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High transport parameters and free volume of perfluorodioxole copolymers

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Abstract

Permeability (P) and diffusion (D) coefficients of perfluoro-2,2-dimethyl-1,3-dioxole–tetrafluoroethylene copolymers were determined with respect to different gases (He, H_2, O_2, N_2, CO_2, hydrocarbons C_1–C_3). The copolymers with large content of perfluorodioxole comonomer exhibit high permeability with respect to lighter gases comparable to that of poly(trimethylsilyl propyne). However, the copolymers studied are much more permselective than the latter polymer. Free volume as estimated via Bondi's method and free volume size distribution parameters which were determined by means of positron annihilation lifetimes (PAL) method are also unusually high if compared with other glassy polymers. A novel correlation of the P and D values, as well as of the solubility coefficients S with the PAL parameter $\tau_4 I_4$ are reported.

Keywords: Perfluorodioxole copolymers; Permeability; Diffusion; Free volume

1. Introduction

Polymeric materials for high performance and high permeability membranes attracted more and more attention during the last decade. In particular, it was shown that several strategies of molecular design of repeating units of glassy polymers can result in strong variation in free volume and permeability (P), and diffusion (D) coefficients [1]. One approach involves an introduction of $Si(CH_3)_3$ groups as side chains, which is accompanied by significant increase in transport parameters (P, D), sometimes not at the expense of permselectivity [2]. This effect is observed independently of the structure of a main chain – for vinylic type polymers, polynorbomenes, derivatives of phenylene oxide, etc. However, the magnitude of these variations strongly depends on the structure of main chains. The most dramatic manifestation of such a behavior is observed in the properties of poly(trimethylsilyl propyne) (PTMSP), a polymer distinctive by the largest permeability coefficients among all the known materials, both rubbery and glassy [3]. It is generally accepted that a drastic increase in permeability, diffusivity, and free volume in this case is a net result of an appearance of bulky trimethylsilyl group attached directly to the stiff polyene main chain. Based on these results obtained for polymers of different classes, an arbitrary assumption might be made

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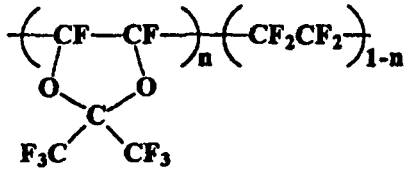
that the only strategy for preparing high free volume, high permeability glassy materials involves the introduction of $Si(CH_3)_3$ or its structure analogs. However, this conclusion needs an experimental corroboration.

Some time ago, permeation rates through the films and membranes prepared from the copolymers of perfluoro-2,2-dimethyl-1,3-dioxole and tetrafluoroethylene were reported [4] where it was shown that these perfluorinated polymers are distinctive by exceedingly high level of gas permeability comparable only to that of PTMSP. However, no data were available on diffusivity and solubility of these amorphous materials with respect to different gases. Accordingly, novel data are reported now on gas permeability, diffusion, and solubility coefficients of two copolymers having different content of perfluoro-2,2-dimethyl-1,3-dioxole comonomer. Additionally, free volume of these copolymers was studied by means of positron annihilation lifetimes technique.

2. Experimental

2.1. Materials

The chemical structures of the copolymers studied are shown below.



Ia: n=0.9 Ib: n=0.65

Such copolymers have been described by Squire [5]. Two compositions of the copolymers were studied with n=0.90 (Ia) and n=0.65 (Ib).

2.2. Film casting procedure

The copolymers studied are soluble in fluorocarbons only. The films were cast from ca. 2 wt% solutions of perfluorotoluene. Polymer solutions were poured into flat metal cylinders with bottoms formed by strongly stretched cellophane film previously wet and dried. The cylinders were placed over the surface of a horizontal table. A strong tendency to form gel was noted for the copolymer Ia. Here, the solvent was allowed to evaporate at 55°C in an oven. The films of the copolymer Ib were prepared at ambient temperature. The films were dried in a vacuum oven at 40–50°C until a constant weight was achieved.

