CHEMISTRY LETTERS, pp. 225-228, 1993.

Selective Permeation of Carbon Dioxide over Nitrogen through Polyethyleneoxide-Containing Polyimide Membranes

Ken-ichi OKAMOTO,* Nobuhiro UMEO, Shuusaku OKAMYO,
Kazuhiro TANAKA, and Hidetoshi KITA
Department of Advanced Materials Science and Engineering,
Faculty of Engineering, Yamaguchi University, Ube 755

Polyethyleneoxide(PEO)-containing copolyimides having microphase separated structure have high permeability to CO_2 and high permselectivity for CO_2 over N_2. The permeation occurs through soft segment phase of PEO and the high permselectivity is ascribed to high solubility selectivity.

Removal of CO_2 from flue gas stream containing 10-20% CO_2 is an important objective in view of the global warming and the recovery of carbon resources. For this purpose, liquid membranes have been investigated.[1)] They have high permselectivity because of the chemical interaction between CO_2 and carrier molecules. However, they have not been used practically because of disadvantages characteristic of liquid membranes. Solid polymeric membranes such as cellulose acetate have been practically used for CO_2 separation for natural gas treating and enhanced oil recovery etc.[2)] They have the permeability coefficient to CO_2, P_{CO2}, of 10 Barrer (1 Barrer = 10^{-10} cm^3(STP) cm^{-1} s^{-1} $cmHg^{-1}$) and the permeability ratio for CO_2 over CH_4, P_{CO2}/P_{CH4}, of 30-40. Fluorine-containing polyimides have P_{CO2} of 10-60 Barrer and P_{CO2}/P_{CH4} of 40-70.[3)] However, these polyimides have low permeability ratio for CO_2 over N_2, P_{CO2}/P_{N2}, of around 20. For practical application, it is necessary to develop membrane materials having the much higher performace; for example, P_{CO2}=100 Barrer and P_{CO2}/P_{N2}= 100.[4)] In this paper, we report excellent performance of the CO_2/N_2 separation of polyethyleneoxide-containing polyimides having microphase separated structure.

Bis(3-aminopropyl)-polyethyleneoxides (BAPEO) having average block-length of polyethyleneoxide (PEO) of 23(PEO-2) and 52(PEO-3), p,p'-oxydianiline (ODA), 3,5-diaminobenzoic acid (DABA), and m-phenylenediamine (PDA) were used as diamines. Pyromellitic dianhydride (PMDA) and 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) were used as acid dianhydrides. Copoly(amic acids) were prepared at a concentration of 15 wt% solids by the addition of a stoichiometric amount of diamines to a mechanically stirred solution of an acid anhydride in N,N-dimethylacetamide (DMAc) under nitrogen atmosphere at room temperature. BAPEO was first added, the solution was stirred for 30 min, and then a co-monomer diamine(s) was added. The polymerization solution was continued to stir for several hours. The copoly(amic acid) solutions thus prepared were filtered, cast onto Teflon plates and then dried at 350 K for 2 h. The copoly(amic acid) films were taken off and thermally imidized at 470 K for 20 h in a vacuum. Film thickness ℓ was ca. 100 μm.

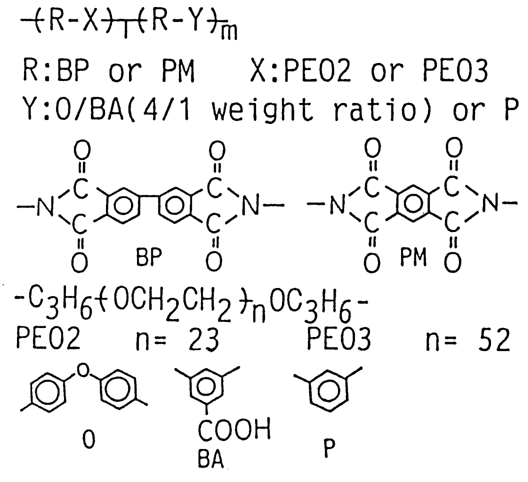

Fig. 1. Chemical structure.

The chemical structures of copolyimides are shown in Fig. 1. Glass transition temperature T_g and melting temperature T_m were determined by the onset point in DSC at a heating rate of 10 K/min. Permeability coefficient P was measured by the vacuum time-lag method at 2 atm. Apparent diffusion coefficient D was calculated from diffusion time-lag θ by the equation, $D=\ell^2/(6\theta)$. The apparent solubility coefficient S was evaluated by the equation $S=P/D$.

