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Advanced CO₂/H₂ Separation Materials Incorporating Active Functional Agents

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Abstract

Polymeric membranes for preferential CO₂ separation over H₂ have been investigated in this project, which can be applicable, for example, in an integrated gasification combined cycle (IGCC) plant with CO₂ capture and storage (CCS). Poly(amidoamine) (PAMAM) dendrimers have been employed as an effective agent for preferential CO₂ separation in this project. Although PAMAM dendrimer containing membranes express excellent CO₂ separation properties under humidified conditions, the separation performance drops sharply with decreasing relative humidity (less than 60 %RH), which indicates CO₂ passes through the membrane most likely in the form of bicarbonate ion.

In this work, selective CO₂ permeation with a different mechanism has been developed by a novel supercritical CO₂ (sc-CO₂) directing method for use under less humid conditions. Sc-CO₂ treatment would work to make a route for CO₂ by a molecular imprinting manner. PAMAM dendrimer was first used for a CO₂ specific compound. Membrane fabrication was tried by photopolymerization of poly(ethylene glycol) dimethylacrylate (PEGDMA) in the presence of PAMAM dendrimer under sc-CO₂. However, due to limited solubility of the dendrimer in sc-CO₂ resulted in inhomogeneous membrane formulation. Then PAMAM dendrimer was first immobilized in a crosslinked PEGDMA, and then incubated in sc-CO₂. In comparison to untreated membrane, the resulting membrane showed higher CO₂ permeance (Q_{CO_2}) and higher separation factor (α_{CO_2/H_2}). When a polymeric membrane containing amino group is kept under sc-CO₂, mechanical properties of the resulting membrane are drastically enhanced. Both of the Young's modulus and elongation-to-break are increased by sc-CO₂ treatment. This can be due to the formation of carbamate linkage, R-NHCOO⁻ ... N⁺H₃-R', between two amino groups and one CO₂. In this case, CO₂ travel through the membrane in carbamate form. In addition, carbamate acts as a quasi-crosslinking point, and the crosslinking is reversible and rearrangeable, which results in the increase of elongation-to-break. Carbamate formation after sc-CO₂ treatment is confirmed by FT-IR. Especially, when the polymeric membrane is fabricated from 2-aminoethyl methacrylate and N-(3-aminopropyl) methacrylamide, increase in a peak at around 1,250 cm⁻¹ is found, which can be assigned to the stretching vibration peak of N-C bonding of carbamate ion (ν_{N-COO^-}). In the sc-CO₂ condition, water content of the polymeric membrane was negligible, so that CO₂ permeated through the membrane in the form of carbamate by hopping between primary amines of PAMAM dendrimers.

The detailed structure of the polymeric membrane was determined by laser scanning confocal microscope. Formation of bicontinuous phase structure was found upon macrophase separation, and the average PAMAM domain size was 2-4 microns depended on the dendrimer concentration and PEG length. On the other hand, glass transition temperature (T_g) of the polymer matrix was -60 °C, and the dendrimer flew at ambient condition. Rearrangement of polymer chains and phase structure can be expected, which would result in losing CO₂ penetrating channel generated by sc-CO₂ treatment over time. PAMAM dendrimer was then immobilized in cellulose acetate. T_g of the polymeric matrix was above 120 °C, which suppressed rearrangement of polymers. However, the resulting polymeric membrane was inhomogeneous, and after sc-CO₂ treatment, it did not show higher CO₂ separation performance as expected. This would be also due to flow nature of the dendrimer. Even CO₂-imprinting by carbamate formation was conducted,

dendrimer could move under ambient conditions. As a result, the polymeric membrane did not hold CO₂ permeation pathway formed under sc-CO₂, and CO₂ separation properties did not change much in comparison to the untreated membrane.

Primary amine is essential for preferential CO₂ permeation, however, intrinsic flow nature of PAMAM dendrimer has been not suitable to fabricate CO₂ penetrating pathway by sc-CO₂ treatment. Then, poly(ethylene imine) (PEI) was used, which was a branching polymer having a number of primary amines. CO₂ separation properties of sc-CO₂ treated PEI membrane was depended on the treatment conditions, and the sc-CO₂ treated membrane for more than 3 hours exhibited higher separation properties than pristine membrane, which indicated CO₂ penetration and formation of carbamate in the membrane required for a couple of hours. Increase in CO₂/He selectivity from 17.7 to 24.8 was accounted for the decrease in He permeance from 1.12×10^{-12} to 5.97×10^{-13} m³(STP)/(m² s Pa) with sc-CO₂ treated time. T_g of PEI was -40 °C and thus rearrangement of polymer chain would take place even after crosslinking in membrane preparation. The high CO₂ separation performance might not last for a period of service time. Finally, we chose methacrylamide or methacrylate monomers bearing primary amines for membrane preparation. Especially, the corresponding polymers obtained by photopolymerization show higher T_g above 100 °C, and thermal rearrangement of polymer chains at the operating condition would be suppressed considerably. After sc-CO₂ treatment, the resulting methacrylamide-base membrane displayed higher CO₂ separation properties over certain period. In addition, under pressurized condition (0.56 MPa of CO₂ partial pressure), CO₂/He selectivity increased with decreasing in He permeance. This could result from “molecular-gate” effect that crosslinks by carbamate inhibited sorption of other gas molecules, leading to high CO₂ separation performance.

Through these investigations, the effect of sc-CO₂ directing method was confirmed for preferential CO₂ permeation, and this technology would provide insights in designing and developing novel CO₂ separation materials.

Introduction

CO₂ capture and storage (CCS) is an important option for mitigating CO₂ emission so as to suppress global warming. However, in terms of present-day technology, CCS consumes a large amount of energy and is costly, especially in CO₂ capturing. Various CO₂ separations have been studied in this research group, including solvent absorption, membrane, membrane-absorption hybrid, and adsorption technologies. Among those separation methods, solvent absorption has gained current acceptance and can be commercialized soon. On the other hand, because membrane separation requires the least energy, it would be the most promising and expected to follow the solvent absorption as a next generation technology. Polymeric membranes for CO₂ separation over H₂ have been investigated extensively for the use in an IGCC plant in this project. Lately, He has been used as a substituent of H₂ as a safety reason.