2.3. Methods of measurements

The method of hydrostatic weighing was used for the determination of film densities. Isopropanol was chosen as a liquid with known density. It is a nonsolvent for the polymers studied and has a relatively low diffusion coefficient. It allows to neglect the effects of absorption and swelling on density measurement. The density was calculated using the formula

$$\rho = W_a/(W_a - W_l)\rho_l$$

where ρ is the density of the sample, W_a the weight of the sample in air, W_l the weight of the sample in isopropanol, and ρ_l the density of isopropanol at the temperature of measurement.

Permeability and diffusion coefficients were determined using a mass spectrometric method that has been described elsewhere [6]. In this method, the permeability coefficient is determined by the slope of the increase in a certain ion current in the mass spectrum of the diffusing gas molecule after attaining steady state conditions, whereas the diffusion coefficient is determined by the time-lag procedure. The measurements were carried out at 22°C and pressures 10–200 mmHg over the film and about 10^{-4} mmHg below the film, i.e. in the receiving volume of the mass spectrometer. MI-1309 and Balzers QMG instruments were used. In no case was any noticeable pressure dependence observed for the permeability and diffusion coefficients. The accuracy of determination of P values was about 10%; D values were measured with somewhat lower accuracy of about 20%. All the values reported were measured at 22±3°C.

Free volume and free volume size distribution in the perfluorodioxole copolymers were investigated by means of positron annihilation lifetimes method. The positron lifetimes were measured on a standard instrument Ortec (USA), which had a resolution function with the full width at half-maximum (fwhm) equal to 300 ps. The radioactive isotope ^{22}Na served

as a source of positrons; it had an activity of about 10 μCi. The spectra were treated using the program with an automatic selection of the parameters of the resolution function and an account for the contribution into lifetimes spectrum from the annihilation in the material of the source.

3. Results and discussion

Some physical properties of the copolymers studied are presented in Table 1. It is seen that both materials have fairly high glass transition temperatures, which increases for larger content of perfluorodioxole comonomer. It is in agreement with the results of Hung's study [7] on glass transition temperature of these copolymers having variable content of tetrafluoroethylene. The presence of a single glass transition temperature in both cases indicates that there is no phase separation in these materials, which are assumed to be random copolymers.

Interestingly, rather low density was found for both copolymers. Thus, the density of polytetrafluoroethylene (PTFE) is equal, according to [8], to 2.15–2.24 g/cm^3 (apparently depending on its crystallinity). Fractional free volume (FFV) of a material can be calculated if the density is known. FFV is defined as

$$FFV = v_f/v_{sp}$$

where v_f is the free volume (cm^3/g^1) and $v_{sp} = 1/\rho$ is the specific volume of the material. According to Bondi [9], v_f can be estimated as

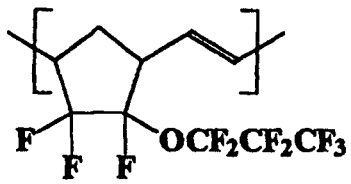
$$v_f = v_{sp} - 1.3v_w$$

where v_w is the van der Waals volume of the repeat unit of the polymer. The latter quantity can be calculated using the group contributions method (see the book by Van Krevelen [10]). Statistical weights of both comonomers were taken into account in these calculations.

Table 1
Physical properties of perfluorodioxole copolymers

Parameter	Ib	Ia
TFE content, %	35	10
Mol. Mass	100.000	300.000
T_g, °C	156	250
Density, g/cm^3	1.7416	1.5950
FFV, %	32.0	37.4

Fractional free volume found for both copolymers seems to be extremely high. In order to compare volumetric and other properties of perfluorodioxole copolymers studied and other materials, three different polymers were selected: PTMSP, PTFE, and a fluorine containing norbornene polymer studied earlier [11] and having relatively high permeation and sorption parameters. Its structure is shown below:



(POFPNB)

Fractional free volume (%) of these polymers found by the same way are presented below:

PTMSP	PTFE	POFPNB
34	14–18	26

So far, PTMSP was considered as a polymer having the highest free volume among all other glassy polymers. It means that fluorine containing polymers studied in the present work are distinctive by a very high free volume too. It is markedly larger than those of PTFE, POFPNB, as well as other glassy polymers [1].

