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Application of organic–inorganic polymer hybrids as selective gas permeation membranes

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The gas permeability of polymer hybrid membranes has been investigated. The membranes were prepared by dip-coating a methanol solution of poly(*N*-vinylpyrrolidone) (PVP) and methyltrimethoxysilane (MTMOS) on porous glass tubes. The permeance was measured by using N_2, CO_2 and He separately at a pressure of 1 kg cm^{-2}. It was found that the permeance of these gases all increased with temperature in the PVP hybrid membranes. In particular, the permeance of He increased at a much greater rate with temperature, resulting in high selectivity against N_2. For instance, the permeance of He is 150 times greater than that of N_2 at 100 °C. The results indicate the dense structure of PVP hybrid membranes as confirmed by SEM observations. The hybrid membranes also exhibited high selectivity of CO_2 against N_2. This could be attributed to the high polarity of amide groups in PVP chains which would facilitate the sorption of CO_2. These polymer hybrid membranes were also found to have high thermal stability compared to organic polymer membranes.

Introduction

We have recently reported the synthesis of a large variety of organic–inorganic polymer hybrids by utilizing the sol–gel reaction of alkoxysilanes. The method comprises initial hydrolysis of the metal alkoxides and subsequent condensation and removal of the solvent, resulting in metal oxides.[1–6] The advantage of the sol–gel technique for the preparation of composite materials is the fact that the reactions can be carried out at ambient temperature, while the conventional melt fusion technique for silica glasses requires high temperature. Thus, it enables the introduction of organic elements into inorganic materials without deteriorating their functionalities. In our group, organic–inorganic polymer hybrids have been prepared utilizing various methods. The most common method for the preparation of polymer hybrids is the utilization of hydrogen bonding interactions between polar functional groups of organic polymers and residual silanol groups of silica gel. Organic polymers such as poly(2-methyl-2-oxazoline), poly(*N*-vinylpyrrolidone) or poly(*N*,*N*-dimethylacrylamide) have been incorporated homogeneously into silica gel by such interactions.[7–12] π–π Interactions between phenyl rings of organic polymers and silica gel may also be of significance for the synthesis of polymer hybrids and we have succeeded in the preparation of hydrophobic polystyrene and silica gel polymer hybrids by utilizing this type of interaction.[13]

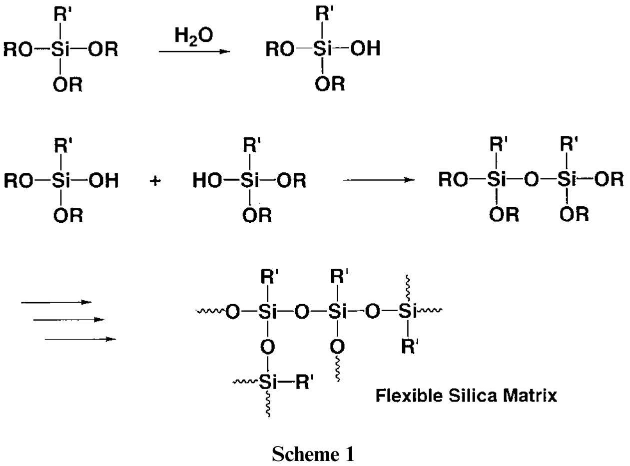
Novel properties have been obtained by the combination of organic and inorganic elements, especially when they were mixed at a molecular level. For instance the mechanical strength of organic polymers can be improved by incorporation of inorganic segments.[14–18] High transparency is another important property of the polymer hybrids and is an indispensable factor for development of optical waveguides,[19–23] optical biosensors,[24] non-linear optical materials[25,26] and other applications such as contact lenses.[27] Combination with inorganic materials also provides high thermal stability to the organic polymers.[28]

