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CO_2/N_2 Gas Separation Properties of Poly(Ethylene Oxide) Containing Polymer Membranes

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High molecular weight branched polyethers P(EO/EM/AGE) were prepared by ring opening copolymerization of ethylene oxide(EO), 2-(2-methoxyethoxy)ethyl glycidyl ether (EM) and allylglycidyl ether (AGE) and their gas permeation properties were investigated. The weight average molecular weight was determined by size exclusion chromatography to be 1750000 - 330000. The films of the branched polyether were self standing elastomers with a favorable mechanical strength. The branched polyethers displayed excellent performance for CO_2/N_2 separation, for example, permeability to CO_2 of 7.7×10^{-8} $cm^3(STP)cm/(cm^2\,s\,cmHg)$ and separation factor of 46 at 308K. Branched polyether is a promising candidate for highly CO_2 selective membrane material.

Key words: Poly(ethylene oxide), Branched Polyether, Gas Separation, Membrane Separation, CO_2 Separation

1. INTRODUCTION

The recovery of CO_2 from flue gas containing 10-20% CO_2 is an important objective in view of global warming. Membrane separation is one of the potential methods to remove CO_2 from flue gas with reduced energy consumption. Selective removal of CO_2, however, cannot be performed economically with the commercial membrane materials such as polyimide and cellulose acetate due to low selectivity of CO_2/N_2.

In previous papers, we reported on the CO_2/N_2 separation performance of poly(ethylene oxide) segmented co-polymers[1-3]. Among them, poly (ethylene oxide) segmented copolyimides (PEO-PI) showed the excellent CO_2/N_2 separation performance[2]. They have microphase-separated structures consisting of rubbery PEO segments and glassy PI segments. Their high CO_2/N_2 separation performance is due to PEO-segment which has specific interaction toward CO_2 [4,5]. PI-segment microdomains contribute to the mechanical properties and film-forming ability.

PIs have good mechanical and thermal properties but have very poor solubility in ordinary solvents, and this sometimes limits the preparation of high performance composite membranes that have very thin dense layer. We prepared composite hollow-fiber membranes of PEO-PIs, of which the CO_2 permeances and CO_2/N_2 selectivities were high enough initially but decreased 40% and 10-20%, respectively, in a month[6]. Furthermore, the PEO containing membrane mentioned above had their PEO contents less than 70% because of the poor film-forming ability of the PEO derivatives.

Here we report gas permeation properties of high molecular weight comb-shaped polyether. The high molecular weight allows self-standing films with high PEO contents.

2. EXPERIMENTAL

High-molecular-weight branched polyethers P(EO/EM/AGE) were prepared by ring-opening copolymerization of ethylene oxide (EO), 2-(2-methoxyethoxy)ethyl glycidyl ether (EM) and allylglycidyl ether (AGE) in hexane, using a condensation product of dibutyltin oxide and tributylphosphate as a highly active catalyst[7]. Figure1 shows the structures of these polymers.

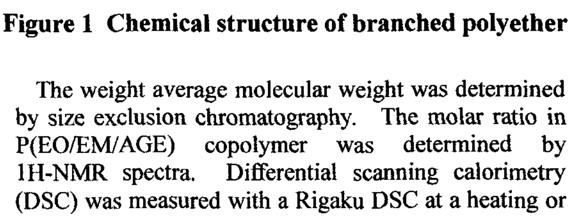

Figure 1 Chemical structure of branched polyether

The weight average molecular weight was determined by size exclusion chromatography. The molar ratio in P(EO/EM/AGE) copolymer was determined by 1H-NMR spectra. Differential scanning calorimetry (DSC) was measured with a Rigaku DSC at a heating or cooling rate of 10K/min.

Membranes were prepared by casting the polymer solution with 3.5 mass% crosslinking agent (phenylene bismaleimide) onto Teflon dishes. The membranes were dried at 373K for 2h in an air oven and further dried at 373K for 3h *in vacuo*.

