(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
17 November 2016 (17.11.2016)

WIPO | PCT

(10) International Publication Number
WO 2016/182889 A1

(51) International Patent Classification:
C07C 7/144 (2006.01) *B01D 71/32* (2006.01)
B01D 69/14 (2006.01)

(21) International Application Number:
PCT/US2016/031140

(22) International Filing Date:
6 May 2016 (06.05.2016)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

62/159,646	11 May 2015 (11.05.2015)	US
62/159,668	11 May 2015 (11.05.2015)	US
62/262,169	2 December 2015 (02.12.2015)	US

(71) Applicant: **COMPACT MEMBRANE SYSTEMS, INC.** [US/US]; 335 Water Street, Newport, DE 19804 (US).

(72) Inventors: **SHANGGUAN, Ning**; 1612 Mayflower Lane, Cherry Hill, NJ 08003 (US). **LOUSENBERG, Robert, Daniel**; 2103 Anson Road, Wilmington, DE 19810 (US). **FEIRING, Andrew, Edward**; 1203 Shallcross Avenue, Wilmington, DE 19806 (US).

(74) Agent: **CITRON, Joel, D.**; 2003 Ferndale Drive, Wilmington, DE 19810 (US).

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

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *of inventorship (Rule 4.17(iv))*

Published:

— *with international search report (Art. 21(3))*

WO 2016/182889 A1

(54) Title: COPOLYMER FOR USE IN ALKENE-ALKANE SEPARATION MEMBRANES

(57) Abstract: Described herein are copolymers derived from certain perfluorinated sulfonyl fluoride monomers, cyclic or cyclizable perfluorinated monomers, and one or both of ethylene and/or vinyl fluoride. Group 11 metal sulfonate ionomers of these copolymers, especially silver ionomers, are useful in membranes which separate olefins from alkanes.

Copolymers for Use in Alkene-Alkane Separation Membranes

Field of the Invention

This invention describes copolymers which can be made into Group 11 metal ionomer which are useful in membranes for the separation of alkenes and alkanes.

Government Rights

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

Technical Background

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 carbon dioxide from methane, or alkenes from alkanes.

The separation of alkenes from alkanes can be accomplished using a silver ionomer of a fluorinated polymer. Usually, perhaps because fluoropolymers are more stable to oxidation than unfluorinated polymers, the Group 11 metal 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.

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 is 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 energy costs. Therefore cheaper, less energy intensive methods of separation are desirable.

U.S. Patent 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. The presently claimed copolymers are not mentioned in Eriksen.

U.S. Patent Application 2015/0025293 to Feiring *et al.* describes the use of a membrane which is a silver ionomer of a perfluorinated polymer. The presently claimed copolymers are not mentioned in Feiring.

Summary of the Invention

This invention concerns a copolymer, comprising repeat units derived from a monomer of the formula $CF_2=CF(OR_f)SO_2F$, one or more cyclic or cyclizable perfluorinated monomers, and one or both of vinyl fluoride and ethylene,, wherein R_f is perfluoroalkylene or ether containing perfluoroalkylene having 2 to 20 carbon atoms, and provided that repeat units derived from $CF_2=CF(OR_f)SO_2F$ are at least one mole percent of total repeat units, units derived from one or more cyclic or cyclizable perfluorinated monomers are at least 1 mole percent of total repeat units, and repeat units derived from both ethylene and vinyl fluoride are in total at least 1 percent of total repeat units.

Also disclosed are copolymers in which the $-SO_2F$ group has been converted to other groups such as sulfonic acid or metal sulfonate salt, membranes comprising one or more layers comprising such copolymers, and a method of separating alkenes from alkanes using such membranes.

Details of the Invention

Herein certain terms are used and they some of the are defined below.

By a "driving force" in the separation of the alkene and alkane in the gaseous state is generally meant that the partial pressure of alkene on the first ("feed") side of the membrane is higher than the partial pressure of alkene on the second ("product") side of the membrane. For instance this may be accomplished by several methods or a combination thereof. One is pressurizing first side to increase the partial pressure of alkene on the first side, second is sweeping the second side by inert gas such as nitrogen to lower the partial pressure of the alkene on the second side, and third is reducing pressure of second side by vacuum pump to lower the partial pressure of the alkene on the second side. These and other known methods in the art of applying a driving force may be used.

