Gas and vapor transport properties of amorphous perfluorinated copolymer membranes based on 2,2-bistrifluoromethyl-4,5-difluoro-1,3-dioxole/tetrafluoroethylene

Ingo Pinnau *, Lora G. Toy

Membrane Technology and Research, Inc., 1360 Willow Road, Suite 103, Menlo Park, CA 94025, USA

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Abstract

Teflon AF 2400 (Du Pont) is an amorphous, glassy perfluorinated copolymer containing 87 mol% 2,2-bistrifluoromethyl-4,5-difluoro-1,3-dioxole and 13 mol% tetrafluoroethylene. The polymer has an extremely high fractional free volume of 0.327. Permeability coefficients for helium, hydrogen, carbon dioxide, oxygen, nitrogen, methane, ethane, propane, and chlorodifluoromethane (Freon 22) were determined at temperatures from 25 to 60°C and pressures from 20 to 120 psig. Permeation properties were also determined at a feed pressure of 200 psig at 25°C with a 2 mol% n-butane/98 mol% methane mixture. Permeabilities of permanent gases in Teflon AF 2400 are among the highest of all known polymers; the oxygen permeability coefficient at 25°C is $1600 \times 10^{-10} \text{cm}^3(\text{STP}) \text{cm}^2 \text{s cmHg}$ and the nitrogen permeability coefficient is $780 \times 10^{-10} \text{cm}^3(\text{STP}) \text{cm}^2 \text{s cmHg}$. The permeabilities of organic vapors increase up to 20-fold as the vapor activity increases from 0.1 to unity, indicating that Teflon AF 2400 is easily plasticized. Although Teflon AF 2400 is an ultrahigh-free-volume polymer like poly(1-trimethylsilyl-1-propyne) [PTMSP], their gas permeation properties differ significantly. Teflon AF 2400 shows gas transport behavior similar to that of conventional, low-free-volume glassy polymers. PTMSP, on the other hand, acts more like a nanoporous carbon than a conventional glassy polymer.

Keywords: 2,2-Bistrifluoromethyl-4,5-difluoro-1,3-dioxole; Tetrafluoroethylene; Copolymer; Gas transport; Vapor separation; Activation energy of permeation; Teflon AF 2400; PTMSP

1. Introduction

In the last decade, remarkable progress has been made in the development of high-performance polymers for gas separations. In particular, glassy polymers such as polyimides [1–3], polycarbonates [4–6], polysulfone, and cellulose acetate have been widely applied to the separation of permanent gas mixtures such as oxygen/nitrogen, carbon dioxide/methane and hydrogen/nitrogen.

Several recent patents and papers describe the synthesis and gas permeation properties of glassy 2,2-bistrifluoromethyl-4,5-difluoro-1,3-dioxole [PDD]-based polymers and copolymers [7–11]. This family of perfluorinated polymers has similar chemical and thermal stability to semicrystalline poly (tetrafluoroethylene) [PTFE] and poly (hexafluoropropylene-
tetrafluoroethylene) [FEP]. However, PDD and PDD-PTFE copolymers containing at least 20 mol% PDD in the repeat unit are amorphous, high-free-volume, glassy materials [9]. PDD-PTFE copolymers with 65 and 87 mol% PDD, respectively, are commercially available from Du Pont (Wilmington, DE) as Teflon AF 1600 and Teflon AF 2400. In this paper, we report the permeability properties of Teflon AF 2400 and compare them to those of poly(1-trimethylsilyl-1-propyne) [PTMSP], a high-free-volume glassy material, and those of polycarbonate, a representative conventional, low-free-volume glassy polymer.

