A compatible crosslinker for enhancement of CO₂ capture of poly(amidoamine) dendrimer-containing polymeric membranes

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Abstract

Poly(amidoamine) (PAMAM) dendrimers are physically immobilized in a crosslinked poly(ethylene glycol) (PEG) upon photopolymerization of PEG dimethacrylates (PEGDMAs) in the presence of the dendrimers in ethanol. The dendrimer-containing polymeric membranes exhibit excellent CO₂ separation properties over smaller H₂. However, immiscibility of PEG matrix and the dendrimer results in the formation of a bicontinuous phase-separated structure on a couple of microns scale, which inhibits to reduce the membrane thickness for enhancement of the CO₂ permeability. A compatible crosslinker, 4GMAP, is developed from the dendrimer and glycidyl methacrylate. Incorporation of the compatible crosslinker in the photopolymerization suppresses the macrophase separation between PAMAM dendrimer and PEG matrix and allows preparation of polymeric membranes as thin as 10 μm with high CO₂ selectivity. The 4GMAP incorporation also endows pressure tolerance by increasing crosslinking density of the resulting polymeric membranes. The CO₂ permeance is elevated from 9.94×10^{-13} to 1.68×10^{-11} m³(STP) m⁻² s⁻¹ Pa⁻¹, by reducing the membrane thickness from 640 to 9.5 μm with 10 of CO₂ selectivity at 313 K and 0.56 MPa of CO₂ partial pressure.

Keywords

CO₂ separation, Crosslinker, PAMAM dendrimer, Phase separation, Polymeric membrane

1. Introduction

Inexperienced rise of atmospheric concentration of CO₂ triggers global warming and climate change, and a number of CO₂ capturing technologies have been studied to mitigate CO₂ emission through the air. Membrane separation would be one of the most promising approaches among them in terms of technological and economic perspectives, and various CO₂ separation materials have been developed [1,2]. Sirkar et al. reported PAMAM dendrimers expressed high CO₂ separation performance over N₂ [3-5] and would hold potential as novel CO₂ separation materials in gas separation. However, flow nature of the dendritic molecules requires stable immobilization into a suitable matrix to fabricate a CO₂ separation membrane. In our research group, various CO₂ separation membranes containing PAMAM dendrimers have been developed [6-8]. Especially, the dendrimer can be readily immobilized in a crosslinked PEG by photopolymerization of PEGDMA in the presence of the dendrimer. The resulting polymeric membrane exhibits excellent CO₂ separation performance over H₂ under humidified conditions [9]. CO₂ absorbed in the membrane turns to bicarbonate ion and carbamate with primary amines of PAMAM dendrimer under the conditions. The former is a major migrating species through the membrane, while the latter results in the formation of quasi-crosslinking of PAMAM, which suppresses H₂ permeation, to give a high selectivity [10]. However, permeability of CO₂ should be enhanced for use such as in an integrated gasification combined cycle (IGCC) plant [11-14]. H₂ separation over CO₂ is indeed technically more accessible, and various separation technologies have been reported such as with palladium membranes [12,15]. However, in the IGCC process, recompression of H₂ after separation results in higher energy requirement rather than CO₂ separation process. On the other hand, the polymeric membrane would have another opportunity at H₂ stations for fuel cell vehicles (FCVs), where H₂ is mostly produced by steam reforming of natural gas or liquid propane gas (LPG) with emission of CO₂ in the PSA off gas. When CO₂ is effectively separated, carbon-free H₂ will be available.

An approach to elevate gas permeability of the polymeric membrane can be reducing the membrane thickness. However, recent intensive investigations of the dendrimer-containing membranes reveal the formation of a bicontinuous structure of PAMAM dendrimer-rich and PEG-rich phases upon

photopolymerization-induced phase separation on a couple of microns scale [16]. When the membrane thickness is less than 200 μm , the resulting membrane loses the high CO_2 separation properties over H_2 because leakage of the physically entrapped dendrimer from the membrane is not negligible. Herein, we develop a compatible crosslinker, 4GMAP [17], which is derived from PAMAM dendrimer. Suppression of the macrophase separation by the incorporation of the compatible crosslinker is investigated. With the resulting polymeric membranes, increase in the CO_2 permeance is examined by reducing the membrane thickness under pressurized conditions.

2. Experimental

2.1. Materials

PAMAM dendrimer (G_0) and glycidyl methacrylate are purchased from Sigma-Aldrich (MO, USA) and Tokyo Chemical Industry (Tokyo, Japan), respectively. A radical initiator, 1-hydroxycyclohexyl phenyl ketone (Irgacure 184), is obtained from Ciba Specialty Chemicals (Tokyo, Japan). Other organic and inorganic compounds are reagent grade and used without further purification.

