PDMS with Tunable Side Group Mobility and Its Highly Permeable Membrane for Removal of Aromatic Compounds

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Abstract: Polydimethylsiloxane (PDMS), as the benchmark of organophilic membrane materials, still faces challenges for removal of aromatic compounds due to the undesirable transport channels. In this work, we propose to reconstruct the PDMS conformation with tunable side group mobility by introducing phenyl as rigid molecular spacer to relieve steric hindrance of large-sized aromatic molecules; meanwhile, polymer segments are loosely stacked to provide additional degrees of freedom as increasing the permeant size. Moreover, the reconstructed PDMS is engineered into the composite membrane with prevention of condensation of aromatic compounds in the substrate pores. The resulting thin-film composite membrane achieved one order of magnitude higher flux (11.8 kg m\(^{-2}\) h\(^{-1}\)) with an equivalent separation factor (12.3) compared with the state-of-the-art membranes for aromatic removal. The permeant-customized membrane molecular and microstructure designing strategy opens a new avenue to develop membranes for specific separation targets.

Introduction

Efficient removal or recovery of volatile organic compounds (VOCs) from aqueous solution has significant environmental and economic value.[9] Aromatic compounds are a typical kind of VOCs with high boiling point and large molecule size. On the one hand, aromatics such as phenol and its derivatives pose threats to public health and aquatic ecosystems. On the other hand, aromatic alcohols such as 2-phenylethanol are high-value natural flavor and fragrance compounds. Selective removal of aromatic compounds currently involves distillation, solvent extraction and adsorption, showing considerable energy-intensity and complex post-treatment.[9] Alternatively, pervaporation membrane technology served as an energy-efficient process is widely used in separation of organic–water[10] or organic–organic mixtures.[9] The separation performance of the pervaporation process relies on the preferential sorption and diffusion of the components in the membrane materials. Therefore, the pervaporation process can overcome the limitation of thermodynamic vapor–liquid equilibrium and consume less energy as only the latent heat of evaporation is required compared with distillation separation.[9] In addition, a pervaporation process that can be operated at moderate temperature is favorable for purification of thermally sensitive organics such as aromatic substances in food industry.

Membranes with highly permeable and selective transport properties are the key component to implement the pervaporation separation process. As the benchmark of organophilic membrane materials, polydimethylsiloxane (PDMS) has been widely studied for VOCs removal.[11] In the past two decades, increasing attention has been paid to developing various approaches to modify the PDMS membrane, and efforts have been successful in promoting selective permeation of small molecules (e.g., ethanol, butanol) over water molecules.[11] However, PDMS-based membranes still face challenges for fast and selective transport of aromatic compounds (e.g., phenol, 2-phenylethanol) with much bigger molecule size over these C\(_{1-4}\) alcohols. On the one hand, chemical modifications of the PDMS membrane have mainly focused on improving the affinity towards organic compounds to enhance the preferential sorption of the permeation process. However, these result in excessive swelling of polymer chains and lead to a deterioration of the membrane selectivity and stability. On the other hand, incorporation of inorganic fillers (e.g., MFI zeolite,[12] ZIF-8 metalorganic framework[13]) with well-defined pores showed great potential in highly enhancing the selective permeation of the PDMS membrane towards C\(_{1-4}\) alcohols. Unfortunately, the pore size of the known inorganic fillers is generally less than 0.5 nm, which is too small to provide fast transport channels for large-sized aromatic molecules. Therefore, the undesirable transport channels in current PDMS-based membranes, resulting from either intrinsic free volume of the polymer chains or incorporated porous fillers, failed to afford efficient and selective permeation of aromatic molecules. Besides, of the materials designed, the membranes for pervaporation removal of aromatic compounds were generally micron-thick or fabricated on arbitrary substrates. The resulting high transport resistance in the selective layer or substrate layer led to unattractive permeation flux for practical aromatic removal processes.

