ABSTRACT: Combinatorial methodology is described for rapid screening of selectivity in polymeric pervaporation membrane materials for alcohol–water separations. The screening technique is demonstrated for ethanol–water separation using a model polyacrylate system. The materials studied are cross-linked random copolymers of a hydrophobic comonomer (n-butyl acrylate, B) and a hydrophilic comonomer (2-hydroxyethyl acrylate, H). A matrix of materials is prepared that has orthogonal variations in two key variables, H:B ratio and cross-linker concentration. For mixtures of ethanol and water, equilibrium selectivities and distribution coefficients are obtained by combining swelling measurements with high-throughput HPLC analysis. Based on the screening results, two copolymers are selected for further study as pervaporation membranes to quantify permeability selectivity and the flux of ethanol. The screening methodology described has good potential to accelerate the search for new membrane materials, as it is adaptable to a broad range of polymer chemistries.

KEYWORDS: combinatorial synthesis, gels, pervaporation membranes, permeability selectivity

INTRODUCTION

Pervaporation is a membrane-based separation process in which a component is selectively removed from a liquid mixture by transport through the membrane into the vapor phase. Pervaporation can be applied to separation of many mixtures, but it is presently receiving attention for energy-efficient recovery of biofuels from aqueous fermentation processes. Recovery of bioalcohols (ethanol, n-butanol) from fermentations usually requires separation of dilute mixtures, for example, solutions having alcohol concentrations less than 20 g/L for n-butanol or less than 100 g/L for ethanol. Pervaporation can be applied either to remove alcohols from dilute aqueous systems or, conversely, to remove residual water from concentrated alcohols, such as the azeotropic mixture of 95.6% w/w ethanol and 4.4% w/w water. Design of effective membranes involves optimization of materials to yield both high selectivity and high flux of the desired permeant. Much recent literature has been devoted to the design of pervaporation membrane materials with high separation factor and high flux, especially those based upon silicone polymers and zeolites, but high-throughput screening techniques to rapidly identify promising candidates from other materials classes are lacking.

Given the inherent variability in biomass-derived feedstocks, it is evident that one membrane material cannot prove optimal for all separations. Techniques are needed for rapid tuning of membrane composition for optimal performance with different separation processes. Testing of the effects of membrane composition, additives and fillers, or other variables is presently done on a membrane-by-membrane basis by fabricating membranes and conducting time-consuming pervaporation trials. High throughput screening techniques potentially allow a researcher to greatly reduce the number of membranes that must be fabricated and tested. Such a methodology is presented here, whereby simple swelling and high performance liquid chromatography (HPLC) experiments are combined to screen materials for equilibrium swelling and selectivity, after which a greatly reduced number of materials is subjected to membrane testing to measure permeability selectivity and flux.

We demonstrate the screening approach with a model polyacrylate system consisting of random copolymers of hydrophilic (H) and hydrophobic (B) repeat units. Copolymers provide flexibility in chemical composition and control over cohesive energy density (CED), permitting straightforward tuning of separation characteristics. Randomly copolymerizing H and B type monomers provides a basis for tuning solvent affinity, as copolymers are expected to have CED lying in between that of the H and B units. Here, 2-hydroxyethyl acrylate is selected as the hydrophilic (H) unit, and n-butyl acrylate is selected as the hydrophobic (B) unit, for example. The methods described herein are broadly applicable to other H/B monomer pairs, provided the monomers are miscible and can undergo copolymerization. It is preferable to select monomers with different CEDs in order to cover a wide range in the copolymers. Materials having high CED are likely to swell to a high degree in water and exhibit poor selectivity for the alcohol, whereas materials having a low CED are likely to exhibit a lower flux of the alcohol with improved selectivity. Screening random copolymers with a wide range of CED
increases the chances of finding a material that offers an acceptable compromise between selectivity and flux.