2.2. Synthesis of compatible crosslinker, 4GMAP

4GMAP is chemically synthesized by the reaction between PAMAM dendrimer (G_0) and glycidyl methacrylate as shown in Fig. 1. In brief, a 10 g of the dendrimer (19.3 mmol) is dissolved in 100 mL ethanol on a crushed ice bath. To the solution is added a 11.0 g (77.2 mmol) of glycidyl methacrylate dissolved in 10 mL ethanol dropwise, and the reaction mixture is stirred for 3 hours at 273 K and then further stirred for 16 hours at ambient temperature.

δ_{H} (400 MHz; $\text{MeOH-}d_4$) 1.94 (12 H, s, CH_3), 2.36 (8 H, CH_2CONH), 2.55 (4 H, s, $\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NHCH}_2$), 2.34 and 2.65 (8 H, NHCH_2CH), 2.67 (8 H, $\text{CONHCH}_2\text{CH}_2$), 2.75 (8 H, $\text{NCH}_2\text{CH}_2\text{CO}$), 4.12 (4 H, CH), 4.21, 3.99 (8 H, CH_2O), 5.63 and 6.14 ppm (8 H, s, $\text{CH}_2=\text{C}$).

2.3. Membrane preparation

PAMAM dendrimer-containing membranes are fabricated by photopolymerization of PEGDMA and

4GMAP with various mixture ratios in the presence of the dendrimer in ethanol as shown in Fig. 1. The preparation conditions are the same in our previous report [9]. A ratio of solutes to ethanol is 2.0 by wt, and a monomer to initiator ratio is 60 by mol. For a laser scanning confocal microscope (LSCM) observation, FITC-PEGMA [16] is incorporated into the photocopolymerization with 1 wt% relative to the monomers. The dendrimer concentration is 50 wt%. The membrane thickness is controlled by sandwiching the reaction mixture with quartz plates and commercial stainless steel spacers with predetermined thickness (10-500 μm) followed by the UV curing. The polymeric membranes obtained are dried under vacuum to eliminate ethanol before use. The membrane thickness is determined by a Keyence VHX-1000 digital microscope (Tokyo, Japan).

2.4. Microscope observations

The polymerization-induced phase separation is examined on a LSM 710 laser scanning confocal microscope (Carl Zeiss, Germany) with an incident laser beam (488 nm) [16]. A band-pass filter (490-735 nm) installed in front of the detector is used to detect only fluorescence from the fluorescent molecules that are introduced only to stain the PEG-rich phase. An oil-immersed $\times 63$ (Plan-Apochromat, Carl Zeiss) objective lens with numerical aperture of 1.4 is used. Scanning electron microscope (SEM) measurement is carried out on a Hitachi S-4800 field emission scanning electron microscope (Hitachi, Japan) after Pt-Pd sputtering on a MSP-1S (Vacuum Device, Japan). Transmission electron microscope observation is also conducted with a Hitachi H-7650 transmission electron microscope. A PEG fraction of the polymeric membrane is stained with Ru tetroxide, and a TEM sample is sliced by using a Leica FC-7 microtome (Leica, Germany) with a thickness of ca. 50 nm.

2.5. Mechanical properties

Mechanical properties of the polymeric membranes are measured using a Shimadzu AGS-X tester (Kyoto, Japan) with a 50 N load cell to find Young's modulus and strain at break. The displacement rate is 10 mm s^{-1} . The polymeric membranes with various 4GMAP contents contain 50 wt% PAMAM dendrimer, and the thickness is ca. 500 μm . They are dried and cut using a custom dog

bone-shaped specimen cutter (JIS K6251, 2 mm wide and 35 mm long). Mechanical testing for each specimen is carried out at least in triplicate under ambient conditions.

2.6. CO₂ separation performance

CO₂ separation properties are studied at 313 K and predetermined relative humidity under various pressures (CO₂ partial pressure $p(\text{CO}_2)$: up to 560 kPa) [9,18]. The polymeric membranes placed on a polyether sulfone support (MW cut-off: 300 kDa, Millipore) are set in a flat-sheet membrane cell and a humidified CO₂/H₂ (80/20 by vol) gas mixture is fed to the cell at a flow rate of 100 mL min⁻¹. Humidified He gas is supplied to collect the permeate at a flow rate of 10 mL min⁻¹. Gas compositions in both feed and permeate sides are analyzed by gas chromatography on a GC-4000 gas chromatograph (GL Sciences Inc., Tokyo, Japan). The stage cut is controlled to less than 0.01, and under these experimental conditions, the pressure ratios of feed to permeate are sufficient to give the separation factor ($\alpha(\text{CO}_2/\text{H}_2)$) as an ideal separation factor. The separation factor and permeance (Q_i) are determined by the following equations:

$$\alpha(\text{CO}_2 / \text{H}_2) = \frac{y_{\text{CO}_2} / y_{\text{H}_2}}{x_{\text{CO}_2} / x_{\text{H}_2}} \quad (1)$$

$$Q_i = \frac{N_i}{A \cdot \Delta p_i \cdot t} \quad (2)$$

where x_i and y_i are the molar fraction of gas i of feed and permeate sides, respectively, and N_i , A , Δp_i , and t are steady-state permeate volume of gas i , effective membrane area, partial pressure difference of the feed and permeate sides of gas i , and transmission time, respectively. In the experimental conditions, $\alpha(\text{CO}_2/\text{H}_2)$ can be equivalent to $Q(\text{CO}_2)/Q(\text{H}_2)$.