We have developed advanced composite materials having a functional agent by nano-architecture controlling technologies in polymeric and inorganic materials. For example,

selective extraction of CO₂ from CO₂ and H₂ gas mixture was enabled by introducing amine, which specifically interacted to CO₂. The materials consisted of the active functional agents in the nanopores of a porous substrate and polymeric matrix. We control the morphology, surface atoms/molecules and the compositions of the pore/matrix and functional compounds to create the desired molecular interaction. Our research is going to provide insights for development of effective and promising CO₂ separation materials.

Basic concept of CO₂ molecular gate membrane

Figure 1 shows the basic outline of the CO₂ “molecular gate” membrane. Free volume of the membrane is occupied by CO₂, which acts as a gate to block the sorption of other gases by forming carbamate with primary amines. As a consequence, permeation of H₂ is significantly suppressed, and high concentrations of CO₂ can be obtained in the permeate. The molecular gate membrane realizes CO₂ separation over smaller H₂ in reverse molecular sieving mechanism. Figure 1 (b) explains details of the preferential CO₂ separation with amine compounds, such as PAMAM dendrimers. A carbamate ion pair is formed with one CO₂ molecule and two amine moieties of the dendrimer. The resulting carbamate ion pair works as a quasi cross-linkage that inhibits H₂ permeation through the membrane. On the other hand, because formation of carbamate ion pairs are in equilibrium with free CO₂ and amine moieties, CO₂ in carbamate form can diffuse into the membrane from feeding side to permeate side to form another carbamate ion pair with free amine moieties next to the carbamate. As a result, CO₂ molecules can permeate the membrane by hopping mechanism.

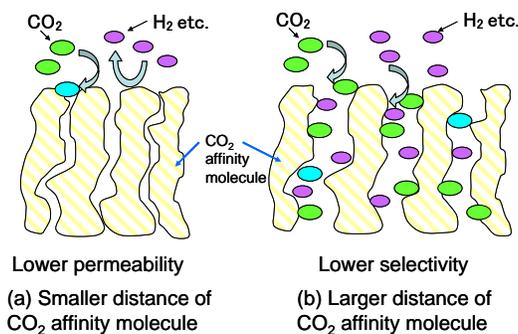


Figure 1: Concept of the CO₂ molecular gate membrane.

The CO₂ molecular gate requires precise alignment of amine moieties. In Figure 1, the distance between two amine moieties should be controlled to express the CO₂ molecular gate function. If the distance is closer than an appropriate distance, the hydrogen bonding formation will be suppressed. As a result, the membrane will not have sufficient CO₂ permeability (Figure 2(a)). On the other hand, if the distance is too far, a quasi cross-linkage to prevent H₂ permeation will not be achieved. Precise control of the molecular alignments will be thus required as represented in Figure 2(b).

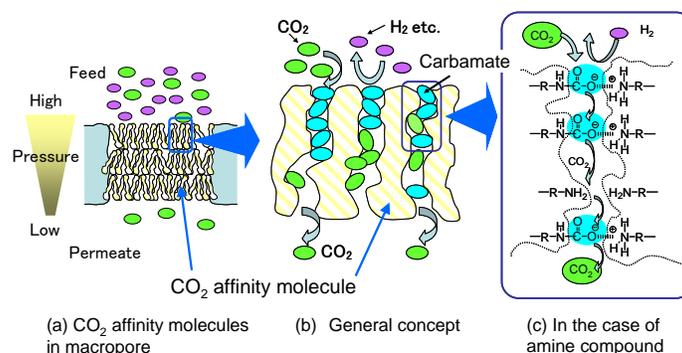
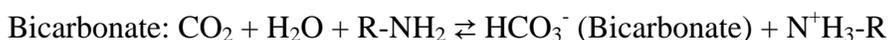


Figure 2: Morphological deformation and the molecular gate function.

Amine compounds react with CO₂ to form both bicarbonate and carbamate ions as follows:



In the presence of water, bicarbonate ion can be formed with one mole of CO₂, H₂O and amine moiety. On the other hand, carbamate ion pair is with one mole of CO₂ and two moles of amine moieties. The bicarbonate formation requires H₂O, while the carbamate formation does not. Our recent results suggest that humidity is crucial to determine the CO₂ separation properties, which means that bicarbonate ion is dominant of CO₂ permeation species in the amine containing polymeric membrane. On the other hand, when CO₂ permeates in the carbamate ion form, H₂O will not give any effect on CO₂ permeation. Thinking of actual use of the polymeric membrane, the membranes insensitive to humidity are preferable, especially, those work under dry operation are sought after. Thus, CO₂ permeation in the form of carbamate ion would be suitable in comparison to the current bicarbonate ion transportation.

CO₂ separation membranes with carbamate transportation mechanism have not been developed because of difficulty in precise control of the alignment of amine moieties. Fine alignment of the moieties would give a suitable conformation for carbamate formation, which would result in rapid hopping of CO₂. Gas separation membranes developed in this research institute showed high CO₂ permeance (Q_{CO_2}) of 1.0×10^{-10} m³(STP)/(m² s Pa) and selectivity ($\alpha_{\text{CO}_2/\text{H}_2}$) of 30 at 80 % relative humidity condition. This membrane needs water to obtain the higher CO₂ separation performance. If the gas separation membrane with high CO₂ gas permeability and high CO₂/H₂ selectivity under less humid or even dry conditions would be developed, this membrane could be useful in a wide area not only in CO₂/H₂ in the IGCC plant but in CO₂/CH₄ separation.

Our methodology

A promising way of creating the best morphology for the hopping of carbamate ion is the rearrangement of amine moiety in the membrane to form the ion hopping channel using structure directing agent. We select sc-CO₂ as a structure directing agent for

rearranging conformation of amino moiety for carbamate ion hopping. Sc-CO₂ will be one of the most promising candidates for the agent, because sc-CO₂ can readily penetrate and diffuse into the pre-formed membrane to act as a structure directing agent to form carbamate ion.

Figure 3 shows a conceptual image of sc-CO₂ treatment of membrane for CO₂ transport pathway. A membrane containing amine compound is treated under sc-CO₂ atmosphere. Sc-CO₂ can easily penetrate into the membrane and swell it. And then, sc-CO₂ triggers rearrangement of amine moieties and polymer chains with the formation of carbamate ion. Because of the near-zero surface tension, after taking out from sc-CO₂, the optimized morphology would be maintained for serving the suitable channel for carbamate ion hopping. Membrane materials and sc-CO₂ treating condition would be critically important to create a channel of carbamate ions for selective CO₂ permeation.

