Silicon-Containing Polypyrrolone for Gas-Separation Application*

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SYNOPSIS

The permeability to H_2, O_2, and N_2 of silicon-containing polypyrrolone (SiDA–OTA) and three silicon-containing polypyrrolone random copolymers was determined at 30°C and 1 atm. The SiDA–OTA shows simultaneously increased permeability and permselectivity over the analogous polyimide (SiDA–ODA). The substitution of SiDA for the BPDA moiety in a polypyrrolone appears to result in a significant increase in gas permeability. The random copolymers contain different amounts of SiDA and DODA, which show lower permeability and higher permselectivity than does SiDA–OTA. Wide-angle X-ray diffraction measurements of the mean intersegmental distance of the materials characterized the packing of different polymer types. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Typically, a trade-off exists between the permeability and the permselectivity of polymer membranes. Work reported by various investigators involving polyimides,[1-4] however, has indicated that simultaneous improvements in permeability and permselectivity are possible. By utilizing a more rigid repeat unit than a polyimide, even greater permeability and permselectivity were anticipated.

Polypyrrolones are condensation polymers obtained from the reaction of aromatic dianhydrides and aromatic tetraamines followed by complete cyclization. The precursor obtained in an aprotic solvent is a soluble poly(amide amino acid) (i.e., A-A-A) that can be thermally cyclized. The resulting polypyrrolone possesses a repeat unit with four condensed rings, imparting a great degree of thermal and chemical resistance, strength, and rigidity. The rigidity of the polypyrrolone repeat unit was expected to provide an usually high size and shape discrimination between the penetrants. With the incorporation of the proper linkages in the repeat unit, the intrinsic rigidity of the polypyrrolone linkage can also inhibit packing, allowing one to increase penetrant mobility without losses in selectivity.

Transport characterization of polypyrrolone for gas separations was first determined by Lu et al.[5] in 1987. Subsequently, a series of polypyrrolones was prepared and the gas permeability of these polypyrrolone membranes for H_2, O_2, He, N_2, CO, CO_2, and CH_4 was studied.[6,7] Then, gas sorption and permeation properties of a polypyrrolone with a hexafluoroisopropylidene moiety were reported by Walker and Koros.[8] Stern and Vaidyanathan reported the permeability of silicon-containing polyimide (SiDA–ODA).[9]

Gases permeate through nonporous polymer membranes, such as used in membrane-separation processes, by a "solution-diffusion" mechanism.[10-13] The permeability, P, can be written as the product of an effective solubility coefficient of the penetrant in the polymer matrix, S, and the diffusivity coefficient of the penetrant through the polymer matrix, D:[14,15]

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

The diffusivity coefficient, D, can be measured by the time lag method,[10,16] as shown in eq. (2):

$$D = \frac{l^2}{6\theta} \tag{2}$$

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* Project supported by National Natural Science Foundation of China.

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Journal of Applied Polymer Science, Vol. 51, 855–861 (1994)
CCC 0021-8995/94/050855-07

where l is the thickness of the membrane, and θ, the lag time. 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 glass polymer.[17-19]

The ideal separation factor α, which is an index of the overall selectivity of a polymer, can be expressed in term of eq. (3):

$$\alpha_{(A/B)} = \frac{P(A)}{P(B)} = \frac{D(A)}{D(B)} \cdot \frac{S(A)}{S(B)} \qquad (3)$$

where $P(A)$ and $P(B)$ are the permeability for gases A and B, when the downstream pressure is negligible, as in our work; the permselectivity $\alpha_{(A/B)}$ 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 or the solubility selectivity, or both.

EXPERIMENTAL

Materials

Silicon-containing Polypyrrolone (SiDA–OTA)

The polymer was prepared by dissolving a small quantity of the 3,3′,4,4′-tetraamino diphenyl ether (OTA) in dimethylacetamide (DMAc) under argon in a three-neck round-bottom flask. An equimolar quantity of the bis(phthalic anhydride)dimethylsilane (SiDA), which was prepared according to the literature,[20] was dissolved in enough DMAc so that the solid was 10% by weight of the mixture. The dianhydride solution was first rapidly and then slowly dripped into the vigorously stirred OTA solution over a period of 2 h to prevent gelation at ambient temperature. The solution of the A-A-A was filtered and stored in a cooler until needed for film casting.