Nemser and Roman have already reported some permeability properties of Teflon AF polymers. Apparently, the polymers are very permeable to permanent gases; the oxygen and nitrogen permeability coefficients of melt-pressed Teflon AF 2400 films were $990 \times 10^{-10}$ and $480 \times 10^{-10}$ cm$^3$(STP) cm$^{-2}$ s$^{-1}$ cmHg respectively [10]. Nemser and Roman also claim that Teflon AF 2400 is essentially impermeable to organic vapors such as n-butane and toluene [10,11]. These results suggest that Teflon AF 2400 may be a candidate membrane material for the separation of organic vapors from air. In contrast to other high-free-volume glassy polymers such as PTMSP, the gas permeability of PDD-based polymers shows good long-term stability [10,11].

2. Experimental

2.1. Materials

Teflon AF 2400, an amorphous PDD-PTFE copolymer containing 87 mol% 2,2-bistrifluoromethyl-4,5-difluoro-1,3-dioxole and 13 mol% tetrafluoroethylene, was obtained from Du Pont (Wilmington, DE). The structure of this copolymer is shown in Fig. 1. Teflon AF 2400 has a glass transition temperature of 240°C and a density of 1.744 g/cm$^3$ at 25°C [9].

The steric bulkiness of two trifluoromethyl substituent groups on the dioxole ring inhibits dense chain packing. The specific free volume (SFV) (free volume/g of polymer) and the fractional free volume (FFV) (free volume/cm$^3$ of polymer), commonly used as measures for the free volume potentially available for gas transport and for the chain packing density of polymers [12-14], are defined as [15]:

$$\text{SFV} = \nu_{sp} - \nu_0 = \nu_{sp} - 1.3 \nu_w$$

(1)

$$\text{FFV} = \text{SFV} / \nu_{sp}$$

(2)

where $\nu_{sp}$ is the specific volume (cm$^3$/g) of the polymer as determined from density or thermal expansion measurements, and $\nu_0$ is the zero point volume at 0 K. The van der Waals volume, $\nu_w$, was calculated using the group contribution method of Bondi [15]. The calculated SFV and FFV of Teflon AF 2400 are 0.192 and 0.327, respectively. These values are much higher than those of other high-free-volume glassy polymers such as fluorinated polyimides or fluorinated polycarbonates [16,17], which typically have fractional free volumes in the range 0.18 to 0.22.

Teflon AF 2400 shows excellent resistance to organic solvents; the only known solvents are perfluorinated compounds [9]. In this study, perfluoro-N-methyl morpholine [C$_3$F$_7$NO] (PF 5052, 3M Company, St. Paul, MN) was used to prepare solution-cast films.

The gases used for the pure gas permeation experiments, nitrogen, oxygen, carbon dioxide, hydrogen, helium, methane, ethane, propane, and chlorodifluoromethane (Freon 22), had a purity of at least 99.5 mol%. Permeation experiments were also performed with a certified gas mixture of 2 mol% n-butane/98 mol% methane.

2.2. Membrane preparation

Isotropic, dense Teflon AF 2400 films were made by casting a 1-wt% polymer solution in perfluoro-N-methyl-morpholine on glass plates with a doctor blade. The films were air-dried overnight at ambient conditions. The clear films were stripped from the glass
plates, and then dried in a vacuum oven at 150°C for three days. To ensure that the films were completely solvent-free, the films were removed from the oven periodically and weighed on an analytical balance. The thicknesses of the films were determined with a precision micrometer. Film samples with thicknesses of 14–20 μm (± 0.5 μm) were used for the permeation experiments.

2.3. Gas permeation measurements

Pure gas measurements

The gas permeation properties of isotropic Teflon AF 2400 films were determined for membrane samples of 12.6 cm²/surface area using the constant pressure/variable volume method [18]. The feed pressure was varied between 20 and 120 psig; the permeate pressure was atmospheric (0 psig). Measurements were carried out at temperatures between 25 and 60°C by immersing the test cell in a constant-temperature (± 0.5°C) water bath. Gas flow rates were determined using soap-film flowmeters. The feed and permeate side of the permeation cell were always purged with the test gas prior to the permeation run. The high gas flow rates through Teflon AF 2400 precluded any back-diffusion of air into the permeation cell. The experimental error in the permeabilities of isotropic Teflon AF 2400 films were estimated to be about ± 5%.

