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# Gas transport in bisphenol A poly(ether ether ketone ketone) membrane

Xin-Gui Li[a,b,*], Mei-Rong Huang[a], Ingo Kresse[b], Jürgen Springer[b]

[a]*Department of Polymer Materials Science and Engineering, College of Materials Science and Engineering, Tongji University, 1239 Siping Road, Shanghai 200092, People's Republic of China*

[b]*Macromolecular Chemistry, Institute of Technical Chemistry, Technical University of Berlin, D-10623 Berlin, Germany*

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## Abstract

A homogeneous dense membrane of bisphenol A poly(ether ether ketone ketone) (PEEKK) has been prepared by a solution casting technique with chloroform as solvent and characterized by wide-angle X-ray diffraction and tensile tester. Permeating characteristics of five pure gases through the membrane has been described systematically. The permeability, diffusivity, solubility, and their selectivities of oxygen, nitrogen, carbon dioxide, methane, and hydrogen through the membrane have been measured by a change in operating temperature and upstream pressure in a time-lag apparatus. A continuously enhanced permselectivity for gas pairs of carbon dioxide/methane, and hydrogen/nitrogen, an enhanced diffusivity selectivity for gas pairs of oxygen/nitrogen, carbon dioxide/methane, as well as a decreased permeability and diffusivity for five pure gases, have been observed with decreasing operating temperature. The solubility of five gases in the PEEKK membrane increases with decreasing temperature. The solubility selectivity hardly ever varies with operating temperature. Especially, the permeability, diffusivity, solubility, and their selectivities in the PEEKK membrane almost maintain constant with changing the upstream pressure. The highest oxygen/nitrogen, carbon dioxide/methane, and hydrogen/nitrogen selectivity coefficients were, respectively, equal to 7.06, 23.1, and 106.1. A relationship between the permeability or diffusivity and molecule diameter of the gases across the PEEKK membrane was discussed. The gas solubility in the membrane is believed to be a linear function of the critical temperature of the gases.

*Keywords*: Bisphenol A poly(ether ether ketone ketone); Homogeneous dense membrane; Gas transport

## 1. Introduction

It is known that wholly aromatic poly(ether ketone) is one of the advanced thermoplastics with excellent mechanical property, high thermal stability, solvent resistance, considerable toughness [1] and sometimes exhibits thermotropic liquid crystallinity [2,3]. Conversely, the poly(ether ketone) is difficult to process by a solution technique due to poor solubility. It is reported that an incorporation of substituent on phenyl rings of poly(ether ether ketone) can improve the solution processability [4,5]. It is found that a blend of sulfonated poly(ether ether ketone) with polysulfone is a good ultrafiltration and nanofiltration membrane with high water flux, high salt rejection, excellent reproducibility and stability, as well as reduced particle adhesion compared to polysulfone membrane [4]. Alkyl poly(ether ether ketone)s exhibit much higher gas permeability and low permselectivity [5]. An addition of isopropylidene group into the backbone of the poly(ether ketone) improves solubility, electrical properties and optical transparency without decreasing thermal stability. Bisphenol A poly(ether ether ketone ketone) (PEEKK) membrane takes a complete amorphous structure if it is prepared from the solution in chloroform [6]. The PEEKK has been believed as a kind of polymer material with better membrane-forming ability, high gas-separation capability, good flexibility, excellent durability, high transparency, and good solubility. Mohr et al. [6] investigated the gas sorption and transport properties of a series of PEEKKs containing two isopropylidene groups per repeat unit. Engelmann et al. [7] described the gas permeability of amorphous membrane made of cardo-poly(ether ether ketone). However, little report concerning a systematical investigation on the permeability, diffusivity, solubility, and their selectivities of oxygen ($O_2$), nitrogen ($N_2$), carbon dioxide ($CO_2$), methane ($CH_4$), hydrogen ($H_2$) through the PEEKK containing only a single isopropylidene group on each repeat unit was found.

In this paper, we attempt to provide a complete

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* Corresponding author. Address: Department of Polymer Materials Science and Engineering, College of Materials Science and Engineering, Tongji University, 1239 Siping Road, Shanghai 200092, People's Republic of China. Fax: +86-21-6579-9455.

*E-mail address:* lixingui@citiz.net (X.-G. Li).

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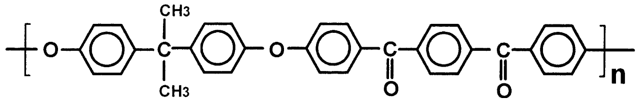


Scheme 1.

understanding of gas transport in the free-standing new PEEKK membrane by investigating, over an unprecedented range of temperature and pressure, the permeability, diffusivity, and solubility of five gases through the membrane, and to elaborate the variation of the permeability, diffusivity, solubility, and their selectivities with temperature and pressure. A relationship between the permeability/diffusivity and molecular diameter of the gases across the PEEKK membrane as well as between the gas solubility in the membrane and the critical temperature of the gases is discussed for the first time.

## 2. Experimental

### 2.1. Materials

Bisphenol A PEEKK particles were Ampek A from Hoechst. The molecular structure of the bisphenol A PEEKK is shown in Scheme 1. Chloroform of analytical reagent grade was directly used without any purification. The gases including $O_2$, $N_2$, $CO_2$, $CH_4$, and $H_2$ were obtained from Messer Griesheim GmbH, Duesseldorf, Germany. The purity of $CH_4$ was higher than 99.5%, and the other gases had the purity of more than 99.99%. The gases were used without any further purification.

### 2.2. Membrane preparation

PEEKK particles of 0.5 g were dissolved in 10 ml chloroform to form a 5 wt% solution. The polymer solution was poured into a Petri dish. Solvent was allowed to evaporate slowly from the solution at 25°C and 60% relative humidity for almost 20 h. The resultant membrane was removed from the Petri dish by pouring some water and dried in a high vacuum at 60°C for 6 h. PEEKK membrane is light yellow, flexible, transparent, and smooth and has a thickness of 40 μm.

### 2.3. Morphology characterization

The PEEKK membrane was characterized by wide-angle X-ray diffraction (WAXD) in a range of Bragg angle 3–50° using the wave length 0.154 nm of CuKα electron beam in step-by-step scanning region and recorded nickel filtered radiation at 25°C with a Bruker Analytical X-ray Systems D8 Advance X-ray Diffractometer made in Germany. The scanning rate is 3°/min. The tensile property of a 12 mm-wide PEEKK membrane was examined by an Instron Tensile Tester model 5565 made in USA.