In this work, emphasis is placed on random copolymerization methods that require only simple apparatus and methods, as opposed to those chemistries requiring more elaborate synthetic techniques. Readily polymerizable monomers such as acrylates, methacrylates, styrenes, functional silicones, and others are amenable to screening, meaning that hundreds of potential monomer combinations are accessible. A very small percentage of these materials have ever been screened for performance as membranes, however, with much of the current literature on polymeric membranes for alcohol–water separations focusing on a relatively small number of polymers. The synthesis and screening techniques described here are extensible to a wide range of polymer chemistries, providing opportunities for discovery of membrane materials with exceptional performance characteristics.

Screening experiments involve both high-throughput synthesis and characterization. A high-throughput synthetic protocol is first employed to prepare a matrix of cross-linked copolymer samples, into which orthogonal gradients in H:B ratio and cross-link density are programmed, providing a two-dimensional parameter space. Equilibrium swelling measurements in pure solvents (water and ethanol) are conducted in order to gain information about the polymers’ affinities for the pure solvents. After swelling the membrane materials in an ethanol–water mixture lying in the composition range of interest, high-throughput HPLC analysis is conducted to obtain experimental measurements of distribution coefficients and equilibrium selectivities. Pervaporation membranes are fabricated from two materials selected from the test matrix based on their swelling characteristics and equilibrium selectivity for ethanol. Pervaporation tests on these membranes yield direct measurements of the permeability selectivity and flux of ethanol.

## RESULTS AND DISCUSSION

### Model Copolymer System

A random copolymer network system consisting of hydrophobic n-butyl acrylate (B) and hydrophilic 2-hydroxyethyl acrylate (H) repeat units was selected to demonstrate the screening approach. The glass transition temperatures of the component homopolymers, poly(n-butyl acrylate) \( T_g \approx -52 \, ^\circ C \) and poly(2-hydroxyethyl acrylate) \( T_g \approx 3.5 \, ^\circ C \), are low enough to yield rubbery copolymers at room temperature. Both acrylate monomers are readily polymerized in bulk or in solution by simple free-radical techniques, and they are miscible across their entire composition range. The H and B monomers have widely different Hansen solubility parameters, 18.5 MPa\(^{0.5}\) for poly(n-butyl acrylate) and 29.7 MPa\(^{0.5}\) for poly(2-hydroxyethyl acrylate), where higher solubility parameter indicates a higher CED. Hansen solubility parameters for ethanol and water are approximately 26.6 MPa\(^{0.5}\) and 47.9 MPa\(^{0.5}\), respectively.

**Combinatorial Synthesis.** The screening procedure begins with high-throughput synthesis of a matrix of samples having orthogonal gradients in composition and cross-linker concentration. The sample matrix provides a library of information regarding two key variables that affect membrane performance. Besides hydrophilicity and cross-link density, it is possible to select from other variables that might affect performance, such as the concentration of a filler or additive. Rapid synthesis of an \( 11 \times 11 \) matrix of samples that covers a wide range of compositional parameter space was accomplished by pipetting techniques in this study, but any simple bulk or solution polymerization methodology can be used, and a smaller matrix can be screened, if desired. All samples were prepared and cured in a single batch under identical conditions to minimize variations in the experimenters’ preparation technique. In the present study, the mole fraction of acrylate groups belonging to H monomers \( x_H \) was varied from 0.0 to slightly less than 1.0, while the mole fraction of acrylate groups belonging to cross-linkers \( x_c \) was varied between 0.0005 and 0.0105, as illustrated in Table 1. Achieving \( x_H = 1 \) or \( x_C = 1 \) is impossible because of the presence of the acrylates belonging to the cross-linker \( x_C \neq 0 \); thus, the table only covers samples having \( x_H \) values up to 0.9895.

**Equilibrium Swelling Experiments: Pure Solvents.** The materials studied in this report are rubbery networks that behave as gels once they are swollen with water or ethanol. Networks having low cross-linker concentration are more likely to absorb the desired permeant to a large extent than heavily cross-linked networks, which is beneficial for increasing flux in a membrane. However, weakly cross-linked materials are also likely to have a higher mass fraction of extractable components. Extractable polymeric components are undesirable for pervaporation membranes, so measurement of the soluble mass fraction by extraction in a thermodynamically good

