

## Supporting Information

**Title: Preparation of water-selective polybutadiene membranes and their use in drying alcohols by pervaporation and vapor permeation technologies**

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Total number of pages: 16 (S1-S16) including 8 Tables, 4 Figures and 4 Equations

### Materials and Methods:

#### Raw materials:

1,2-polybutadiene (1,2-PB) was purchased from Scientific Polymer Products, Inc. (catalog #688, Ontario, NY). Properties of the 1,2-PB used are presented in **Table S1**. Solvents, including toluene and tetrahydrofuran (THF) (analytical grade) were purchased from Sigma-Aldrich Corporation Inc. Feed solutions were prepared from ethanol (200 proof, PHARMCO-AAPER, Shelbyville, KY), 2-propanol (HPLC-grade, Fisher Chemical), methanol (HPLC-grade, Fisher Chemical), or 1-butanol (Certified ACS grade, Fisher Chemical) and deionized (DI) water. For some membranes, a coating of polydimethyl siloxane (PDMS), aka silicone rubber, was applied on top of the PB layer to ensure a defect-free dense layer. The PDMS consisted of a vinyl-terminated PDMS (DMS-V41, molecular weight  $\approx 63,000$ , Gelest) and a poly(methylhydrosiloxane-dimethylsiloxane) copolymer containing 5-7 mol% MeHSiO (HMS-064, molecular weight  $\approx 63,000$ , Gelest). Platinum divinyltetramethylidisiloxane complex in xylene (2.1-2.4 wt% platinum concentration, SIP6831.2, Gelest) was used as the hydrosilylation catalyst. Microporous poly(vinylidene fluoride) (PVDF) membranes served as mechanical supports for thin 1,2-PB films (Sepro200, Sepro Membranes, Oceanside CA, now a part of Nanostone Water, Inc., and membrane distillation membranes from Aquatech International Corporation).

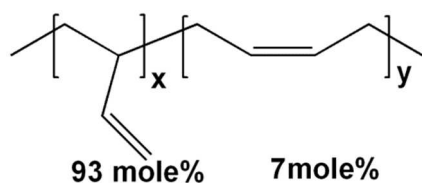


Figure S1. Chemical structure of polybutadiene used in this study.

**Table S1. Properties of the 1,2-polybutadiene used in this study (as reported by Scientific Polymer Products, Inc.)**

Composition	93 mol% vinyl-1,2 7 mol% <i>cis</i> -1,4
Crystallinity	29%
Ave. Molecular Weight ( $M_w$ )	100,000 g/mol
Melting Point ( $T_m$ )	90 °C
Glass Transition Temperature ( $T_g$ )	-14 °C
Vicat Softening Point	66 °C
Density ( $\rho$ )	0.91 g/cm <sup>3</sup>
Melt Flow Index	3 g/10 min @ 150 °C

**Membrane preparation:**

Spray coating thin films on microporous support: The procedure for preparing a 1,2-PB thin film on a microporous PVDF support was as follows: 1,2-PB was dissolved in toluene with the aid of a 40 W probe-type sonicator (Kontes Model KT40) and heating to 80 °C for 1 h to yield a 2.5 wt% polymer solution. The solution was then allowed to cool to room temperature. The solution was spray-coated on a 23 cm × 16 cm piece of microporous PVDF membrane, taped to a glass plate, using an airbrush (Model H#3, Paasche Airbrush Co.) with nitrogen as the carrier gas. Approximately 30-40% of the material did not make it onto the membrane, due to overspray losses or residual material in preparation/spray containers. Toluene was allowed to evaporate from the membrane layer for at least 30 min at room temperature. For thicker layers, this procedure was repeated one or more times.

UV Treatment: A subset of the PB films was exposed to UV radiation for various periods of time to functionalize and crosslink the PB materials. The UV exposure was carried out inside a photochemical safety reaction cabinet (ACE Glass, model 7836-20) using a 450 W medium pressure quartz mercury vapor arc lamp (0.28 m arc length, ACE Glass, model 7825-35) placed inside a quartz immersion well (ACE Glass model 7874-38) cooled with room temperature water. The reaction cabinet is equipped with a ventilation fan that maintained temperatures in the cabinet near room temperature. The PB film was taped to a glass plate that was atop a laboratory jack stand used to adjust the distance between the film and the UV lamp, thereby adjusting the intensity of the UV radiation. For samples wider than 5 cm, the film was placed in a curved holder made of corrugated aluminum so that all regions of the film were equidistant from the cylindrical lamp. The spectral characteristics of the arc lamp as provided by the manufacturer are listed in **Table S2**. As noted, the intensity of UV radiation is roughly the same in the Far, Middle, and Near UV wavelengths.

**Table S2. Spectral energy characteristics of the medium pressure mercury arc lamp used for UV treatment of PB films (as provided by lamp supplier).**

Far UV Energy UV-C (W) 220-280 nm	Middle UV Energy UV-B (W) 280-320 nm	Near UV Energy UV-A (W) 320-400 nm	Visible Energy (W) 400-600 nm	Infrared Energy (W) 1000-1400 nm	Total Radiated Energy (W)
27.0	28.7	28.0	75.7	16.4	175.8

**Thermal Treatment:** For thermal treatment, films were placed, usually taped to a glass plate, in a convective air oven at a set temperature for set periods of time, after which they were removed to ambient conditions. A membrane treated for 96 h at 120 °C was selected for presentation here because these conditions yielded almost complete vinyl group conversion (based on FTIR traces).

