Study of Effect of pressure and temperature on the gas separation properties of a novel copolyimide membrane with flexible moieties

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Abstract

In this research a novel copolyimide was synthesized with aliphatic diamine, which composed of 3,3□4,4□-Benzophenonetetracarboxylic dianhydride (BTDA), 4,4□-Oxydianyline (ODA) and 4,9-dioxa-1,12-dodecacanediamine monomers. Synthesis was performed by thermal imidization in a two-pot procedure that carried out by unique block copolymerization method. The physical properties of the copolyimide were characterized by FT-IR and XRD. The permeability properties of O_2, N_2, CH_4, and CO_2 gases of synthesized copolyimide at different pressures and temperatures has been evaluated. The permeability coefficients of O_2, N_2, CH_4, and CO_2 decrease slightly with increasing pressure but for CO_2 was more intense. The percentages of permeability decay increase exactly in the order of CO_2 (3.30 Å), O_2 (3.46 Å), N_2 (3.64 Å), and CH_4 (3.80 Å). Increasing temperature promoted permeability and diffusion coefficients which demonstrated reverse behavior with increasing pressure. Also, selectivity was observed to show the same trend for temperature as pressure effect. Compared with fully aromatic BTDA-ODA structure, the gas permeability and diffusion coefficients increased with adding aliphatic diamine because of flexible moieties in this monomer; however, the permselectivity of gas pairs such as O_2/N_2, CO_2/CH_4 and CO_2/N_2 was slightly decreased.

Keyword: Polyimide, aliphatic diamine, gas separation membrane, permeability, selectivity

Introduction

In the past decades membranes have been widely used in gas separation because this technique has advantages over traditional separation processes. Much of the membrane research work is being devoted to the proposal of new membrane materials and the development of new membrane structures that exhibit both a higher selectivity and intrinsic permeability to specific gases. Polyimides have been found to have high intrinsic gas permeability as well as a high permselectivity in comparison to polycarbonate, polysulfone and other polymeric materials [1]. It is well known that the performance of polyimide membranes in separation applications relies on the chemical structure of the polyimide, the fractional free volume (FFV) and crystallinity degree of the polyimide, and the membrane structure [2-5].

Experimental

1. Material
The dianhydride monomer used in this study was 3, 3□ , 4, 4□-Benzophenonetetracarboxylic dianhydride (BTDA) which purchased from Sigma-Aldrich. The aliphatic diamine monomer used was 4,9-dioxa-1,12-dodecacanediamine and aromatic diamine monomer used was 4,4□-Oxydianyline (ODA) which both

obtained from Merck (GERMANY) Also dimethylacetamide (DMAc) as solvent was obtained from Merck (GERMANY).

2. Polymer synthesis

For synthesis block polyimide, into a three-necked flask ODA dissolved at DMAc and then all of the anhydride added to mixture. The mixture stirred for 12 hr until reaction between anhydride and ODA entirely carried out. Aliphatic diamine was added to polyamic acid solution. Finally, Thermal imidazation carried out for convert polyamic acid to polyimide. The PAA solution casted on a glass plate and left at 80°C over night. Film was imidized by sequential heating at100, 125, 150, 175, and 200 °C for each 1 hr, respectively. Then film heated for 30 min at 220 and 250 °C.

Results and Discussion

1. FTIR spectra

The IR analysis of polyimide showed peak at around1780 cm^{-1} (attributed to C=O asymmetric stretch of imide groups), 1724 cm^{-1} (attributed to C=O symmetric stretch of imide groups), and 1396 cm^{-1} (attributed to C-N stretch of imide groups). Fig.1 shows FTIR-ATR spectra of this polymer.

