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# Development of poly(amidoamine) dendrimer/ poly(ethylene glycol) hybrid membranes for CO<sub>2</sub> capture at elevated pressures

Shuhong Duan, Teruhiko Kai\*, Ikuo Taniguchi<sup>1</sup> and Shingo Kazama<sup>2</sup>

*Research Institute of Innovative Technology for the Earth (RITE)  
9-2 Kizugawadai, Kizugawa-shi, Kyoto 619-0292, Japan*

## Abstract

To improve CO<sub>2</sub> separation performance of Poly (amidoamine) (PAMAM) dendrimer at pressure difference conditions, hybrid membranes have been developed by immobilizing of PAMAM dendrimer into a cross-linked poly(ethylene glycol) dimethacrylate (PEGDMA) polymer matrix. A multifunctional cross-linker (MFX) such as trimethylolpropane trimethacrylate (TMPTMA) was used to enhance membrane separation performance at elevated pressures. The resulting hybrid membrane PAMAM dendrimer / PEGDMA/TMPTMA hybrid membrane exhibited an excellent CO<sub>2</sub>/H<sub>2</sub> selectivity of 30 and above with CO<sub>2</sub> permeance of  $2.1 \times 10^{-12} \text{m}^3(\text{STP})/(\text{m}^2 \text{ s Pa})$  at 660 kPa CO<sub>2</sub> partial under 820 kPa feed pressure with 80% relative humidity at 40 °C. The PAMAM dendrimer/cross-linked PEG hybrid membrane shows great potential for CO<sub>2</sub> separation from H<sub>2</sub> in high pressure applications, such as IGCC process.

A compatible crosslinker (CPC) was used to prepare the composite membrane with a thin selectivity layer to enhance CO<sub>2</sub> permeance. An isopropyl alkyl hindered amine IAM, tertiary amine TA1 and TA2 were added to the formation solution of membrane for investigating the effect of additive on CO<sub>2</sub> separation performance.

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\* Corresponding author. Tel.: +81-774-75-2305; fax: +81-774-75-2318.

E-mail address: [kai.te@rite.or.jp](mailto:kai.te@rite.or.jp)

Present Address:

1) International Institute for Carbon-Neutral Energy Research (WPI-I2CNER), Kyushu University,  
744 Motoooka, Nishi-ku, Fukuoka 819-0395, Japan.

2) Technical Development Bureau, Nippon Steel Corporation, 2-6-1Marunouchi, Chiyoda-ku, Tokyo100-8071, Japan

*Keywords:* CO<sub>2</sub> separation; Poly(amidoamine) dendrimer; Poly(ethylene glycol); hybrid membrane; IGCC

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## 1. Introduction

Carbon dioxide capture and storage (CCS) is an effective way to mitigate global warming. The first step of CCS is to separate CO<sub>2</sub> from other gases, such as H<sub>2</sub>, N<sub>2</sub> and CH<sub>4</sub>. The cost of CO<sub>2</sub> capture has been reported more than 60% of the total cost of CCS, and thus reducing the cost of CO<sub>2</sub> capture is a critical if CCS is to be implemented. Coal-based plants for electricity generation are major CO<sub>2</sub> emission sources. IGCC (the integrated coal gasification combined cycle) with CCS is expected to be an efficient and environmentally-friendly power generation system. The driving force of gas separation is pressure difference between feed and permeate sides without requiring additional energy, so that the pressurized gas stream in the IGCC plant would be directly applicable to membrane separation, which would result in reducing CO<sub>2</sub> capture cost. In IGCC process, H<sub>2</sub> is primarily produced from water gas shift (WGS) reaction of synthesis gas, and the gas consists of CO<sub>2</sub> and H<sub>2</sub>. Thus, the development of a CO<sub>2</sub>-selective membrane with both high CO<sub>2</sub> permeability and high CO<sub>2</sub>/H<sub>2</sub> selectivity is very important [1-3].

Sirkar and coworkers were the first to find an effective CO<sub>2</sub> selectivity of poly(amidoamine) (PAMAM) dendrimer in a liquid immobilized membrane (ILM) [4, 5]. However, PAMAM dendrimer ILM had insufficient pressure tolerance for practical use because of the flow nature of the PAMAM dendrimer at or above room temperature.

