Selective Recovery of n-Butanol from Aqueous Solutions with Functionalized Poly(epoxide ionic liquid)-Based Polyurethane Membranes by Pervaporation

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ABSTRACT: In this study, hydroxyl-terminated polybutadiene–poly(epoxide ionic liquid)–poly(urethane urea) (HTPB-PEIL-PU) membranes, HTPB-PEIL1-PU and HTPB-PEIL2-PU, were prepared by the reaction of functionalized PEIL, poly(1-methylimidazole-3-methyl-ethyloxy)hexafluorophosphate or poly(1-methylimidazole-3-methyl-ethyloxy)bistrifluoromethanesulfonimide, respectively, with HTPB using 4,4′-diphenylmethane diisocyanate (MDI) as the chain extender. The HTPB-PEIL-PU and HTPB membranes were investigated for the selective recovery of n-butanol from aqueous solutions by pervaporation. PEIL was confirmed to be successfully embedded in the PU membranes by 1H NMR, Fourier transform infrared, and differential scanning calorimetry measurements. According to our mechanical measurements, the HTPB-PEIL-PU membranes retain the mechanical properties of the original PU membrane. PEIL was shown to enhance the diffusion rate of n-butanol significantly based on swelling behavior tests. The pervaporation flux through the HTPB-PEIL1-PU membrane increased with increasing feed temperature and feed concentration. In contrast, the separation factor of the HTPB-PEIL1-PU membrane increased with increasing feed temperature but decreased with increasing feed concentration. In addition, the HTPB-PEIL2-PU membrane exhibited an optimal separation factor of up to 29.2 at a feed concentration of 3% and a feed temperature of 70 °C, which is superior to that (22.7) through pure HTPB membranes. Furthermore, the HTPB-PEIL1-PU and HTPB-PEIL2-PU membranes show better long-term stability than other supported ionic liquid membranes.

1. INTRODUCTION

n-Butanol is an important fine chemical that is extensively used in the areas of medicine and chemical engineering, as well as coating industries. In addition, several large chemical industry enterprises have been established to commercialize biobutanol.1,2 However, a drawback of commercial biobutanol production is that the concentration of biobutanol in the fermentation broth is very low, and this is a bottleneck problem in the separation and purification process.3 The main methods of dealing with n-butanol from aqueous solutions are distillation, absorption, gas stripping, and liquid–liquid extraction. Unfortunately, these methods require significant energy or are complex, which restricts their broader application.

Pervaporation has gained popularity in the past few years because of its superiority in removing trace organics from aqueous solutions.4–7 Compared with other methods of separating organic wastewater, pervaporation has many advantages such as device simplicity, environmentally friendly operation, low cost, and low energy consumption.8,9 Many polymer materials such as polydimethylsiloxane (PDMS), zeolite or silicalite-filled siloxane, polyether block amide, and poly(urethane urea) (PU) have been shown to have greater affinity for n-butanol than water in pervaporation.10–14

Because of their excellent ability to solubilize a large range of organic molecules, as well as their thermal stability, ionic liquids (ILs) are an important substitute for classical organic solvents.15,16 ILs can be filled into the pores of porous membranes, forming so-called supported ionic liquid membranes (SIMs). SIMs have several merits; for example, molecular diffusion is enhanced by the appropriate choice of IL components and is much higher in ILs than in polymers.17–19 Thus, many studies concerning pervaporation by SIMs have been reported, particularly because SIMs exhibit high fluxes and excellent separation. Plaza reported20 sweep gas pervaporation with gelled SIMs prepared by gelating [bmim][PF6] into porous polytetrafluoroethylene hollow fibers. Heitmann utilized21 SIMs filled with tetracyanoborate and triis(pentafluorophenyl)trifluorophosphate ILs for pervaporation.

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Cascon used SILMs to recover \( n \)-butanol from dilute aqueous solutions by pervaporation, and hydrophobic ammonium- and phosphonium-based room temperature ILs were used as the liquid fillers in the SILMs. The abovementioned studies of SILMs for pervaporation all demonstrate their good pervaporation performance.

