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A CO_2-selective molecular gate of poly(amidoamine) dendrimer immobilized in a poly(ethylene glycol) network

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ABSTRACT

A polymeric membrane composed of poly(amidoamine) (PAMAM) dendrimer immobilized in a poly (ethylene glycol) (PEG) network expresses excellent CO_2 separation properties over smaller H_2. The preferential CO_2 permeation can be explained by specific interaction between CO_2 and primary amine of the dendrimer, which enhances CO_2 solubility into the polymeric membrane. CO_2 forms carbamate with the amines or bicarbonate in the presence of water determined by inverse-gate decoupled ^{13}C NMR. The resulting carbamate ion pair works to form a quasi-crosslinking, which would suppress H_2 permeation by a CO_2-selective Molecular Gate, while bicarbonate ion can be a major moving species to pass through the polymeric membrane. Attenuated total reflection (ATR) indicates the formation of carbamate. Small-angle X-ray scattering (SAXS) reveals increase in scattering intensity under CO_2 atmosphere due to the formation of scattering particles, which can be a cluster of the dendrimer-CO_2 crosslinks. Tensile testing of the membrane exhibits increase in both Young's modulus and elongation-to-break by CO_2 treatment, suggesting that the crosslinking is reversible and rearrangeable. Differential scanning calorimetry (DSC) also shows an exothermic peak at 120 °C, which is associated with dissociation of the crosslinks.

1. Introduction

Since the development of dendrimers by Vogtle et al. in 1978 [1], such starburst-macromolecules have gained particular attention in both basic science [2,3] and applications [4,5], and various dendrimers have been introduced. PAMAM dendrimers are one of the most studied [2] and the first commercialized dendrimers. Recently, Sirkar and co-workers inspired a novel aspect of PAMAM dendrimers, which represented an excellent CO_2 separation performance with an immobilized liquid membrane system by so called “a CO_2-selective Molecular Gate” [6]. However, the detailed mechanism has not been made clear. In addition, the dendrimers flow at ambient conditions, which has been one of the shortcomings to limit use in practical CO_2 separation.

We have investigated CO_2 separation membranes with PAMAM dendrimers and succeeded stable immobilization of them in a crosslinked PEG by photopolymerization of PEG dimethacrylates (PEGDMAs) in the presence of the dendrimers [7]. The resulting polymeric membrane expresses excellent CO_2 separation properties over H_2. In addition, various real-space and Fourier-space investigations revealed the formation of a bicontinuous structure of PAMAM dendrimer-rich and PEG-rich phases upon macrophase separation [8]. As well as the dendrimer generation and fraction, the phase-separated structure, PEG length, and humidity are key factors to characterize CO_2 separation properties of the polymeric membrane [9,10].

However, the mechanism of preferential CO_2 permeation through the polymeric membrane has not been studied explicitly. For example, at 5 kPa of CO_2 partial pressure and 25 °C, the polymeric membrane exhibits the following performance under 80% relative humidity with a He sweep. Permeability of H_2 (P_{H_2}) decreased from 2.39×10^{-15} to 4.72×10^{-17} $m^3(STP)/(m^2\ s\ Pa)$ sharply with increase of the dendrimer fraction from 0 to 50 wt% in the polymeric membrane, while that of CO_2 (P_{CO_2}) increased slightly from 1.63×10^{-14} to 2.60×10^{-14} $m^3(STP)/(m^2\ s\ Pa)$. As a consequence, a drastic increase in the selectivity (α_{CO_2/H_2}) was found with increasing PAMAM dend rimer content from 10 to 550 under the isobaric condition [7]. This result suggests the dendrimer suppresses H_2 permeation rather than enhancing CO_2 permeation by the conventional carrier-mediated facilitated transportation mechanism [11]. In the polymeric membrane, CO_2 will form carbamate with two primary amines of the dendrimer, which act as a quasi-crosslink,

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and the resulting crosslinks would inhibit H_2 permeation by the Molecular Gate mechanism [6]. We herein investigate crosslinking of PAMAM dendrimer with CO_2 by the formation of carbamate upon CO_2 sorption in the polymeric membrane.

2. Experimental

2.1. Materials and membrane fabrications

PEGMA (average M_n 750), 1-hydroxycyclohexyl phenylketone, and PAMAM dendrimer in methanol (0th generation, 50 wt%) were obtained from Sigma-Aldrich (MO, USA). Other chemicals were reagent grade and used without further purification. A polymeric membrane was fabricated by photopolymerization of PEGDMA in the presence of PAMAM dendrimer in ethanol. The details were described in the previous paper [7]. UV irradiation for 90 s gave macroscopically homogeneous polymeric membranes. The dendrimer concentration was kept to 50 wt% in the membrane, and considerable leakage of the dendrimer was not found in the fabrication procedures. The membrane thickness was ca. 400 μm after removing ethanol under vacuum.

