Silicon-containing polyimides for gas separation

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In this paper, three novel silicon-containing polyimides (abbreviated as SiDA-TDA, SiDA-DDA and SiDA-BDA) were synthesized. The permeability to H_2, O_2 and N_2 of these polymer membranes was determined at 30°C and at 1 atm. The introduction of bis(phenylcarboxylic dianhydride)dimethylsilane (SiDA) into the backbone of polyimides appears to result in a significant increase in gas permeability, without a correspondingly large decrease in permselectivity. The relationships between chemical structure and permeability of polyimides were also discussed. Wide-angle X-ray diffraction measurements of the average segmental spacing of the membrane materials characterized the packing of the different polymer types.

(Keywords: Si-containing polyimides; gas separation; membrane)

INTRODUCTION

Systematic variations in chemical structure have been found to lead to significant changes in permeability and permselectivity[1–3]. Introduction of a bulky central moiety such as hexafluoroisopropylidene[1] or dimethylsilylene[4] into the backbone of a polyimide can achieve significant increase in permeability.

The present work extends the study of silicon-containing polyimides by determining the effect of side groups of the diamines on the permeability and permselectivity of polyimides. Moreover, the effect of a soft central moiety in the diamine in silicon-containing polyimides was investigated.

Background and theory

Gases permeate through non-porous polymer membranes, such as used in membrane separation processes, by a 'solution–diffusion' mechanism[5–8].

The permeability P can be written as the product of an effective solubility coefficient S of the penetrant in the polymer matrix and the diffusivity coefficient D of the penetrant through the polymer matrix[9,10]:

$$P = DS \tag{1}$$

The diffusivity coefficient D can be measured by the method of time lag[5,11], as shown in the following equation:

$$D = l^2/(6\theta) \tag{2}$$

where l is the thickness of the membrane, and θ is the time lag. The diffusivity coefficient, which is a kinetic factor, is a measure of the mobility of the penetrant between the upstream and downstream conditions in the membrane. This parameter is determined by the packing and motion of the polymer segments and by the size of the penetrant molecule.

The solubility coefficient S can be determined by dividing the penetrant's permeability by the penetrant's diffusivity coefficient. The solubility coefficient S is thermodynamic in nature and is influenced by the inherent condensability of the penetrant, by polymer–penetrant interactions, and by the amount of excess volume existing in the glassy polymer[12–14].

The ideal separation factor α, which is an index of the overall selectivity of a polymer, can be expressed in the following terms:

$$\alpha_{A/B} = \frac{P_A}{P_B} = \frac{D_A}{D_B}\frac{S_A}{S_B} \tag{3}$$

where P_A and P_B are the permeabilities for gases A and B. When the downstream pressure is negligible, as in our experiments, the separation factor $\alpha_{A/B}$ is equal to the ratio of permeability of gases A and B, D_A/D_B is the diffusivity selectivity and S_A/S_B is the solubility selectivity. Clearly, if one can increase the diffusivity or the solubility of a desired gas by altering the structure of the polymer, the permeability of the gas will be raised proportionately. Similarly, to improve the permselectivity of one gas over another, one must increase either the diffusivity selectivity, the solubility selectivity, or both.

EXPERIMENTAL

Materials

Four types of silicon-containing polyimides, abbreviated as SiDA-TDA, SiDA-DDA, SiDA-BDA and SiDA-ODA, the structures of which are shown in *Table 1*, were synthesized by reacting bis(phenyldicarboxylic anhydride)dimethylsilane (SiDA)[15] with 4,4′-oxydianiline (ODA), 3,3′-dimethylbenzidine (TDA), benzidine (BDA) or 3,3′-dimethoxybenzidine (DDA). Stoichiometric amounts of diamine and dianhydride at a concentration of 15% solids in N,N-dimethylacetamide (DMAc) were mechanically stirred in a polymerizing reactor for 4 h at