However, the ILs in SILMs are easily and gradually lost with increasing experimental time. Thus, a kind of solidified poly(epoxide ionic liquid) (PEIL)-based polyurethane membrane has been designed to improve membrane stability and maintain the good separation performance of the ionic liquid. To date, this concept has not been investigated in depth. In this study, these novel PEIL-based polyurethane membranes were prepared for pervaporation as follows: (1) first, polyepichlorohydrin (PECH) was produced by the ring opening polymerization of epichlorohydrin (ECH) and was subsequently reacted with \( n \)-methylimidazole and potassium hexafluorophosphate (KPF\(_6\)) or lithium difluoromethane sulfonylimide (LiTf\(_2\)N), thus yielding PEIL. Thus, hydroxyl groups on both sides of polymer chains are introduced via these processes. (2) Second, to obtain the desired structure and good performance of the polyurethane membrane, isocyanate was reacted with the hydroxyl groups of PEIL and 1,4-butanediol (BDO) was used to extend the chains. In addition, the separation performance and the stability of PEIL-based polyurethane membranes was measured and evaluated for the pervaporation of \( n \)-butanol/water solution.

In this paper, we report a new kind of solidified PEIL-based polyurethane membrane for pervaporation. This membrane solves several serious defects of SILMs, such as low load capacity and easy release of ILs, and could increase the efficiency of the industrial separation of \( n \)-butanol.

2. RESULTS AND DISCUSSION

2.1. \(^1\)H NMR Analysis. The \(^1\)H NMR spectra of PECH, PEIL1, and PEIL2 in Figure 1 confirm the presence of the introduced H-containing groups. As shown in Figure 1, the signals for protons at 3.36 and 2.50 ppm are the absorption peaks of dimethyl sulfoxide (DMSO). The \(^1\)H NMR spectra show that the peaks at 8.95, 7.70, and 7.60 ppm emerge, as shown in Figure 1b,c. These peaks are attributed to the protons of \( n \)-methylimidazole introduced into PECH through the quaternization reaction. The strong resonance absorption peaks at 3.65 ppm in Figure 1a are assigned to \(-\text{CH}_2\text{Cl}\), but the corresponding peaks are weakened in the spectra as shown in Figure 1b,c because \(-\text{Cl}\) has been replaced by an imidazole ring. The spectra in Figure 1b,c are similar because of similar frameworks. The above data confirm that \( n \)-methylimidazole had been grafted onto the PECH chain successfully.

2.2. FTIR Analysis. Figure 2 shows the Fourier transform infrared (FTIR) spectra of PECH, PEIL1, and PEIL2. For PECH, the strong absorption peak at 1128 cm\(^{-1}\) is attributed to the C–O–C stretching vibration. The absorption peaks observed at 2875 and 748 cm\(^{-1}\) are assigned to the \(-\text{CH}_2\) and the C–Cl group stretching vibrations, respectively. An intense \(-\text{OH}\) vibration is observed at 3475 cm\(^{-1}\). For PEIL1, the C–Cl absorption peak is weakened and replaced by those corresponding to the vibrations of the imidazole ring at 1570 and 1450 cm\(^{-1}\), which indicates that the quaternization reaction was successful. The absorption peak at 836 cm\(^{-1}\) is assigned to the P–F stretching vibration. For PEIL2, peaks at 1195 and 1350 cm\(^{-1}\) correspond to the C–F symmetric and asymmetric vibrations.

![Figure 1. \(^1\)H NMR spectra of (a) PECH, (b) PEIL1, and (c) PEIL2.](image1)

![Figure 2. FTIR spectra of PECH, PEIL1, and PEIL2.](image2)
stretching vibrations, respectively. These findings are consistent with the \(^1\)H NMR results.

Figure 3 shows the FTIR spectra of the hydroxyl-terminated polybutadiene (HTPB)-PU, HTPB-PEIL1-PU, and HTPB-PEIL2-PU membranes. In Figure 3, the absorption peaks at 1705 and 1531 cm\(^{-1}\) are attributed to C=O and N=C stretching vibrations, respectively, which proves the formation of the urethane group (\(-\text{NHCOO}–\)). However, in the spectrum of the HTPB-PEIL1-PU membrane, a strong P-F stretching vibration at 840 cm\(^{-1}\) appears because of the successful introduction of PEIL1 into HTPB-PU. Meanwhile, peaks at 1203 and 1353 cm\(^{-1}\) corresponding to the C-F symmetric and asymmetric stretches, respectively, are observed in the spectrum of the HTPB-PEIL2-PU membrane, which confirms that PEIL2 molecules are cross-linked with HTPB and 4,4'-diphenylmethane diisocyanate (MDI).