### 2.4. Gas permeation measurements

The gas permeation performance of the PEEKK membrane was measured using a constant volume, variable pressure approach with a self-built vacuum time-lag apparatus [7–9]. All parts are held at a constant temperature (±0.2°C) in an air bath inside a thermostatic housing. The effective permeation area was 7.07 $cm^2$. After both sides of a membrane were evacuated, the pure gas was introduced to the upstream side of the membrane at a certain pressure, and was allowed to permeate to the downstream side at a pressure of 0.00001 bar. On the downstream side, a chamber of 43.8 $cm^3$ constant volume connected with a pressure gauge was attached to the membrane. After a certain period of time, a steady state was reached at which the amount of gas permeated increases linearly with time. The upstream and downstream pressures were measured by two pressure sensors and recorded online. The software developed in Technical University of Berlin ensures automated measurement with an automatically adapting data sampling rate to yield at least 600 data points and to describe time-lag and steady-state gas transport completely. Feed pressure was adjusted from 5 to 20 bar. The permeate pressure was recorded up to 10 mbar, depending on the feed gas. The permeability coefficient, $P$, was calculated from the slope of the straight line in the steady-state region. These measurements were carried out at 25°C for oxygen, nitrogen, carbon dioxide, methane, and hydrogen. The apparent diffusion coefficient $D$ was estimated from the time-lag $\tau$ by $D = l^2/6\tau$ ($l$ being the membrane thickness). The apparent solubility coefficient $S$ was calculated from $S = P/D$. When the downstream pressure is negligible relative to the upstream pressure, the ideal separation factor of a membrane for a gaseous mixture of A and B can be related simply to the ratio ($P_A/P_B$) of the permeabilities of A and B. Diffusion selectivity and solubility selectivity were defined as $D_A/D_B$ and $S_A/S_B$, respectively. The experimental errors vary with the magnitudes of the permeability and time-lag. The estimated errors in gas permeability, diffusivity, and solubility are about 3% for oxygen, carbon dioxide, and hydrogen, and about 5% for nitrogen and methane.

## 3. Results and discussion

### 3.1. Membrane characteristics

The PEEKK membrane looks homogeneous and lustrous with a naked eye. A WAXD diagram of the PEEKK membrane is shown in Fig. 1. Two major diffraction peaks at $d$-spacing of 0.283 nm or Bragg angle of 31.6° (stronger) and 0.446 nm or Bragg angle of 18.9° (weaker) are broad. These suggest that the PEEKK membrane is indeed amorphous. Almost the same diffraction angles were observed in the equatorial scan for oriented wholly aromatic PEEK film [10], but their diffraction intensities

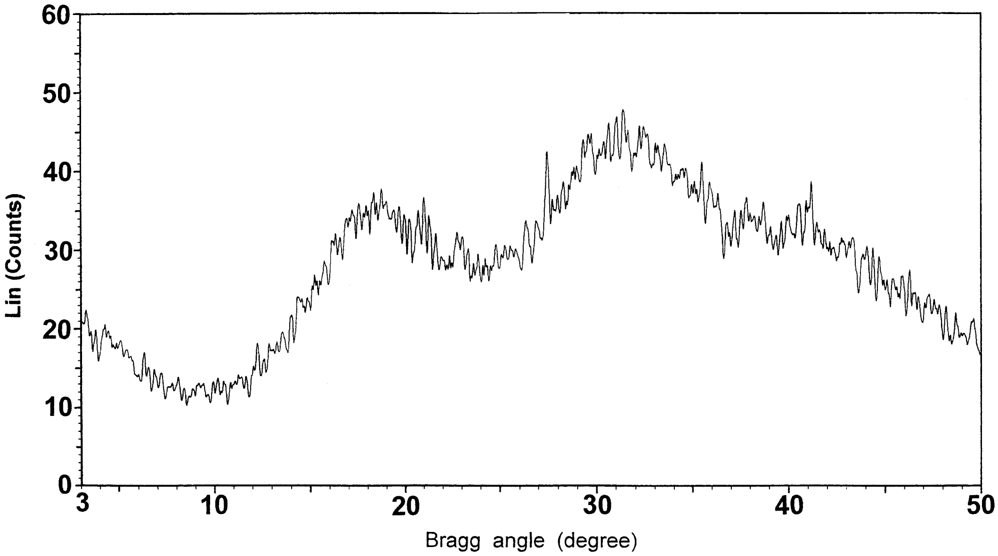


Fig. 1. WAXD diagram of bisphenol A PEEKK membrane.

are opposite, i.e. the peak at the Bragg angle of 30.4° is much weaker and the peak at 18.8° is much stronger and also sharper. Note that there is a scatter at the Bragg angle of around 3° shown in Fig. 1, implying there seems some domain with larger size. The tensile stretching behavior of the PEEKK film indicates that the tensile strength and initial modulus of the membrane are >70 and 1238 MPa, respectively. This result implies that the PEEKK membrane can be served as a gas-separation membrane that resists a large tensile stress.

### 3.2. Gas permeation performance

Five gases permeate the PEEKK membrane in different ways. $H_2$ permeates the membrane very rapidly after the shortest time-lag of 2 s because the molecular size of $H_2$ is small enough to pass freely through the free volume in the PEEKK membrane due to a short-range motion of chain molecules such as the vibrational and/or rotational motions of side chains. $O_2$ permeates the membrane at the third fastest rate after the second shortest time-lag of 150 s. $CO_2$ can permeate the membrane very rapidly after a long time-lag of 372 s. $CH_4$ permeates the membrane very slowly after the longest time-lag of 1670 s, whereas $N_2$ exhibits the second slowest permeation rate through the membrane with the second longest time-lag of 610 s. It is because of the different permeation characteristics of various gases through the membrane that the PEEKK membrane can be served as a high-performance membrane for gas separation. It should be noted that the PEEKK dense membrane with the thickness of less than 40 μm can withstand high temperature (55°C) and very high pressure difference (20 bar) for a long period of time without any membrane destructure and permselectivity loss. This observed behavior may have practical utility when good performance stability is an issue. It should be noted that not completely the same characteristics of permeation of five gases through the ethylcellulose membrane was found [11].

The $O_2$ permeation through the PEEKK membrane was investigated with increasing upstream pressure from 5 to 20 bar at 35°C. It can be found that the downstream pressure of the membrane increases rapidly after a small initial time-lag. The increase rate of downstream pressure with permeating time is strongly dependent on the upstream pressure. The slope of straight line of downstream pressure versus permeating time in a steady-state region has been used to calculate the permeability.

