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Gas permeation and sorption properties of non-ionic and cationic amino-hydroxy functionalized poly(dimethylsiloxane) membranes

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Abstract

In order to improve the permselectivity of poly(dimethylsiloxane) (PDMS) membrane without much reduction in permeability value, a new type of poly(dimethylsiloxane) membranes containing different concentrations of non-ionic and cationic amino-hydroxy functionalities has been prepared. IR, ^{1}H NMR and ^{13}C NMR, GPC, DSC, TGA and WAXD techniques were used to characterize the prepared membranes. The gas transport properties, viz., permeability, solubility and diffusivity of the prepared membranes were determined for N_2, O_2, CH_4 and CO_2 gases. The fractional free volume present in the PDMS membrane was found to decrease with increasing amino-hydroxy functionality. The permselectivity values for O_2/N_2 and CO_2/CH_4 gas pairs were found to increase with increasing concentrations of amino-hydroxy functionalized siloxane. The effect of temperature on gas permeabilities was studied and activation energy was determined for the studied gases.

Keywords: Gas separation; Poly(dimethylsiloxane); Functionalized membrane

1. Introduction

In the past two decades, gas separation through membrane technology has settled down at several industrial processes and applications [1–3]. The development of new membrane materials with both high permeability and high selectivity could play a significant role in the future success of gas separations [4,5]. Modification of the chemical structure of a polymer chain often leads to the improvement in permeability coefficient at the cost of selectivity [1,4,5] and vice-versa. The permeation of gas molecule through a polymeric membrane largely depends on the nature of the gas molecule and its interaction with polymer in question. The molecular structure related factors such as polarity, hydrogen bonding, cohesive energy density, chain flexibility, steric hindrance, side group substitution and crystallinity affects the permeation process in some manner [1,6]. Attempts were made by many scientists to modify the chain stiffness, packing density and fractional free volume to obtain material with optimized transport properties by the incorporation of rigid and bulky groups into the polymer chain [7–9]. Koros et al. [8] and Stern et al. [9] observed that introduction of polar functional groups and bulky groups have greater effect on the gas transport properties of the polymers.

Poly(dimethylsiloxane) (PDMS) membranes were known to have considerable commercial applications in the field of gas separations for a long time due to its more permeable nature because of high chain flexibility [10]. The high permeability of siloxane membrane combined with inherent thermal stability, hydrophobicity and flexibility, conferred by the Si–O–Si backbone, makes them more suitable for various commercial applications such as oxygen enrichment from air, artificial lungs, polymer electrolyte, metal catalyst support, catalyst, organometallic species, etc. [11]. The limitations with PDMS membrane are their poor permselectivity for gases and mechanical strength. One way of improving the separation characteristic of a membrane is to incorporate different functional groups into the polymer matrix. Recently, there has been increased attention in the modification of basic PDMS framework with different functional groups like amide, imide, phenyl, ester, urethane, etc., in order to extend the chemistry and application of this unique material [12–16]. The scope of this research work is to improve the permselec-

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tivity of PDMS membrane without drastically affecting its permeability coefficient for various gases through the structural modification by incorporating bulky functional groups. This article deals with the preparation of different concentrations of non-ionic and cationic amino-hydroxy functionalized PDMS membranes and examine its effect on the transport properties, viz., Permeability, solubility and diffusivity, for N_2, O_2, CH_4 and CO_2 gases. Only very few studies about amine functionalized PDMS membrane was available in the literature. It is also expected that this work will help to determine the role of functional groups during gas transport through the membrane and get a better understanding of the transport mechanism.