Fig. 1. Synthetic scheme of a compatible crosslinker, 4GMAP (upper) and schematic drawing of photocopolymerization of PEGDMA and 4GMAP in the presence of PAMAM dendrimer (bottom).

3. Results and Discussion

The compatible crosslinker, 4GMAP, is derived from the parent dendrimer as shown in Fig. 1, and Fig. 2 shows ^1H NMR spectrum of the crosslinker in deuterated methanol. By ring-opening reaction of the epoxide of glycidyl methacrylate, a peak shift of methine proton from 3.25 to 4.12 ppm indicates introduction of the polymerizable methacrylate group into the branching end of the dendrimer. The ring-opening reaction competes with Michael addition reaction between $\text{C}=\text{C}$ bonds and primary amines, however, steric hindrance by the methyl group of methacrylate would be expected to inhibit the addition reaction. A small hill at around 1.1 ppm can be assigned to methylene protons formed as a result of the addition reaction, and thus Michael addition reaction is considerably suppressed in the reaction conditions.

Fig. 2. ^1H NMR spectrum of 4GMAP in methanol- d_4 at 298 K.

Polymeric membranes are readily prepared by the photopolymerization. Progress of the photopolymerization reaction is also studied by NMR. The monomers, PAMAM dendrimer, and the initiator are dissolved in methanol- d_4 , where the ratio of PEGDMA/4GMAP/PAMAM dendrimer is 42.5/7.5/50 by wt. The mixture is transferred into a $\phi 5$ mm quartz NMR tube (Shigemi, Tokyo, Japan) and then exposed to UV for 90 s. ^1H and ^{13}C NMR of the sample before and after the UV curing are recorded on a Bruker Ascend 600 NMR spectrometer as shown in Fig. 3. Peaks of allyl protons of the monomers are seen at 5.6 and 6.1 ppm in ^1H NMR and 136.3 and 125.3 ppm in ^{13}C NMR (black lines). Methyl protons of the monomers also give a strong singlet peak at 1.94 ppm in ^1H NMR. Those characteristic peaks have disappeared after the UV curing (red lines), which suggests that the photopolymerization is completed by the experimental conditions.

Fig. 3. ^1H NMR (top) and allyl proton region of ^{13}C NMR (bottom) spectra of the reaction mixture before (black) and after (red) the UV irradiation in methanol- d_4 at 303 K.

Fig. 4 displays various images of the polymeric membranes with or without the compatible crosslinker. Photopolymerization without 4GMAP gives an opaque polymeric membrane due to the polymerization-induced macrophase separation between PAMAM dendrimer and PEG matrix as represented in Fig. 4a [16]. On the contrary, incorporation of 4GMAP results in the formation of a macroscopically transparent membrane in Fig. 4b, which indicates suppression of the phase separation on a micron scale. 4GMAP is derived from PAMAM dendrimer and can be a compatibilizer in the UV curing. The LSCM observation is a suitable tool to investigate the detail morphology of polymeric blend on a micron scale [19-21] and captures macrophase separation when a polymeric membrane is prepared without 4GMAP in Fig. 4c. Here, the bright and dark fields are PEG-rich and PAMAM dendrimer-rich phases, respectively [16]. However, the macrophase separation is completely suppressed in the spatial range by the incorporation of 4GMAP when the content is not less than 7.5 wt% as shown in Fig. 4d. The phase separation is also examined by TEM. In the absence of 4GMAP, macrophase separated structure is clearly seen in Fig. 4e, which is well

consistent to the LSCM results. On the contrary, the phase separation takes place on a submicron range by the addition of the compatible crosslinker in Fig. 4f.

Fig. 4. PAMAM dendrimer-containing polymeric membranes (a) without 4GMAP and (b) with 4GMAP (7.5 wt%); LSCM images (c) without 4GMAP and (d) with 4GMAP (7.5 wt%); TEM images (e) without 4GMAP and (f) with 4GMAP (7.5 wt%); [PAMAM dendrimer]=50 wt%.

Fig. 5. SEM images of cross section of the polymeric membranes after ethanol extraction of PAMAM dendrimer with (a) 3.75; (b) 5.0; (c) 7.5 and (d) 10 wt% 4GMAP; [PAMAM dendrimer]=50 wt% in the membrane fabrication.

