A bio-inspired CO$_2$-philic network membrane for enhanced sustainable gas separation†

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For the first time, the exciting reaction between the bio-inspired dopamine and the epoxy functional poly(ethylene oxide) (PEO) at elevated temperatures was found and utilized for fabricating dopamine/poly(ethylene oxide) (PEO) network membranes for sustainable gas separation. The gas transport properties of the synthesized novel membrane were investigated aiming at energy (H$_2$) purification and CO$_2$ capture. The membrane was confirmed to be CO$_2$ selective and exhibited relatively high selectivity especially for CO$_2$/N$_2$ separation. Importantly, the flexible incorporation of low-molecular-weight poly(ethylene glycol) dimethyl ether (PEGDME) into the swollen network membrane greatly improved the gas transport performance and the CO$_2$ permeability was increased by 550%. Furthermore, the temperature and upstream pressure dependence of our developed membranes have been examined in detail. Surprisingly, the plasticization phenomena in the membranes at higher upstream pressure can be harnessed to enhance the gas transport performance by increasing both the CO$_2$ permeability and the CO$_2$/other tested gas selectivity mainly due to the network structure and CO$_2$-philic character. This report will expedite the rapid discovery of new materials derived from bio-inspired dopamine for possibly solving energy and environmental issues.

Introduction

Greenhouse gas carbon dioxide (CO$_2$) capture from flue gas (N$_2$) has attracted significant attention due to the global warming in recent years. Meanwhile, during the clean energy (H$_2$) and traditional energy (CH$_4$) production, CO$_2$ as the by-product and impurities must be separated and removed for highly efficient energy utilization.1–4 Traditional gas separation technologies such as pressure swing adsorption (PSA) are applicable but at the expense of secondary pollution and high costs. Therefore, developing “green” and low cost methods to efficiently separate various gases is imperative. Nowadays, membrane technology is believed to be an efficient “green” technology for gas separation with low cost and low carbon footprints.5–10 Conventional glassy polymer membranes, such as polyimide-based membranes mainly based on the diffusion discrimination of various gas molecules for separation, have been investigated extensively.11,12 However, glassy polymer membranes are not the ideal choice to separate CO$_2$ from flue gas and syngas due to the reduced gas separation efficiency arising from the unavoidable plasticization phenomenon or the limited H$_2$/CO$_2$ discriminating ability. Therefore, CO$_2$-philic membranes based on high CO$_2$ solubility providing fast CO$_2$ transportation have attracted great interest for CO$_2$ related gas separation.7,13 Most recently, PEO containing ethylene oxide (EO) units with a strong affinity to acid gases such as CO$_2$ have been screened out as the state-of-the-art CO$_2$-philic membrane material for CO$_2$ capture and energy purification.14–16 As a primary factor dominating the preferential CO$_2$ sorption, the inherent solubility parameter of the EO unit should match the optimal solubility parameter (22 MPa$^{1/2}$) to benefit the CO$_2$ transport.17

On the other hand, bio-inspired dopamine and its self-polymerization product of polydopamine (PDA) designed by nature have attracted great attention due to their excellent adhesion on virtually any type of inorganic and organic substrates.18,19 Although the self-polymerization mechanism of dopamine is extremely complicated and has not been thoroughly clarified until now, dopamine and its derivatives have been extensively applied to biomineralization, surface modification, nanomaterial functionalization, catalysts, and many other dynamic fields with a superfast speed.18,20,21 For membrane separation applications,
PDA (or dopamine or the derivatives) as a smart coating material has been widely utilized to decorate membranes for improving the water treatment performance.\textsuperscript{23,24} For example, Xi et al. modified the surface of hydrophobic polymer membranes using 3,4-dihydroxyphenylalanine (DOPA) and dopamine to improve the membrane hydrophilicity for water treatment.\textsuperscript{23,24} PDA coating followed by the hydrolysis of ammonium fluorotitanate was used for modifying the polyvinylidene fluoride (PVDF) ultrafiltration (UF) membranes.\textsuperscript{23} Furthermore, a one-step strategy via simultaneous polymerization of mussel-inspired dopamine and hydrolysis of various silanes was explored to modify PVDF membranes for oily water (oil-in-water emulsion) treatment.\textsuperscript{23} A simple and low-cost approach was reported recently to tailor the material surface using dopamine toward superhydrophobicity, which was utilized to build a mini-boat for self-driven oil spill cleanup.\textsuperscript{26} However, as far as we know, there are few literature studies reporting on the direct application of dopamine or PDA for synthesizing gas separation membranes.\textsuperscript{27}