Table 2 gives the permeability coefficients of the two perfluorinated copolymers and, for comparison, PTMSP and POFPNB. The permeability coefficients of Ia are very high and comparable, especially for lighter gases, to those of PTMSP. More accurate comparison of the permeabilities of these two materials is hampered by a wide variation in P values reported for PTMSP [2], probably owing to aging behavior of this material. However, for larger gas molecules, the P values of Ia are significantly lower than those of PTMSP. It means that the latter material is distinguished by higher permselectivity. We shall consider this subject in more detail below.

Recently, Pinnau and Toy [18] reported permeability coefficients of the copolymer Ia in both individual gas and mixed gas permeation experiments. The P values observed in both studies are rather close although those found in [18] are systematically higher

Table 2
Permeability coefficients P (Barrer) at 22–30°C

Gas	Ia	Ib	PTMSP	POFPNB [11]
He	2740	830	2200 [12],5500 [13]	–
H_2	2400	500	5200 [12], 17000 [14]	130
O_2	1140	170	2600 [15],5800 [13]	55
N_2	554	55	1500 [15],6200 [13]	17
CO_2	2600	530	19000 [12], 37000 [13]	200
CH_4	435	41	2700 [15], 4300 [12]	18
C_2H_2	480	53	2000 [15]	–
C_2H_4	325	26	2200 [15], 24000[16]	–
C_2H_6	252	16	1800 [15], 16700[17]	14
C_3H_8	97	2	1900 [15], 12600[17], 24000 [16]	–
n-C_4H_{10}	138	–	2300[15], 14460[17]	–

1 Barrer=10^{-10} cm^3(STP) cm/cm^2 s cmHg.

by a factor of about 1.3–1.4. It can be speculated that a possible reason for it can be related to differences in the conditions of film formation. In [18], the films were prepared from a solution in perfluoro-*N*-methylmorpholine, whereas in the present work the films were formed from perfluorotoluene solutions at 55°C. Maybe, it is the temperature difference that is most relevant for films properties. Indeed, the melt-pressed films [4] exhibit permeability coefficients very similar to the ones observed in this work.

When the content of perfluorodioxole comonomer decreases, permeability of the copolymer decreases too. Nevertheless, the P values found for Ib are still fairly high. Table 2 shows that the P values are substantially larger than those observed for POFPNB, which belongs to a group of high permeability glassy polymers like poly(vinyltrimethyl silane) or poly(phenylene oxide) [2]. For light gases (He, H_2), permeability of Ib is similar to that of a highly permeable rubbery material – polydimethylsiloxane.

It is of interest to find permeability of the homopolymer of perfluorodioxole. Poor film forming properties of the latter prevent direct determination of it. However, this can be estimated approximately using the dependencies of P vs. the composition of copolymers. Such dependencies have proved to hold for completely miscible polymer blends [19] or random copolymers [20]. The permeability coefficient of a copolymer can be approximately given by the equation:

$$l_g P_m = a_1 \cdot l_g P_1 + a_2 \cdot l_g P_2$$

where P_1 and P_2 are permeability coefficients of corresponding homopolymers, and a_1 and a_2 the concentrations of comonomers, respectively. Since the permeability coefficients P_2 of PTFE have been reported [21–23], the values of P_1 for various gases can be found. Unfortunately, it is not always clear what is the crystallinity of the PTFE samples studied in these works, and how to make allowance for the content of crystalline phase. However, the difference between permeation rates in PTFE and perfluorodioxole copolymers is so significant that this circumstance does not seriously affect the results of the calculation.