We hypothesized that the permeation of large-sized aromatics through PDMS is not only determined by the free volume cavities that is common for small-sized C\(_{1-4}\) alcohols, but is also affected by the side group mobility for which there is a lack of understanding and manipulation methods.
Herein, we proposed to introduce rigid side groups into the PDMS chains as molecular spacers to tune the mobility and packing of side groups and main chains, thereby creating a selective transport highway for aromatic molecules through the membrane. As illustrated in Figure 1, \( p \)-dimethyl side groups on the main chain (Si–O–Si) of PDMS are partially replaced by \( p \)-diphenyl groups that act as the rigid molecular spacers between the adjacent polymer chains. As a result, the chain distance can be enlarged, allowing the remaining methyl side groups on the main skeleton higher mobility due to the lower steric hindrance. Meanwhile, the bulky phenyl side groups are expected to suppress the cooperative motion of the main skeleton and thus the entanglement of polymer chains. Therefore, lower resistance and additional degrees of freedom could be offered to transport aromatic molecules whose size is very close to the free volume size of the polysiloxane chains, thereby promoting the membrane permeation towards large-sized aromatic compounds. Furthermore, the PDMS with reconstructed molecular structure was engineered into a submicron-thick thin-film composite membrane with a highly reduced transport resistance to break the trade-off between the permeation flux and the separation factor that exists in state-of-the-art membranes for aromatic removal from water.

**Results and Discussion**

The flexibility between the main backbone (Si–O–Si) and two side groups (–CH\(_3\)) promotes polymer chains of PDMS stacking as a highly tangled structure. Regards membrane separation, the PDMS polymer is often crosslinked by tetraethoxysilane to form a crosslinked network for molecular transport. In this work, to reconstruct the polymer structure and tune the membrane transport properties, we replaced some of the \( p \)-dimethyl side groups in PDMS with \( p \)-diphenyl groups that act as rigid molecular spacers in the polysiloxane chains (Figure 2a). The sample is denoted as PDMS-(C\(_6\)H\(_5\))\(_2\). According to the analysis of the \(^1\)H NMR spectra (Figure S3), one-third of the \( p \)-dimethyl groups (molar ratio) was substituted by \( p \)-diphenyl groups. As control samples, side groups of phenyl or \( n \)-hexyl (C\(_6\) in linear structure) were introduced into the PDMS network by replacing the conventional tetraethoxysilane crosslinker.

![Figure 1](image1.png)

*Figure 1. Schematic of membrane structure design and its selective transport of phenol over water. Chain conformation of PDMS (side groups: \( p \)-dimethyl) and PDMS-(C\(_6\)H\(_5\))\(_2\) (side groups: \( p \)-dimethyl and \( p \)-diphenyl with a molar ratio of 2), the permeation direction is along the \( y \) axis. The rigid phenyl takes the function of spacer to provide extra degrees of freedom to the methyl rotation. Twisted bars, exhibiting a softer status, are adopted to show the higher mobility and dynamic process of methyl. The PDMS membrane material with a minimal thickness is supported on a porous substrate that is applied for the pervaporation recovery of phenol from aqueous solution.*
Firstly, we rationalized the reconstruction of the PDMS chain by using ab initio molecular dynamics (AIMD) simulations. The root mean square deviation (RMSD) is widely used in molecular dynamic simulations to reveal the difference between two structures, which can indicate the flexibility of polymer chains.\cite{bio1} We calculated the RMSD of the –CH$_3$ side groups for PDMS and PDMS-(C$_6$H$_5$)$_2$, along the AIMD trajectories. As shown in Figure 2b, the RMSD and its fluctuation amplitude for PDMS-(C$_6$H$_5$)$_2$ are larger than those for PDMS after the equilibration (>5 ps). This demonstrates that the –CH$_3$ side groups of PDMS-(C$_6$H$_5$)$_2$ are more flexible than those of PDMS. To probe the underlying mechanism, we conducted single-point calculations on the last frame of the AIMD trajectory of PDMS or PDMS-(C$_6$H$_5$)$_2$ at the PBE/6-311G** level of theory. The obtained wavefunctions were used to perform the non-covalent interaction (NCI)\cite{bio1} analysis through the Multiwfn package.\cite{bio1} The \(\rho\)\text{sign}(\(\lambda\)) mapped RDG (reduced density gradient) isosurfaces are shown in Figures 2c,d, revealing the locations, types and strengths of the weak interactions. The green and brown isosurfaces imply that the van der Waals interaction and the steric interaction maintain the PDMS main structure. In PDMS-(C$_6$H$_5$)$_2$, the isosurfaces between phenyl groups show the colors from brown to red, which indicates that there are strong repulsive steric interactions between phenyl groups. These will impede the movement of the phenyl groups and the –Si–O–Si– backbone chain, resulting in a more rigid main backbone, which possibly leaves more spaces for methyl side groups to move. Comparatively, in PDMS, the green and light brown isosurfaces indicate that the –CH$_3$ side groups mainly have van der Waals interactions and weak steric interactions with the surroundings, leading the polymer chains to be more contracted compared with PDMS-(C$_6$H$_5$)$_2$. This can be depicted by shorter interatomic distances in PDMS (Figure 2b,c) with respect to those in PDMS-(C$_6$H$_5$)$_2$, therefore, leaving relatively less space for movement of the –CH$_3$ side groups.