In this study, a CO\textsubscript{2}-philic membrane with a network structure is fabricated for the first time by reacting dopamine with epoxy functional PEO via a thermo-induced reaction, which is inspired by our experimental discovery on the easy reaction between dopamine and epoxy functional monomers at elevated temperatures. The physicochemical properties of dopamine/PEO (D-PEO) membranes have been characterized by FTIR, XPS, XRD and SEM, and the gas transport performance has been investigated as well. The possible cross-linking mechanism is proposed based on the analysis of the experimental results and the literature reported on the dopamine induced reactions. Furthermore, D-PEO is simply immersed into poly(ethylene glycol) dimethyl ether (PEGDME) water solution. Driven by membrane swelling, D-PEO can readily swallow low-molecular-weight PEGDME for significantly enhanced gas transport performance. This study can greatly expand the application areas of the bio-inspired dopamine and its derivatives for sustainable development.

Experimental section

Preparation of the D-PEO membrane

Poly(ethylene glycol) diglycidyl ether (PEO-526, molecular weight of 526 g mol\textsuperscript{-1}), dopamine hydrochloride (DA) and poly(ethylene glycol) dimethyl ether (PEGDME, molecular weight of 250 g mol\textsuperscript{-1}) were purchased from Sigma-Aldrich and used as received. Ethanol, acetone and dichloromethane were purchased from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China). 2 g DA and 8 g PEO-526 were mixed directly according to the molar ratio of reactive groups with magnetic stirring at 80 °C for at least 6 h. After ultrasonication for 10 min to remove the trapped air, the solution was cast slowly onto a glass plate and then heated at 120 °C for 6 h and 160 °C for another 2 h. The thickness of the as-synthesized membranes is about 150 μm. The as-synthesized membranes were immersed into deionized water to remove the unreacted monomers for at least 2 days, and then the insoluble fractions were dried at 80 °C for 48 h to constant weight. The final obtained network membranes (called D-PEO) were ready for characterization. For the immersion process, the pristine D-PEO membrane (m\textsubscript{1}) with a known weight was immersed in the PEGDME water solution (30/70 wt%) at room temperature for 12 h to incorporate the PEGDME molecule into D-PEO, and then the impregnated D-PEO (called D-PEO-I) was washed gently with distilled water to remove the residual PEGDME-water solution on the surface of the membrane. The D-PEO-I was dried at 60 °C under vacuum for 48 h and weighed as m\textsubscript{2}. The PEGDME loading ratio of D-PEO-I is calculated as (m\textsubscript{2} – m\textsubscript{1})/m\textsubscript{1} × 100%. Finally, the D-PEO-I with a PEGDME loading ratio as high as 40.1 wt% was obtained via this simple post-treatment approach.

