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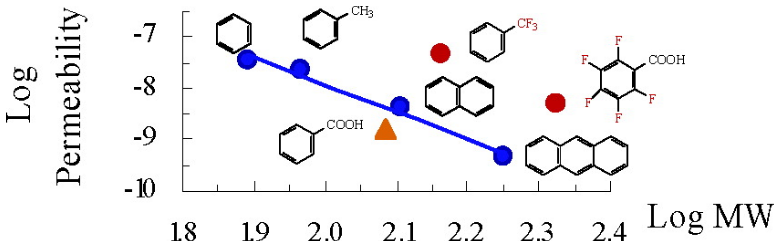

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Transport of Organic Solutes through Amorphous Teflon AF Films

Hong Zhao,[†] Jie Zhang,[†] Nianqiang Wu,[‡] Xu Zhang,[†] Katie Crowley,[†] and Stephen G. Weber*,[†]

Contribution from the Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260, and Keck Interdisciplinary Surface Science Center, NUANCE, Northwestern University, Evanston, Illinois 60208-3108

Received May 2, 2005; E-mail: sweber@pitt.edu

Abstract: Fluorous media have great potential for selective extraction (e.g., as applied to organic synthesis). Fluorous polymer films would have significant advantages in fluorous separations. Stable films of Teflon AF 2400 were cast from solution. Films appear defect-free (SEM; AFM). Rigid aromatic solutes are transported (from chloroform solution to chloroform receiving phase) in a size-dependent manner (log permeability is proportional to −0.0067 times critical volume). Benzene's permeability is about 2 orders of magnitude higher than in comparable gas-phase experiments. The films show selectivity for fluorinated solutes in comparison to the hydrogen-containing control. Transport rates are dependent on the solvent making up the source and receiving phases. The effect of solvent is, interestingly, not due to changes in partition ratio, but rather it is due to changes in the solute diffusion coefficient in the film. Solvents plasticize the films. A less volatile compound, −COOH-terminated poly(hexafluoropropylene oxide) (**4**), plasticizes the films ($T_g = -40$ °C). Permeabilities are decreased in comparison to **4**-free films apparently because of decreased diffusivity of solutes. The slope of dependence of log permeability on critical volume is not changed, however.

Introduction

The goal of extraction is selective removal of target species from their matrix to another phase. Artificial receptor-based molecular recognition can enhance the selectivity of extraction and minimize the consumption of solvents.[1−3] Hydrogen bond-based artificial receptors selectively associate with target species through specific hydrogen bonds between the target species and the complementary receptor. Studies of solvent influences on hydrogen bond-based molecular recognition of phenobarbital[4−6] have revealed that solvent properties (π^*, α, β)[7] affect the equilibria relevant to solute distribution (partitioning, association with the receptor, and the solubility of the receptor) differently. We postulate that selectivity can be improved by a judicious choice of solvent that maximizes the extraction of the target solute, while minimizing the extraction of interfering species. However, it is definitely not a trivial task to investigate a series of solvents for each receptor. A general way to encourage the desired hydrogen bonding and inhibit nonspecific extraction of interfering species becomes important.

The unique nature of fluorocarbon solvents makes them significant in selective extraction. The poor solubility of most hydrocarbons in fluorous phases has been useful in synthesis by simplifying the postreaction purification process.[8] Fluorous biphasic synthesis and fluorous biphasic catalysis have been attractive in recent years and have provided understanding about solubility, partitioning, and reactivity in fluorous phases.[9−14] Selectivity is achieved by attaching a fluorocarbon tag to one of the reactants, followed by separation of the desired products according to the solubility in fluorous solvents. The fluorocarbon-tagged products or reagents can be removed easily by extraction with fluorocarbon solvents.

In practical situations, dimensionally stable solvents such as supported liquids contained in polymer membranes are beneficial.[15−17] We therefore investigated an amorphous glassy

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[†] University of Pittsburgh.

[‡] Northwestern University.

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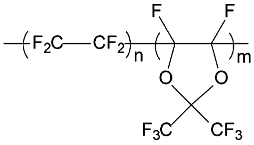

Figure 1. Teflon AF.

fluorous polymer, Teflon AF, as a transport medium for solutes. Teflon AF is a copolymer of tetrafluoroethylene (TFE) and 2,2-bistrifluoromethyl-4,5-difluoro-1,3-dioxole (PDD) (Figure 1). Two products available are Teflon AF 2400 (87 mol % PDD, T_g 240 °C, **1**) and Teflon AF 1600 (65% mol PDD, T_g 160 °C).[18] While sharing many significant characteristics of other known Teflon polymers, such as chemical inertness and thermal stability, Teflon AF is highly permeable to low molecular weight gases and has been studied in gas separation[19−22] and pervaporation.[23,24] Teflon AF polymers are mechanically stiff and are moderately soluble in some fluorinated solvents at room temperature; thus thin and dimensional stable films can be prepared easily through solvent casting. The film is transparent within a wide UV−vis and IR range,[18] which enables analysis of the films with these spectroscopic techniques.