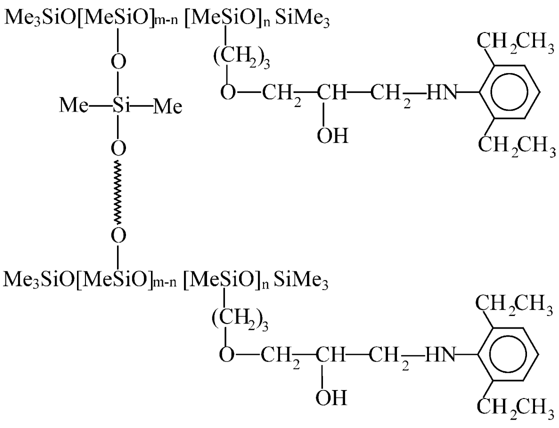
2. Experimental section

2.1. Materials

Allyl-2,3-epoxypropylether (Merck) was used as received. 2,6-Diethylaniline (Fluka) was used after distilling under reduced pressure. Linear poly(methyl hydrogen siloxane), $Me_3SiO[MeSi(H)O]_xSiMe_3$ having a molecular weight of 1900 was purchased from Lancaster and stored in a sealed container in the absence of moisture or oxygen. Hydroxy terminated poly(dimethylsiloxane) having a molecular weight of 6100 was purchased from Aldrich and used as such. Toluene was purified by distilling at 110 °C and finally dried over Na wire.

2.2. Preparation of amino-hydroxy functionalized poly(dimethylsiloxane) membrane

A three-step procedure reported in our previous work [17] was employed for the synthesis of five different concentrations of non-ionic and cationic amino-hydroxy functionalized PDMS membrane. However, only a brief description about the preparation of 2,6-diethylphenyl amino-hydroxy functionalized PDMS was provided here.



2,6-diethylphenyl amino-hydroxy functionalized PDMS

crosslinked with OH-terminated PDMS

2.3. Preparation of 2,6-diethylphenyl amino-hydroxy functionalized PDMS

Into a 250 ml three-necked round bottom flask, equipped with a reflux condenser and a nitrogen inlet, 18.63 g (5 M excess) of 2,6-diethylaniline dissolved in 50 ml of toluene was taken. 4.75 g (1 mmol) of the prepared epoxy functionalized siloxane [17] was slowly added into the content of the flask at 70 °C. After the addition was over, the contents in the flask were refluxed at 120 °C under nitrogen atmosphere for 7 h. The amino-hydroxy functionalized siloxane was obtained as a brownish yellow gum material by removing solvent and excess amine under vacuum at 90 °C. The product obtained was purified from the un-reacted compounds by dissolving it using minimum quantity of toluene and re-precipitated by pouring the solution over a beaker containing ethyl methyl ketone.

2.4. Gas permeation measurements

The permeability of the prepared non-ionic and cationic membranes for single gases such as O_2, N_2, CH_4 and CO_2 are measured using constant pressure/variable volume method [18,19] following the experimental procedure reported in our previous work [17].

2.5. Gas sorption measurements

The equilibrium uptake of N_2, O_2, CH_4 and CO_2 gases in non-ionic and cationic amino-hydroxy functionalized siloxanes were determined using barometric method with a dual volume and dual transducer apparatus [20].

2.6. Characterization

IR spectrum was recorded using Perkin-Elmer 20 DXB FT-IR spectrophotometer and the solid sample, which is grinded with potassium bromide and pressed into a transparent disk, is directly placed in the infrared beam. Both ^{1}H and ^{13}C NMR spectra were recorded using 15–20 wt.% of polysiloxanes in $CDCl_3$ solution on JEOL 300 MHz NMR instrument. ^{13}C measurements were made at 67.8 MHz and the chemical shifts were referenced to $CDCl_3$ (77 ppm). Weight average molecular weights (M_w) were determined by Waters 510 gel-permeation chromatography using polystyrene standards and tetrahydrofuran as eluant. The glass transition temperature (T_g) was determined using DSC-7 Perkin-Elmer analyzer at a heating rate of 5 °C/min under nitrogen atmosphere. The thermogravimetric analysis (TGA) was carried out on Mettler TA 3000 thermal analyzer and the thermograms were recorded at a heating rate of 10 °C/min in nitrogen atmosphere. Wide-angle X-ray diffraction (WAXD) spectra were recorded using Philips model APD-3720 X-ray diffraction instrument. The X-rays were produced by Cu-Kα source. The voltage and current settings