Silicon-containing Polypyrrolone Copolymers and Nonsilicon-containing Polypyrrolone (BPDA–OTA)

SiDA was substituted with a mixture of SiDA and DODA in different amounts; then the copolymerization was carried out according to what has been described in the last paragraph. BPDA–OTA was prepared by the reaction of BPDA with OTA according to the same procedure shown in the last paragram.

Silicon-containing Polyimide (SiDA–ODA)

Polymerization was carried out according to Ref. 9. Monomers and polymers used in this study are shown in Figures 1 and 2. Compositions of copolymers are shown in Table I.

Film Preparation

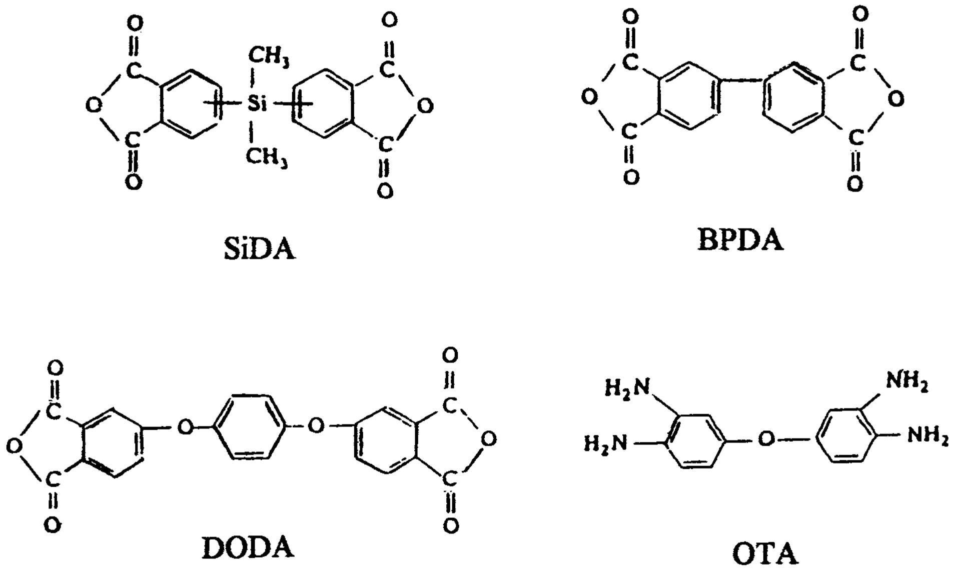
Film was prepared by casting an appropriate volume of A-A-A solution on a clean glass plate. Then, it was heated on a hot plate at 85°C for 1 h to evaporate most of the solvents and, the glass plate was next placed into an oven while the temperature was gradually increased to 300°C and kept at that point for 2 h by a slow flow of argon into the oven. After cooling, the membrane was removed from the glass plate by soaking in water and then 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 an RSK Model K-315N-01 gas transmission rate measurement apparatus produced by RSK Rikaseiki Kogyo Co. The gases were represented as having a minimum purity of 99.5 mol % and were used without further purification.

X-ray Diffraction

The WAXD measurements were performed on a Rigaku Dmax-3B X-ray diffractometer with CuKα radiation, with wave length equal to 1.54 Å. The mean intersegmental distance was taken to be represented by the d-spacing obtained from maxima in wide-angle X-ray diffraction spectra as suggested by O'Brien et al.[21] The d-spacing of the polymers is shown in Table II.



SiDA BPDA

DODA OTA

Figure 1 Monomers used in this study.