Teflon AF 2400 has a large fractional free volume (FFV) of 0.327.[22] This is much larger than most glassy plastics, including other Teflon polymers. Transport of gas-phase species (penetrants) through Teflon AF films has shown that the films have large permeability coefficients for gases that are second only to poly(trimethylsilyl propyne) (PTMSP), a well-known highly permeable polymer.[20,22] The films demonstrate moderate selectivity to a variety of gases. Studies of sorption[25−28] and diffusion[29−31] of penetrants in Teflon AF films have led to insights into how gases are separated with these films. Permeability of organic vapors increases with the vapor pressure, which suggests possible plasticization of the polymer.[22,32] Large free volume elements on the order of 5−7 Å exist in the polymer as determined by positron annihilation lifetime spectroscopy.[20,32,33] A study of penetrant diffusion in Teflon AF 1600 films by NMR also showed that the films contain large disordered regions that consist of these high free volume elements.[29,30] The disordered regions appeared to be interspersed with lower free volume regions, and the apparent diffusion constants of penetrants showed strong dependence on diffusion time. A recent study demonstrated enhancement of permeability for large molecules by physically dispersing silica nanoparticles in the Teflon AF polymer films.[34,35] The reports of pervaporation of organic solvents through these films also showed high permeability of volatile organic compounds.[23,24]

We have recently communicated the first transport data for solutes permeating films of Teflon AF 2400 (**1**) in contact with their solutions.[36] This work demonstrated that the films absorb a substantial amount of solvent ($CHCl_3$) to which they are exposed. As a result, organic solutes have high permeability in the films compared to the penetrants of similar size in gas permeation. The high permeability arises from increased diffusion coefficients of the solutes in the film. For benzene, the partition ratio is 0.04 from chloroform to the film, lower than the value of benzene partitioning from the same solution to a imaginary “dry film” of **1** (0.34).[36] By dry film, we mean a film that has not been exposed to solvents. It is evident that the solvent plays an important role in solute transport through these films. In this article, we report the results from our investigation of the factors that affect the solute permeability through the films of **1**. These factors include the characteristics of the solutes (solute size, polarity, and structure) and the solvents (chloroform, methanol, water, 1,1,2-trichlorotrifluoroethane). Films of **1** doped with a fluorous plasticizer are reported for the first time and are compared with films of **1**.

Experimental Section

Reagents. Teflon AF 2400 (**1**) was purchased from DuPont (Wilmington, DE). FC-72 (perfluorohexanes) was obtained from 3M (Minneapolis, MN). Acid red 37 (**2**) and Reichardt’s dye (**3**) were purchased from Aldrich (Milwaukee, WI). Krytox 157 FSH (FW 7000−7500, **4**) was from Miller-Stephenson Chemical Company Inc. (Danbury, CT). 1,1,2-Trifluorotrichloroethane (TCTFE), spectrophotometric grade chloroform, and the solutes used in transport experiments were from Aldrich (Milwaukee, WI). All aqueous solutions were prepared with deionized water produced from a Milli-Q A10 system (Millipore, Bedford, MA).

Apparatus. The surfaces and the cross sections of the films were imaged by scanning electron microscopy FE-SEM (Philips, model XL 30 FEG). The topography of the film was imaged by atomic force microscopy (AFM) (Digital Instruments, model NanoScope IIIa). UV absorbance measurements were carried out on a UV−vis diode array spectrophotometer (Agilent, model 8453E, Palo Alto, CA). Quartz cuvettes with path lengths of 0.1 and 1.0 cm were purchased from Starna Cells (Atascadero, CA). IR spectra were obtained from an Excalibur FTS 3000 spectrometer (DigiLab, Randolph, MA). Multiple transport experiments were carried out on a 15-position stirrer (Cole-Parmer, Chicago, IL) equipped with a stirring speed controller. The homemade glass transport cuvette (1 × 1 × 4 cm^3) had well-polished walls and a hole of 0.5 cm i.d. on the wall in contact with the film. Film thicknesses were measured by a Starrett micrometer (Athol, MA) with an accuracy of ±1 μm.

Preparation of the Films. Films of **1** were cast from a 1 wt % Teflon AF 2400 polymer solution in FC-72. A defined amount of solution was transferred into a glass Petri dish that had a flat bottom

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(diameter 7.5 cm) and was covered by a glass plate. The solvent was allowed to evaporate overnight at room temperature. The formed film was stripped from the Petri dish. Soaking the film in water for a short time helped peel off the film more easily. The film was dried in an oven at 110 °C for 2 h and stored in a container at room temperature. For use in transport experiments, the film was cut into small pieces (about 1 × 1 cm^2) with scissors.

To prepare films doped with Krytox 157 FSH, the dopant was dissolved in FC-72 and mixed with 1% Teflon AF 2400 polymer solution in the desired proportions. The films were formed under the conditions described above. The formed film was readily peeled off with a scalpel without the water-soaking procedure. The film was then left in a vacuum oven for 1 h at room temperature. Drying at high temperature was not used because the doped films shrank at elevated temperatures.