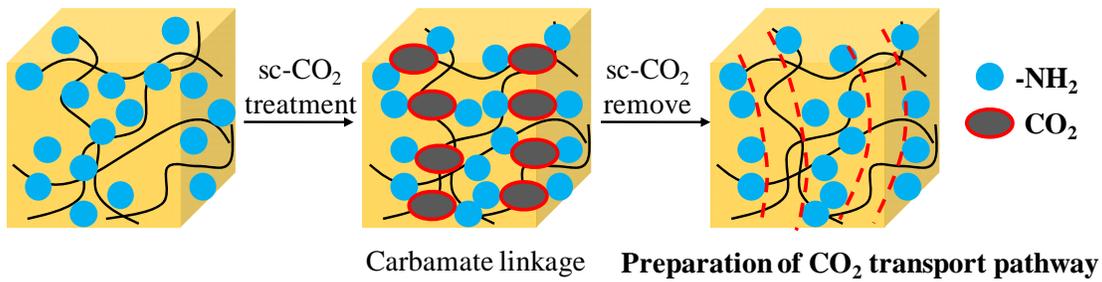


Figure 3: Schematic drawing of formation of CO₂ pathway by sc-CO₂ treatment.

The amino groups are crucial to fabricate CO₂ separation membrane. However, the CO₂ gas separation membrane did not show higher CO₂ separation performance at lower relative humidity condition. One of the reasons would be due to the random distribution of the amino group. To obtain higher CO₂ permeance and CO₂/H₂ separation, precise control of the alignment of amino groups would be required as seen in Figure 4. In other words, formation of CO₂ transport pathway should be established. The CO₂ transport pathway will be organized by fine alignment of amino groups in the membrane by sc-CO₂ treatment.

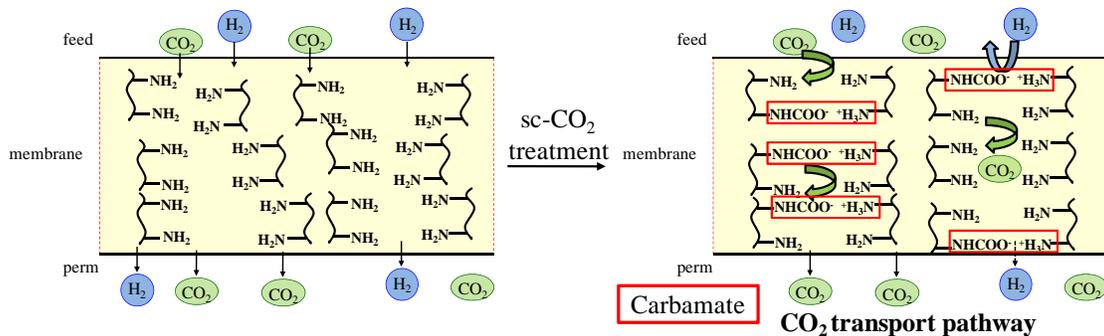


Figure 4: Sc-CO₂ directing carbamate formation

Background

Preparation of a CO₂/H₂ separation membrane has been a topic in gas separation research. Our institute has been leading the CO₂ separation technologies and developed PAMAM dendrimer containing membranes as a novel CO₂ separation materials. Quite high CO₂ separation performance of PAMAM dendrimer membrane was first reported by Sirkar and coworkers at New Jersey Institute of Technology as an immobilized liquid membrane for CO₂/N₂ separation [1]. A liquid state dendrimer has been successfully and stably retained in a polymer matrix as a composite hollow fiber membrane in this institute [2]. Polymeric membranes developed hold the world record for CO₂/H₂ separation properties (CO₂/H₂ selectivity: 30) at an elevated CO₂ pressure (0.56 MPa of p_{CO_2}). With the membrane, PAMAM dendrimer was incorporated into a cross-linked polymeric matrix, whereby a continuous channel of PAMAM dendrimer through membrane was formed. Further improvement of the dendrimer membrane and morphological control of the dendrimer channel is required.

In CO₂ separation over H₂ with polymeric membranes, Freeman et al. at the University of Texas at Austin also has developed very good CO₂/H₂ separation membranes of cross-linked poly(ethylene glycol) (PEG) network, which show a selectivity of 10 at 30 °C and an elevated CO₂ pressure with high CO₂ permeability [3]. Ho et al. at Ohio State University has reported a cross-linked poly(vinyl alcohol) membrane containing amine compounds [4]. Matsuyama et al. at Kobe University in Japan has also reported a gel membrane, which consists of poly(vinyl alcohol)/poly(acrylic acid) co-polymer and an amine as CO₂ carrier [5]. Those membranes exhibit high CO₂/H₂ selectivity at an elevated temperature with relatively lower CO₂ partial pressure.

The word “molecular gate” is sometimes used in the field of separation membranes. The term was first proposed by Sirkar, however, the detailed concept was not clearly described in his reports [1]. The concept of the “CO₂ molecular gate” mentioned above was developed in this institute, and the idea is now being confirmed. Molecular gate membranes developed represent excellent CO₂ separation properties only at highly humidified condition (> 80 RH%). “CO₂ molecular gate” membrane would work and show excellent CO₂ separation properties even under dry or less humid conditions. In this research, CO₂ transportation by carbamate ion hopping has been investigated. Sc-CO₂ is selected as a structure-directing agent of the CO₂/H₂ separation membrane for the reasons above mentioned.

Results

We have developed CO₂ molecular gate membranes using PAMAM dendrimer immobilized in a polymer matrix. PAMAM dendrimer was successfully immobilized in a PEG network by photopolymerization of PEGDMA in the presence of the dendrimer [6]. The resulting membrane shows bicontinuous structure of the dendrimer-rich and PEG-rich phases upon macrophase separation. The result indicates that the dendrimer channel penetrates through the membrane, where CO₂ would pass through [7]. Figure 5 shows a 3D reconstructed image of the membranes observed by a laser scanning confocal

microscope. In Figure 5, PEG-rich phase is colored green while the dendrimer phase remains empty. An average PAMAM dendrimer domain size was calculated by summation of a series of 2D-sliced fluorescent images and was about 2-4 μm in proportion to PAMAM dendrimer concentration in the polymeric membrane. Such controlled structure, or the dendrimer channel, would be critical to design and fabricate polymeric membranes for preferential CO_2 permeation.

