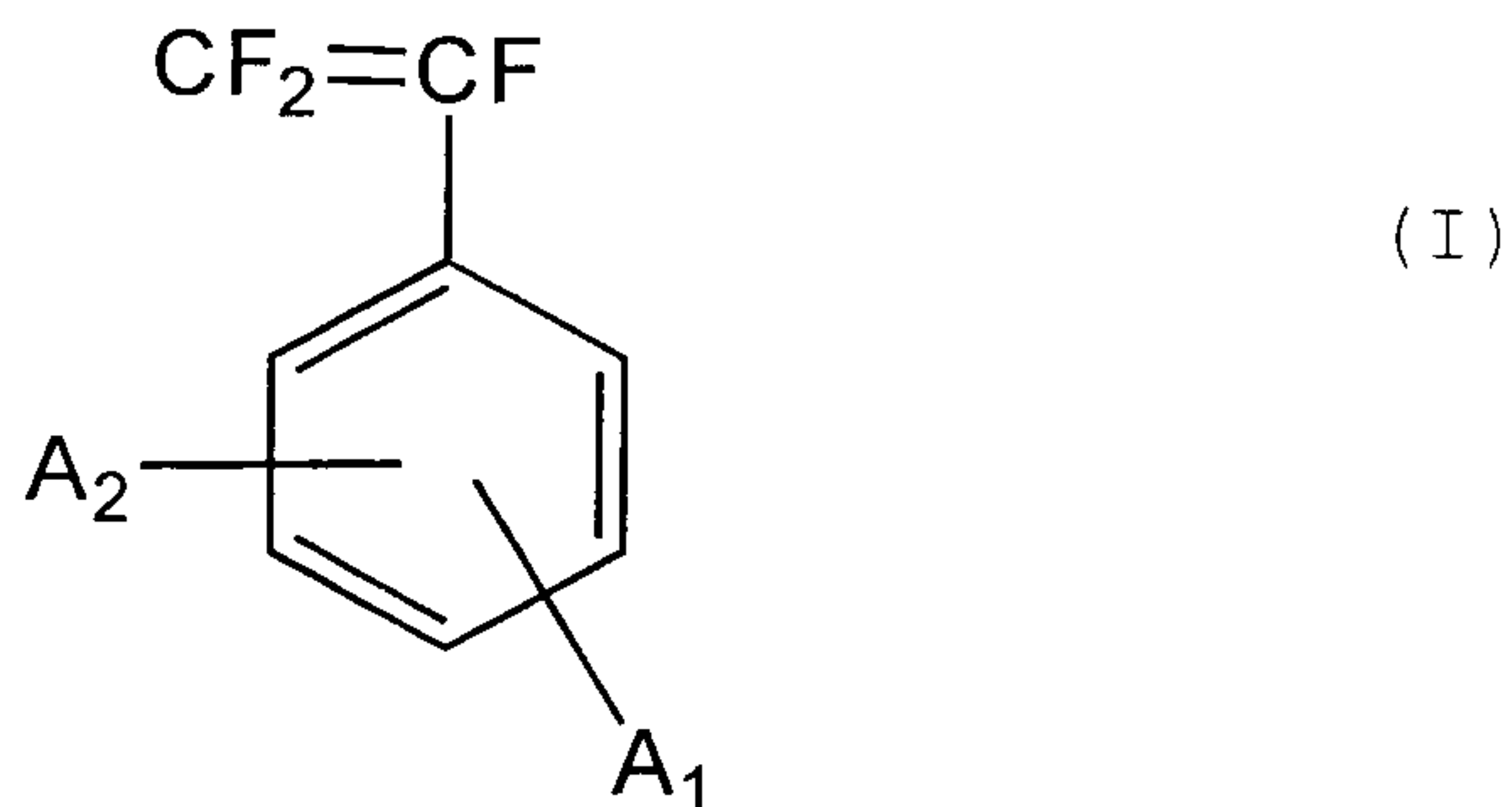
wherein in the selected monomer at least one of A_1 , A_2 , and at least one of B_1 , B_2 is a substituent other than hydrogen which activates said monomer with respect to said graft polymerizing, and said method further comprises: introducing a sulfonate group into at least a portion of said graft polymerized monomer units; and converting at least a portion of said substituent to substituent which are deactivating with respect to desulfonation.

