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(54) **IMPROVED MEMBRANES FOR SEPARATION OF ALKENES FROM ALKANES**

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(57) **ABSTRACT**

Ionomers of Group 11 metals which include repeat units from vinylidene fluoride, can separate alkenes from alkanes when comprising a layer of a membrane. These membranes have excellent permeability and/or selectivity for alkenes in the separation of alkenes from alkanes.

IMPROVED MEMBRANES FOR SEPARATION OF ALKENES FROM ALKANES

GOVERNMENT RIGHTS

[0001] Support was provided under Department of Energy awards of DE-SC0004672 and DE-SC0007510. The U.S. government has rights in this patent application.

FIELD OF THE INVENTION

[0002] Membranes containing Group 11 metal ionomers comprising repeat units derived from vinylidene fluoride have exceptionally good permanences and/or selectivities for alkenes compared to other membranes, when used to separate alkenes from alkanes in mixtures of these types of compounds.

TECHNICAL BACKGROUND

[0003] Nonporous, but permeable, membranes have been used to separate various types of chemicals for a long time. For instance certain types of semipermeable membranes are used to separate water from seawater, or oxygen from nitrogen, or alkenes from alkanes.

[0004] The separation of alkenes from alkanes is usually accomplished using a silver ionomer of a fluorinated polymer. Often, because fluoropolymers are more stable to oxidation than unfluorinated polymers, the silver ionomers of fluorinated polymers are often more stable than unfluorinated polymers. Also polymers which contain fluoro substituents near, for instance sulfonic acid or carboxyl groups tend to be very strong acids (sometimes called "super acids), the silver salts may be more stable.

[0005] In oil refineries or olefin polymerization plants sometimes one has mixtures of alkenes and alkanes and one desires to separate the alkenes from the alkanes. This may be relatively easy if these two types of compounds have significant differences in boiling points, but separation of such compounds with similar boiling points are more difficult and expensive, especially if the boiling points are lower in temperature. For instance propane boils at −44.5° C. and propylene boils at −47.8° C. Separation of these two compounds by cryogenic distillation is very expensive because of high equipment and energy costs. Therefore cheaper, less energy intensive methods of separation are desirable.

[0006] U.S. Pat. No. 5,191,151 to Erikson et al. describes the separation of lower alkenes (containing 2 to 4 carbon atoms) from lower alkanes (containing one to six carbon atoms) using a membrane which is a silver ionomer of a polymer of tetrafluoroethylene (TFE) and a perfluorovinyl ether containing a terminal precursor group to a sulfonic acid.

[0007] U.S. Patent Application 2015/0025293 to Feiring et al. describes the use of a membrane which is a silver ionomer of a fluorinated polymer. The ionomer includes repeat units derived from perfluorinated cyclic monomers.

[0008] L. Sauguet, et al., *Fluorinated Copolymers and Terpolymers Based on Vinylidene Fluoride and Bearing Sulfonic Acid Side-Group, Journal of Polymer Science, Part A:, Polymer Chemistry,* Vol. 45, (2007), p. 1814-1834, reports the synthesis of a wide range of fluorinated polymers containing repeat units derived from vinylidene fluoride and an olefinic sulfonyl fluoride. There is no mention of using such polymers or their ionomers to separate alkenes from alkanes, and only ionomers of alkali metals such as potassium are discussed.

[0009] U.S. Pat. No. 6,025,093 to Doyle, et al., describes ionomers of univalent metals which contain repeat units derived from vinylidene fluoride and a perfluorinated sulfonic acid precursor.

[0010] The present invention results in membranes which have higher permanences and separation alkene/alkane separation coefficients, and longer useful lives over previously used alkene/alkane separation membranes.

SUMMARY OF THE INVENTION

[0011] This invention concerns, an ionomer of a Group 11 metal, comprising repeat units derived from vinylidene fluoride and a monomer containing a precursor to a sulfonic acid group or a sulfonic acid group, and provided that carbon-fluorine groups are at least 30% of the total of said carbon-fluorine groups and carbon-hydrogen groups present in said ionomer.