**PDMS overcoating:** To ensure a defect-free coating on the microporous PVDF support, some of the PB films were overcoated with a layer of PDMS. Such overcoating of the selective dense film with a layer of high permeability/low selectivity material as a means to ensure no defects or to enhance mechanical properties is known in the field. Vinyl-terminated DMS-V41 and hydrosilane crosslinker HMS-064 in a 16:1 mass ratio were dissolved in toluene at 10 wt% total polymer. Platinum catalyst SIP6831.2 was added to this PDMS solution at 1  $\mu$ L per gram polymer and mixed for 1 min using the probe-type sonicator. The mixture was immediately spray-coated on top of the PB film in the same manner as was the PB film. Such overcoating was done after UV or thermal treatment of the PB. Toluene was allowed to evaporate from the PDMS layer for at least 30 min at room temperature, and then the film was crosslinked for 1 h at 80 °C.

**Cast coating of thicker PB films:** For tests requiring thicker films, 2.0 g 1,2-PB was dissolved in 38.0 g toluene with heating (5 h @ 80 °C), then cooled to room temperature with strong stirring to yield a transparent 5 wt% PB solution. The solution was cast on a flat 23 cm  $\times$  23 cm glass or fluoropolymer surface (Bytac surface protector, Saint Gobain Performance Plastics) using a universal blade applicator with adjustable gap height (Paul N Gardner Co., Inc., Pompano Beach FL) to produce a dried film thickness of about 50  $\mu$ m. Alternatively, foam tape was placed at the perimeter of the glass or fluoropolymer surface and the polymer solution was allowed to pool inside the border while sitting on a level surface. The films were dried overnight at room temperature and then heated to 80 °C to complete solvent evaporation. The film was then peeled from the glass surface. Film thickness was measured with a coating thickness gage (Positector®6000-FNS2, DeFelsko Corporation, USA) with an accuracy of 2  $\mu$ m. The reported thickness of cast films is the average of 5 measurements.

### **Membrane Characterization**

#### ***Scanning Electron Microscopy (SEM)***

SEM images of membrane cross-sections were used to estimate the thickness of the permselective layer of each supported film. Prior to SEM imaging, the membranes were fractured after immersing in liquid nitrogen, mounted on an SEM stub, and coated with gold. The SEM instrument was a JEOL model JSM-6490LV operating at 15-30 kV voltages.

### ***Fourier Transform Infrared (FTIR) Spectroscopy***

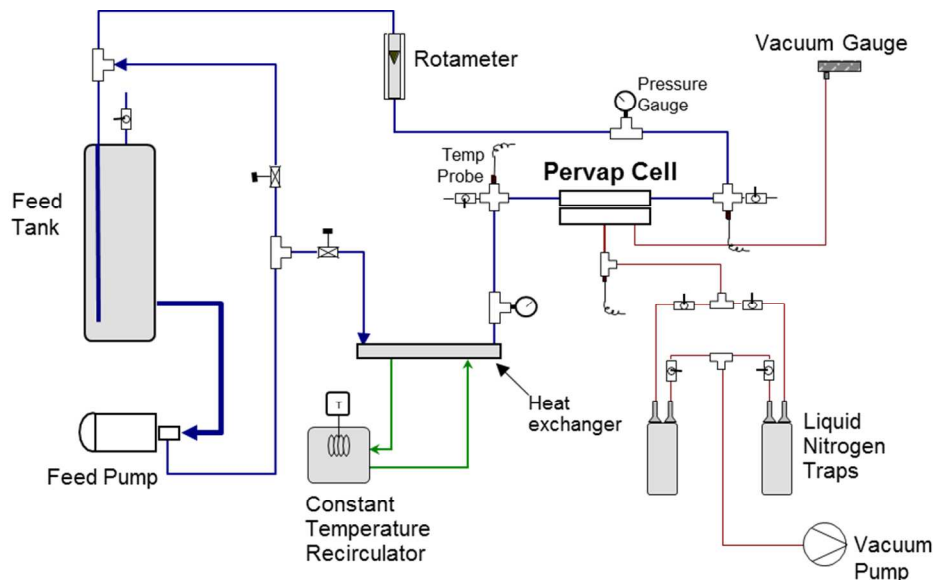
FTIR spectra were measured on a Spectrum 2000 (Perkin Elmer) or a Cary 660 (Agilent Technologies) instrument with 16 scans over the wavenumber range of 4000 to 500  $\text{cm}^{-1}$  with 4  $\text{cm}^{-1}$  resolution. For reflectance measurements, each instrument was equipped with a diamond crystal attenuated total reflectance (ATR) accessory.

### ***Pervaporation test***

Prior to testing, the membrane was checked for defects by wiping the coated side with ethanol/water (~80/20 w/w) liquid and looking for pinhole wetting through membrane. Any pinholes found were either patched by applying a small amount of 10 wt% PB/toluene solution to the spot with a Pasteur pipet and checked again or rejected.

A schematic diagram of the system used to carry out the ethanol dehydration pervaporation experiments is shown in **Figure S2**. It consisted of a two-chamber stainless steel membrane cell. The upper chamber held the inlet and outlet ports for the alcohol-water feed liquid. The lower chamber was coupled to liquid nitrogen traps and a vacuum pump. An oval section of membrane (approximately 4 cm  $\times$  20 cm) was sealed with O-rings between the two chambers, supported by a porous sintered stainless steel inlay. The active membrane area was 39  $\text{cm}^2$ . The liquid stream leaving the membrane cell, the “retentate”, was returned to the feed tank. Feed temperature was maintained ( $\pm 0.1$   $^\circ\text{C}$ ) with a constant temperature heat exchange bath. The feed flow rate through the membrane cell was kept constant at 2 L/min which corresponded to an average fluid velocity of 0.73 m/s in the 1.9 mm tall  $\times$  24.0 mm wide  $\times$  162.5 mm long rectangular flow gap above the membrane. The hydraulic diameter of the channel is 3.5 mm. The Reynolds number for the benchmark 80/20 w/w ethanol/water solution at 50  $^\circ\text{C}$  was calculated to be 3200, assuming a density of 799  $\text{kg}/\text{m}^3$  and a viscosity of  $6.37 \times 10^{-4}$   $\text{kg}/\text{m}\cdot\text{s}$  (calculated with ChemCAD software by Chemstations, Inc.), indicating turbulent flow. Using boundary layer mass transfer correlations for turbulent flow in a rectangular channel<sup>1</sup> and the observed membrane permeances (maximum of  $\sim 10^{-6}$   $\text{mol}/\text{m}^2\cdot\text{s}\cdot\text{Pa}$ ), the boundary layer resistance was estimated to be less than 2% of the membrane mass transfer resistance for all conditions reported herein. Thus, the flow conditions were determined to be sufficient to avoid liquid boundary layer effects on mass transfer.