To improve CO<sub>2</sub> separation performance at pressure difference conditions, hybrid membranes have been developed by incorporating or immobilizing of PAMAM dendrimer into a polymer matrix in our research group [6-9]. We have succeeded in immobilizing the dendrimer in a cross-linked poly(ethylene glycol) (PEG) obtained by photopolymerization of PEG dimethacrylate (PEGDMA), and reported that PAMAM/PEGDMA hybrid membrane containing 50 wt.% PAMAM dendrimer showed high CO<sub>2</sub> separation properties over H<sub>2</sub>, for example Selectivity CO<sub>2</sub>/H<sub>2</sub> > 500 at 5 kPa CO<sub>2</sub> partial pressure and 80 % relative humidity under ambient conditions.

In this study, a multifunctional cross-linker trimethylolpropane trimethacrylate (TMPTMA) was used to enhance membrane separation performance at elevated pressures. To enhance CO<sub>2</sub> permeance by decreasing membrane thickness, CPC was used to prepare the composite membrane with a thin selectivity layer [10]. The composite membranes, which consisted with PAMAM dendrimer / PEGDMA/CPC hybrid thin layer supported on substrate membrane, were successfully prepared. An isopropyl alkyl hindered amine IAM, tertiary amine TA1 and TA2 were added to the formation solution of membrane for investigating the effect of additive on CO<sub>2</sub> separation performance [11].

## 2. Experimental

### 2.1. Materials

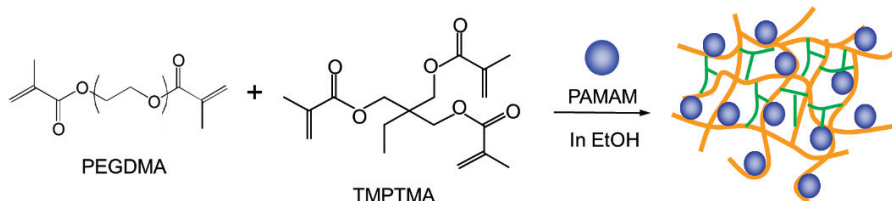
PEGDMAs with PEG length (EG unit: 14 (550)), PAMAM dendrimers in methanol solution, and 1-hydroxycyclohexyl phenylketone (HCPK) were obtained from Aldrich (WI). Other organic and inorganic materials were reagent grade and used without further purification. Polyethersulfone (PES) porous support membrane with 30kDa NMWCO was purchased from Millipore Com (Tokyo, Japan).

### 2.2. Membrane preparation

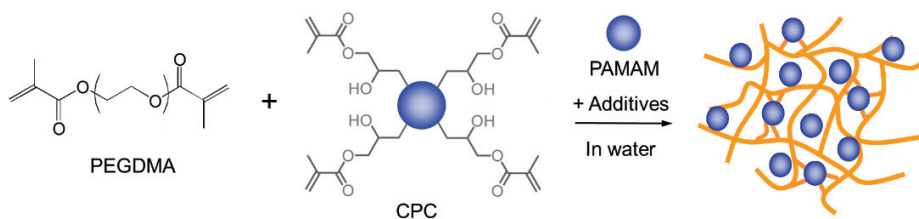
PAMAM dendrimer/PEGDMA/TMPTMA hybrid membranes (free-standing films) were prepared by casting solution of different weight of the reaction mixture of PAMAM, PEGDMA and TMPTMA on a Teflon dish (I.D.: 6.0 cm), followed by curing at 365 nm UV for 3 min in ethanol. PAMAM dendrimer/PEGDMA/CPC hybrid membranes (free-standing films) were prepared by casting solution of different weight of the reaction mixture of PAMAM dendrimer(50-x wt. %)/Additive(x wt. %)/PEGDMA/CPC on a Teflon dish (I.D.: 6.0 cm), followed by

curing at 365 nm UV for 3 min in ethanol and at 312 nm UV for 3 min in water. The composite membrane of smaller thickness was prepared by casting precursor solution of PAMAM dendrimer(50-x wt. %)/Additive(x wt. %)/PEGDMA/CPC in water on a quartz plate, followed by the UV curing at 312 nm UV for 1.5 min and transferred onto PES support membrane. The membrane thickness was controlled by sandwiching the reaction mixture with quartz plates and stainless steel spacers (20  $\mu\text{m}$  in thick). Fig. 1. Shows schematic diagrams of membrane fabrication, chemical structure of PAMAM dendrimer (generation 0) and the resulting free-standing membranes.

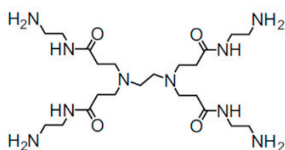
(a) Fabrication of PAMAM dendrimer/PEGDMA/TMPTMA hybrid membranes.



