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Hybrid membranes of nanostructrual copolymer and ionic liquid for carbon dioxide capture

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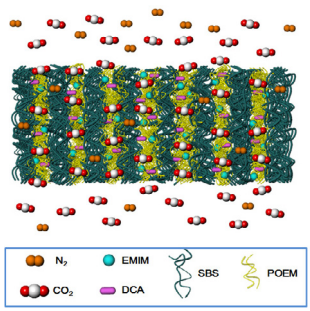
HIGHLIGHTS

- Efficient CO_2 capture membranes were prepared using hybrid of SBS-*g*-POEM and IL.
- SBS-*g*-POEM was synthesized via mass-producible, low-cost radical polymerization.
- IL was efficiently and uniformly distributed due to good miscibility and interactions.
- SBS-*g*-POEM exhibited enhancement in CO_2 permeability and selectivity.
- SBS-*g*-POEM/IL15% hybrid showed the best performance due to unique nanostructure and morphology.

GRAPHICAL ABSTRACT



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ABSTRACT

Efficient CO_2 capture membranes were prepared using a hybrid comprising the poly(styrene-*block*-butadiene-*block*-styrene)-*graft*-poly(oxyethylene methacrylate) (SBS-*g*-POEM) nanostructural copolymer and the ionic liquid (IL) 1-ethyl-3-methylimidazolium dicyanamide (EMIMDCA). The SBS-*g*-POEM copolymer was synthesized via a mass-producible, cheap, free-radical polymerization process. The specific interaction of SBS-*g*-POEM with EMIMDCA and the good miscibility of these species were confirmed by Fourier transform infrared spectroscopy (FT–IR) and wide angle X-ray scattering (WAXS) and by using a universal testing machine (UTM). The microphase-separated nanostructure of the membranes and uniform distribution of EMIMDCA were also observed using transmission electron microscopy (TEM) and small angle X-ray scattering (SAXS). The neat SBS membrane exhibited a CO_2 permeability of 372 Barrer (1 Barrer = 10^{-10} cm^3(STP)·cm/(cm^2·s·cmHg) and CO_2/N_2 selectivity of 16.4; these values increased to 407 Barrer and 21.6, respectively, for the SBS-*g*-POEM membrane due to the high CO_2 affinity of the polar POEM side chains. Upon incorporation of EMIMDCA, the CO_2 permeability increased to 514 Barrer without a large sacrifice of the selectivity. In contrast, the blend of neat SBS and EMIMDCA did not show any gas separation ability due to the inhomogeneity and poor mechanical properties, indicating the importance of grafting POEM to the SBS main chains.

1. Introduction

Recently, global warming has gained recognition as a serious issue. Global warming is attributed to a large increase in CO_2 emis-

Abbreviations: EMIMDCA, 1-ethyl-3-methylimidazolium dicyanamide; COFs, covalent organic frameworks; IL, ionic liquid; MOF, metal-organic framework; PEO, poly(ethylene oxide); SBS-*g*-POEM, poly(styrene-*block*-butadiene-*block*-styrene)-*graft*-poly(oxyethylene methacrylate).

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sion; thus, CO_2 emission is regulated at the national level. Fuel combustion for generating energy and heat has led to a gradual increase in annual global CO_2 emission levels [1]. In order to address this problem, various efforts have been made to develop new and economical technologies for carbon capture and storage, such as adsorption [2–4] and absorption [5,6]. Membrane technology has gained recognition due to various advantages such as easy manufacture, low energy consumption, low operating costs, environmental safety, and facile application of functionalized nanomaterials such as metal-organic frameworks (MOFs) [7–16]. Due to these advantages, membrane technology has become a vital part of CO_2 separation and capture. Although membrane technology has evolved in various directions in recent decades, there are still drawbacks that need to be addressed, such as the low permeability, selectivity, and weak mechanical strength of existing membranes. Generally, the permeability and selectivity of conventional polymer membranes have a trade-off relationship, i.e., membranes with higher permeability typically show lower selectivity and vice versa [17]. Thus, it is very important to improve both the membrane permeability and selectivity simultaneously.

Extensive research has been conducted on polymers containing ether groups, such as poly(ethylene oxide) (PEO), that undergo Lewis acid-base interactions, where the oxygen atoms of the ether group act as the Lewis base and CO_2 acts as the Lewis acid [18,19]. Due to the specific affinity and selective interactions with CO_2, PEO-based membranes generally exhibit good CO_2 permeability and high selectivity. However, unmodified, neat PEO membranes have limited applicability as gas separation membranes due to the difficulty in controlling their high crystallinity. Poly(oxyethylene methacrylate) (POEM) is an amorphous PEO with limited applications in membranes due to its poor, liquid-like mechanical properties. To address these issues, nanostructural block copolymers based on poly(amide-*b*-ethylene oxide), well known as Pebax, have been intensively used as gas separation membranes [20–24]. However, the synthesis of Pebax is highly sensitive to impurities such as H_2O and O_2 and requires expertise with accompanying high costs.