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

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

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 on the first (feed) side, and $P2_a$ is the partial pressure on the second (product) side.

By a membrane containing one or more Group 11 metal ionomers is meant a membrane comprising a thin nonporous layer of the metal ionomer and one or more other polymeric layers which physically support or reinforce the Group 11 metal ionomer layer. Preferably the Group 11 metal 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. The 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.

The Group 11 metal ionomer described here is prepared from a copolymer comprising repeat units derived from a compound of the formula $CF_2=CF(OR_f)SO_2F$, one or more cyclic or cyclizable perfluorinated monomers, and one or both of vinyl fluoride (VF) and ethylene (E), wherein R_f is perfluoroalkylene or ether containing perfluoroalkylene having 2 to 20 carbon atoms. The resulting polymer contains sulfonyl flu rode groups ($-SO_2F$) which may be readily converted to sulfonic acid, a metal sulfonate salt, etc. see for instance US Patent Application 14/334,605, US Provisional Applications 62/159,646, 62/159,668, and 62/262,169 (now PCT applications _____, respectively), A. van Zyl, *et al., Journal of Membrane Science,* **133**, (1997), pp. 15-26, O.I. Eriksen, *et al., Journal of Membrane Science,* **85** (1993), pp. 89-97, and A.J. van Zyl, *Journal of Membrane Science,* **137** (1997), pp. 175-185, and U.S. Patent 5,191,151, all of which are hereby included by reference. Thus the repeat unit in the polymer derived from $CF_2=CF(OR_f)SO_2F$ may be represented as

$$-CF_2-CF-$$
$$\quad\quad\quad|$$
$$\quad\quad O\text{-}R_f\text{-}SO_2Y$$

wherein Y is fluorine, -OH, or –OM wherein M is a metal cation, preferably univalent metal cation. Preferred metal cations are alkali metal cations such as Na^+ and/or K^+, and Group 11 metal cations such as Cu^+ and/or Ag^+. Group 11 metal cations are preferred and silver is especially preferred.

Another type of useful monomer is a perfluorinated cyclic or cyclizable monomer. 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. Preferably repeat units derived from one perfluorinated cyclic or cyclizable monomer are present in the polymer. Of course the exact structure of a repeat unit from a perfluorinated cyclic or cyclizable monomer will depend on the particular monomer used.

Repeat units derived from ethylene and vinyl fluoride are those usually obtained in such similar fluorinated polymers, $-CH_2CH_2-$ and $-CH_2CHF-$. respectively.

At least one mole percent (preferably at least about 5 percent) of the repeat units present in the polymer are derived from each of $CF_2=CF(OR_f)SO_2F$, and one or more cyclic or cyclizable perfluorinated monomers. At least one percent (preferably at least about 5 percent) of the repeat units are derived from the total repeat units derived from E and VF. Preferably repeat units derived from $CF_2=CF(OR_f)SO_2F$ are about 10 mole percent to about 40 mole present of total repeat units in the polymer, more preferably about 25 mole percent to about 40 mole percent. Preferably repeat units derived from one or more cyclic or cyclizable perfluorinated monomers are about 5 mole percent to about 30 mole present of total repeat units in the polymer, more preferably about 10 mole percent to about 25 mole percent. Preferably the total repeat units derived from E and VF are about 10 mole percent to about 60 mole present of total repeat units in the polymer, more preferably about 20 mole percent to about 50 mole percent. In one preferred form all of the repeat units in the polymer consist essentially of those derived from $CF_2=CF(OR_f)SO_2F$, one or more cyclic or cyclizable perfluorinated monomers, and one or both of E and VF. In one preferred form ,the copoltmer consists essentially of repeat units derived from $CF_2=CF(OR_f)SO_2F$, one or more cyclic or cyclizable perfluorinated monomers, and repeat units derived from one of VF and/or E

Other useful comonomers include tetrafluoroethylene, vinylidene fluoride and chlorotrifluoroethylene.