The steady-state flux, J, measured by the constant pressure/variable volume method, is given by:

\[
J = \frac{273.15 p_a}{767 A} \left( \frac{dV}{dt} \right)
\]

where J is the steady-state gas flux (cm³(STP)/cm²·s), A is the membrane area (cm²), p_a is the atmospheric pressure (cmHg), T is the gas temperature (K), and dV/dt is the volumetric displacement rate of the soap film in the glass capillary (cm³/s). Transport of gases through isotropic polymer films is characterized by the relationship:

\[
P = \frac{J}{p_2 - p_1}
\]

where P is the permeability coefficient (cm³(STP)/cm²·s·cmHg), \( \ell \) is the membrane thickness (cm), and p_2 and p_1 are the upstream (feed) and downstream (permeate) pressures (cmHg), respectively. The permeability coefficient depends on the nature of the penetrant, the polymer type, the temperature and, in the case of strongly interacting, condensable gases, on the feed and permeate pressures.

The pure gas selectivity, α, of an isotropic film is defined as the ratio of the permeability coefficients of gas A and gas B:

\[
\alpha_{A,B} = \frac{P_A}{P_B}
\]

Gas transport through nonporous polymer films is commonly described as a solution-diffusion process. The permeability coefficient defined in Eq. (4) can be expressed as

\[
P = DS
\]

where D is an average diffusion coefficient (cm²/s) and S is the solubility coefficient (cm³(STP)/cm³·cmHg). The selectivity defined in Eq. (5), can then be expressed by:

\[
\alpha_{A,B} = \frac{\left( \frac{D_A}{D_B} \right) \left( \frac{S_A}{S_B} \right)}
\]

Selectivity, as defined in Eq. (7), is the product of two terms. The first term, \( (D_A/D_B) \), is the ratio of the diffusion coefficients and is often called the mobility or diffusivity selectivity. This term reflects the size of the penetrants relative to the chain mobility and inter- and intra-molecular chain spacing of the polymer. In the case of the separation of organic vapors from permanent gases, such as nitrogen, the diffusion coefficient of the organic vapor is always less than that of nitrogen, and thus the mobility selectivity is less than one. The second term is the sorption or solubility selectivity, \( (S_A/S_B) \), and reflects the relative sorption of the gases. In general, the more condensable the component, the higher its sorption. Hence, in the separation of organic vapors from nitrogen, the sorption selectivity term will always be greater than one. Whether a particular membrane material is organic-vapor-selective or permanent-gas-selective depends on the balance between these two terms for the particular material.

Gas mixture permeation measurements

Permeation experiments were performed at 25°C with a 20-μm-thick Teflon AF 2400 film using a 2 mol% n-butane/98 mol% methane feed gas mixture.
Table 1
Pure gas permeabilities of Teflon AF 2400 at 25°C and a feed pressure of 50 psig. Permeate pressure: atmospheric (0 psig)

<table>
<thead>
<tr>
<th>Film thickness (μm)</th>
<th>Permeability coefficient × 10^{-6} (cm^3(STP)/cm^2 s cmHg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CO_2  He  H_2  O_2  N_2  CH_4  C_2H_6  C_3H_8</td>
</tr>
<tr>
<td>14</td>
<td>3600  3300  1500  780  630</td>
</tr>
<tr>
<td>18</td>
<td>3900  3600  3300  1600  790  660  380  200</td>
</tr>
<tr>
<td>20</td>
<td>3900  3600  3400  1600  780  660  370  200</td>
</tr>
</tbody>
</table>