### 3.3. Effect of temperature on gas permeability and its selectivity

A typical relationship between gas permeability or permselectivity through the PEEKK membrane and reciprocal absolute temperature is shown in Fig. 2. The gas permeability through the membrane increased with an increase in temperature in a considered range of 25–55°C at a constant upstream pressure of 10 bar and is found to follow the Arrhenius law:

$$P = P_0 \exp\left(\frac{-E_P}{RT}\right) \tag{1}$$

The activation energy ($E_P$) values for $CO_2$, $H_2$, $O_2$, $N_2$, and $CH_4$ permeation through the membrane calculated by the Arrhenius law are 6.2, 6.9, 8.3, 11.4, and 12.6 kJ/mol, respectively. It was reported that the permeation activation energy through other polymer [7–9,11–14] and supported carbon molecular sieve membranes [15] follows almost the same trend with a variation of permeation gas, that is, the $E_P$ value for $CO_2$ is the smallest but the $E_P$ value for $CH_4$ is the largest. Note that the activation energy of permeation for the gases calculated in this paper is lower than that for two cardo-poly(ether ether ketone)s [7,14] possibly due to the

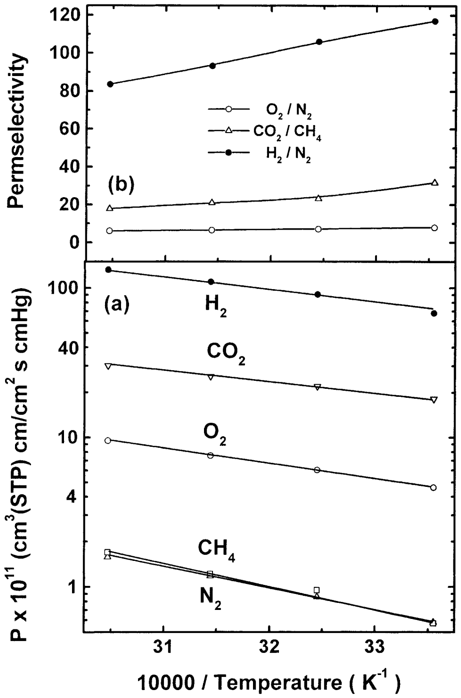


Fig. 2. The variation of permeability (a) and permeability selectivity (b) through bisphenol A PEEKK membrane with temperature at an upstream pressure of 10 bar.

difference of the molecular structure of the polymers. Additionally, as shown in Fig. 2(b), there is a linear relation between the permselectivity of three gas pairs and reciprocal temperature. The permselectivity increases with enhancing reciprocal absolute temperature where $P_{H_2}/P_{N_2}$ exhibits the strongest dependence on reciprocal temperature. This is a normal trend for most polymer membranes except for the liquid crystal membranes [16–19]. This significant decrease in the selectivity of three gas pairs is likely due to the dramatic increase of permeability of two slow gases $N_2$, and $CH_4$ from low temperature to high temperature, whereas the permeability of $H_2$, and $CO_2$ increases less. However, it is apparent that the selectivity of these gas pairs is high at lower temperature.

It can be seen from Fig. 2 that the permeability coefficients for the PEEKK membrane all over the temperature increase in the order of gases

$$P_{N_2} \leq P_{CH_4} < P_{O_2} < P_{CO_2} < P_{H_2}$$

The lowest $P_{N_2}$ is attributed to both a low diffusivity and the lowest solubility while the highest $P_{H_2}$ should be caused by its highest diffusivity of the five gases regardless of its lowest solubility, as discussed below. Three alkyl poly(ether ether ketone)s [5] and two isopropylidene-containing PEEKKs [6] also exhibit lower $P_{N_2}$ than $P_{CH_4}$. However, poly(ether ether ketone) [5], hexafluoroisopropylidene group-containing PEEKK [6] and cardo-poly(ether ether ketone) [7] appear to exhibit lower $P_{CH_4}$ than $P_{N_2}$.

### *3.4. Effect of temperature on gas diffusivity and its selectivity*

A typical relationship between gas diffusivity/its selectivity and reciprocal absolute temperature for PEEKK membrane is shown in Fig. 3. The gas diffusivity through the membrane increased with an increase in temperature in a considered range of 25–55°C at a constant upstream pressure of 10 bar and is found to follow the Arrhenius law:

$$D = D_0 \exp\left(\frac{-E_D}{RT}\right) \tag{2}$$

The activation energy ($E_D$) values for the $H_2$, $CO_2$, $O_2$, $N_2$, and $CH_4$ diffusion through the membrane calculated by the Arrhenius law are 12.8, 13.2, 15.3, 17.1, and 19.4 kJ/mol, respectively. It was reported that the diffusion activation energy through tetramethyl hexafluoro polycarbonate [20] and polypyrrolone [13] membranes follows almost the same trend with a variation in gas, that is, the $E_D$ value for $H_2$ is the smallest but the $E_D$ value for $CH_4$ is the largest. Additionally, as shown in Fig. 3(b), there is a substantially linear relation between the diffusivity selectivity of three gas pairs and reciprocal temperature. The diffusivity selectivity increases slightly with enhancing reciprocal temperature where $D_{CO_2}/D_{CH_4}$ exhibits slightly strong dependence on reciprocal temperature. This is a general trend for most polymer membranes.

It can be seen from Fig. 3 that the trend of the diffusion coefficients for five gases is quite different from the

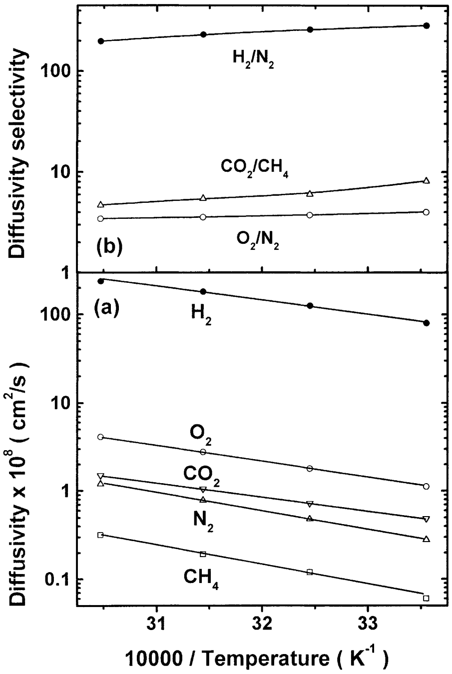


Fig. 3. The variation of diffusivity (a) and diffusivity selectivity (b) through bisphenol A PEEKK membrane with temperature at an upstream pressure of 10 bar.

