PDMS thin-film composite membrane fabricated by ultraviolet crosslinking acryloyloxy-terminated monomers

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A B S T R A C T

Polydimethylsiloxane (PDMS), as a representative membrane material with superior permeability, attracts great attention in gas separation, pervaporation and nanofiltration. However, the fabrication of defect-free ultrathin PDMS membrane remains great challenge mainly due to the difficulty in controlling the processability and substrate pore penetration of casting solution. In this work, for the first time, we employed PDMS monomer terminated with acryloyloxy groups (AC-PDMS) to implement fabrication of thin-film composite (TFC) membrane. The ultraviolet (UV) reactivity between acryloyloxy groups induced fast curing of AC-PDMS casting solution, thereby realizing formation of ultrathin selective layer (~260 nm) and inhibition of substrate pore penetration. By optimizing the UV wavelength, irradiation time and polymer concentration, the resulting AC-PDMS TFC membrane achieved attractive CO$_2$ permeance of 9635 GPU, with CO$_2$/N$_2$ selectivity of 11.5. Furthermore, chain crosslinking and packing behavior, fabrication of TFC membrane and transport property of AC-PDMS were compared with conventional hydroxyl-terminated PDMS (OH-PDMS). Together with the potential in scalable fabrication, the strategy based on UV crosslinking acryloyloxy-terminated monomers provides a new avenue to produce ultrathin PDMS membranes toward practical application in molecular separation.

1. Introduction

Extensive efforts has been plunged into the ablation of carbon dioxide emission which induced increasing environmental issues [1]. Membrane technology is regard as an essential and feasible strategy for efficient carbon capture [2,3]. However, so far, membranes for gas separation require further improvement of separation performance to meet the practical application, owing to high energy consumption and undesirable selectivity [4–7]. In this regard, thin film composite (TFC) membrane endows distinct advantage in fast and selective permeation during practical process [8–10]. One of the critical factors of forming ultrathin selective layer is controlling the extent of pore penetration [11–13]. The influence of pore penetration on composite membrane is a double-edged sword. On the one hand, the mechanical interlocking between the polymer and substrates is essential to ensure the interfacial adhesion and mechanical properties [14,15]. On the other hand, the excessive pore penetration increases the transport resistance and thus reduce the permeance. For achieving a positive holistic effect, it is essential to customize the fabrication method according to characteristics of membrane material.

A series of polymer materials have been developed for the efficient separation of CO$_2$/N$_2$. Among them, the glassy polymers such as PIM [16,17] exhibit high permeability, and the block-co-polymer Pebax [18] shows high affinity toward CO$_2$. Polydimethylsiloxane (PDMS), as the benchmark of rubbery membrane materials with high permeability, has been widely studied for gas separation, pervaporation and nanofiltration [19–22]. Low concentration of PDMS casting solution is normally required to fabricate a thin selective layer on a porous substrate. The high fluidity of solution is inevitable to intrude into the pore of substrate, causing excessive pore penetration and possible defects. To address this issue, highly permeable polymer or inorganic material with high porosity was introduced as a gutter layer to fabricate PDMS TFC.

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membranes [23–26]. This strategy complicates the membrane fabrication process. Alternatively, Wang and co-workers fabricated a high-performing PDMS TFC membrane by integrating the advantage of casting method and doping method [27,28]. The key factor of this process is the design of casting blade. Aside from the reconstruction of equipment, introduction of functional groups into PDMS crosslinking process could improve the processability of casting solution. Qin and co-workers proposed UV-induced polymerization to implement fast curing process could improve the processability of casting solution. This process was based on condensation reaction between OH-PDMS monomer and crosslinker (Fig. 1). The fast curing of casting solution effectively inhibited the penetration of dilute PDMS solution into the substrate pores, thereby enabling the formation of ultra-thin and defect-free PDMS layer for efficient separation of CO₂/N₂. Moreover, the A4-sized AC-PDMS TFC membrane was successfully prepared, demonstrating the potential in scalable fabrication.