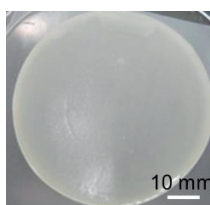
(b) Fabrication of PAMAM dendrimer/PEGDMA/CPC hybrid membranes.



(c) PAMAM dendrimer (generation 0).



(d) The resulting hybrid membrane of (a).



(e) The resulting hybrid membrane of (b).

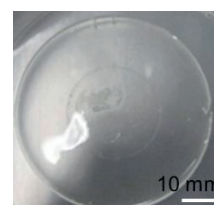


Fig. 1. Schematic diagrams of membrane fabrication and the resulting hybrid membrane

### 2.3. Permeation experiments

A schematic diagram of the gas separation experiment setup is shown in [6]. A  $\text{CO}_2/\text{H}_2$  (80/20 by vol.) gas mixture was humidified at 80 % relative humidity and then fed to a flat-sheet membrane cell at a flow rate of 100 ml/min. As we reported in our previous papers, our membrane needs relative humidity as high as 80 RH% to show high separation performance [9]. The  $\text{CO}_2$  partial pressures of the feed side were from 80 to 660 kPa. Dry He was supplied at a flow rate of 10 ml/min to the permeate side of the cell as a sweep gas. The test operating temperatures

were at 40 °C. The CO<sub>2</sub> and H<sub>2</sub> concentrations in both feed and permeate gas were measured by gas chromatography. Permeance, Q, and selectivity, CO<sub>2</sub>/H<sub>2</sub> were calculated as expressed in [6, 7].

#### 2.4. Membrane characterization

The morphologic analysis of composite membrane was performed using scanning electron microscopy (SEM, HitachiS-4800), at an accelerating voltage of 1.0 kV. Cross-sections of the composite membrane were obtained by fracturing the membrane in liquid N<sub>2</sub>, and these sections were made conductive by coating with Pt/Pd.

### 3. Results and discussion

#### 3.1. Membrane characterization via SEM images and photos

SEM images of PAMAM/IAM/PEGDMA/CPC hybrid composite membrane and PES substrate are shown in Fig. 2. From cross-sectional images of SEM, the thickness of PAMAM/IAM/PEGDMA/CPC hybrid membrane layer was observed to be about 10 μm from top to PES substrate surface and soaked into PES inner surface about 15 μm deep in Fig. 2 (a, b).

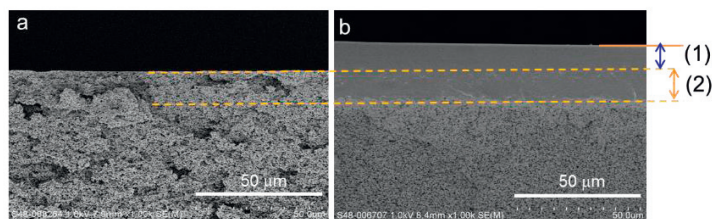
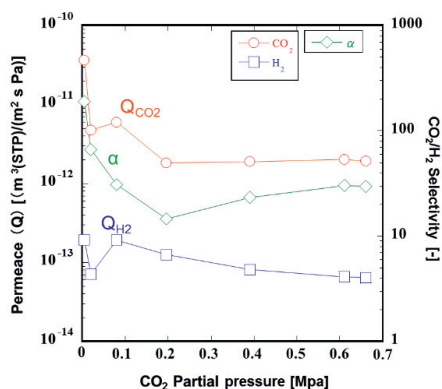
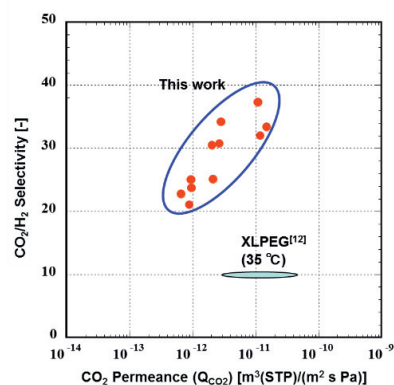


Fig. 2. SEM cross-sectional images. (a) PES substrate, (b) composite membrane with selectivity layer PAMAM/IAM/PEGDMA/CPC on PES. (1) 10 μm selectivity layer PAMAM/IAM/PEGDMA/CPC. (2) 15 μm soaked into PES inner surface.