On account of the spatial dynamic of groups imparting vital change on the structure, we further employed dielectric relaxation spectroscopy technique (DRS) to analyze the segmental dynamics of PDMS samples. This technique provides us unique perspectives to understand the motion characteristics of side groups, main chains and segments from sub-nano to nano scale.\cite{bio1} On the basis of the results (Figures S5,6), all of these PDMS samples contain two relaxation processes from low temperature (around glass transition temperature, \(T_g\)) to high temperature (above \(T_g\), representing \(\beta\) and \(\alpha\) relaxation processes, respectively.\cite{bio1} The relaxation time (\(\tau\)) depends on temperature (\(T\)) and frequency (\(f\)), relating to responding dipoles experiencing orientation polarization in amorphous regions with different
As the surrounding temperature is lower than \( T_g \), lattices restrain the motions of bulk chains and only side groups are able to rotate. The resulting \( \beta \) relaxation is affected by the physico-chemical structure of sub-nano units of the polymers, which can be described by the Arrhenius equation. By fitting the \( \tau_{\text{max}} \) vs. \( f \) during \( \beta \) relaxation, the activation energy (\( E \)) of side groups for the PDMS samples were obtained (Figure 3a). It is found that the PDMS-(C\( _{5} \)H\( _{5} \)) \((56.9 \text{ kJ mol}^{-1})\) or PDMS-C\( _{6} \)H\( _{5} \) \((53.9 \text{ kJ mol}^{-1})\) containing phenyl side groups reveal much lower activation energy than the others with all dimethyl (PDMS, 70.1 kJ mol\(^{-1}\)) or doping with n-hexyl side groups (PDMS-C\( _{5} \)H\( _{15} \), 66.5 kJ mol\(^{-1}\)). This suggests that the side groups of PDMS-(C\( _{5} \)H\( _{5} \)) and PDMS-C\( _{6} \)H\( _{5} \) possess higher mobility, which seems to be contradictory to the inherently higher rotation steric hindrance of phenyl than methyl and n-hexyl. This was appreciable when taking the total contributions of all kinds of side groups on the chain into account. In other words, the phenyl with a small amount (1/3 molar ratio) acting as spacer provided extra free volume cavities for the major methyl to rotate and keep pace with the frequency change during DRS analysis. The expected slightly lower activation energy of PDMS-C\( _{5} \)H\( _{5} \) than PDMS-(C\( _{5} \)H\( _{5} \))\(_{2} \) is attributed to the higher content of methyl groups.

To further investigate the effect of side groups on segmental motions at the nanoscale, the \( \alpha \) relaxation process was studied in detail. On increasing temperature, the crystalline region and transition region start melting and release large amounts of dipoles; meanwhile, the self-motion of the bulky polymer segments and the interaction with adjacent segments begin to emerge, thus the DRS signal at this moment reflects the motions of Si–O–Si main chains at the molecular scale. The fragile factor (\( m \)), which is used to quantify the steepness of the temperature dependence of the segmental relaxation time,\(^{[16]}\) was analyzed to evaluate the stacking status of the PDMS main chains.\(^{[17]}\) As shown in Figure 3b, the fragile factor of pristine PDMS is 84, which is in agreement with the value from other reports.\(^{[18]}\) It increased sharply to 208 and further enlarged to 261 when phenyl (PDMS-C\( _{5} \)H\( _{5} \)) and \( p \)-diphenyl (PDMS-(C\( _{5} \)H\( _{5} \))\(_{2} \)) side groups, respectively, were attached onto the Si–O–Si main chains. In contrast, the introduction of flexible n-hexyl softened the PDMS main chains, as evident from a reduced fragile factor of 42 in PDMS-C\( _{5} \)H\( _{15} \). It is interesting to find that rigid molecular spacers endowed the methyl side groups with higher mobility, but lower mobility to the Si–O–Si main chains. As shown in the schematic of Figure 3b, the cooperative motion of the soft main skeleton was suppressed