Characterization

To confirm the cross-linked structure of pristine D-PEO, the prepared D-PEO was divided by 1.5 cm × 1.5 cm, and then immersed into various solvents for about 12 h for obtaining the digital photographs. In particular, the size of the water swollen D-PEO without drying was measured. The swelling ratio of D-PEO in water can be calculated by (L\textsubscript{sw} – L\textsubscript{d})/L\textsubscript{d} × 100%, where L\textsubscript{d} and L\textsubscript{sw} are the lengths of D-PEO before and after swelling in water. The surface morphologies and elemental mapping of the D-PEO membranes were characterized using a scanning electron microscope (SEM, S-4500, Hitachi, Japan). FTIR measurements were carried out using a Spectrum One (Perkin Elmer, USA). The scan range was from 4000 to 600 cm\textsuperscript{-1}. The gel contents of the cross-linked D-PEO membranes were measured by extracting the as-synthesized membrane in deionized water at room temperature for at least 2 days. The insoluble fractions were dried at 80 °C for 48 hours to constant weight. The gel content was calculated as: gel% = (W’/W) × 100%, where W and W’ are the initial weight and the insoluble fraction weight of the cross-linked membrane, respectively. The wide-angle X-ray diffraction (XRD) spectra were recorded using a RINT D/MAX-2500/PC XRD instrument (Cu K\textsubscript{α1} λ = 0.154 nm, 40 kV × 30 mA, Rigaku, Japan). The samples were measured with a 2θ scan from 2° to 50° with 0.02° step. X-ray photoelectron spectroscopy (XPS) was used to determine the surface chemical composition. XPS measurements were carried out using an AXIS ULTRA DLD spectrometer (SHIMADZU, Japan) with a monochromatized Al K\textsubscript{α} X-ray source (1486.6 eV photons) at a constant dwell time of 250 ms and a pass energy of 40 eV. Differential scanning calorimetry (DSC) was performed on a DSC-Q2000 (TA, USA) from −100 to 140 °C with a heating and cooling rate of 5 °C min\textsuperscript{-1} under dry N\textsubscript{2} purge (50 mL min\textsuperscript{-1}). Two heating cycles of the D-PEO membrane were performed due to the water absorbency of PEO, and the glass transition temperature was obtained from the second heating cycle.

Measurements of pure gas transport properties

Generally, the gas transport properties of the dense polymeric membranes can be explained via the solution-diffusion model. The permeability (P) with the unit of Barrer (1 Barrer = 10\textsuperscript{-10} cm\textsuperscript{3} (STP) cm per cm\textsuperscript{2} per s per cmHg) can be described as:\textsuperscript{29}

\[ P = D \times S \]

(1)
where $D$ and $S$ with the unit of $\text{cm}^2 \text{s}^{-1}$ and $\text{cm}^3$ (STP) per $\text{cm}^3$ polymer cmHg are the diffusivity and solubility coefficients, respectively. The ideal selectivity of a membrane for gas A and gas B can be calculated by eqn (2):

$$
\alpha_{AB} = \frac{P_A}{P_B} = \left(\frac{D_A}{D_B}\right) \times \left(\frac{S_A}{S_B}\right)
$$

A constant volume method was used to characterize the pure gas permeability. The test sequence of gas permeability follows $H_2$ (kinetic diameter: 2.89 Å), $N_2$ (kinetic diameter: 3.64 Å), $CH_4$ (kinetic diameter: 3.80 Å) and $CO_2$ (kinetic diameter: 3.30 Å) with the testing temperature gradually increasing from 30 to 50 °C. The gas permeability was calculated by eqn (3):

$$
P = \frac{273 \times 10^{10}}{760} \left(\frac{V}{AT(p_2 \times \frac{76}{14.7})}\right) \left(\frac{dp}{dt}\right)
$$

where $P$ is the permeability of a membrane to a gas with the unit of Barrer. The rate of downstream-pressure increase $(dp/dt)$ was obtained when the permeation reached the steady state. $V$ is the volume of the downstream chamber ($\text{cm}^3$) and $l$ is the membrane thickness (cm). $A$ is the effective area of the membrane ($\text{cm}^2$). $T$ and $p_2$ are the testing temperature (K) and the upstream operating pressure (psi), respectively. $D$ can be obtained by the time-lag method according to eqn (4), and then the solubility can be deduced by eqn (1).