Table I Characterization of polymers

Polymer (molar ratio)	EO content [wt %]	Glass transition temperature (Tg) [K]	Melting temperature (Tm) [K]	Weight-average molecular weight (Mw) (X10^6)
EO/EM/AGE (80/20/2)	85	204	ND	1.59
EO/EM/AGE (77/23/2.3)	84	205	ND	1.75
EO/EM/AGE (96/4/2.5)	93	209	305	0.33
PMDA/mPD/PEO (50/42.5/7.5)	56	211	ND	-
PDMS	0	150	-	-

EO: ethylene oxide, EM: 2-(2-methoxyethoxy)ethyl glycidyl ether, AGE: allylglycidyl ether,
PMDA: pyromellitic dianhydride, mPD: 1,3-phenylenediamine, PEO: poly(ethylene oxide) (PEO),
PDMS: polydimethyl siloxane
ND: no observed corresponding DSC signal

The permeability coefficient P of the membrane was measured by a vacuum time-lag method. The effective membrane area was 19cm^2 and the membrane thickness was about 50 μ m. The solubility coefficient S was measured using an electronic microbalance (Sartorius S3D-P). The diffusion coefficient D was evaluated by equation D=P/S.

3. RESULTS AND DISCUSSION

Table I lists the characterization results of the branched polyethers, PEO-segmented copolyimide, and PDMS. The characterization result of PEO-segmented copolyimide is cited from ref. 2. The P(EO/EM/AGE) copolymer have fairly high molecular weight. Reflecting the high molecular weights, the films of the copolymer are self standing elastomers with a favorable mechanical strength. The P(EO/EM/AGE)(80/20/2 molar ratio, Mw=1.6 × 10^6) copolymer film showed tensile strength at break of 1.8 MPa and elongation at break of 202 %.

It is well known that high molecular weight PEO is crystalline polymer and the crystalline part does not contribute to permeation at all, which cause a decrease of gas permeability coefficient. However, the melting temperature (Tm) of the copolymer was observed only for P(EO/EM/AGE) with EO content of 96 mol%. By the copolymerization of EO with EM and AGE, the crystallinity of the PEO segments in the copolymer became small or disappeared. The glass transition temperature (Tg) values of the copolymer were at 204 to 209 K and were lower than those of PEO-PI copolymer and PEO homopolymer[2], which suggests that the mobility of PEO segment of the copolymer is higher than those of PEO-PI. Thus, we can expect the P(EO/EM/AGE) copolymer to be a better CO_2 permeable membrane than the PEO polymers reported previously[1-6, 8-13].

Figure 2 shows permeabilities as a function of penetrant size for a branched polyether P(EO/EM/AGE(80/20/2)), polydimethyl siloxane (PDMS), poly(ethylene oxide) segmented copolyimide (PMDA/mPD /PEO(50/42.5/7.5)), and cellulose acetate membrane. In glassy polymers, such as cellulose acetate, the mobility of gases, characterized by their diffusion coefficients, is usually dominant, so permeability generally decreases strongly with increasing gas size and small molecules permeate preferentially. When used to separate CO_2 from N_2, the ideal selectivity (P_{CO2}/P_{N2}) is relatively low, for example cellulose acetate shows the selectivity of 27 at 298 K, since the molecular size of these gases differ by only a few tenth of one angstrom. In rubbery polymers, the sorption selectivity is usually dominant, so permeability increases with increasing gas size and large molecules permeate preferentially. The silicone rubber (PDMS) membrane is highly permeable. The permeability of P(EO/EM/AGE) is one order of magnitude lower than that of PDMS. However, CO_2 permeability of P(EO/EM/AGE) was only 4 times lower compared with that of PDMS. Thus, when used to separate CO_2 from N_2, the ideal selectivity is up to 46 at 308 K.