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**Figure 3.** Chain conformations of PDMS at the atomic scale and the molecular scale. a) Temperature (\( T \)) dependence of the maximum relaxation time (\( \tau_{\text{max}} \)) during the \( \beta \) relaxation process of DRS. An Arrhenius fit (dashed line) is used to obtain the rotation activation energy of side groups (values are given in the inset). The schematic illustrates the \( \beta \) relaxation of PDMS and PDMS-(C\( _{5} \)H\( _{5} \)) chains, highlighting the mobility of the methyl side groups before and after introducing the rigid phenyl molecular spacers. b) Temperature (\( T \)) dependence of the maximum relaxation time (\( \tau_{\text{max}} \)) during the \( \alpha \) relaxation process of DRS. The fragile factor (\( m \)) was obtained by a VFT fit (dashed line) at maximum relaxation time (1 s) and the values are given in the inset. The schematic illustrates the stacking status of the main chains of PDMS and PDMS-(C\( _{5} \)H\( _{5} \)) reflected by the \( \alpha \) relaxation process. c) XRD spectra and the corresponding \( d \)-spacing calculated by the Bragg equation. d) Loss factor (\( \tan \delta \)) measured by DMA. The glass transition temperature (\( T_g \)) was determined by the peak of the \( \tan \delta \) curve indicated by a dashed line.
in the PDMS doped with phenyl side groups. We then supposed that the stiffened PDMS segments tended to stack in a looser structure and the degree of chain entanglement was reduced. To verify this hypothesis, XRD analysis was used to study the packing behavior of PDMS chains. As shown in Figure 3c, the pristine PDMS exhibits a characteristic peak at 12.1°, corresponding to a d-spacing of 3.67 Å calculated by the Bragg equation, which is in agreement with values in the literature. After introducing $C_6$ side groups of phenyl or $n$-hexyl with larger size than methyl, the d-spacing of PDMS increased. Particularly, PDMS-($C_6H_{13}$)$_2$ and PDMS-C$_2$H$_6$ underwent substantial d-spacing enlargement compared with PDMS and PDMS-C$_3$H$_7$, indicating the critical role of rigid phenyl side groups on intercalating the polymer chains. Compared with the random single phenyl side group introduced by crosslinking, the regular $p$-diphenyl side groups with 1/3 substitution of methyl side groups on the main chain ($p$-dimethyl) generates the most significant spacing effect and the largest d-spacing of 3.93 Å.

The interaction between the PDMS segments was quantified by the loss factor ($\tan \delta$) determined by a dynamic mechanical analysis (DMA) measurement. The higher the loss factor is, the more energy will be consumed due to the friction between polymer segments. As shown in Figure 3d, PDMS-($C_6H_{13}$)$_2$ shows the highest loss factor, which is far superior to the other PDMS samples, and PDMS-C$_2$H$_6$ comes second. As discussed above, the introduction of a rigid molecular spacer (phenyl) with high steric resistance inhibited the segment mobility, including torsion and twist of the main chain. However, the main chain with intrinsic low-mobility relieved excessive entanglement of segments, inducing the segment stacking in a loose status. The friction was enhanced due to the reduction of the interaction between the neighboring segments. The stronger friction further produced the possibility for creating extra free volume cavities. Moreover, the loss factor is also very sensitive to the glass transition temperature ($T_g$) of polymers that can also quantitatively reflect the chain mobility. Again, the mobility of the main chains was confirmed by the highest $T_g$ observed in PDMS-($C_6H_{13}$)$_2$, followed by PDMS-C$_2$H$_6$, PDMS and PDMS-C$_3$H$_7$. Such $T_g$ order is consistent with the results measured by differential scanning calorimetry (DSC) in Table S1.