[0012] Also described herein is a partially fluorinated polymer, comprising repeat units derived from vinylidene fluoride; and a monomer containing a precursor to a sulfonic acid group or a sulfonic acid group, provided that carbon-fluorine groups are at least 30% of the total of said carbon-fluorine groups and carbon-hydrogen groups present in said ionomer.

[0013] Also described herein is a process for separating one or more alkanes from one or more alkenes, comprising:

[0014] (a) providing a membrane comprising a layer of an ionomer, said ionomer comprising repeat units derived from vinylidene fluoride and a monomer containing a precursor to a sulfonic acid group or a sulfonic acid group, said membrane having a first side and a second side, providing that carbon-fluorine groups are at least 30% of the total of said carbon-fluorine groups and carbon-hydrogen groups present in said ionomer;

[0015] (b) exposing said first side to a feed composition comprising a mixture of one or more alkanes and one or more alkenes;

[0016] (c) providing a driving force; and

[0017] (d) producing a second mixture, on a second side of said membrane, having a higher ratio of alkene to alkane than said first mixture.

DETAILS OF THE INVENTION

[0018] Herein certain terms are used, and some of them are defined below:

[0019] Of the total of the carbon-hydrogen groups and the carbon fluorine groups in the ionomer, 30% or more are carbon-fluorine groups, preferably 60% or more, and more preferably 80% or more are carbon fluorine groups. By a carbon-hydrogen group is meant a hydrogen atom bound directly to a carbon atom, while a carbon-fluorine group is a fluorine atom bound directly to a carbon atom. Thus $—CF_2—$ groups contains 2 carbon fluorine groups, while a $—CH_3$ group contains 3 carbon-hydrogen groups. In a homopolymer of vinylidene fluoride, in which the repeat groups are $—CH_2CF_2$-the carbon-hydrogen groups and the carbon fluorine groups are each 50% of the total of carbon-hydrogen plus carbon-fluorine groups present. In a copolymer of 20 mole percent $CF_2═CFOCF_2CF(CF_3)OCF_2CF_2SO_2F$ and 80 mole percent vinylidene fluoride the

carbon-hydrogen groups are 27.6% of the total of the carbon-fluorine plus carbon hydrogen groups present. The relative amount of carbon-fluorine and carbon hydrogen groups present can be determined by NMR Spectroscopy, for instance using ^{14}C NMR, or a combination of ^{19}F and proton spectroscopy.

[0020] By a "monomer containing a precursor to a sulfonic acid group" is meant a monomer, when part of the polymer after polymerization, that can be readily converted to a sulfonic acid. Such groups include sulfonyl halides, especially sulfonyl fluorides, sulfonyl esters, sulfonamides, etc. It will be understood by those skilled in the art that the "monomer containing a precursor to a sulfonic acid group" is converted to the sulfonic acid group, often by hydrolysis, after chemical treatment of the polymer formed by the initial polymerization. Also that in the ionomeric form the "sulfonic acid" group is actually at least partly the sulfonate salt of a Group 11 metal. For the sake of simplicity herein, in the hydrolyzed or otherwise reacted original polymer, and in the ionomer, these are sometimes referred to herein as sulfonic acid groups.

[0021] By a "driving force" in the separation of the alkene and alkane by the membrane is generally meant that the effective concentration of the alkene on the first ("feed") side of the membrane is higher than on the second ("product") side of the membrane. This may be accomplished by, if the separation is on a gaseous feed, having higher partial pressure of the alkene on the feed side of the membrane. Thus the gaseous feed may be at a higher pressure than the product side, and/or the alkene may be swept away from the product side of the membrane by an "inert" gas such as nitrogen to lower the partial pressure of the alkene on the product side. If a liquid feed is being separated, the feed side may be at a higher pressure, and/or the alkene may be swept away by an inert liquid on the product side. These and other known methods in the art of applying a driving force may be used.

[0022] This may be quantified for a separation of gases to some extent by a mathematical relationship:

$$Q_a \alpha F_a(P1_a - P2_a)$$

[0023] wherein Q_a is the flow rate of component "a" through the membrane, F_a is the permeance of component a through the membrane, $P1_a$ is the partial pressure of a on the first (feed) side, and $P2_a$ is the partial pressure of a on the second (product) side.