2. Experimental

2.1. Materials

Acryloyloxy-terminated PDMS (Mw = 2500) and hydroxyl-terminated PDMS (Mw = 8000), photo-initiator 1173 (2-hydroxy-2-methylpropio phenone), tetraethylorthosilicate (TEOS), dibutyltin dilaurate (DBTDL) and n-heptane were purchased from Sigma-Aldrich. All chemical reagents were used as received without further purification. The Polycrylonitrile (PAN) substrate with average pore size of 25 nm was supplied by Beijing Haicheng Shijie Filter Equipment Co., Ltd.

2.2. Membrane fabrication

2.2.1. Fabrication of AC-PDMS/PAN composite membrane

A certain amount of AC-PDMS was dissolved into n-heptane and mixed for 10 min to obtain homogenous solution. Then, the photo-initiator 1173 was added into the solution, the mass ratio of polymer to photo-initiator was 10:1. The solution was exposed to the UV light for several minutes by using a set of tunable ultraviolet generator under nitrogen atmosphere. Before casting, the PAN substrate was immersed into water to prevent possible pore penetration. The AC-PDMS composite membrane was fabricated by a casting blade with adjustable clearance. The composite membrane was placed into UV irradiation box for crosslinking. The wavelength of the light source are 365 nm and 254 nm, respectively. At last, the composite membrane was thermally treated at 80 °C for 10 min to evaporate extra solvent and photo-initiator. The preparation of A4-sized composite membrane is consistent with aforementioned procedure by using 10 wt% AC-PDMS casting solution to avoid possible defect.

2.2.2. Fabrication of OH-PDMS/PAN composite membrane

The casting solution was prepared by mixing OH-PDMS, crosslinking agent (TEOS) and catalyst (DBTDL) into n-heptane. The weight ratio of polymer: crosslinker: catalyst = 100:10:1. Before casting, the PAN substrate was immersed into water to prevent possible pore penetration. When the casting solution achieved suitable viscosity, casting blade was applied to fabricate OH-PDMS/PAN composite membranes. After evaporating solvent at room temperature for 24 h, the composite membrane was thermally treated at 80 °C for 12 h to form the final OH-PDMS composite membrane.

2.2.3. Fabrication of AC-PDMS and OH-PDMS free-standing membranes

A certain amount of AC-PDMS casting solution (polymer concentration: 10 wt%) was poured into petri dishes. Then, these dishes were migrated to the glove box for isolation of oxygen. Because the amount of casting solution is much more than that for the composite membrane fabrication, the absence of oxygen is critical to the full curing of AC-PDMS membrane. After 10 min UV irradiation with combined...
wavelength, the crosslinked AC-PDMS membrane was heated at 80 °C for 1 h to evaporate extra solvent and photo-initiator. The preparation of OH-PDMS free-standing membrane is similar to AC-PDMS except of not using UV irradiation. Moreover, OH-PDMS membrane was placed into atmosphere under room temperature for 5 h. After curing, a post-heating process with 80 °C was adopted for further crosslinking to fabricate the final OH-PDMS free-standing membrane. These free-standing membranes were utilized to study the intrinsic transport behavior of gas molecules.

2.3. Characterizations

The chemical structures of OH-PDMS and AC-PDMS were analyzed by Fourier transform infrared (FTIR, Thermo AVATAR-FT-IR-360, USA). The X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha, USA) was applied to detect the process of chemical bond transition on the AC-PDMS membrane surface. The single component adsorption isotherm test was carried out by BELSORP-HP (MicrotracBEL Corp., Japan). Film extensometer was adopted to measure the critical tensile load.