The above characterizations of PDMS chains clearly demonstrated that introducing rigid molecular spacers reconstructed the polymer structure from sub-nano to nanoscale in two aspects: i) enhancing the mobility of side groups while stiffening the main chains; ii) inhibiting the chain packing and increasing the frictions between the segments. We assumed that the achieved reconstruction of PDMS at the atomic and molecular level would have a more significant influence on the molecular transport through the PDMS membrane as the size of permeant is closer to the free volume size. It was expected that on increasing the size of permeant, the transport resistance reduced by the rotation of side groups or the extra free volumes resulting from local segmental motions will be more remarkable.

The hypothesis was probed by exploring the selective permeation properties of a group of practically important VOCs with different molecular sizes (Figure 4c), including ethanol (4.5 Å), n-butanol (5 Å), phenol (6.9 Å), phenyl methanol and 2-phenyl ethanol over water (3 Å), through the pristine and modified PDMS membranes. The kinetic diameters of phenyl methanol and 2-phenyl ethanol are unavailable, while their geometric mean radii are larger than that of phenol (Table S2). The permeation flux and separation factor (a parameter that evaluates selectivity) of the PDMS membranes for pervaporation removal of the VOCs from its dilute aqueous solution are summarized in Figures 4a,b. Interestingly, flux for small-sized VOCs (ethanol or n-butanol) in all the PDMS membranes is similar, while flux for large-sized VOCs (phenol, phenyl methanol or 2-phenyl ethanol) in PDMS-($C_6H_{13}$)$_2$ and PDMS-C$_2$H$_6$ is noticeably higher than that for PDMS and PDMS-C$_3$H$_7$. Moreover, the separation factor of PDMS-($C_6H_{13}$)$_2$ is lower for small-sized VOCs but higher for large-sized VOCs compared with that in PDMS and PDMS-C$_3$H$_7$. It was found that the structure of PDMS is more suitable for recovery of n-butanol than PDMS-($C_6H_{13}$)$_2$. The high-content phenyl could enhance the transport of water and n-butanol molecules simultaneously, leading to a low separation factor. By contrast, PDMS-C$_2$H$_6$ possesses the blend polymer conformation, combing the characteristics of PDMS and PDMS-($C_6H_{13}$)$_2$. As n-butanol molecules passed through the PDMS-C$_2$H$_6$ membrane, the higher affinity towards n-butanol increased the separation factor.

To further confirm the benefit of a rigid molecular spacer on the transport of large-sized VOCs, we mixed pristine PDMS and PDMS-($C_6H_{13}$)$_2$ polymers with various weight ratios (2/8, 4/6, 6/4, 8/2) to fabricate a PDMS/PDMS-($C_6H_{13}$)$_2$ blending membrane with identical thickness (Figure S7). In the phenol/water separation measurement, the membrane permeation flux was enhanced gradually by increasing the $p$-diphenyl side groups in the polysiloxane chains, while the separation factor was maintained at ≈15 (Figure S8). The substantial enhancement of selective permeation of phenol molecules in PDMS-($C_6H_{13}$)$_2$ is consistent with the result shown in Figure 4b. Apparently, the introduction of rigid molecular spacers only promoted the selective permeation of large-sized VOCs over water molecules. As assumed above, the key inducement might be the size difference between the permeant and membrane free volume, and how the size difference influences molecular transport through the pristine and reconstructed PDMS membranes. This motivated us to measure the free volumes of the polysiloxane membranes by using positron annihilation spectroscopy (PAS).

Two different PAS sources were used to obtain a reproducible result (Figure 4e). The spectra exhibited a classic bimodal distribution. Surprisingly, the size of free volumes that can be used for VOCs or water transport is almost constant at equivalent pore diameter of 7.88–7.94 Å ($R_p$) in the four PDMS samples. It is inferred that the change of chain conformation induced cavity variation was nearly offset by the variation in space occupied by the substituted side groups. For instance, in PDMS-($C_6H_{13}$)$_2$ and PDMS-C$_2$H$_6$, the bulky phenyl occupies larger spaces than the methyl side group. This could balance the extra free volumes
resulting from the enlarged chain distance and looser chain packing compared with pristine PDMS. Moreover, the free volume size could be maintained as the space between the adjacent methyl was increased, which endowed the methyl with higher mobility. Taking the size of VOCs molecules and free volume into account, we envision that the free volume cavity (R4) can accommodate only one phenol molecule or one butanol molecule coupled with a few water molecules (Figure 4d). Similar size effects apply for the other aromatic molecules and ethanol. As the permeant size is closer to the cavity size (e.g., ethanol, butanol), the transport of a single permeant molecule is less affected by the methyl side groups, while the transport of the coupled water molecules might be promoted by the methyl side groups with higher mobility. This effect accounts for the similar ethanol or butanol permeation flux but lower separation factor over water on introducing phenyl spacers into PDMS.