Preferred specific monomers of the type $CF_2=CF(OR_f)SO_2F$ include $CF_2=CFOCF_2CF_2SO_2F$, $CF_2=CFOCH_2CF_2CF_2SO_2F$

CF_2=$CFOCF_2CF(CF_3)OCF_2CF_2SO_2F$, CF_2=$CFOCF_2CF(CF_3)OCF_2CF_2SO_2F$ and CF_2=$CFOCF_2CF_2SO_2F$ for the. CF_2=$CF(OR_f)SO_2F$ type monomer, and preferred cyclic or cyclizable perfluorinated monomers 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-trifluoromethoxy-1,3-dioxole, and perfluoro(2,2-dimethyl-1,3-dioxole) is more preferred. Preferably one of each type of these preferred monomer, a sulfonyl fluoride containing monomer and a preferred cyclic or cyclizable perfluorinated monomer is copolymerized with one or both of VF and E to form a preferred copolymer. It is to be understood that any of the preferred monomers mentioned in this paragraph can be combined with another preferred comonomer and one or both of VF and E to form a preferred copolymer. Also preferably, only one of VF and E is used to form a copolymer.

Polymers containing a single CF_2=$CF(OR_f)SO_2F$ type monomer and a single cyclic or cyclizable perfluorinated monomer, which are also preferred, can be analyzed for mole percent repeat units by doing an elemental analysis of the polymer for C, H and S if the copolymer contains only one of VF and E. This is because the CF_2=$CF(OR_f)SO_2F$ type monomer is the only source of sulfur in the copolymer, and E or VF is the only source of hydrogen in the copolymer when Y is F. If repeat units derived from both E and VF are present in the copolymer a combination of the elemental analysis plus a H^1 NMR, which can readily determine the molar ration of VF and E derived repeat units can be used to determine the molar ratios of repeat units in the copolymer. All of the calculations to determine the ratios of repeat units in the copolymer can be carried out using standard, well known, chemical stoichiometric methods.

The polymers can be made by typical liquid (often water) phase free radical polymerization, see for instance US Patent Application 14/334,605, US Provisional Applications 62/159,646, 62/159,668, and 62/262,169 (now PCT applications _____, respectively), all of which are hereby included by reference.

Preferably the various forms of the 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.

As noted above, the originally formed sulfonyl fluoride containing polymer may be modified to form a sulfonic acid containing polymer, or a metal sulfonate salt of the polymer, an ionomer. Group 11 metal ionomers, especially silver ionomers, are particularly useful in membranes for the separation of alkenes from alkanes, see for instance US Patent Application 14/334,605, US Provisional Applications 62/159,646, 62/159,668, and 62/262,169 (now PCT applications _____, respectively), A. van Zyl, *et al., Journal of Membrane Science,* **133**, (1997), pp. 15-26, O.I. Eriksen, *et al., Journal of Membrane Science,* **85** (1993), pp. 89-97, and A.J. van Zyl, *Journal of Membrane Science,* **137** (1997), pp. 175-185, and U.S. Patent 5,191,151, all of which are hereby included by reference. Membranes containing dense layers of one or more Group 11 metal ionomers of the present copolymers have been shown to have excellent permeance and/or selectivity in the separation of alkenes from alkenes. Separations of alkenes from alkene/alkane mixtures can be done with mixtures in either the gas or liquid phase., it is preferred to carry out the membrane separation of alkene/alkane mixtures in the gas phase and/or using humidified gas streams. To carry out such separations, a driving force is usually applied across the membrane.

In the Examples certain abbreviations are used, and they are:

HFPO – hexafluoropropylene oxide (For preparation of HFPO dimer peroxide see US Patent 7,112,314, which is hereby included by reference).

PDD – perfluoro(2,2-dimethyl-1,3-dioxole)

SEFVE - CF_2=$CFOCF_2CF(CF_3)OCF_2CF_2SO_2F$

PPSF- CF_2=$CFOCF_2CF_2SO_2F$

VF- vinyl fluoride (H_2C=CHF)

Determination of Permeance and Selectivity for Alkene/Alkane Separations

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.