The experiments were performed with the constant pressure/variable volume method described above. The feed pressure was 200 psig and the permeate pressure was atmospheric (0 psig). The compositions of residue and permeate were determined with a gas chromatograph equipped with a TCD detector. The permeate to feed flow rate, that is the stage-cut, was always less than 1%. Under these conditions, the residue composition was essentially equal to the feed composition. The permeability coefficient of each gas component in the mixture was calculated from the relationship:

\[
P = \frac{x_{\text{perm}}}{x_{\text{feed}}} \times \left( \frac{p_{\text{feed}}}{p_{\text{perm}}} \right)
\]

(8)

where \(x_{\text{perm}}\) and \(x_{\text{feed}}\) are the mole fractions of the gas components in the permeate and feed streams, respectively, \(J_{\text{perm}}\) is the total permeate flux (cm^3/cm^2 s), and \(p_{\text{feed}}\) and \(p_{\text{perm}}\) are the pressures (cmHg absolute) on the feed and permeate side of the membrane, respectively. The gas mixture selectivity was then calculated using Eq. (5).

3. Results and discussion

3.1. Pure gas permeation properties of Teflon AF 2400

The permeability coefficients of helium, hydrogen, carbon dioxide, oxygen, nitrogen, methane, ethane and propane for solution-cast Teflon AF 2400 films determined at 25°C and a pressure difference of 50 psig are summarized in Table 1. The permeability coefficients of films with thicknesses of 14, 18 and 20 μm agree within 5% of each other, demonstrating good reproducibility of the permeation measurements. The permeability coefficients of Teflon AF 2400 increase in the order: propane < ethane < methane < nitrogen < oxygen < hydrogen < helium < carbon dioxide. The extraordinarily high permeabilities for permanent gases (helium, hydrogen, nitrogen, oxygen) in Teflon AF 2400 are more than two orders of magnitude higher than those of conventional, low-volume, glassy polymers such as polycarbonate. In fact, gas permeabilities of Teflon AF 2400 are only exceeded by those of poly(1-trimethylsilyl-1-propyne) [PTMSP], a glassy, ultrahigh-free-volume polyacetylene-based polymer [19,20].

The permeability coefficients of Teflon AF 2400; polycarbonate, an example of a low-volume glassy polymer (FFV = 0.16); and PTMSP, an example of an ultrahigh-free-volume (FFV = 0.32) glassy polymer, as a function of the kinetic diameters of several gases are compared in Fig. 2. In Teflon AF 2400, the permeability decreases as the molecular size of the gas molecule increases. A similar trend is observed for the low-volume, glassy polycarbonate. This behavior is typical for glassy polymers in which gas transport is controlled primarily by the diffusivity term in Eq. (6) [21]. PTMSP shows markedly different behavior; the permeability coefficients for more condensable gases with large kinetic diameters, such as propane, are higher than those of small, noncondensable gases such as helium or hydrogen. The helium permeability coefficient of PTMSP is higher than that of Teflon AF 2400 by a factor of only 1.5. Because the solubility of helium...
Table 2
Gas/nitrogen selectivities of Teflon AF 2400 at 25°C and a feed pressure of 50 psig. Permeate pressure: atmospheric (0 psig)

<table>
<thead>
<tr>
<th>Film thickness (μm)</th>
<th>Selectivity gas/nitrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CO₂</td>
</tr>
<tr>
<td>14</td>
<td>4.6</td>
</tr>
<tr>
<td>18</td>
<td>4.9</td>
</tr>
<tr>
<td>20</td>
<td>5.0</td>
</tr>
</tbody>
</table>

is very low and of similar value for different polymers, it is reasonable to assume that the diffusion coefficients in Teflon AF 2400 and PTMSP are on the same order of magnitude. On the other hand, the propane permeability coefficient of PTMSP is about 150 times higher than that of Teflon AF 2400. We suggest that the remarkable difference in propane permeability results from a large difference in propane solubility in the two polymers.