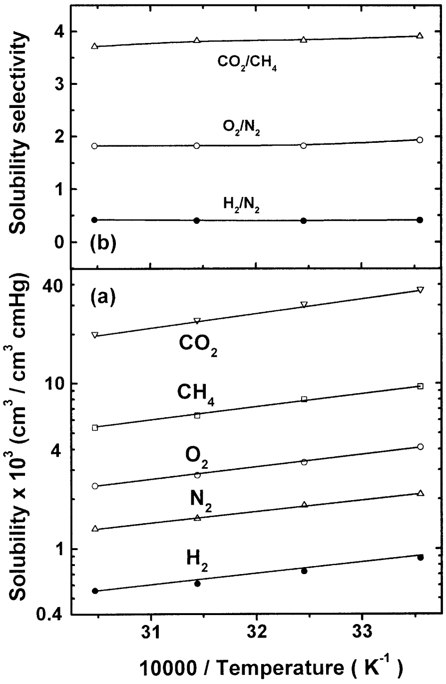


Fig. 4. The variation of solubility (a) and solubility selectivity (b) in bisphenol A PEEKK membrane with temperature at an upstream pressure of 10 bar.

permeability coefficients as follows:

$$D_{CH_4} < D_{N_2} < D_{CO_2} < D_{O_2} < D_{H_2}$$

It should be noted that the $D_{H_2}$ is the greatest since $H_2$ molecule has the smallest molecular diameter in the five gases. On the contrary, the smallest $D_{CH_4}$ should be due to its largest molecular diameter.

### *3.5. Effect of temperature on gas solubility and its selectivity*

A typical relationship between gas solubility or its selectivity in the PEEKK membrane and reciprocal absolute temperature is shown in Fig. 4. The gas solubility in the membrane increased with a decrease in temperature in a temperature range of 25–55°C at a constant upstream pressure of 10 bar and is found to follow the van't Hoff relationship:

$$S = S_0 \exp\left(\frac{-\Delta H_S}{RT}\right) \tag{3}$$

The solution heat ($\Delta H_S$) values for $H_2$, $N_2$, $O_2$, $CH_4$, and $CO_2$ in the membrane calculated by the van't Hoff relationship are 5.1, 5.7, 6.3, 6.8, and 7.3 kJ/mol, respectively. It was reported that the solution heat in tetramethyl polycarbonate membrane follows almost the same order with a variation of solution gas [20], that is, the $-\Delta H_S$ value for $CO_2$ is the largest. Additionally, as shown in Fig. 4(b), there is a substantially linear relation between the solubility selectivity of three gas pairs and reciprocal temperature. Their solubility selectivity increases with enhancing reciprocal temperature.

Fig. 4 also shows that the trend of the solubility coefficients for five gases is different from the trend of permeability and diffusivity.

$$S_{H_2} < S_{N_2} < S_{O_2} < S_{CH_4} < S_{CO_2}$$

The lowest $S_{H_2}$ is due to its weakest interaction with the membrane. The greatest $S_{CO_2}$ and $CO_2/CH_4$ solubility selectivity in the membranes are attributed to the relatively high solidification point and the strongest interacting of $CO_2$ with the membrane as compared with other gases, because the more condensable the gas is, the higher the gas solubility.

The values of permeability, diffusivity, and solubility of various gases measured at 35°C and upstream pressure 10 bar are summarized in Table 1. The highest permeability of the smallest $H_2$ molecule arises from its highest diffusivity, whereas $CO_2$ is the second most highly permeable because of its highest solubility. The lowest permeability of $N_2$ is mainly attributed to a cooperating effect of its second lowest diffusivity and the second lowest solubility. Table 2 summarizes the selectivity values of permeability, diffusivity, and solubility of three gas pairs at 35 and 55°C. Apparently, the highest permselectivity of $H_2/N_2$ is mainly due to their largest diffusivity selectivity, whereas the second highest permselectivity of $CO_2/CH_4$ is mainly due to its largest solubility selectivity. When the temperature is elevated to 55°C, the permselectivity of three gas pairs decreases because their diffusivity selectivity decreases significantly but their solubility selectivity remains almost a constant value, as shown in Fig. 2(b). The $H_2/N_2$ permselectivity is the most adversely affected, but $O_2/N_2$ permselectivity is the least affected. Therefore, the noticeable difference in permselectivity loss for these three gas pairs with increasing temperature should be nearly completely dependent on the diffusivity selectivity. This could be explained by considering the relative penetrant sizes. $H_2$ and $N_2$ molecules have the largest difference in diffusion activation

Table 1
Kinetic molecule diameter ($\sigma_K$), effective molecule diameter ($\sigma_{eff}$), and critical temperature ($T_C$) of gases and their permeability (*P*), diffusivity (*D*), and solubility (*S*) across bisphenol A PEEKK membrane at 35°C and 10 bar

| | Gas | | | | |
|---|---|---|---|---|---|
| | $H_2$ | $O_2$ | $CO_2$ | $N_2$ | $CH_4$ |
| $\sigma_K$ (nm) | 0.289 | 0.346 | 0.330 | 0.364 | 0.380 |
| $\sigma_{eff}$ (nm) | 0.290 | 0.344 | 0.363 | 0.366 | 0.381 |
| $T_C$ (°C) | 33.3 | 154.4 | 304.2 | 126.2 | 190.7 |
| $P^a$ | 90.7 | 6.04 | 21.9 | 0.87 | 0.84 |
| $D^b$ | 125 | 1.79 | 0.72 | 0.45 | 0.11 |
| $S^c$ | 0.73 | 3.37 | 30.4 | 1.9 | 8.0 |

[a] The unit of *P* is $10^{-11}$ $cm^3$(STP) cm/$cm^2$ s cmHg.
[b] The unit of *D* is $10^{-8}$ $cm^2$/s.
[c] The unit of *S* is $10^{-3}$ $cm^3$(STP)/$cm^3$ cmHg.

Table 2
The selectivity of permeability, diffusivity, and solubility of gases across bisphenol A PEEKK membrane at an upstream pressure of 10 bar

| Selectivity | 35°C | | | 55°C | | |
|---|---|---|---|---|---|---|
| | $O_2/N_2$ | $CO_2/CH_4$ | $H_2/N_2$ | $O_2/N_2$ | $CO_2/CH_4$ | $H_2/N_2$ |
| Permeability | 6.86 | 22.8 | 103.1 | 6.02 | 17.7 | 83.5 |
| Diffusivity | 3.78 | 6.00 | 277 | 3.43 | 4.69 | 198 |
| Solubility | 1.77 | 3.8 | 0.38 | 1.76 | 3.69 | 0.37 |

energy due to the largest size difference (0.075 nm), whereas $O_2$ and $N_2$ molecules have the smallest difference in diffusion activation energy due to the smallest size difference (0.018 nm). It is reported that the separation dependent on large size difference is undermined to a greater extent by increasing temperature since the diffusivity of larger molecules benefits more from increased polymer chain motion [13]. In addition, the diffusivity of $O_2$ and $N_2$ undergoes a comparable increase with increasing temperature, allowing the membrane to better maintain $O_2$ over $N_2$ separation capability. Similar results have been observed for aromatic polypyrrolone [13] and supported carbon membrane [15].