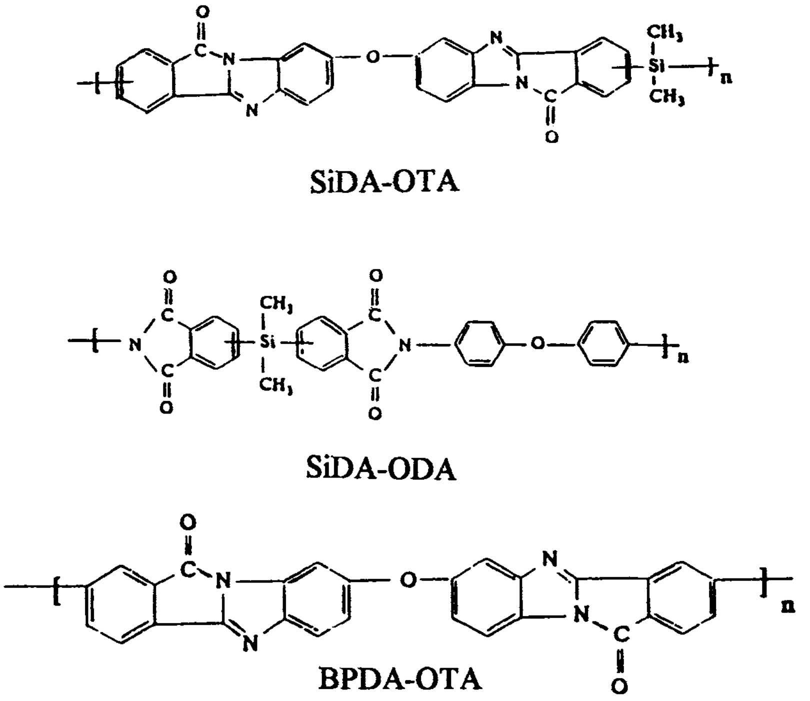
RESULTS AND DISCUSSION

The permeability, diffusivity, and solubility coefficient data measured at 30°C and 1 atm for H_2, O_2, and N_2 for five silicon-containing polypyrrolones and polyimide and one nonsilicon-containing polypyrrolone are summarized in Tables III–V.

Referring to Table III, it is seen that the permeability for H_2, O_2, and N_2 in all the membrane materials studied here decreases in the following order:

$$P_{H_2} > P_{O_2} > P_{N_2}$$

which is also the order of increasing kinetic molecular diameter and, probably, of decreasing diffusivity (D) of the three gases. Hence, the overall gas permselectivity of these membrane materials appears to



SiDA-OTA

SiDA-ODA

BPDA-OTA

Figure 2 Polymers used in this study.

Table I Compositions of Copolymers

Copolymer	SiDA (Mol %)	DODA (Mol %)	OTA (Mol %)
A	75	25	100
B	50	50	100
C	25	50	100

be largely controlled by the mobility (or diffusivity) selectivity.

Comparison of SiDA-OTA and Its Copolymers

Table III shows that the permeability of the silicon-containing polypyrrolone homopolymer (SiDA-OTA) is higher than that of the copolymers. The permeability of the copolymers to any given gas decreases from copolymer A to B to C, i.e., with decreasing mol % of SiDA.

Similarly, the diffusivity coefficient of these four polymers decreases in the same order of the permeability. This result indicates that the diffusivity is the principal factor that alters the permeability and permselectivity of these materials. The results of WAXD also show that the mean intersegmental distance of the four polymers decreases with the reduction of mol % of SiDA. The larger $-Si(CH_3)_2-$ central moiety may act as "spacers" in polymer backbone chains,[9] leading to a simultaneous disruption in intersegmental chain packing and suppression of intrarotational flexibility in the dianhydride segment of these polymers. This results in a significant increase in permeability of all gases and a small decrease in permselectivity. The higher the content of the $-Si(CH_3)_2-$ central moiety is, the further the permeability of the membrane would increase.

Correspondingly, the H_2/N_2 permselectivity of SiDA-OTA is lower than that of the copolymers, i.e., with the increase of the mol % of the $-Si(CH_3)_2-$ central moiety. However, the O_2/N_2 permselectivity behaves irregularly. Figures 3-6 describes the trend of the permeability, diffusivity, and solubility coefficient for H_2, O_2, and N_2 and the permselectivity of H_2/N_2 with increase of the mol % of the $-Si(CH_3)_2-$ central moiety.

Table II The *d*-Spacing of Polymers Studied

Polymer	*d*-Spacing (Å)
SiDA-OTA	5.7
SiDA-ODA	5.1
BPDA-OTA	5.4
Copolymer A	5.3
Copolymer B	5.2
Copolymer C	5.0

Table III Permeability 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-OTA	12.7	0.63	0.102	123.8	6.17
SiDA-ODA	5.21	0.33	0.058	89.6	5.61
BPDA-OTA	6.56	0.24	0.023	287.0	10.6
Copolymer A	9.25	0.51	0.068	136.4	7.53
Copolymer B	6.92	0.29	0.044	159.0	6.72
Copolymer C	6.39	0.29	0.036	176.3	7.91

Unit: 10^{-10} cm^3 (STP) cm/cm^2 s cmHg.