57. A method of preparing a membrane, said method comprising graft polymerizing to a polymeric base film a monomer selected from the group consisting

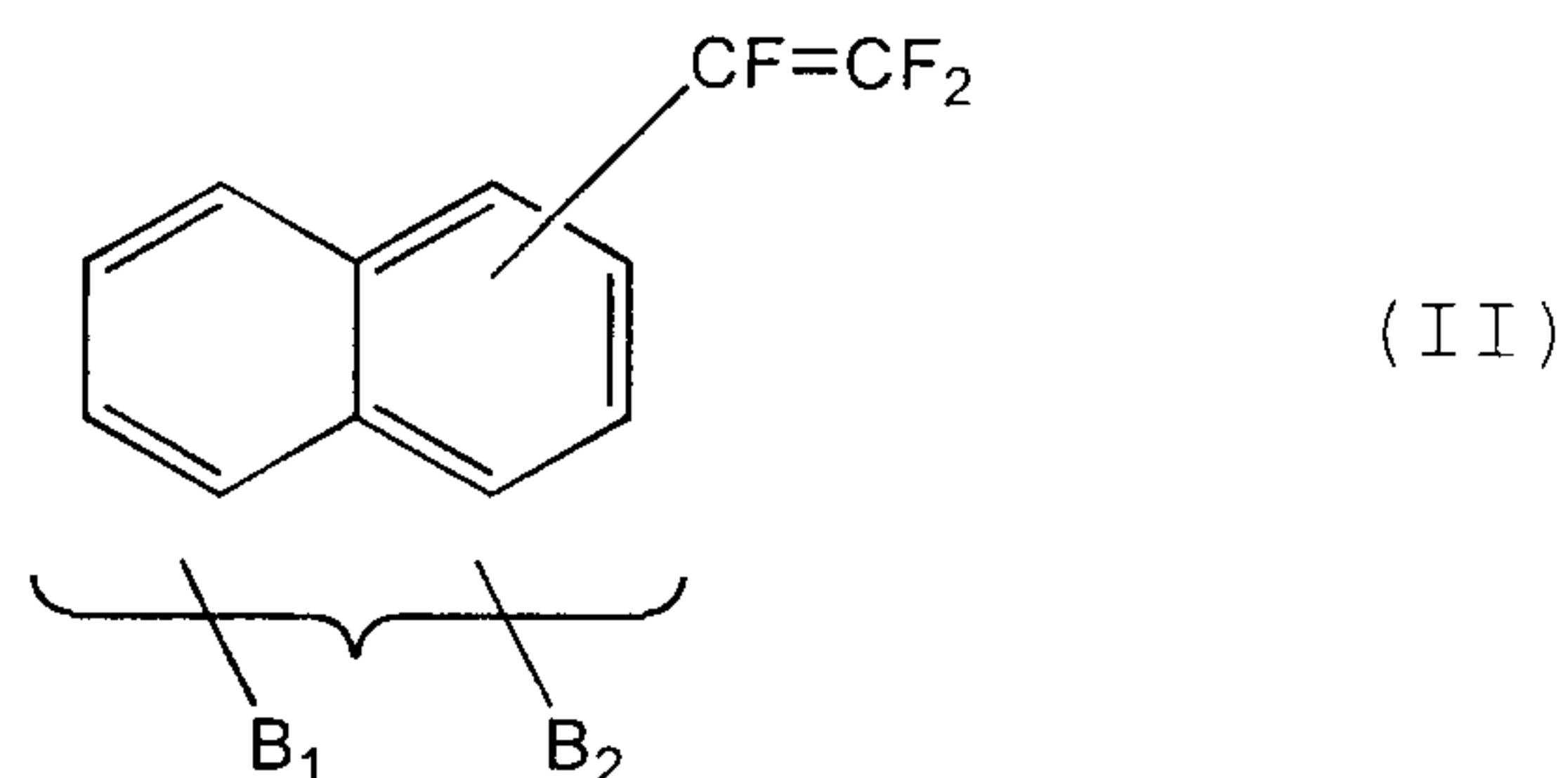
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of monomers of formula (I)



and formula (II)



where A_1 , A_2 , and B_1 , B_2 are independently selected from the group consisting of:

20 hydrogen, lower alkyl, lower fluoroalkyl,
 cyclic alkyl,
 aryl (where aryl is other than Ph),
 CH(X)Ph, where X is selected from the group
 consisting of fluorine, lower alkyl, lower
 25 fluoroalkyl and Ph,

 PRR' and P(OR)(OR') (where R and R' are
 independently selected from the group consisting
 of lower alkyl, cyclic alkyl and Ph, and where R
 and R' can be the same or different, and

30 wherein A_1 , A_2 , B_1 , and B_2 can be the same or
 different, provided that in each monomer at least
 one of the substituents A_1 , A_2 , B_1 , B_2 is other
 than hydrogen.