2.3. Differential Scanning Calorimetry Analysis. Table 1 lists the glass transition temperature (\(T_g\)) of different samples.

Table 1. Glass Transition Temperature of Different Samples

| samples          | \(T_g/\degree C\) |
|------------------|-------------------|
| PEIL1-PU         | 63.54             |
| PEIL2-PU         | 48.96             |
| HTPB-PEIL1-PU    | 48.96             |
| HTPB-PEIL2-PU    | -15.29            |

The \(T_g\) values of PEIL1 and PEIL2 are 63.54 and -8.56 °C, respectively, so they are solid and liquid at room temperature, respectively. A \(T_g\) value could not be obtained for HTPB-PU because the heating range used was -50 to 150 °C, whereas the theoretical \(T_g\) value of HTPB-PU is around -75 °C.\(^3\) However, new \(T_g\) values were observed for both the HTPB-PEIL1-PU membrane (48.96 °C) and HTPB-PEIL2-PU membrane (-15.29 °C) after PEIL1 and PEIL2 had been introduced into the HTPB-PU membrane. These \(T_g\) values are both lower than the \(T_g\) value of primary PEIL. The above changes in the \(T_g\) values may be attributed to microphase separation. When the hard segments of PEIL are connected with the soft segments of HTPB by MDI the membrane has poor compatibility, which results in the new \(T_g\) values of the HTPB-PEIL-PU membranes.

2.4. Mechanical Properties. Tensile testing was performed on the HTPB-PU, HTPB-PEIL1-PU, and HTPB-PEIL2-PU membranes, and the analytical results are shown in Figure 4 and Table 2. The tensile strength of HTPB-PEIL2-PU is almost the same as that of the initial PU membrane, whereas that of HTPB-PEIL1-PU dropped by just 13.7%. Compared with the elongation at the break of HTPB-PU (1688.5%), that of HTPB-PEIL1-PU dropped to 1307.8%, whereas that of HTPB-PEIL2-PU increased to 1557.8%. The above phenomenon is due to the addition of the crisper PEIL. The modified HTPB-PU maintained its excellent mechanical properties in the solid PU membranes; thus, the new material could be used for the subsequent pervaporation experiments.

2.5. Swelling Properties of the Membranes and Diffusion Coefficients. Figure 5 shows the different swelling behaviors of the membranes in pure n-butanol and water. The degrees of equilibrium swelling in pure n-butanol are 14.33, 12.57, and 11.43% for the HTPB-PU, HTPB-PEIL1-PU, and HTPB-PEIL2-PU membranes, respectively. The equilibrium swelling times for the HTPB-PEIL1-PU and HTPB-PEIL2-PU membranes in pure n-butanol are almost two times lower than that of the original HTPB-PU membrane. However, the above membranes seem not to swell in water, which indicates that the membranes are suitable for the separation of n-butanol from water.

The diffusion coefficient for Fickian diffusion can be obtained using eq 1.\(^28\)

\[
W_c(\infty) = W_c(0) - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp \left( -\frac{D(2n+1)^2 \pi^2 t}{l^2} \right)
\]

where \(W_c\) and \(W_{c0}\) are the sorption mass at equilibrium and at time \(t\), respectively, and \(l\) is the thickness of the dried membrane. The application of eq 1 requires the following conditions: (a) steady-state operation; (b) minimal external mass and heat-
transfer resistance (by achieving a sufficiently high flow rate on both sides of the membrane); thus, only intraparticle diffusion is considered; and (c) the reactor external wall is adiabatic.