### Table 1. Layout of Combinatorial Sample Matrix

<table>
<thead>
<tr>
<th>mole fraction of acrylates belonging to cross-linker ( x_c )</th>
<th>0</th>
<th>0.1</th>
<th>0.2</th>
<th>0.3</th>
<th>0.4</th>
<th>0.5</th>
<th>0.6</th>
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<td>KH</td>
<td>Kl</td>
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<td>AG</td>
<td>AH</td>
<td>AI</td>
<td>AJ</td>
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</tbody>
</table>

*Each column contains a gradient in cross-linker concentration, while each row contains a gradient in the mole fraction of hydrophilic monomer. Samples are hereafter referred to by the names in this table.*
Determined by ethanol extraction (Table 2). The measured necessarily the optimal composition for pervaporation, as other produce a selective membrane. However, this material is not.

The networks in the model system tested had a very low extractable mass fraction (w_{sol}), as determined by ethanol extraction (Table 2). The measured w_{sol} was less than 0.01 for the majority of samples and less than 0.02 for even the most weakly cross-linked samples. Only previously extracted networks were used for subsequent tests with mixed solvents. The leaching of soluble polymeric components can provide inaccurate measurements of the equilibrium swollen mass until the solubles are removed exhaustively. As a safeguard, the solvent should be decanted and replaced daily until the membrane reaches an equilibrium swollen mass (M_s). Soxhlet extraction potentially provides a convenient means to extract solubles continuously for individual samples, but it is less tractable when large numbers of samples are involved. Thus, the simpler approach of swelling the samples in closed containers with periodic replacement of the solvent was followed in this study.

The measurement of equilibrium mass swelling ratios for extracted samples was conducted in both ethanol and water in this study. It should be noted that these measurements are not absolutely necessary to determine selectivities and distribution coefficients, which can be obtained from mixed-solvent swelling experiments and HPLC alone. However, the swelling in pure solvents was carried out to illustrate the relative affinities for water and ethanol among the copolymer samples. In addition, it may be desired to extract polymer—solvent thermodynamic interaction parameters from the swollen samples for modeling purposes later, in which case swelling in pure solvents provides a wealth of information.

Figure 1 presents the equilibrium swelling behavior of all networks in pure ethanol and in pure water. The largest ethanol swelling ratio is observed in membranes having x_{H} ≈ 0.3 and x_C ≈ 0.001. The swelling ratio of this copolymer is higher than that of either of the respective homopolymers, suggesting its CED is close to that of ethanol. The membrane having x_{H} = 0.3 and x_C ≈ 0.001 absorbed more than 200% of its initial (dry) mass in pure ethanol, while absorbing less than 2% of its mass in pure water. In addition, the swelling maximum for water is located at x_{fl} ≈ 1, far away in compositional parameter space, indicating that the chosen monomer pair has good potential to produce a selective membrane. However, this material is not necessarily the optimal composition for pervaporation, as other factors must be considered, such as swelling in mixed solvents and the material’s ability to provide an adequate flux of ethanol.

The effects of cross-linker concentration are also readily apparent from Figure 1. Weakly cross-linked systems (low x_C) have enhanced equilibrium swelling in both solvents, as expected. However, low values of x_C are also more likely to produce membranes with high w_{sol} which is undesirable. While the system studied always yielded w_{sol} < 0.02, not all systems are expected to behave so well as cross-linker concentration is lowered. The screening approach is valuable for evaluating this trade-off in properties and identifying the minimum value of x_C that produces an acceptably low value of w_{sol}.

**Distribution Coefficient and Selectivity: HPLC Analysis**. From mixed-solvent swelling experiments, the distribution coefficients for water and ethanol are found (Distribution coefficients are defined by eqs 5 and 6 in the Experimental Procedures). Previously extracted and dried samples are swollen to equilibrium in an ethanol—water mixture having a concentration in the range of interest for the intended pervaporation process. Figure 2 shows the results of swelling the materials to equilibrium in 100 g/L ethanol (aq). The measured swelling ratios follow essentially the same trend as the swelling results in pure water (Figure 1) because the solvent mixture contains a large excess of water over ethanol. The most highly swelling materials are therefore those consisting of cross-linked HEA homopolymer. The effects of cross-linker concentration on swelling are weak in this system, suggesting that any cross-linker concentration in the matrix is adequate for membrane testing. The mass fraction of ethanol in the external liquid at equilibrium is obtained directly from HPLC analysis. By gravimetric measurement, the combined mass of water and ethanol absorbed, (M_s−M_0), is obtained. The masses of water and ethanol inside and outside the network can then be calculated by a mass balance on the system, as in eqs 4a and 4b. Values of k_α, k_β, and α_α are thereby obtained for each sample in the test matrix.