In addition, we understood the transport mechanism by using the solution–diffusion model that is commonly applied for pervaporation separation of 1 wt% phenol/water mixtures at 50°C.
for the pervaporation membrane process. Molecular permeation through the membrane (permeability, $P$) can be deconvolved into the product of sorption coefficient ($S$) and diffusion coefficient ($D$). As an example, the separation of phenol/water mixtures is discussed here. Free-standing membranes were prepared and used to obtain reliable $P$, from the pervaporation test. $S$ was obtained by the sorption isotherms of the membranes in the liquid$^{[22]}$ (Figure S10) and $D$ was calculated using the measured $P$, and $S$. First, the sorption coefficient represents the affinity of the membrane material towards organic compounds, which mainly depends on the functional groups in the material. Replacing methyl side groups on the PDMS chains with phenyl or n-hexyl could improve the affinity towards phenol, as evidenced by the higher phenol sorption in the modified PDMS free-standing membranes (Figure S11). Specifically, the phenol sorption coefficient shows the order of PDMS-$(\text{C}_6\text{H}_5)_5 \text{PDMS-CH}_5 \text{PDMS-CH}_3 > \text{PDMS}$ (Figure 4f), reflecting the stronger affinity of phenyl than n-hexyl towards phenol. Second, phenol molecules diffused fastest in the PDMS-(CH$_3$)$_5$ membrane (diffusion coefficient of PDMS-(CH$_3$)$_5$ is the highest), confirming our assumption that the methyl side groups with higher mobility on polysiloxane could promote the diffusion of aromatic molecules through the cavity even with almost the free volume size (Figure 4e). Furthermore, the water transport also affects the separation performance. As shown in Figure S12, water sorption coefficients of PDMS-(CH$_3$)$_5$ and PDMS-CH$_3$ are similar to that of PDMS, while that of PDMS-(CH$_3$)$_5$ is slightly lower due to the introduced higher hydrophobicity and denser stacking status. The much larger water diffusion coefficient combined with the similar sorption coefficient generates the higher water permeability. In addition, there is a similar degree of enhancement in phenol permeability and thus the constant perm-selectivity for phenol/water in the four PDMS membranes.

The aforementioned experiments and discussions proved that PDMS-(CH$_3$)$_5$ possessed the optimal transport properties for selective permeation of aromatic compounds over water. For use in a practical separation processes, micron-thick free-standing membranes suffer from a lack of mechanical strength and essential permeation flux, so a porous substrate is often employed to fabricate thin-film composite membranes. Recent innovations highlight the importance of interfacial properties between the selective layer and substrate layer.$^{[25]}$ However, matching the physicochemical properties between the mesoporous or micro-porous substrate and the molecules to be separated, which may have a notable influence on the pervaporation separation performance, was often overlooked. In this work, we investigated four kinds of the mostly used commercial substrates to fabricate the PDMS-(CH$_3$)$_5$ composite membranes. As shown in Figures 5a and S13, the polyvinylidene fluoride (PVDF) and polytetrafluoroethylene (PTFE) substrates are hydrophobic and have homogeneous sponge-like pores with an average size of 220 nm. The polyacrylonitrile (PAN) and polyethersulfone (PES) substrates are hydrophilic and have asymmetric structures consisting of two layers: a top sponge pore layer and a bottom finger-like pore layer. The average surface pore size of the PAN and PES substrate was $\approx 25$ nm.