Equation 1 can be simplified into eq 2 by truncation at the first term in the summation.

\[
\frac{W_f}{W_c} = 1 - \frac{8}{\pi^2} \exp\left(-\frac{D\pi^2}{l^2}\right)
\]

(2)

According to the hypothesis that the diffusion coefficient is constant, eq 2 can be rewritten as eq 3.

\[
\ln\left(1 - \frac{W_f}{W_c}\right) = -D\pi^2 \left(\frac{t}{l^2}\right) + \ln\frac{8}{\pi^2}
\]

(3)

The graph of \(\ln(1 - W_f/W_c)\) as a function of \(t/l^2\) is a straight line within the normal limits of experimental error. Therefore, the diffusion coefficient can be acquired from the slope of the straight line. The linear relationship of \(\ln(1 - W_f/W_c)\) versus \(t/l^2\) for n-butanol through different membranes is shown in Figure 6.

The diffusion coefficients for n-butanol through different membrane samples were calculated according to the slopes of different lines in Figure 6 and are listed in Table 3. It was found that the diffusion coefficient through the HTPB-PEIL1-PU membrane is more than double that through the initial membrane. In addition, the HTPB-PEIL2-PU membrane exhibits the highest diffusion coefficient (\(2.475 \times 10^{-11} \text{ m}^2 \cdot \text{s}^{-1}\)) of the three membranes. Thus, the introduction of PEIL, especially PEIL2, can significantly enhance the diffusion rate of n-butanol.

2.6. Pervaporation Experiment Results. Figure 7 shows the effects of the feed concentration and feed temperature on the permeation flux of the HTPB-PEIL1-PU membrane at a fixed downstream pressure of 1000 Pa. It was observed that the permeation flux of the HTPB-PEIL1-PU membrane significantly increased with increasing feed temperature. The permeating molecules diffuse through the free volume of the membrane in the pervaporation process. Free volume is randomly produced in amorphous regions by the thermal motion of the polymer chains. The amplitude and frequency of polymer chain jumping increase with increasing feed temperature, resulting in larger free volumes in the membrane. At the same time, the mobility of the permeating molecules is improved. Therefore, the diffusion rate of each permeating molecule increases with increasing feed temperature, which leads to higher flux.

Meanwhile, the pervaporation flux at feed concentrations of 5% through the membranes is much higher than that at feed concentrations of 3 and 1%. The relationship between the concentrations in the two phases (vapor–liquid) with permeation flux is shown in eq 4 for the recovery of volatile organic compounds (VOCs) from aqueous solution.

\[
J = K\rho(1 - C_l/C_v)
\]

(4)

Table 3. Diffusion Coefficient for n-Butanol through the Three Membranes

| Membrane          | Diffusion Coefficient (m²·s⁻¹) |
|-------------------|-------------------------------|
| HTPB-PU           | 0.746 \times 10^{-11}         |
| HTPB-PEIL1-PU     | 1.745 \times 10^{-11}         |
| HTPB-PEIL2-PU     | 2.475 \times 10^{-11}         |

*Swelling temperature is 25 °C.
where $K_i$ (m s$^{-1}$), $\rho$ (mol m$^{-3}$), $(C)_L$ (dimensionless), and $(C)_V$ (dimensionless) denote the coefficient of total mass transfer rate, feed total molar density, concentration of bulk liquid phase (mole fraction), and concentration of bulk vapor phase (mole fraction), respectively, for component $i$. $(C)_L$ is dominant because it is much larger than $(C)_V$. As a result, increasing the feed concentration will lead to enhanced permeation flux. The above effects of feed temperature and feed concentration on the pervaporation performance in Figure 7 are similar to those reported by Dong and Choudhari.$^{29,30}$

Figure 8 shows the effects of the feed concentration and temperature on the separation factor of the HTPB-PEIL1-PU membrane at a fixed downstream pressure of 1000 Pa. The separation factor of the HTPB-PEIL1-PU membrane increased with increasing temperature. This is attributed to the increase in the amplitude and frequency of the polymer chain jumping with increasing feed temperature, which results in the fluxes of $n$-butanol and water increasing simultaneously. However, for PU membranes, the selectivity for $n$-butanol is greater than that for water. This can be explained by the Arrhenius equation, eq 5.$^{5}$

$$J_i = J_{i,0} \exp \left( -\frac{E_i}{RT} \right)$$

where $E_i$ is the activation energy, $J_i$ is the solute flux, and $J_{i,0}$ and $R$ are both constants.