2. X- ray diffraction

The analyses of X-ray diffraction in a range of 2Ө between 0° and 60° were carried out using a Rigaku model D-Max III C device, lamp of CuKa and filter of Nickel. The d-spacings (dsp) of each synthesized membrane were determined by Bragg's equation (Eq. (1)). Fig.2 show X-ray of polyimide.
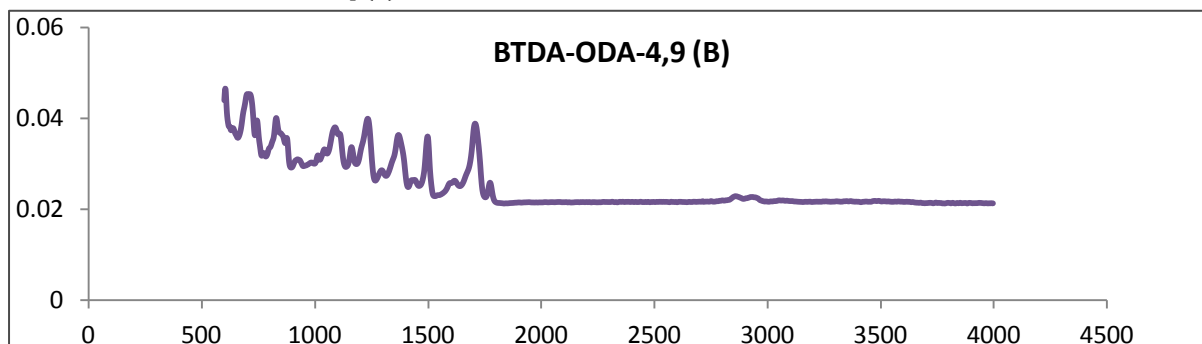
$$n\lambda = 2dsin\,Ө \qquad \text{Eq.(1)}$$

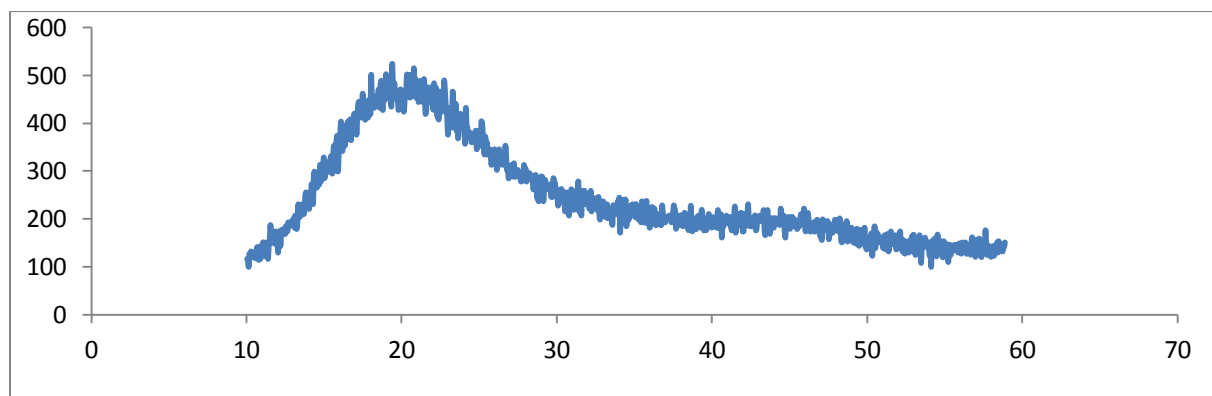**Fig.1 FTIR-ATR spectra of BTDA-ODA- 4,9 polyimide**

Fig.2 X-ray diffraction of BTDA-ODA-4,9 polyimide

3. The effect of pressure on the gas transport property

The permeabilities and diffusivities of O_2, N_2, CH_4, and CO_2 were measured as a function of upstream pressure and at 35°c and the results are reported in Table1, 2. The permeability coefficients of O_2, N_2, CH_4, and CO_2 decrease slightly with increasing pressure but for CO_2 was more intense because molecular size of CO_2 is smallest than others. Also for the reason, permselectivity of CO_2/CH_4 has more decay than O_2/N_2. This phenomena of pressure dependence on permeability is consistent with the dual-mode transport model used to describe the gas transport behavior of glassy polymers, which is represented as the sum of the Henry mode and the Langmuir mode as follows:

$$P = k_D D_D + \frac{C'_H D_H b}{(1+bp)}$$

For most glassy polymers at a low pressure environment, gas molecules are sorbed into Langmuir mode sites (intersegmental packing defects) more easily than into Henry's mode sites. The situation changes at a high-pressure environment, because the capacity of Langmuir mode sites is saturated. Thus, Henry's mode becomes predominant for further sorption. Depending on the partial immobilization theory, gas molecules sorbed into Henry's mode sites may have greater diffusivity than those into Langmuir mode sites.