[0024] By a membrane comprising the silver ionomer is meant a membrane comprising a thin nonporous layer of the silver ionomer and one or more other polymeric layers which physically support or reinforce the silver ionomer layer. Preferably the silver ionomer layer is about 0.1 μm to about 1.0 μm thick, more preferably about 0.2 μm to about 0.5 μm thick. These other layer(s) should preferably be relatively permeable to the alkenes and alkanes to be separated, and not themselves have much if any tendency to separate alkenes and alkanes.

[0025] In one preferred embodiment of the invention the Group 11 metal is copper or silver, more preferably silver.

[0026] In the ionomer, and its precursor acidic form, the repeat units that contain the pendant sulfonic acid groups are preferably at least about 5 mole percent of the total repeat units present, more preferably at least about 10 mole percent, very preferably at least about 20 mole percent, and especially preferably at least about 25 mole percent. It is preferred that the repeat units that contain the pendant acid groups are no more than 45 mole percent of the repeat units present in the silver ionomer or its precursor acid form. It is to be understood that any minimum amount of such repeat units and any maximum amount of such repeat units may be combined to form a preferred range of the amount of these repeat units.

[0027] Useful monomers containing a sulfonic acid group or a precursor to a sulfonic acid group include one or more of $CF_2{=}CFOCF_2CF_2SO_2F$, $CF_2{=}CFOCH_2CF_2CF_2SO_2F$ and $CF_2{=}CFOCF_2CF(CF_3)OCF_2CF_2SO_2F$, and $CF_2{=}CFOCF_2CF(CF_3)OCF_2CF_2SO_2F$ is preferred. In another type of preferred monomer containing a sulfonic acid or its precursor the carbon atom bound to the sulfonic acid group has at least one fluorine bound to that carbon atom.

[0028] Preferably the various forms of the VF2 copolymer described herein (referring to what exactly "Y" is, especially when Y is a Group 11 metal cation) are so-called "glassy" copolymers. By that is meant the copolymer has no melting point above about 30° C. with a heat of fusion of 3 J/g or more when measured by Differential Scanning calorimetry using ASTM Test D3418-12e1 using a heating and cooling rate of 10° C./min, and measured on the second heat. Also a glassy copolymer has a Glass Transition Temperature (Tg) above about 40° C., more preferably about 40° C. The Tg is measured according to ASTM Test D3418-12e1 at a heating and cooling rate of 10° C./min, and the Tg is taken as the midpoint (inflection point) of the transition on the second heat. Preferably the Tg is less than about 220° C., because for instance if the Tg is too high it may be difficult to dissolve the polymer to form a coating or layer.

[0029] Preferably the Group 11 metal ionomer is produced by contacting, in a liquid medium, a fluorinated polymer containing pendant sulfonic acid groups (not metal sulfonate salts) with a Group 11 metal salt whose anion's conjugate Bronsted acid has a pKa in water at 25° C. of less than 1.0.

[0030] The polymeric portion of the ionomers may contain repeat units derived from other monomers, as long as other compositional limits of the polymer, such as the minimum fraction of carbon-fluorine groups present. Useful monomers include one or more of tetrafluoroethylene, chlorotrifluoroethylene, vinyl fluoride, trifluororethylene hexafluoropropylene, and ethylene.

[0031] It is preferred that repeat units derived from cyclic or cyclizable perfluorinated monomers not be present in the ionomer. By a cyclic perfluorinated monomer is meant a perfluorinated olefin wherein a double bond of the olefin is in the ring or the double bond is an exo double bond wherein one end of the double bond is at a ring carbon atom. By a cyclizable perfluorinated monomer is meant a noncyclic perfluorinated compound containing two olefinic bonds, and that on polymerization forms a cyclic structure in the main chain of the polymer (see for instance N. Sugiyama, *Perfluoropolymers Obtained by Cyclopolymereization and Their Applications,* in J. Schiers, Ed., *Modern Fluoropolymers*. John Wiley & Sons, New York, 1997, p. 541-555, which is hereby included by reference). Such perfluorinated cyclic and cyclizable compounds include perfluoro(2,2-dimethyl-1,3-dioxole), perfluoro(2-methylene-4-methyl-1,3-dioxolane), a perfluoroalkenyl perfluorovinyl ether, and 2,2,4-trifluoro-5-trifluoroimethoxy-1,3-dioxole.