Dielectric relaxation spectroscopy (DRS, Concept 800, Germany) was used to study the intrinsic transport behavior of gas membranes. The preparation of PDMS-UVAC membranes fabricated by UVAC combined light source was evaluated via a constant volume/variable pressure method. When the system reached steady state, the permeation test was carried out at 0.1 MPa and 25 °C. All the test was repeated for at least three times. The gas permeance of component $i$ was calculated by the following equation:

$$P_i = \frac{\frac{dp}{dt} \times V}{A \times F \times d\rho}$$

where $P_i$ is the gas permeance (1 GPU = 10⁻⁶ cm² (STP) cm⁻² s⁻¹ cmHg), $F$ is the effective membrane area, $T$ is the testing temperature (°C), $dp/dt$ represents the slope of the permeate pressure change. The membrane ideal selectivity, $\alpha_{ij}$, is determined by the ratio of the permeance of the fast gas ($i$) to the slow gas ($j$):

$$\alpha_{ij} = \frac{P_i}{P_j}$$

The mixed-gas permeation test (CO₂: N₂, 15 vol%: 85 vol%) was similar with the test process of pure gas except for the gas chromatography (Agilent 8890) was applied to analyze the components of binary gas mixtures. In addition, the stage-cut of feed was maintained less than 1% to avoid the concentration polarization by a back-pressure controller.

3. Results and discussion

3.1. Effect of fabrication conditions

We investigated a series of factors to optimize the fabrication conditions of AC-PDMS TFC membrane. Firstly, the wavelength of UV light is essential to the formation of membrane. The UV light can be divided into three kinds on the account of wavelength: UVA (320 nm–400 nm), UBV (275 nm–320 nm) and UVC (200 nm–275 nm). For convenience of labeling, we named membranes fabricated by different light sources as AC-PDMS-UVA, AC-PDMS-UVC and AC-PDMS-UVAC. UVAC means the combination of UVA and UVC. As shown in Fig. 2, the membranes fabricated by UVC showed conspicuous disadvantage on the permeance, only 4378 GPU, comparing to other kinds of UV light. However, AC-PDMS-UVAC membranes fabricated by UVAC combined light source...
exhibited the highest permeance (6944 GPU) and intrinsic selectivity (11.7) of PDMS material. UVC meet the demand of sufficient energy for surface curing, while was disabled to penetrate through the whole selective layer that caused the incomplete curing of underneath casting solution. The fluidity of casting solution led to pore penetration and thus the decline of CO$_2$ permeance. The UVA with the longest wavelength shows advantage to the penetration ability [35], ensuring the deep curing and restrain the pore penetration. However, the low energy intensity of UVA caused the incomplete crosslinking polymer matrix with higher transport resistance, inducing the slight decline of CO$_2$ permeance comparing to AC-PDMS-UVAC. Therefore, combining UVC with UVA as the light source could completely crosslink the whole AC-PDMC selective layer.

For further verification our inferences, XPS spectra was applied to determine the surface chemical properties of membrane fabricated by different UV light sources. As shown in Fig. 3, the C1s spectrum of AC-PDMS-UVA exhibited four peaks at the binding energies of 287.8, 285.8, 284.8, 283.8 eV, corresponding to C=O, C–C, C-Si and C–C, respectively. Compared with AC-PDMS-UVC and AC-PDMS-UVAC, the existence of C–C on the surface of AC-PDMS-UVA indicated that the crosslink reaction on the surface was incomplete. The content of C–C groups in AC-PDMS-UVC and AC-PDMS-UVAC implied all of C–C groups took conversion into C–C. In addition, the power of light source is another critical factor influencing the crosslinking reaction extent. The UVAC combined light source possessing higher intensity and power enhanced the bulkily curing of membrane. In summary, UVAC combined light source assembled the advantage of UVA and UVC to fabricate the AC-PDMC TFC membrane with the optimal crosslinked network and composite membrane structure.