Here, we present an application of poly(*N*-vinylpyrrolidone) and silica gel polymer hybrids as gas selective membranes. It is of interest to obtain membranes that can provide high selectivities for certain gases. Membranes possessing high selectivity at high temperatures are especially desirable for practical applications. As stated above, the integration of organic elements and inorganic elements at a molecular-level may induce physical as well as chemical properties that are different from original materials. Modification in the mechanical flexibility of polymer hybrids may provide crack free membranes suppressing Knudsen flow. Such suppression is an effective method to obtain membranes having high selectivity, since Knudsen flow gives rise to high selectivity of gases only when permeant molecules have large differences in molecular weights.[29–31] Improvement in the thermal stability was also expected for the polymer hybrid membranes since the rigid structure of silica gel suppresses the deformation of organic polymers above the glass transition temperature.[28] For the synthesis of polymer hybrid membranes, we employed mono-alkyl substituted methyltrimethoxysilane (MTMOS) instead of tetraalkoxysilanes. It has been reported that the flexibility of silica gel was improved by the replacement of an alkoxy group with alkyl group which does not undergo hydrolysis and provides a less cross-linked silica gel (Scheme 1).[32,33]

Experimental

Materials

Methyltrimethoxysilane (MTMOS) (Tokyo Kasei Kogyo Co., Ltd.) was used after distillation under N_2. Methanol (Wako

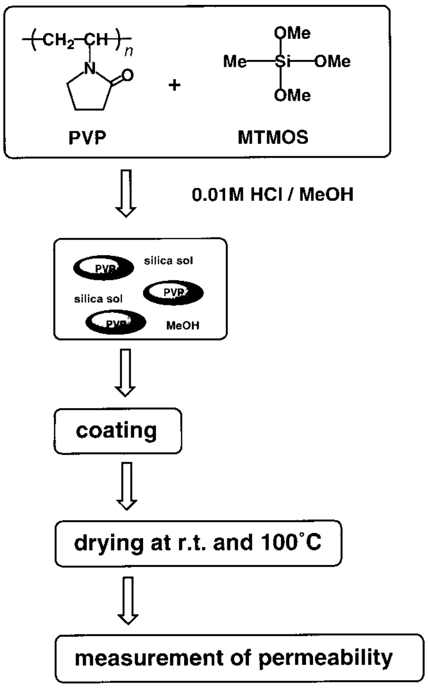


Scheme 1

Pure Chemical Industries, Ltd.) was used after distillation with sodium under N_2. Poly(*N*-vinylpyrrolidone) (PVP) (Tokyo Kasei Kogyo Co., Ltd., average M_w *ca.* 630 000) and 0.01 M HCl (Wako Pure Chemical Industries, Ltd.) were used as supplied. He, N_2 and CO_2 gases were used as supplied.

Preparation of PVP–silica hybrid membranes (Scheme 2)

Prescribed amounts of PVP and MTMOS were dissolved in methanol (20 ml). To the solution was added 0.01 M aqueous HCl as a catalyst for the sol–gel reaction. The total weight of PVP and MTMOS was fixed at 10 g and the amount of aqueous HCl was varied to contain 3 mol of water per mol MTMOS. The initial weight ratios of PVP and MTMOS are given in Table 1. The mixture was then stirred at room temperature for 0.5 h in air. Porous glass tubes of 4 nm diameter pores were dipped in the solution at a constant rate (1.2 mm s^{-1}) for the preparation of polymer hybrid membranes with constant thickness. The tube was of length 8.5 cm, diameter 0.54 cm and thickness 0.73 mm. The dipped tube was then dried in air at room temperature for 1 h to promote the growth of the silica gel. This procedure was repeated four times and the polymer hybrid membranes were obtained on the surface and inside the glass tubes. The membranes obtained were denoted as membrane(x) depending on the initial weight ratio (x) of PVP to MTMOS. The membranes were subjected to gas permeability measurements on porous glasses. The obtained polymer hybrid membranes were allowed to stand for two weeks at room temperature in air, during which gelation of MTMOS proceeded. Further drying of the membranes was conducted just before the measurement of gas permeation at 100 °C *in vacuo* to allow completion of gelation and to remove residual water and solvent.