### 3.6. *Effect of upstream pressure on gas permeability and its selectivity*

The permeability of five gases through the PEEKK membrane at 35°C is shown in Fig. 5 as a function of upstream pressure from 5 to 20 bar. The $O_2$ permeability does not appear to be affected by pressure up to 20 bar, the permeability of $N_2$, $CO_2$, and $CH_4$ decreases with an increase in upstream pressure and approaches a limiting value at elevated upstream pressure, while $H_2$ permeability seems to increase slightly. It should be noted that $P_{H_2}$ slightly increases with increasing pressure, leading to a significant increase in $P_{H_2}/P_{N_2}$ in the corresponding pressure range, although $P_{O_2}/P_{N_2}$ and $P_{CO_2}/P_{CH_4}$ also increase with the upstream pressure. A similar $P_{H_2}$ versus upstream pressure relationship has been reported for ethyl cellulose [11] and polyamide 6 [21]. A contrary dependence of $P_{CO_2}/P_{CH_4}$ on upstream pressure has been observed for the polyimide membrane [22]. Negative $P_{N_2}$, $P_{CO_2}$, and $P_{CH_4}$ dependences on upstream pressure have been also observed for the other ether ketone polymer [5–7,23], polyimide [22], and polyamide 6 membranes [21]. This is a general phenomenon for the glassy polymers, because the free volume within the polymer might be reduced to some extent, therefore, the mobility of $N_2$, $CO_2$, and $CH_4$ molecules with larger molecular diameter decreases significantly with increasing upstream pressure [21]. In fact, the permeability dependence of $CH_4$ with the largest molecular diameter on upstream pressure is the strongest, as shown in Fig. 5(a). The mobility of $O_2$ with the second smallest molecular diameter almost remains constant with an increase in pressure, whereas the mobility of $H_2$ with the smallest molecular diameter is nearly not affected by the upstream pressure, because the reduction of free volume induced by increasing upstream pressure up to 20 bar has no effect upon the $H_2$ transportation in the polymer.

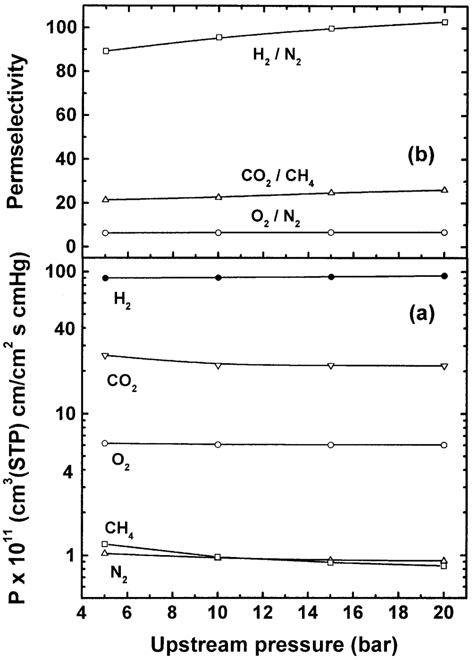


Fig. 5. The variation of permeability (a) and permeability selectivity (b) through bisphenol A PEEKK membrane with upstream pressure at 35°C.

### 3.7. *Effect of upstream pressure on gas diffusivity and its selectivity*

The diffusivity of five gases through the PEEKK membrane at 25°C is shown in Fig. 6 as a function of upstream pressure from 5 to 20 bar. The diffusivity of $O_2$, $N_2$, $CH_4$ and $H_2$ through the PEEKK membrane maintains nearly constant but the $CO_2$ diffusivity increases slightly with increasing upstream driving pressure, leading to almost constant $D_{O_2}/D_{N_2}$ and $D_{H_2}/D_{N_2}$ values in the corresponding pressure range. The positive pressure-dependent $D_{CO_2}$ and $D_{O_2}/D_{CH_4}$ have been interpreted by using a partial immobilization model. A similar result has been observed for the cardo-poly(ether ether ketone) membrane [7] as found for glassy polymers.

### 3.8. *Effect of upstream pressure on gas solubility and its selectivity*

The solubility of five gases in the PEEKK membrane at 25°C is shown in Fig. 7 as a function of upstream pressure from 5 to 20 bar. The $H_2$ solubility in the PEEKK membrane remains constant at a very low value with increasing upstream pressure, the solubility of $O_2$ and $N_2$ decreases slightly, but the solubility of $CO_2$ and $CH_4$ decreases significantly. Especially $CO_2$ solubility decreases steadily at the fastest rate, leading to a significant decline of $S_{CO_2}/S_{CH_4}$ values in the corresponding pressure range. The negative

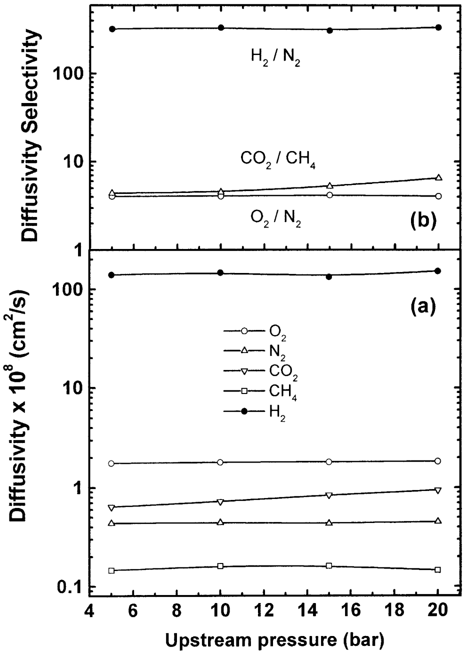


Fig. 6. The variation of diffusivity (a) and diffusivity selectivity (b) through bisphenol A PEEKK membrane with upstream pressure at 35°C.

pressure-dependent solubility has been interpreted by using a partial immobilization model [11]. Quite the contrary, $S_{O_2}/S_{N_2}$ exhibits a slight increase trend since $S_{N_2}$ decreases at a faster rate than $S_{O_2}$. $S_{H_2}/S_{N_2}$ keeps at a very low and constant value with the variation of pressure due to a very low and constant $S_{H_2}$ value.

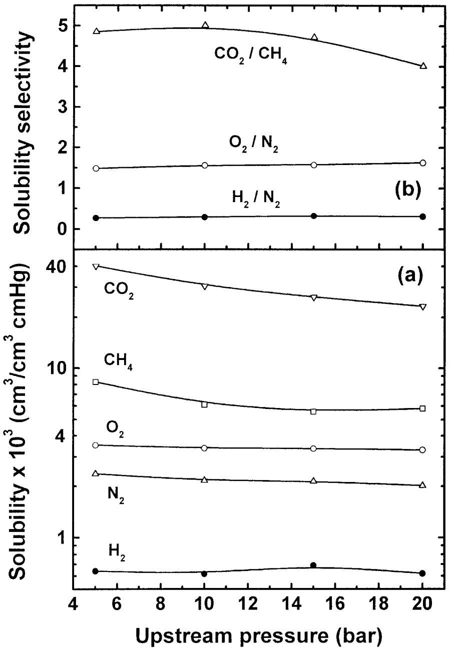


Fig. 7. The variation of solubility (a) and solubility selectivity (b) in bisphenol A PEEKK membrane with upstream pressure at 35°C.