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 (alkene) (propylene) gas and a paraffin (alkane) (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.

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.

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 (0.32mm, 30m) 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.

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).

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.

Example 1

Synthesis of PDD/VF/SEFVE (feed ratio 100:100:150) Copolymer and Hydrolysis

Into a 150 mL stainless steel pressure vessel, after argon purging for 5 minutes, were added a magnetic stirring bar, 3.66g PDD, 10.04 g SEFVE, 12 mL of Vertrel ®XF, 0.6 mL of HFPO dimer peroxide solution (0.12M), and then charged 0.69 g of vinyl fluoride gas at 0 °C. The reaction mixture was sealed in the pressure vessel and stirred at room temperature in a water bath. After 3 hours of reaction, the reaction vessel was opened to ambient air, 10 mL acetone and 40 mL methanol was added to the reaction mixture. The resulting gel like precipitate was transferred to a glass dish and dried in oven at 100 °C overnight to yield 5.5 g PDD/VF/SEFVE terpolymer as a colorless solid (Tg 37 °C).

Into a 250 mL round bottom flask, were added 3.75 g of the terpolymer synthesized in the previous paragraph, 20 mL deionized water, 60 mL of methanol, 1.85 g ammonium carbonate and a magnetic stirring bar. The reaction mixture was stirred and maintained at 50-60 °C. After overnight reaction, a clear solution was obtained. 80 mL 2.0 M hydrochloric acid was added to the mixture and methanol in the mixture was evaporated under heating to form a gel like precipitate. The liquid was decanted and 50 mL of 2.0 M hydrochloric acid was added and stirred for 30 minutes. The liquid was decanted and 80 mL of deionized water was added and then stirred for 30 minutes. After the liquid decanting, the water washing was repeated twice and the solid residue was dried in a vacuum oven at 60 °C for 3 hours. A brownish solid (2.7 g) containing free sulfonic acid groups was obtained.

Example 2

Synthesis of PDD/VF/SEFVE (feed ratio 100:200:150) Copolymer and Hydrolysis.

Into a 150 mL stainless steel pressure vessel, after argon purging for 5 minutes, were added a magnetic stirring bar, 3.66g PDD, 10.04 g SEFVE, 15 mL of Vertrel ®XF,

0.6 mL of HFPO dimer peroxide solution (0.12M), and then charged 1.38 g of vinyl fluoride gas at 0 °C. The reaction mixture was sealed in the pressure vessel and stirred at room temperature in a water bath. After 5.5 hours of reaction, the reaction vessel was opened to ambient air, 10 mL acetone and 40 mL methanol was added to the reaction mixture. The resulting gel like precipitate was transferred to a glass dish and dried in oven at 100 °C overnight to yield 9.1 g PDD/VF/SEFVE terpolymer as a colorless solid (Tg 18 °C). Anal: Found: C, 24.92; H, 0.55; S, 5.01. Intrinsic viscosity (in Novec® HFE-7200 at 25°C): 0.389 dL/g. From the elemental analysis, the polymer composition was estimated as 21% PDD, 43 % VF and 37 % SEFVE.

Into a 250 mL round bottom flask, were added 5.8 g of the terpolymer synthesized in the previous paragraph, 20 mL deionized water, 80 mL of methanol, 2.0 g ammonium carbonate and a magnetic stirring bar. The reaction mixture was stirred and maintained at 50-60 °C. After overnight reaction, a clear solution was obtained. 80 mL 2.0 M hydrochloric acid was added to the mixture and methanol in the mixture was evaporated under heating to form a gel like precipitate. The liquid was decanted and 50 mL of 2.0 M hydrochloric acid was added and stirred for 30 minutes. The liquid was decanted and 80 mL of deionized water was added and then stirred for 30 minutes. After the liquid decanting, the water washing was repeated twice and the solid residue was dried in a vacuum oven at 60 °C for 3 hours. A brownish solid (4.6 g) containing free sulfonic acid groups was obtained.