Effect of 4GMAP content on the phase-separated structure is then studied by SEM. Since the dendritic molecules are physically entrapped in the PEG network, they can be eluted out from the polymeric membranes by immersing in ethanol. About 0.6 g of the polymeric membrane with various 4GMAP contents was immersed in 50 mL ethanol, and the effluent was collected by changing the eluent every 12 hours for 3 days. When the crosslinker content was below 5.0 wt%, the polymeric membranes turned to white after the ethanol extraction. On the other hand, the membranes were transparent after the extraction with above 7.5 wt% of 4GMAP content. The cross sections of the resulting polymeric membranes are displayed in Fig. 5a-d. When 4GMAP weight fraction is below 5.0 wt% (Fig. 5a,b), a porous structure is found, which indicates the formation of a bicontinuous phase-separated structure of PAMAM dendrimer-rich and PEG-rich phases on a micron scale [16] corresponded to the results of the LSCM and TEM experiments in Fig. 4c and 4e, respectively. With increase of the weight fraction of 4GMAP, morphology of the polymer matrix after the ethanol extraction changes drastically due to increase in compatibility between PEG matrix

and PAMAM dendrimer by 4GMAP, and the resulting matrix loses the porous structure when the weight fraction of 4GMAP is above 7.5 wt%.

Fig. 6. ^1H NMR spectra of effluent after ethanol extraction of PAMAM dendrimer (50 wt%) containing polymeric membranes with various amount of 4GMPA in methanol- d_4 at 298 K.

The effluent is collected and analyzed by ^1H NMR, which reveals that the resulting effluents are exactly identical to PAMAM dendrimer independent of 4GMAP content as shown in Fig. 6. The peaks at 2.38 (*t*), 2.57 (*s*), 2.73 (*t*), 2.78 (*t*), and 3.24 (*t*) ppm are assigned to the proton resonances of $\text{CH}_2\text{-CONH}$, $\text{N-CH}_2\text{CH}_2\text{-N}$, $\text{N-CH}_2\text{CH}_2\text{-CONH}$, $\text{CH}_2\text{-NH}_2$, and CONH-CH_2 of PAMAM dendrimer. The ratios of integral values are also reasonably fit to the chemical structure. If residual PEGDMA comes out from the membrane, peaks of allyl protons are seen at 5.6 and 6.1 ppm. In addition, polymerized PEG or reactant between PEGDMA and PAMAM dendrimer gives a peak at 3.7 ppm. The effluent can be thus determined as PAMAM dendrimer, indicating that PAMAM dendrimer stays intact in the PEG network. The dendrimers can be recovered quantitatively, and thus unfavorable side reactions, such as Michael addition reaction between primary amines of PAMAM dendrimers and $\text{C}=\text{C}$ bonds of monomers, would not take place under the photopolymerization conditions.

The CO₂ separation properties of the polymeric membranes under different pressures are displayed in Fig. 7. At 0.082 kPa of $p(\text{CO}_2)$ under isobaric conditions, the separation factor is ca. 50, and then decreases with increase in $p(\text{CO}_2)$, which is most likely due to decrease in $Q(\text{CO}_2)$ while $Q(\text{H}_2)$ stays constant. The CO₂ permeation undergoes on a facilitated transportation via carrier-mediated diffusion mechanism [22]. Without 4GMAP, the polymeric membranes can not tolerate under pressure above 0.23 MPa of $p(\text{CO}_2)$ and 0.29 MPa of total pressure. In contrast, the polymeric membranes with 4GMAP exhibit high CO₂ separation performance under higher pressurized conditions. The $\alpha(\text{CO}_2/\text{H}_2)$ and $Q(\text{CO}_2)$ are 17.4 and $4.92 \times 10^{-12} \text{ m}^3(\text{STP}) \text{ m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$, respectively, at 0.56 MPa of $p(\text{CO}_2)$ and 0.70 MPa of total pressure. Incorporation of the compatible crosslinker results in increase of crosslinking density, which endows the polymeric membranes with pressure tolerance.

Fig. 7. CO₂ separation properties of PAMAM dendrimer-containing polymeric membranes as a function of CO₂ partial pressure at 313 K and 80 % relative humidity: (a) PAMAM dendrimer/PEGDMA=50/50 by wt., 75 μm in thickness; (b) PAMAM dendrimer/PEGDMA/4GMAP=50/42.5/7.5 by wt., 71 μm in thickness; circle: $Q(\text{CO}_2)$; diamond: $Q(\text{H}_2)$; cube: $\alpha(\text{CO}_2/\text{H}_2)$.

As shown in Fig. 8b, when the ratio of PEGDMA/4GMAP/PAMAM is 42.5/7.5/50 by wt and the thickness of the membrane is 10 μm , the polymeric membrane retains the gas permeances over 16 h at 0.7 MPa of total pressure (0.56 MPa of CO₂ partial pressure). And the selectivity is thus constant

and 10 during the period. The $Q(\text{CO}_2)$ is $1.68 \times 10^{-11} \text{ m}^3(\text{STP}) \text{ m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$. When the membranes reach steady state in the separation conditions, the separation properties become constant and do not change over the period. Deactivation or leakage of the dendrimer can be thus negligible. On the other hand, the membrane without the crosslinker (ca. 180 μm in thickness) loses preferential CO_2 permeation above 0.30 MPa of total pressure (0.24 MPa of CO_2 partial pressure) in Fig. 8a, and it is obvious that the compatible multi-arm crosslinker endows pressure tolerance to the polymeric membrane.