One source of error in the approach is that the values of k_α, k_β, and α_α might depend on the external concentration of alcohol at equilibrium. Although the initial concentration of the alcohol is the same for all membranes, the final external concentration of the alcohol is different for each sample due to differences in selectivity and distribution coefficient. To check whether concentration dependence of the properties is an issue, the mixed-solvent swelling can be repeated with different amounts of external liquids, or with different initial alcohol concentrations, if desired.

### Table 2. Soluble Mass Fractions (w_{sol}) of Copolymer Networks Determined by Ethanol Extraction

<table>
<thead>
<tr>
<th>mole fraction of acrylates belonging to cross-linker (x_C)</th>
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<th>0.3</th>
<th>0.4</th>
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<th>0.6</th>
<th>0.7</th>
<th>0.8</th>
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<td>w_{sol} vs composition</td>
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</tr>
<tr>
<td>mole fraction of acrylates belonging to hydrophilic monomer (x_H)</td>
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<td></td>
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<td>0.021</td>
<td>0.020</td>
<td>0.022</td>
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<td>0.011</td>
<td>0.013</td>
<td>0.011</td>
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</tr>
<tr>
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<td>0.021</td>
<td>0.018</td>
<td>0.021</td>
<td>0.018</td>
<td>0.012</td>
<td>0.010</td>
<td>0.010</td>
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<td>0.025</td>
<td>0.017</td>
<td>0.007</td>
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<td>0.022</td>
<td>0.018</td>
<td>0.021</td>
<td>0.004</td>
<td>0.007</td>
<td>0.003</td>
</tr>
</tbody>
</table>
Each membrane sample was swelled in a precisely determined mass of 100 g/L ethanol (aq) in a sealed container until the equilibrium swollen mass was reached. Figures 3 and 4 show measured values of $k_a$ and $k_w$, respectively. The measured $k_a$ ranges from 0.1 to 0.7, and $k_w$ is in all cases much higher than $k_a$. The reported distribution coefficients have values less than 1.0 because they include the volume occupied by polymer in the membrane phase, rather than considering only the liquid components. Membranes consisting of cross-linked poly(2-hydroxyethyl acrylate) ($x_H = 0.9895$) have the highest $k_a$ and $k_w$ values. It is noteworthy that the highest $k_a$ value was not observed in the material that appeared to have the highest affinity for alcohol based on pure solvent swelling experiments (Figure 1), illustrating the necessity of the mixed-solvent swelling measurements. Figure 5 shows the measured equilibrium selectivity ($\alpha_a^*$) for all samples in 100 g/L ethanol (aq). The most selective materials for ethanol are the hydrophobic polymers having $x_M \approx 0$ and high $x_C$. The highest $\alpha_a^*$ values (about 15−20) were found for the samples with $x_M = 0$ (AA through KA in Table 1). The presence of hydrophobic (B) monomers discourages water from entering the network, leading to higher alcohol selectivity. As is often the case, there is a trade-off between selectivity and absorption capacity (the latter of which affects flux). The materials showing the highest selectivity for alcohol also absorbed the least amount of mixed solvents at equilibrium.
Pervaporation Membrane Trials. In the next stage of screening, the solubility selectivity and swelling data are used to guide selection of promising materials for pervaporation tests. Here, two membranes were fabricated and tested in order to evaluate $\alpha_a$ and ethanol flux. Sample KK from Table 1 (HEA homopolymer) was selected to represent a highly swelling material, and sample KD from Table 1 (30% HEA copolymer) was selected to represent a membrane with higher equilibrium ethanol selectivity. The selection of materials for further testing is somewhat subjective, as permeability selectivity is not known quantitatively beforehand.