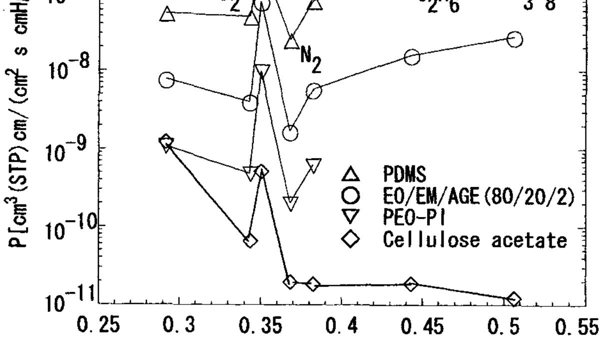

Fig. 2 Permeabilities as a function of penetrant size for a branched polyether, PDMS, PEO-PI and cellulose acetate

Table II Permeabilities and permselectivities of branched polyether membranes

Polymer (mol ratio)	Temp	Permeability			Selectivity			
	[K]	H_2	CO_2	O_2	CO_2/N_2	CO_2/H_2	CO_2/CH_4	O_2/N_2
EO/EM/AGE (80/20/2)	308	78.0	773	40.7	46	9.9	13	2.4
EO/EM/AGE (77/23/2.3)	308	67.8	680	38.1	44	10	13	2.4
EO/EM/AGE (96/4/2.5)	308	52.7	580	29.6	48	11	14	2.4
PMDA/mPD/PEO (50/42.5/7.5)	308	10.8	99	4.90	50	9.2	16	2.5
PDMS	298	550	2700	500	11	4.9	3.4	2.0
Cellulose acetate	298	13	5.5	0.70	27	0.42	28	3.4

Permeability: $10^{-10}cm^3(STP)cm/(cm^2 s cmHg)$

Furthermore, the gas permeability of P(EO/EM/AGE) is one order of magnitude larger than those of PEO-PIs.

The gas separation performances are listed in Table II. The permeability and the selectivity were independent of feed pressure up to 5 atm as shown in Figure 3. In the case of branched polyethers, CO_2 are much more permeable than the other gases considered and the CO_2 selectivity is up to 48 for CO_2/N_2 and 10 for CO_2/H_2. Gas permeability of P(EO/EM/AGE) decreases at high EO content (96 molar ratio) probably due to the crystalline behavior of this polymer mentioned above, whereas variations in selectivity were rather small. This high CO_2 selectivity is due to the high solubility selectivity. Branched polyethers display higher CO_2 solubility due to the interaction between the polar nature of PEO and a high quadrupole moment of CO_2. In the case of P(EO/EM/AGE(80/20/2)), the ratio of the solubility coefficient for CO_2/N_2 at 308 K and 1 atm was 60.

In conclusion, branched polyethers displayed larger CO_2 permeability and selectivity compared with other polymers. This result suggests that such branched polyethers may be a promising candidate for highly CO_2 selective membrane material.

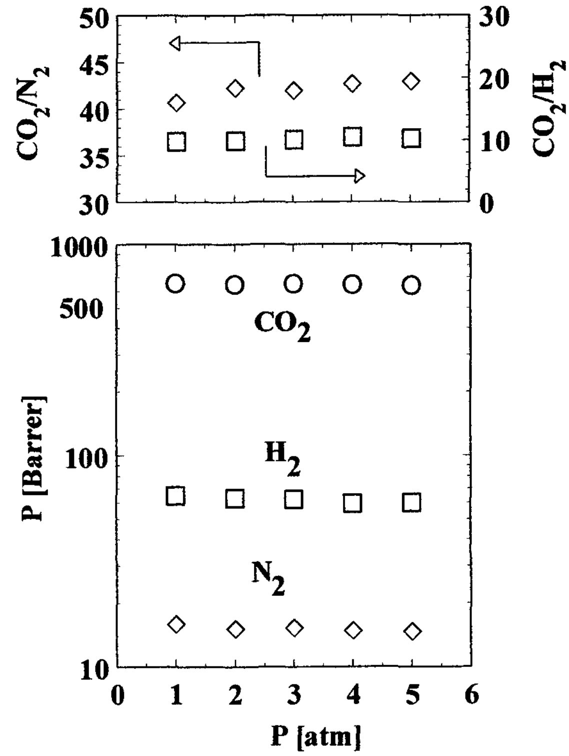

Fig. 3 Pressure dependence of permeability and selectivity for P(EO/EM/AGE(80/20/2)) membrane

4. REFERENCES

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