

열적 변형 유리상 고분자막의 기체분리특성

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Gas permeation properties of thermally transformed superglassy polymer membranes

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1. Introduction

The gas separation performances of polymer membranes have been continuously improved since 1980s and many researches to seek smart polymer with better separation properties have been still progressed. However, presently we have witnessed that a number of attempts to obtain polymer membranes suitable for further practical and economical applications seems to be failed because of limitations in their structural modification and strong trade off between permeability and selectivity shown in the semi empirical relationship of enormous data in the literature[1,2]. Therefore, we have investigated new class of polymeric gas separation membrane to overcome the unavoidable limitation of conventional polymer membranes and examined the structure-gas permeation property relationships.

Recently, it was reported that hydroxy-containing polyimide could be thermally transformed into polybenzoxazole in a solid state[3]. In general, hydroxy-containing polyimides have been regarded as potential high glass transition temperature (T_g), thermally stable polymers for photoresist and non-linear optical (NLO) applications[4]. During thermal conversion process, two moles of carbon dioxide molecules in repeating unit of polymer are

removed, which may accompany different chain conformations depending upon initial amorphous chain structure. The polybenzoxazole membranes obtained from above thermal conversion display excellent thermal stability, good solvent and chemical resistance. In most cases, natural and synthetic polymers have non-porous characteristics while the present thermally transformed polybenzoxazole membranes show some micropore characteristics similar to microporous carbons due to high fractional free volume formed during thermal rearrangement process. Here, we will discuss the gas permeation properties of polybenzoxazole membranes and their structure - gas permeation property relationships.

2. Experimental

For preparation of polybenzoxazole (PBO) membranes, we synthesized five kinds of hydroxy containing polyimides (HPIs) with conventional thermal imidization method using NMP as a solvent. The anhydrides used in this study were 4,4' - (hexafluoroisopropylidene) - diphthalic anhydride (6FDA), 4,4'- oxydiphthalic anhydride (ODPA), 3,3',4,4' - biphenyltetracarboxylic dianhydride (BPDA), pyromellitic anhydride (PMDA), benzophenone - 3,3,4,4 - tetracarboxylic dianhydride (BTDA). Bis(3 - amino - 4 - hydroxy - phenyl) hexafluoropropane (APAF) was used as a diamine in all polyimide preparation. After thermally cycled imidization, flexible hydroxy-containing polyimide films were obtained. The films were placed in the target temperature range (400°C - 500°C) in order to achieve PBO membranes. Thermally converted PBOs were characterized using a FT-IR spectroscopy, a thermo-gravimetric analysis, a X-ray diffraction pattern, a BET adsorption measurement, a density measurement. Eventually, gas permeation experiments were carried out using pure single gases such as He, H₂, O₂, N₂, and CO₂.

3. Results and Discussion

From TGA curves of PBOs, the first weight loss was observed at about 350 - 500 °C mainly due to CO₂ removal, and then the second weight loss appeared around 500 °C due to the decomposition of main chains. All PBO samples showed approximately the weight losses of 9-11%. Nitrogen adsorption and desorption isotherms were measured and the pore volume and the surface area of PBO membranes are summarized in Table 1. The nitrogen

sorption isotherm of PBO samples is Type I isotherm represented by a plateau which is nearly or quite horizontal, and which may cut the p/p^0 (relative pressure) = 1 axis sharply or may show a tail as saturation pressure is approached. In addition, there exists hysteresis over the whole ranges in desorption isotherms of all samples, indicating the retention of significant quantities of nitrogen at the end of the depressurization cycle.

Table 1. Nitrogen adsorption and desorption results of PBOs

Sample Name	Single point surface area at $P/P_0 = 0.18$ (m^2/g)	Single point total pore volume of pores less than 782.4 diameter at $P/P_0 = 0.97$ (cm^3/g)
6F-PBO	410	0.22
O-PBO	158	0.09
B-PBO	194	0.10
P-PBO	226	0.12
Et-PBO	70	0.04

Gas permeation results at 25 °C are shown in Fig 1. In the present study, the gas permeation properties of PBO membranes were investigated in terms of their structural differences. 6F-PBO shows highest gas permeability of all tested gases but the selectivity was relatively lowest as compared to other PBO samples. This might be caused by the formation of high fractional free

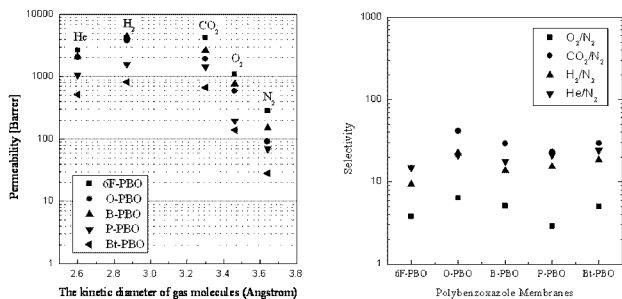


Fig 1. Gas permeabilities of various PBO membranes and their selectivities

volume due to the existence two hexafluoroisopropylidene groups and by the change of chain conformation in highly chain mobility-restricted solid state during thermal conversion process from HPI to PBO. Other PBO samples were also affected by the similar effects but, the extent was relatively small. In addition, the gas permeabilities of PBO membranes was largely affected by the chemical structure of the polyimide. For instance, the oxygen permeabilities were varied 10 folds from lowest B PBO to highest 6F PBO.

4. Conclusions

We carried out the single gas permeation experiments of PBO membranes with various chemical structure. The presnet PBO membranes exhibited high gas selectivity as well as ultrapermeable gas permeability. T gas permeability and selectivity could be controlled by changing their main chain structure. It may be anticipated that the PBOs, which can be readily prepared from simple starting materials and simple thermal treatment, will cover the field of possible applications such as adsorption, catalysis and gas separation process, even under harsh conditions (e.g. harsh temperature and corrosive environment) because of their superior stability in the presence of organic vapours or solvents (including strong acids) and higher thermal stability.

References

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