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Random and block copolymer membranes based on flexible etheric-aliphatic soft segments designed for CO_2/CH_4 separation

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ABSTRACT

Air pollution gradually aggravated, which accelerates the demand of clean energy (in particular clean natural gas) because of its abundant storage worldwide. However, raw natural gas commonly contains impurity gases, such as CO_2 and N_2, which reduce the heat of its combustion. Here, we reported new polyamide-poly(propylefne glycol) (PA-PPG) random and block copolymer materials with excellent CO_2/CH_4 separation performance. These copolymers were characterised by Fourier-transform infrared spectroscopy (FTIR), nuclear magnetic resonance spectroscopy (^{1}H NMR), UV–vis absorption spectrum and X-ray diffraction (XRD). The gas permeation properties of these copolymers were investigated by using five single gases (CO_2, H_2, O_2, CH_4 and N_2) at different temperatures (298–328 K) and a feed pressure of 76 cmHg. The effects of chemical structure, PPG content and operating temperature on the gas permeation properties of these copolymers were also further discussed. Results showed that PA-PPG random copolymer membranes exhibited better gas permeation properties than those of PA-PPG block copolymer membranes. PA-PPG random copolymer membrane with 20 wt% PPG exhibited the highest selectivity ($CO_2/CH_4 = 37.31$ and $H_2/CH_4 = 33.44$) at 298 K and 76 cmHg. The CO_2 and H_2 permeability values were 5.97 Barrer and 5.19 Barrer, respectively.

1. Introduction

Natural gas has attracted extensive attention because of its lower carbon footprint than those of other fossil energies, such as gasoline or coal (Luo et al., 2017). In the past decades, the demand for the use of natural gas has steadily increased, and it will further increase in the future (Heck et al., 2017). The raw natural gas composition varies largely, depending on its origin. Currently, raw natural gas contains not only a large amount of methane but also a considerable amount of CO_2 impurity in China, which does not satisfy the pipeline requirement and simultaneously corrodes the natural gas pipeline (Amedi and Aghajani, 2016). To improve energy value, meet the requirements for pipelines, and protect natural gas pipeline (Tena et al., 2013; Azizi et al., 2017), most of raw natural gas requires methane enrichment, the process of separating CO_2 from methane (Jomekian et al., 2016).

Currently, CO_2 separation technologies mainly include pressure swing adsorption, cryogenic distillation and membrane separation (Alkhouzaam et al., 2016). Among these technologies, polymeric membrane separation technology has attracted significant attention due to its inherent advantages, such as low operating cost, high energy efficiency, easy operating process and small footprint (Gin and Noble, 2011; Paul, 2012; Fu et al., 2016; Zhao et al., 2014; Qiu et al., 2016; Mahdavi et al., 2017). In the last decades, polymeric membranes have been widely studied with regard to CO_2 separation from raw natural gas. When CO_2-philic materials are used as CO_2 gas separation membranes, their CO_2 permeability values are higher than those of other gases, although their molecular kinetic diameters are smaller (Dai et al., 2017; Liu et al., 2013; Quan et al., 2015a). In recent years, polymeric membranes containing flexible etheric–aliphatic soft segments are considered ideal CO_2-philic membranes because of their excellent CO_2 separation performances (Quan et al., 2015b; Lee et al., 2016).

Poly(ethylene glycol) (PEG) and poly(propylene glycol) (PPG) are considered ideal CO_2-philic rubbery materials due to the inherent attraction between the polar ether groups and the CO_2 molecules (Khosravi and Omidkhah, 2015; Jung et al., 2017; Lin and Freeman, 2004, 2005; Li et al., 2017). Nevertheless, PEG, a semi-crystalline material at room temperature, prevents gas molecules through the PEG-based membranes (Dai et al., 2017; Jiang et al., 2017; Luo et al., 2016). Therefore, PPG is selected an ideal CO_2-philic membrane material because of its amorphous structure at room temperature (Li et al., 2011), but many challenges are limiting its further industrial application. Firstly, PPG-based membranes possess relatively poor mechanical properties, which result in some problems in the process of membrane production and fabrication. Secondly, PPG-based membranes suffer

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from serious plasticisation at high CO_2 feed pressures, which deteriorates the selectivity of CO_2/light gases.