Figure 9 shows Arrhenius plots of $\ln J$ versus $1/T$ for the HTPB-PU, HTPB-PEIL1-PU, and HTPB-PEIL2-PU membranes at a fixed concentration of 3% and a downstream pressure of 1000 Pa. According to the slopes of the Arrhenius plots, the permeation activation energies of $n$-butanol through the HTPB-PU, HTPB-PEIL1-PU, and HTPB-PEIL2-PU membranes are 58.68, 60.99, and 62.69 kJ mol$^{-1}$, respectively, and those of water are 9.17, 18.21, and 19.44 kJ mol$^{-1}$, respectively. The larger permeation activation energy of $n$-butanol than that of water reveals that the $n$-butanol permeation flux is more sensitive to increasing temperature than the water permeation flux.

The separation factor at feed concentrations of 1 and 3% through the membranes is much higher than that in feed concentrations of 5%. HTPB-PEIL1-PU has a strong affinity for $n$-butanol, so the $n$-butanol flux increases with increasing feed concentration. Nevertheless, because there is a coupling effect between water and $n$-butanol during pervaporation and water molecules penetrate the membranes along with $n$-butanol, there is a reduction in the separation factor.

However, the separation factors at feed concentrations of 1 and 3% are similar. Combining the excellent permeation flux results shown before, 3% was chosen as the optimal feed concentration for our subsequent experiments.

Figure 10 compares the flux and separation factors of HTPB-PU, HTPB-PEIL1-PU, and HTPB-PEIL2-PU membranes at a fixed concentration of 3% and downstream pressure of 1000 Pa. It is demonstrated that the separation factors of the three membranes under the same pervaporation conditions can be ranked in the following order: HTPB-PEIL2-PU > HTPB-PEIL1-PU > HTPB-PU. The introduction of the ionic liquid into the HTPB-PEIL2-PU membranes makes it more hydro-
phobic than the HTPB-PU membrane itself. As n-butanol and water molecules pass the membrane, a large number of water molecules are blocked by the membrane. In addition, as demonstrated in Figure 5, the diffusion rate of n-butanol molecules is much faster through the modified membranes than that through the initial HTPB-PU membrane. As shown in Figure 10, HTPB-PEIL2-PU shows better separation performance than HTPB-PEIL1-PU because of the stronger hydrophobicity of the Tf$_2$N$^-$ groups in the former compared with the PF$_6$ groups in the latter. Izak reported that the diffusion coefficients of n-butanol in 1-ethyl-3-ethyl-imidazolium hexafluorophosphate-PDMS exceed those in PDMS alone. The enrichment factors and superior permeation flux of n-butanol in IL-PDMS result from the higher diffusion coefficient. Uragami reported that when aqueous solutions of 0.05 wt % VOCs permeated through poly(styrene)-b-poly-(dimethylsiloxane) (PSt-b-PDMS) membranes containing 1-allyl-3-butylimidazoliumbis(trifluoromethane sulfonylimide (ABIM)TFSI) ionic liquid ([ABIM]TFSI/PSt-b-PDMS), the prepared membranes had strong VOC/water selectivity. The separation performance of the [ABIM]TFSI/PSt-b-PDMS membranes was enhanced by increasing the [ABIM]TFSI content. All the above results indicate that the introduction of a hydrophobic ionic liquid is very helpful for the absorption of organic compounds.

On the other hand, the permeation fluxes through the three membranes show the opposite trend to that of the separation factor. It is obvious that PEIL has a strong affinity for n-butanol but is incompatible with water; thus, the total fluxes of the n-butanol aqueous solution at low feed concentrations through the HTPB-PEIL2-PU and HTPB-PEIL1-PU membranes are lower than that through the HTPB-PU membrane.

2.7. Membrane Stability. Figure 11 shows the pervaporation results for the HTPB-PEIL1-PU and HTPB-PEIL2-PU membranes after two weeks. Over the two week period, the used film was soaked in distilled water in a beaker, sealed with a plastic wrap, and kept at room temperature. The flux and separation factors at this time were maintained at almost the same values as those of the original membranes. Thus, the long-term stabilities of the HTPB-PEIL1-PU and HTPB-PEIL2-PU membranes were better than those of previously reported supported IL membranes, which may result from the strong interactions between the PEIL moiety and PU membrane because of covalent bonding.