Transport of Solutes through Films. Transport of solutes was carried out on a homemade, three-phase transport device at room temperature (24 ± 2 °C).[37] The subject film was held between two pieces of viton rubber in which holes of a diameter of 0.5 cm (an area of 0.196 cm^2) were cut to define the transport area. The rubber-secured film was then clamped between two transport cuvettes. A multiple position stirrer controlled the small stirring bar in each cuvette at a stirring speed of 300 rpm. The source phase contained 3 mL of solute-containing solution at a defined concentration. The receiving phase contained 3 mL of solvent at the beginning of the experiments. The solute concentration in the receiving phase was monitored by UV spectrophotometry until steady transport was reached. The steady-state flux, J, of a solute through the film is given by eq 1.

$$J = (\mathrm{d}C_\mathrm{r}/\mathrm{d}t)(V/A) \quad (\mathrm{mol{\cdot}s^{-1}{\cdot}cm^{-2}}) \tag{1}$$

A is the effective film area, V is the volume of the receiving phase, and $\mathrm{d}C_\mathrm{r}/\mathrm{d}t$ is the accumulation rate of the solute in the receiving phase at steady state. The permeability coefficient, P, can be calculated from the flux,

$$P = J{\cdot}l/(C_\mathrm{s} - C_\mathrm{r}) \approx J{\cdot}l/C_{\mathrm{s}0} \quad (\mathrm{cm^2{\cdot}s^{-1}}) \tag{2}$$

where l is the thickness of the film. C_s and C_r are the concentration of the solute in the source phase and the receiving phase, respectively. Because C_r is negligible at the beginning, $C_\mathrm{s} - C_\mathrm{r}$ is close to the initial concentration of the solute in the source phase, $C_{\mathrm{s}0}$. The permeability coefficient depends on the nature of the solute, the film type, and the temperature.

Determination of Diffusion Coefficients (D) and Partition Ratios of Solutes (K_D). The experiment was carried out in a similar transport device while a quartz cuvette was employed for the receiving phase to obtain continuous UV measurement of the receiving phase.[36] Thick films (200−300 μm) were used to observe the whole kinetic process from the start of transport to the steady state. The thick film was prepared by firmly stacking multiple thin films (about 20 μm) together after dipping the thin films in a mixture of 4% FC-72 and 96% TCTFE briefly. The film was then washed with dichloromethane and dried at 110 °C in an oven. In the transport experiment, the concentration of a solute in the receiving phase was recorded as a function of time. The diffusion coefficient and partition ratio of a solute were obtained through nonlinear curve fitting according to eq 3,[36] in which we assume that the solute in the membrane is initially at zero concentration and also maintains zero concentration in the receiving phase during the initial transport period.

$$Q_\mathrm{t} = K_\mathrm{D}Cl\left[\frac{Dt}{l^2} - \frac{1}{6} - \frac{2}{\pi^2}\sum_{1}^{\infty}\frac{(-1)^n}{n^2} - \exp(-Dn^2\pi^2t/l^2)\right] \tag{3}$$

Q_t denotes the total amount of a solute transported through the film at time t, which can be calculated from the recorded concentration in the receiving phase. C is the concentration of the solute in the source phase, and l is the film thickness. This equation is an infinite series. We determined that 10 terms ($n = 10$) was sufficient.

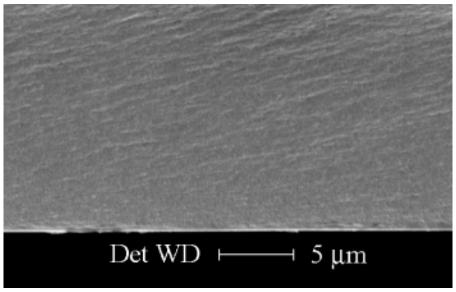


Figure 2. SEM image of the cross section of a film of **1**.

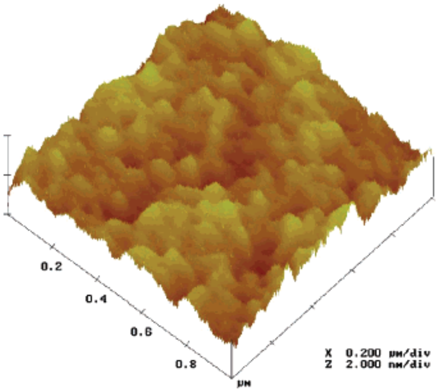
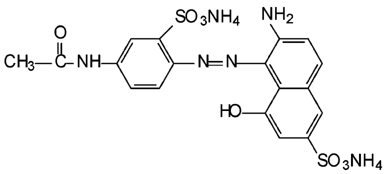


Figure 3. SEM image of the topography of a film of **1**.



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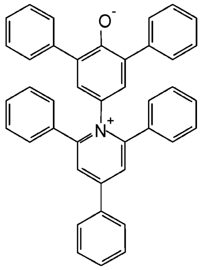

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Figure 4. Acid red 37 (**2**) and Reichardt's dye (**3**).

Results and Discussion

Film Integrity and Transport Experiments. SEM and AFM were used to image the topography and possible defects of the film (Figures 2 and 3). The cast film appears homogeneous both on the film surface and through the cross section, with no obvious pinholes or cracks. AFM images indicated a smooth surface of the film with RMS roughness of 0.4 nm over a 10-μm scan range. The smooth surface of the film cast from **1** has enabled applications of Teflon AF polymers in surface polishing[38] and allows for preparation of thin stable films containing minimal defects.

The integrity of the film and the transport device was tested with two dyes that have high molecular weight, high molar absorptivity, but different polarities (Figure 4). An aqueous solution of **2** and a chloroform solution of **3** were used as the source phases, while water or chloroform were employed as the receiving phases, respectively. No measurable absorbance

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Table 1. Permeability Coefficients of Benzene through Films of **1** with Various Thicknesses

film thickness (μm)	film density (g·mL^{-1}) (± SEM, number)	P/(10^{-9} cm^2·s^{-1}) (± SEM, number)
7.8	1.61 ± 0.10 (5)	41 ± 5 (2)
12	1.65 ± 0.06 (5)	33 ± 1 (2)
37	1.74 ± 0.07 (9)	37 ± 3 (9)
269[a]	nd	33 ± 6 (7)

[a] The films were prepared by stacking multiple thin films (about 20 μm) together.

was observed in the receiving phase after 3 days in repeated experiments. In light of the detection sensitivity, the permeability coefficients are estimated to be no more than 1.1 × 10^{-12} cm^2·s^{-1} for **2** and no more than 1.2 × 10^{-12} cm^2·s^{-1} for **3**. This proved that the film did not contain defects that allowed significant passage of somewhat polar molecules of ~500 Da.