Scheme 2

Measurement

Bulk polymer hybrids were prepared from the same mixture as above by conducting the reaction in a polypropyrene container at room temperature. After removal of solvents, transparent glass-like polymer hybrids were obtained and were subjected to further drying at room temperature for two weeks. Thermal properties were measured for these polymer hybrids. Thermogravimetry (TG) was performed on a Shimadzu TG-30, TGC-30 with a heating rate of 10 °C min^{-1} in air for the measurement of ceramic yield which was calculated at 900 °C. Differential scanning calorimetry (DSC) was performed on a Seiko DSC 200. Glass transition temperatures (T_g) were estimated from the second scan (−10 to 150 °C, 10 °C min^{-1}) after the first scan (20–100 °C, 10 °C min^{-1}) and cooling (110 to −10 °C, 50 °C min^{-1}). Scanning electron microscopy (SEM) measurements were conducted with a JEOL JSM-5200 at 15 kV.

Measurement of gas permeation

The permeation properties of the hybrid membranes were investigated with N_2, He and CO_2. Each gas was provided separately at a pressure of 753 mmHg and the membrane was evacuated to 0.3 mmHg on the downstream side. As is illustrated in Fig. 1, the flux of each gas was read with a mass flow meter (STEC Inc. SEF-410) which was connected to the downstream side. To control the temperature of measurement, the experimental module was placed in a thermostated oven. The permeability was evaluated from the steady-state gas permeation rate.

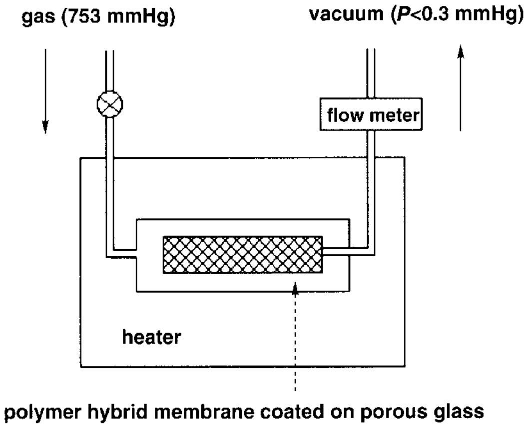


Fig. 1 The gas permeability measurement apparatus.

Table 1 Preparation of PVP–silica hybrid membranes

	PVP/MTMOS (wt/wt)	Ceramic yield[a,b]			
		Obs.(%)	Calc.(%)[c]	Obs./Calc.(%)	T_g[a,d]
Membrane(0)	0/1	73.8	89.5	82.5	—
Membrane(1/4)	1/4	82	62.5	131.2	142
Membrane(3/7)	3/7	35.2	51.4	68.5	131
Membrane(1/1)	1/1	23	32.8	70.1	148

[a]Properties of the transparent bulk polymer hybrids. [b]The ceramic yield was calculated by thermogravimetry. (The samples were heated to 30–900 °C in air.) [c]Ceramic yield = [wt[$RSi(OR)_3$] × {$M(SiO_2)/M[RSi(OR)]$}/wt[$RSi(OR)_3$] × {$M(RSiO_{1.5})/M[RSi(OR)_3]$} + wt(PVP)]. [d]Calculated from DSC. T_g of PVP = 84.8 °C.

Results and discussion

Structure of PVP–silica polymer hybrid membranes

To elucidate the mechanism of gas permeation in the polymer hybrid membranes, we investigated the temperature dependence of the permeation rate. The heating profile used entailed heating the films from 30 to 150 °C and the flux was recorded at 10 °C intervals. Initially the membrane prepared only from MTMOS was subjected to gas permeability measurements. It was found that membrane(0) showed a negative temperature dependence as shown in Fig. 2. The permeation rate of N_2, He and CO_2 decreased with increasing temperature, the values showing a linear relationship with $T^{-\frac{1}{2}}$ (Fig. 3). The results indicate that the diffusion of gases in the membrane follows a Knudsen mechanism.[29] As such, the membrane prepared from MTMOS was suspected to have a porous structure.