Comparison of SiDA-OTA and BPDA-OTA

SiDA-OTA is more permeable than is BPDA-OTA. Its permeability increases by 94, 162, and 343% for H_2, O_2, and N_2, respectively. Correspondingly, the permselectivity of H_2/N_2 and O_2/N_2 decreases by 57 and 42%.

Replacement of the rigid BPDA moiety in BPDA-OTA with SiDA probably leads to simultaneous disruption in the intersegmental chain packing and suppression of the intrarotational flexibility because the larger $-Si(CH_3)_2-$ central moiety may act as "spacers." As a result, the gas permeability of SiDA-OTA is higher than that of BPDA-OTA, whereas the permselectivity of the former polymer is lower than that of the latter.

The increased packing disruption is reflected in the data in Table II with an increased *d*-spacing of SiDA-OTA (d = 5.7 Å) over that of the BPDA-OTA (d = 5.4 Å). The larger diffusivity difference between the two membrane materials for the penetrants also demonstrates that the introduction of $-Si(CH_3)_2-$ central moiety in BPDA-OTA would increase the chain-packing disruption.

Comparison of SiDA-OTA and SiDA-ODA

Polypyrrolone (SiDA-OTA) is more permeable than is polyimide (SiDA-ODA) by 76% or more for all

Table IV Diffusivity 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-OTA	124	0.84	0.18	689	4.66
SiDA-ODA	52.1	0.72	0.19	274	3.79
BPDA-OTA	35.9	0.35	0.05	718	7.00
Copolymer A	111	0.74	0.14	613	5.33
Copolymer B	73.5	0.42	0.12	598	3.43
Copolymer C	52.1	0.31	0.11	478	2.87

Unit: 10^{-8} cm^2/s.

Table V Solubility 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-OTA	10.1	75.1	56.2	0.180	1.34
SiDA-ODA	10.0	45.1	30.1	0.332	1.50
BPDA-OTA	18.1	68.3	44.6	0.406	1.53
Copolymer A	8.32	68.9	48.8	0.170	1.41
Copolymer B	9.42	69.3	35.6	0.265	1.95
Copolymer C	12.3	91.6	33.4	0.368	2.74

Unit: 10^{-4} cm^3 (STP)/cm^3 cmHg.

the gases studied in this work. The increased permeability is due primarily to an increase in the diffusivity of these penetrants. For H_2 and O_2, the diffusivity is increased by 138 and 16%, respectively, but for N_2, the diffusivity is decreased by 5%. This leads to a greater increase in diffusivity selectivity of H_2/N_2 and O_2/N_2.

The greater diffusivity of polypyrrolone relative to polyimide may be due to the inhibition of intersegmental chain packing in polypyrrolone. The backbone of polypyrrolone contains a four-condensed-ring structure, which shows extreme high rigidity compared with that of polyimide with a two-condensed-ring structure. The rigid structure of polypyrrolone may inhibit intersegmental chain packing, which is reflected in the values of *d*-spacing, 5.7 and 5.1 Å, respectively, for polypyrrolone and polyimide.

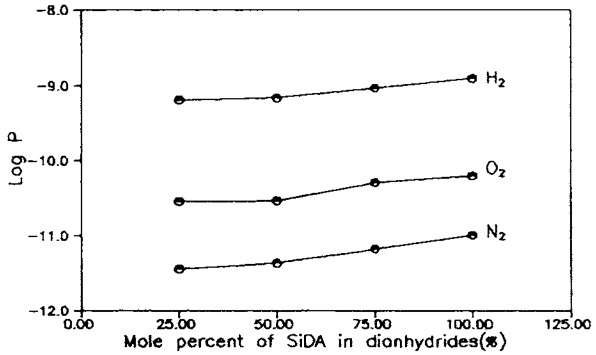


Figure 3 Dependencies of the permeability of H_2, O_2, and N_2 on the mol % of SiDA-OTA in anhydride.