3. CONCLUSIONS

In this study, HTPB-PEIL-PU membranes were prepared by the reaction of PEIL1 or PEIL2 with HTPB and MDI to improve the membrane stability and maintain good separation performance of the ionic liquid. The pervaporation recovery of n-butanol from aqueous solutions was investigated thoroughly. The results indicate that the permeation flux through the HTPB-PEIL1-PU membranes increases as the feed temperature and feed concentration increase. The separation factor of the HTPB-PEIL1-PU membranes increases with increasing feed temperature but decreases with increasing feed concentration. In addition, HTPB-PEIL2-PU exhibits an optimal separation factor of up to 29.2 at a feed concentration of 3% and a temperature of 70 °C compared to that of 22.7 through the pure HTPB membrane. Furthermore, it was found that the HTPB-PEIL1-PU and HTPB-PEIL2-PU membranes show better long-term stability than those of SILMs. Possibly, the solidified PEIL-based polyurethane membranes with good total flux and high n-butanol/H$_2$O selectivity may be an attractive alternative or supplement to conventional polymeric membranes and SILMs for the separation of n-butanol from water.

The selection and pairing of the types of anions and cations in ILs is one of the important factors affecting pervaporation performance; thus, a systematic study of the HTPB-PEIL-PU membranes with various types of IL anions and cations is required.

4. EXPERIMENTAL SECTION

4.1. Materials. LiTf$_2$N, KPF$_6$, n-methylimidazole, tin (IV) chloride (SnCl$_4$), trifluoroacetic acid (CF$_3$COOH), and MDI were purchased from Shanghai Aladdin Co., Ltd., China. ECH, BDO, ethylenediaminetetraacetic acid disodium salt (EDTA-Na$_2$), 1,2-dichloroethane, and methanol were procured from Shanghai Lingfeng Co., Ltd., China. The abovementioned reagents were of analytical grade and employed without further purification. Hydroxyl-terminated polybutadiene (HTPB, hydroxyl value = 0.68 mmol KOH g$^{-1}$) with a molecular weight of 2950 (M$_n$) was supplied by Shandong Zibo Qilong Co., Ltd., China. 1-Methyl-2-pyrrolidinone (NMP) and tetrahydrofuran (THF) solvents were supplied by Sinopharm Chemical Reagent Co., Ltd., China, dried with molecular sieves and distilled under nitrogen. Deionized water was used directly throughout the study.

4.2. Preparation of PEIL. 4.2.1. Synthesis of PECH. PECH was prepared by the ring opening polymerization of ECH as follows. First, 1.8 g BDO, 25 mL 1,2-dichloroethane, 0.234 mL SnCl$_4$, and 0.613 mL CF$_3$COOH as a co-catalyst were added to a flask. Secondly, 121.2 g ECH was added dropwise to the flask with stirring at 0−5 °C for 1 h. Afterward, the solution was kept stirring at 65−70 °C for another 2 h. Then, the reaction mixture was returned to room temperature, and 70 g of aqueous 10% methanol solution containing 0.8 g EDTA-Na$_2$ was added to terminate the reaction. The organic phase was extracted twice with 70 g of aqueous 10% methanol solution and concentrated by rotary evaporation under reduced pressure at 70 °C. The remaining viscous solution was dried for 24 h under vacuum at 90 °C. The synthetic process is shown in Scheme 1.
the reaction of PECH and n-methylimidazole in a Cl:n-methylimidazole molar ratio of 2:3 in nitrogen for 24 h at 100 °C.