Permeability studies of PVP–silica polymer hybrid membranes were conducted under the same conditions. Initial contents of PVP and MTMOS were varied as shown in Table 1. The permeance of these gases in the polymer hybrid membranes exhibited quite different behavior from that of membrane(0). The permeance in membrane(1/4) along with other polymer hybrid membranes having different compositions is plotted as a function of temperature in Fig. 4. In contrast to the negative dependence of permeance with temperature in membrane(0) the permeance of each gas was increased with temperature, though the values themselves were much lower than that of membrane(0). The permeance of He for the polymer hybrid membranes remained in the range of 10^{-5} $cm^3(STP)\,cm^{-2}\,s^{-1}\,cmHg^{-1}$ while membrane(0) exhibited values as high as 10^{-4} $cm^3(STP)\,cm^{-2}\,s^{-1}\,cmHg^{-1}$. These results indicate the lack of pores in the polymer hybrid membranes and a very dense structure. Assuming that the temperature dependence of permeability is mainly governed by the diffusion of penetrant molecule, the low permeation rate and positive dependence on temperature could be attributed to a dissolution and diffusion mechanism for the polymer hybrid membranes, which is applied to non-porous membranes.[34–37] The non-porosity of the polymer hybrid membranes is a consequence of their flexibility; incorporation of organic polymers into the inorganic segments would provide flexibility to the matrix.[38] When the sol–gel reaction proceeds in the presence of organic polymers, the mass fractal structure of silica gel is retained by the integrated polymer chains, suppressing the collapse into silica particles having sharp interfaces.[39,40] The change in the segmental structure of silica gel is expected to contribute to the improvement of flexibility as a whole. Although membrane(1/4) contained only 18% of the organic component, this quantity was sufficient to dramatically affect the structure of the silica gel. The resulting flexibility presumably suppresses the formation of micropores during the drying process.

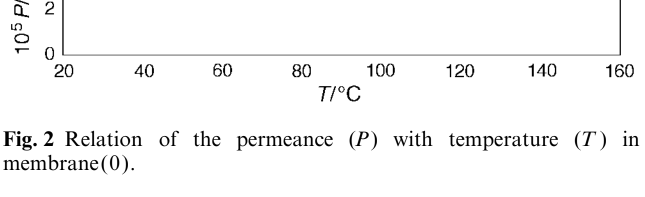


Fig. 2 Relation of the permeance (P) with temperature (T) in membrane(0).

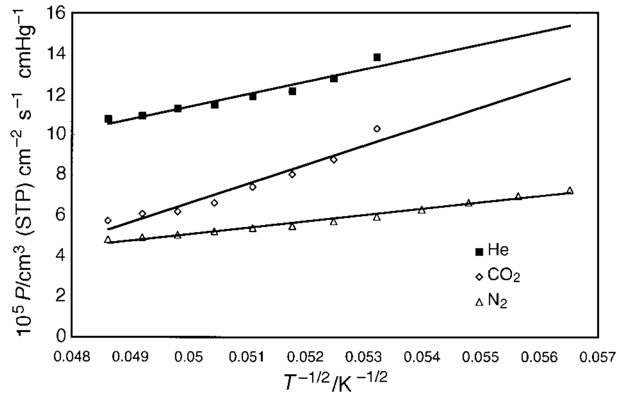


Fig. 3 Dependence of the permeance (P) with $T^{-\frac{1}{2}}$ in membrane(0).

