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

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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 1600×10^{-10} cm^3(STP) cm/cm^2 s cmHg and the nitrogen permeability coefficient is 780×10^{-10} cm^3(STP) cm/cm^2 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-bis-trifluoromethyl-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-

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tetrafluoroethylene) [FEP]. However, PDD and PDD-PTFE copolymers containing at least 20 mol% PPD 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-pro-pyne) [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 990×10^{-10} and 480×10^{-10} cm^3(STP) cm/cm^2 s 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]:
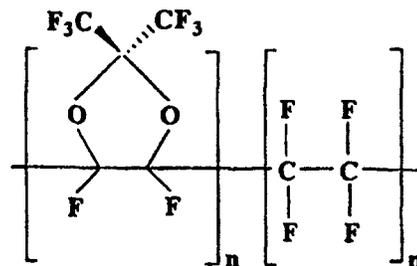

Fig. 1. Repeat unit of poly(2,2-bistrifluoromethyl-4,5-difluoro-1,3-dioxole) [PDD]/PTFE. The copolymer containing 87 mol% PDD and 13 mol% PTFE is commercially available as Teflon AF 2400 from Du Pont (Wilmington, DE).

$$SFV = \nu_{sp} - \nu_0 = \nu_{sp} - 1.3\nu_w \qquad (1)$$

$$FFV = SFV/\nu_{sp} \qquad (2)$$

where ν_{sp} is the specific volume (cm^3/g) of the polymer as determined from density or thermal expansion measurements, and ν_0 is the zero point volume at 0 K. The van der Waals volume, ν_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$_5$F$_{11}$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 cm^2 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 $\pm 5\%$.

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

$$J = \frac{273.15 p_a}{76 T A}\left(\frac{dV}{dt}\right) \tag{3}$$

where J is the steady-state gas flux (cm^3(STP)/cm$^2\cdot$s), A is the membrane area (cm^2), 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 (cm^3/s). Transport of gases through isotropic polymer films is characterized by the relationship:

$$P = \frac{J_i \cdot \ell}{(p_2 - p_1)} \tag{4}$$

where P is the permeability coefficient (cm^3(STP) cm/cm^2 s cmHg), ℓ is the membrane thickness (cm), and p_2 and p_1 are the upstream (feed) and downstream (permeate) pressures (cmHg), respectively. The per-

meability 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:

$$\alpha_{A,B} = \frac{P_A}{P_B} \tag{5}$$

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

$$P = DS \tag{6}$$

where D is an average diffusion coefficient (cm^2/s) and S is the solubility coefficient (cm^3(STP)/cm^3 cmHg). The selectivity defined in Eq. (5), can then be expressed by:

$$\alpha_{A,B} = \left(\frac{D_A}{D_B}\right)\left(\frac{S_A}{S_B}\right) \tag{7}$$

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)

Film thickness (μm)	Permeability coefficient $\times 10^{10}$ (cm^3(STP)cm/cm^2 s cmHg)							
	CO_2	He	H_2	O_2	N_2	CH_4	C_2H_6	C_3H_8
14	3600		3300	1500	780	630		
18	3900	3600	3300	1600	790	600	380	200
20	3900	3600	3400	1600	780	600	370	200

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:

$$P = \frac{x_{perm}J_{perm}\ell}{(p_{feed}x_{feed}) - (p_{perm}x_{perm})} \tag{8}$$

where x_{perm} and x_{feed} are the mole fractions of the gas components in the permeate and feed streams, respectively, J_{perm} is the total permeate flux (cm^3/cm^2 s), and p_{feed} and p_{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 per-

meability 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-free-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-free-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-free-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
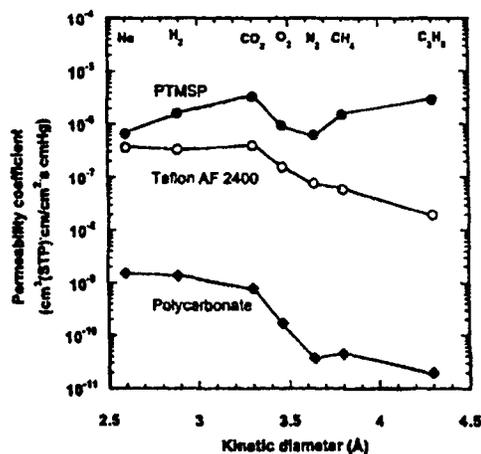

Fig. 2. Permeability coefficients of various gases at 25°C and a feed pressure of 50 psig in Teflon AF 2400, poly(1-trimethylsilyl-1-propyne) (PTMSP) [22], and polycarbonate [23] as a function the kinetic diameters of the penetrants.