The membranes were tested on the same day they were installed in the membrane cell. After installation, permeate vacuum and feed liquid flow were applied. After allowing 2 h for the system to reach steady state, permeate vapor from the lower chamber was collected in a liquid nitrogen trap for up to 3 h, but typically 1-2 h, and the mass and composition of the collected permeate was determined. Permeate pressure was maintained below 1 torr (0.13 kPa) during permeate collections. The benchmark feed liquid temperature was 50  $^\circ\text{C}$ . For select experiments, the feed temperature was 40, 60, or 70  $^\circ\text{C}$ . Although the membranes continuously removed solvents and water from the feed, the rate of removal was low relative to the volume in the feed tank so that the feed concentration remained approximately constant during an experiment. Between experiments, water and/or alcohol were added to maintain the desired feed concentration. Membranes were usually tested on multiple days. When permeate was not being collected in liquid nitrogen traps, feed liquid flow and temperature were maintained and permeate vapor was processed through a diaphragm vacuum pump to maintain the permeate pressure below 15 torr (2 kPa) to prevent condensation in the vacuum lines and maintain a partial pressure driving force across the membrane.



**Figure S2. Schematic diagram of bench-scale pervaporation system used to evaluate membranes.**

Feed and retentate samples were acquired at the beginning and end of each permeate collection period. Samples were diluted, as needed, with deionized (DI) water or 1-propanol prior to GC analysis. Duplicate analyses were performed on each sample. The results for a given experiment represent the average of four permeate values from two permeate collections. In some cases, multiple membranes from the same preparation or from multiple preparations were tested. On selected days, permeate and feed/retentate collections were made to assess long-term pervaporation performance trends.

Pervaporation results were analyzed in terms of the conventional parameters of separation factor ( $\beta$ ) and mass flux of each component ( $J_i$ ) as well as the more descriptive driving force-normalized parameters of permeance ( $\Pi_i$ ), molar gas permeability ( $P_i$ ), and molar permselectivity ( $\alpha$ ). Flux is defined as the mass permeating a unit area of membrane per unit of time. The separation factor of species 1 relative to species 2 ( $\beta_{12}$ ) is defined as the ratio of the permeate compositions ( $c_i^V$ ) divided by the ratio of the feed compositions ( $c_i^L$ ) as follows:

$$\beta_{12} = \frac{(c_1^V/c_2^V)}{(c_1^L/c_2^L)} = \frac{(J_1/J_2)}{(c_1^L/c_2^L)} \quad \text{Equation S1}$$

Component permeances and permeabilities were calculated based on the flux of the component; component mole fraction ( $x_i$ ), activity coefficient ( $\gamma_i$ ), and saturated vapor pressure ( $p_i^{sat}$ ) associated with the feed liquid; component mole fraction ( $y_i$ ) and total pressure ( $p_{total}^V$ ) in the permeate vapor; membrane thickness ( $\ell$ ); and molecular weight ( $MW_i$ ) as follows:

$$\Pi_i = \frac{P_i}{\ell} = \frac{J_i}{(x_i \gamma_i p_i^{sat} - y_i p_{total}^V) MW_i} \quad \text{Equation S2}$$

Common units for permeance are gas permeation units (GPU) where  $1 \text{ kmol/m}^2 \cdot \text{s} \cdot \text{kPa} = 2.99 \times 10^9 \text{ GPU}$  and  $1 \text{ GPU} = 10^{-6} \text{ cm}^3(\text{STP})/\text{cm}^2 \cdot \text{s} \cdot \text{cmHg}$ . Common units for permeability are Barrer where  $1 \text{ kmol} \cdot \text{m}/\text{m}^2 \cdot \text{s} \cdot \text{kPa} = 2.99 \times 10^{15} \text{ Barrer}$  and  $1 \text{ Barrer} = 10^{-10} \text{ cm}^3(\text{STP}) \cdot \text{cm}/\text{cm}^2 \cdot \text{s} \cdot \text{cmHg}$ . Molar permselectivity ( $\alpha_{12}$ ) is the ratio of the molar permeabilities or permeances of the two species through the membrane:

$$\alpha_{12} = \frac{P_1}{P_2} = \frac{\Pi_1}{\Pi_2} \quad \text{Equation S3}$$

Activity coefficients for binary solvent-water mixtures were calculated using ChemCAD 6.5 (Chemstations) with the NRTL thermodynamics model and the parameters presented in Table S3. For example, the model predicted  $\gamma_{\text{EtOH}}$  of 1.115 and  $\gamma_{\text{H}_2\text{O}}$  of 1.732 for an 80/20 w/w ethanol/water solution at 50 °C. The saturated vapor pressure of the compounds was calculated using the Antoine equation with published Antoine parameters. The feed-side partial pressures ( $x_i \gamma_i p_i^{\text{sat}}$ ) of ethanol and water for the 80/20 w/w ethanol/water feed solution at 50 °C were calculated to be 20.13 and 8.37 kPa, respectively.