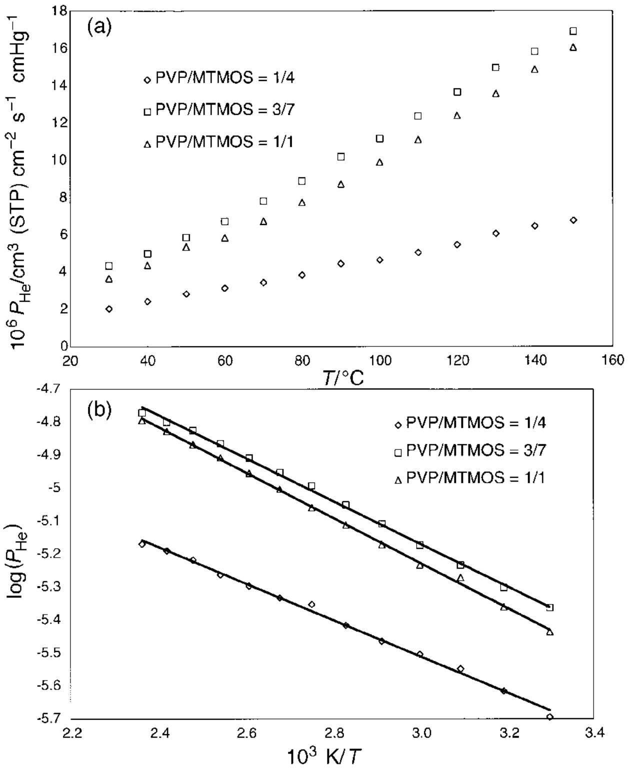


Fig. 4 (a) Relation of temperature (T) with the permeance of He (P_{He}) in the polymer hybrid membranes. (b) Arrhenius plot of the permeance of He (P_{He}) in the polymer hybrid membranes.

Differences of permeability with change of composition can be clearly observed by comparing the apparent activation energy of these polymer hybrid membranes calculated from an Arrhenius plot of the permeance. As shown in Fig. 4(b), a logarithmic plot of the permeance in the hybrid membranes *vs.* the reciprocal of the temperature shows a linear relationship and the activation energy for the permeation of He was calculated from the slope, which was found to be in the same range as observed in previous studies.[41,42] As shown in Table 2, the activation energy was found to increase with an increase of the initial PVP content from 1/4 to 3/7, *i.e.* the permeability

Table 2 Apparent activation energies for the permeation of He

	PVP/MTMOS (wt/wt)	Activation energy/ kJ mol^{-1}
Membrane(1/4)	1/4	6.9
Membrane(3/7)	3/7	10.7
Membrane(1/1)	1/1	12.1

of He became more temperature-dependent as the PVP content was increased. It can be speculated that some pores existed in polymer hybrid membranes when the PVP content was small, leading to some contribution from Knudsen flow in the pores as well as diffusion through the segments of the membrane, resulting in the reduction of the activation energy. On the other hand, a further densification of the membranes was achieved with an increase of PVP content, which leads to the suppression of Knudsen flow and relative increase of permeation through the segmental motion of the membranes. This leads to the more temperature dependent permeation of penetrant molecules in PVP rich polymer hybrid membranes.

Differences in the porosity of the hybrid membranes and MTMOS membranes could be clearly observed by SEM measurements. High porosity of the membrane prepared from MTMOS is seen in Fig. 5(a); although no cracks were observed it was found to have a very rough surface. A porous structure is formed in silica gel prepared by the sol–gel reaction of alkoxysilanes[6] and the roughness of the surface indicates an open structure. Even though the silica gel prepared from MTMOS possesses flexibility to an extent to form crack free membranes, the rigid nature of the silica gel matrix is expected to lead to a roughly packed structure giving rise to pores at an Å scale. On the other hand, as shown in Fig. 5(b)–(d), the polymer hybrid membranes showed a very smooth surface, quite different from that of membrane(0). As noted above, the polymer hybrids possessed more flexibility and drying would proceed without formation of cracks and pores. From the SEM image, it is also seen that the polymer hybrids were very homogeneous with no evidence for phase separation at a sub-micrometer scale. The non-porous nature of such polymer hybrid membranes has been also confirmed by Saegusa *et al.*, by employing atomic force microscopy (AFM) and nitrogen porosimetry, which also confirmed the homogeneity of the polymer hybrids at an Å scale.[43]