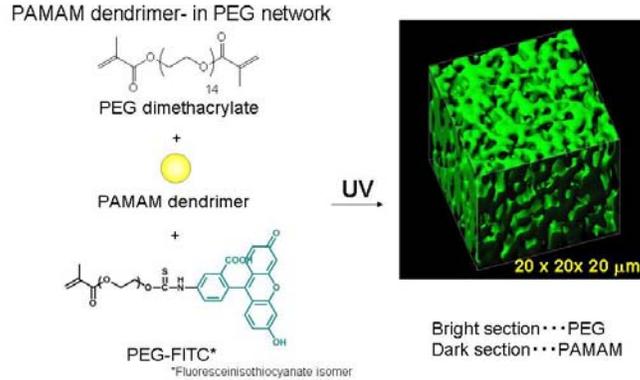


Figure 5: A 3D reconstructed image of PAMAM dendrimer (empty) immobilized in PEG network (green).

Structure control in further smaller scale such as nanometric scale would be attained by a structure-directing agent. CO_2 itself will be used as a structure-directing agent for building an ideal CO_2 molecular gating structure. Figure 6 shows the basic concept of sc- CO_2 directing method for preparing ideal CO_2 transporting channel with CO_2 molecular gating function. Precise structural control of the CO_2 transporting channel surrounded by CO_2 affinity materials such as PAMAM dendrimer will be crucial. In the figure, CO_2 works as a structure-directing agent to form a CO_2 penetrating channel with finely aligned CO_2 -affinity moieties. CO_2 would pass through the membrane in Carbamate form by hopping mechanism.

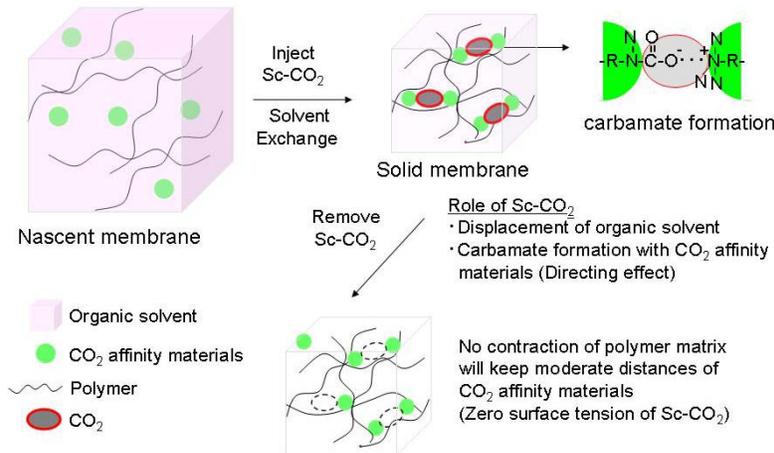


Figure 6: Sc- CO_2 as a structure-directing to form CO_2 penetrating channel.

Figure 7 shows an experimental set-up of sc-CO₂ directing method. The set-up consists of a syringe pump, high-pressure view cell with a sapphire window, a back pressure regulator and a monitoring camera. A nascent membrane containing a solvent was formed on a glass plate, followed by set in the high-pressure cell. CO₂ was injected gradually into the cell with a high-pressure pump to make supercritical condition at 40 °C. Pressure was kept for a while at 10 MPa, and then released at a rate of 0.1 MPa/min to form a CO₂ penetrating channel.

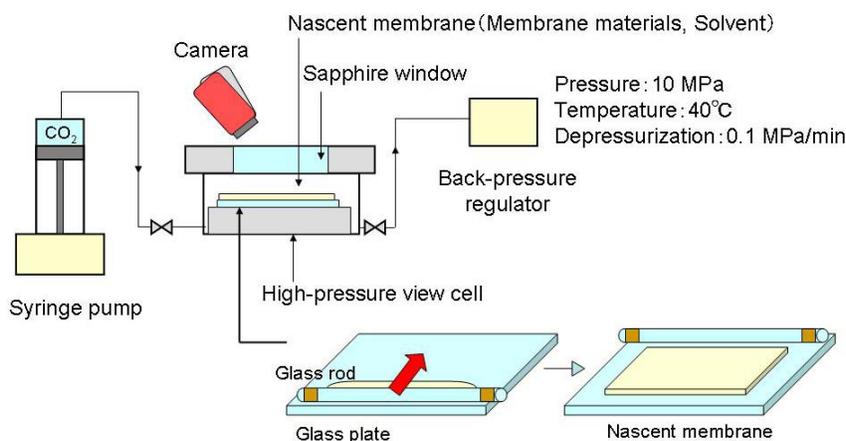


Figure 7: Experimental set-up of membrane fabrication under sc-CO₂.

For producing an ideal CO₂ channel with molecular gate function, a dense and macroscopically homogeneous membrane incorporating CO₂ affinity materials such as PAMAM dendrimer was treated by sc-CO₂. Both of choosing polymeric materials and optimizing the sc-CO₂ condition would be important. PAMAM dendrimer was immobilized in a polymer network from copolymerization of PEGDMA and trimethylolpropane trimethacrylate (TMPTMA) in the presence of PAMAM dendrimer. Figure 8 shows chemical structures of the compounds used.

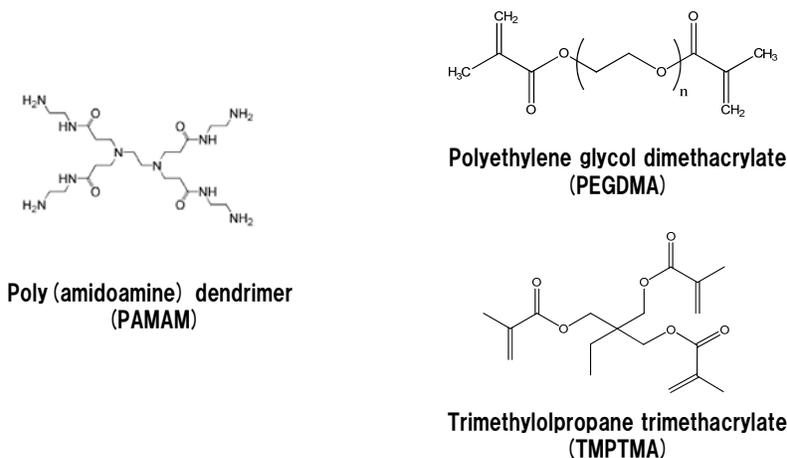


Figure 8: Chemical structure of PAMAM dendrimer, PEGDMA, and TMPTMA.