Example 3

Synthesis of PDD/VF/PPSF (feed ratio 100:100:150) Copolymer and Hydrolysis,

Into a 150 mL stainless steel pressure vessel, after argon purging for 5 minutes, were added a magnetic stirring bar, 3.66g PDD, 6.3 g PPSF, 12 mL of Vertrel ®XF, 0.6 mL of HFPO dimer peroxide solution (0.12M), and then charged 0.96 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, 10 mL acetone and 40 mL methanol was added to the reaction mixture. The resulting gel like precipitate was transferred to a glass dish and dried in oven at 100 °C overnight to yield 6.0 g PDD/VF/PPSF terpolymer as a colorless solid (Tg 58 °C).

Into a 250 mL round bottom flask, were added 4.0 g of the terpolymer synthesized in the previous paragraph, 20 mL deionized water, 60 mL of methanol, 1.5 g ammonium carbonate and a magnetic stirring bar. The reaction mixture was stirred and maintained at 50-60 °C. . After overnight reaction, a clear solution was obtained. 80 mL 2.0 M hydrochloric acid was added to the mixture and methanol in the mixture was evaporated under heating to form a gel like precipitate. The liquid was decanted and 50 mL of 2.0 M hydrochloric acid was added and stirred for 30 minutes. The liquid was decanted and 80 mL of deionized water was added and then stirred for 30 minutes. After the liquid decanting, the water washing was repeated twice and the solid residue was dried in a vacuum oven at 60 °C for 3 hours. A slight brownish solid (3.0 g) containing free sulfonic acid groups was obtained.

Example 4

Membrane Formation and Testing

A solution was prepared using 0.200 g of polymer from example 1 and 20 % by weight of silver nitrate in isopropanol to form a 2 % polymer solution. A substrate was prepared by coating a 0.3 wright % solution of Teflon® AF2400 (available from the DuPont Co, Wilmington, DE 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, MN, USA) on a PAN350 membrane made by Nanostone Water, 10250 Valley View Rd., Eden Prairie, MN 53344, USA) (It is believed that the PAN350 membrane is made from polyacrylonitrile and it is believed that this is a microporous membrane). The coating of the silver ionomer was done at < 30% relative humidity. Similar membranes were formed from the polymers from examples 2 and 3. Permeability and selectivity results are shown in Table 1

Table 1

Polymer from	Permeance (GPU)		Selectivity
	propane	propylene	
Example 1	2.70	125.81	46.7
Example 2	4.65	282.44	60.8
Example 3	2.5	161.56	75.3

Example 5

Synthesis of PDD/Ethylene/SEFVE Copolymer and Hydrolysis

A pressure reactor that comprised an Ace Glass pressure tube (60-mL) was assembled in a fume hood. The pressure tube had PTFE #25 and #7 Ace-thread top- and side-addition ports, respectively. A hole through the top-port plug was threaded and the top-port was connected to a 1/4" stainless steel union cross (Parker®). A thermocouple was mounted through the cross fitting, which also connected the reactor to a 3-way stainless steel inlet valve and ¼" stainless steel tubing to a pressure gauge and relief (100-psig). The reactor was magnetically stirred and was leak tested with 80-psig nitrogen prior to operation. A polycarbonate safety shield was placed in front of the reactor when pressurized. Perkadox® 16 (150-mg) and Vertrel® HFE-4310 (18-mL) were added through the side port. The reactor was chilled using liquid nitrogen to less than -40°C. SEFVE (10.5-g) and PDD (7.5-g) were added by syringe through the side port. The stirred reactor was de-gassed while cold by briefly evacuating until bubbling indicative of boiling (out gassing) was observed. The reactor was back-filled with argon. The degassing was repeated two more times with the reactor remaining under vacuum after the last degassing. Ethylene was added in increments as the reactor warmed with oil bath heating. A constant 50-psig ethylene pressure was maintained as the reactor was stirred at 43 to 45°C for 5 hours. The reactor was depressurized and the contents were purged with nitrogen prior to transferring into a tarred 250-mL wide-mouth jar. The jar was loosely capped and excess monomers and solvent were carefully removed by vacuum oven drying (65°C) to constant weight (yield = 7.8-g). The polymer was colorless and transparent. The intrinsic viscosity was measured by Ubbelohde viscometry in Novec® HFE-7200 at 25°C and was 0.28-dL/g. Reflectance FTIR spectroscopy showed absorbances at 1466-cm^{-1} and 2850 to 2960-cm^{-1} that were indicative of SO_2F and CH groups in the polymer, respectively. Anal. Found: C,25.67; H, 0.79; S, 4.47. From the elemental analysis, the polymer composition was estimated as 28 % PDD, 42 % ethylene and 30 % SEFVE.