Selectivity towards gases of the polymer hybrid membranes

The polymer hybrid membranes prepared from PVP and MTMOS were found to possess a non-porous structure which would suppress Knudsen flow. The suppression of Knudsen flows supposedly provides higher selectivity than that resulting simply from differences in molecular weights of penetrants. The selectivity of CO_2 or He against N_2 was measured as a factor of temperature. The permeance of CO_2 and N_2 in the polymer hybrid membranes was measured by the same method as described above. The selectivity of each membrane against N_2 at a given temperature was calculated by simply dividing the permeance of the studied molecule by that of N_2.

The selectivity in membrane(0) was almost constant with temperature (Fig. 6). When a gas permeates through a membrane following Knudsen flow, the selectivity of the gas is simply a function of molecular weight, *i.e.* proportional to the inverse square root of molecular weight, and independent of temperature.[30] For He, the selectivity relative to N_2 (P_{He}/P_{N_2}) is 2.6 if the flow follows this mechanism. The experimental value of *ca.* 2.4 thus indicates Knudsen flow in membrane(0).

By contrast, the selectivity in the polymer hybrid membranes is temperature dependent and remarkably exceeds the value calculated for the Knudsen flow. Values obtained for P_{He}/P_{N_2} were at least >20. Although the selectivity of these gases in these polymer hybrid membranes exhibited some randomness, it should be noted that the selectivity of He against N_2 decreases with increasing temperature. (Any pertubations can