For the organic solutes that we have investigated, the relative standard deviations of the measured permeability coefficients are from 10 to 14% within the same batch of films, and 12 to 25% among different batches of films in over three years of study. The films had good long-term stability and showed no changes in transport properties after months of storage at room temperature.

The permeability coefficients of benzene measured from films of various thickness agreed within the variation between different batches of films, indicating that permeability coefficients are independent of the film thickness (Table 1, first three entries). The evaporation conditions during film preparation were found to affect the density of the formed films and result in variation of the film permeability. Compared to thin films, it is more difficult to control the density of thick films with the same preparation procedures. Therefore, the thick films used in kinetic transport experiments were prepared by stacking a number of thin films together. The thickness of thick films prepared in this way was measured and compared with the sum of the thicknesses of the individual films of the stack. Stacks with thicknesses more than 20% different than expected were not used. The quality of the thick films was confirmed by comparing the permeability coefficients of solutes with the values obtained from the thin films. The average permeability coefficient of benzene through the thick films is 3.3 × 10^{-8} cm^2·s^{-1}, which is close to that through thin films (Table 1).

Dependence of Permeability Coefficients on the Solute Molecular Size. Neutral, rigid aromatic molecules were used to investigate the dependence of permeability on the molecular size of the solutes. The permeation of the dissolved solutes through Teflon AF films was found to be much higher than that of gas-phase penetrants. For example, the permeability coefficient of benzene is about 2 orders of magnitude higher than the value extrapolated from gas permeation[23,32] (see Supporting Information). Although films of **1** are highly permeable, the permeability of solutes decreases rapidly as molar volume increases. The permeability coefficient of anthracene was only 1/74 of benzene, indicating the size-sieving characteristics of the film. The critical volume (V_c) is a convenient measure of the size of a solute. A plot of the permeability coefficients and the critical volumes (V_c)[39] of the solutes is shown in Figure 5. Linear regression of log P versus V_c for these solutes gave a slope of −0.0067 and a correlation coefficient of 0.99. This observation is in agreement with other reports about separation of gases through Teflon AF films[22,27,32] and pervaporation of organic liquids through these films[23] where high molecular weight gases or organic liquids had lower permeability than the smaller ones. The slope of −0.0067 observed from solute transport is comparable to that obtained in these reports but is smaller than those strongly size-sieving glassy polymers such as polysufone (PSF) and polycarbonate.[23]

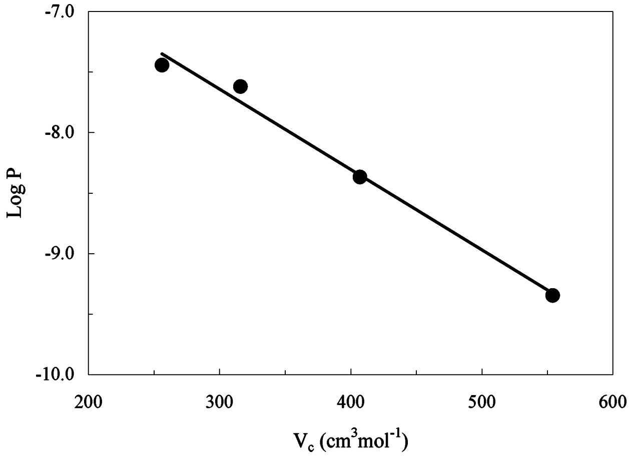

Figure 5. Dependence of permeability coefficients (cm^2·s^{-1}) on solute size.

Dependence of Permeability on the Concentration of Solutes in the Receiving Phase (C_{s0}). Benzene and pyrazine in chloroform showed constant permeability coefficients regardless of the initial concentrations in the source phase (Figure 6), which agrees with the solution-diffusion transport mode.[40] In this transport mode, the transport process consists of partitioning a solute from the source phase into the film, diffusion of the solute through the film, and release of the solute to the receiving phase. The permeability coefficient (P) is the product of the diffusion coefficient (D) and the partition ratio of a solute from the source phase to the film (K_D) as shown in eq 4.[41] In this case, the permeability coefficient is independent of the solute concentration.

$$P = D \cdot K_D \tag{4}$$

However, solutes such as benzoic acid and pentafluorobenzoic acid showed changing permeability coefficients with C_{s0} (Figure 7), with higher permeability coefficients at lower C_{s0}. Carboxylic acids are well-known to dimerize. Benzoic acid has been reported to have a dimerization constant of 87 in 1,2-dichloroethane (37 °C)[42] and 516 in benzene (25 °C).[43] Dimerization of carboxylic acids is solvent-dependent; higher dimerization constants have been demonstrated in solvents with lower dielectric constants.[44] Considering that the dielectric constant of chloroform ($\epsilon = 4.8$) is between those of 1,2-dichloroethane ($\epsilon = 10.36$) and benzene ($\epsilon = 2.3$),[42] it is reasonable to assume that the dimerization constant of benzoic acid is in the range of 10^2 M^{-1} in chloroform. With this dimerization constant, the