$$
D = \frac{l}{\theta}
$$

The effect of temperature on the gas permeability, solubility and diffusivity is typically described using the Van’t Hoff–Arrhenius equation:

$$
P_A = P_{A0} \exp \left(\frac{-E_P}{RT}\right)
$$

$$
S_A = S_{A0} \exp \left(\frac{-\Delta H_S}{RT}\right)
$$

$$
D_A = D_{A0} \exp \left(\frac{-E_D}{RT}\right)
$$

where $P_{A0}$, $S_{A0}$, and $D_{A0}$ are the pre-exponential factors, $R$ is the universal gas constant, $T$ is the absolute temperature (K), and $E_P$, $\Delta H_S$, and $E_D$ are the activation energy of gas permeation (kJ mol$^{-1}$), enthalpy of sorption (kJ mol$^{-1}$), and activation energy of diffusion (kJ mol$^{-1}$), respectively. The relationship between $E_P$ and $\Delta H_S$, $E_D$ can be described as eqn (8):

$$
E_P = -\Delta H_S + E_D
$$

**Results and discussion**

Initially, a simple “eye-guided” method by immersing the D-PEO membrane in various solvents was used to confirm the cross-linked structure of the D-PEO membranes fabricated via the thermo-induced reaction between bio-inspired DA and epoxy functional PEO. Fig. 1 shows the digital photographs of D-PEO membranes before and after soaking in water and other organic solvents. Obviously, the D-PEO membrane cannot be dissolved by any solvent including water, ethanol, acetone and dichloromethane. In fact, the solvent-immersed D-PEO membrane tends to swell, instead of dissolution in the solvents. Such results readily confirm the existence of the cross-linked network in the D-PEO membrane. Interestingly, water is the best solvent to swell D-PEO with the largest swelling ratio up to 60% by calculation. This should be due to the inherent hydrophilic character of PEO materials. After drying, the gel content of the D-PEO membrane immersed in water is more than 80%, indicating that the cross-linked structure can be effectively formed. In addition, the swelling character should allow low molecular-weight PEG to be imbedded into the swollen D-PEO via the simple post-immersion approach that may effectively enhance the gas transport properties.

To explore the possible mechanism of the discovered reaction between bio-inspired DA and epoxy functional PEO, chemical characterization was carried out. Fig. 2 demonstrates the FTIR spectra of DA, epoxy functional PEO (PEO-526), D-PEO and D-PEO-I membranes for comparison. The peak of pure dopamine at 1615 cm$^{-1}$ belongs to the N–H stretching vibration. The peaks at 3356 and 3260 cm$^{-1}$ are the characteristic peaks of the primary amine groups of dopamine. For epoxy functional PEO, the peaks at 915 and 3060 cm$^{-1}$ are the characteristic peaks of epoxy groups. By contrast, the peaks of epoxy groups and primary amine groups disappear in the synthesized D-PEO membrane. The new peak at 3200–3600 cm$^{-1}$ belonging to the secondary amine of N–H and O–H stretching appears, indicating that DA has reacted with epoxy groups of PEO-526 instead of just playing a role of an initiator. Besides, the peaks at 1625 and 1520 cm$^{-1}$ can be attributed to the secondary amine N–H stretching and C=C from benzene vibration resonance, respectively. For comparison, the FTIR results of the D-PEO-I are also shown in Fig. 2. The FTIR results imply that there are no significant differences between D-PEO and D-PEO-I since the preparation of D-PEO-I is a physical process without any chemical structure change.

The chemical composition of the D-PEO surface was determined by XPS analysis. Fig. 3 shows the XPS wide spectra and C 1s curve-fitting results of the D-PEO membrane. The D-PEO membrane is composed of C, O and N elements, as shown in

![Fig. 1 The photographs of original D-PEO (a) and swollen D-PEO using solvents of (b) H2O, (c) ethanol, (d) acetone, and (e) dichloromethane.](image-url)
Fig. 3(a). Since the unreacted monomers in the D-PEO membranes have been removed thoroughly by washing before characterization, DA cannot be determined in the XPS spectra if DA plays a role of an initiator. Definitely, the N 1s peak, appeared in the wide spectra, undoubtedly emerges from DA, indicating that DA has taken part in the reaction with PEO-526, rather than as an initiator. Based on Fig. 3(b), the C 1s peak can be well resolved into four peaks corresponding to C=O (288.8 eV), C–N (286.3 eV), C–O (286.0 eV) and C–C/H (284.6 eV), which are consistent with FTIR results. In addition, the surface morphology and elemental mapping of the D-PEO membrane, Fig. 4, indicate that the elements of C, O and N in the D-PEO membrane are distributed homogeneously, proving that the DA monomers have readily reacted with PEO-526 without large-scale self-polymerization.