Table 2
Gas/nitrogen selectivities of Teflon AF 2400 at 25°C and a feed
pressure of 50 psig. Permeate pressure: atmospheric (0 psig)

Film thickness (μm)	Selectivity gas/nitrogen						
	CO_2	He	H_2	O_2	CH_4	C_2H_6	C_3H_8
14	4.6		4.2	1.9	0.8		
18	4.9	4.6	4.2	2.0	0.8	0.5	0.25
20	5.0	4.6	4.3	2.0	0.8	0.5	0.25

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 perme-
ability 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 com-

pared to those reported by Nemser at 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 agree-
ment with each other. The differences in gas
permeabilities between melt-processed films and solu-
tion-cast films are in qualitative agreement with pre-
vious 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 per-
meabilities between melt-pressed and solution-cast Tef-
lon 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 pres-
sure. 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 inde-
pendent of gas pressure under the experimental condi-
tions 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, indi-
cating 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]

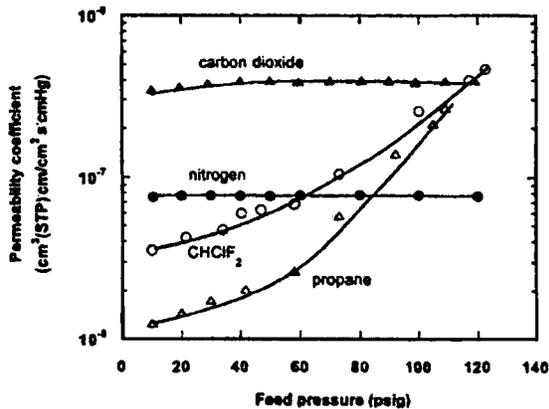| Gas	Permeability $\times 10^{10}$ (cm^3(STP)cm/cm^2 s cmHg)		Selectivity gas/nitrogen	
	Solution-cast film (this work)	Melt-pressed film [10]	Solution-cast film	Melt-pressed film
CO_2	3900	2800	5.0	5.7
He	3600	2700	4.6	5.5
H_2	3400	2200	4.4	4.5
O_2	1600	990	2.0	2.0
N_2	780	490		
CH_4	600	340	0.8	0.7
C_2H_6	370	180	0.5	0.4

Fig. 3. Permeability coefficients of nitrogen, carbon dioxide, chlorodifluoromethane, and propane in Teflon AF 2400 as a function of the feed pressure. Temperature: 25°C; permeate pressure: 0 psig.
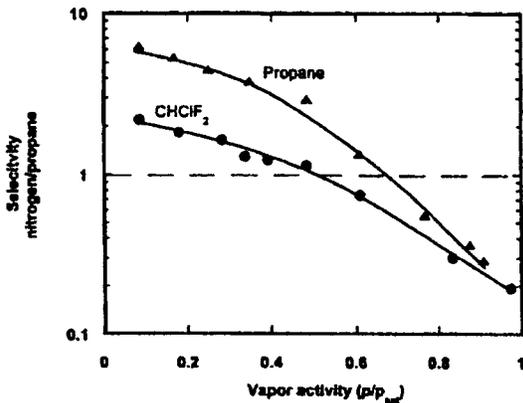