The characterization results for the copolyimides are listed in Table 1. These copolyimides have two glass transition temperatures and one melting temperature. The T_g and T_m of BAPEO were 204 and 311 K, respectively, for PEO2 and 207 and 316 K for PEO3. Therefore, the lower glass transition temperature T_{g1} and T_m of the copolyimides are attributed to the PEO segments and the higher one T_{g2} is attributed to polyimide segments of comonomer diamine moieties. This indicates that they have micro-

Table 1. Characterization of PEO-containing polyimides

Code	Polymer[a)]	η[b)] dl g^{-1}	Density g cm^{-3}	T_{g1} K	T_{g2} K	T_m k	PEO content[c)] wt%
B1	BP-O/BA/PEO2(70)	2.18	1.318	231	511	301	43.3
B2	BP-O/BA/PEO2(80)	0.68	1.272	229	514	303	53.4
B3	BP-O/BA/PEO3(80)	0.84	1.259	217	522	293	57.4
P1	PM-P/PEO3(80)	0.43	1.323	211	459	303	55.9

a) The figure in parenthesis refers to feed ratio (wt%) of BAPEO to total diamines. b) η is the inherent viscosity at 0.5 wt% and 308 K of poly(amicacid) in DMAc solution. c) Calculated from the feed amount of BAPEO.

phase separated structure consisting of the hydrophilic and soft segment phase of PEO and the hydrophobic and hard segment phase of polyimide. The T_{g2}s of B1-3 are slightly lower than T_g (531 K) of BPDA-ODA/DABA(4/1) polyimide, whereas the T_{g2} of P1 is much lower than that (above 773 K) of PMDA-PDA polyimide. It has been found from the effect of PEO content on the pervaporation of organic liquids through the copolyimide membranes that the permeation occurrs through the continuous phase of rubbery PEO segment and that the polyimide segment phase contributes to mechanical properties, film forming ability and durability to solvents.$^{5)}$

The P, D, and S data for the copolyimides are listed in Table 2. Figure 2 shows that the PEO-containing copolyimides have high membrane performances for CO_2/N_2 separation; they have more than three times larger values of P_{CO2}/P_{N2} as compared with other imide and non-imide polymers having similar value of P_{CO2}. This high permselectivity is due to the high solubility selectivity. As shown in Fig. 3, there is linear relationship between log S and Lennard-Jones force constant ε/k of gases for glassy and rubbery polymers. For the PEO-containing copolyimides, the slopes of the correlation lines are larger than those for other polyimides and nonpolar rubbery polymers and the S_{CO2} values are about twice larger than those predicted by the correlation lines, suggesting strong affinity of CO_2 molecules to the polar PEO segments. CO_2 is nonpolar but has the high polarizability and the high quadrupole moment as compared with other gases. This may be the reason of the strong affinity of CO_2 molecules to the polar PEO segments.

With an increase in the content of PEO, P_{CO2} increases significantly, whereas P_{CO2}/P_{N2} hardly varies. With an increase in the average block lenth of PEO, P_{CO2} increases significantly with accompanying a little decrease in P_{CO2}/P_{N2}. The kind of acid anhydride and comonomer diamine also affect the membrane performance. The copolyimides consisting of soft

Table 2. P, D, and S data for copolyimides$^{a)}$

Code	$\frac{T}{K}$	P_{CO2}	P_{N2}	$\frac{P_{CO2}}{P_{N2}}$	D_{CO2}	D_{N2}	$\frac{D_{CO2}}{D_{N2}}$	S_{CO2}	S_{N2}	$\frac{S_{CO2}}{S_{N2}}$
B1	308	14.3	0.25	57	11.5	11.3	1.02	12.3	0.22	56
B2	298	24.2	0.32	76	17.7	15.2	1.16	13.7	0.21	65
	308	36.0	0.64	56	(40)	(29)	(1.4)	(9)	(0.2)	(45)
B3	298	50.2	0.73	69	25.3	26	0.97	19.9	0.28	71
P1	298	77.0	1.15	67	33.5	39	0.86	23.0	0.29	79
	308	98.8	1.99	50	53.4	-	-	18.5	-	-

a) P is in Barrer. D is in $10^{-8}cm^2s^{-1}$. S is in $10^{-3}cm^3(STP)cm^{-3}cmHg^{-1}$.

