

CO₂ Removal by Branched Polyether Membranes

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Branched polyether was selected as a gas separation membrane with high CO₂ permeability and good mechanical strength. Five branched-based copolymers with different number of oxyethylene unites in a side chain were considered as the best candidates. Molecular design was performed from the view point of crystallinity and molecular weight. The branched polyethers of ethylene oxide / side chain-containing monomer / allyl glycidyl ether by the dispersion polymerization method using the catalyst system of organic tin and phosphorous acid ester was carried out. All of the polyethers had high weight-averaged molecular weights over 10⁵. From the result of thermal analysis, the polymers had glass transition temperature near -70°C and the extremely low crystallinity. The branched polyethers displayed excellent performance for CO₂/N₂ separation, for example, CO₂ permeability of 770 Barrer (1 Barrer= 10⁻¹⁰cm³(STP)cmcm⁻²s⁻¹cmHg⁻¹) and CO₂/N₂ permselectivity of higher than 46 at 35°C. High permselectivity of these membranes were attributed to the solubility selectivity of the membrane due to the specific interaction between the polar nature of PEO and a high quadrupole moment of CO₂. This result suggests that such branched polyethers may be a promising candidate for highly CO₂ selective membrane material.

Key words: Membrane separation, CO₂ separation, Branched polyether, Poly(ethylene oxide)

1. INTRODUCTION

Separation processes play critical roles in manufacturing and their proper application can significantly reduce costs and increase profits. Thus, alternative energy-saving and high efficiency separation process are strongly expected to be applied to many industries [1]. Membrane separation appears to be promising candidate for CO₂ removal because of low energy consumption, compact unit, simple operation, and low environmental impact [2]. Therefore, strong interest exists in the recovery of CO₂ from flue gas containing 10-20 % CO₂ by membrane separation. However, selective removal of CO₂ cannot be performed economically with the commercial membrane materials such as polyimide and cellulose acetate due to low selectivity of CO₂/N₂.

In previous papers, we reported on the CO₂/N₂ separation performance of poly(ethylene oxide) segmented co-polymers [3-6]. Among them, poly(ethylene oxide) segmented copolyimides (PEO-PI) showed the excellent CO₂/N₂ separation performance[4] compared with other polyethylene oxide containing polymers [7-11]. They have microphase-separated structures consisting of rubbery PEO segments and glassy PI segments. PEO-PIs have good CO₂/N₂ separation performance but have very poor solubility in ordinary solvents and this sometimes limits the preparation of high performance membranes that have very thin

dense layer. 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.

Recently, we reported preliminary results concerning excellent CO₂/N₂ separation performance of high molecular weight branched polyether membranes [12]. The high molecular weight allows self-standing membranes with high PEO content. In this study, we report transport properties of branched polyether membranes with various side chain types for CO₂ separation.

2. BACKGROUND

Membrane-based separation processes can separate the components of gas mixture on the basis of their difference of permeation rates through a membrane. The separation mechanism of non-porous polymeric membranes is described in terms of a solution-diffusion mechanism, where the penetrant gas dissolves at the upstream side of the membrane and then diffuses in the membrane matrix toward the downstream side. The gas permeability through a membrane of thickness l is defined as

$$P = \frac{J \times l}{p_1 - p_2} \quad (1)$$

where J is the steady state gas flux through the membrane and p_1 and p_2 are the upstream

pressure and the downstream pressure ($p_1 > p_2$), respectively. It can also be shown that P is the product of the diffusion coefficient D , reflects the mobility of the penetrant molecules in the membrane, and the sorption coefficient S , reflects the amount of penetrant molecules in the membrane, that is,

$$P = D \times S \quad (2)$$

The overall selectivity of a polymer membrane toward two different penetrant gases is commonly expressed in terms of an ideal separation factor, $\alpha_{id}(i/j)$, which is calculated as the P ratio of single gases i and j , and is expressed by the product of the D and S ratios of the single gases, i.e. diffusivity selectivity and solubility selectivity.

These ratios represent contributions to the overall selectivity due to the differences in the

$$\alpha_{id}(i/j) = \frac{P_i}{P_j} = \left(\frac{D_i}{D_j} \right) \times \left(\frac{S_i}{S_j} \right) \quad (3)$$

diffusivities and solubilities of gases i and j in a polymer.

3. EXPERIMENTAL

3.1 Membrane preparation and characterization

Fig. 1 shows the chemical structures of branched polyether used in this study. The branched polyethers were prepared by ring-opening copolymerization of ethylene oxide (EO), allylglycidyl ether (AGE) and 2-(2-methoxyethoxy)ethyl glycidyl ether (EM-2), propylene oxide (PO) or epichlorohydrin (EP) in hexane using a condensation product of dibutyltin oxide and tributylphosphate as a highly active catalyst[13]. The molar ratio of these monomers in branched polyethers was determined from ¹H-NMR spectra. The weight average molecular weight was determined by size exclusion chromatography. Glass transition temperature (T_g) and melting temperature (T_m) were determined by differential scanning calorimetry (DSC).