58. A method according to claim 57, wherein A_1 and B_1 are independently selected from the group consisting of

an aryl group selected from the group consisting of monocyclic heteroaromatics, fused polycyclic heteroaromatics, and heteroaromatic ring assemblies having at least one nitrogen atom, and

phosphines of the formula PRR' and phosphites of formula $P(OR)(OR')$ where R and R' are independently selected from the group consisting of lower alkyl, cyclic alkyl and Ph and where R and R' can be the same or different, and

A_2 and B_2 are hydrogen, the method further comprising alkylating or benzylating at least a portion of any of said nitrogen atoms of said aryl group, or the phosphorus atoms of said phosphine or phosphite.

59. A method according to claim 57, wherein A_1 and B_1 are independently selected from the group consisting of

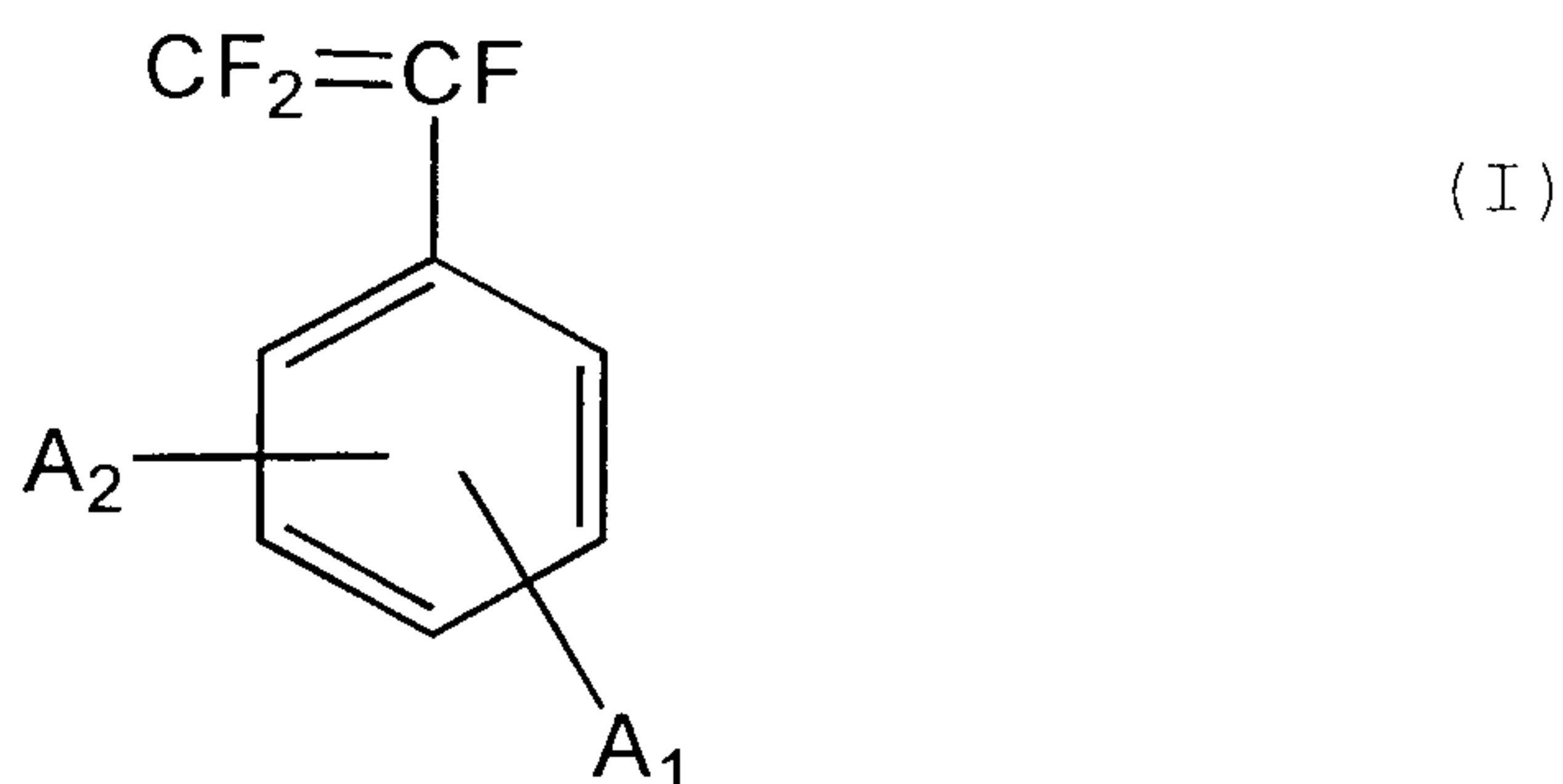
phosphines of the formula PRR' and phosphites of formula $P(OR)(OR')$ where R and R' are independently selected from the group consisting of lower alkyl, cyclic alkyl and Ph, and where R and R' can be the same or different, and