The post-heating process is critical to evaporate solvent and other additives, and ensure the extent of vulcanization. In general, OH-PDMS membrane was heated to construct integral network [36,37]. Because the extra Si–OH groups require high temperature (60 °C–120 °C) and sufficient time to react with the crosslinker under non-solvent environment [38]. AC-PDMS membranes also need post-heating process, which however would not involve the deeper crosslinking since the reaction between acryloyloxy stops immediately once removing the UV light. As shown in Fig. 4, the mass loss curve of AC-PDMS exhibited a stage from 80 °C to 305 °C, which was owing to the desorption of photo-initiator 1173 with boiling point of 80 °C. Moreover, the mass loss fraction was corresponded with the concentration of photo-initiator. It should be noted that the photo-initiator could transit from grand state to excited state after UV irradiation, accompanied by releasing abundant free radical for promoting the crosslinking of AC-PDMS monomers via the addition reaction [39,40]. Therefore, the photo-initiator would not participate in the actual crosslinking reaction and affect the separation performance.

Before membrane casting, the pre-crosslinking of the casting solution to a suitable viscosity is essential to fabricate a defect-free TFC membrane [39,41]. It is difficult for conventional OH-PDMS to control the viscosity, because the condensation reaction will be hardly stopped once beginning [42]. In contrast, the addition reaction between AC-PDMS can cease immediately by removing the UV light. In view of this property, we can easily control the viscosity of casting solution by intermittent UV irradiation. As shown in Fig. 5, the viscosity of casting solution was positively associated with the polymer concentration. After 200 s UV irradiation, the viscosity of 5 wt% polymer concentration reached 43 cP, which is suitable for the membrane coating and fabricating a thin selective layer on top of the porous substrate. Moreover, the viscosity of
casting solution increased with the irradiation time. When the irradiation time was more than 200 s, the solution viscosity increased dramatically, and the casting solution would transform into gel if continuously extending the irradiation time. It was noted that continuous N\textsubscript{2} flow is necessary to eliminate oxygen from the reaction system [43].

After membrane casting, an indispensable irradiation duration is another critical factor. The membrane without UV irradiation did not possess the ability of efficient separation (Fig. 6). In contrast, the permeance of CO\textsubscript{2} and CO\textsubscript{2}/N\textsubscript{2} selectivity increased rapidly after only 3 s UV irradiation, implying such short irradiation time was sufficient to construct integrated selective layer. By further extension of irradiation time, the denser crosslinking network contributed to the slight enhancement of selectivity from 11.3 to 12 and the CO\textsubscript{2} permeance nearly unchanged. Because of the ultrafast solidification, the casting solution could not penetrate into the substrate, thereby avoiding additional transport resistance for the AC-PDMS TFC membrane. Furthermore, the extreme short curing time was expected to save energy compared with thermal crosslinking process for conventional OH-PDMS membrane.

Finally, we investigated the effect of polymer concentration on the AC-PDMS TFC membrane performance. Generally, membrane thickness increases with polymer concentration of the casting solution, leading to the decline of gas permeance. The result of Fig. 7a also abided by this trend. As the polymer concentration decreasing to 5 wt%, CO\textsubscript{2} permeance reached the highest value of 9635 GPU and intrinsic CO\textsubscript{2}/N\textsubscript{2} selectivity of PDMS material (11.5). As shown in Fig. 7b, although without introducing a gutter layer, the AC-PDMS TFC membrane possessed an ultrathin selective layer of 260 nm and the boundary between selective layer and substrate layer could been clearly observed. By further increasing the polymer concentration, combined with higher viscosity of the casting solution (Fig. 5), the membrane thickness varied from 260 nm to 2.5 \( \mu \)m (Fig. 7b–f), but the selectivity decreased slightly. It could be owing to that penetrating capacity of UV light was too weak to allow the complete curing of selective layer with high thickness and the irradiation time was also too short. The fluidity of deep casting solution and pore penetration further induced the surface collapse and appearance of few defects. We further tested the mixture gas (15 vol %/85 vol% CO\textsubscript{2}/N\textsubscript{2}, 0.1 MPa) separation performance of membranes fabricated by 10 wt% and 25 wt% polymer concentrations. The result showed that membrane fabricated by 25 wt% polymer concentration possessed CO\textsubscript{2} permeance of 1036 GPU and the selectivity was 10.2, which was lower than the membrane fabricated by 10 wt% polymer concentration (CO\textsubscript{2} permeance: 4079 GPU, selectivity: 12.3). Namely, the selectivity observed in mixture gas test was also decreased with increasing polymer concentration. When it comes to free-standing membranes with around 100 \( \mu \)m, it required enough irradiation time (10 min) to ensure the integrity curing. Moreover, the problem of pore penetration was avoided without substrate and each side of films could obtain efficient irradiation. Hence, free-standing membranes could reach intrinsic selectivity (around 12). The specific data will be discussed later in Fig. 12.