Polyether membranes were prepared by the solvent casting method. 1.5 g of the polymer, 0.0525 g (3.5 mass% of the polymer) of crosslinking agent (m-phenylene bismaleimide) and 0.015 g of benzoyl peroxide were dissolved in 13 g of acetonitrile in an Erlenmeyer flask equipped with a mechanical stirrer at a room temperature for overnight. The solutions were cast onto a silicone-treated PET film attached with glass plate, followed by evaporating the solvent at 50° C for 2 h in an air oven and further dried at 100° C for 3h *in vacuo*. The membrane thickness was about 50 μ m.

3.2 Gas permeation and sorption experiments

Permeability coefficients P of CO₂, H₂ and N₂ for the polyether membranes were measured using the constant volume and variable pressure technique at 25-35° C. The membrane was heated at 70° C *in vacuo* prior to a series of permeation experiments. The upstream

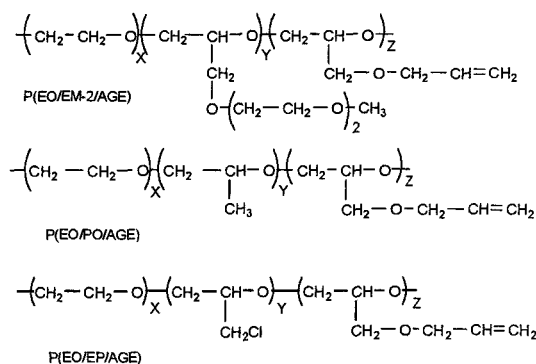


Fig. 1 Chemical structures of branched polyether.

pressure was varied between 1 and 10 atm and the downstream pressure was initially at vacuum. The downstream pressure gradually increased with time and the permeate amount of gas through the membrane was determined in a steady state permeation using a pressure-transducer. The effective membrane area was 19 cm². The mixed gas permeation experiments were also carried out at 35° C and 1 atm, followed by gas chromatographic analysis of the permeate. Separation factor $\alpha(i/j)$ was calculated by the equation: $\alpha(i/j) = (y_i/y_j)/(x_i/x_j)$ where x_i and y_i are the mole fraction of component i in the feed and the permeate gases, respectively.

Gas sorption amount was measured by a sorption cell equipped with a Sartorius S3D-P model electronic microbalance at 35° C and 1-10 atm. Solubility coefficients S of CO₂ and N₂ were calculated as the ratio of the sorption amount to the equilibrium pressure. Diffusion coefficients D of CO₂ and N₂ were evaluated from the equation $D = P/S$.

4. RESULTS AND DISCUSSION

Table I lists the characterization results of the branched polyethers together with other PEO containing polymers. Weight average molecular weights of the branched polyethers were higher than 10⁵. Thus, the membranes of the branched polyethers were self standing elastomers with a favorable mechanical strength [12]. Although high molecular weight

Table I Characterization results of polymers.

Polymer (molar ratio)	EO [wt%]	M _w (X10 ⁶)	T _g [°C]	T _m [°C]	Ref.
EO/AGE (92/8)	89	-	-63	31	this study
EO/EM-2/AGE (96/4/2.5)	93	0.33	-64	32	this study
EO/EM-2/AGE (80/20/2)	85	1.59	-69	ND	this study
EO/PO/AGE (81/19/2)	91	3.3	-68	ND	this study
EO/EP/AGE (52/43/5)	64	-	-48	ND	this study
PMDA/pDDS/ PEO4 (50/46/4)	69	-	-62	30	7

ND = Not detected,

poly(ethylene oxide) is crystalline polymer, copolymerization of EO with EM-2 and AGE effectively reduces the crystallinity. The melting temperature of the branched polyethers was observed only for P(EO/EM-2/AGE) with low content of EM-2 and P(EO/AGE) without EM-2. Furthermore, the degree of crystallinity of P(EO/EM-2/AGE) (96/4/2.5) and P(EO/AGE) (92/8), evaluated from the heat of fusion by DSC, is 40 and 26 %, respectively, which is considerably lower than that of high molecular weight poly (ethylene oxide) (normally higher than 70 %).