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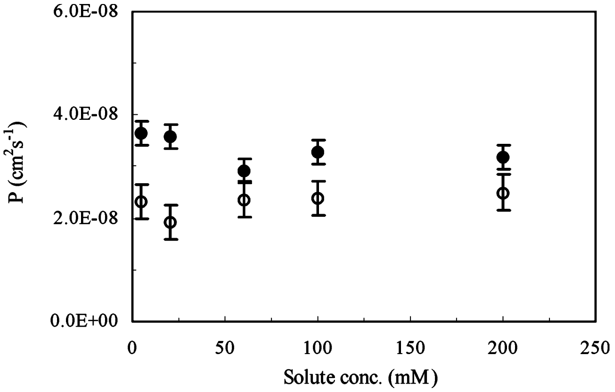

Figure 6. Dependence of the permeability coefficients of benzene and pyrazine on the initial concentrations of solutes in the source phase. The initial concentrations of benzene (●) and pyrazine (○) in the source phase were 5, 20, 60, 100, and 200 mM. The error bars are from a pooled standard deviation.

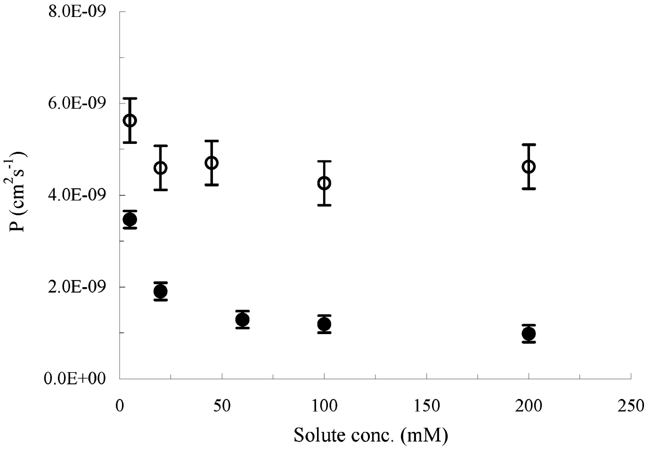

Figure 7. Dependence of the permeability coefficients of benzoic acid and pentafluorobenzoic acid on the initial solute concentrations (C_{s0}). The experimental conditions were the same as in Figure 6. Solutes: benzoic acid (●) and pentafluorobenzoic acid (○). The error bars are from a pooled standard deviation.

monomer fraction in the concentration range of 5−200 mM changes from about 60% (at 5 mM) to about 15% (at 200 mM). Transport through films of **1** is sensitive to the molecular size of the solutes. Therefore, the monomer has a much larger permeability than the dimer. Dimerization of benzoic acid leads to a lower concentration of benzoic acid monomer in the source phase, which results in a decreased permeability coefficient.

Worthy of mention is that the dimerization constant of benzoic acid is probably higher in the film than in chloroform, considering the nonpolar nature of the film. However, the partition ratios of solutes from chloroform to the film are generally small, for example, 0.04 for a nonpolar molecule, benzene, and 0.02 for a polar molecule, 3-hydroxypyridine. As a result, the concentration of benzoic acid monomer in the film is small, and the dimerization equilibrium in the film does not likely affect the permeability strongly. The correspondence of the concentration range over which the permeability changes and the dissociation constant in chloroform supports the notion that the dimerization equilibrium in the film has a small effect on permeability. Pentafluorobenzoic acid has a smaller dimerization constant than benzoic acid.[45] We observed that the concentration affected the permeability coefficients of pentafluorobenzoic acid to a smaller degree.

Table 2. Permeability Coefficients of Solutes through Films of **1**[a]

solutes	number	P/(10^{-9} cm^2·s^{-1})[b]	P/(10^{-9} cm^2·s^{-1})[c]
α,α,α,-trifluorotoluene	1	47	/
benzene	2	33	36
toluene	3	24	/
pyrazine	4	21	23
pyridine	5	14	/
benzyl alcohol	6	6.2	/
pentafluorobenzoic acid	7	4.8	5.6
naphthalene	8	4.3	/
benzoic acid	9	1.5	3.5
anthracene	10	0.45	/
2-hydroxypyridine	11	0.13	0.38

[a] Transport was carried out with solutes in chloroform as the source phase through the film with an effective area of 0.20 cm^2 and a thickness of 9 ± 1 μm at room temperature (24 ± 2 °C). The reported permeability coefficients are the mean values of duplicate measurements, with a pooled relative standard deviation as 16.4%, so the standard error of the mean is 12%. [b] 0.1 M solution. [c] 0.005 M solution as the source phase.

As the concentration of carboxylic acid increases, the activity coefficient decreases (extrapolated infinite dilution standard state), but the activity itself increases. The observation that permeability decreases as concentration increases is therefore certainly a kinetic, not a thermodynamic, effect.