### 3.9. The relationship between gas permeability and molecular diameter

Fig. 8 gives plots of the gas permeability vs. kinetic molecular diameter listed in Table 1 for five penetrants through the PEEKK membrane. The permeability increased linearly as the kinetic diameter of the gases decreased, indicating that the behavior of permeation appears to follow the transport mechanism dependent on the molecular sieving. This is similar with the relationship between the permeance and kinetic diameter of gas through non-oxidized dense carbon membrane showing high $O_2/N_2$ permselectivity 11.4 and $CO_2/CH_4$ permselectivity 120 [24]. The apparent activation energy $E_P$ of permeation of the gases through the PEEKK membrane as a function of kinetic diameter of the gases is also shown in Fig. 8. The activation energy of the permeation for $CO_2$, $O_2$, $N_2$, and $CH_4$ increased with the increase of the gas size, whereas it decreased slightly with increasing gas size for $H_2$ and $CO_2$. The larger penetrants such as $O_2$, $N_2$, and $CH_4$ caused an increase in the permeation activation energy owing to molecular sieving effect rather than adsorption effect [25], which is consistent with the decrease of permeability caused by molecular sieving effect. Note that the transport of $CO_2$ and $H_2$ might be governed by the adsorption process, leading to high $CO_2/CH_4$ permselectivity [25]. A similar relationship between permeation activation energy and gas size has been observed for the carbonized hollow fiber membranes [25].

### 3.10. The relationship between gas diffusivity and molecular diameter

Fig. 9(a) gives plots of the gas diffusivity vs. square value of effective molecular diameters at different temperatures or upstream pressures on the basis of the empirical relationship between gas diffusivity and effective diameter ($\sigma_{\text{eff}}$) of gas molecules listed in Table 1 by Eq. (4):

$$D = K_1 \exp[-K_2(\sigma_{\text{eff}})^2] \qquad (4)$$

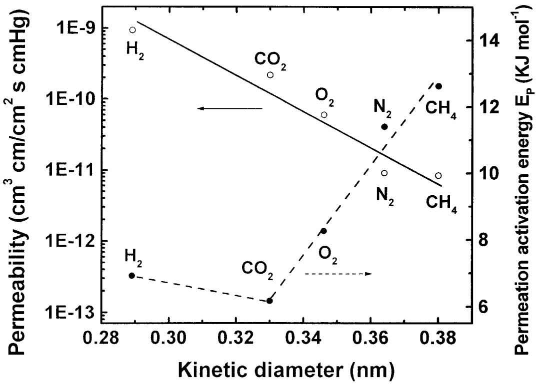


Fig. 8. Gas permeability and permeation activation energy across bisphenol A PEEKK membrane as a function of the kinetic diameter of gases at 35°C and an upstream pressure of 20 bar.

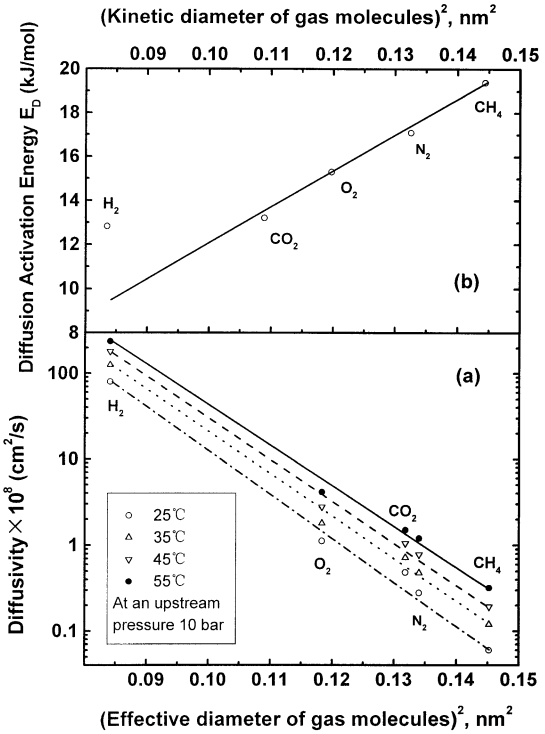


Fig. 9. Gas diffusivity (a) and diffusion activation energy (b) across bisphenol A PEEKK membrane as a function of the square of gas molecule diameter at four temperatures and an upstream pressure of 10 bar.

where $K_1$ and $K_2$ are constants and

$$(\sigma_{\mathrm{eff}})^2 = (\text{collision diameter} \times \text{kinetic diameter}) \qquad (5)$$

Four straight lines with different slopes are obtained. It appears that the slope of the line decreases with increasing temperature. That is to say, the dependence of gas diffusivity on the effective molecule diameter becomes weaker with increasing temperature. Note that only $CO_2$ and $O_2$ data points deviate sometimes from the straight lines. A very similar result has been obtained for ethyl cellulose membrane [11]. It was reported that the diffusion process of the gas penetrant occurs along a cylindrical volume defined by the kinetic diameter of penetrant, $\sigma_K$ (Table 1), and the average length of its diffusional step, $\lambda$. The product of the cylindrical volume and the cohesive energy density, $E_{\mathrm{coh}}$, of the polymer equals the activation energy for diffusion as follows [20]:

$$E_D = \frac{\pi}{4}\sigma_K^2 \lambda E_{\mathrm{coh}} \qquad (6)$$

On the basis of Eq. (6), Fig. 9(b) shows a reasonable relationship between $E_D$ values and the square of the kinetic diameter ($\sigma_K$) of gases. If the kinetic diameter, $\sigma_K$, is replaced with effective diameter, the linearity of the relationship will be poorer. Note that the $E_D$ values for $CO_2$ and $N_2$ appear to be slightly low. Quite the contrary, the $E_D$ value of $H_2$ apparently deviates from the straight line. Very similar relation between $E_D$ values and the square of the molecular diameter of gases through tetramethyl hexafluoro polycarbonate [20] and polypyrrolone [13] was reported. The linear relation between $E_D$ and $\sigma_K^2$ follows the interpretation for penetrant diffusion through polymer matrices [13].