T_g values of branched polyethers except for P(EO/EP/AGE) with low EO content were lower than -60 °C. The higher T_g values of P(EO/AGE) and P(EO/EM-2/AGE) with EM-2 mol ratio of 4 % than those of P(EO/EM-2 or PO/AGE) with EM-2 or PO mol ratio of 20 % can be assigned to the presence of crystallinity. It can be noticed from Table 1 that T_g values of branched polyethers were lower than those of PEO-PIs and PEO-crosslinked polymers prepared by plasma polymerization of PEO-containing acrylate monomers [8], which suggests that the mobility of polymer chain of the branched polyethers is higher than those of PEO-PIs and PEO-crosslinked copolymers.

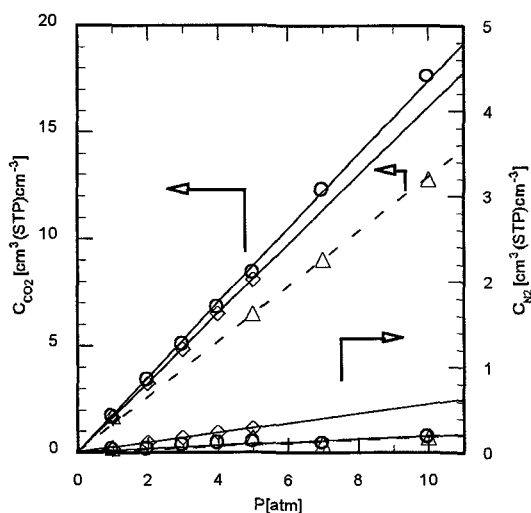


Fig.2 Sorption isotherms of CO₂ and N₂ for branched polyethers at 35°C. P(EO/EM-2/AGE)(80/20/2) (○), P(EO/PO/AGE)(81/19/2) (□), P(EO/EP/AGE)(52/43/5) (△).

Fig. 2 shows the sorption isotherms of CO₂ and N₂ for the branched polyether membranes at 35 °C. The gas sorption amount is proportional to the applied pressure, which is consistent with sorption results in other rubbery polymers. Solubility coefficients of CO₂ and N₂ were independent of pressure. CO₂ sorption amount of the branched polyethers is in the following order: P(EO/EM-2/AGE) > P(EO/PO/AGE) > P(EO/EP/AGE). P(EO/EM-2/AGE) copolymer has EO segment in the side chain. EM-2 segment seems to be polar and hydrophilic enough to enhance CO₂ solubility, but PO and EP segments are less hydrophilic than EM-2 segment. On the other hand, N₂ sorption amount of branched polyether is in the following order: P(EO/PO/AGE) > P(EO/EP/AGE) ≈ P(EO/EM-2/AGE). It follows that P(EO/EM-2/AGE) copolymers have much higher solubility selectivity of CO₂ over N₂ than P(EO/PO/AGE) and P(EO/EP/AGE) copolymers.

The gas separation performances of the branched polyethers are listed in Table 2. The branched polyether membranes are much more permeable to CO₂ than to the other gases such as H₂, O₂ and CH₄, which is consistent with the results in other rubbery polymers such as polydimethylsiloxane (PDMS). It is well known that the solubility selectivity is usually dominant in rubbery polymers, while the diffusivity selectivity is relatively small because diffusion coefficients in these polymers decrease slowly with increasing penetrant size. The difference of diffusivity selectivity for CO₂/N₂ is small also in the branched polyethers as shown in Table 2, although diffusion coefficient of CO₂ is in the following order: P(EO/PO/AGE) > P(EO/EM-2/AGE) >> P(EO/EP/AGE). On the other hand, solubility selectivity for CO₂/N₂ is much larger in these polymers than in other rubbery polymers. Compared with PDMS which is known to be high permeable polymer, the diffusivity of P(EO/PO/AGE) and P(EO/EM-2/AGE) is one order of magnitude lower than that of PDMS. However, CO₂ permeability of these polymers is only 2 or 3 times lower and membrane selectivity for CO₂/N₂ is much higher than that of PDMS, due to higher solubility selectivity for CO₂/N₂ of EO containing polymers. This is because the polar nature of PEO seems to enhance the solubility of

Table 2 Permeability, diffusion, and solubility coefficients of CO₂ and N₂ for polymer membranes at 35°C.^a

Polymer(molar ratio)	EO[wt%]	P_{CO_2}	P_{H_2}	P_{CO_2}/P_{N_2}	P_{CO_2}/P_{H_2}	D_{CO_2}	D_{CO_2}/D_{N_2}	S_{CO_2}	S_{CO_2}/S_{N_2}
EO/EP/AGE(52/43/5)	64	57	13	38	4.6	33	0.84	1.7	45
EO/PO/AGE(81/19/2)	91	917(930)	94	35(36)	9.8	430	0.94	2.1	38
EO/EM-2/AGE(80/20/2)	85	773(770)	78	46(43)	9.9	350	0.78	2.2	59
EO/EM-2/AGE(96/4/2.5)	93	580(610)	53	48(47)	11	-	-	-	-
EO/AGE(92/8)	89	294	30	42	9.7	-	-	-	-
PMDA/pDDS/PEO4 ⁷	69	238	-	49	-	116	0.82	2.0	61
PDMS ^b	-	2700	550	11	4.9	1500	1.0	1.8	11

^a P, D, S are in barrer [$10^{-10} \text{cm}^3(\text{STP}) \text{cm}^{-2} \text{s}^{-1} \text{cmHg}^{-1}$], $10^{-8} \text{cm}^2 \text{s}^{-1}$, and $10^{-2} \text{cm}^3(\text{STP}) \text{cm}^{-3} \text{cmHg}^{-1}$, respectively.