2.2. Inverse-gate decoupled ^{13}C NMR experiment

An equal amount of PAMAM dendrimer and D_2O was mixed in a sealed NMR tube with a rubber septum, and CO_2 was flushed through a syringe with 20 mL/min at ambient temperature for 24 h, when equilibrium of the CO_2 sorption was confirmed by monitoring pH value. CO_2 was humidified by passing through deionized water prior to introduction to the NMR tube to avoid water evaporation. Inverse-gate decoupling technique was employed to give a quantitative ^{13}C NMR spectrum, and the spectrum was obtained by accumulation of 1000 resonances with a long relaxation time (60 s) to minimize Nuclear Overhauser effect of carbonyl carbons.

2.3. FT-ATR measurement

Formation of carbamate ion pair was examined by infrared microspectrometry-ATR on a JASCO IRT-7000 (Tokyo, Japan). A polymeric membrane was kept under 1.0 MPa of CO_2 for 24 h at ambient temperature in a pressure chamber (Syn Corporation, Kyoto, Japan). ATR spectrum of the incubated specimen was collected right after taking it out from the chamber. A total of 256 scans were collected at an instrument resolution of 4 cm^{-1} over the spectral range from 4000 to 650 cm^{-1}. As a control experiment, a non-treated polymeric membrane was also measured.

2.4. SAXS measurement

SAXS was performed on a Rigaku Nano-viewer (RA-Micro7 generator) with Cu-Kα (λ:1.5418 Å) radiation operated at 40 kV and 20 mA (Tokyo, Japan). A specimen was set in an *in situ* cell (Rigaku), where atmosphere and relative humidity were controlled at 47 °C and 80%, respectively, under N_2 or CO_2 atmosphere. A Pilatus 100K/RL 2D detector (Dectris, Baden, Switzerland) was used to collect the scattering. The camera length and exposure time were 600 mm and 10 min, respectively.

2.5. DSC measurement

Thermal analysis is conducted on a Netzsch DCS 204 HP calorimeter (Kanagawa, Japan), which allows DSC measurement under pressure. The sample was equilibrated under 1.0 MPa of N_2 or CO_2 atmosphere for 24 h at 30 °C before running, and the thermal transition was recorded from 30 to 200 °C with a heating rates of 10 °C/min under 1.0 MPa of the gas pressure. DSC measurements were also carried out under ambient pressure. The pre-incubation and operation conditions were the same but done under ambient pressure.

2.6. Tensile testing

Mechanical properties of the polymeric membranes were measured using a Shimadzu AGS-X tester (Kyoto, Japan) with a 50 N load cell to find Young's modulus and strain-to-break at ambient conditions. The displacement rate was 10 mm/s. Samples, with or without CO_2 treatment under 1.0 MPa for 24 h at ambient temperature, were cut using a custom dogbone-shaped specimen cutter (JIS K6251, 2 mm wide and 35 mm long). Tensile testing was conducted at least in triplicate.

3. Results and discussion

A polymeric mixture of PAMAM dendrimer physically immobilized in a PEG network has been explored as a membrane material for preferential CO_2 separation. The excellent CO_2 separation properties over H_2 of the polymeric membrane can be explained by significant suppression of H_2 permeation [7]. In the gas separation experiment, CO_2 will show a higher solubility than H_2 in the polymeric membrane because of the specific interaction to primary amine of the dendrimer. The absorbed CO_2 would form carbamate with two primary amines to crosslink the dendrimer. The resulting quasi-crosslinking formation would inhibit permeation of H_2 with increase in crosslinking density, relating to a CO_2-selective Molecular Gate effect [6]. The mechanism of preferential CO_2 permeation was studied by various investigations described below.

3.1. CO_2 in dendrimer solution

Since the polymeric membrane swells under humidified conditions by absorbing water, and the weight fraction of water can be ca. one-third of the swelled membrane ([PAMAM] = 50 wt%), which means PAMAM:PEG matrix:H_2O = 1:1:1 by wt [9,10]. Due to low sensitivity, ^{13}C NMR measurement of the solid membrane will not give precise information of CO_2 in the membrane. The dendrimer was thus mixed with the same amount of D_2O, and the mixture was equilibrated with humidified CO_2 flush. Inverse-gate decoupled ^{13}C NMR of the resulting mixture was conducted as a model experiment to see the interaction between PAMAM dendrimer and CO_2. Fig. 1a represents a ^{13}C NMR spectrum of carbonyl region of the dendrimer solution. As a control, the NMR measurement of $NaHCO_3$ aqueous solution (pH 8.0) was conducted in Fig. 1b. The absence of a peak at 125 ppm suggests that CO_2 does not exist as a gas molecule in the dendrimer solution. Peaks at 161 and 164 ppm are found only after introduction of CO_2 and can be assigned carbonyl carbons of bicarbonate and carbamate, respectively. Formations of carbamate and bicarbonate are expressed by the following reaction schemes. A peak at 174–175 ppm was from amide carbon of the dendrimer. Exhange of proton for deuterium resulted in the splitting pattern.

$$CO_2 + 2R\text{–}NH_2 \rightarrow R\text{–}NH\text{–}COO^- \cdot N^+H_3\text{–}R$$

$$CO_2 + H_2O \rightarrow HCO_3^- + OH^-$$

The inverse-gate decoupling method allows quantitative analysis. The amount of absorbed CO_2 and ratio of the ions can be calculated. A 5.6 mmol of CO_2 was absorbed per g-dendrimer, and the molar