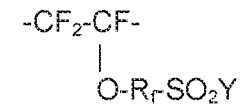
Polymer Hydrolysis. 4.04-g of the polymer was hydrolyzed with 2.5-g of KOH dissolved in a mixture of 75-mL of methanol and 8-mL of Novec® HFE-7200. The polymer dissolved as it hydrolyzed with heating up to 60°C for 3 hours. The resulting solution was transparent and very slightly yellow. The solution was poured into a large dish and the solvents were slowly evaporated. The polymer was removed from the dish and

washed with water on a filter funnel, acid exchanged with three successive portions of 1-M nitric acid, and water washed to remove excess acid. The white polymer was vacuum oven dried (50°C) and Reflectance FTIR showed that the SO_2F absorbance at 1466-cm^{-1} had disappeared. 1.5-g of the hydrolyzed and acid exchanged polymer was dissolved to approximately 5% in isopropanol and gently roll milled for 1.5 hours with 1.5-g of Amberlyst® 15 ion exchange resin, to ensure complete acid exchange. The solution was syringe filtered (1-µm glass fiber) and the solids content of the filtered solution was determined gravimetrically by hot plate drying (110°C). Solution aliquots were diluted (~3X) with excess isopropanol and were titrated with 0.0200-M aqueous sodium hydroxide to a phenolphthalein end-point. The equivalent weight was 1157-g/mole for the polymer free acid.

Claims

1. A copolymer, consisting essentially of repeat units derived from a monomer of the formula $CF_2=CF(OR_f)SO_2F$, one or more cyclic or cyclizable perfluorinated monomers, and one or both of vinyl fluoride and ethylene,, wherein R_f is perfluoroalkylene or ether containing perfluoroalkylene having 2 to 20 carbon atoms, and provided that repeat units derived from $CF_2=CF(OR_f)SO_2F$ are at least one mole percent of total repeat units, units derived from one or more cyclic or cyclizable perfluorinated monomers are at least 1 mole percent of total repeat units, and repeat units derived from both ethylene and vinyl fluoride are in total at least 1 percent of total repeat units.

2. The copolymer as recited in claim 1 wherein said repeat unit derived from $CF_2=CF(OR_f)SO_2F$ has the formula



wherein Y is fluorine, -OH, or --OM wherein M is a univalent metal cation.

3. The copolymer as recited in claim 2 wherein Y is M, and M is a silver cation Ag^+.

4. The copolymer as recited in any one of claims 1 to 3 where said cyclic or cyclizable perfluorinated monomer is perfluoro(2,2-dimethyl-1,3-dioxole).

5. The copolymer as recited any one of claims 1 to 4 wherein $CF_2=CF(OR_f)SO_2F$ is one or more of $CF_2=CFOCF_2CF_2SO_2F$, $CF_2=CFOCH_2CF_2CF_2SO_2F$ $CF_2=CFOCF_2CF(CF_3)OCF_2CF_2SO_2F$, $CF_2=CFOCF_2CF(CF_3)OCF_2CF_2SO_2F$ and $CF_2=CFOCF_2CF_2SO_2F$.

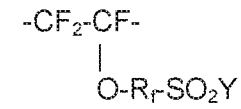
6. The copolymer as recited in claim 5 wherein repeat units from only one type of monomer with the formula $CF_2=CF(OR_f)SO_2F$ is present.