Figure 9 shows a membrane under sc-CO₂ in a high-pressure cell. A membrane containing PAMAM dendrimer was placed on a glass plate. Sc-CO₂ causes negligible deformation of the structure upon solvent removal, due to the near-zero surface tension. The sc-CO₂ directing method will provide an ideal CO₂ penetrating channel structure by carbamate ion hopping. Table 1 shows CO₂ separation properties of the polymeric membrane before and after sc-CO₂ treatment. Gas permeation data was taken under atmospheric pressure and 40 °C. Feed gas contained 80 % of CO₂ and 20% of H₂ at 80 % relative humidity (80 %RH).



Figure 9: PAMAM dendrimer containing PEGDMA/TMPTMA membrane under sc-CO₂.

Table 1: CO₂ separation properties of PAMAM dendrimer containing PEGDMA/TMPTMA membrane before and after sc-CO₂ treatment.

Membrane	Temp./°C	$10^{12} Q_{CO_2}$	$10^{14} Q_{H_2}$	α_{CO_2/H_2}
Before treatment	-	4.38	2.98	144
After treatment	40	8.80	3.62	243
	60	8.52	4.00	213

Q: m³(STP)/(m² s Pa), sc-CO₂ conditions: 10 MPa for 4 h.

The original membrane containing PAMAM dendrimer showed 4.38×10^{-12} and 2.98×10^{-12} m³(STP)/(m² s Pa) for Q_{CO_2} and Q_{H_2} , respectively. On the other hand, Q_{CO_2} and Q_{H_2} increased to 8.80×10^{-12} and 3.62×10^{-12} m³(STP)/(m² s Pa), respectively, by sc-CO₂ at 40 °C. The increment of Q_{CO_2} was larger than that of Q_{H_2} , which gave higher CO₂/H₂ selectivity. Higher separation properties were obtained by elevating operation treatment (at 60 °C), Q_{CO_2} and Q_{H_2} of 8.52×10^{-12} and 4.00×10^{-12} m³(STP)/(m² s Pa), respectively, were obtained. It was obvious that sc-CO₂ treatment gave rise to improving the CO₂ separation properties. However, the effect of improvement on CO₂ permeance is not as large as expected. The reason might be low T_g of PEG matrix, which would cause rearrangement of polymer chains or phase structure aligned under sc-CO₂.

Cellulose acetate was then selected as one of the candidate matrices for PAMAM dendrimer, and the T_g was above 120 °C. Cellulose acetate and *N*-methylpyrrolidone (NMP) was placed in a high-pressure cell, followed by gradually increasing CO₂ pressure

up to 10 MPa at 40 °C to reach sc-CO₂ condition. CO₂ was fed at a rate of 2 mL(STP)/min for 240 min under the Sc-CO₂ condition to remove NMP. After that CO₂ pressure decreased gradually to obtain an intended membrane. A polymeric membrane with a thickness of 70 μm was obtained by this method. Figure 10 shows a series of photo images during membrane formation under Sc-CO₂ and a SEM image of the resulting membrane. In the photo images, transparent nascent membrane (upper left) became opaque with operation time due to removal of NMP under sc-CO₂ condition, indicating formation of a phase-separated structure. On the contrary, a dense homogeneous structure was confirmed by SEM.

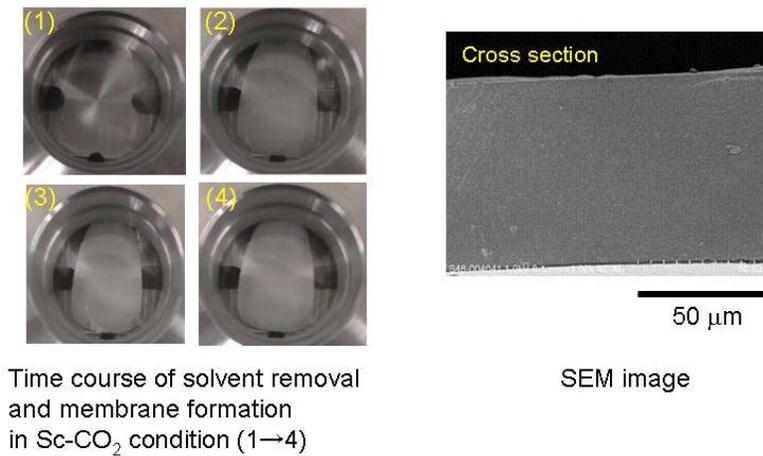


Figure 10: Photo images of membrane formulation under sc-CO₂ and a SEM image of the resulting membrane cross-section.

CO₂/H₂ separation properties of the resulting membrane were shown in Figure 11. In the figure, CO₂/H₂ selectivity (α) for 35 wt% of PAMAM dendrimer concentration was 4, which was slightly larger than that of cellulose acetate itself. Such lower concentration was not enough for the dendrimer to form CO₂ penetrating pathway. It might mean that a continuous PAMAM dendrimer channel would not be formed for the PAMAM dendrimer concentration of 35 wt%. For 52 wt% dendrimer membrane, the selectivity was increased up to about 16. This result is the first accomplishment of reasonably high CO₂/H₂ selectivity by novel sc-CO₂ directing method, even though the value of CO₂/H₂ selectivity was still not enough for ideal CO₂ molecular gate. The result encourages sc-CO₂ directing method to provide a novel method for preparing CO₂ molecular gate membrane.

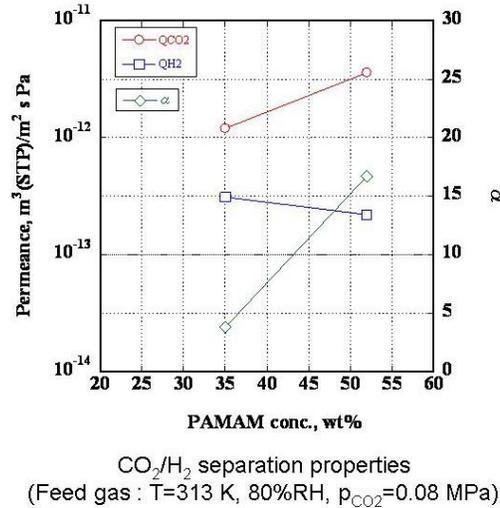


Figure 11: CO₂/H₂ separation properties of membrane prepared by sc-CO₂ directing method (thickness: 70 μm).