Fig. 8. Time course of CO_2 separation properties of PAMAM dendrimer-containing polymeric membranes at 313 K and 80 % relative humidity under various pressures; $\text{CO}_2/\text{H}_2=80/20$ by vol.; (a) PAMAM dendrimer/PEGDMA=50/50 by wt., 175 μm in thickness; (b) PAMAM dendrimer/PEGDMA/4GMAP=50/42.5/7.5 by wt., 9.5 μm in thickness; cube: $Q(\text{CO}_2)$; diamond: $Q(\text{H}_2)$; triangle: CO_2 partial pressure.

Fig. 9. Mechanical properties of PAMAM dendrimer (50 wt%) containing polymeric membranes with various 4GMAP contents. Error bar denotes standard deviation (n=at least 3).

Mechanical properties of the polymeric membranes are examined by tensile testing in Fig. 9. The Young's modulus increases about 3-fold when 4GMAP content is incorporated from 0 to 30 wt%. On the other hand, the elongation at break decreases with increase of the crosslinker. The polymeric membrane loses the elasticity and becomes brittle due to increase in the crosslinking density. On the other hand, CO₂-induced plasticization has an important impact on various polymeric membranes, which might cause a reduction in the physicochemical properties [23]. When the polymeric membranes are equilibrated under 0.7 MPa of CO₂ at 298 K, the polymeric membrane without 4GMAP swells by absorbing CO₂ and the thickness increases from 440±4 to 454±6 μm. In contrast, the membrane thickness with the crosslinker does not change much before (403±1 μm) and after (400±2 μm) the equilibration. These results also support the increase in crosslinking density by incorporation of 4GMAP. Polymeric membranes with 4GMAP show slightly higher CO₂ separation performance than those without the crosslinker, although the crosslinking density is increased. Hydroxyl groups of 4GMAP formed as a result of ring-opening reaction of the epoxide may result in the increase in hydrophilicity, which is one of the most crucial factors to determine the CO₂ separation properties [24].

Fig. 10. Effect of the membrane thickness on the CO₂ separation properties of PAMAM dendrimer-containing polymeric membranes at 313 K and 90 % relative humidity under 0.56 MPa of $p(\text{CO}_2)$ and 0.70 MPa of total pressure; circle: $Q(\text{CO}_2)$; diamond: $Q(\text{H}_2)$; cube: $\alpha(\text{CO}_2/\text{H}_2)$; PAMAM dendrimer/PEGDMA/4GMAP=50/42.5/7.5 by wt.

With the polymeric membranes containing 7.5 wt% 4GMAP, change in gas permeance as a function of the membrane thickness is studied at 313 K and 90 % relative humidity under pressurized conditions, 0.56 MPa of $p(\text{CO}_2)$ and 0.70 MPa of total pressure, as shown in Fig. 10a. It is found that thinner membranes give higher CO₂ permeation properties as expected, and the $Q(\text{CO}_2)$ reaches ca. $1.68 \times 10^{-11} \text{ m}^3(\text{STP}) \text{ m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ when the membrane thickness is 10 μm. The selectivity is mostly above 10 under the pressurized conditions when the thickness is between 10 to 100 μm in Fig. 10b, which is higher than that of various CO₂-philic polymers, such as polydimethylsiloxane [25]. The CO₂ permeation of PAMAM dendrimer-containing polymeric membranes can be increased by reducing the membrane thickness. Although the required CO₂ permeance would be above $7.5 \times 10^{-10} \text{ m}^3(\text{STP}) \text{ m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ for use in an IGCC plant based on our calculations [18], and further enhancement of the CO₂ separation performance is required under pressurized conditions. However, the dendrimer-containing polymeric membranes exhibit excellent CO₂ separation properties over H₂ especially when the $p(\text{CO}_2)$ is low [9] and thus would have greater opportunity for CO₂ capture in a H₂ station for FCVs. After steam reforming of natural gas or LPG, H₂ generated is purified by a pressure-swing adsorption (PSA) method. The off-gas from PSA consists of H₂ and CO₂ at ambient conditions and reused as a fuel for the reforming reaction. When CO₂ is separated over H₂ in the

off-gas before the introduction to a reformer, the CO₂ emission in this system is considerably reduced as well as elevating the combustion efficiency.

In contrast to CO₂ separation membranes over larger molecules such as N₂ [26-30], only limited successful examples have been reported in CO₂/H₂ separation under pressurized conditions [31-39].

Table 1 makes a comparison of the membrane performance with literature values. The PAMAM dendrimer-containing polymeric membranes developed work under pressurized conditions and hold potential as effective CO₂ separation materials.

Table 1. Comparison of the CO₂ separation performance of PAMAM/PEGDMA/4GMAP membranes with literature values.

