Selective Permeation of Carbon Dioxide through Amine-modified Polyimide Membranes

Ken-ichi Okamoto,* Norimitsu Yasugi, Takashi Kawabata, Kazuhiro Tanaka, and Hidetoshi Kita
Department of Advanced Materials Science & Engineering, Faculty of Engineering, Yamaguchi University,
Tokiwadai, Ube, Yamaguchi 755

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Amine-modified polyimide membranes were prepared by immersing methyl-brominated polyimide membranes into aqueous amine solutions. They displayed high performance for CO_2/N_2 separation especially in the presence of water vapor; for example, permeability to CO_2 of 36 Barrer and separation factor of 81 at 2 atm, 298 K and relative humidity of 75%.

Recovery of CO_2 from flue gas containing 10-20% CO_2 is an important objective in view of the global warming. Membrane separation is one of the potential method to remove CO_2 from flue gas with reduced energy consumption. Facilitated transport of CO_2 through ion exchange membranes containing organic amine counterions have been intensively investigated because of their high permselectivity.[1,2] They have much better durability than liquid membranes, but still have their characteristic shortcomings; they can be used only in water-swollen state. From the practical viewpoint, use of solid polymeric membranes is more suitable than that of liquid or ion exchange ones. There have been developed polyimides having high performance for CO_2/CH_4 separation.[3] However, they have rather low permselectivity for CO_2/N_2 separation because of low diffusivity selectivity due to the similarity of molecular size between CO_2 and N_2. For much higher permselectivity, it is essential to enhance the solubility selectivity by introducing functional groups into polymeric membranes that have specific interaction toward CO_2 molecules.[4,5] Yoshikawa et al. have reported that membranes of poly(2-(N,N-dimethyl)aminoethyl methacrylate-co-acrylonitrile) had high permeability ratio of CO_2 over N_2, P_{CO2}/P_{N2}, of 60-90 at low upstream pressures of CO_2 and 298 K due to the acid-base interaction between CO_2 molecules and the tertiary amine moieties.[5] However, they displayed very low permeability coefficients to CO_2, P_{CO2}, of 0.1-0.5 Barrer (1 Barrer = 10^{-10} cm^3(STP)/(cm s cmHg)). For practical application, it is necessary to develop membrane materials having higher performance. Here, we report preparation of amine-modified polyimide membranes and their excellent performance of CO_2/N_2 separation.

The polyimide from 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) and 2,4,6-trimethyl-1,4-phenylene diamine (TrMPD) had less efficient packing of polymer chains and displayed high permeability and low selectivity for gas separations; for example, P_{CO2} =200 Barrer and P_{CO2}/P_{N2} =20 at 10 atm and 308 K.[6] In order to enhance the permselectivity with keeping the high permeability, this polyimide was chemically modified as follows.

BPDA-TrMPD polyimide was brominated on methyl-side groups by adding 2.2 mole-equivalent of N-bromosuccinimide to a 0.5% methylene chloride solution of the polyimide and refluxing the reaction mixture under illumination with a W-halogen lamp for 4-5 h. The degree of bromination was determined from the intensity ratio of-CH_2Br (4.2-4.4 ppm) to -CH_3 (2.0-2.2 ppm) in a ^{1}HNMR spectrum (270MHz,$CDCl_3$), and the values ranged from 50 to 70%.

Membranes of brominated polyimide BPDA-TrMPD(Br) were prepared by casting from methylene chloride solution onto glass plates and dried at 323 K in vacuo. Amine-modification of the membranes was achieved by the reaction of CH_2Br groups with amines; the membranes were immersed in aqueous amine solutions at room temperature. Amines used are diethanol amine (DEA), morphorine(MP), ammonia (A), hydroxyl amine (HA), diethylene triamine (DETA) and poly(ethylene imine) (PEI). The chemical structures of amine-modified polyimides are shown in Figure 1. Amine modification was confirmed by solubility, density, IR spectra, and elementary analysis. The amine-modified membranes were heat-treated at 373 K for 5 h in vacuo prior to permeation measurements. The membrane thickness was 30-40 μm.