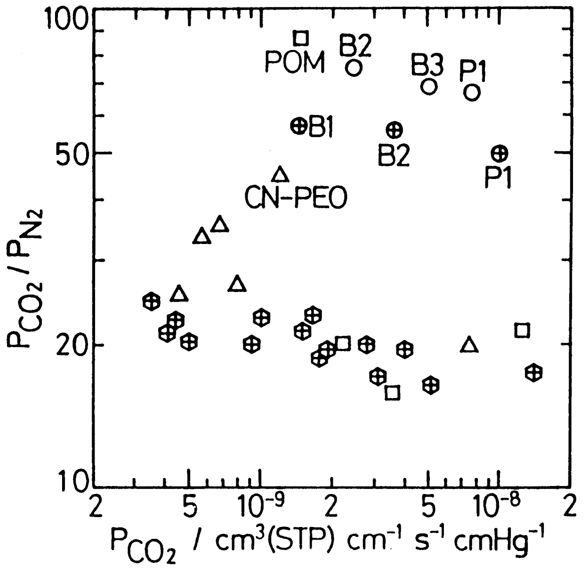

Fig. 2. Plots of P_{CO2}/P_{N2} vs. P_{CO2} for PEO-containing copolyimides (○, ⊕), other polyimides (⊕), non-imide glassy polymers (△), and rubbery polymers (□) at 298 K (⊕ and ⊕ ; at 308 K). POM: polyoxymethylene,[6] CN-PEO: cellulose nitrate/PEO blend.[7]

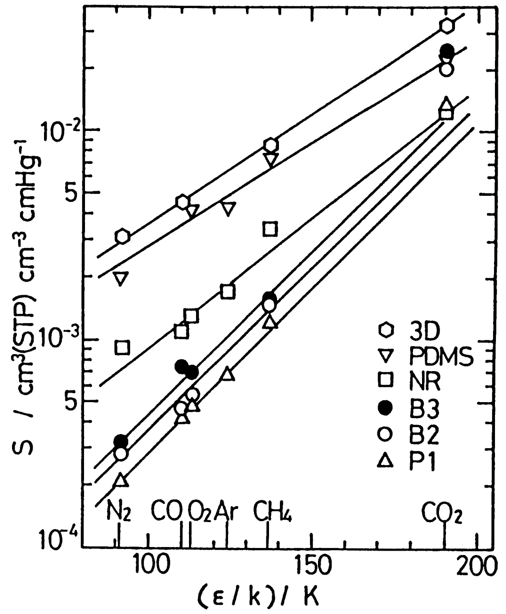

Fig. 3. Plots of log S vs. ε/K at 298 K. 3D: polyimides from 3,3',4,4'-benzophenonetetracarboxylic dianhydride and ODA, PDMS: polydimethylsiloxane, NR: natural rubber.

PEO segments and hard polyimide segments are very attractive as CO_2/N_2 separation membrane materials because of both the excellent thin-film-forming property and the excellent membrane performance. Further investigation is in progress.

The present work was supported in part by a research grant from Iketani Science and Technology Foundation.

References

1) J. D. Way, R. D. Noble, D. L. Reed, and G. M. Ginley. AIChE J., **33**, 480 (1987), and the references cited therein.
2) W. J. Schell, J. Membr. Sci., **22**, 218 (1985).
3) K. Tanaka, H. Kita, M. Okano, and K. Okamoto, Polymer, **33**, 585 (1992).
4) A. Nakamura, Preprints of the 24th Autumn Meeting of The Society of Chemical Engineers, Japan, SK203 (1991).
5) N. Umeo, K. Tanaka, H. Kita, and K. Okamoto, Prep. of the 57th Annual Meeting of The Society of Chemical Engineers, Japan, B318 (1992).
6) S.T. Hawang, C.K. Choi, and K. Kammermeyer, Separ. Sci., **9**, 461 (1974).
7) M. Kawakami, H. Iwanaga, Y. Hara, M. Iwamoto, and S. Kagawa, J. Appl. Polym. Sci., **27**, 2387 (1982).

(Received October 5, 1992)