According to the above-mentioned gel content (including swelling properties), FTIR, XPS and SEM characterization, the interesting cross-linking reaction between the bio-inspired dopamine and the epoxy functional PEO happened at elevated temperatures for forming the cross-linked network. However, DA polymerization in almost all the currently available literature studies is achieved under alkaline conditions (for example, Tris buffer with pH = 8.5) and at room-temperature, and the exact polymerization and interaction mechanism of DA is still not clear so far because of various possible reaction routes of the fascinating monomer of DA. As far as we know, the thermo-induced reaction of DA lacks study and its mechanism should be very interesting considering its possible promising applications. Based on our analysis of physicochemical properties of D-PEO, the possible reaction mechanism between DA and PEO-526 at elevated temperatures is proposed as shown in Scheme 1. Theoretically, the cross-linking reaction should happen by using the monomers with multi-functional groups. The pure PEO-526 cannot be cross-linked simply by thermal treatment without DA, which has been proved by our experiments (referring to Fig. S1, ESI†). Considering only two functional groups in PEO-526, the number of functional groups in DA for the thermo-induced reaction with PEO-526 to form a cross-linked structure should be at least 3. Generally, the primary amine in DA can react with epoxy groups, which accounts for one functional group. Therefore, where are other functional groups accounting for the cross-linking reaction in DA? Then, we have thermally treated the mixture of DA and PEO-526 especially under vacuum conditions. It is noted that the cross-linked membrane can still be obtained even without any oxygen involved (referring to Fig. S2, ESI†), which excludes the possible contribution of the complicated DA oxidation conditions to the cross-linking reaction. Therefore, the most possible functional groups from DA for reacting with epoxy groups in PEO-526 should be the phenolic hydroxyl groups, which account for 2 functional groups. As a result, the possible cross-linking mechanism should be attributed to both phenolic hydroxyl groups and amine groups of DA to react with the epoxy groups of PEO-526 at elevated temperatures. However, further study should be carried out in-depth to clarify the self-polymerization mechanism of DA.

In theory, the crystalline status of gas separation membranes strongly affects the gas transport properties since the crystallization region is considered to be impermeable for gas transport. The high crystallization tendency of PEO materials is basically due to the highly ordered arrangement of chain segments and the chain regularity must be limited for efficient gas separation applications. Therefore, XRD has been carried out for detecting the crystalline status of the samples and Fig. 5.
showed the XRD results of PEO-10k (molecular weight of 10 000 g mol$^{-1}$), DA, D-PEO and D-PEO-I. Obviously, several sharp peaks of DA and PEO-10k are exhibited due to their crystalline structure. However, both D-PEO and D-PEO-I membranes exhibit a broad halo, indicating that the introduced DA serves as a cross-linker and restrains the crystallization of PEO macromolecules by disturbing the chain regularity. In addition, further incorporation of PEGDME into D-PEO has no great influence on the crystalline status. The $d$-space is calculated by Bragg’s law:

$$d = \frac{\lambda}{2 \sin \theta}$$

where $\lambda$ is the wavelength of Cu Kα radiation (1.54 Å), and $\theta$ is the angle of the reflection peak. The $d$-space value can be related to the space between the polymer chains and the fractional free volume (FFV) of cross-linked membranes, i.e. gas permeability. The $d$-space of D-PEO is calculated to be 4.20 Å approximately, which is smaller than those of pure cross-linked PEO membranes (4.28 Å and 4.30 Å). This phenomenon is due to the smaller molecular weight of DA reagents. As expected, the $d$-space of D-PEO-I is 4.26 Å, which is larger than that of D-PEO. This result indicates that the incorporation of PEGDME can effectively expand the interchain space which is in favor of the gas transport by enhancing the diffusion process. Besides, the XRD results of D-PEO are also consistent with the FTIR and XPS results. The characteristic crystal peak would be determined if the self-polymerization of PEO-526 had occurred. However, the broad halo of D-PEO makes it clear that DA only serves as a cross-linker rather than an initiator, in the reaction system for creating an amorphous PEO network structure.