Membrane	Thickness/ μm	Temp./ $^{\circ}\text{C}$	$p(\text{CO}_2)/\text{atm}$	$p_{\text{total}}/\text{atm}$	$P(\text{CO}_2)/\text{barrer}^*$	$Q(\text{CO}_2)/\text{GPU}^{**}$	$\alpha(\text{CO}_2/\text{H}_2)$	Ref.#
PEGDME	152	37	0.2	1	814	5.4	11	31
PTMEGDAC	152	37	0.2	1	956	6.3	9	31
GTA	152	37	0.2	1	1,844	12.1	9	31
PPGDME	152	37	0.2	1	518	3.4	6	31
PDMS (5 cSt)	152	37	0.2	1	2,194	14.4	4	31
PDMS (100 cSt)	152	37	0.2	1	1,517	10.0	4	31
PBGDAc	152	37	0.2	1	289	1.9	3	31
PFPE GPL100	152	37	0.2	1	1220	8.0	3	31
PFPE GPL107	152	37	0.2	1	283	1.9	2	31
PAO	152	37	0.2	1	47	0.3	3	31
PTMEGDA	150-170	37	0.2	1	329	2.1	6	31
PEGDA	150-170	37	0.2	1	52	0.3	5	31
PDMS	150-170	37	0.2	1	2,848	17.8	4	31
PPGDA	150-170	37	0.2	1	103	0.6	3	31
PEPF	150-170	37	0.2	1	338	2.1	2	31
PBGDA	150-170	37	0.2	1	21	0.1	2	31
[H ₂ NC ₃ mim][Tf ₂ N]	-	85	0.2	1	8,000	-	18	32
PAA/x-PVA	25	110	0.4	2	55	2.2	17	33
PAA-C(CH ₃) ₃ /x-PVA	25	110	0.4	2	119	4.8	34	33
PAA-C ₄ H ₉ /x-PVA	25	110	0.4	2	159	6.4	23	33
PAA-C ₃ H ₇ /x-PVA	25	110	0.4	2	297	11.9	40	33
PAA-C ₃ H ₇ /x-PVA-P(siloxane)	25	110	0.4	2	6,577	263.1	340	34
PAA/x-PVA-P(siloxane)	25	110	0.4	2	3,952	158.1	191	34
Syngas-PVA-3	15	106	3	15	915	61.0	38	35
Arginine salt-chitosan	64	110	0.5	-	600	9.4	20	36
x-PVA (DMG-Li, PEI)	15	80	0.5	-	750	50.0	25	36
x-PVA (PAA, AIBA-K)	60	110	0.6	-	4,000	66.7	170	36
PTMSP ([C(CH ₃) ₄ N]F ₄ H ₂ O)	-	50	0.9	-	-	11.9	55	36
	-	50	1.3	-	-	8.1	30	36
PVA-PPOS/FS (FS: 23.5 wt%)	24-32	107	3	15	1,296	41.0	87	36
PVA-PPOS/FS (FS: 4.2 wt%)	24-32	107	1	5	2,901	104.0	138	36
(PEO-r-PPO/T)-T6T6T	100	-10	19	-	510	5.1	29	37

x-PEGDA/PEGMEA	70	-20	17	-	410	5.9	31	38
	70	35	17	-	440	6.3	9.4	38
PVBTMAF-CsF	-	23	0.4	1.2	510	-	127	39
PAMAM/PEGDMA/4GMAP	71	40	0.8	1	131.6	1.9	50	This work
			2.4	3	75.3	1.1	27	
			4.0	5	54.7	0.8	21	
			5.6	7	46.6	0.7	17	
	9.5	40	5.6	7	21.3	2.2	9	

*1 barrer = $1 \times 10^{-10} \text{ cm}^3(\text{STP}) \text{ cm cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$, **1 GPU = $1 \times 10^{-6} \text{ cm}^3(\text{STP}) \text{ cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1} = 7.5 \times 10^{-10} \text{ m}^3(\text{STP}) \text{ m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$.

Conclusions

A compatible cross linker, 4 GMAP, is prepared from PAMAM dendrimer (*G* 0) by the reaction with glycidyl methacrylate. Macrophase separation of PAMAM dendrimer-containing polymeric membranes is completely suppressed by the addition of the crosslinker with above 7.5 wt% relative to the membrane in the photopolymerization. By reducing the membrane thickness, the CO₂ permeability is enhanced with high CO₂/H₂ selectivity. In addition, incorporation of the compatible multi-arm crosslinker increases crosslinking density of the resulting polymer membrane to enhance the mechanical properties and pressure tolerance. As a consequence, the polymeric membranes with as thin as 10 µm in thickness express high CO₂ permeance and selectivity under pressurized conditions.