**Table S3. NRTL thermodynamic parameters used with ChemCAD software to estimate partial feed pressures for pervaporation experiments with binary solvent (1)-water (2) mixtures.**

Solvent (1)	$B_{12}$ (K)	$B_{21}$ (K)	$\alpha$
Ethanol	-55.16	670.44	0.303
Methanol	-24.49	307.17	0.300
2-Propanol	20.06	832.98	0.326
1-Butanol	307.45	1218.53	0.432

### ***Vapor Permeation Testing***

The main difference between vapor permeation and pervaporation is the state of the feed stream: a liquid in pervaporation and a vapor in vapor permeation. A schematic diagram of the bench-scale vapor permeation test apparatus is shown in **Figure S3**. To create a vapor feed, a liquid mixture of ethanol and water was metered into a plate heat exchanger heated with a recirculated heat transfer fluid (Dyanalene 600, Dynalene Inc.) at 130 °C with a downstream tube-in-tube heat exchanger to ensure complete evaporation of the liquid. The feed vapor formed was transferred through heat-traced tubing to the membrane cell. The membrane cell was the same design as that described above for the pervaporation bench-scale tests. The total feed-side pressure was adjusted using a back-pressure regulator on the retentate stream leaving the feed-side of the membrane cell. The retentate was then condensed at atmospheric pressure in a glass condenser cooled with 4 °C water/glycol coolant. To prevent condensation in process components before the retentate condenser and to maintain constant temperature, all tubing and components were either heat traced or housed in a heated enclosure set to the desired feed vapor temperature, usually 115 °C. This temperature was sufficient to prevent condensation under all of the feed conditions tested: up to 40 wt% water and 1800 torr pressure (240 kPa).

Permeate handling was the same as that described above for pervaporation tests. Retentate condensate was collected during the period of time a permeate sample was collected. The

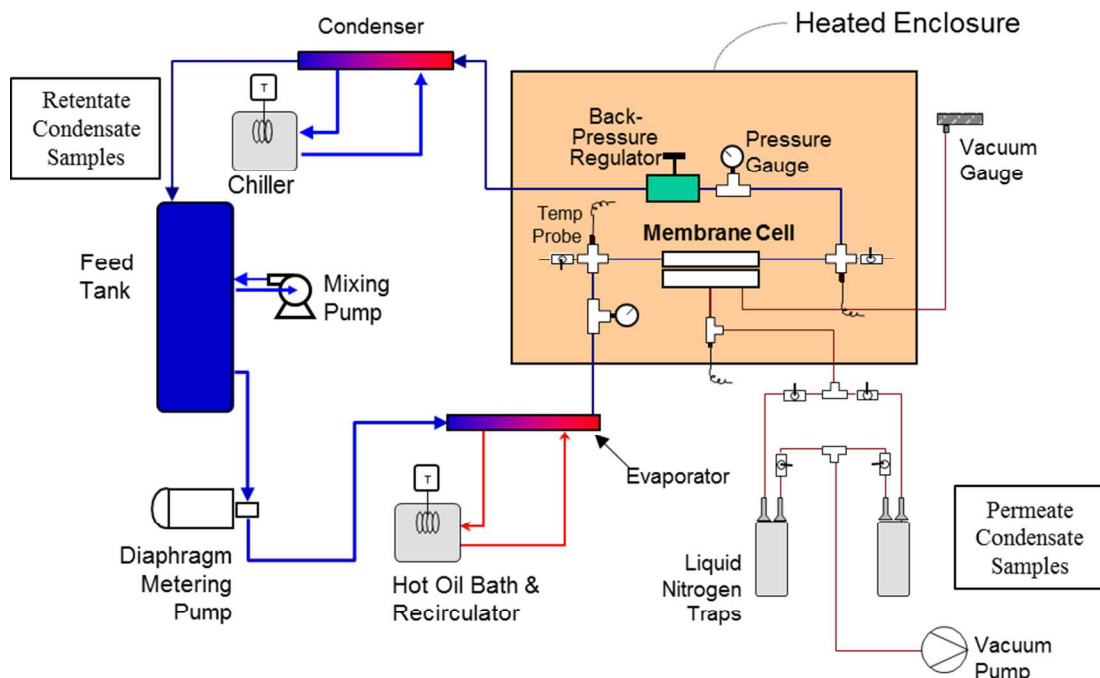
masses and compositions of the permeate and retentate samples was determined. The composition and amount of feed material was calculated as the sum of the retentate and permeate streams. The permeance of each compound was then calculated according to the following equation:

$$\Pi_i = \frac{P_i}{\ell} = \frac{J_i}{(x_i p_{total}^F - y_i p_{total}^V) MW_i} \quad \text{Equation S4}$$

Where  $p_{total}^F$  is the total pressure of the feed-side vapor. The product  $x_i p_{total}^F$  is the partial pressure of component  $i$  on the feed side of the membrane. Here, the log-mean average of the feed and retentate vapor partial pressures was used to represent the feed-side partial pressure.

Between experiments, water and/or ethanol were added to maintain the desired feed concentration. Membranes were usually tested on multiple days with the same or altered conditions. When permeate was not being collected in liquid nitrogen traps, feed vapor flow and temperature were maintained and permeate vapor was processed through a scroll vacuum pump to maintain the permeate pressure below 20 torr (2.66 kPa) to prevent condensation in the vacuum lines and maintain a partial pressure driving force across the membrane.