3.2. Fabrication of A4-sized AC-PDMS TFC membrane

For exploration of the feasibility of scale-up fabrication of AC-PDMS TFC membrane, we amplified the substrate to the size of A4 paper (length 297 mm, width 210 mm). The fabricated membrane was cut into 12 portions equally and evaluated the separation performance and morphology (Fig. 8a). The CO\textsubscript{2} permeance of each part was almost ~7900 GPU and the CO\textsubscript{2}/N\textsubscript{2} selectivity was ~10 (Fig. 8b). Only #3 and #8 membrane exhibited relatively low selectivity due to the locally tiny defects. As shown in Fig. 8c, the averaged thickness of selective layer was around 550 nm. All the membrane samples didn’t exist obvious pore penetration, thereby contributing to the high gas permeance. The result
Fig. 8. Scale-up fabrication of AC-PDMS TFC membrane. (a) Digital photos of A4-sized AC-PDMS TFC membrane, (b) The CO₂/N₂ separation performance and (c) cross-sectional SEM images of 12 portions of the A4-sized AC-PDMS TFC membrane (membrane fabrication conditions: 5 s irradiation time, 10 wt% polymer concentration, UVAC light source; test conditions: pure gas, 0.1 MPa, 25 °C).

Fig. 9. Influence of (a) feed pressure and (b) operation time on the separation performance of AC-PDMS TFC membrane; SEM images of membrane cross-section (c) and surface (d) after continuous test (membrane fabrication conditions: 10 wt% polymer concentration, 5 s irradiation time, UVAC light source; test conditions: 15 vol%/%85 vol% CO₂/N₂ at 0.1 MPa and 25 °C).
demontated the great potential of AC-PDMS TFC membrane in scale-up fabrication.

We randomly chose one from the 12 portions of the A4-sized PDMS TFC membrane to investigate the mixed-gas separation performance (15 vol%/85 vol% CO2/N2). The effect of feed pressure and operation time on the separation performance were investigated to verify the stability of AC-PDMS membrane. The decline of permeance and selectivity was owing to the sorption competition [11,44-47] that often observed in the mixed-gas permeation (Fig. 9a). The result of Fig. 9b confirmed that AC-PDMS TFC membrane exhibited satisfied stability during 120 h continuous operation. After the continuous test, there were no obvious defects and structural collapse observed in the AC-PDMS TFC membrane according to the SEM images of Fig. 9c and d, further confirming the outstanding mechanical property.