Permeability of Fluorinated Solutes and Polar Solutes. The permeability coefficients of fluorinated solutes and polar solutes are shown in Table 2. The four neutral aromatic hydrocarbons are included in the table for comparison. For some of the solutes, the permeability coefficients obtained at a lower concentration (5 mM) are also listed. Fluorinated solutes showed higher permeability than their nonfluorinated analogues. The permeability coefficient of α,α,α-trifluorotoluene is twice the value of toluene, and the permeability coefficient of pentafluorobenzoic acid is three times the value of benzoic acid. Films of **1** have been reported to have a higher dissolving power for perfluorocarbon gases than their hydrocarbon analogues because of the fluorous nature of the polymer.[27] For example, the concentration of C_2F_6 sorbed in **1** is 13% higher than that of C_2H_6 at 15 atm feed pressure. However, because of the larger molecular size of the perfluorocarbons, perfluorocarbon gases have significantly lower permeability than the hydrocarbon analogues despite favorable solubility.[27] In contrast, in this work, the permeability coefficients of dissolved fluorinated solutes are still higher than the values of the hydrocarbon analogues. Preference of films of **1** for fluorocarbons hints at possible applications in separation of fluorocarbons from hydrocarbons with this type of films.

The polarity of the solutes was found to influence the permeability. In the group of solutes benzene, pyridine, and pyrazine that have similar molecular size, the permeability decreased with increased polarity. The same phenomenon was found in the group of solutes toluene and benzyl alcohol. The observation is consistent with the general view that polar solutes having smaller partition ratios into the fluorous environment thus results in lower permeability.

2-Hydroxypyridine has a remarkably low permeability coefficient considering its molecular size. 2-Hydroxypyridine dimerizes and tautomerizes in solvents.[46−48] Keto-monomer (2-

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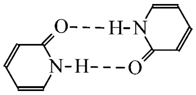

Figure 8. 2-Pyridone dimer.

Table 3. Permeability Coefficients of Pyrazine in Different Solvents[a]

solvent	$P/(10^{-9}\ \mathrm{cm^2 \cdot s^{-1}})$	ratio
chloroform	21 ± 0.7	1.0
methanol	6.6 ± 0.4	0.32
water	4.1 ± 0.1	0.20

[a] Transport was carried out through films of **1** with 20 mM pyrazine in each solvent as the source phase. Other conditions were the same as in Table 2. The ratios are the permeability coefficients compared to the value obtained from chloroform.

pyridone) is more stable than enol-monomer (2-hydroxypyridine) in chloroform, and thus the dimeric equilibrium is primarily between 2-pyridone and its dimer[47] (Figure 8). The self-association constant of 2-pyridone is large and increases when the polarity of the solvent decreases. Dimerization constants are reported to be $6.5 \times 10^2\ M^{-1}$ in $CHCl_3$ and $2.5 \times 10^4\ M^{-1}$ in CCl_4.[47] The low permeability of 2-pyridone in transport is a result of the low fraction of monomer in the chloroform solution (8.4% in a 0.1 M solution) and the cyclic structure of the dimer. In contrast to benzoic acid discussed in the former section, dimerization of 2-pyridone is stronger and the dimer has a more rigid structure. Self-association of 2-pyridone is likely stronger as well in the film. All these factors lead to a very low permeability coefficient.

Solvent Effects on Solute Transport. Pyrazine was chosen as the solute because it presents satisfactory solubility in solvents with a large range of polarities. Chloroform, methanol, and water influence the transport of pyrazine as shown in Table 3. In chloroform, the permeability was three times higher than that in methanol and five times higher than that in water.

The permeability coefficient is the product of the partition ratio and the diffusion coefficient. The effect of solvents on the permeability coefficient can be predicted if we assume that the solvent does not influence the film properties, and thus the diffusion coefficients of the solute in the film will be identical in all experiments. The only effect of solvents on permeability would then be the difference in partition ratios. If we define the permeability of a solute in the film in the presence of solvent j as P_j, and similarly, if we define the partition ratio of a solute from solvent j to solvent k as $K_{j,k}$, we obtain eq 5.

$$P_{H_2O}/P_{CHCl_3} = K_{H_2O,film}/K_{CHCl_3,film} = K_{H_2O,CHCl_3} \tag{5}$$

If solvent does not influence diffusion coefficient in the film, then the ratio of the permeability coefficients for pyrazine (P_{H_2O}/P_{CHCl_3}) should be comparable to the partition ratio $K_{H_2O,CHCl_3}$. The former is 0.20, whereas the latter is 3.9.[49] The two values are clearly not identical. This tells us that the assumption that solvent does not influence the diffusion of the solutes is wrong. Solvents act not only to influence the partitioning, but also to influence the diffusion coefficients of solutes in the film. In an investigation of pervaporation of organic solvents through Teflon AF films, Polyakov and co-workers found that 10 organic solvents with a wide range of polarity showed small difference of solubility in the films (within a factor of 2), which is substantially smaller than the variation of their permeability coefficients.[23] We have measured the partition ratios of two solutes with very different polarities, benzene and 3-hydroxypyridine, from $CHCl_3$ to films of **1**. The values are remarkably similar, 0.04 and 0.02, respectively. All of this indicates that the changes among permeability coefficients of pyrazine (solute) in various solvents primarily come from the differences in its diffusion coefficient in the film, not from the differences in its partition ratio. This is likely caused by partitioning of the solvent into the film, altering its properties.[23,36]