Fig. 4. Nitrogen/propane and nitrogen/chlorodifluoromethane selectivities of Teflon AF 2400 as a function of vapor activity (p/p_{sat}) at 25°C. Permeate pressure: atmospheric (0 psig). Selectivities calculated from pure gas permeation experiments.
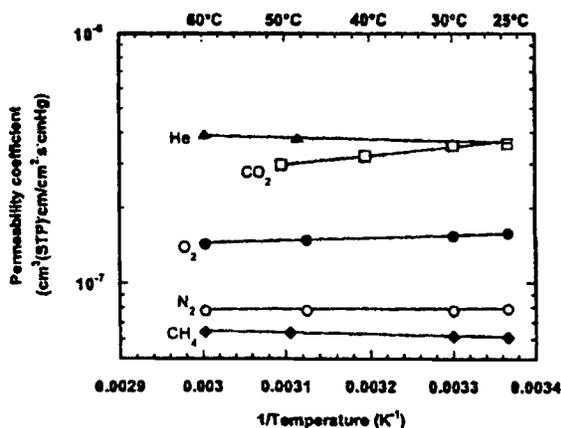

Fig. 5. Permeability coefficients of Teflon AF 2400 as a function of reciprocal temperature. Feed pressure: 50 psig; permeate pressure: atmospheric (0 psig).

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:

$$P = P_0 \exp\left(\frac{-E_p}{RT}\right) \qquad (9)$$

where P_0 is a pre-exponential factor, E_p 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_p, 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_p, 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:

$$E_p = E_d + H_s \qquad (10)$$

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]

Polymer	Activation energy of permeation, E_p (J/mol)				
	N_2	O_2	He	CH_4	CO_2
PTMSP	−5100	−6100	−400	−6300	−9700
Teflon AF 2400	−400	−2500	+1600	+1300	−6700
Polycarbonate	+25 000	+19 700	+17 600	+26 000	+12 600

trant, the intra- and inter-molecular gaps between polymer chains, and the chain mobility. For activated diffusion processes, E_d is positive, that is, diffusion coefficients increase with increasing temperature. The heat of sorption is related to the thermodynamic interaction of the penetrant with the polymer. Sorption of gases in polymers is typically an exothermic process. Thus, solubility of gases in polymers decreases with increasing temperature, and H_s is negative.

In essentially all conventional glassy polymers, gas permeability increases with increased temperature, because $E_d + H_s > 0$ or $|E_d| / |H_s| > 1$. An exception to this rule is the temperature dependence of gas permeability in ultrahigh-free-volume PTMSP. Masuda et al. showed that gas permeabilities in PTMSP decrease with increased temperature, i.e. $|E_d| / |H_s| < 1$. The heat of sorption in PTMSP is similar to that of low-free-volume glassy polymers [19]. Therefore, negative activation energies of permeation in PTMSP result from very small activation energies of diffusion [19].

The activation energies of permeation in Teflon AF 2400 are only slightly higher than those of PTMSP, but are significantly lower than those of low-free-volume polycarbonate, as shown in Table 4. The E_p values for nitrogen, oxygen, and carbon dioxide in Teflon AF 2400 are negative, indicating that $|E_d| / |H_s| < 1$. In glassy polymers, negative activation energies of permeation have only been observed for ultrahigh-free-volume polymers such as PTMSP and Teflon AF 2400. On the other hand, negative activation energies of permeation are routinely observed for microporous solids in which the pore dimensions are relatively large in comparison with the diffusing gas molecules [25]. It is reasonable, therefore, to suggest that the ultrahigh-free-volume glassy polymers resemble microporous solids and comprise a network of interconnected gaps with dimensions large compared to the diffusing gas molecules.

3.4. 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 ultrahigh-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)cm/cm² s cmHg

Polymer	Permeability coefficient (gas mixture) (Barrer)		Permeability coefficient (pure gas) (Barrer)	Permeability ratio (gas mixture/pure gas)	Selectivity (gas mixture)
	$n\text{-}C_4H_{10}$	CH_4	CH_4	CH_4	C_4H_{10}/CH_4
Teflon AF 2400	260	550	600	0.92	0.5
PTMSP	52 900	1840	16 700	0.11	29.0

tivity was 2. This behavior is typical for glassy polymers in which the diffusivity selectivity, $(D_{CH_4}/D_{C_4H_{10}})$, is larger than the solubility selectivity, $(S_{C_4H_{10}}/S_{CH_4})$. 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 $(S_{C_4H_{10}}/S_{CH_4})$ is much greater than $(D_{CH_4}/D_{C_4H_{10}})$. 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].

Acknowledgements

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