### *3.11. The relationship between gas solubility and critical temperature ($T_C$)*

The gas solubility in the membrane is correlated with critical temperature ($T_C$) listed in Table 1 by Eq. (7):

$$\ln S = \ln S_0 + K_C T_C \qquad (7)$$

where $S_0$ and $K_C$ are constants. The critical temperature is a measure of the condensation tendency for gaseous molecules. The solubility of five gases in the PEEKK membrane as a function of critical temperature is shown in Fig. 10(a). It is seen that the solubility increases almost linearly as the critical temperature increases and the dependency of the solubility on the critical temperature becomes weaker with increasing operating temperature. Only the $CH_4$ data points deviate positively from the straight line but the $N_2$ data points deviate negatively from the straight line. In addition, the solution heat seems to be substantially correlated with critical temperature of gases, as shown in Fig. 10(b). Note that the solution heat for $CH_4$ and $O_2$ deviates positively from the straight line, but the solution heat for $N_2$ deviates negatively from the straight line possibly due to the difference of the interaction of these gases with PEEKK as

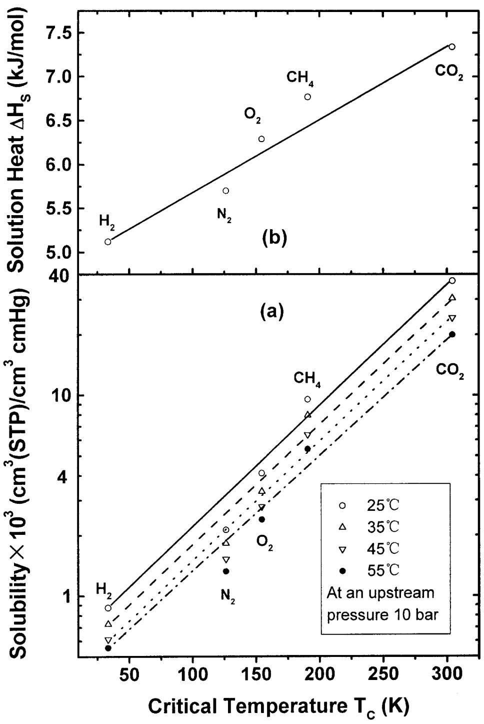


Fig. 10. Gas solubility (a) and solution heat (b) in bisphenol A PEEKK membrane as a function of critical temperature at an upstream pressure of 10 bar and four temperatures.

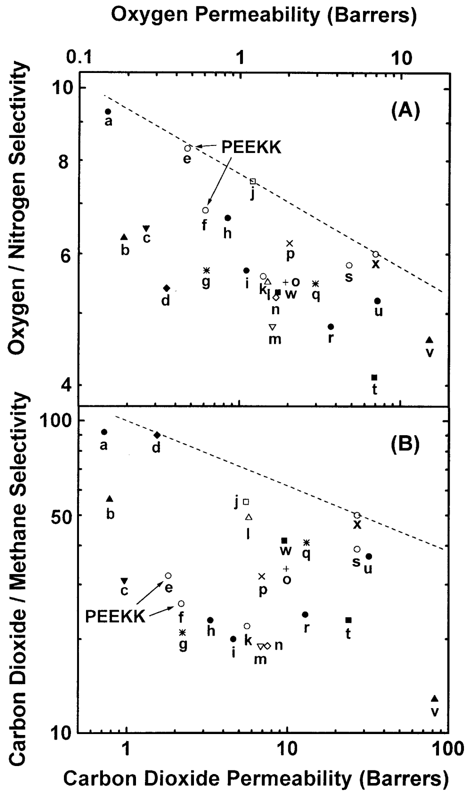


Fig. 11. Comparison of oxygen/nitrogen (A) and carbon dioxide/methane (B) permselectivity in various glassy aromatic polymers exhibiting higher permselectivity reported recently: (a) polyaniline [27,28]; (b) polysulfone amide [29]; (c) poly(ether ether ketone) [5]; (d) polyamide imide [8]; (e) PEEKK at 25°C and (f) PEEKK at 35°C in this study; (g) poly(*o*-phenetidine) [30]; (h) poly(4-vinylpyridine) [31]; (i) poly(ether ketone) [6]; (j) polytriazole [32]; (k) polysulfone [33]; (l) fluorinated polyamide imide [34]; (m) polycarbonate [35]; (n) polyarylate [31]; (o) hexafluoro polythioether imide [36]; (p) poly(*N*-methylpyrrole) [37]; (q) hexafluoro polysulfone imide [36]; (r) dodecylfluoro poly(ether ketone) [6]; (s) pentylmethyl polyether imide [38]; (t) hexafluoro polycarbonate [35]; (u) hexafluoro polytetramethylterphenylene imide [39]; (v) poly(2,6-dimethylphenylene oxide) [40]; (w) hexafluoro polyamide imide [41]; (x) polypyrrolone [13,42].

compared with $CO_2$ and $H_2$ [20]. A similar correlation of solution heat with the critical temperature of gases in ethyl cellulose [11] and bisphenol A polycarbonate has been observed [20].

### *3.12. Comparison of gas transport in PEEKK membrane and various aromatic polymer membranes*

Table 3 lists the gas permeation properties of 10 types of ether ketone polymers including PEEKKs, poly(ether ether ketone)s, and poly(ether ketone ketone)s. It is seen that wholly aromatic poly(ether ketone ketone)s exhibits the highest $O_2/N_2$ and $H_2/N_2$ selectivities in the 10 polymers but the lowest $O_2$ and $H_2$ permeability. Tetramethylbiphenyl unit-containing poly(ether ether ketone) has the highest $O_2$ and $CO_2$ permeability, but its $O_2/N_2$ and $CO_2/CH_4$ permselectivities are low as compared with most of other polymers listed in Table 3. The bisphenol A PEEKK prepared in this study shows the second highest $O_2/N_2$, $CO_2/CH_4$, and $H_2/N_2$ selectivity, being accompanied with relatively low gas permeability. By the way, incorporating *tert*-butyl or tetramethyl or cardo groups into the ether ketone polymers, increasing the content of *tert*-butyl side group or isopropylidene unit in the backbone of the polymers, and fluorinating the isopropylidene inside the ether ketone polymers, all increase their gas permeability but decrease the selectivity, because the free volume in the polymers is increased.