The benchmark conditions for vapor permeation tests were a feed vapor temperature of 115 °C, vapor feed rate of 1.5 kg/h, atmospheric feed pressure (101 kPa), total permeate pressure of 10 torr (1.33 kPa), and a feed containing 10 wt% water. Feed conditions studied included: feed compositions from 1 to 40 wt% water, feed pressures from 101 to 240 kPa, and feed temperatures from 102 to 115 °C. Care was taken to maintain at least 5 °C of superheat in the feed stream to prevent condensation. At a feed pressure of 106 kPa, the Reynolds number was calculated to be 2700 based on a density of 1.34 kg/m<sup>3</sup>, velocity of 6.8 m/s, and viscosity of 1.2×10<sup>-5</sup> kg/m·s (calculated with ChemCAD software program). Using boundary layer mass transfer correlations for turbulent flow in a rectangular channel and the observed membrane permeances for the vapor permeation tests (maximum of ~0.2×10<sup>-6</sup> mol/m<sup>2</sup>·s·Pa), the boundary layer resistance was estimated to be less than 2% of the membrane mass transfer resistance for all conditions reported herein. Thus, the flow conditions were determined to be sufficient to avoid significant liquid boundary layer effects on mass transfer.



**Figure S3. Schematic diagram of vapor permeation test apparatus.**

### *Pervaporation and Vapor Permeation Alcohol/Water Sample Analysis*

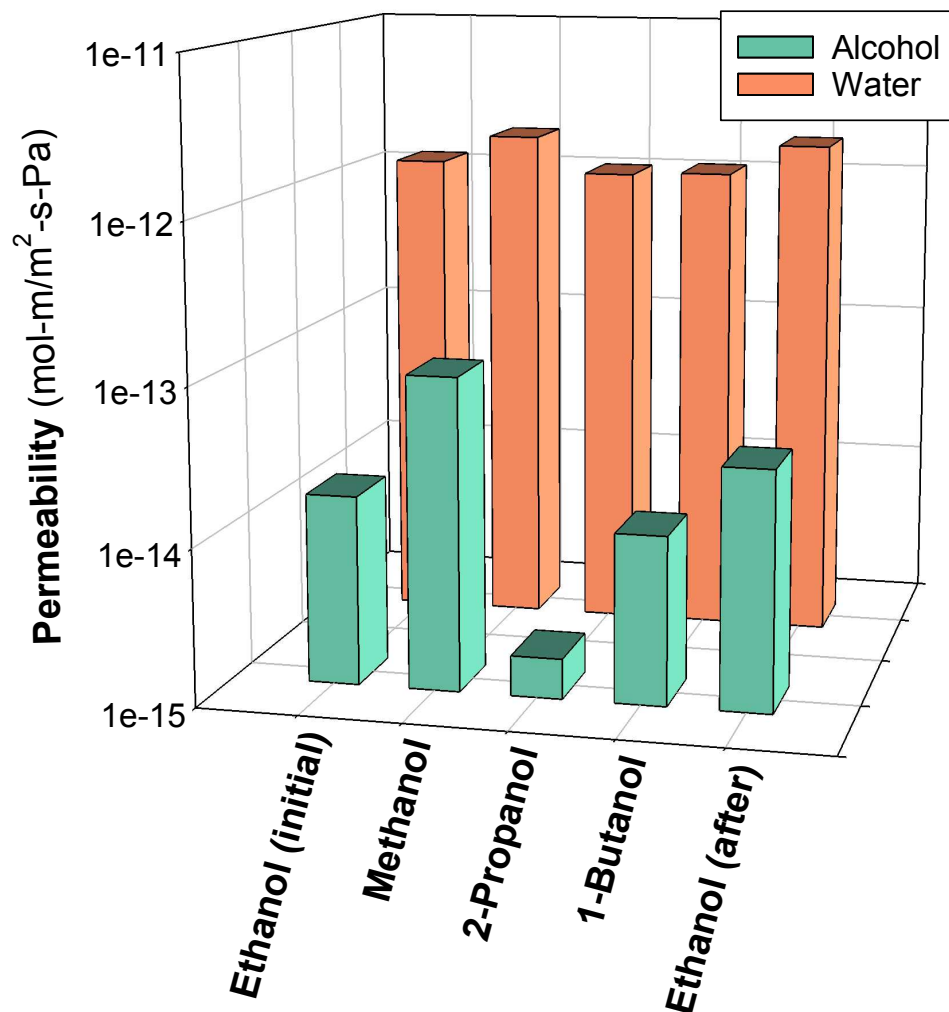
Gas chromatography (GC) analyses: Membrane testing was carried out in two facilities and each had a separate GC system to analyze liquid samples to determine alcohol and/or water concentrations. In one, a GC/Mass spectrometer (GC/MS) (Agilent Technologies 7890/5975) with HP INNOWax column and a CombiPAL liquid autosampler was utilized to quantitate both alcohol and water concentrations. In the other a GC/Thermal Conductivity Detector/Flame Ionization Detector (GC/TCD/FID) system (Agilent Technologies 6890) with Restek Rtx®-624 fused silica column and CombiPAL liquid autosampler was utilized. The FID detector was used to quantitate ethanol in permeate samples with ethanol concentrations of less than 20 wt% while the TCD detector was used to quantitate both ethanol and water in samples.

Linear calibration curves were established using multiple standard alcohol/water mixtures. Samples were analyzed within 24 h or stored in sealed vials at 4 °C. Relative percent differences (RPD) of ethanol concentrations for duplicate samples were always less than 10 % and usually less than 5 %. The GC calibrations were checked daily using standard solutions. Ethanol concentration approximations were made by refractive index (RI) with handheld refractometers (MISCO PA203 or APT HR 110.008).

*Karl Fischer Titration:* Feed and retentate vapor condensates from vapor permeation experiments with water concentrations of less than 30 wt% were analyzed by coulometric Karl Fischer titration using either a Metrohm 831 Coulometer with Diaphragm or a Denver Instruments model 260 titration controller and model KF275 coulometric titration module. The coulometric Karl Fischer method is a sensitive and specific method for the determination of water, even at low levels. Samples are introduced into a sealed titration cell. The titrator automatically senses the presence of water and passes a quantity of electricity (“coulombs”)



through the cell to electrochemically generate iodine, which reacts with water. The titrator determines when all of the water has been consumed. The anolyte and catholyte liquids were Hydranal® Coulomat AG and Coulomat CG, respectively (Riedel-de Haën). A 1.000 wt% water standard (Hydranal®-Water Standard 10.0, Riedel-de Haën) was analyzed before and after each set of samples to ensure proper operation of the instrument. The relative standard deviation of duplicate samples was always less than 0.5%.