The data in parentheses were obtained for mixed-components system. ^b 25°C

quadrupolar CO₂ due to favorable dipole-quadrupole interaction.

In rubbery polymers, the gas permeability and permselectivity hardly depend on feed pressure and partial pressure for gas pair of CO₂/N₂. In mixed components, CO₂ permeability and CO₂/N₂ permselectivity of the branched polyethers hardly changed compared with those of single gas permeation. The branched polyether membranes containing ethylene oxide group in the side chain displayed excellent CO₂/N₂ separation performance in the mixed-components permeation.

Fig. 3 shows the effects of PEO segment content ([PEO]) on the CO₂/N₂ gas separation properties of the PEO-copolymer membranes at 35°C. Permeability of CO₂ of PEO-PIs and of branched polyether membranes increased with increasing [PEO] content. Typical PEO-PIs with [PEO] of about 60 wt% displayed CO₂ permeability of 150 Barrer (1 Barrer = 10⁻¹⁰ cm³ (STP)cmcm⁻²s⁻¹cmHg⁻¹) and permselectivity of CO₂ over N₂ of 52 at 35°C [4]. CO₂ permeability increased with increasing [PEO] up to 91 wt%. In spite of higher PEO content (more than 80 wt%), the present branched polyethers are self standing membranes and they remain the completely amorphous state of PEO. CO₂ permeability of the branched polyether membranes showed more than 500 Barrer. Permselectivity of CO₂ over N₂ slightly decreased with increasing [PEO]. With further increasing [PEO] up to 93 %, CO₂

permeability of the branched polyether slightly decreased probably due to the crystallinity of PEO mentioned above.

Thus, it can be concluded that the introduction of ethylene oxide group in the side chain of branched polyether is very effective for CO₂/N₂ separation. Branched polyether is a promising candidate for highly CO₂ selective membrane material.

5. CONCLUSIONS

High molecular weight branched polyethers having more than 80 wt% of PEO-content have been shown to be effective CO₂ separation membrane material. By copolymerization of EO with EM-2 and AGE, the crystallinity of the PEO segments in the copolymer became smaller or disappeared. The branched polyether P(EO/EM-2/AGE), which contains ethylene oxide group in their side chain of the polymer, displayed excellent performance for CO₂/N₂ separation, for example, permeability to CO₂ of 770 Barrer and separation factor of 46 at 35°C.

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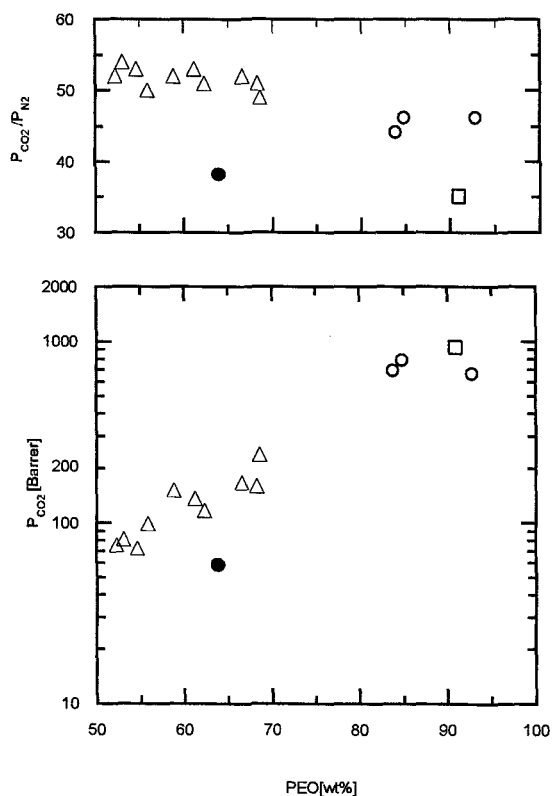


Fig.3 P_{CO_2} and P_{CO_2}/P_{N_2} as a function of [PEO] for branched polyether (○;EO/EM-2/AGE, ●;EO/EP/AGE, □; EO/PO/AGE) and PEO-segmented polyimide[4](□) at 35°C.