Due to the flow nature of PAMAM dendrimer at ambient conditions and microscopically inhomogeneous structures would lead to change in morphology. CO₂ pathway formed under sc-CO₂ thus might be disturbed over long-term use, resulting in decrease of CO₂ separation properties. Here after, polyethyleneimine (PEI) bearing primary amine used in the following investigations as a substituent of PAMAM dendrimer and polymer matrix. The polymeric membrane was prepared by solution-casting method with a cross-linker. Operating temperature and gas pressure of the sc-CO₂ treatment condition are fixed at 50 °C and 10 MPa, respectively. The sc-CO₂ treatment time was varied from 1 to 4 h. Figure 12 shows preparation procedures of PEI polymer membrane.

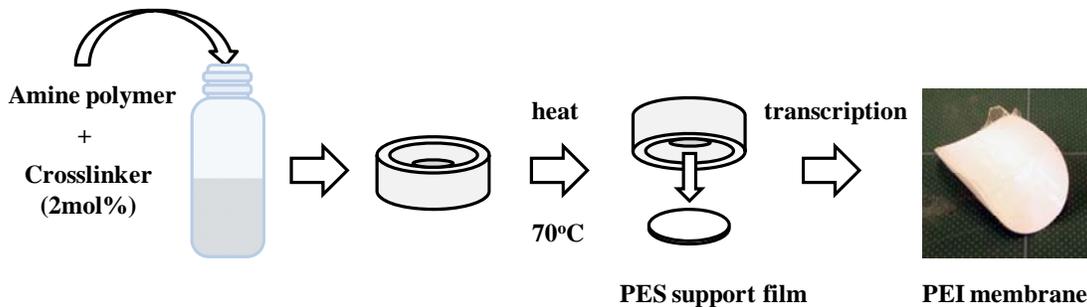


Figure 12: Preparation of PEI membrane.

The CO₂ separation properties of sc-CO₂ treated CO₂ membrane were represented in Figure 13. The Q_{CO2} increased by sc-CO₂ treatment for 1 h, and then it remained unchanged (ca. 1.8 × 10⁻¹¹ m³(STP)/(m² s Pa)). The Q_{He} also increased by the treatment for first 1 h, however, it decreased with the treatment time. As a consequence, CO₂/He selectivity was increased with incubation time under sc-CO₂. Increase in Q for the first 1 h would be due to swelling of the membrane by sc-CO₂. After that time period,

carbamate formation took place in the membrane by rearranging the polymer chain, which made CO₂ penetrating pathway, and the quasi cross-linking between CO₂ and primary amines would suppress He permeation.

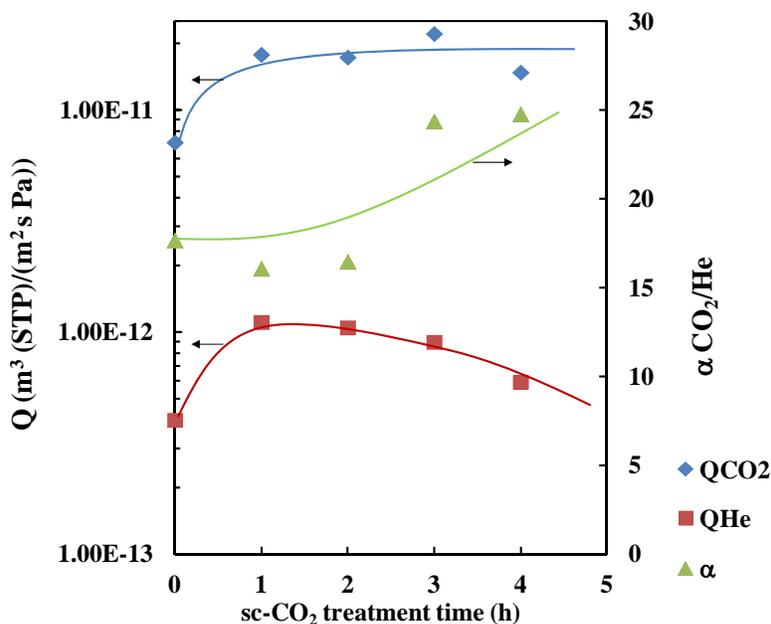


Figure 13: Gas permeance and selectivity of CO₂ separation membrane with sc-CO₂ treatment.

PEI membranes exhibited effect of structure-directing method by sc-CO₂, although the T_g (-40 °C) of PEI was far below from ambient temperature and thus the conformational change might occur during long time use. In the extended period of this project, amine-bearing polymers with high T_g were employed as a membrane material.

Experimental

Material: 2-Aminoethyl methacrylate hydrochloride (AEM), *N*-(2-aminoethyl) methacrylamide hydrochloride (AEMA), and *N*-(3-Aminopropyl) methacrylamide hydrochloride (APMA) are shown in Figure 14. The three monomers, tri(ethylene glycol) dimethacrylate (TEGDMA), and Irgacure 2959 were purchase from Sigma-Aldrich (MO, USA). Other chemicals used were analytical grade and used as received.

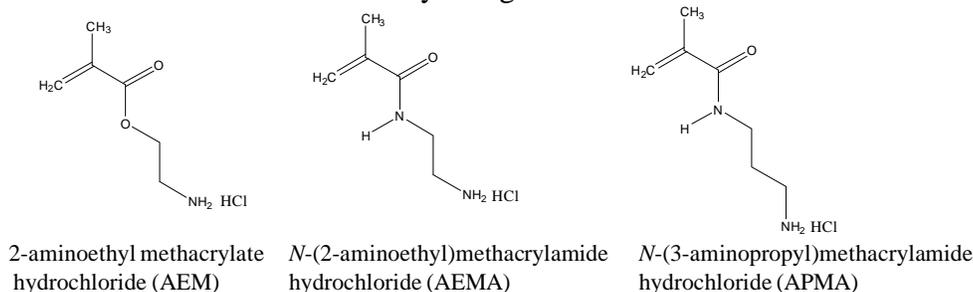


Figure 14: Chemical structures of AEM, AEMA and APMA.