[0032] Preferably the Group 11 metal ionomer has no melting point above about 0° C. with a heat of fusion of 3

J/g or more when measured by Differential Scanning calorimetry using ASTM Test D3418-12e1 using a heating rate of 10° C./min, and measured on the second heat. Also preferably the ionomer has no Glass Transition Temperature (Tg) above 50° C. The Tg is measured according to ASTM Test D3418-12e1 at a heating rate of 10° C./min, and the Tg is taken as the midpoint of the transition. Preferably there is no Tg above 30° C., and more preferably above 10° C. Alternatively when actually doing a separation of one or more alkanes from one or more alkenes, the Tg of the ionomer (if present) is below the temperature at which the process is run.

[0033] The ionomers may be produced by methods described in this application, US Patent Application 2015/0025293 to Feiring et al., U.S. Pat. No. 5,191,151 to Erikson et al. and L. Sauguet, et al., *Fluorinated Copolymers and Terpolymers Based on Vinylidene Fluoride and Bearing Sulfonic Acid Side-Group, Journal of Polymer Science, Part A:, Polymer Chemistry,* Vol. 45, (2007), p. 1814-1834, all of which are hereby included by reference. Some compositions of polymers useful in this invention are also described in Feiring et al., and such polymers described therein containing pendant acidic groups may also be treated as described herein to form silver ionomers.

[0034] Determination of Permeance and Selectivity for Olefin/Alkane Separations

[0035] For determinations of permeance (GPU, reported in units of sec/cm^2.s.cm Hg) and selectivity the following procedure was used. A 47 mm flat disc membrane was punched from a larger flat sheet 3 inch composite membrane. The 47 mm disc is then placed in a stainless steel cross flow testing cell comprised of a feed port, retentate port, a sweep inlet port, and a permeate port. Four hex bolts were used to tightly secure the membrane in the testing cell with a total active area of 13.85 cm^2.

[0036] The cell was placed in a testing apparatus comprising of a feed line, a retentate line, a sweep line, and a permeate line. The feed consisted of a mixture of an olefin (propylene) gas and a paraffin (propane) gas. Each gas was supplied from a separate cylinder. For olefin, polymer grade propylene (99.5 vol % purity) was used and for paraffin, 99.9 vol % purity propane was used. The two gases were then fed to their respective mass flow controllers where a mixture of any composition can be made. The standard mixing composition was 20 vol % olefin and 80 mol % paraffin at a total gas flow rate of 200 mL/min. The mixed gas was fed through a water bubbler to humidify the gas mixture bringing the relative humidity to greater than 90%. A back pressure regulator is used in the retentate line to control the feed pressure to the membrane. The feed pressure was normally kept at 60 psig (0.41 MPa) after the back pressure regulator the gas is vented.

[0037] The sweep line consisted of a pure humidified nitrogen stream. Nitrogen from a cylinder was connected to a mass flow controller. The mass flow controller was set to a flow of 300 mL/min. The nitrogen was fed to a water bubbler to bring the relative humidity to greater than 90%. After the bubbler the nitrogen was fed to the sweep port of the membrane to carry any permeating gas through to the permeate port.

[0038] The permeate line consisted of the permeated gas through the membrane and the sweep gas as well as water vapor. The permeate was connected to a three way valve so flow measurements could be taken. A Varian® 450 GC gas chromatograph (GC) with a GS-GasPro capillary column (0.32 mm, 30 m) was used to analyze the ratio of the olefin and paraffin in the permeate stream. The pressure in the permeate side was typically between 1.20 and 1.70 psig (8.3 to 11.7 kPa). Experiments were carried out at room temperature.

[0039] During experiment the following were recorded: feed pressure, permeate pressure, temperature, sweep-in flow rate (nitrogen+water vapor) and total permeate flow rate (permeate+nitrogen+water vapor).