Batch pervaporation with 100 g/L ethanol as the starting material was conducted in this study, and $\alpha_a$ was calculated by periodically measuring the residual concentration of ethanol in the remaining liquid (raffinate) by HPLC. Conducting membrane testing by unsteady-state, batch pervaporation can provide additional information about the concentration dependence of $\alpha_a$ as the ethanol concentration in the feed becomes depleted.

For experimental convenience, pervaporation was conducted with very thick (5 mm) membranes. Practical applications benefit from thin membranes (for example, silicone membranes less than 50 μm thick are typical), which provide higher flux. Here, composite membranes were produced by cross-linking the polymers inside a 5 mm thick glass frit filter with pore size of approximately 10 to 15 μm, which provided a mechanically robust membrane. In each membrane, a solvent (dimethyl sulfoxide for KK and 2-butoxyethanol for KD) was added during cross-linking in order to leave space for swelling of the polymer with water and ethanol inside the pores. Solvents of low volatility were selected to discourage evaporation during polymerization at elevated temperature. The solvent used during cross-linking was completely extracted out by soaking the membranes in 100 g/L ethanol in water prior to use; no trace of 2-butoxyethanol or dimethyl sulfoxide was detected in subsequent HPLC experiments.

Figure 6 shows the results of a pervaporation trial at 55 °C with the membrane fabricated from material KD, which has $x_H = 0.3$, $x_C = 0.0105$, and $x_B = 0.6895$. The starting concentration of ethanol was 100 g/L. The calculated concentration of ethanol in the permeate was initially 280 g/L, but it dropped gradually to 240 g/L (on the basis of condensed liquid) over a period of 100 h. The initial flux of ethanol in this membrane (6.0 g m⁻² h⁻¹) at the start of the experiment was comparatively low because of the material’s low swelling capacity in the dilute ethanol–water mixture. The initial flux of water was 15.2 g m⁻² h⁻¹, yielding an initial permeability selectivity of 3.6 by eq 8. Permeability selectivity remained within the range 3.6 to 4.0 during the course of the pervaporation test.

Figure 7 shows the results of the second pervaporation trial at 55 °C with the membrane fabricated from material KK, which has $x_H = 0.9895$, $x_C = 0.0105$, and $x_B = 0.0$. The calculated concentration of ethanol in the permeate dropped from 182 to

**Figure 4.** Experimentally determined distribution coefficient of water ($k_w$) for copolymer networks immersed in 100 g/L ethanol (aq) (initial concentration).

**Figure 5.** Experimentally determined equilibrium selectivity for ethanol ($\alpha_a^*$) for copolymer networks immersed in 100 g/L ethanol (aq) (initial concentration).

**Figure 6.** Pervaporation trial with composite membrane based on material KD in Table 1, which exhibits good selectivity for ethanol, but swells to a low degree in 100 g/L ethanol compared to material KK.
The matrix-based synthetic approach is most readily applicable to polymerization processes that can be accomplished in a single step in the liquid state without requirements for extreme purity, complex apparatus, or secondary processing. It is easily extensible to other acrylate and methacrylate monomers, step-growth polymers, styrenic monomers, “click” reaction polymerizations, and hydrosilylation-cure silicone systems. This range of polymerization chemistries provides a diverse array of materials candidates that can be screened for performance in pervaporation processes.

Pure solvents and their mixtures were studied in this work for illustrative purposes, but the methods were developed with the more complex mixtures derived from fermentations in mind. The swelling and HPLC techniques are still applicable to these mixtures with minimal modifications. With addition of suitable characterization techniques, the screening method could be extended to evaluate other important membrane characteristics such as resistance to fouling.

## EXPERIMENTAL PROCEDURES

### Synthesis of Test Matrix Samples

Polyacrylate networks were synthesized by thermally initiated, bulk free radical polymerization of a mixture of 2-hydroxyethyl acrylate (96%, Aldrich), n-butyl acrylate (≥99%, Aldrich), cross-linker pentaerythritol tetraacrylate (PETA, 10%–40% triester, Aldrich), and initiator 2,2’-azobis(isobutyronitrile) (AIBN, 98%, Aldrich). Acrylate monomers initially contained hydroquinone monomethyl ether as inhibitor, which was removed by passing them through a Sigma-Aldrich 306312-IEA column. The concentration of AIBN in all samples was 0.5 mass % of the total mixture. AIBN was dissolved into each monomer immediately before mixing of the components.