**Figure S4. Water and alcohol permeabilities for UV-treated 1,2-PB membrane from pervaporation tests at 50 °C with ~20 wt% water in feed. Data given in Table S4.**

Table S4. Expanded data for results presented in Table 1 in the manuscript

Entry No.	Alcohol	Water Conc. (wt%)	Temp. (°C)	Membrane Treatment	Dense Layer Thickness (μm)	Permeate Water Conc. (wt%)	Total Flux (kg/m <sup>2</sup> ·h)	Water Permeability (10 <sup>-12</sup> mol·m/m <sup>2</sup> ·s·Pa)	Water-Alcohol Selectivity
1	Ethanol	19.8	50	None	4.5	46.8	0.348	1.37	5.5
2	Ethanol	19.9	50	UV:0.5h @ 8cm	4.5	63.2	0.907	4.80	10.7
3	Ethanol	19.3	50	UV:1h @ 8cm	4.5	86.5	0.209	1.54	41.0
4	Ethanol	17.7	50	Thermal: 96 h @ 120 °C in air	2.9	83.4	0.362	1.73	34.4
5	Ethanol	15.3	50	UV:2h @ 8cm, PDMS overcoat	3.6**	82.7	0.564	3.57	36.5
6a	Ethanol	17.8	50	UV:2h @ 8cm	3.4	91.9	0.201	1.22	75.7
6b	Methanol	18.8	50	Same membrane	-	59.9	0.334	1.85	18.8
6c	2-Propanol	20.5	50	Same membrane	-	99.2	0.219	1.08	604.0
6d	1-Butanol	18.7	50	Same membrane	-	98.8	0.260	1.13	95.5
6e	Ethanol	18.1	50	Same membrane – day 37	-	88.4	0.303	1.75	50.4
6f	Ethanol	21.3	50	Same membrane – day 104	-	89.8	0.330	1.84	52.0
7*	Ethanol	19.4		None – PDMS membrane	11.1	15.0	3.94	12.5	1.1
8a	Ethanol	16.5	50	UV:2h @ 8cm	3.4	96.6	0.105	0.71	206
8b	Ethanol	16.3	70	Same membrane		84.7	0.272	0.72	127

Internal references for membranes listed in Table S4:

1 = LMV-081-027A  
 2 = LMV-081-027C  
 3 = LMV-081-027D

4 = LMV-078-070B  
 5 = LMV-078-052A  
 6 = LMV-078-100B

7 = LMV-081-156A  
 8 = LMV-078-100C, PV test after VP runs

Table S5. Pervaporation data for Figures 2B, 2C, and 2D. Overall thickness of the PB and PDMS layers was 3.6  $\mu\text{m}$ . Support was a Sepro 200 ultrafiltration membrane. The thickness of each layer was estimated to be one-half of the total. The PB layer was treated with UV radiation for 2 h at a distance of 8 cm prior to being coated with PDMS layer. Pervaporation tests carried out at 50  $^{\circ}\text{C}$ .

Elapsed time (days)	Water in Feed Liquid (wt%)	Water in Permeate (wt%)	Total Flux ( $\text{kg}/\text{m}^2\cdot\text{h}$ )	Water Permeability ( $10^{-12} \text{ mol}\cdot\text{m}/\text{m}^2\cdot\text{s}\cdot\text{Pa}$ )	Ethanol Permeability ( $10^{-12} \text{ mol}\cdot\text{m}/\text{m}^2\cdot\text{s}\cdot\text{Pa}$ )	Water/Ethanol Selectivity
0	15.3	82.7	0.564	3.57	0.098	36.5
1	14.8	79.9	0.599	3.72	0.120	31.1
6	2.29	41.9	0.315	4.56	0.142	32.3
7	1.91	34.2	0.367	5.17	0.185	27.9
8	1.37	26.6	0.358	5.39	0.199	27.1
9	1.74	29.8	0.393	5.25	0.211	24.9
13	1.60	26.9	0.423	5.50	0.236	23.3
14	1.31	22.8	0.423	5.65	0.247	22.9
15	12.7	67.7	0.713	4.09	0.222	18.4
27	16.9	72.9	0.779	4.11	0.217	19.0
28	49.0	90.1	0.758	3.58	0.106	33.7
29	48.3	91.1	0.725	3.47	0.091	38.2
30	93.5	99.68	0.431	1.98	0.0069	285.9
31	94.0	99.72	0.416	1.91	0.0063	301.7
35	99.98	100.00	0.388	1.75		N/A
36	48.5	94.58	0.617	3.06	0.047	65.1
37	17.1	82.7	0.613	3.66	0.109	33.4

Table S6. Water/ethanol vapor-liquid equilibrium (VLE) values presented in Figure 2D. These values were calculated using Chemstations ChemCAD software with the non-random two liquid (NRTL) Thermodynamic model at an equilibrium temperature of 50 °C. NRTL parameters were  $B_{ij} = 670.441$  K,  $B_{ji} = -55.1581$  K,  $\alpha = 0.303$  (i = water, j = ethanol).