Membrane preparation: Poly(2-Aminoethyl methacrylate) (PAEM) membrane was prepared as follows. AEM and TEGDMA were dissolved in deionized water at 25 °C. Irgacure 2959 as an initiator for photopolymerization was added to the solution, and the resulting mixture was stirred for 10 min at room temperature. The reaction mixture was cast on a PET film and irradiated UV (312 nm) for 10 min. Poly(2-aminoethyl) methacrylamide (PAEMA) and poly(3-aminopropyl) methacrylamide (PAPMA) membrane were also prepared by the same procedures. The thickness of the membranes were approximately 50 µm in each case. The resulting membranes were treated under sc-CO₂. Operating temperature and CO₂ pressure were fixed at 40 °C and 10 MPa, respectively. The sc-CO₂ treated PAEM, PAEMA and PAPMA membranes were denoted as sc-PAEM, sc-PAEMA and sc-PAPMA, respectively.

Characterization of gas separation membrane: The thermal behavior of the polymeric membranes was evaluated by thermogravimetric analysis under nitrogen atmosphere at a heating rate of 10 °C/min (Pyris 1 TGA, PerkinElmer, MA, USA). The infrared (FT-IR) spectra were collected using an IRT-5000 FT-IR (Jasco Co., Tokyo, Japan). A CO₂/He (80/20 by vol.) gas mixture was humidified at 90 RH% and then fed to a flat-sheet membrane cell at a flow rate of 100 mL/min. The CO₂ partial pressures of the feed side were 5 (100) and 560 kPa (700 kPa), the total absolute pressure shown in parentheses. Dry He was supplied at a flow rate of 10 mL/min to the permeate side of the cell as a sweep gas to collect the permeate. The operating temperature was 40 °C. The CO₂ and He concentrations in both feed and permeate sides were measured by gas chromatography with a pulsed discharge detector (GC-4000, GL Sciences Inc., Tokyo, Japan). Under these experimental conditions, the pressure ratio of feed to permeate was sufficient to give the separation factor as an ideal separation factor (selectivity).

Obtained Results

The thermal stability of the polymer membrane was investigated by TGA measurements. Figure 15 showed TGA curves of the polymer membranes before and after sc-CO₂ treatment. All the polymeric membranes showed the weight loss around 100 °C because of desorption of water in the membrane. Decomposition temperatures (T_d) of PAEM, PAEMA and PAPMA were 247.5, 259.0 and 281.4 °C, respectively. The T_d was slightly increased by sc-CO₂ directing method in all the cases, and the T_{ds} of sc-PAEM, sc-PAEMA, and sc-PAPMA were 251.1, 259.1, and 284.8 °C, respectively. This result suggests that CO₂ introduced under sc-CO₂ may form carbamate with primary amines, leading to increase in thermal stability.

The structural change of the polymeric membrane was evaluated by FT-IR measurement. Figure 16 displayed the FT-IR spectra of the polymer membranes before and after sc-CO₂ treatment. The peak at 1150 cm⁻¹ in PAEM spectrum was assigned to C-O-C stretching, and 1200 cm⁻¹ in PAEMA and PAPMA was represent the C-O-C stretching of TEGDMA. The peaks at 3000 and around 1500 cm⁻¹ were due to the NH group of the polymer. The peaks at 1620 cm⁻¹ was attributed to the C=O stretching of the polymer. The peak at 3400 cm⁻¹ in PAEMA and PAPMA was assigned to the amide group absorption. After sc-CO₂ treatment, the peak at 1720 cm⁻¹ in sc-PAPMA was disappeared. This result indicated that the residual C=C was reacted. The peak intensity

at 3400 cm^{-1} in sc-PAEMA and sc-PAPMA assigned to the amide group increased by sc- CO_2 treatment due to formation of carbamate linkage between amine groups and CO_2 .

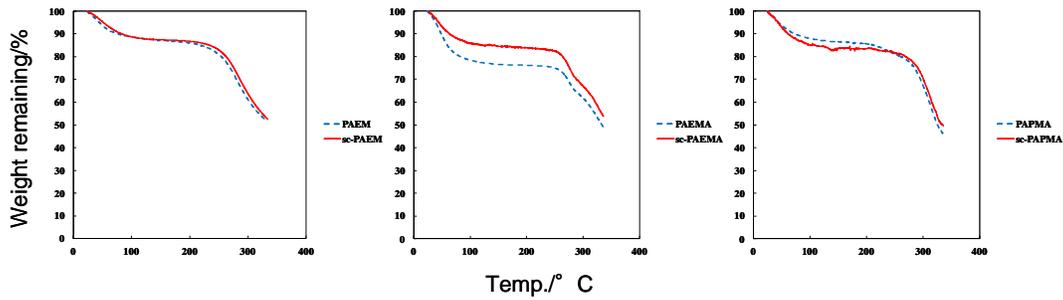


Figure 15: TGA curves of various polymeric membranes before and after sc- CO_2 treatment.

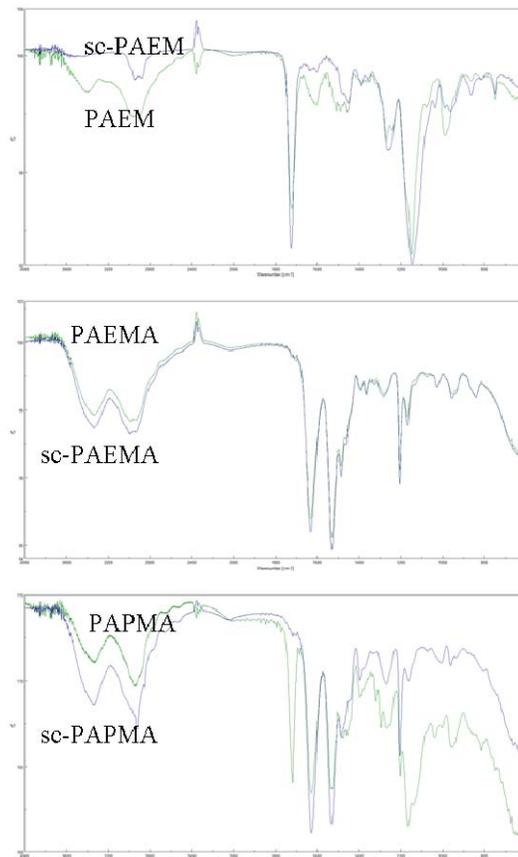


Figure 16: FT-IR spectra of various polymeric membranes before and after sc- CO_2 treatment.