#### 3.2. Effect of CO<sub>2</sub> Partial Pressure on CO<sub>2</sub> Separation Properties

The effect of CO<sub>2</sub> partial pressures on CO<sub>2</sub> separation properties using PAMAM/PEGDMA/TMPTMA hybrid membranes with 500 μm thick. In general, as observed in Fig. 3, CO<sub>2</sub> permeance decreased with increasing CO<sub>2</sub> partial pressures in the feed gas, but kept constant over 200 kPa CO<sub>2</sub> partial pressure. Conversely, H<sub>2</sub> permeance was relatively constant and only decreased slightly as CO<sub>2</sub> partial pressure increased. As a result, the membrane showed high Q<sub>CO<sub>2</sub></sub> ( $2.1 \times 10^{-12}$  m<sup>3</sup> (STP)/(m<sup>2</sup> s Pa)) and α<sub>CO<sub>2</sub>/H<sub>2</sub></sub> (31) even at a high CO<sub>2</sub> partial pressure (i.e., 660 kPa) and 40 °C. CO<sub>2</sub> separation properties of 40~60 °C were summarized as shown in Fig. 4.

A comparison between our membranes and cross-linked PEG (XLPEG) membranes reported in reference [12] for CO<sub>2</sub>/H<sub>2</sub> separation is shown in Fig. 4. As shown in Fig. 4, CO<sub>2</sub>/H<sub>2</sub> selectivity of XLPEG membranes is around 10 at 35 °C. On the other hand, PAMAM/PEGDMA/TMPTMA hybrid membranes showed CO<sub>2</sub>/H<sub>2</sub> selectivity as high as 30 or more at 40~60 °C, which is required for IGCC process.

Fig. 3. The effect of CO<sub>2</sub> Partial Pressure on CO<sub>2</sub> Separation PropertiesFig. 4. A comparison of CO<sub>2</sub> /H<sub>2</sub> Separation Properties

### 3.3. Effect of additives on CO<sub>2</sub> Separation Properties

PAMAM dendrimer with 4 primary amino groups exhibits high CO<sub>2</sub> selective absorbability. PAMAM dendrimer is a basic molecule that would facilitate conversion of CO<sub>2</sub> into a bicarbonate ion in the presence of H<sub>2</sub>O. CO<sub>2</sub> absorption and transport in the form of a bicarbonate ion were facilitated by the PAMAM dendrimer in the presence of H<sub>2</sub>O [13, 14]. CO<sub>2</sub> is a weak acidic gas that is absorbed into a solvent containing the amine, (a weak base), where RNHCOO<sup>-</sup> is carbamate ion which is formed with both primary and secondary amines, but tertiary amines (and hindered amines) form the bicarbonate ion in a reaction with water. IAM, TA1 and TA2 tertiary amine were added to the formation solution of membrane for investigating the relationship between chemical structure of additives and CO<sub>2</sub> separation membrane properties to suggestion of the new separation function material.

Composite membranes with selectivity layer PAMAM/IAM/PEGDMA/CPC by wt. in water/PES were prepared from 0 to 50 wt% with IAM / (IAM +PAMAM). Fig. 5 shows CO<sub>2</sub>, H<sub>2</sub> gas permeances and CO<sub>2</sub>/H<sub>2</sub> selectivity for hybrid composite membranes prepared from different IAM concentration. As shown in Fig. 5, both Q<sub>CO2</sub> and CO<sub>2</sub>/H<sub>2</sub> selectivity increased with increasing IAM concentration. And Q<sub>H2</sub> kept constant with increasing IAM concentration. Membrane performances can be explained by steric hindrance effect. The bulky alkyl group attached to the amino group lowers the tendency to form carbamate ions and therefore increases the CO<sub>2</sub> loading capacity, and resulted in CO<sub>2</sub> permeance increased 4 times with 50 wt% IAM addition.

To investigate the effect of tertiary amines additive, composite membranes with selectivity layer PAMAM/TA1 (or TA2)/PEGDMA/CPC with 50 wt% addition in water/PES were prepared. Fig. 6 shows that the three hindered amines demonstrated all the effect of Q<sub>CO2</sub> increasing at a high CO<sub>2</sub> partial pressure (i.e., 560 kPa). Among of them, IAM showed the best effect of Q<sub>CO2</sub> increasing. The reason is that IAM has the smallest steric hindrance and the highest reaction rate of the formation of HCO<sub>3</sub><sup>-</sup> compared with others. Hinder amine with isopropyl group is optimum structure for Q<sub>CO2</sub> increasing.