An ionic liquid (IL) is a salt in the liquid state, the melting point of which is below 100 °C, and it typically consists of an organic cation and an inorganic or organic anion. ILs have unique physicochemical properties such as high affinity/solubility for CO_2 and low volatility, and the structure may be modified to change the properties. These features provide new opportunities for the application of ILs in CO_2 separation membranes, where membrane separation is a more energy-saving and environmentally friendly process than other separation technologies. There has been growing interest in the use of ILs for polymer-based gas separation membranes because the addition of ILs can lead to an increase in the flexibility of the polymer and the affinity for CO_2 [25–29]. Klähn et al. reported that ILs undergo slight ion displacement for equal cation-anion radial distribution and it is possible to achieve CO_2 insertion into the unoccupied space in the IL [30]. It has also been suggested that the solubility of CO_2 in ILs is proportional to the unoccupied space, i.e., the free volume of the ILs [30]. Due to these unique properties, ILs can show enhanced CO_2 permeability without deteriorating the selectivity.

Poly(styrene-*block*-butadiene-*block*-styrene) (SBS) block copolymer is a thermoplastic elastomer that is relatively cheap and has the unique properties of plastic and rubber simultaneously. Due to these important properties, SBS has been widely used in industry and daily life as a plastic modifying agent, an asphalt modifying agent, and in adhesives. The well-defined nanostructural morphology of the SBS block copolymer is of scientific interest for various applications such as proton exchange membranes for proton transport in fuel cells [31], as polymer electrolytes to deliver ions in solid-state supercapacitors [32], and as structure-directing agents to prepare well-organized metal oxide films for dye-sensitized solar cells [33]. However, the use of the SBS block copolymer for CO_2 separation membranes has not been intensively investigated due to the low selectivity of such membranes despite their good permeability [34]. Thus, it is proposed that the grafting of amorphous POEM chains to the SBS block copolymer could lead to improved CO_2 separation performance without deteriorating the mechanical properties of the membranes, which is the motivation of this study.

In this paper, we report an efficient hybrid membrane based on the poly(styrene-*block*-butadiene-*block*-styrene)-*graft*-poly (oxyethylene methacrylate) (SBS-*g*-POEM) nanostructural copolymer, synthesized via low-cost, free radical polymerization for CO_2 capture. SBS-*g*-POEM is combined with the IL 1-ethyl-3-methylimidazolium dicyanamide (EMIMDCA) to investigate the effect of the IL on the structure and permeation properties. The morphology and structure of the materials were characterized using Fourier transform infrared spectroscopy (FT–IR), thermogravimetric analysis (TGA), wide-angle X-ray scattering (WAXS), small angle X-ray scattering (SAXS), and transmission electron microscopy (TEM), and a universal testing machine (UTM). The gas separation performance of the membranes was measured at 35 °C via the time-lag and continuous-flow techniques.

2. Experimental

2.1. Materials

Poly(styrene-*block*-butadiene-*block*-styrene) (SBS, styrene 30 wt%, M_w = 140,000 g·mol^{-1}), poly(oxyethylene methacrylate) (POEM, M_n = 500 g·mol^{-1}), dicumyl peroxide (DCP, 98%) and 1-ethyl-3-methylimidazolium dicyanamide (EMIMDCA) were purchased from Sigma Aldrich. Toluene, tetrahydrofuran (THF), and methanol (MeOH) were purchased from J.T. Baker. All of the chemicals were used as received without further purification.

2.2. Synthesis of SBS-g-POEM nanostructural copolymer

First, 8 g of SBS was dissolved in 100 ml of toluene in a 250 mL rounded-bottom flask and allowed to stand for 2 h at room temperature. A 24 mL aliquot of POEM (the ratio of SBS to POEM was set to 1:3) and 0.6 g of DCP were then added to the flask with vigorous stirring. For homogenization, the mixture was further stirred for 2 h and purged with N_2 gas for 1 h. The flask was transferred to a thermal reactor where the polymerization proceeded at 100 °C for 15 h. After the polymerization process, the resultant polymer solution was poured into a large amount of MeOH. The precipitate was dissolved in THF again and then slowly precipitated in a large amount of MeOH. The product was washed with MeOH several times to eliminate unreacted residuals. The obtained SBS-*g*-POEM nanostructural copolymer was completely dried in a vacuum oven at 50 °C overnight.

2.3. Preparation of hybrid membranes

First, 0.3 g SBS-*g*-POEM (or neat SBS) was dissolved in 5 mL of THF in separate vials. Varying amounts of the IL, i.e., EMIMDCA (5%, 10%, 15%, and 20% wt% with respect to SBS-*g*-POEM) were added to each solution. The mixture was vigorously stirred for 6 h for homogenization. The solution was then poured into a glass dish (5 cm in diameter) and slowly dried at 50 °C in a drying oven for 15 h. After evaporation of the solvent, the membrane was detached from the glass dish and transferred to a vacuum oven at 50 °C and kept for two days to completely eliminate the residual