Definitely, the amorphous structure of novel PEO-based membranes confirmed by XRD can be beneficial to enhance the gas permeability. Fig. 6(a) and (b) show pure gas permeabilities of the novel D-PEO membrane and PEGDME-imbedded D-PEO-I as a function of testing temperature, respectively. H$_2$ is tested at 3.5 atm for safety reasons and other gases are tested under 10 atm for accurate selectivity calculation. CO$_2$ is tested at both 3.5 and 10 atm.

According to Fig. 6(a), the permeabilities of all tested gases increase with an increase in the temperature, which can be attributed to the enhanced membrane chain flexibility at a higher temperature. For instance, as the testing temperature increases from 30 to 50 °C, the CO$_2$ permeability of D-PEO increases from 36.9 to 90.3 Barrer at 3.5 atm. In addition, the CO$_2$ permeability of D-PEO is much larger than that of the other three gases, indicating the CO$_2$-philic character of D-PEO due to the existence of EO groups. The CO$_2$ permeability tested at 10 atm is larger than that at 3.5 atm, indicating that the upstream pressure influences the gas transport properties, which will be discussed later in this paper. Moreover, the relationship between the gas permeability and the testing temperature is linear, instead of appearing as a big jump. In fact, the gas permeability properties of D-PEO are still unsatisfactory, though the formation of the amorphous structure results in a much higher CO$_2$ permeability (49 Barrer at 35 °C and 3.5 atm) than that of the semi-crystalline PEO membranes (12 Barrer at 35 °C and 4 atm). Inspired by the inherent swelling properties of the cross-linked network structure of D-PEO in solvents as Fig. 1 shows, the D-PEO was further modified by imbedding low-molecular-weight PEG (PEGDMA) via a facile post-treatment strategy. As a result, D-PEO-I with a PEGDME loading of 40.1 wt% can be simply obtained. Surprisingly, the gas permeabilities of D-PEO-I significantly increase compared with those of D-PEO according to Fig. 6(b). For example, the CO$_2$ permeability increases by 550%, respectively, in D-PEO-I at 30 °C and 3.5 atm, from 43 to 281 Barrer after imbedding PEGDME into D-PEO membranes. The great performance enhancement can be mainly attributed to the changed physicochemical
environment (such as the interchain space) by the incorporated PEGDME for the easier gas transport, which will be further discussed in the following activation energy part.

The gas permeability is contributed by both solubility and diffusivity by means of a solution-diffusion model. Fig. 7 shows the gas solubility and apparent diffusivity of D-PEO (a) and D-PEO-I (b) as a function of testing temperature. The H₂ diffusivity cannot be determined due to the extremely short H₂ time lag. As Fig. 7(a) shows, the N₂ and CH₄ solubilities of the D-PEO membrane almost remain constant with the testing temperature. However, the CO₂ solubility is considerably larger than that of any other gas due to the strong interaction between CO₂ and PEO as mentioned above, also indicating the CO₂-philic character of D-PEO. The apparent diffusivities of all the tested gases increase with an increase in the temperature in D-PEO, attributing to the enhanced chain segment flexibility at higher temperature. Generally, the order of gas apparent diffusivity should be kept the same as the gas molecular dynamic diameter. The H₂ diffusivity should be much larger than that of other three gases due to its smaller kinetic diameter (2.89 Å) than N₂ or CH₄, though the H₂ diffusivity cannot be determined accurately by our available equipment. Interestingly, the N₂ apparent diffusivity is larger than that of CO₂, though the N₂ kinetic diameter (3.64 Å) is larger than the CO₂ kinetic diameter (3.30 Å). This is due to the strong interaction between CO₂ and}

EO groups retarding the CO₂ diffusion, which had been proved in our previous work. Even so, D-PEO exhibits a higher CO₂ permeability than that of N₂ due to the considerable CO₂ solubility, the CH₄ apparent diffusivity is the lowest among the tested gases resulting from the larger kinetic diameter (3.80 Å).