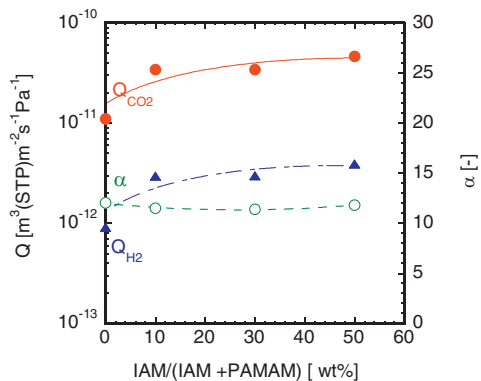


Fig. 5. The effect of IAM concentration on CO<sub>2</sub> separation properties at 560 kPa of CO<sub>2</sub> partial pressure and 80 %RH at 40 ° C.

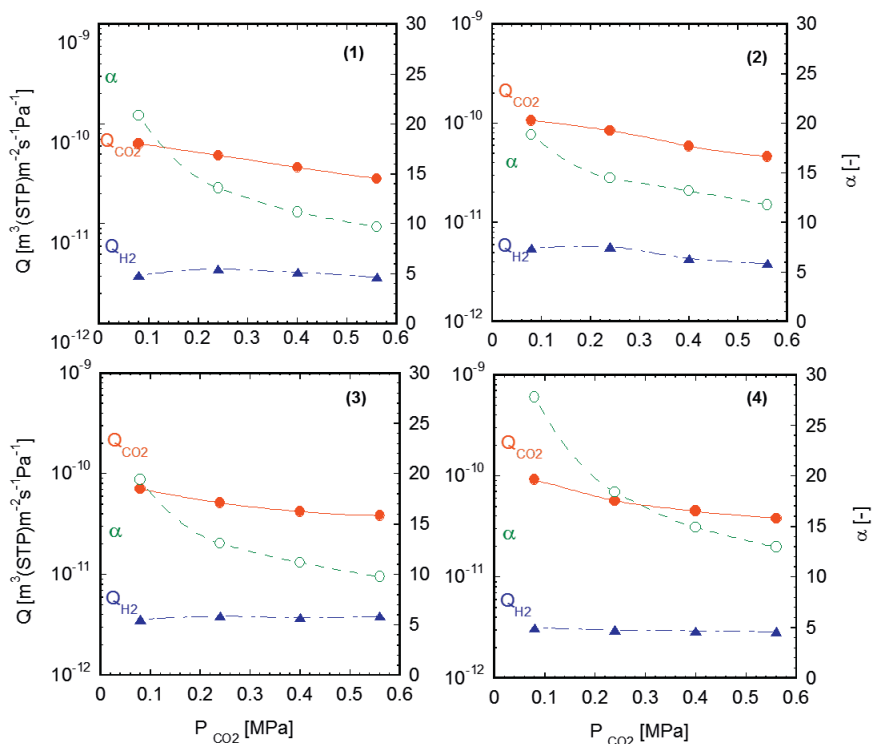


Fig. 6. The effect of additives on CO<sub>2</sub> separation properties at 560 kPa of CO<sub>2</sub> partial pressure and 80 %RH at 40 ° C. Hybrid composite membranes of PAMAM/Additive/PEGDMA/CPC (1) without additive (2) IAM (3) TA1 (4) TA2

#### 4. Conclusions

The multifunctional cross-linker TMPTMA exhibited the enhancement of CO<sub>2</sub> membrane separation performance at elevated pressures. PAMAM dendrimer / PEGDMA/TMPTMA hybrid membrane exhibited an excellent CO<sub>2</sub>/H<sub>2</sub> selectivity of 30 and above with CO<sub>2</sub> permeance of  $2.1 \times 10^{-12} \text{m}^3(\text{STP})/(\text{m}^2 \text{ s Pa})$  at 660 kPa CO<sub>2</sub> partial under 820 kPa feed pressure with 80% relative humidity at 40 °C. The PAMAM dendrimer/cross-linked PEG hybrid membrane shows great potential for CO<sub>2</sub> separation from H<sub>2</sub> in high pressure applications. Composite membrane with a thin selectivity layer were prepared successfully with compatible cross-linker CPC. The effect of IAM additive on CO<sub>2</sub> permeance showed that the balance of optimum steric hindrance and high reaction rate of is very important to suggestion of the new separation function material for CO<sub>2</sub> separation.

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