Figs. 11 and 12 show the relationship between $O_2$ permeability and $O_2/N_2$ selectivity, $CO_2$ permeability and $CO_2/CH_4$ selectivity, $H_2$ permeability and $H_2/N_2$ selectivity through various glassy aromatic polymers reported recently. The PEEKK membrane prepared in this study has higher comprehensive $O_2/N_2$ permselectivity and $H_2/N_2$ permselectivity than most of the polymers shown. $CO_2/CH_4$ permselectivity of the PEEKK is not good enough. It appears that more aromatic nitrogen-containing polypyrrolone exhibits the impressive comprehensive $O_2/N_2$, $CO_2/CH_4$, and $H_2/N_2$ permselectivities. Another more aromatic nitrogen-containing polytriazole also exhibits good comprehensive $O_2/N_2$ permselectivity. Pentylmethyl polyether imide and polyamide imide exhibit better comprehensive $H_2/N_2$ and $CO_2/CH_4$ separation performance, respectively. It should be noted that a common problem of polytriazole, polypyrrolone, pentylmethylpolyether imide, and polyamide imide is that their chemical composition is complicated and their preparation is difficult. For example, polytriazole is synthesized by a slow condensation reaction for ca. 6 days at 179–190°C in nitrogen [32], leading to an increase in membrane

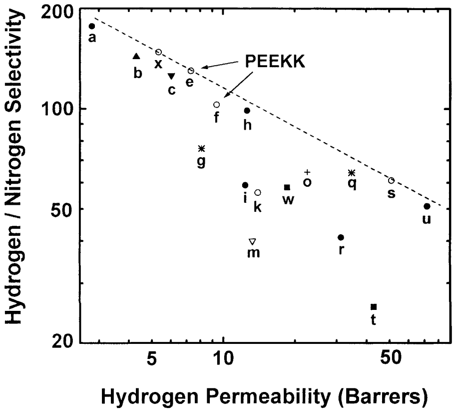


Fig. 12. Comparison of hydrogen over nitrogen permselectivity in various glassy aromatic polymers exhibiting higher permselectivity reported recently as follows: (a) polyaniline [27,28]; (b) polysulfone amide [29]; (c) poly(*o*-anisidine) [30]; (e) PEEKK at 25°C; (f) PEEKK at 35°C in this study; (g) poly(*o*-phenetidine) [30]; (h) poly(4-vinylpyridine) [31]; (i) poly(ether ketone) [6]; (k) polysulfone [33]; (m) polycarbonate [35]; (o) hexafluoro polythioether imide [36]; (q) hexafluoro polysulfone imide [36]; (r) dodecylfluoro poly(ether ketone) [6]; (s) pentylmethyl polyether imide [38]; (t) hexafluoro polycarbonate [35]; (u) hexafluoro polytetramethylterphenylene imide [39]; (w) hexafluoro polyamide imide [41]; (x) polypyrrolone [42].

Table 3
Comparison of gas transport in various aromatic poly(ether ketone) membranes

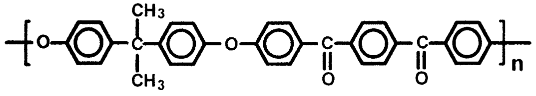
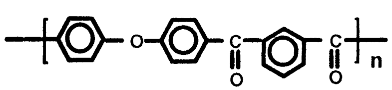
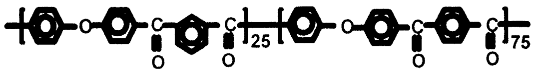
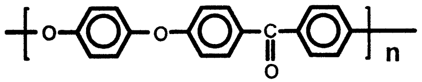
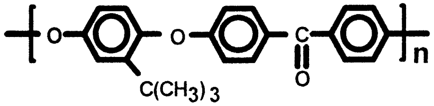
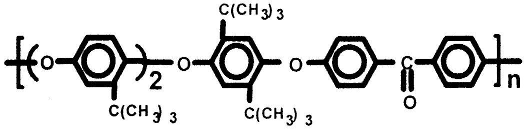
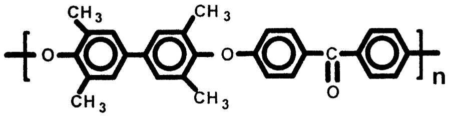
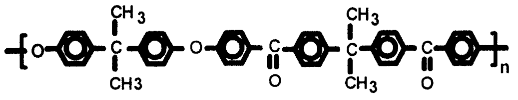
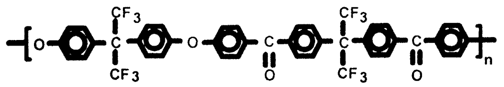
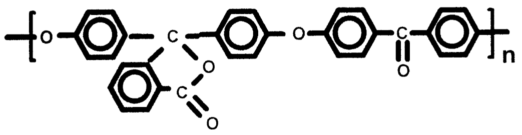
| Polymer chain structure | Temperature (°C) | Permeability (Barrers) | | | Selectivity | | | Refs. |
|---|---|---|---|---|---|---|---|---|
| | | $O_2$ | $CO_2$ | $H_2$ | $O_2/N_2$ | $CO_2/CH_4$ | $H_2/N_2$ | |
|  | 25 | 0.47 | 1.81 | 7.31 | 8.3 | 32 | 130 | This study |
|  | 35<br>30 | 0.61<br>0.09 | 2.18<br>– | 9.38<br>2.50 | 6.86<br>8.1 | 26<br>– | 103<br>220 | This study<br>[26] |
|  | 30 | 0.17 | – | 2.90 | 8.3 | – | 140 | [26] |
|  | 35 | 0.26 | 0.96 | – | 6.5 | 31 | – | [5] |
|  | 35 | 1.39 | 4.65 | – | 6.4 | 21 | – | [5] |
|  | 35 | 2.19 | 6.91 | – | 6.3 | 18 | – | [5] |
|  | 35 | 4.76 | 19.4 | – | 4.9 | 19 | – | [5] |

Table 3 (*continued*)

| Polymer chain structure | Temperature (°C) | Permeability (Barrers) | | | Selectivity | | | Refs. |
|---|---|---|---|---|---|---|---|---|
| | | $O_2$ | $CO_2$ | $H_2$ | $O_2/N_2$ | $CO_2/CH_4$ | $H_2/N_2$ | |
|  | 35 | 1.1 | 4.6 | 12.4 | 5.7 | 20 | 59 | [6] |
|  | 35 | 3.7 | 12.9 | 31.4 | 4.8 | 24 | 41 | [6] |
|  | 25 | 1.0 | 2.7 | 5.0 | 5.7 | 32 | 32 | [14] |

cost. The productivity, separation efficiency, durability of the membrane must be balanced against cost in all cases [43].

## 4. Conclusions

The temperature dependence of permeability, diffusivity, and solubility through and in the PEEKK membrane is in accordance to Arrhenius equation and a van't Hoff relationship, respectively. The activation energy $E_P$ of gas permeation is primarily governed by changes in diffusion activation energy since $|E_D| > |\Delta H_S|$ for each gas. Different upstream pressure-dependent behaviors for the permeation, diffusion, and solution of gases through and in the PEEKK membrane have been observed. The size of gas molecules affects significantly the permeation and diffusion performances through the membrane. A linear relationship between effective molecule diameter of the gases and their diffusivity or between kinetic molecule diameter and permeability or activation energy of permeation or diffusion through the PEEKK membrane has been found. There is an almost linear relationship between the critical temperature and solubility or solution heat of the gases in the PEEKK membrane. The PEEKK membrane may be useful as a membrane for gas separation based on a careful comparison of gas permeability and permselectivity through various glassy aromatic polymers reported recently.

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