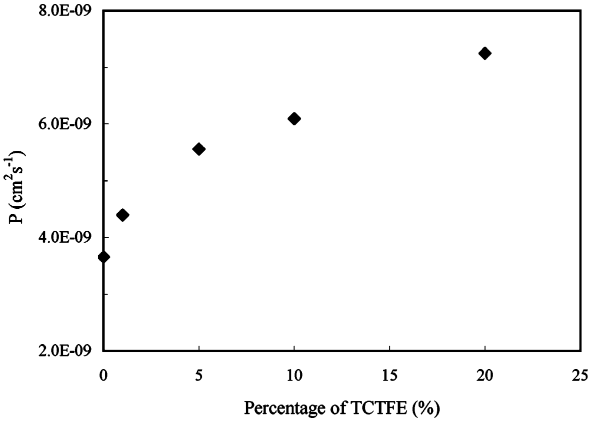

Figure 9. Addition of 1,1,2-trichlorotrifluoroethane to chloroform in the source phase enhanced the permeability of naphthalene. The percentage of TCTFE mixed with chloroform (v/v) in the source phase varied as 0, 2, 5, and 20%. The receiving phase contained only chloroform.

If solvents influence permeability by increasing solute diffusion coefficients, we hypothesized that a cosolvent that was compatible both with the source (and receiving) phase and the film would have a significant effect. The effect of halogen atoms on solubility has been demonstrated in the pervaporation study through Teflon AF films.[23] The solubility of chlorinated methane increases in the order of $CCl_4 > CHCl_3 > CH_2Cl_2$, with the solubility of CCl_4 twice the value of CH_2Cl_2. TCTFE is a good solvent for many fluorinated and nonfluorinated compounds and is soluble in chloroform (used as a source/receiving phase solvent). A variety of proportions of TCTFE were mixed with chloroform solutions of naphthalene, which was used as the source phase. Results shown in Figure 9 demonstrate that addition of TCTFE in the source phase enhanced the permeability. It is likely that fluorinated solvents such as TCTFE could have higher solubility than nonfluorinated solvents in Teflon AF films, which plasticize the films and increase the transport of solutes.

To understand the role that solvents play in transport of dissolved solutes, it is helpful to measure the solvent uptake in the films. Uptake of solvents is often obtained by soaking a film in solvents and then monitoring the weight increase of the film.[23,50] Having concerns that the volatility of the organic solvents might affect the measurement, we developed a method to determine the solvent sorption in the film by FTIR.[36] Films of **1** in an IR flow cell were allowed to contact the saturated vapor of the solvent, chloroform in this case. The IR absorbance

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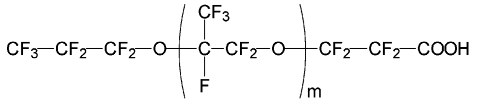

$$CF_3-CF_2-CF_2-O-\left(\overset{CF_3}{\underset{F}{\overset{|}{\underset{|}{C}}}}-CF_2-O\right)_m-CF_2-CF_2-COOH$$

Figure 10. Krytox FSH (**4**).

of the solvent vapor in the flow cell was monitored by an FTIR spectrometer until equilibrium was reached. The equilibrium concentration of chloroform in the film is measured to be 7.9 ± 0.2 g/100 g of polymer (SEM, $n = 5$ (1.13 M)),[36] which is close to the value reported by Polyakov et al. in a pervaporation study measured by the weighing method (9.11 g/100 g of polymer).[23] They also examined the sorption of a couple of other common solvents in the films of **1**. The solubility of methanol was determined to be 1.84 g/100 g of polymer (0.99 M) and that of water was determined to be negligible. The concentrations of the sorbed chloroform and methanol in the film are similar. However, the influence of the two solvents on the permeability of pyrazine is not comparable. Clearly, the chemical nature of the solvent, not just its ability to fill space, influences solute permeability.

Due to the high concentration of solvents sorbed in the films, the films in contact with organic solvents become somewhat like a supported liquid membrane. Solvent uptake results in partitioning and diffusion behavior of solutes that is quite different from the same species acting as gas-phase penetrants. Benzene vapor has been reported to have a diffusion coefficient of 4.9×10^{-10} $cm^2{\cdot}s^{-1}$ in Teflon AF 1600.[51] Benzene liquid in a pervaporation study has a diffusion coefficient of 4.93×10^{-8} $cm^2{\cdot}s^{-1}$ in Teflon AF 1600 films and 1.9×10^{-7} $cm^2{\cdot}s^{-1}$ in Teflon AF 2400 films.[23] We have measured the diffusion coefficient of benzene in the solute (chloroform solution) transport experiments to be $(1.2 \pm 0.3) \times 10^{-6}$ $cm^2{\cdot}s^{-1}$.[36] The diffusion coefficient of benzene in chloroform-containing films is remarkably larger than that of the benzene gas as a result of plasticization.

Transport through Films of 1 Doped with Perfluoroether 4. The apparent plasticization of the films by organic solvents is interesting and leads to very large increases in solute diffusivity. It would be significant if the film could be plasticized in the absence of organic solvent. It is intriguing to explore fluorous additives as plasticizers of films of **1**. Part of the significance is to maintain the fluorous nature of the film while gaining better control of the solute diffusion and the solute solubility that affect the selectivity[37,52] of the film. Poly(hexafluoropropylene oxide) terminated with a carboxylic acid (**4**) (Figure 10) was found to be miscible with **1** in any proportion. It is known that **4** has an IR absorbance at 1775 cm^{-1} from the C=O stretch of the carboxylic acid dimer.[53] Films of **1** doped with various percentages of **4** showed the expected absorption peak around 1774 cm^{-1} (Figure 11). We did not see any IR evidence for the dissociation of the carboxylic acid dimer into the monomer.