Table 2 summarized the CO_2 separation properties of the polymeric membranes before and after sc- CO_2 treatment at $40\text{ }^\circ\text{C}$ and 90 \%RH . PAEMA membrane showed preferential permeation of CO_2 at ambient pressure, while PAEM did lower CO_2/He selectivity. Both of the membranes were not tolerate use under pressure. PAPMA

membrane was fragile and the gas separation test was not done. On the other hands, sc-CO₂ treated polymeric membranes demonstrated increase in elastic modulus determined by AFM force curve (data not shown), which would be due to formation of carbamate quasi-crosslinking, although sc-PAEM membrane was not allowed CO₂ separation properties even at ambient pressure. Interestingly, with PAEMA and PAPMA membranes, $\alpha_{\text{CO}_2/\text{He}}$ values are increased under higher pressure from 11.7 to 13.3 for PAEMA and from 7.28 to 11.2 for PAPMA. This was because of decrease in Q_{He} while Q_{CO_2} did not change much. The obtained results strongly suggested the “CO₂ molecular gate” effect. The selectivities were still lower than that expected, however, T_g s of the polymeric membrane were above 100 °C. The separation properties were thus kept for a long time.

Table 2: CO₂ separation properties of various polymeric membranes before and after sc-CO₂ treatment.

Membrane	sc-CO ₂	Pressure/MPa	Q_{CO_2}	Q_{He}	$\alpha_{\text{CO}_2/\text{He}}$
PAEM	before	0.1	2.33	1.03	2.27
		0.7	n.a.	n.a.	n.a.
	after	0.1	n.a.	n.a.	n.a.
		0.7	n.a.	n.a.	n.a.
PAEMA	before	0.1	4.47	0.30	14.7
		0.7	n.a.	n.a.	n.a.
	after	0.1	3.56	0.31	11.7
		0.7	3.48	0.26	13.3
PAPMA	before	0.1	n.a.	n.a.	n.a.
		0.7	n.a.	n.a.	n.a.
	after	0.1	2.68	0.37	7.28
		0.7	2.46	0.22	11.2

Q_{CO_2} and Q_{He} : $\times 10^{-11} \text{ m}^3(\text{STP})/(\text{m}^2 \text{ s Pa})$, membrane thickness: 50 μm , at 40 °C and 90 %RH, CO₂: 80 %.

Conclusions

CO₂ separation membranes will take an advantage of CO₂ capture from a pressurized gas stream in such as IGCC plant with CCS. CO₂ separation membranes would be also one of the powerful candidates of CO₂ removal from higher CO₂ content natural gases. In addition, CO₂ separation membranes are considered as an example of CO₂ capture from a flue gas in a coal-power plant. In this project, various polymeric membranes have been developed for preferential CO₂ separation. Sc-CO₂ was employed as a structure-directing method in order to fabricate CO₂ penetrating channel upon formation of carbamate quasi cross-linkage, which inhibit permeation of other gases. As a consequence, higher CO₂ selectivity was attained even over smaller H₂ or He. CO₂ separation properties should be enhanced in the actual use, however, carbamate transportation studied would have greater opportunities in comparison to bicarbonate transportation.

An IGCC power plant of 300 MW would emit about one million metric tons of CO₂ a year. Assuming 90% CO₂ recovery by the membrane system, the GCEP outcome will potentially contribute to a CO₂ reduction of 0.9 million metric tons per 300 MW power plant. When the membrane system is installed in 100 IGCC plants, annual CO₂ reduction can be 90 million metric tons. Additionally, the GCEP outcomes by the CO₂ membrane research might be applicable to the existing power plants such as coal-fired thermal power plants. A 1000 MW coal-fired power plant emits about five million metric tons of CO₂ a year. Significant improvement of CO₂ permeability is required for effective CO₂ membrane separation from those power plants, however, when it comes, more than four million metric tons of CO₂ would be captured annually from a 1 GW coal-fired power plant. Our final goal is to establish novel CO₂ separation membrane system with a game-changing technology, which can be applied in the existing power plants and steel works, as well as the next generation plants, for example IGCC.

Publications

1. Shimizu, R, Duan, S. Taniguchi, I., Kai, T., Kazama, S., Fujioka, Y., Advanced CO₂/H₂ Separation Materials Incorporating Active Functional Agents, GCEP Res. Symp., 2009.
2. Kazama, S., Advanced CO₂/H₂ Separation Materials Incorporating Active Functional Agents, GCEP Res. Symp. 2011.

References

1. Kovvali, A. S., Chen, H., Sirkar, and K. K., Dendrimer Membranes: A CO₂-Selective Molecular Gate, *J. Am. Chem. Soc.*, 122, 7594-7595, 2000.
2. Kouketsu, T., Duan, S., Kai, T., Kazama, S., and Yamada, K., PAMAM Dendrimer Composite Membrane for CO₂ separation: Formation of a Chitosan Gutter Layer, *J. Membr. Sci.*, 287, 51-59, 2007.
3. Lin, H., Wagner, E. V., Freeman, B. D., Toy, L.G., and Gupta, R. P., Plasticization-Enhanced Hydrogen Purification using Polymeric Membranes, *Science*, 311, 639-642, 2006.
4. Zou, J. and Ho, W. S. W., CO₂-selective polymeric membranes containing amines in crosslinked poly(vinyl alcohol), *J. Membr. Sci.*, 286, 310-321, 2006.
5. Yegani, R., Hirozawa, H., Teramoto, M., Himei, H., Okada, O., Takigawa, T., Ohmura, N., Matsumiya, N., and Matsuyama, H., Selective separation of CO₂ by using novel facilitated transport membrane at elevated temperatures and pressures, *J. Membr. Sci.*, 291, 157-164, 2007.
6. Taniguchi, I., Duan, S., Kazama, S., and Fujioka, Y., Facile fabrication of a novel high performance CO₂ separation membrane: Immobilization of poly(amidoamine) dendrimers in poly(ethylene glycol) networks, *J. Membr. Sci.*, 322, 277-280, 2008.
7. Taniguchi, I., Kazama, S., and Jinnai, H., Structural analysis of poly(amidoamine) dendrimer immobilized in cross-linked poly(ethylene glycol), *J. Polym. Sci. Part B: Polym. Phys.*, 50, 1156-1164, 2012

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