To overcome these challenges, various effective and practical strategies, mainly including preparations of PPG-based copolymer membranes (Jung et al., 2017), PPG-based blend membranes (Khosravi and Omidkhah, 2015) and PPG-based cross-linked membranes (Dastgir et al., 2005; Barillas et al., 2011), have been investigated. Among these strategies, covalently cross-linked PPG membrane presents a promising strategy to improve gas separation efficiency. Nonetheless, PPG membranes, even at high cross-linked degrees, are still confronted with problems on thermal and mechanical stabilities, which limit their industrial application. Therefore, the use of PPG-based copolymer membranes by copolymerising PPG with glassy polymers is considered an ideal strategy to improve gas separation and membrane performance. The copolymer hard segment provides mechanical strength and thermal stability and hinders CO_2 plasticisation at high CO_2 feed pressure (Vaughn et al., 2012); CO_2 permeation occurs preferentially through the PPG soft segment of the copolymer because of the inherent attraction between the polar ether groups and the CO_2 molecules (Ahmadpour et al., 2014). Luo et al. (2016) prepared a series of polyimide-poly(ethylene oxide) (PI-PEO) block copolymer membranes by combining glassy PI blocks with rubbery PEO blocks. The effects of the molecular weight of PEO and the weight content of PEO on CO_2 separation performance were discussed. Results showed that PEO with molecular weight of 2000 $g{\cdot}mol^{-1}$ and 60% of PEO content in PI-PEO block copolymer membranes exhibits the highest CO_2 permeability (39 Barrer) and selectivity of CO_2/light gases ($CO_2/H_2 = 4.1$, $CO_2/N_2 = 46$ and $CO_2/CH_4 = 20$).

In the present study, polyamide-poly(propylene glycol) (PA-PPG) random and block copolymers were designed by the polycondensation reaction of 4,4′-oxybis(benzoic acid) (OBA) and the corresponding amounts of PPG and 4,4′-(9-fluorenylidene)dianiline (9FDA). The aromatic OBA and 9FDA hard segments provide these copolymers with mechanical strength and thermal stabilities, and CO_2-philic PPG soft segments are beneficial to pass through CO_2 molecules. The weight content of PPG was systematically adjusted in these copolymer membranes. We mainly discussed the effects of PPG content, chemical structure and operating temperature on the performance of CO_2 separation.

2. Experimental

2.1. Materials

All chemicals and reagents were used without further purification. 4,4′-oxybis(benzoic acid) (OBA, 98%) were purchased from Meryer Chemical Technology Co., Ltd., China. Poly(propylene glycol) bis(2-aminopropyl ether) (PPG) with molecule weights of 2000 $g{\cdot}mol^{-1}$ was obtained from Aladdin (China). 4,4′-(9-fluorenylidene)dianiline (9FDA) was synthesised according to the reported procedure (Zhu et al., 2017; Biolley et al., 1991). Toluene, tetrahydrofuran (THF), N, N-dimethylformamide (DMF), N, N-dimethylacetamide (DMAc), chloroform ($CHCl_3$), 1-methyl-2-pyrrolidinone (NMP), dimethyl sulfoxide (DMSO) and methanol were supplied by Tianjin Reagent Co., Ltd., China. Triphenyl phosphite (TPP, 99%), pyridine (Py, 99%) and calcium chloride were purchased from Sinopharm Chemical Reagent Co., Ltd., China. Cylinders of single gas CO_2, O_2, H_2, CH_4 and N_2 (99.9%) were purchased from Gas Production Plant, Taiyuan, China. The more detailed list of all used materials is listed in Table 1.