According to Fig. 7(b), the same order of the tested gas solubility is confirmed in D-PEO-I, i.e. CO₂ > CH₄ > N₂. Interestingly, the CO₂ and CH₄ solubilities of D-PEO-I are higher than those of D-PEO, which may be caused by the incorporation of PEGDME with much more EO content. The N₂ solubility seems to remain unchanged after the incorporation of PEGDME into the D-PEO membrane.

As expected, the apparent diffusivities of all tested gases increase with an increase in the temperature in D-PEO-I. The gas diffusivities of D-PEO-I increase markedly compared with those of D-PEO at the same temperature. For example, the apparent diffusivity values of the tested three gases increase by an order of magnitude compared to that of D-PEO at 50 °C. This phenomenon can be attributed to the imbedded low-molecular-weight PEGDME, which plays a role of a plasticizer. The imbedded PEGDME molecules can be located between the polymer chains to improve the chain mobility and to increase the chain distance, i.e. increase the FFV. This phenomenon has been proved by the XRD results mentioned above. The d-space increases from 4.20 Å of D-PEO to 4.26 Å of D-PEO-I, which makes the gas diffusion easier. The simultaneous increment of gas diffusivity and solubility of D-PEO-I compared with that of D-PEO validated our strategy that the incorporation of low-molecular-weight PEG into the D-PEO membrane by the versatile post-treatment method is highly effective for enhancing the gas transport properties.

The effect of temperature on the gas permeability, apparent diffusivity and solubility can be described by the Van’t Hoff–Arrhenius equation. The CO₂ negative adsorption enthalpy in both D-PEO and D-PEO-I (Table S1, ESI†) caused its decrease with an increase in the temperature. All the E_p values of various gases in D-PEO-I membranes are smaller than those in D-PEO

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Fig. 6 Pure gas permeabilities of (a) D-PEO and (b) D-PEO-I membranes as a function of temperature.

Fig. 7 Temperature dependence of gas solubility and diffusivity of D-PEO (a) and D-PEO-I (b).
membranes, indicating the lower barrier of D-PEO-I for gas transport.

In addition, the permeability of D-PEO and D-PEO-I was compared with other PEO-based membranes, Table S2, ESL†. Both the LCM membrane and XLPEGDA are prepared using pure PEO with different end groups. The gas permeability value of Am PEO (fully amorphous PEO) is theoretically estimated.† The gas permeabilities of D-PEO are lower than those of LCM and XLPEGDA. However, after simply soaking in PEGDME solution, D-PEO-I exhibits significantly higher gas permeabilities than LCM or XLPEGDA. In order to determine the principle of the increased gas permeability in D-PEO-I, the gas solubilities and apparent diffusivities of D-PEO-I and LCM as a function of testing temperature were compared† (Fig. S3, ESL†). As Fig. S3(a)† shows, the gas solubility values of D-PEO-I and LCM are approximately similar since they both are PEO-based membranes, indicating that DA does not affect the gas solubility obviously. Surprisingly, the gas apparent diffusivity of D-PEO-I is greatly different from that of LCM. As shown in Fig. S3(b),† the gas apparent diffusivities of D-PEO-I as a function of testing temperature are much larger than those of LCM, resulting in much larger gas permeabilities. Since the gas apparent diffusivity can be strongly influenced by the membrane fractional free volume (FFV),39 the larger gas diffusivity of D-PEO-I indicates an increment of the FFV due to the imbedded PEGDME molecule to some extent.