Samples were prepared by pipetting calculated volumes of monomers and cross-linker into an 11 × 11 matrix of 1.8 mL sealed glass vials. Dilute stock solutions of the initiator (AIBN) and cross-linker (PETA) were prepared beforehand in one of the monomers to aid in dispensing small quantities of these reagents accurately with a pipet or with a 10 μL syringe. The composition of each sample was mapped to a two-dimensional parameter space. The rows and columns of the sample matrix had orthogonal gradients in the mole fraction of reactive groups belonging to cross-linker (xC) and the mole fraction of acrylates belonging to the hydrophilic monomer (xH), respectively. The range of xC covered was from 0.0005 to 0.0105 in increments of 0.001. xH ranged from 0 to 0.9895 in increments of approximately 0.1. All of the samples had the same initial volume (1500 μL) and were cured at 47 °C in a temperature-controlled water bath overnight. Care was taken to prevent water from entering the sample containers.

For swelling-based analysis, the networks cannot contain bubbles that might affect measurement of equilibrium swelling. Bubble formation was minimized by conducting polymerizations in sealed containers under slightly elevated pressure. Because of the exothermic nature of acrylate polymerizations, the temperature of the monomer/polymer mixture can greatly exceed the temperature of the surroundings, leading to unexpected boiling and pressurization. The temperature rise is an important safety consideration when acrylate polymerizations are conducted in bulk, especially in sealed containers; a solvent can optionally be added to act as a heat sink. For the system studied, only a minimal amount of bubbles formed at the tops of a few samples after polymerization in a reservoir at 47 °C. In these cases, bubbles were eliminated by trimming a...
piece from the sample prior to conducting swelling experiments.

**Swelling Experiments in Pure Solvents.** Each sample was immersed in a comparatively large volume of ethanol and swollen at room temperature until equilibrium mass \( M_e \) was reached (generally 3 to 5 d). The ethanol was replaced daily to remove any dissolved, extractable components. Drying was accomplished by placing the gel in air for 2 d, followed by drying under vacuum until the mass of the sample reached an equilibrium value \( M_0 \). The soluble mass fraction \( (\omega_{\text{sol}}) \) of each sample was then determined by comparing the original, unextracted mass \( M_0 \) to \( M_e \).

\[
\omega_{\text{sol}} = 1 - \frac{M_\text{ex}}{M_0} \quad (1)
\]

Dried samples were reswollen in pure solvents to determine their equilibrium swelling ratios. The mass equilibrium swelling ratios of \( (Q_{se}) \) and \( Q_{sw} \) of each network in ethanol and water were calculated according to eq 2.

\[
Q_{se} = \frac{M_{se}}{M_s} \quad \text{and} \quad Q_{sw} = \frac{M_{sw}}{M_s} \quad (2)
\]

In eq 2, \( M_{se} \) and \( M_{sw} \) are the swollen masses at equilibrium in pure ethanol and pure water, respectively.

**Swelling in Mixed Solvents: HPLC Analysis.** Extracted networks were soaked in a precisely measured volume of 10.05 wt % (100 g/L) ethanol (aq) for several days in a sealed vial with minimal air space. The mass of liquid added to each vial was 1.5 times the dry mass of the polymer. After several days, the ethanol concentration in the external liquid was measured by HPLC and the swollen mass of the polymer network was recorded. In cases where all of the solvent mixture is absorbed by HPLC and the swollen mass of the polymer network was reached (generally 3 to 5 d). The ethanol was replaced daily to remove any dissolved, extractable components. Drying was accomplished by placing the gel in air for 2 d, followed by drying under vacuum until the mass of the sample reached an equilibrium value \( M_0 \). The soluble mass fraction \( (\omega_{\text{sol}}) \) of each sample was then determined by comparing the original, unextracted mass \( M_0 \) to \( M_e \).

