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Asymmetric hollow fibre membranes based on ring-substituted polyaniline and investigation towards its gas transport properties

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ABSTRACT

A more soluble polyaniline derivative, i.e. poly(*o*-anisidine), (POAn), was synthesized in-house for this study by using an ortho substituted aniline monomer. It was observed that the prepared dope solution was more homogeneous with less visible agglomerates as compared to previously prepared polyaniline (PAni) solution. Integrally skinned hollow fibre membranes were successfully prepared by dry-jet wet spinning from POAn with N-methyl-2-pyrrolidone as a solvent and a more volatile tetrahydrofuran as a co-solvent for gas separation. The spinning air-gap lengths were varied to promote the formation of the membrane skin layer. POAn membranes prepared at higher air gap were more orientated with packed structure and good gas separation characteristics. They showed selectivities of O_2/N_2, CO_2/N_2, H_2/N_2 and H_2/CO_2 of about 13, 89, 370 and 4.2, respectively with permeation rates of H_2, CO_2 and O_2 about 10.4, 2.5 and 0.37×10^{-6} cm^3 (STP)/cm^2 s cmHg, respectively. Presence of methoxy group in POAn showed substantial enhancement in gas permeation properties compared to previously developed PAni membranes. The H_2/N_2 and CO_2/N_2 selectivities were improved by 3 and 7 times, respectively as compared to PAni membranes. Development of hollow fibre membranes using polyaniline derivative with improved processability and excellent gas separation performance depicts their potential for industrial gas separation applications.

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1. Introduction

Membrane based gas separation processes have had considerable interest for years due to its inherent advantages over traditional methods (cryogenic distillation, adsorbent bed processes and adsorption processes, such as pressure swing adsorption and thermal swing adsorption). Current studies projected that the combined sales of membrane products in the U.S market for gas separation, pervaporation and other novel related processes was $180 million. This was forecast to increase at a compound annual growth rate (CAGR) of 6.6% to $247 million by 2015 [1]. This huge market has definitely intensified the interest in finding new materials that are suitable for producing synthetic membrane that can cater for the gas separation related industries. An important concern in membrane gas separations is to produce a membrane process that is economically feasible while maintaining a high permeability and selectivity. For an asymmetric membrane useful for gas separation, its skin layer must be almost defect free to assure that permeation is exclusively controlled by a solution-diffusion mechanism to achieve the maximum permselectivity, and its skin layer must be as thin as possible to maximize the membrane productivity. In addition to produce defect-free membrane [2,3], a simpler and more practical approach of sealing the hollow fibres surface defects with silicone rubber coating is also widely practiced [4]. There are various factors that govern the formation of gas selective hollow fibre membranes such as dope formulation, fibre spinning parameters like polymer extrusion rate, fibre take up rate, air gap distance, coagulation rate. Significant progresses have been made in membrane materials [5,6], dope formulation [7,8], hollow fibre fabrication [2,3,7,8], and fundamental understanding of membrane formation [5,9,10]. Kesting et al. reported that 17% polysulfone (PS) was needed to fabricate an ultrafiltration hollow fibre, while 37% PS was required to produce an air-separation fibre [11]. Similar results were also reported in Dow's patent where they fabricated tetrabromobisphenol-A polycarbonate hollow fibre with different concentrations [12]. Fibres spun with low dope concentration gave poor O_2/N_2 selectivities than those spun from high concentration dopes. Chung et al. [7] hypothesized that one of the requirements to obtain an air-separation hollow fibre with minimum defects is to ensure the dope solution to be prepared with concentration exhibiting significant chain entanglement. Besides the concentration and spinning parameters other factors such as

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