4. The effect of temperature on the gas transport property

The effect of temperature on permeabilities and diffusion coefficients of O_2, N_2, CH_4, and CO_2 were investigated with an upstream pressure of 10 atm. As shown in table1, 2 the gas permeabilities and diffusivities increase with temperature. Although, permeability coefficients increase with temperature, permselectivities for gas pairs of O_2/N_2 and CO_2/CH_4 decrease due to differences in permeation activation energies for various gas pairs. In most cases, a larger penetrant exhibits greater activation energy for permeation. Thus, an increase in temperature results in a higher percentage of permeability increase for a larger penetrant than for a small penetrant, which consequently reduces the permselectivity. The CO_2/CH_4 permselectivity exhibits much higher temperature dependence than that of the O_2/N_2 pair, because the former has a much greater difference in activation energies of permeability than the latter.
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Table1. Permeability coefficients and permselectivities as a function of pressure and temperature

Pressure	temperature	permeability coefficient (barrer)[a]				permselectivity	
		O_2	N_2	CH_4	CO_2	O_2/N_2	CO_2/CH_4
10	25	0.104	0 .0176	0.009	0.418	5.9	46.44
10	35	0.11	0.024	0.0125	0.433	4.58	34.64
3	35	0.16	0.034	0.0171	0.69	4.7	40.35
5	35	0.143	0.031	0.016	0.594	4.67	37.12

[a] 1 Barrer = 1×10^{-10} cm^3(STP)cm/cm^2 s cmHg

Table2. diffusion coefficient and selectivity as a function of pressure and temperature

Pressure	temperature	diffusion coefficient					selectivity	
		O_2	N_2	CH_4	CO_2		O_2/N_2	CO_2/CH_4
10	25	29.31	6.066	2.082	12.55		4.88	6.02
10	35	47.87	12.76	4.51	24.65		3.46	5.35
3	35	21.764	6.395	2.035	14.71		3.4	7.22
5	35	29.9	7.517	2.66	15.36		3.97	5.77

5. The effect of adding aliphatic diamine on the gas transport property

In this work also compared this copolyimide membrane with fully aromatic BTDA-ODA structure, the gas permeability and diffusion coefficients increased with adding aliphatic diamine because of flexible moieties in this monomer that caused packaging reduced and fraction free volume (FFV) increased thus permeability of these gases enhanced; however, the permselectivity of gas pairs such as O_2/N_2, CO_2/CH_4 and CO_2/N_2 was slightly decreased. Also the results show an adequate correlation between the permeation coefficients $P_{CO2} > P_{O2} > P_{N2} > P_{CH4}$ and their kinetic diameters $\sigma_{kCO2} < \sigma_{kO2} < \sigma_{kN2} < \sigma_{kCH4}$.

Conclusion

The intrinsic gas separation performance of membrane has been investigated. It is found that O_2, N_2, CH_4, and CO_2 permeability coefficients decrease slightly with increasing pressure. This phenomenon can be explained using the partial immobilization dual-sorption model. Since the diffusion coefficients of CO_2 and CH_4 increase, it suggests that Langmuir sorption mainly dominates the pressure-dependent gas permeation. Because the diffusivity is a stronger function of temperature, gas permeability increases with temperature. It is found that E_p increases with the molecular size of a penetrant gas in the order of CO_2, O_2, N_2, and CH_4. Also showed Compared with fully aromatic BTDA-ODA structure, the gas permeability and diffusion coefficients increased with adding aliphatic diamine because of flexible moieties in this monomer.

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