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References

- [1] D.F. Sanders, Z.P. Smith, R. Guo, L.M. Robeson, J.E. McGrath, D.R. Paul, B.D. Freeman, Energy Efficient Polymeric Gas Separation Membranes for a Sustainable Future: A Review, *Polymer* 54 (2013) 4729-4761.
- [2] J.K. Adewole, A.L. Ahmad, S. Ismail, C.P. Leo, Current challenges in membrane separation of

- CO₂ from natural gas: A review, *Int. J. Greenh. Gas Con.* 17 (2013) 46-65.
- [3] A.S. Kovvali, H. Chen, K.K. Sirkar, Dendrimer Membranes: A CO₂-Selective Molecular Gate, *J. Am. Chem. Soc.* 122 (2000) 7594-7595.
- [4] A.S. Kovvali, K.K. Sirkar, Dendrimer Liquid Membranes: CO₂ Separation from Gas Mixtures, *Ind. Eng. Chem. Res.* 40 (2001) 2502-2511.
- [5] A.S. Kovvali, K.K. Sirkar, Carbon Dioxide Separation with Novel Solvents as Liquid Membranes, *Ind. Eng. Chem. Res.* 41 (2002) 2287-2295.
- [6] S. Duan, T. Kouketsu, S. Kazama, K. Yamada, Development of PAMAM dendrimer composite membranes for CO₂ separation, *J. Membr. Sci.* 283 (2006) 2-6.
- [7] T. Kouketsu, S. Duan, T. Kai, S. Kazama, K. Yamada, PAMAM dendrimer composite membrane for CO₂ separation: Formation of a chitosan gutter layer, *J. Membr. Sci.* 287 (2007) 51-59.
- [8] S. Duan T. Kai, I. Taniguchi, S. Kazama, Development of poly(amidoamine) dendrimer/poly(vinyl alcohol) hybrid membranes for CO₂ separation, *Desalin. Water Treat.* 51 (2013) 5337-5342.
- [9] I. Taniguchi, S. Duan, S. Kazama, Y. Fujioka, Facile Fabrication of a Novel High Performance CO₂ Separation Membrane: Immobilization of Poly(amidoamine) Dendrimers in Poly(ethylene glycol) Networks, *J. Membr. Sci.* 322 (2008) 277-280.
- [10] I. Taniguchi, H. Urai, T. Kai, S. Duan, S. Kazama, A CO₂-selective molecular gate of Poly(amidoamine) dendrimer immobilized in a poly(ethylene glycol) network, *J. Membr. Sci.* 444 (2013) 96-100.
- [11] J. Franz and V. Scherer, An evaluation of CO₂ and H₂ selective polymeric membranes for CO₂ separation in IGCC processes, *J. Membr. Sci.* 359 (2010) 173-183.
- [12] C.A. Scholes, K.H. Smith, S.E. Kentish and G.W. Stevens, CO₂ capture from pre-combustion processes-Strategies for membrane gas separation, *Int. J. Greenh. Gas Con.* 4 (2010) 739-755.
- [13] T.C. Merkel, M. Zhou, R.W. Baker, Carbon dioxide capture with membranes at an IGCC power plant, *J. Membr. Sci.* 389 (2010) 441-450.
- [14] K. Ramasubramanian, Y. Zhao, W.S.W. Ho, CO₂ capture and H₂ purification: Prospects for CO₂-selective membrane processes, *AIChE J.* 56 (2013) 1033-1045.
- [15] S. Yun, S. T. Oyama, Correlations in palladium membranes for hydrogen separation: A review, *J. Membr. Sci.* 375 (2011) 28-45.