As shown in Figure 5b, it is found that PDMS-(CH$_3$)$_5$ composite membranes fabricated by using hydrophobic substrates (PVDF, PTFE) exhibited much higher phenol flux and phenol/water separation factor than that using hydrophilic substrates (PAN, PES). Such a huge separation performance difference among these membranes was surprising because they possessed the same materials and identical thickness of the selective layer (Figure S14). Moreover, this phenomenon wasn’t observed in the pervaporation removal of ethanol from its aqueous solution. Indeed, the ethanol flux and ethanol/water separation factor of the four PDMS-(CH$_3$)$_5$ composite membranes are independent on the kinds of substrates. It seems like the substrate only affects the transport of phenol/water mixtures, and the hydrophobic substrate is favorable for promoting the selective permeation of phenol over water. We further used hydrophobic PTFE substrates with smaller pore sizes (50 nm, 110 nm) to fabricate two kinds of PDMS-(CH$_3$)$_5$ composite membranes. It turns out that the phenol/water separation performance started to drop as the substrate pore size decreased to 50 nm (Figure S15). This result points out that the pore size of the substrate is the dominant factor affecting the overall separation performance, rather than the substrate hydrophobicity.

During the pervaporation separation process, molecules pass through the substrate in the gaseous state when reaching the boundary of the selective layer. Once the mean free path of the permeant is larger than the pore size of the substrates, the permeant will transport as Knudsen flow which would cause a rapid partial pressure drop.$^{[24]}$ Phenol, having a lower saturated vapor pressure than ethanol, is more sensitive to the pressure drop. The pore condensation occurs easier in the Knudsen area, and becomes notable on increasing the boiling point of the permeant (lower critical condensation pressure) and decreasing the pore size of the substrate.$^{[25]}$ It accounts for our observation that the substrate pore size of the PDMS-(CH$_3$)$_5$ composite membrane significantly affected the pervaporation separation of phenol/water compared to ethanol/water (Figure 5b).

Besides optimizing the transport properties of the substrate layer, efficient reduction of the thickness of the selective layer is another critical approach to achieve a highly permeable membrane. In this regard, substrates with a pore size of tens of nanometers are often employed to fabricate ultra-thin selective layers by avoiding the pore penetration of the casting solution. However, according to the above-mentioned pore condensation effect on the aromatic transport, small-pore-sized substrates would highly reduce the separation performance of ultra-thin composite membranes. Indeed, the fabricated 690-nm-thick PDMS-(CH$_3$)$_5$ composite membrane using a substrate with a pore size of $\approx 25$ nm showed a very poor separation factor for phenol removal from water (blue line in Figure 5d). Apparently, despite the great challenge, substrates with a large pore size ($>100$ nm) is an inevitable choice to fabricate ultra-thin composite membranes for aromatic removal. The key to address this challenge is inhibiting penetration of the
casting solution into the substrate pores that would form defects in the selective layer and increase the transport resistance. It was found that by reducing the thickness of the selective layer from micrometer to sub-micrometer on top of using a substrate with a large pore size, the separation factor was significantly decreased by using the conventional casting method. There is a trade-off between permeation flux and separation factor, as indicated by the black line in Figure 5d.

Here, we pre-coated a very dilute casting solution on the substrate (pore size: 110 nm) to reduce the surface roughness and the pore penetration of the subsequent coating. Meanwhile, a hydrophilic PVDF substrate was chosen to facilitate the use of water as a substrate-pore-plugging agent to further inhibit the casting solution penetration. As shown in Figure 5c and S16, the EDX mapping of elemental Si (from PDMS) across the composite membrane confirmed that the PDMS solution penetration was highly suppressed with our modifications to the conventional casting method. The selective layer thickness could be successfully reduced down to sub-micrometer without introducing defects. It was evidenced by the 2–3 fold enhancement in flux, while maintaining a well-preserved separation factor, breaking the trade-off limit (red line in Figure 5d). A minimum membrane thickness was required to fully cover the substrate surface roughness to ensure a defect-free selective layer. Substrates with smaller pores have a lower surface roughness but higher pore condensation effect. By balancing the two factors, we found that 580 nm is an optimal PDMS-(C₆H₅)₂ membrane thickness to achieve the best aromatic removal performance.