The selectivities of Teflon AF 2400 for various gases over nitrogen are shown in Table 2. The selectivities of permanent gases over nitrogen are low. The oxygen/nitrogen, hydrogen/nitrogen and carbon dioxide/nitrogen selectivity of Teflon AF 2400 are 2.0, 4.3 and 5.0, respectively. As discussed above, Teflon AF 2400 is more permeable to nitrogen than to hydrocarbons. The selectivity of nitrogen over hydrocarbons increases as the size of the hydrocarbon increases. The nitrogen/methane, nitrogen/ethane, and nitrogen/propane selectivity at 25°C and a feed pressure of 50 psig are 1.3, 2.0 and 3.9, respectively.

The permeability coefficients and selectivities of a solvent-cast Teflon AF 2400 film of this study are compared to those reported by Nemser et al. [10] for a melt-pressed film in Table 3. The permeabilities of the solution-cast film are between 30% (helium) and 80% (methane) higher than those reported for the melt-pressed film. The selectivities are in fairly good agreement with each other. The differences in gas permeabilities between melt-processed films and solution-cast films are in qualitative agreement with previous studies. Maeda showed that melt-extruded polysulfone films had between 10 and 20% lower gas permeabilities than solution-cast polysulfone films [13]. The reason for the larger difference in gas permeabilities between melt-pressed and solution-cast Teflon AF 2400 films is not known.

3.2. Influence of pressure on gas transport properties of Teflon AF 2400

The permeabilities of solution-cast Teflon AF 2400 films were determined as a function of the feed pressure. The measurements were carried out with nitrogen, carbon dioxide, chlorodifluoromethane (Freon 22), and propane at 25°C and pressures up to 120 psig. The permeabilities of nitrogen and carbon dioxide are independent of gas pressure under the experimental conditions of this study, as shown in Fig. 3. On the other hand, the permeabilities of the more condensable gases, propane and chlorodifluoromethane, depend strongly on feed pressure.

The permeabilities of chlorodifluoromethane and propane increase 12- and 20-fold, respectively, by increasing the feed pressure from 10 to 110 psig, indicating that Teflon AF 2400 is easily plasticized by

Table 3
Pure gas permeability coefficients and selectivities of solution-cast Teflon AF 2400 films (this study) and melt-pressed Teflon AF 2400 films [10]

<table>
<thead>
<tr>
<th>Gas</th>
<th>Permeability × 10⁻¹⁰ (cm³(STP)cm²s cmHg⁻¹)</th>
<th>Selectivity gas/nitrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>3900</td>
<td>2800</td>
</tr>
<tr>
<td>He</td>
<td>3600</td>
<td>2700</td>
</tr>
<tr>
<td>H₂</td>
<td>3400</td>
<td>2200</td>
</tr>
<tr>
<td>O₂</td>
<td>1600</td>
<td>990</td>
</tr>
<tr>
<td>N₂</td>
<td>780</td>
<td>490</td>
</tr>
<tr>
<td>CH₄</td>
<td>600</td>
<td>340</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>370</td>
<td>180</td>
</tr>
</tbody>
</table>
organic vapors. This result is in agreement with studies by Nemser and Roman, who reported a similar pressure dependence for a melt-pressed Teflon AF 2400 film with dichlorodifluoromethane (Freon 12) [10]. As a result, the pure gas nitrogen/organic vapor selectivity of Teflon AF 2400 is highly pressure-dependent, as shown in Fig. 4. At vapor activities of less than 0.6–0.7, Teflon AF 2400 is more permeable to nitrogen than to propane or chlorodifluoromethane; however, at activities of 0.7 or higher, the polymer is more permeable to organic vapors than to nitrogen. The dramatic dependence of selectivity on vapor activity limits the use of Teflon AF 2400 as a membrane material for organic vapor separation to very dilute organic vapor/air streams.