[0040] From the results recorded the following were determined: all individual feed partial pressures based on feed flows and feed pressure; all individual permeate flows based on measured permeate flow, sweep flows, and composition from the GC; all individual permeate partial pressures based on permeate flows and permeate pressures. From these the transmembrane partial pressure difference of individual component were calculated. From the equation for permeance

$$Q_i = F_i/(A.\Delta p_i)$$

wherein, Q_i=permeance of species 'i', F_i=Permeate flow rate of species 'i' Δp_i=transmembrane partial pressure difference of species 'i', and A is the area of the membrane (13.85 cm^2), the permeance(Q_i) was calculated.

[0041] In the Examples certain abbreviations are used, and they are:

[0042] HFPO—hexafluoropropylene oxide (For preparation of HFPO dimer peroxide see U.S. Pat. No. 7,112,314, which is hereby included by reference. HFPO dimer [2062-98-8] is available from Synquest Laboratories, Alachua, Fl., USA)

[0043] PDD—perfluoro(2,2-dimethyl-1,3-dioxole)

[0044] SEFVE—CF_2═$CFOCF_2CF(CF_3)OCF_2CF_2SO_2F$

[0045] VF2—vinylidene fluoride (H_2C═CF_2)

Comparative Example A

[0046] Synthesis of PDD/SEFVE (Feed ratio; 100/200 total) Copolymer and Hydrolysis

[0047] Into a 100 mL pear shape glass reaction flask, after argon purging for 5 minutes at 0° C., were placed a magnetic stirring bar, 4.0 g of PDD, 29.3 g SEFVE, 10 mL of 2,3-dihydrodecafluoropentane (Vertrel® XF specialty fluid, E.I. DuPont de Nemours & Co., Inc., Wilmington, Del. 19898, USA), and 0.8 mL of an initiator solution in Vertrel® XF of hexafluoropropylene oxide (HFPO) dimer peroxide (0.12 M) (see U.S. Pat. No. 7,112,314, which is hereby included by reference, for synthesis of this peroxide) made from the reaction of CF3CF3CF3OCF(CF3)CFO with basic hydrogen peroxide. The reaction mixture was sealed with a rubber septum, protected with an argon balloon, stirred, and allowed warm to room temperature in a water bath. After stirring overnight, 4.0 g of PDD and 0.8 mL of the HFPO dimer peroxide solution (0.12 M) was added into the reaction mixture by a syringe. After stirring for one more day, the flask was opened to ambient air and 40 mL of acetone was added into the mixture. The liquid was decanted after stirring for 15 min and 40 mL of fresh acetone was added. After stirring for 15 min, the liquid was again decanted and the solid residue was transferred to a watch glass. Drying in an oven at 100° C., overnight yielded 10.0 g of a white solid, PDD/SEFVE copolymer.

[0048] Into a round bottom 250 mL glass flask, were added 10.0 g of PDD/SEFVE copolymer synthesized in the

above procedure, 60 mL of deionized water, 60 mL ethanol, 3.0 g potassium hydroxide and a magnetic stirring bar. The reaction mixture was heated to reflux and stirred overnight. Ethanol in the mixture was evaporated and 100 mL of 2.0 M hydrochloric acid was added to the mixture. The solid was filtered from the mixture and then immersed in 100 mL of 2.0 M hydrochloric acid twice. The resulting solid was washed three times with 100 mL of deionized water and filtered after each washing. Finally it was dried in oven at 100° C. for 3 hours to yield 9.4 g of a brownish solid, the hydrolyzed copolymer PDD/SEFVE containing sulfonic acid groups. This copolymer had a Tg of 39° C.

[0049] Into a glass bottle were added 1 g of the polymer made in the immediately preceding paragraph Fluorinet® FC770 (available from 3M Corp., 3M Center, St. Paul, Minn., USA) and 30 mL of 30% hydrogen peroxide. The reaction mixture was stirred overnight at ambient temperature and then the polymer filtered off and dried under vacuum. Dried polymer (0.1 g) was added to a bottle containing 3.5 g of isopropyl alcohol and 1.5 g of Novec® 7300 and then 47 mg of $AgNO_3$ was added and the initial mixture stirred for 1-2 hours until the polymer was completely dissolved, and the solid $AgNO_3$ was not visible. The solution was then filtered through a glass fiber filter having a 1.2 μm nominal pore size.