Water in Liquid Phase (wt fraction)	Water in Vapor Phase (wt fraction)
0	0
0.001	0.00105
0.01	0.0103
0.02	0.0202
0.05	0.0475
0.1	0.0857
0.2	0.140
0.3	0.174
0.4	0.198
0.5	0.216
0.6	0.235
0.7	0.262
0.8	0.311
0.9	0.431
0.95	0.581
0.99	0.864
1	1

Table S7. Vapor permeation data for Figures 3A, 3B, and 3C. Thickness of the PB layer was 3.4  $\mu\text{m}$ . Support was a PVDF membrane distillation membrane. The PB layer was treated with UV radiation for 2 h at a distance of 8 cm. Elapsed time reflects time from initiation of feed vapor flow and permeate vacuum. Membrane was heated at 115  $^{\circ}\text{C}$  for 2 days prior to start of feed flow.

Elapsed time (days)	Water in Feed Vapor (wt fraction)	Water in Permeate Vapor (wt fraction)	Total Feed Pressure (kPa)	Feed Temperature ( $^{\circ}\text{C}$ )	Total Flux ( $\text{kg}/\text{m}^2\cdot\text{h}$ )	Water Activity	Ethanol Activity	Water Permeability ( $\text{mol}\cdot\text{m}/\text{m}^2\cdot\text{s}\cdot\text{Pa}$ )	Ethanol Permeability ( $\text{mol}\cdot\text{m}/\text{m}^2\cdot\text{s}\cdot\text{Pa}$ )	Water/Ethanol Selectivity
3	0.0487	0.8285	108.1	115.7	0.123	0.0746	0.2598	4.47E-13	4.52E-15	99.0
4	0.0482	0.8378	108.7	115.7	0.120	0.0742	0.2615	4.36E-13	4.14E-15	105.5
5	0.0481	0.8389	107.9	115.7	0.123	0.0736	0.2598	4.53E-13	4.26E-15	106.5
6	0.0795	0.9036	109.4	115.6	0.188	0.1179	0.2437	4.63E-13	4.15E-15	111.3
7	0.1075	0.9350	110.5	115.7	0.237	0.1548	0.2292	4.57E-13	3.74E-15	122.2
12	0.0640	0.8974	111.3	115.7	0.155	0.0984	0.2569	4.56E-13	3.45E-15	131.9
13	0.0751	0.9259	111.3	115.6	0.177	0.1142	0.2512	4.64E-13	2.92E-15	158.7
14	0.0899	0.8649	240.3	115.5	0.769	0.2851	0.5207	7.45E-13	1.11E-14	67.3
17	0.0927	0.8733	241.6	115.6	0.832	0.2958	0.5216	7.88E-13	1.13E-14	69.9
18	0.0915	0.8883	202.3	115.7	0.601	0.2455	0.4374	6.99E-13	8.56E-15	81.7
19	0.0975	0.8981	203.4	115.6	0.624	0.2613	0.4341	6.88E-13	8.17E-15	84.2
20	0.0959	0.8674	203.7	115.6	0.614	0.2583	0.4367	6.59E-13	1.04E-14	63.3
21	0.1237	0.9039	204.8	115.3	0.750	0.3262	0.4143	6.74E-13	9.83E-15	68.6
24	0.1369	0.9235	205.5	115.3	0.799	0.3569	0.4032	6.68E-13	8.56E-15	78.0
25	0.1643	0.9402	205.0	115.4	0.911	0.4120	0.3754	6.70E-13	8.18E-15	81.9
26	0.1793	0.9491	204.6	115.4	0.943	0.4401	0.3609	6.53E-13	7.49E-15	87.2
33	0.1831	0.9511	205.6	115.4	0.938	0.4489	0.3586	6.39E-13	7.19E-15	88.8
34	0.1924	0.9512	205.7	115.4	0.959	0.4662	0.3504	6.28E-13	7.48E-15	84.0
35	0.1959	0.9554	206.2	115.4	0.968	0.4740	0.3484	6.27E-13	6.97E-15	89.9
39	0.1877	0.9532	206.9	115.5	0.951	0.4600	0.3564	6.32E-13	7.02E-15	90.1
41	0.1996	0.9586	205.4	115.4	0.994	0.4799	0.3446	6.38E-13	6.72E-15	94.9
42	0.2307	0.9677	206.2	115.3	1.094	0.5364	0.3202	6.35E-13	6.21E-15	102.1
46	0.2444	0.9708	206.2	115.5	1.146	0.5588	0.3093	6.39E-13	6.09E-15	104.9
47	0.2668	0.9743	207.5	115.4	1.253	0.5988	0.2946	6.54E-13	6.16E-15	106.2