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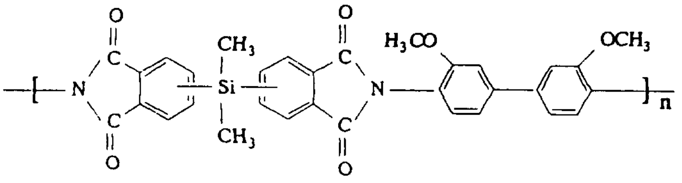
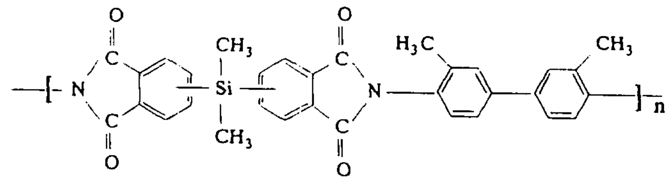
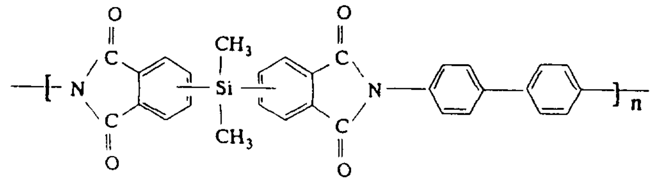
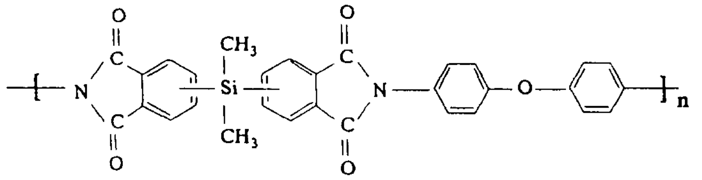
Table 1 Structures of four silicon-containing polyimides

Structure of polymers	Abbreviation[a]
	SiDA-DDA
	SiDA-TDA
	SiDA-BDA
	SiDA-ODA

[a] See text for full names

ambient temperature. The solution of the precursor poly(amic acid) was filtered and stored in a cooler until needed for film casting.

Film preparation

Films were prepared by casting the appropriate volume of the poly(amic acid) solution on a clean glass plate, followed by heating on a hot plate at 85°C for 1 h to evaporate most of the solvent. Then, the glass plate was put into an oven while the temperature was gradually raised to 300°C and kept at that point for 2 h by a slow flow of argon into the oven. After cooling, the membranes were removed from the glass plate by soaking in water and dried. All membranes were stored in a desiccator for 10 days prior to use.

Apparatus and gases

All the gas permeability properties were measured with a RSK Model K-315N-01 Gas Transmission Rate Measurement Apparatus produced by RSK Rikaseiki Kogyo Co. Ltd.

The gases were represented as having a minimum purity of 99.5 mol%.

X-ray diffraction

The WAXD measurements were performed on a Rigaku Dmax-3B X-ray diffractometer with Cu Kα radiation, wavelength = 1.54 Å. The mean intersegmental distance was taken to be represented by the *d*-spacings obtained from maxima in wide-angle X-ray diffraction spectra as suggested by O'Brien *et al.*[16]. The *d*-spacings are shown in *Table 2*.

Table 2 The *d*-spacings of polymers studied

Polymer	*d*-spacing (Å)
SiDA-TDA	5.8
SiDA-DDA	5.7
SiDA-BDA	5.3
SiDA-ODA	5.1

RESULTS AND DISCUSSION

The permeability, diffusivity and solubility coefficient data measured at 1 atm and 30°C for H_2, O_2 and N_2 for four silicon-containing polyimides are summarized in *Tables 3*, *4* and *5*.

Comparison of SiDA-BDA with SiDA-TDA and SiDA-DDA

The permeability of H_2 in SiDA-TDA and SiDA-DDA is higher than that of SiDA-BDA. However, the permeability of O_2 and N_2 in SiDA-TDA and SiDA-DDA is slightly lower than that of SiDA-BDA.

Table 3 Permeability coefficient[a] and permselectivity of polymers

Polymer	P_{H_2}	P_{O_2}	P_{N_2}	α_{H_2/N_2}	α_{O_2/N_2}
SiDA-TDA	10.9	0.663	0.094	116.4	7.1
SiDA-DDA	9.33	0.530	0.096	97.0	5.5
SiDA-BDA	8.38	0.677	0.109	76.9	6.2
SiDA-ODA	5.21	0.326	0.058	89.6	5.6

[a] Unit: 10^{-10} cm^3(STP) cm cm^{-2} s^{-1} cmHg^{-1}

Table 4 Diffusivity coefficient[a] and diffusivity selectivity of polymers

Polymer	D_{H_2}	D_{O_2}	D_{N_2}	D_{H_2}/D_{N_2}	D_{O_2}/D_{N_2}
SiDA-TDA	11 600	125	20.0	580	6.25
SiDA-DDA	9080	104	21.6	420	4.81
SiDA-BDA	8330	124	42.9	194	2.89
SiDA-ODA	5210	72	19.3	270	3.73

[a] Unit: 10^{-10} cm^2 s^{-1}

Table 5 Solubility coefficient[a] and solubility selectivity of polymers

Polymer	S_{H_2}	S_{O_2}	S_{N_2}	S_{H_2}/S_{N_2}	S_{O_2}/S_{N_2}
SiDA-TDA	9.45	53.2	46.9	0.201	1.13
SiDA-DDA	10.3	50.8	44.5	0.231	1.14
SiDA-BDA	10.1	54.6	25.3	0.399	2.16
SiDA-ODA	10.1	45.1	30.1	0.332	1.50