A_2 and B_2 are hydrogen, the method comprising the sequential steps of introducing a nitro group into at least a portion of the grafted monomer units of said membrane and

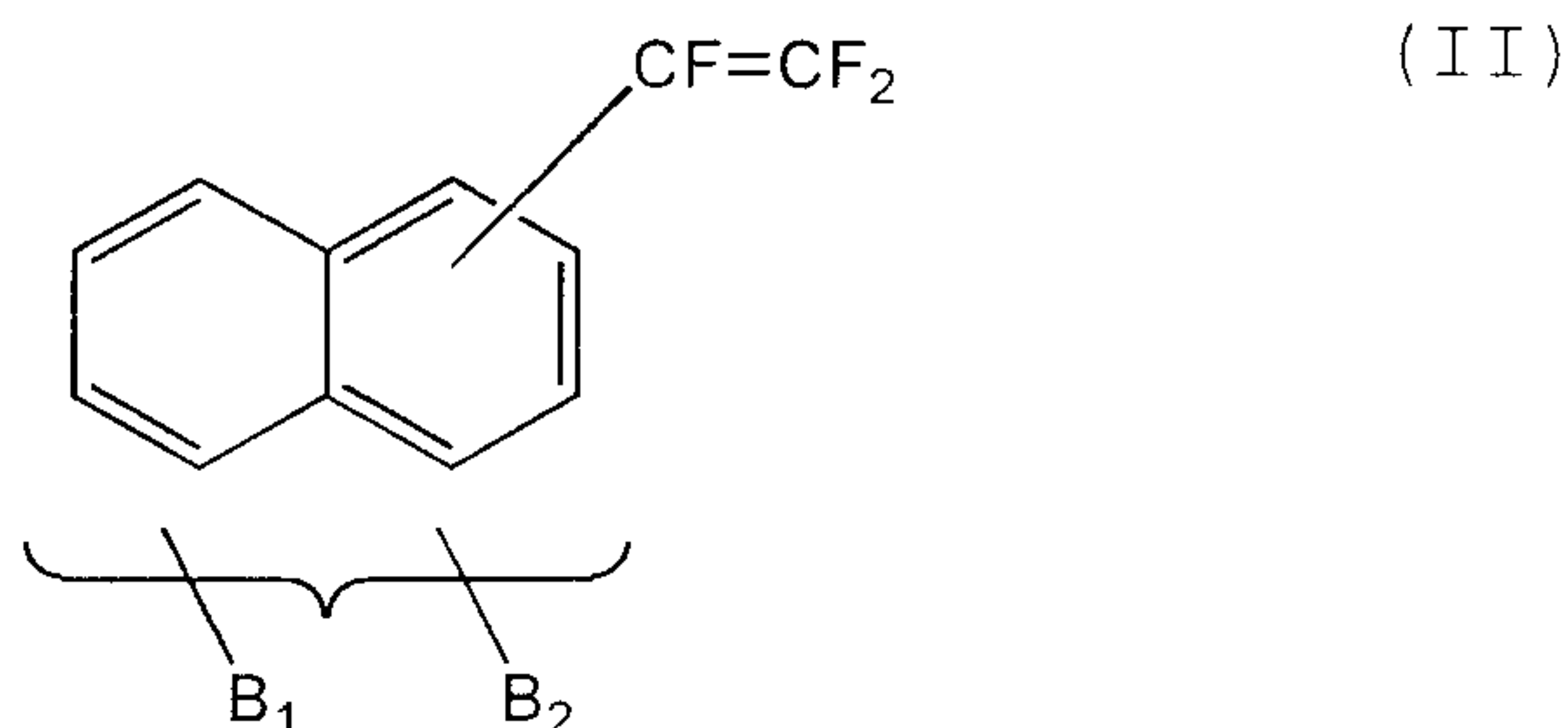
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converting at least a portion of said nitro groups
to quaternary ammonium groups,
the method optionally further comprising
converting said phosphine or phosphite to an ion-
exchange substituent.

60. A method of preparing a membrane comprising graft
polymerizing to a polymeric base film a monomer
selected from the group consisting of monomers of
formula (I)



and formula (II)



where A_1 and B_1 are independently selected from
the group consisting of

PRR' , $P(OR)(OR')$, and SR where R and R' are
independently selected from the group consisting
of lower alkyl, cyclic alkyl and Ph , and where R
and R' can be the same or different, and

A_2 and B_2 are the same as A_1 and B_1 respectively or hydrogen,

the method further comprising oxidizing at least a portion of the PRR', P(OR)(OR'), or SR groups.