3.3. Comparison with traditional PDMS membrane

We further compared the fabrication, structure and transport properties of the AC-PDMS membrane with traditional OH-PDMS membrane. As shown in Fig. 10a, the CO2 permeance of AC-PDMS composite membranes was nearly twice higher than OH-PDMS composite membranes, although the selective layer thickness of both membranes was ~500 nm (Fig. 10b). The slight decline of selectivity may be owing to the lower gas solubility (will be discussed in later) and tiny defects of the membrane layer. Assuming the intrinsic transport property of AC-PDMS and OH-PDMS is similar (will be discussed later), the half permeance indicated that excessive pore penetration of OH-PDMS composite membranes increased the gas transport resistance. As confirmed by EDX mapping shown in Fig. 10c-e, stronger Si signal was observed within the substrate layer of OH-PDMS membrane. It can be inferred that the fast curing of AC-PDMS casting solution takes obvious effect on the suppression of pore penetration. Meanwhile, this method omits the introduction of gutter layer which is often utilized to fabricate ultra-thin membrane. Fig. 10f-g shows FTIR spectra of AC-PDMS membrane and OH-PDMS membrane. Both samples exhibited representative adsorption peaks of PDMS, where the adsorption peaks at 1257 cm−1 and 1019 cm−1 are ascribed to bending vibration of Si–CH3 and asymmetrical stretching vibration of Si–O–Si. Importantly, the peak of C≡C at 1670 cm−1 was not observed in AC-PDMS membrane [29], suggesting that C≡C bonds on the AC-PDMS monomers were completely consumed after UV radiation and the AC-PDMS membrane was thoroughly cured.

Essential differences between AC-PDMS and OH-PDMS, including the chemical and physical properties can be attributed to the distinct crosslinking mechanism. The conventional OH-PDMS was tend to conform into spatial polymerization network by the condensation between PDMS with hydroxyl and crosslinker with ethoxy (e.g. tetraethylorthosilicate, vinyltriethoxysilane). However, the length of AC-PDMS segments increased rapidly by the addition reaction between vinyl groups under ultraviolet irradiation. Hence, the entanglement of liner-type polymer chains led to the curing of polymer matrix (Fig. 11a). It is interesting to investigate the detail information on segment stacking status that may result in the different gas transport behavior in the PDMS membrane.

Dielectric relaxation spectroscopy technique (DRS) is an accessible avenue to explore the stacking status from segment dynamic characteristics [34]. As shown in Fig. 11b, the relaxation process of PDMS samples took strong dependence of temperature. When the temperature is closer to the glass transition temperature (Tg), the side groups of AC-PDMS segments could respond to the change of electric field, leading to the β relaxation. When the temperature is higher than the Tg, stronger mobility of the AC-PDMS main chains enhances the dielectric loss which occurs the α relaxation. During the relaxation process, the orientation polarization could overcome the thermal motion of segments and caused the loss of electrical energy. This effect was expressed in the form of dielectric loss peak. It was obviously found that the α relaxation peak of AC-PDMS shifted to lower temperature area. It induced that the segments of AC-PDMS possessed higher mobility and lower molecular weight. The loss peak value of AC-PDMS was also higher than OH-PDMS demonstrating the thermal motion of short AC-PDMS segments was stronger. Fig. 11c exhibited the dependence of frequency, when the frequency of electric field is lower than 10 Hz, the dipoles orientation polarization happens which take pace with the change of alternating electric field. At this moment, the direct conduction contributes the major dielectric loss. As the increase of frequency, the relaxation process also can be divided into β relaxation and α relaxation. The data of α relaxation was fit by HN equation and VFT equation to obtain the fragile factor, which is adopted to demonstrate the stacking status of polymer segments. As shown in Fig. 11d, the fragile factor of AC-PDMS is much lower than the OH-PDMS. It means the polymer segments of AC-PDMS stack more densely than OH-PDMS [48]. Furthermore, the result of XRD (Fig. 11e) showed that the characteristic peak position of AC-PDMS was shifted from 12.1° to 12.9° compared with OH-PDMS. According to the Bragg equation, OH-PDMS possesses larger segment d-spacing (3.67 A) than AC-PDMS (3.47 A).

The structure of polymer network has great effect on the material mechanical property. We measured the critical tensile load of PDMS free-standing membranes and composite membranes to compare the mechanical property. As shown in Fig. 12, for the free-standing membranes, the critical tensile load of AC-PDMS (2.28 N) was lower than that of OH-PDMS (3.39 N), owing to the lower physical entanglement of AC-PDMS segments. Nevertheless, after coating on the porous substrate, owing to the robust substrate and interfacial adhesion, the AC-PDMS
composite membrane and OH-PDMS composite membrane possessed similar critical tensile load (Fig. 12b), which is favorable for practical application.