[a] Unit: 10^{-4} cm^3(STP) cm^{-3} cmHg^{-1}

The large side groups in the biphenylene ring can inhibit intersegmental chain packing, which appears to increase the permeability of gas penetrants, and the hindrance of chain packing of SiDA-DDA and SiDA-TDA would appear from the wide-angle X-ray diffraction measurements of the average spacing between adjacent polymer chains. The *d*-spacings of SiDA-DDA and SiDA-TDA are 5.7 and 5.8 Å, while it is 5.3 Å for SiDA-BDA. On the other hand, the large side groups in the biphenylene ring can also inhibit intrasegmental rotation of the connected benzene rings and imide rings, which would probably increase the permselectivity of gas pairs. As a result, instead of increasing, the permeability of large-size gas penetrants decreased, even if the inhibition of intersegmental chain packing may allow for the increase of the permeability of penetrants.

The data on diffusivity can also reflect the disadvantage of large-size gas penetrants such as O_2 and N_2 in SiDA-TDA and SiDA-DDA: the diffusivity of O_2 and N_2 in SiDA-TDA and SiDA-DDA is no more than that is SiDA-BDA. The diffusivity selectivity of H_2/N_2 in SiDA-TDA and in SiDA-DDA is much higher than in SiDA-BDA. If the diffusivity selectivity of H_2/O_2 were calculated, the same law would be found.

So, from the results of the experiments, we can form a hypothesis: the introduction of large side groups in the biphenylene ring moiety in polyimides would increase the permeability of small-size gas penetrants, and simultaneously the permselectivity between small- and large-size gas penetrants would also increase.

Comparison of SiDA-BDA and SiDA-ODA

Generally, the permeability increased when soft moieties were introduced into the polymer backbone. Stern *et al.* reported the permeability of two types of silicon-containing polyimides, SiDA-ODA and SiDA-PDA[4]. The permeability of SiDA-PDA was significantly lower than that of SiDA-ODA because of the rigid *p*-phenylenediamine (*p*-PDA) linkage in the former polymer. In contrast, the permselectivity of SiDA-PDA was larger for the same reason.

However, in our work, we found that the permeability of SiDA-BDA, which was derived from benzidine, is significantly higher than that of SiDA-ODA. This result may be concerned with the introduction of the $-Si(CH_3)_2-$ central moiety. The $-Si(CH_3)_2-$ central moiety has a large volume, which tends to increase the average segmental spacing of the polymer. SiDA-ODA is likely to be packed tightly because the soft ODA may make segmental motion easier. However, SiDA-BDA expresses more inhibition of chain packing over SiDA-ODA owing to the rigidity of the biphenylene moiety. This is reflected in the *d*-spacing value, 5.3 Å for SiDA-BDA but 5.1 Å for SiDA-ODA. In contrast to SiDA-PDA, the SiDA-BDA has a biphenylene moiety. The long rigid biphenylene can inhibit the intersegmental chain packing much more than the phenylene, so that SiDA-PDA is less permeable than SiDA-ODA, whereas SiDA-BDA is more permeable than SiDA-ODA.

The data of diffusivity of SiDA-BDA and SiDA-ODA contribute to the hypothesis of more inhibition of chain packing in SiDA-BDA over SiDA-ODA: the diffusivity of SiDA-BDA for H_2, O_2 and N_2 was increased more than 60% over that of SiDA-ODA.

The solubility of O_2 of SiDA-BDA is higher than that of SiDA-ODA, while the solubility of N_2 of SiDA-BDA is lower than that of SiDA-ODA. Hence, the O_2/N_2 solubility selectivity of SiDA-BDA is much higher than for SiDA-ODA. This makes a great contribution to the increase of α_{O_2/N_2} of SiDA-BDA over SiDA-ODA.

CONCLUSIONS

The permeability of H_2 for two silicon-containing polyimides with large side groups in the polymer backbone, SiDA-TDA and SiDA-DDA, is higher than that for the silicon-containing polyimide without side groups, SiDA-BDA, whereas the permeability of O_2 and N_2 for the latter is slightly higher than for SiDA-TDA and SiDA-DDA. The permselectivity of H_2/N_2 for SiDA-TDA and SiDA-DDA is also higher than for SiDA-BDA.

The relatively rigid silicon-containing polyimide SiDA-BDA shows higher permeability for all gas penetrants studied here than the soft one, SiDA-ODA, whereas the permselectivity was decreased, for the soft segments of SiDA-ODA may promote intersegmental chain packing. As a result, the average segmental spacing of SiDA-ODA is smaller than that of SiDA-BDA.

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