Then, KPF₆ or LiTf₂N was added to the P[MIEO][Cl] aqueous solution in a PF₆⁻ (or Tf₂N⁻):Cl⁻ molar ratio of 1.2:1 with mechanical stirring for 2 h. The water-insoluble solid of poly(1-methylimidazole-3-methyl-ethyloxy)-hexafluorophosphate ionic liquid (P[MIEO][PF₆], PEIL1) or poly(1-methylimidazole-3-methyl-ethyloxy)-bistrifluoromethanesulfonimidate ionic liquid (P[MIEO][Tf₂N], PEIL2) was filtered out of aqueous solution after ion exchange. The filtered precipitates were rinsed several times with deionized water until the concentration of chlorine ions in the filtrate was below 5 mg L⁻¹. The products were dried under vacuum at 60 °C for 24 h in an oven. The synthetic process is also shown in Scheme 1.

4.3. Preparation of the HTPB-PEIL-PU Membrane. Prepolyurethane was synthesized by an −NCO-terminated reaction of HTPB, PEIL1 (or PEIL2), and MDI with an −OH:−NCO molar ratio of 1:2 at 80 °C for 1 h under nitrogen. BDO dissolved in NMP (or THF) was added to the prepolyurethane in an −OH:−NH₂ molar ratio of 1 for chain extension at 40 °C for 30 min, and the solvent content was kept at 70 wt %. Thus, the HTPB-PEIL-PU casting solution was obtained.

Then, the above casting solution was coated on glass plates after vacuum degassing and then exposed to air for cross-linking. Finally, the prepared membranes were put in an oven under vacuum and step-heated at 50 and 70 °C for 6 and 24 h, respectively. The thickness of the HTPB-PEIL-PU membrane was about 120 μm in this study. The preparation process is shown in Scheme 2.

4.4. Characterization. ¹H NMR spectra of PECH, PEIL1, and PEIL2 were recorded on an AVII-400 MHz spectrometer (Bruker Co. Ltd, Germany) using deuterated DMSO as an internal standard.

The chemical composition of the PECH, PEIL1, PEIL2, and HTPB-PU membranes, HTPB-PEIL1-PU membrane, and HTPB-PEIL2-PU membrane was analyzed using an FTIR spectrophotometer (NICOLET iS10, Thermo Electron Corporation, USA). Each spectrum was captured by averaging 32 scans at a resolution of 4 cm⁻¹.
The temperature of the feed solution was varied between 40 and 70 °C to explore the influence of feed temperature on mass transfer in the HTPB-PEIL1-PU membranes. The second set of test conditions had a fixed feed temperature and a downstream pressure of 1000 Pa, but the feed concentration was varied between 1 and 5 wt % to evaluate the influence of the feed concentration on the mass transfer in the HTPB-PEIL1-PU membranes. The third set of test conditions had a constant feed concentration of 3 wt % and a downstream pressure of 1000 Pa, but the feed temperature was varied between 40 and 70 °C to compare the pervaporation performance of the HTPB-PU, HTPB-PEIL1-PU, and HTPB-PEIL2-PU membranes.

The permeation flux (J) at the steady state depends on the weight (M_p) of the collected permeate and is given by eq 7.

\[ J = \frac{M_p}{At} \]  

where \( M_p \) denotes the weight of the collected permeate measured using an electronic balance (Mettler AT21, P. R. China), A is the effective membrane surface area and \( t \) is the test time interval for pervaporation.

The selective permeability of the membrane depends on the separation factor (\( \alpha \)), which is calculated using eq 8.

\[ \alpha = \frac{X_b/X_w}{Y_b/Y_w} \]  

where \( X \) denotes the weight fractions of the species in the feed and \( Y \) denotes the weight fractions of species in the permeate. The subscript “b” denotes n-butanol and “w” denotes water.

The concentration of the aqueous n-butanol solution was measured by preparing standard curves of the concentration versus the density. All measurements were carried out using a densitometer (Anton Paar DMA 5000, Austria) and measured in triplicate. Average values are presented.

**4.7. Membrane Stability Experiments**

After the pervaporation measurements on the HTPB-PEIL1-PU and HTPB-PEIL2-PU membranes had been performed, the membranes were immersed in distilled water. Two weeks later, the separation performance of the above samples was measured again for comparison.

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**Image 12.** Pervaporation experimental setup (1) calorstat (2) reservoir (3) thermometer (4) pump (5) rotometer (6) membrane cell (7) membrane (8) triple valve (9) refrigerator (10) liquid nitrogen cold trap (11) collecting bottle (12) vacuum.

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