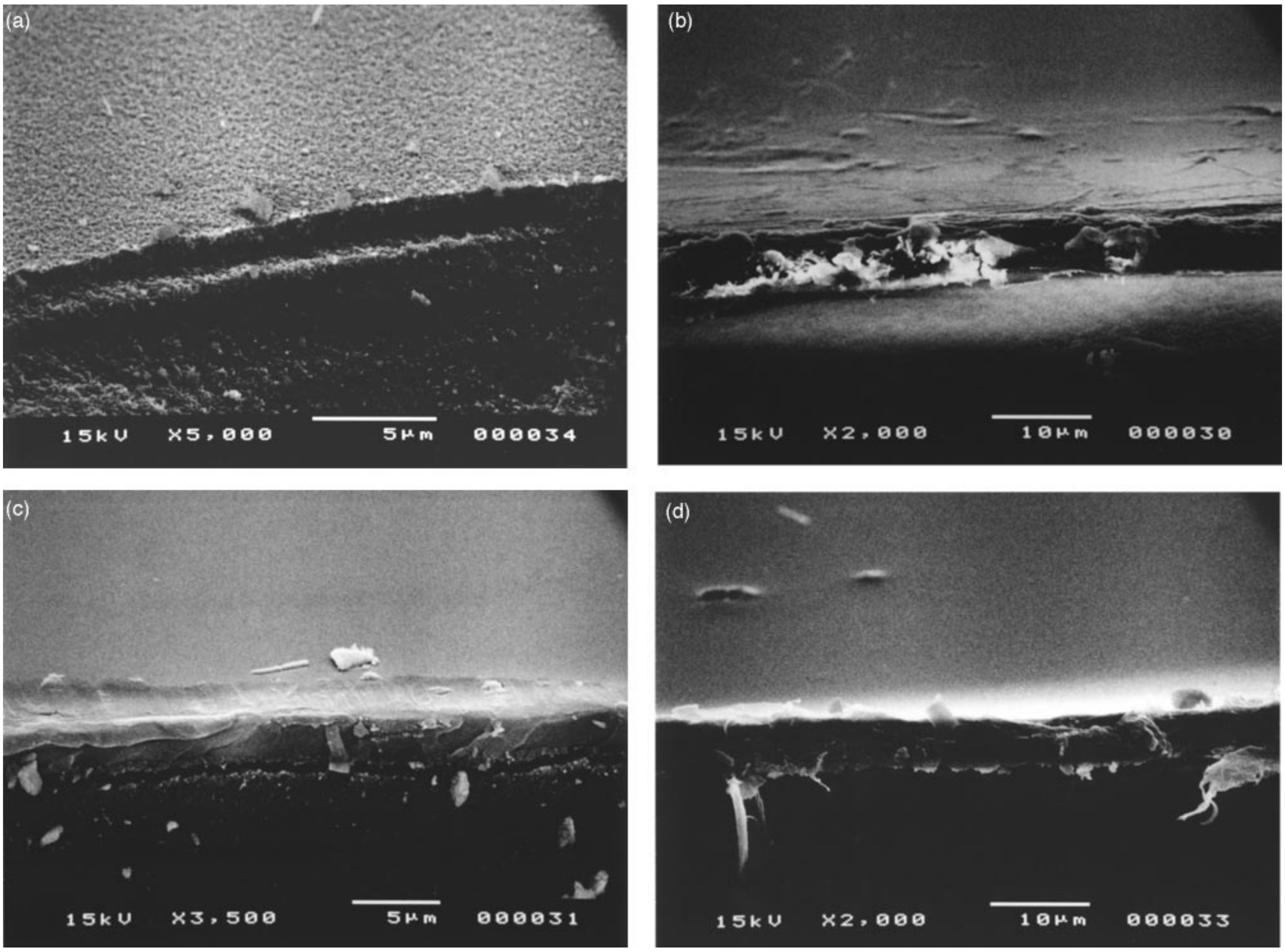


Fig. 5 SEM images of the silica membrane and polymer hybrid membranes: (a) membrane(0), (b) membrane(1/4), (c) membrane(3/7), (d) membrane(1/1).

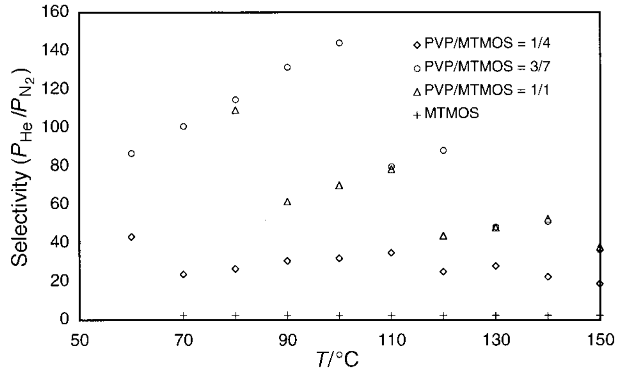


Fig. 6 Relation of temperature (T) with selectivity of He against N_2 (P_{He}/P_{N_2}).

be attributed to experimental error caused by the low performance of a flow meter used in the experiment which cannot measure a subtle increase of the flow with increasing temperature for N_2 permeability. For the same reason, the small value of N_2 permeation could not be detected below 50 °C making it impossible to calculate the selectivity.) The overall reduction in the selectivity with increasing temperature is caused by an increase of flow of N_2, which is the denominator in the selectivity coefficient. These polymer hybrid membranes exhibited high selectivity of He, with the high selectivity of He against N_2 attributable to the difference of the size of penetrant molecules, assuming the dissolution and diffusion mechanism for permeation in the membrane. The smaller a molecule, the larger the expected diffusion rate, resulting in the improvement of selectivity of He against N_2.[44–46]

The selectivity at each temperature increased with an increase in PVP content from 1/4 to 3/7. At low temperatures, the selectivity exceeded 100 for membrane(3/7). As discussed above, it is expected that the matrix becomes more flexible with increase in the organic polymer component, which results in the densification of the matrix and contributes to the further suppression of N_2 permeation and the reduction of Knudsen type diffusion. Further increase of PVP content to 1/1, however, did not lead to much change, which might be attributed to little further morphological change in the hybrid membrane with the membrane(3/7) already possessing a densely packed structure.