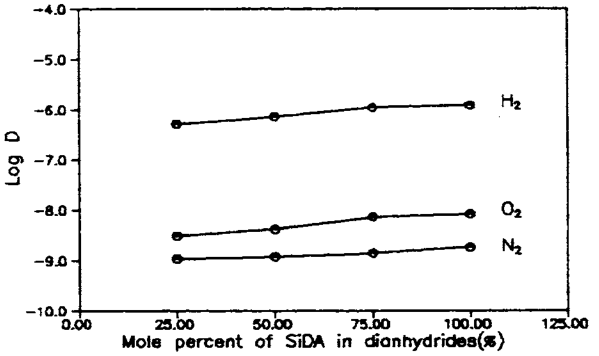


Figure 4 Dependencies of the diffusivity coefficient of H_2, O_2, and N_2 on the mol % of SiDA-OTA in anhydride.

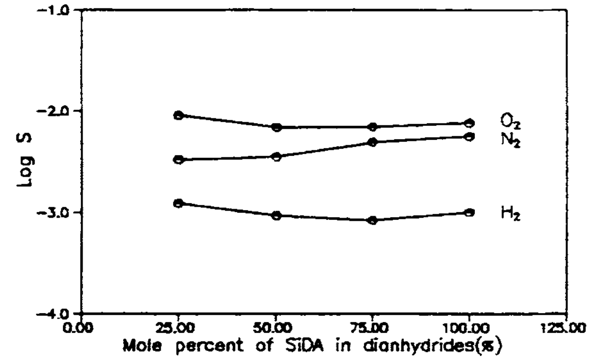


Figure 5 Dependencies of the solubility coefficient of H_2, O_2, and N_2 on the mol % of SiDA–OTA in anhydride.

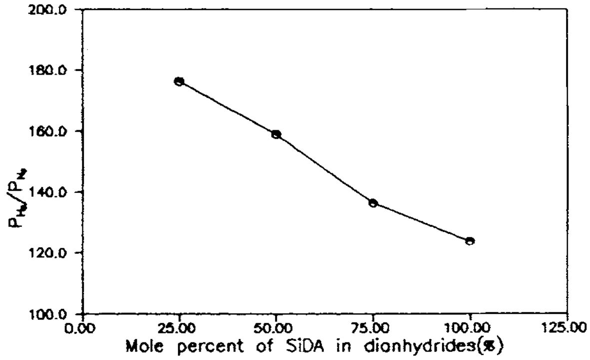


Figure 6 Dependencies of the permselectivity of H_2/N_2 on the mol % of SiDA–OTA in anhydride.

It has been demonstrated that a significant increase in diffusivity and diffusivity selectivity can be obtained by simultaneously inhibiting intrasegmental motions and intersegmental chain packing.[1,2] For polypyrrolone, the four-condensed-ring moiety in it can inhibit not only intersegmental chain packing but also intrasegmental motions about flexible linkages in the polypyrrolone backbone. This tends to increase the diffusivity while maintaining diffusivity selectivity. Furthermore, the rigid moiety may decrease the concentration of mobile linkages in the polymer repeat unit to increase the diffusivity selectivity without decreasing the diffusivity significantly.

So, though the great hindrance of intersegmental chain packing may allow for high permeability and relatively low permselectivity, the inhibition of intrasegmental motions about flexible linkages and the decrease of concentration of mobile linkages in the polymer repeat unit can greatly increase the permselectivity. As a result, the permeability and permselectivity of polypyrrolone are all higher than that of the polyimide. The permselectivity of H_2/N_2 and O_2/N_2 of polypyrrolone is 28 and 10% higher, respectively, than that of polyimide.

CONCLUSION

Compared with polyimide, polypyrrolone has a lower concentration of mobile linkages and possesses great permselectivity. The increase in permselectivity is due primarily to the increase in diffusivity selectivity. The ring closure also increases the mean intersegmental distance, leading to a greater increase in permeability. The increase in permeability is due primarily to the increase in diffusivity.

Silicon-containing polypyrrolone SiDA–OTA has a higher permeability for all gases studied here than that of nonsilicon-containing polypyrrolone BPDA–OTA, whereas the permselectivity of SiDA–OTA is lower than that of BPDA–OTA.

The permeability of silicon-containing polypyrrolones increases with the rise of the mol % of the $—Si(CH_3)_2—$ central moiety in the backbone chains. The permselectivity of H_2/N_2 decreases with the increase of the mol % of the $—Si(CH_3)_2—$ central moiety.

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Received March 11, 1993
Accepted June 30, 1993