- [16] I. Taniguchi, S. Kazama, H. Jinnai, Structural analysis of poly(amidoamine) dendrimer immobilized in cross-linked poly(ethylene glycol), *J. Polym. Sci. B: Polym. Phys.* 50 (2012) 1156-1164.
- [17] 4GMAP: 11,11'-(ethane-1,2-diyl)bis(2,20-dihydroxy-24-methyl-8,14,23-trioxo-22'-oxa-4',7',11',15',18'-pentaazapentacos-24-ene-11,1-diyl) bis(2-methylacrylate).
- [18] S. Duan, I. Taniguchi, T. Kai, S. Kazama, Poly(amidoamine) dendrimer/poly(vinyl alcohol) hybrid membranes for CO₂ capture *J. Membr. Sci.* 423-424 (2012) 107-112.
- [19] H. Jinnai, Y. Nishikawa, T. Koga, T. Hashimoto, Direct Observation of Three-Dimensional Bicontinuous Structure Developed via Spinodal Decomposition, *Macromolecules* 28 (1995) 4782-4784.
- [20] H. Jinnai, T. Koga, Y. Nishikawa and T. Hashimoto, Curvature Determination of Spinodal Interface in a Condensed Matter System, *Phys. Rev. Lett.* 78 (1997) 2248-2251.
- [21] H. Jinnai, Y. Nishikawa, H. Morimoto, T. Koga, T. Hashimoto, Geometrical Properties and Interface Dynamics: Time Evolution of Spinodal Interface in a Binary Polymer Mixture at the Critical Composition, *Langmuir* 16 (2000) 4380-4393.
- [22] J.S. Schultz, J.D. Goddard, S.R. Suchdeo, Facilitated transport via carrier-mediated diffusion in membranes: Part I. Mechanistic aspects, experimental systems and characteristic regimes, *AIChE J.* 20 (1974) 417-445.
- [23] A.F. Ismail, W. Loma, Penetrant-induced plasticisation phenomenon in glassy polymers for gas separation membrane, *Sep. Purif. Technol.* 27 (2002) 173-194.
- [24] I. Taniguchi, S. Duan, T. Kai, S. Kazama, H. Jinnai, Effect of phase-separated structure on CO₂ separation performance of poly(amidoamine) dendrimer immobilized in a poly(ethylene glycol) network, *J. Mater. Chem. A* 1 (2013) 14514-14523.
- [25] M.K. Barillas, R.M. Enick, M. O'Brien, R. Perry, D.R. Luebke, B.D. Morreale, The CO₂ permeability and mixed gas CO₂/H₂ selectivity of membranes composed of CO₂-philic polymers, *J. Membr. Sci.* 372 (2011) 29-39.
- [26] K. Nagai, T. Masuda, T. Nakagawa, B.D. Freeman, I. Pinnau, Poly[1-(trimethylsilyl)-1-propyne] and related polymers: Synthesis, properties and functions, *Prog. Polym. Sci.* 26 (2001) 721-798.
- [27] N.B. McKeown, B. Gahnm, K. Msayib, P.M. Budd, C. Tattershall, K. Mahmood, S. Tan, D. Brook, H.W. Langmi, A. Walton, Towards polymer-based hydrogen storage materials: Engineering ultramicroporous cavities within polymers of intrinsic microporosity, *Angew. Chem. Int. Ed.* 45 (2006) 1804-1807.

- [28] N. Du, H.B. Park, G.P. Robertson, M.M. Cal-Cin, T. Visser, L. Scoles, M.D. Guiver, Polymer nanosieve membranes for CO₂-capture applications, *Nat. Mater.* 10 (2011) 372-375.
- [29] H.B. Park, C.H. Jung, Y.M. Lee, A.J. Hill, S.J. Pas, S.T. Mudie, E.V. Wagner, B.D. Freeman, D.J. Cookson, Polymers with Cavities Tuned for Fast Selective Transport of Small Molecules and Ions, *Science* 318 (2007) 254-258.
- [30] H.M. El-Kaderi, J.R. Hunt, J.L. Mendoza-Cortés, A.P. Côté, R.E. Taylor, M. O’Keeffe, O.M. Yaghi, Designed Synthesis of 3D Covalent Organic Frameworks, *Science* 316 (2007) 268-272.
- [31] M.K. Barillas, R.M. Enick, M. O’Brien, R. Perryc, D.R. Luebkea, B.D. Morreale, The CO₂ permeability and mixed gas CO₂/H₂ selectivity of membranes composed of CO₂-philic polymers, *J. Membr. Sci.* 372 (2011) 29-39.
- [32] C. Myersa, H. Pennlinea, D. Luebkea, J. Ilconichb, J.K. Dixonc, E.J. Maginnc, J.F. Brennekec, High temperature separation of carbon dioxide/hydrogen mixtures using facilitated supported ionic liquid membranes, *J. Membr. Sci.* 322 (2008) 28–31.
- [33] Y. Zhao, W.S.W. Ho, Steric hindrance effect on amine demonstrated in solid polymer membranes for CO₂ transport, *J. Membr. Sci.* 415–416 (2012) 132–138.
- [34] Y. Zhao, W.S.W. Ho, CO₂□Selective Membranes Containing Sterically Hindered Amines for CO₂/H₂ Separation, *Ind. Eng. Chem. Res.* 52, (2013) 8774–8782.
- [35] H. Bai, W.S.W. Ho, Carbon Dioxide-Selective Membranes for High-Pressure Synthesis Gas Purification, *Ind. Eng. Chem. Res.* 50 (2011) 12152-12161.
- [36] R. Xing, W.S.W. Ho, Crosslinked polyvinylalcohol-polysiloxane/fumed silica mixed matrix membranes containing amines for CO₂/H₂ separation, *J. Membr. Sci.* 367 (2011) 91-102.
- [37] S.R. Reijerkerka, K. Nijmeijera, C.P. Ribeiro Jr., B.D. Freeman, M. Wessling, On the effects of plasticization in CO₂/light gas separation using polymeric solubility selective membranes, *J. Membr. Sci.* 367 (2011) 33-44.
- [38] H. Q. Lin, E.V. Wagner, B.D. Freeman, L.G. Toy, R.P. Gupta, Plasticization-enhanced hydrogen purification using polymeric membranes, *Science* 311 (2006) 639-642.
- [39] J. Zou, W.S.W. Ho, CO₂-selective polymeric membranes containing amines in crosslinked poly(vinyl alcohol), *J. Membr. Sci.* 286 (2006) 310-321.

Suppression of phase separation

Compatible x-linker

4GMAP