The reconstruction of PDMS stacking status may domain the change of molecular transport behavior. According to the solution-diffusion model, the gas permeation ($P_i$, permeability) through the membrane is the product of the sorption coefficient ($S_i$) and the diffusion coefficient ($D_i$). The permeabilities of CO$_2$ and N$_2$ of PDMS free-standing membranes were tested under the same condition to the PDMS TFC membrane (0.1 MPa and 25 $^\circ$C). As shown in Fig. 13a, the permeability of OH-PDMS was slightly higher than the AC-PDMS and the selectivity was almost the same. According to the XRD analysis, the permeability
adsorption experiments were carried out to determine the affinity of PDMS polymer segments and higher transport resistance compared with OH-PDMS decline of AC-PDMS could be owing to the denser stacking status of HF: hollow fiber.

Table 1

<table>
<thead>
<tr>
<th>Composite membrane</th>
<th>Feed pressure/Temperature (MPa/°C)</th>
<th>P CO₂ (GPU)</th>
<th>a CO₂/N₂</th>
<th>Reference</th>
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<td>10.5</td>
<td>[27]</td>
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<td>3003</td>
<td>13</td>
<td>[23]</td>
</tr>
<tr>
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<td>2700</td>
<td>10</td>
<td>[11]</td>
</tr>
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<td>4050</td>
<td>9</td>
<td>[49]</td>
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<tr>
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<td>2865</td>
<td>9</td>
<td>[13]</td>
</tr>
<tr>
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<td>10.4</td>
<td>[50]</td>
</tr>
<tr>
<td>AC-PDMS/PAN</td>
<td>0.1/25</td>
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<td>11.5</td>
<td>This work</td>
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</table>

HF: hollow fiber.

g., depositing an intermediate layer). Moreover, PDMS TFC membrane with CO₂ permeance >5000 GPU was rarely reported, except the recent work of Wang and co-workers by developing a novel casting blade to fabricate ultrathin PDMS/PSF TFC membrane. In contrast, in this work, the facile strategy operated on fast UV crosslinking of acryloyloxy-terminated PDMS monomers, endowed the resulting defect-free AC-PDMS TFC membrane with obvious superiority in CO₂ permeance.

4. Conclusions

In summary, for the first time, AC-PDMS monomer was adopted to implement the fast fabrication of TFC PDMS membrane by ultraviolet-induced crosslinking. Comparing to the conventional OH-PDMS, the addition reaction between AC-PDMS monomers led to the fast curing of casting solution and effectively inhibited the pore penetration. After optimization of UV light wavelength, viscosity of casting solution, and irradiation time, the fabricated AC-PDMS TFC membrane exhibited remarkable improvement in CO₂ permeance, reaching to 9635 GPU with CO₂/N₂ selectivity of 11.5. Moreover, this strategy simplifies the fabrication of PDMS TFC membrane, exhibiting great potential in scale-up. The distinct crosslinking process of AC-PDMS resulted in difference on the segments stacking status compared with OH-PDMS, further taking effect on the gas transport properties in the membrane. We expected that the strategy of fabricating PDMS TFC membrane via UV crosslinking of acryloyloxy-terminated monomers would have broad application in other membrane molecular separation processes.

Credit authorship contribution statement

Yang Pan: Investigation, Methodology, Formal analysis, Writing - original draft, review & editing.
Guining Chen: Investigation. Methodology, Formal analysis.
Jiangying Liu: Investigation.
Jiahui Li: Investigation.
Xi Chen: Formal analysis, Suggestion.
Haipeng Zhu: Characterizations, Writing - review & editing.
Gongping Liu: Conceptualization, Writing - review & editing, Supervision.
Guangru Zhang: Writing - review & editing.
Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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References