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An “equilibrium selectivity” \( \alpha_s^* \) is defined as the selectivity of the network for alcohol when swollen to thermodynamic equilibrium in the water/alcohol mixture.

\[
\alpha_s^* = \frac{\alpha_{sw} \omega_{sw}}{\alpha_{se} \omega_{se}} = \frac{k_s}{k_w} \quad (6)
\]

In eq 7, the diffusivities of water and alcohol are taken as average or effective values over the membrane, including the effects of concentration dependence.

For a membrane separation an alcohol–water mixture, \( \alpha_s \) is related to the concentrations of alcohol and water in the permeate (vapor) and raffinate (remaining liquid) by eq 8.

\[
\alpha_s = \frac{(C_A/C_W)_{\text{permeate}}}{(C_A/C_W)_{\text{raffinate}}} \quad (8)
\]

For the membrane experiments in this report, the instantaneous value of \( \alpha_s \) was calculated from eq 8 based on knowledge of the concentration of alcohol in the raffinate (from HPLC) and the mass of the liquid remaining in the raffinate.

**Membrane Fabrication and Pervaporation Experiments.** Two composite pervaporation membranes were fabricated by curing the polyacrylate materials inside the pores of a medium porosity glass frit housed inside a 60 mL filtration funnel (Synthware, SYN6F04060M). Average pore size quoted by the supplier was 10 to 15 μm and the thickness of the fritted disks was 5.0 mm. Supporting the polymers inside a porous glass disk provides mechanical stability and avoids issues of swelling and warping associated with highly swelling polymers. To leave enough space for the polymer to swell in ethanol–water mixtures, a solvent was added to the polymers prior to curing. Material KK (Table 1, cross-linked HEA copolymer) was cured in 66% w/w dimethyl sulfoxide, whereas material KD (Table 1, 30% HEA copolymer) was cured in 100% dimethyl sulfoxide and mixed with 2 wt % of the cross-linking agent DVB (Table 1). The supporting medium porosity glass frit was fabricated by curing the polyacrylate materials inside the pores of a medium porosity glass frit housed inside a 60 mL filtration funnel (Synthware, SYNF604060M). Average pore size quoted by the supplier was 10 to 15 μm and the thickness of the fritted disks was 5.0 mm. Supporting the polymers inside a porous glass disk provides mechanical stability and avoids issues of swelling and warping associated with highly swelling polymers. To leave enough space for the polymer to swell in ethanol–water mixtures, a solvent was added to the polymers prior to curing. Material KK (Table 1, cross-linked HEA copolymer) was cured in 66% w/w dimethyl sulfoxide, whereas material KD (Table 1, 30% HEA copolymer) was cured in 100% dimethyl sulfoxide and mixed with 2 wt % of the cross-linking agent DVB (Table 1).
cured in 4% w/w 2-butoxyethanol. Solutions of the monomers and initiators were degassed and purged with nitrogen, added to preheated glass frits and cured under nitrogen. The polymerization temperature was 50 °C for material KK and 95 °C for material KD. Membranes thus obtained were extracted in a large volume of 100 g/L aqueous ethanol prior to conducting pervaporation tests in order to extract the solvents and soluble fraction and swell the material to equilibrium in the ethanol–water mixture.

Pervaporation tests were conducted at 55 °C after adding 29.0 g of 100 g/L ethanol (aq) to the top portion of the filter funnel, sealing the top of the funnel with aluminum foil to prevent evaporation, and equilibrating the apparatus in an oven for 1 h at 55 °C. The bottom surface of the membrane was thereafter placed under vacuum, corresponding to the start of pervaporation, and 50 μL samples of the raffinate liquid were taken with a syringe at regular intervals for HPLC analysis without removing the Al foil cover. Standard solutions of ethanol ranging from 40 to 100 g/L were used to calibrate the HPLC system. The entire apparatus was weighed periodically to determine the total mass of water and ethanol lost through the membrane. Instantaneous permeate concentrations reported were calculated based on mass balances on the system.

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Notes
The authors declare no competing financial interest.

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■ REFERENCES