[0050] A 0.3% solution of Teflon® AF2400 (available from the DuPont Co, Wilmington, Del. 19898, USA) (for further information about Teflon® AF, see P. R. Resnick, et al., *Teflon AF Amorphous Fluoropolymers,* J. Schiers, Ed., *Modern Fluoropolymers,* John Wiley & Sons, New York, 1997, p. 397-420, which is hereby included by reference) in Fluorinert® 770 (available from 3M Corp., 3M Center, Sty. Paul, Minn., USA) was coated onto a PAN350 membrane made by Nanostone Water, 10250 Valley View Rd., Eden Prairie, Minn. 53344, USA) (It is believed that the PAN350 membrane is made from polyacrylonitrile and that it is a microporous membrane) to form a bilayer membrane, and then dried at 100° C. for 1 h. Preferably the thickness of the Teflon AF2400 layer is about 0.1 to about 0.2 μm. At a relative humidity of <30% the solution of silver ionomer prepared in the previous paragraph was then coated onto the Teflon AF2400 layer of bilayer membrane, and then dried at 100° c for 1 h.

Example 1

[0051] Synthesis of VF2/SEFVE (Feed ratio; 200/100) Copolymer and Hydrolysis, and Membrane of Silver Ionomer

[0052] Into a 150 mL stainless steel pressure vessel , after argon purging for 5 minutes, were added a magnetic stirring bar, 6.69 g of SEFVE, 20 mL of Vertrel® XF, 0.7 mL HFPO dimer peroxide solution (0.12 M) and 1.92 g of vinylidene fluoride gas all at 0° C. The reaction mixture was sealed in the pressure vessel and stirred at room temperature in a water bath. After overnight reaction, the reaction vessel was opened to ambient air and 30 mL of Novec®7100 fluorinated solvent (methyl perfluoropropyl ether, available from the 3M Company, Electronic Materials Solutions Div., St. Paul, Minn. 55144, USA) was added to the reaction mixture. The whole solution was transferred to a glass dish and dried in a fume hood at room temperature for 3 h and then in oven at 100° C. overnight to yield 7.0 g of VF2/SEFVE copolymer as a colorless sticky foam. This polymer had a Tg of 39° C.

[0053] Into a 250 mL round bottom glass flask, were added 5.4 g VF2/SEFVE copolymer synthesized in the above procedure, 20 mL of deionized water, 40 mL of methanol, 2.7 g of ammonium carbonate and a magnetic stirring bar. The reaction mixture was stirred and maintained at 50-60° C. overnight. Then methanol in the mixture was evaporated and 50 mL of 2.0 M hydrochloric acid was added to the mixture. The liquid was decanted after stirring for 15 min and 50 mL of 2.0 M hydrochloric acid was added. After stirring for 15 min, the liquid was again decanted and 50 mL of deionized water was added. The water washing was repeated twice and the solid residue was dried in oven at 100° C. overnight. The 5.0 g of brownish solid obtained was the VF2/SEFVE copolymer having free sulfonic acid groups. This polymer has a Tg of 39° C.

[0054] A membrane containing having a layer of the silver ionomer of the sulfonic acid containing polymer made in the previous paragraph was made by the same method described in Comparative Example A.

Example 2

[0055] Synthesis of VF2/SEFVE (Feed ratio; 100/100) Copolymer and Hydrolysis, and Membrane of Silver Ionomer.

[0056] Into a 150 mL stainless steel pressure vessel, after argon purging for 5 minutes, were added a magnetic stirring bar, 8.92 g of SEFVE, 15 mL of Vertrel® XF, 0.5 mL of HFPO dimer peroxide solution (0.12 M), and then charged 1.28 g of vinylidene fluoride gas at 0° C. The reaction mixture was sealed in the pressure vessel and stirred at room temperature in a water bath. After overnight reaction, the reaction vessel was opened to ambient air and 30 mL of Novec® 7100 fluorinated solvent was added to the reaction mixture. The whole solution is transferred to a glass dish and dried in a fume hood at room temperature for 3 hours and then in oven at 100° C. overnight to yield 7.0 g VF2/SEFVE copolymer as a colorless sticky foam.