2.2. Synthesis of PA-PPG random copolymers

As shown in Scheme 1, PA-PPG random copolymers containing flexible etheric–aliphatic soft segments were synthesised via the polycondensation reaction among 9FDA, PPG and OBA. The PA-PPG random copolymers were named as RPA-PPG (x%), where x represents the weight content of PPG. For instance, RPA-PPG (10%) random copolymer contains 10% of PPG by weight. The synthesis of a copolymer with 20 wt% of PPG is provided as an example as follows: a mixture of OBA (0.294 g, 1.14 mmol), 9FDA (0.362 g, 1.04 mmol), PPG (0.200 g, 0.10 mmol), Py (1.4 mL), TPP (1.4 mL, 5.34 mmol), NMP (5 mL) and calcium chloride (0.36 g) was transferred into a 100 mL round-bottom flask equipped with a reflux condenser and a nitrogen inlet. The reaction mixture was heated at 383 K for 48 h with continuous stirring. Afterwards, the mixture was poured gradually into 100 mL of methanol to obtain crude products. The crude products were filtered and washed several times with methanol and subsequently with hot and cold deionised water to remove the adsorbed solvent and residual $CaCl_2$. The final products were dried in a vacuum oven at 338 K for 24 h. The obtained yield was 94.6%. A series of PA-PPG random copolymers was synthesised following the same procedure. The yields of the prepared PA-PPG random copolymers are presented in Table 2.

2.3. Synthesis of PA-PPG block copolymers

As illustrated in Scheme 2, all PA-PPG block copolymers based on flexible etheric–aliphatic soft segments were polymerised by the polycondensation reaction of OBA, 9FDA and PPG. The PA-PPG block copolymers were named as BPA-PPG (y%), where y represents the weight content of PPG. For example, BPA-PPG (10%) block copolymer contains 10% PPG by weight. A typical procedure for the synthesis of BPA-PPG (20%) is as follows: OBA (0.294 g, 1.14 mmol), 9FDA (0.362 g, 1.04 mmol), Py (1.4 mL), TPP (1.4 mL, 5.34 mmol), NMP (4 mL) and $CaCl_2$ (0.36 g) were dissolved in a 100 mL round-bottom flask equipped with a reflux condenser and a nitrogen inlet. After the reaction was carried out at 383 K for 24 h, PPG (0.200 g, 0.10 mmol) and NMP (2 mL) were added into the round-bottom flask. The reaction mixture continued to react at 383 K for 48 h, and it was poured gradually into 100 mL of methanol to obtain crude products. Subsequently, the crude products were filtered and washed several times with methanol and deionised water (hot and cold). The resultant products were dried at 338 K under vacuum for 24 h. The obtained yield was 93.8%. A series of PA-PPG block copolymers was synthesised following the same procedure. The yields of the prepared PA-PPG block copolymers are listed in Table 2.

2.4. Preparation of PA-PPG random and block copolymer dense membranes

The homogeneous solutions of PA-PPG random and block copolymers were prepared by dissolving the polymers in NMP solutions (8% [w/v]). Afterwards, the homogeneous solutions were filtered using a 20–30 μm syringe filter to remove any undissolved material and dust particle. Polymer solutions were treated by ultrasound and left untouched for 12 h to remove gas bubbles. The dense membranes were fabricated by casting the solutions onto a clean and levelled glass plate by using a doctor blade. The polymers on the plate were dried at 353 K for 12 h and placed in a vacuum oven at 393 K for 12 h to remove the residual solvent. The dense membranes were peeled off from the glass plate with the thickness of approximately 35 μm. The photographs of the PA-PPG random and block copolymer dense membranes are shown in Fig. 1.

2.5. Characterisation

FTIR measurements were recorded on a Bruker TENSOR II FTIR spectrometer (Germany) in the range of 4000–400 cm^{-1}.^1H NMR spectra were performed on a 400 MHz Bruker AVANCE IIITM NMR spectrometer (Germany) using DMSO-d_6 as the solvent at room temperature. The solubility of each polymer was tested by dissolving 20 mg of polymer in 1 mL of different solvents, followed by continuous stirring for 24 h at 298 K. Then, the solubility of each polymer was determined by visual observation (observing state of polymer powder and

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