49	0.2854	0.9751	204.5	115.5	1.297	0.6192	0.2775	6.55E-13	6.55E-15	99.9
55	0.3894	0.9821	203.9	115.2	1.547	0.7492	0.2221	6.55E-13	6.98E-15	93.8
56	0.3763	0.9854	203.8	115.4	1.714	0.7474	0.2204	7.27E-13	6.40E-15	113.7
60	0.3777	0.9833	205.5	115.3	1.676	0.7522	0.2248	7.07E-13	7.06E-15	100.2
61	0.3745	0.9831	205.8	115.2	1.686	0.7568	0.2246	7.09E-13	7.20E-15	98.5
62	0.3761	0.9862	169.3	115.0	1.210	0.6250	0.1842	6.19E-13	5.15E-15	120.1
63	0.3773	0.9858	170.7	115.3	1.201	0.6243	0.1868	6.12E-13	5.17E-15	118.4
68	0.3738	0.9865	170.3	115.4	1.143	0.6189	0.1878	5.89E-13	4.65E-15	126.6
69	0.3705	0.9870	102.2	115.4	0.576	0.3751	0.1102	4.90E-13	3.84E-15	127.4
82	0.3775	0.9912	101.1	108.3	0.548	0.4676	0.1364	4.73E-13	2.51E-15	188.4
83	0.3777	0.9907	101.2	108.3	0.549	0.4663	0.1375	4.74E-13	2.64E-15	179.6
84	0.3750	0.9910	101.1	108.2	0.545	0.4678	0.1378	4.71E-13	2.54E-15	185.9
87	0.3754	0.9921	101.6	102.1	0.580	0.5733	0.1653	4.97E-13	2.38E-15	208.6
88	0.3790	0.9919	101.6	102.2	0.580	0.5719	0.1657	4.98E-13	2.43E-15	205.1
89	0.3780	0.9910	101.7	115.0	0.540	0.3771	0.1084	4.60E-13	2.53E-15	181.8
90	0.3826	0.9905	101.6	115.2	0.535	0.3750	0.1087	4.56E-13	2.65E-15	171.8
94	0.3807	0.9871	200.4	115.1	1.487	0.7313	0.2200	6.47E-13	4.94E-15	131.0
95	0.3728	0.9872	200.4	115.4	1.508	0.7327	0.2170	6.53E-13	5.02E-15	130.1
97	0.3765	0.9696	201.3	115.2	0.883	0.5051	0.3512	5.74E-13	4.53E-15	126.7
98	0.2045	0.9797	200.8	115.1	1.220	0.6500	0.2802	6.18E-13	5.21E-15	118.6
101	0.2930	0.9777	202.0	115.4	1.154	0.6145	0.2953	6.11E-13	5.10E-15	119.8
103	0.2711	0.9665	202.8	115.2	0.879	0.4889	0.3577	5.84E-13	4.83E-15	120.9
108	0.1964	0.9456	205.0	115.5	0.683	0.3789	0.4109	5.71E-13	5.28E-15	108.2
109	0.1416	0.9477	204.2	115.2	0.670	0.3734	0.4146	5.73E-13	4.97E-15	115.3
111	0.1387	0.9214	204.6	115.3	0.485	0.2704	0.4633	5.59E-13	4.84E-15	115.6
112	0.0946	0.9134	205.5	115.5	0.482	0.2659	0.4629	5.55E-13	5.26E-15	105.5
115	0.0932	0.9102	205.0	115.2	0.467	0.2565	0.4720	5.62E-13	5.24E-15	107.3
118	0.0886	0.8637	206.4	115.3	0.329	0.1702	0.5116	5.64E-13	5.12E-15	110.0
123	0.0562	0.9209	102.8	115.1	0.219	0.1243	0.2281	5.37E-13	4.33E-15	124.1
124	0.0886	0.9245	103.5	115.1	0.215	0.1249	0.2297	5.28E-13	4.02E-15	131.2

Table S8. Pervaporation data for Figure 3D. Thickness of the PB layer was 3.4  $\mu\text{m}$ . Support was a PVDF membrane distillation membrane. The PB layer was treated with UV radiation for 2 h at a distance of 8 cm. Pervaporation tests carried out at 50  $^{\circ}\text{C}$ .

Elapsed time (days)	Alcohol	Water in Feed Liquid (wt%)	Water in Permeate (wt%)	Total Flux ( $\text{kg}/\text{m}^2\cdot\text{h}$ )	Water Permeability ( $10^{-12} \text{ mol}\cdot\text{m}/\text{m}^2\cdot\text{s}\cdot\text{Pa}$ )	Alcohol Permeability ( $10^{-12} \text{ mol}\cdot\text{m}/\text{m}^2\cdot\text{s}\cdot\text{Pa}$ )	Water/Alcohol Selectivity
0	Ethanol	18.11	92.03	0.192	1.15	0.015	76.5
1	Ethanol	17.48	91.67	0.211	1.29	0.017	74.9
5	Methanol	4.25	17.74	0.304	1.765	0.142	12.4
6	Methanol	21.12	60.24	0.337	1.870	0.099	18.9
7	Methanol	20.92	59.63	0.332	1.830	0.098	18.6
12	Methanol	46.73	79.27	0.391	1.868	0.086	21.8
26	2-Propanol	4.84	97.69	0.070	0.75	0.0012	613.7
27	2-Propanol	21.62	99.25	0.218	1.06	0.0016	647.7
28	2-Propanol	21.04	99.20	0.219	1.07	0.0017	617.1
29	2-Propanol	47.32	99.41	0.271	1.22	0.0018	694.6
33	2-Propanol	18.94	99.05	0.221	1.11	0.0020	547.3
34	1-Butanol	3.84	96.99	0.102	0.80	0.0097	82.8
35	1-Butanol	19.21	98.84	0.261	1.13	0.0119	94.6
36	1-Butanol	18.16	98.84	0.260	1.13	0.0117	96.3
37	Ethanol	18.07	88.36	0.303	1.75	0.0348	50.4
41	Ethanol	100.00	100.00	0.181	0.77	0.0000	N/A
43	Ethanol	18.50	89.70	0.298	1.73	0.0304	56.8
50	Ethanol	18.84	89.86	0.307	1.77	0.0311	57.1
57	Ethanol	20.46	90.04	0.316	1.76	0.0322	54.9
64	Ethanol	17.49	88.76	0.300	1.77	0.0330	53.7
71	Ethanol	18.98	88.91	0.314	1.78	0.0348	51.3
78	Ethanol	4.04	65.98	0.120	1.49	0.0309	48.0
79	Ethanol	3.62	62.13	0.118	1.52	0.0336	45.1
83	Ethanol	51.79	94.48	0.440	2.02	0.0331	61.1
84	Ethanol	51.30	94.70	0.414	1.91	0.0298	64.1
86	Ethanol	21.50	90.27	0.321	1.76	0.0323	54.4
92	Ethanol	22.74	90.44	0.342	1.83	0.0343	53.4
99	Ethanol	20.84	89.82	0.330	1.82	0.0344	52.8
104	Ethanol	21.77	89.94	0.339	1.84	0.0354	52.0

1. Green, D. W.; Perry, R. H. Chapter: Membrane Separation Processes. In *Perry's Chemical Engineers' Handbook, Eighth Edition*, McGraw-Hill: New York, 2008.