For pure gas permeation, the vacuum time-lag method was used. For mixed gas permeation, the feed gas (CO_2/N_2: 18/82 in %, flow rate 50 cm^3/min) and sweep gas (He, usually 20 cm^3/min) were supplied to a permeation cell at 2 atm and atmospheric pressure, respectively. The outlet sweep gas was analyzed by gas chromatography. For wet mixed gas permeation, both gas streams were humidified by bubbling them through thermostated water columns.

Table 1 lists amine-modified polyimide membranes used here. For comparison, polyimides from 2-bis(3,4-dicarboxyphenyl)- hexafluoropropane dianhydride (6FDA) and TrMPD or 2,7-diaminofluorene (DAF) and polysulfone(PSF) were also used. Figure 2 shows permeation results as plots of P_{CO2} versus P_{CO2}/P_{N2} or separation factor α. The P_{CO2} values are much smaller for the amine-modified membranes, especially for the ones having

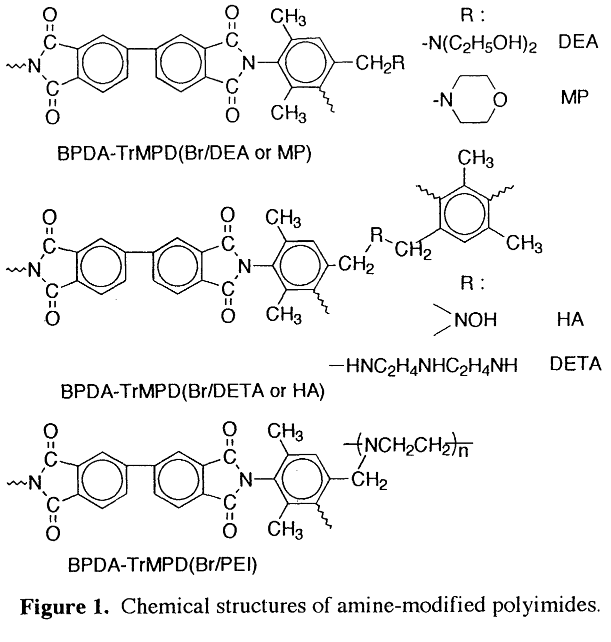

Figure 1. Chemical structures of amine-modified polyimides.

Table 1. Amine-modified polyimide membranes and other membranes

No	Membrane[a]	Amine-modification concentration [wt%]	conditions time [h]
1	BPDA-TrMPD		
2	BPDA-TrMPD(Br70)		
3	BPDA-TrMPD(Br50/A)	1.0	3
4	BPDA-TrMPD(Br50/EDA)	1.0	3
5	BPDA-TrMPD(Br70/DETA)	0.5	10
6	BPDA-TrMPD(Br70/HA)	0.5	10
7	BPDA-TrMPD(Br70/DEA)	0.5	10
8	BPDA-TrMPD(Br60/DEA)	0.5	10
9	BPDA-TrMPD(Br60/MP)	0.5	10
10	BPDA-TrMPD(Br50/PEI)	3.0	3
11	BPDA-TrMPD(Br70/PEI)	5.0	3
30	6FDA-TrMPD		
31	6FDA-DAF		
32	PSF		

[a] For example, (Br50/A) refers to bromination degree of 50% and modification with ammonia (A).