To further explore the potential of the reconstructed PDMS (i.e., PDMS-(C₆H₅)₂) membrane for practical aromatic removal processes, a high operating temperature, a high feed concentration, and a continuous separation process were adopted to validate the membrane stability. The separation performance of conventional polymeric membranes would be easily lowered by the high temperature or feed concentration induced excessive membrane swelling. It is worth noting that our sub-micron-thick PDMS-(C₆H₅)₂ composite membrane exhibited remarkable anti-swelling performance with a feed temperature as high as 80°C and a feed concentration as high as 2.5 wt % for phenol/water mixtures (Figure 6a,b). These harsh operating conditions could even enhance the phenol recovery performance. Indeed, the permeation flux was enhanced by 146 % and 530 % on increasing the phenol feed concentration from 0.5 wt % to 2.5 wt % and elevating the operating temperature from 40°C to 80°C, respectively; meanwhile, the...
separation factor was well maintained or even promoted. Such a desirable response to the operating conditions could be attributed to the introduction of the rigid phenyl that restricted the mobility of the polymer chains and suppressed the polymer swelling. Moreover, during 300 hours continuous removal of phenol under harsh conditions (2.5 wt % aqueous solution at 80°C), the PDMS-(C$_6$H$_5$)$_2$ composite membrane possessed outstanding stability both in terms of permeation flux and separation factor.

We compared our membrane performance with the state-of-the-art membranes for aromatic removal from water. Both rubbery polymers such as PDMS, poly (ether block amide) (PEBA) and glassy polymers such as polyimide (PI) and polymers of intrinsic micro-porosity (PIMs) have been studied for phenol recovery from aqueous solution. In addition, inorganic fillers such as silica, MFI zeolite and MAF-6 MOF were incorporated into polymers to fabricate mixed-matrix membranes. The phenol/water separation performance is summarized in Figure 5d and Table S5. It can be seen that most polymeric membranes generally showed unattractive flux (<500 g m$^{-2}$ h$^{-1}$). Although the flux of some mixed-matrix membranes was higher than 1000 g m$^{-2}$ h$^{-1}$, the separation factor was rather poor (<5). The PEBA membranes exhibited an attractive separation factor, while they were mostly in a free-standing form that remains challenging in terms of long-term stability and practical implementation.\[26\] In comparison, our PDMS-(C$_6$H$_5$)$_2$ composite membrane exhibited superior performance for removing phenol from water, as well as recovering valuable aromatic compounds (e.g., 2-phenyl ethanol, phenyl methanol) from aqueous solution (Table S5). The PDMS material with tunable side group mobility designed in this work successfully addressed the challenges of current membranes in terms of flux-separation factor trade-off and structural stability for aromatic removal from water.

**Conclusion**

We presented a facile methodology to promote the selective transport of aromatic compounds over water through a PDMS benchmark organophilic membrane by introducing phenyl side groups as rigid molecular spacers. The phenyl not only increased the mobility of the methyl side groups at atomic scale but also reconstructed the stacking of polymer segments into looser conformation at the molecular scale. The lowering of the steric hindrance significantly enhanced the transport of permeant whose molecular size is close to the free volume size of the polysiloxane. Moreover, the substrate layer was optimized to facilitate the aromatic

Figure 6. Separation performance of the PDMS-(C$_6$H$_5$)$_2$ composite membrane. Effect of a) feed concentration (feed temperature: 50°C); and b) feed temperature (feed concentration: 1.0 wt %) on the phenol/water separation performance of a 580-nm-thick membrane. c) Long-term stability of a 3-μm-thick membrane during continuous separation of 2.5 wt % phenol/water mixtures at 80°C. d) Performance comparison with the state-of-the-art membranes for phenol recovery from aqueous solution, in which the dashed line is a guide to indicate the general trade-off between total flux and separation factor. More details on the membranes and the operating conditions are provided in Table S5.
transport with evitable pore condensation, and a submicron-thick selective layer was fabricated to achieve highly permeable removal of aromatics. The resulting PDMS-(C$_8$H$_{16}$)$_2$ composite membrane exhibited outstanding performance during continuous removal of phenol from aqueous solution under a wide range of operating conditions, showing great potential for practical implementation. The fundamental insights obtained in this work should inspire the design of customized membranes for selective permeation of target molecules that are essential in the chemical, food and medical industry. For instance, by considering both the affinity and diffusion effects, the size and mobility of side groups of PDMS can be rationally designed to accommodate and rapidly transport the specific VOC molecule with a high perm-selectivity over water.

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Conflict of Interest

The authors declare no conflict of interest.

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The introduction of phenyl side groups as rigid molecular spacers into polydimethylsiloxane (PDMS) imparted the methyl side groups with higher mobility and additional degrees of freedom for fast transport of aromatic compounds. Combined with the engineering design of the transport highway, the membrane achieved outstanding performance for aromatic removal.