It is of considerable interest that CO_2 showed a higher permeation rate than N_2, even though the size of a CO_2 molecule is larger than that of N_2 (Fig. 7). The result could be explained by an uneven charge distribution within the CO_2 molecule resulting from the differing electronegativities of carbon and oxygen, which might lead to interaction with polar amide and silanol groups within the polymer hybrid membranes. The stronger interaction of the CO_2 molecule with the membranes may contribute to an improvement in dissolution rate of the molecule into the membranes.

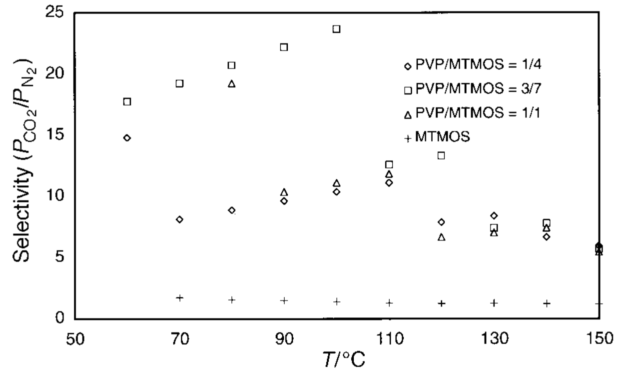


Fig. 7 Relation of temperature (T) with selectivity of CO_2 against N_2 (P_{CO_2}/P_{N_2}).

The selectivity of CO_2 against N_2 also increased with an increase in the PVP content from 1/4 to 3/7 as was found in the measurement of He selectivity. This result is also explained by the further densification of the membrane, resulting in the suppression of N_2 permeation. Increased polarity with an increase in PVP content further contributes to the improvement of CO_2 selectivity owing to improved dissolution of the molecule. The selectivity of CO_2 to N_2 could not be obtained below 50 °C again owing to poor instrumental performance; however, the value of P_{CO_2}/P_{N_2} exceeds 20 at 100 °C in membrane(3/7).

The polymer hybrid membranes were also found to possess high thermal stability. The high selectivity of He and CO_2 against N_2 was maintained even when temperature was raised above the glass transition temperature of the organic polymer. High thermal stability was also observed in membrane(1/1) consisting of 77 wt% organic polymer. We assume that the improved thermal stability in the polymer hybrid membranes was induced by the rigid matrix of the inorganic gel. The effect of the rigid silica matrix on the morphology of organic polymers has been intensely studied by Landry *et al.* who found suppression of deformation of the polymer matrix above the glass transition temperature in polymer hybrids.[39,47] We also observed the influence of the silica gel in changing the glass transition temperature (T_g). PVP shows a T_g of *ca.* 80 °C but when combined with silica gel, T_g shifts to 140 °C (Table 1). The increase in T_g indicates the reduction in the mobility of PVP chains, which influences the thermal properties.

Conclusion

The incorporation of organic polymers into silica gel dramatically influences the gas permeability. Knudsen diffusion was found to dominate over the dissolution and diffusion mechanism for membranes prepared only from MTMOS. With the integration of only 20 wt% of PVP, polymer hybrid membranes became densely packed. The dense structure of the polymer hybrids led to a dissolution mechanism for the permeation of gases and led to a much higher selectivity for He against N_2 in the polymer hybrid membranes than that calculated for Knudsen type flow. The polymer hybrid membranes also exhibited high selectivity for CO_2 against N_2, which could be attributed to the polar environment of the polymer hybrids induced by amide and silanol groups. These results demonstrate the dramatic modification of inorganic silica gel membranes by combination with organic polymer. The polymer hybrid membranes were also found to have high thermal stability. The high selectivities of He and CO_2 against N_2 were retained even at 150 °C due to the thermally stable rigid silica matrix which suppresses deformation of the polymer hybrid membranes.

Acknowledgements

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