RSC Advances

PAPER

Cite this: *RSC Adv.*, 2016, **6**, 35751

Synthesis, characterization and gas separation properties of novel copolyimide membranes based on flexible etheric–aliphatic moieties

Milad Khoshkam,[a] Morteza Sadeghi,*[b] Mahdi Pourafshari Chenar,[a] Mahdi Naghsh,[b] Mohammad J. Namazi fard[b] and Mohammadreza Shafiei[c]

Received 24th February 2016
Accepted 4th April 2016

DOI: 10.1039/c6ra04973g

www.rsc.org/advances

The structural properties and gas permeation of a group of copolyimide membranes were investigated. The copolyimides used in this study were prepared using 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA) and 4,4′-oxydianyline (ODA) as aromatic diaminens and 4,9-dioxa-1,12-dodecanediamine (DODD), 1,13-diamino-4,7,10-trioxatridecane (TODD) and 1,8-diamino-3,6-dioxaoctane (DOO) as aliphatic diamines. Polymers were synthesized using random and block copolymerization methods *via* thermal imidization in a two step procedure. Reflectance-Fourier transform infrared spectroscopy (ATR-FTIR), dynamic mechanical thermal analysis (DMTA), thermal gravimetric analysis (TGA) and X-ray diffraction analysis (XRD) have been performed to characterize the synthesized copolyimides. The copolyimide with BTDA–ODA diamines showed higher T_g compared to the other polymers due to its fully aromatic structure. Gas permeation results reveal that the type of aliphatic diamines and polymer morphology can greatly affect the permeability of membranes for pure CO_2, CH_4, O_2 and N_2 gases. The gas permeability and selectivity of random copolyimides were higher than those of block copolyimides. The effects of temperature and feed pressure were also investigated. The permeability of all gases decreases slightly with increasing pressure. The results revealed that an increase in the temperature of the polymer matrix is able to increase the diffusivity and permeability of the membrane.

1. Introduction

Membranes offer an attractive alternative to cryogenic or pressure swing adsorption processes for gas separation applications.[1–3] Polymeric gas separation membranes are used in a wide variety of areas such as air separation, separation of carbon dioxide from natural gas and removal of hydrogen from mixtures with hydrocarbons in petrochemical processing.[4,5]

Some glassy polymers such as polyimides, polysulfones, polycarbonates and cellulose acetates and some rubbery polymers such as polyurethanes and polydimethylsiloxanes are introduced as proper polymers in manufacturing of gas separation membranes. Satisfactory results have been obtained in gas separation properties particularly for polyimides and polyurethane in glassy and rubbery polymers.[6–9] The improvement of the gas separation property of the polymeric membrane is the target of most research in this area.[10,11] Polymeric membranes with high permeability and high selectivity are desired for gas separation, but most materials known for this application follow trade off relation between permeability and selectivity.[12,13] Changing the chemical structure of polymer is the most common way to increase the membrane permeability without reduction in selectivity.[14–16]

A lot of researches have been carried out to find the relationship between the chemical structure and gas separation properties of polyimides.[17–24] Polyimide membranes are synthesized using various diamines and dianhydrides in order to achieve better gas separation properties. These properties are directly related to the structure of polyimides, including the fractional free volume and inter chain distances that is affected by crystallinity of the polymer.[25–30]

Up to now, many polyimide structures have been synthesized, however few of them are commercialized.[31,32] One of the famous commercial polyimide membrane is matrimid 5218 with permeabilities of about 2 and 4 barrer for O_2 and CO_2 gases, respectively.[33,34]

Copolyimide structures can provide particular membranes by combining two monomers with different properties that cannot be achieved by homopolyimides.[35–40] Copolyimide structures are mostly synthesized using aromatic diamines but there are a few researches were reported on copolyimides with aliphatic diamines.

Tena *et al.* studied a set of copoly(ether-imide)s, synthesized by the reaction between an aromatic dianhydride (BPDA),

[a]*Chemical Engineering Department, Faculty of Engineering, Ferdowsi University of Mashhad, Mashhad, 91775-1111, Iran*

[b]*Department of Chemical Engineering, Isfahan University of Technology, Isfahan 84156-83111, Iran. E-mail: m-sadeghi@cc.iut.ac.ir; Fax: +98 31 33912677; Tel: +98 31 33915645*

[c]*McKetta Department of Chemical Engineering, University of Texas at Austin, TX, USA*