7. The copolymer as recited in any one of claim 1 to 3 wherein repeat units derived from $CF_2=CF(OR_f)SO_2F$ are about 10 mole percent to about 40 mole present of total repeat units in the polymer, repeat units derived from one or more cyclic or cyclizable perfluorinated monomers are about 5 mole percent to about 30 mole present of total repeat units in the polymer, and the total repeat units derived from ethylene and vinyl fluoride are about 10 mole percent to about 60 mole present of total repeat units in the polymer.

8. The copolymer as recited in claim 7 where said cyclic or cyclizable perfluorinated monomer is perfluoro(2,2-dimethyl-1,3-dioxole), and the repeat units

derived from $CF_2=CF(OR_f)SO_2F$ is one of $CF_2=CFOCF_2CF_2SO_2F$, $CF_2=CFOCH_2CF_2CF_2SO_2F$ $CF_2=CFOCF_2CF(CF_3)OCF_2CF_2SO_2F$, $CF_2=CFOCF_2CF(CF_3)OCF_2CF_2SO_2F$ and $CF_2=CFOCF_2CF_2SO_2F$.

9. The copolymer as recited in claim 8 wherein said repeat unit derived from $CF_2=CF(OR_f)SO_2F$ has the formula



wherein Y is fluorine, -OH, or –OM wherein M is a univalent metal cation.

10. The copolymer as recited in claim 9 wherein Y is M, and M is a silver cation Ag^+.

11. The copolymer as recited in any of claims 1 to 10 which consists esstentially of repeat units derived from a monomer of the formula $CF_2=CF(OR_f)SO_2F$, one or more cyclic or cyclizable perfluorinated monomers, and one or both of vinyl fluoride and ethylene,, wherein R_f.is perfluoroalkylene or ether containing perfluoroalkylene having 2 to 20 carbon atoms.,

12. A process for the separation of alkenes from alkanes in a gaseous stream using a membrane to carry out said separation, wherein the improvement comprises, using a membrane comprising a least one dense layer of a Group 10 metal ionomer of a copolymer of any one of claims 2, 3, 9 or 10.

13. The process as recited in claim 12 wherein said Group 11 metal is silver.

14. A membrane comprising at least one dense layer of a Group 11 metal ionomer of a copolymer of any one of claims 2, 3, 9 or 10.

15. The membrane as recited in claim 14 wherein said Group 11 metal is silver.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 16/31140

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 5-6 and 11-15
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 16/31140

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - C07C 7/144; B01D 69/14; B01D 71/32 (2016.01)
CPC - B01D67/0093; B01D71/32; B01D69/142; B01D71/76; C07C7/144; B01D71/36
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(8): C07C 7/144; B01D 69/14; B01D 71/32 (2016.01)
CPC: B01D67/0093; B01D71/32; B01D69/142; B01D71/76; C07C7/144; B01D71/36

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC: 95/50; 585/818; 585/843-844 (Keyword limited, terms below)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PatBase, Google Patents, Google Scholar (NPL); Keywords: fluoropolymer/fluorinated polymer/copolymer/ionomer, SEFVE/PPSF, perfluoro(2,2-dimethyl-1,3-dioxole), silver, exchange, alkane/alkene gas separation

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2015/0025293 A1 (Feiring et al.) 22 January 2015 (22.01.2015) para [0001], [0014], [0015], [0039]-[0047], [0063], [0069], [0071], [0072]	1-4, 7-10
Y	US 2015/0119577 A1 (Campos et al.) 30 April 2015 (30.04.2015) para [0010], [0017]-[0018]	1-4, 7-10
A	US 2012/0097612 A1 (Nemser et al.) 26 April 2012 (26.04.2012) entire document	1-4, 7-10
A	US 2003/0104150 A1 (Bonnet et al.) 05 June 2003 (05.06.2003) entire document	1-4, 7-10
A	US 2001/0025819 A1 (Bowser) 04 October 2001 (04.10.2001) entire document	1-4, 7-10

☐ Further documents are listed in the continuation of Box C. ☐

* 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 application or patent 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

Date of the actual completion of the international search	Date of mailing of the international search report
27 June 2016 (27.06.2016)	08 AUG 2016
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

Form PCT/ISA/210 (second sheet) (January 2015)