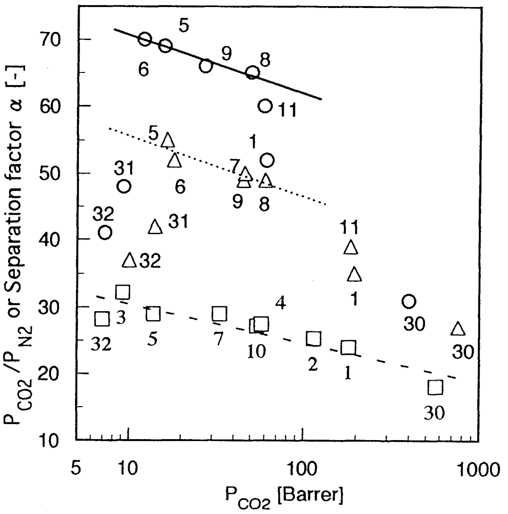

Figure 2. Comparison of membrane performance for CO2/N2 seperation at 308K and 2atm. □: pure gas, △: dry mixed gas (CO2/N2 = 18/82 in %) ○: wet mixed gas at relative humidity of 70-80%.

crosslinking structures such as No. 3 and 5, than for the base and brominated polyimide membranes (No. 1 and 2), but still larger than 10 Barrer. For pure gas permeation, the plots of P_{CO2} vs. P_{CO2}/P_{N2} fall on a trade-off line shown by the broken line irrespective of the amine modification, indicating that there is no special effect of amine moieties on pure gas permeation at 2 atm.

For dry mixed gas permeation at 2 atm (CO_2 partial pressure of 0.4 atm), both P_{CO2} and α were higher as compared with the pure gas permeation, as shown by triangle symbols in Figure 2. For the unmodified membranes the higher values are attributed mainly to the difference in the feed pressure dependence of the permeability between CO_2 and N_2; with a decrease in feed pressure, P_{CO2} increased fairly largely, whereas P_{N2} increased little. The increases in α are partly attributed to decreases in P_{N2} as a result of competition of the mixed penetrants for sorption sites amine-modified membranes are larger than those for the characteristic of glassy polymers.[7] However, the increases in α for the unmodified membranes as a result of larger decreases in P_{N2}. This is probably because the interaction between CO_2 and the amine moieties reduces the sorption of N_2 in competitive sorption between CO_2 and N_2.

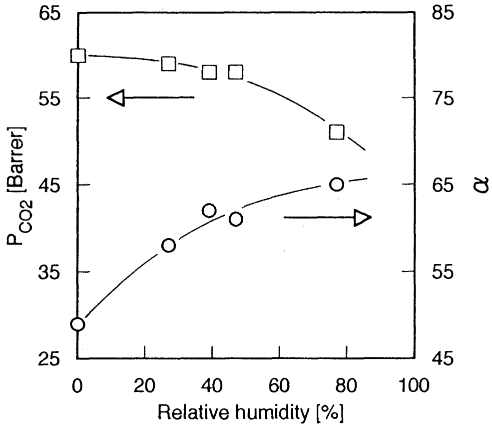

Figure 3. Relative humidity dependance of P_{CO2}(□) and α (○) for BPDA-TrMPD(Br60/DEA) membrane(No.8) at 308K and 2atm for mixed gas (CO_2/N_2=18/82 in %).

The data for wet mixed gas permeation at the relative humidity of 70-80 % are shown by circle symbols in Figure 2. Coexisting water vapor decreased P_{CO2} but increased α. For the amine-modified membranes, the increases in α are fairly large, whereas the decreases in P_{CO2} are rather small. Thus, they displayed high membrane performance; for example, for BPDA-TrMPD (Br60/DEA) membrane (No. 8), P_{CO2}=36 Barrer and α =81 at 2 atm, 298 K and relative humidity of 75 %. The water sorption of the amine modified membranes was around 10 % to the dry membranes at 308 k and the relative humidity of 75 %. The sorbed water might enhance the interaction between the amine moieties and CO_2 molecules and/or polarity of the membrane matrix to enhance the solubility selectivity of CO_2 over N_2. With increasing relative humidity, α increased rapidly in the region of low humidity, whereas P_{CO2} decreased very slowly as shown in Figure 3. Thus, the enhancement effect of coexisting water vapor on α is high even at the low humidities. This becomes advantageous in practical application for flue gas.

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