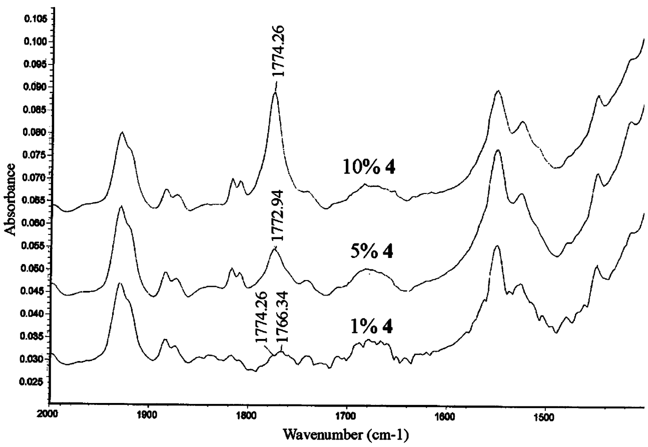

Figure 11. IR spectra of films of **1** doped with varied percentages of **4** (w/w).

Table 4. Permeability Coefficients of Solutes through Films of **1** Doped with 50% **4** (w/w)

solute	$P_2/(10^{-9}\ cm^2{\cdot}s^{-1})^a$	$P_1/P_2{}^b$
α,α,α-trifluorotoluene	6.0	7.7
benzene	3.5	9.7
toluene	2.5	9.7
naphthalene	0.33	13
anthracene	0.043	10

[a] The experimental conditions were the same as those in Table 2, except that the films of **1** were replaced with the doped films. The permeability coefficients are the mean values of duplicate experiments. [b] P_1/P_2 is the ratio of average permeability coefficients through a film of **1** and the doped film.

Table 5. Partition Ratios and the Diffusion Coefficients of Benzene in the Film of **1** and the Doped Film[a]

	partition ratio	diffusion coefficient $(cm^2{\cdot}s^{-1})^{36}$
film of **1**	0.04 ± 0.01	$(1.2 \pm 0.3) \times 10^{-6}$
doped film	0.03 ± 0.003	$(9.5 \pm 0.8) \times 10^{-8}$

[a] The reported values are the average and the standard deviation of the mean from seven measurements for film of **1** and from three measurements for the doped film (50% **1**-50% **4**, w/w).

It was found that **4** plasticized films of **1**. The glass transition temperature, T_g, of **1** doped with 50% **4** (w/w) was measured to be −40 °C, compared to 240 °C for film of **1**.[36] The solute permeability coefficients in **4**-doped films are shown in Table 4. For better comparison, the ratios of the permeability coefficients in the two types of films (films of **1** and the doped films, P_1/P_2) are also presented.

The permeability of benzene through **4**-doped films is still considerably larger than its permeability as a gas-phase penetrant. However, its permeability and the permeabilities of other solutes are lower than the permeabilities in the absence of **4**. The average ratio of the permeability coefficients in the two types of films (P_1/P_2) is about 10. Interestingly, the linear correlation of log P and the critical volume of the four neutral aromatic solutes hold, giving a slope of −0.0066 and a correlation coefficient of 0.98. This slope is essentially the same as the value of −0.0067 for films of **1**, which shows that the doped film is sensitive to the critical volume of the solutes to the same degree as films of **1**. There are two possible reasons for reduced permeation, namely, decreased partitioning of solutes from the solvent into the film and decreased diffusion of solutes in the film. Table 5 lists the partition ratios and the diffusion coefficients of benzene in the two types of film. The partition ratio of benzene in the doped film is not significantly

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smaller than that in the film of **1**. On the other hand, the diffusion coefficient decreases about a factor of 10 in the doped film, changing from 1.2×10^{-6} $cm^2 \cdot s^{-1}$ in the film of **1** to 9.5×10^{-8} $cm^2 \cdot s^{-1}$ in the doped film.

We speculate that the occupation of free volume by **4** significantly alters the diffusion of small molecules even as it increases Teflon AF 2400 chain mobility. We are led to this conclusion from considering that our work presented here and earlier[36] and other studies of solute dynamics[19,28−30,32] in the films are consistent with the idea that diffusion takes place by solute moving from one region of free volume to another. Plasticization by low molecular weight solvents enhances solute diffusion even as it occupies free volume because the solvent molecules themselves are diffusing rapidly. When plasticization is by polymeric **4**, however, the free volume is lowered while the environment within the free volume becomes viscous in comparison to solvent-saturated films, although the environment becomes less restricted than that of dry films. The observed decrease in permeability with the addition of **4** compared to the case in films of **1** alone bears a resemblance to the phenomenon of antiplasticization,[54−56] which occurs when small volume fractions (∼10−30%) of plasticizers actually increase tensile strength and decrease permeability by a reduction of free volume. Larocca and Pessan[57] noted that compatibility (i.e., similar values of solubility parameter) between additive and polymer was one important factor in the additive's ability to decrease free volume. The system under investigation in this article differs from the studies described in that we are comparing films either plasticized with chlorform or plasticized with **4** and chloroform. We are not comparing films of pure **1** with films of **1** containing some fraction of **4**. Nonetheless, there is the similarity to antiplasticization that a polymer-compatible additive apparently decreases film permeability.

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Supporting Information Available: Calculation of the permeability coefficient of benzene in barrers. This material is available free of charge via the Internet at http://pubs.acs.org.

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