5

61. The method of claim 60 further comprising introducing ion-exchange substituents into at least a portion of said monomer units.

10

62. The method of claim 60, wherein A_1 and B_1 are independently selected from the group SR, where R is selected from the group consisting of lower alkyl, cyclic alkyl and Ph, and A_2 and B_2 are the same as A_1 and B_1 respectively or hydrogen, and wherein the method comprises converting at least a portion of the SR groups to sulfonate or sulfonic acid groups.

15

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FIG. 1

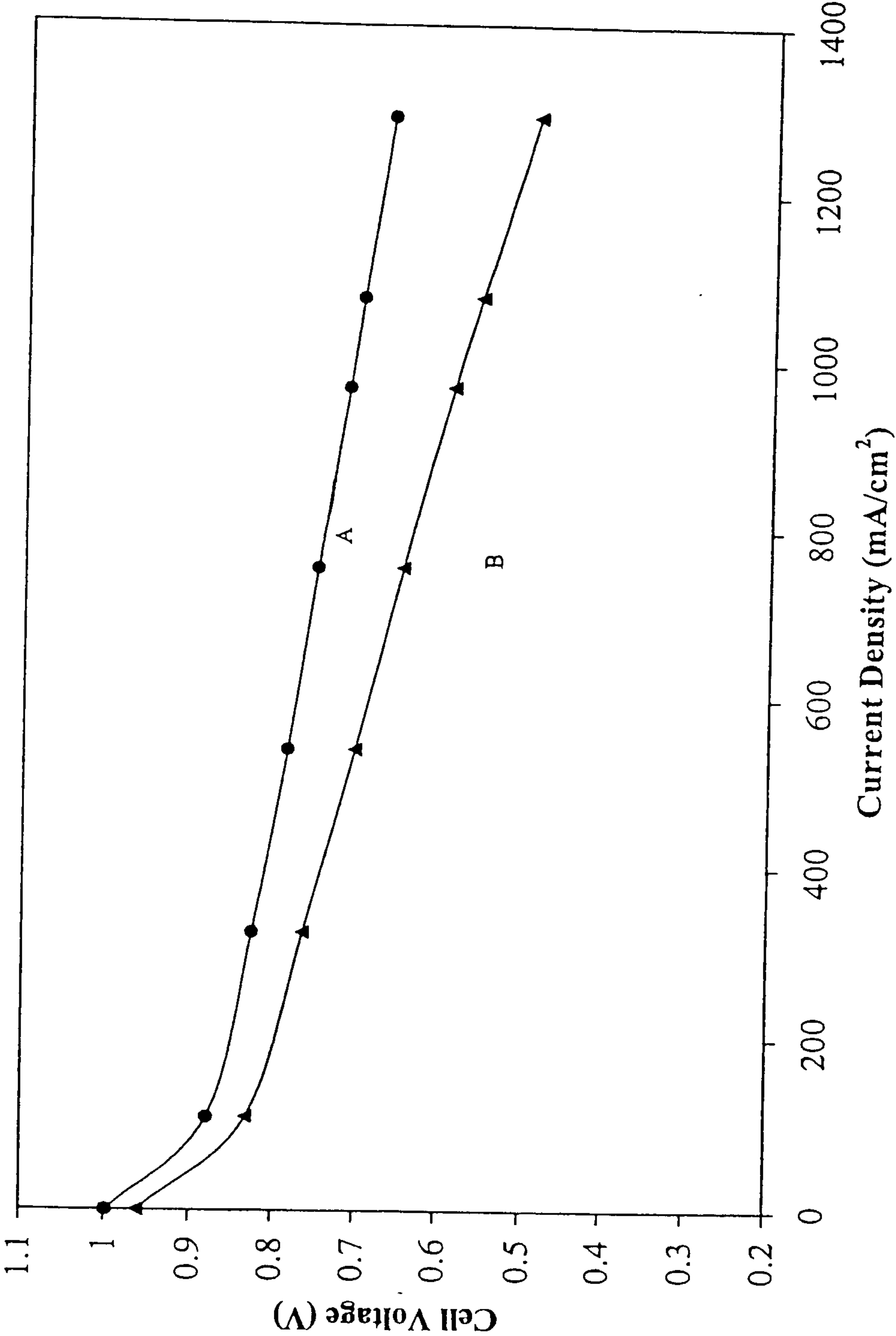


FIG. 2

