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A compatible crosslinker for enhancement of CO_2 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 CO_2 separation properties over smaller H_2. 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 CO_2 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 CO_2 selectivity. The 4GMAP incorporation also endows pressure tolerance by increasing crosslinking density of the resulting polymeric membranes. The CO_2 permeance is elevated from 9.94×10^{-13} to 1.68×10^{-11} m^3(STP) m^{-2} s^{-1} Pa^{-1}, by reducing the membrane thickness from 640 to 9.5 μm with 10 of CO_2 selectivity at 313 K and 0.56 MPa of CO_2 partial pressure.

1. Introduction

Inexperienced rise of atmospheric concentration of CO_2 triggers global warming and climate change, and a number of CO_2 capturing technologies have been studied to mitigate CO_2 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 CO_2 separation materials have been developed [1,2]. Sirkar et al. [3–5] reported PAMAM dendrimers expressed high CO_2 separation performance over N_2 and would hold potential as novel CO_2 separation materials in gas separation. However, flow nature of the dendritic molecules requires stable immobilization into a suitable matrix to fabricate a CO_2 separation membrane. In our research group, various CO_2 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 CO_2 separation performance over H_2 under humidified conditions [9]. CO_2 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 H_2 permeation, to give a high selectivity [10]. However, permeability of CO_2 should be enhanced for use such as in an integrated gasification combined cycle (IGCC) plant [11–14]. H_2 separation over CO_2 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 H_2 after separation results in higher energy requirement rather than CO_2 separation process. On the other hand, the polymeric membrane would have another opportunity at H_2 stations for fuel cell vehicles (FCVs), where H_2 is mostly produced by steam reforming of natural gas or liquid propane gas (LPG) with emission of CO_2 in the PSA off-gas. When CO_2 is effectively separated, carbon-free H_2 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

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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 of regent 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 of 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 h at 273 K and then further stirred for 16 h at ambient temperature.

δ_H (400 MHz; MeOH-*d4*) 1.94 (12H, s, CH_3), 2.36 (8H, CH_2CONH), 2.55 (4H, s, $CH_2NHCH_2CH_2NHCH_2$), 2.34 and 2.65 (8H, $NHCH_2CH$), 2.67 (8H, $CONHCH_2CH_2$), 2.75 (8H, NCH_2CH_2CO), 4.12 (4H, CH), 4.21, 3.99 (8H, CH_2O), 5.63 and 6.14 ppm (8H, s, $CH_2{=}C$).

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 as those of 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 ×63 (Plan-Apochromat, Carl Zeiss) objective lens with numerical aperture of 1.4 is used. A scanning electron microscope (SEM) measurement is carried out on a

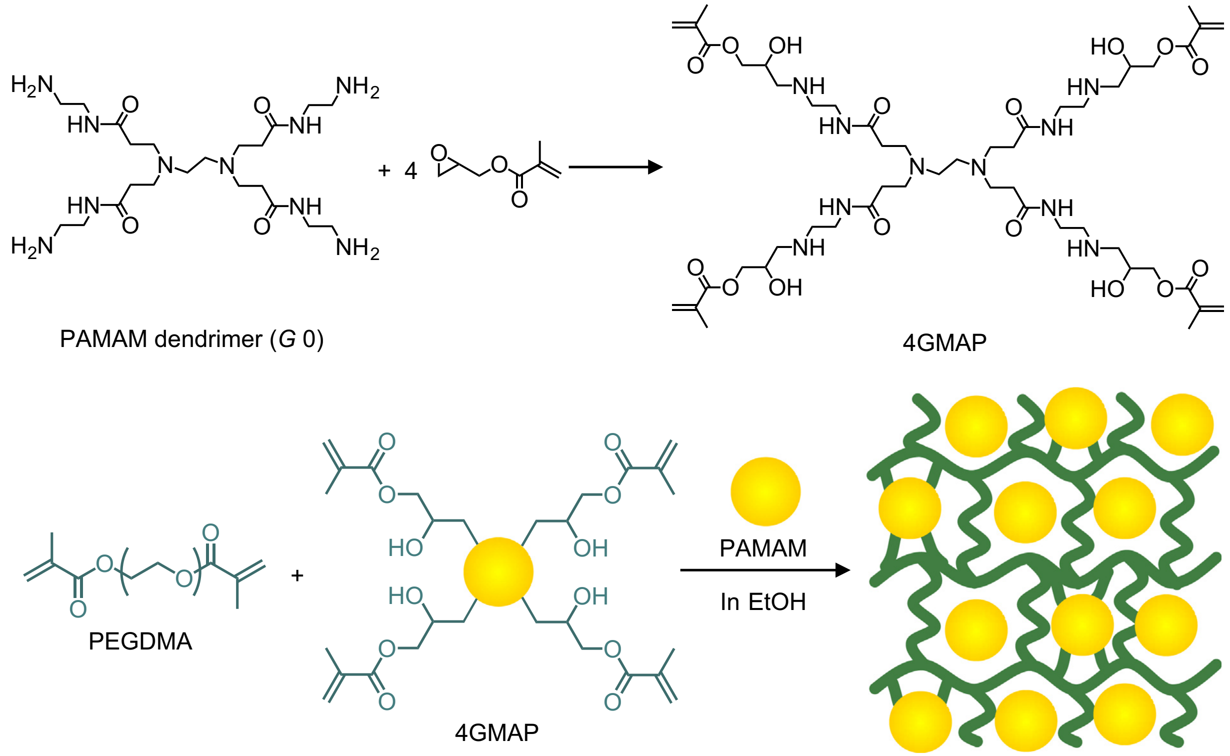

Fig. 1. Synthetic scheme of a compatible crosslinker, 4GMAP (upper) and schematic drawing of photocopolymerization of PEGDMA and 4GMAP in the presence of PAMAM dendrimer (bottom).