3.3. Influence of temperature on gas transport properties of Teflon AF 2400

The permeability coefficients of Teflon AF 2400 for methane, nitrogen, oxygen, carbon dioxide, and helium were determined at a feed pressure of 50 psig and a temperature range from 25 to 60°C. The temperature dependence of gas permeation through polymers without any thermal transitions is given by the Arrhenius relationship:

$$P = P_0 \exp \left( \frac{-E_a}{RT} \right)$$  \hspace{1cm} (9)

where $P_0$ is a pre-exponential factor, $E_a$ is the activation energy of permeation (J/mol), $R$ is the gas constant (8.314 J/mol K) and $T$ is the gas temperature (K). The Arrhenius plots of the gas permeabilities in Teflon AF 2400 are shown in Fig. 5.

The activation energies of permeation, $E_a$, determined from the slope of the Arrhenius plots are shown in Table 4 and compared to those of polycarbonate, a conventional, low-free-volume glassy polymer, and to PTMSP, an ultrahigh-free-volume glassy polymer.

The activation energy of permeation, $E_a$, provides a qualitative measure of the free volume and the size of molecular gaps between chain segments. The activation energy of permeation is the sum of the activation energy of diffusion, $E_d$, and the heat of sorption, $H_s$:

$$E_a = E_d + H_s$$  \hspace{1cm} (10)

The activation energy of diffusion is a size-related parameter; its value depends on the size of the pene-
Table 4
Activation energies of permeation ($E_p$) for Teflon AF 2400, PTMSP [19], and polycarbonate [24]

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$E_p$ (J/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$N_2$</td>
</tr>
<tr>
<td>PTMSP</td>
<td>-5100</td>
</tr>
<tr>
<td>Teflon AF 2400</td>
<td>-400</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>+25000</td>
</tr>
</tbody>
</table>

4. Gas mixture permeation properties of Teflon AF 2400 and PTMSP

The gas mixture transport properties of poly(1-trimethylsilyl-1-propyne) (PTMSP) differ significantly from those of conventional, low-free-volume glassy polymers. As a result of its extremely high sorption capacity, PTMSP is more permeable to organic vapors than to permanent gases. Moreover, recent studies showed that selectivities of PTMSP determined with gas mixtures are significantly higher than those calculated from pure gas measurements [25–27]. These higher gas selectivities result from a dramatic reduction in the permeability of permanent gases in the presence of an organic vapor. The gas mixture selectivities of higher hydrocarbons ($C_3^+$) over methane are the highest of any known polymer [26,27]. In addition, the gas mixture $C_3^+$ permeabilities of PTMSP are substantially higher than those of any polymer, including polydimethylsiloxane, the most vapor-permeable rubber known. The combination of the highest $C_3^+$ / methane selectivity and the highest $C_3^+$ permeability in PTMSP is in singular contrast to the typical permeability-selectivity trade-off observed for polymers for the separation of permanent gas mixtures [28]. Because Teflon AF 2400 can be classified as an ultra-high-free-volume polymer like PTMSP, it is of interest to compare the permeation properties of these two polymers with gas mixtures.

Permeation experiments were carried out with a gas mixture containing 2 mol% $n$-butane/98 mol% methane at 200 psig feed pressure at 25°C. The results are summarized in Table 5.

The gas mixture permeation properties of Teflon AF 2400 and PTMSP are entirely different, as shown in Table 5. First, Teflon AF 2400 preferentially permeates methane, the smaller and less condensable gas component of the mixture; the methane/butane selec-
Table 5
Gas mixture permeation properties of Teflon AF 2400 and poly(1-trimethylsilyl-1-propyne) (PTMSP). Feed: 2 mol% n-butane/98 mol% methane; feed pressure: 200 psig; permeate pressure: atmospheric (0 psig); temperature: 25°C; 1 Barrer = 10⁻¹⁰ cm³ (STP) cm² s cmHg⁻¹.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Permeability coefficient (gas mixture) (Barrer)</th>
<th>Permeability coefficient (pure gas) (Barrer)</th>
<th>Permeability ratio (gas mixture/pure gas)</th>
<th>Selectivity (gas mixture)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n-C₅H₁₀</td>
<td>CH₄</td>
<td>CH₄</td>
<td>CH₄</td>
</tr>
<tr>
<td>Teflon AF 2400</td>
<td>260</td>
<td>550</td>
<td>600</td>
<td>0.92</td>
</tr>
<tr>
<td>PTMSP</td>
<td>52 900</td>
<td>1840</td>
<td>16 700</td>
<td>0.11</td>
</tr>
</tbody>
</table>