[0057] Into a 250 mL round bottom glass flask, were added 7.0 g of the copolymer synthesized in the previous paragraph, 30 mL of deionized water, 60 mL of methanol, 3.5 g of ammonium carbonate and a magnetic stirring bar. The reaction mixture was stirred and maintained at 50-60° C. After overnight reaction, methanol in the mixture was evaporated and 50 mL of 2.0 M hydrochloric acid was added to the mixture. The liquid was decanted after stirring for 15 minutes and 50 mL of 2.0 M hydrochloric acid was added. After stirring for 15 minutes, the liquid was again decanted and 50 mL of deionized water was added. The water washing was repeated twice and the solid residue was dried in oven at 100° C. overnight. A brownish solid copolymer (5.5 g) containing free sulfonic acid groups was obtained. The copolymer had a Tg of 52° C.

[0058] A membrane containing a layer of a silver ionomer was made by the same method described in Example 1, except only 31 mg of $AgNO_3$was used.

Example 3

[0059] Table 1 lists the initial permeances of the membranes from Examples A, 1 and 2. The membrane cell for the permeance measurements used a 47 mm diameter flat membrane sheet. The feed gas composition was humidified, by passing through an aqueous bubbler, and was 20 mole % propylene (polymer synthesis grade), and 80% propane at

room temperature. The total flow rate of both gases was 200 mL/min. The feed gas (mixture of propylene and propane) pressure was 60 psig, and the sweep gas on the second side of the membrane was humidified nitrogen at a pressure of 0.0 to 0.3 psig. The permeate from the second side of the membrane was analyzed by FTIR to determine the total permeate amounts of propane and propylene. Permeances (GPU) are given in $cm^3/cm^2/sec/cm\ Hg \times 10^6$.

TABLE 1

	Permeance		Selectivity
Example	C_3H_8	C_3H_6	C_3H_6/C_3H_8
A	0.84	161.3	193
1	0.37	235.2	634
2	0.44	221.7	509

[0060] Table 1 shows that ionomers of the present composition surprisingly have superior permeances and/or selectivities for alkenes than prior art membranes.

1. A process for separating one or more alkanes from one or more alkenes using a membrane, wherein the improvement consists of using a membrane comprising a nonporous layer of an ionomer of a Group 11 metal, comprising repeat units derived from vinylidene fluoride and a monomer containing a precursor to a sulfonic acid group or a sulfonic acid group, provided that carbon-fluorine groups are at least 30% of the total of said carbon-fluorine groups and carbon-hydrogen groups present in said ionomer, and wherein said ionomer does not comprise repeat units derived from a cyclic or cyclizable perfluorinated monomer.

2. The process as recited in claim wherein id Group 11 metal is silver.

3. The process as recited in claim **2** wherein the repeat units that contain said pendant sulfonic acid groups or a monomer containing a precursor of a sulfonic acid group at least about 10 mole percent of said repeat units present.

4. The process as recited in claim **2** wherein said carbon-fluorine groups are at least about 60% of the total of said carbon-fluorine and said carbon hydrogen groups present in said ionomer.

5. The process as recited in claim **2** wherein said precursor is one or r ore of CF2═CFOCF2CF2SO2F, CF2═CFOCH2CF2CF2SO2F and CF2═CFOCF2CF(CF3)OCF2CF2SO2F.

6. The process as recited in claim **2** wherein said ionomer additionally comprises repeat units derived from one or more of tetrafluoroethylene, chlorotrifluoroethylene, vinyl fluoride, trifluororethylene hexafluoropropylene, and ethylene.

7. The process of claim **1** wherein said alkanes and alkenes are gases.

8. The process of claims **2** herein said alkanes and alkenes are gases.

9. The process of claims **3** wherein said alkanes and alkenes are gases.

10. The process of claims **4** wherein said alkanes and alkenes are gases.

11. The process of claims **5** wherein said alkanes and alkenes are gases.

12. The process of claims **6** wherein said alkanes and alkenes are gases.

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