Fig. 8 shows the pure gas selectivity of D-PEO (a) and D-PEO-I (b) membranes as a function of testing temperature. The CO2/N2 and CO2/CH4 selectivities of both D-PEO and D-PEO-I membranes decrease with an increase in the testing temperature due to the relatively low increment of the CO2 permeability compared with that of N2 or CH4, which is mainly caused by the declined CO2 solubility. However, the CO2/H2 selectivity of both D-PEO and D-PEO-I membranes slightly decreases with an increase in the testing temperature, indicating that the CO2/H2 selectivity is less sensitive to the temperature. The CO2/N2 and CO2/CH4 selectivities of D-PEO-I are smaller than those of D-PEO, attributing to a larger increment of N2 or CH4 permeability than that of CO2. The aforementioned enhanced FFV could improve gas diffusivities, especially for N2 and CH4. However, the existence of PEGDME restrains the CO2 diffusion process due to the strong interaction between CO2 and EO groups, resulting in a less pronounced increment of CO2 permeability than that of N2 or CH4.

For glassy polymeric gas separation membranes, the permeabilities of low-sorbing gases (such as N2, H2 and CH4) are essentially independent of the upstream pressure, while the permeabilities of high-sorbing gases (i.e. CO2) increase with an increase in the operating pressure.22,23 Typically, the CO2 permeability of the glassy polymeric membrane increases obviously with an increase in the upstream pressure resulting from the CO2-induced plasticization phenomenon. This phenomenon seriously deteriorates the membrane performance for practical applications because the gas pair selectivity of the plasticized membrane will generally decrease. Here, various gas permeabilities of the D-PEO and D-PEO-I membranes as a function of upstream pressure were determined at 35 °C and the results are shown in Fig. 9. As expected, the CO2 permeability increases obviously with an increase in the upstream pressure, indicating the remarkable plasticization phenomenon due to the enhanced CO2-polymer interactions in the CO2philic D-PEO and D-PEO-I membranes. In addition, a higher CO2 permeability increment of D-PEO-I can be found compared with that of D-PEO, mainly due to the imbedded PEGDME leading to a higher EO content and interchain space. In contrast, the permeabilities of other three tested gases of both D-PEO and D-PEO-I membranes remain the same or slightly decrease, which may be attributed to the reduced FFV by pressure-induced compaction in the membrane without the strong gas–polymer interactions. Interestingly, different from traditional glassy polymeric membranes, the pure gas selectivities including CO2/H2, CO2/N2 and CO2/CH4 notably increase with an increase in the upstream pressure. Therefore, thanks to the CO2philic character and the cross-linked network structure, our novel developed membranes can utilize the plasticization phenomenon for achieving a better gas separation performance with both enhanced CO2 permeability and higher CO2/N2 (CO2/H2 or CO2/CH4) selectivity.

![Fig. 8](image_url)  
*Fig. 8* Temperature dependence of gas permeability selectivity of D-PEO (a) and D-PEO-I (b).

![Fig. 9](image_url)  
*Fig. 9* Gas permeabilities of D-PEO (a) and D-PEO-I (b) and CO2/gas selectivity (c) as a function of upstream pressure at 35 °C.
Conclusions

A novel CO2-phlic network (D-PEO) membrane has been successfully prepared via the thermo-induced reaction by simply mixing bio-inspired DA and epoxy functional PEO. The cross-linked structure had been observed by the gel content (including swelling properties), FTIR and XPS results. The XRD results confirmed the amorphous structure of our developed membranes due to the disruption of PEO chain regularity. The gas transport properties of the D-PEO membrane are characterized, showing due to the disruption of PEO chain regularity. The gas transport properties of the cross-linked network membrane. And the membranes can be applied for energy puri

Other tested gas selectivity. Therefore, these novel DA/PEO phenomena in both D-PEO and D-PEO-I membranes at higher increase in the temperature. Interestingly, the plasticization solubility of any other tested gas almost remains constant with an decreases with an increase in the temperature although the

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References


38 X. P. Miao, Y. Meng and X. Y. Li, Polymer, 2015, 60, 88–95.