Activity was 2. This behavior is typical for glassy polymers in which the diffusivity selectivity, \(D_{\text{CH₄}}/D_{\text{C₅H₁₀}}\), is larger than the solubility selectivity, \(S_{\text{C₅H₁₀}}/S_{\text{CH₄}}\). PTMSP, on the other hand, is substantially more permeable to n-butane, the larger and more condensable gas component; the butane/methane selectivity of PTMSP was 29, indicating that \(S_{\text{C₅H₁₀}}/S_{\text{CH₄}}\) is much greater than \(D_{\text{CH₄}}/D_{\text{C₅H₁₀}}\). Second, the methane permeability coefficient of Teflon AF 2400 was essentially equal to that obtained from pure gas measurements, as shown in Table 5. In contrast, the methane permeability coefficient of PTMSP was lower than the pure methane permeability by a factor of 10. The reduction in methane permeability results from preferential adsorption of butane in the free volume of the polymer. As a result, the unoccupied space available for methane diffusion in PTMSP is reduced significantly. This unique gas mixture permeation behavior of PTMSP is similar to that observed for nanoporous carbon membranes [27,29,30]. PTMSP can, therefore, be classified as a nanoporous polymeric adsorbent.

4. Conclusions

Teflon AF 2400 exhibits substantially higher gas permeabilities than conventional glassy polymers. The permeabilities of permanent gases (helium, hydrogen, nitrogen, oxygen) are exceeded only in PTMSP, the most permeable polymer known. Teflon AF 2400 and PTMSP are both ultrahigh-free-volume glassy polymers, but their gas permeation properties differ significantly. Although Teflon AF 2400 has very high gas permeabilities, its general transport behavior is similar to that of conventional, low-free-volume glassy polymers. PTMSP, on the other hand, acts more like a nanoporous carbon than a conventional glassy polymer. Permeabilities of small gas molecules in Teflon AF 2400 are higher than those of large, condensable gases, indicating that the high gas permeabilities result from very high diffusion coefficients. PTMSP, on the other hand, is more permeable to large, condensable gases than to permanent gases. The very high gas permeabilities of PTMSP result, therefore, from very high diffusion coefficients and very high solubility coefficients. Permeation studies with gas mixtures confirmed that the selectivity of Teflon AF 2400 is controlled by differences in diffusivity of the gas components, whereas the selectivity of PTMSP is controlled by large differences in their solubility.

Teflon AF 2400 shows only a very weak dependence of gas permeability on temperature. The activation energies of permeation for nitrogen, oxygen, and carbon dioxide were slightly negative, that is, permeability decreased with increased temperature. The vapor permeabilities of Teflon AF 2400 increase greatly with the vapor activity, indicating that the polymer is easily plasticized. The propane permeability coefficient increased 20-fold with an increase in the propane feed pressure from 20 to 110 psig. As a result, the gas/organic vapor selectivity is strongly dependent on vapor activity. At vapor activities of less than 0.7, Teflon AF 2400 is nitrogen-selective, but at higher activities the polymer becomes organic-vapor-selective. The low nitrogen/organic vapor selectivity and the strong dependence of selectivity on vapor activity severely limit the use of Teflon AF 2400 as a membrane material for the separation of air from organic vapors. Because Teflon AF 2400 has very high gas permeabilities and excellent chemical resistance, the polymer could find use in membrane applications as a protective coating for composite and asymmetric membranes [31].
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References