Fig. 1 gives examples of such dependencies for several gases in PTFE, Ib, and Ia. Extrapolation of linear dependencies to zero content of tetrafluoroethylene comonomer gives the permeability coefficients of the homopolymer. They are presented in Table 3. It is seen that the level of permeability of this polymer, with respect to light gases, is close to the one reported for PTMSP. No other polymers, including different silicon and fluorine containing polymers have so high gas permeability coefficients. This also indicates that the strategy adopted in dealing with polyacetylenes, i.e. the search for polymers with rigid main chains combined with bulky side groups, is not the only way to achieve high free volume and permeability of glassy polymers. The chemical structure of perfluorodioxole polymers is quite different, however, some of their important properties like permeability for light gases and free volume as revealed by the Bondi method and positron annihilation technique (see below) are similar to those of PTMSP. However, as we shall see further, there are significant differences too between these two high free volume materials.

Permselectivity is another important characteristic of membrane materials. Separation factors $\alpha_{ij} = P_i/P_j$ of the copolymers Ia and Ib are given in Table 4. Once again, PTMSP and POFPNB were used for comparison. There is another possibility to assess membrane properties of the materials studied. Robeson [24] analyzed numerous data on permeability and permselectivity of rubbery and glassy polymers, and reported the correlations between permeability coefficients P_i and separation factors for different gas pairs. It was shown that all these correlations reveal an upper bound (U.B.) relationship for these binary mixtures, i.e. the lines showing the best achieved combination between the P_i and α_{ij} values. For the

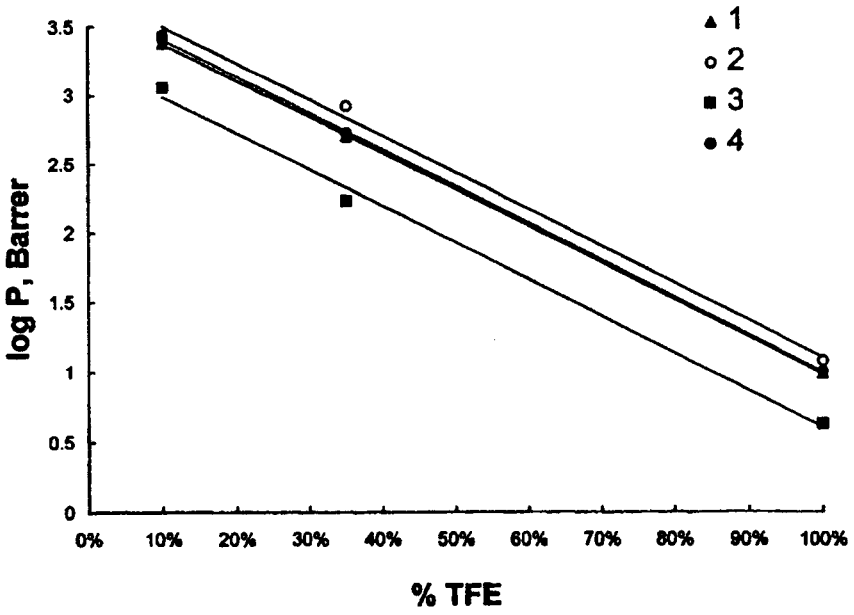


Fig. 1. Permeability coefficients of perfluorodioxole copolymers and PTFE. (1) H_2, (2) He, (3) O_2, and (4) CO_2.

Table 3
Estimated permeability of perfluorodioxole homopolymer *P* (Barrer)

Gas	*P*	Gas	*P*
H_2	4300	CO_2	4700
He	5800	CH_4	470
O_2	1800	C_2H_6	370
N_2	800	C_3H_8	90

comparison, the "upper bound" separation factors corresponding, according to the correlations of Robeson, to the permeability coefficients of Ia and Ib were included.

It can be seen that the copolymer Ia having larger permeability is distinctive by lower permselectivity for all the gas pairs. However, the separation factors of Ia are, in a majority of the cases, higher than those of PTMSP, the polymer having a similar level of permeability. The separation factors of Ib are approximately the same as those of POFPNB, the polymer having some similarities in its chemical structure but much lower permeability. By finding the location, in the correlations of Robeson, of the points corresponding to the polymers studied in this work, one can conclude that experimental separation factors for many gas pairs are close to the "upper bound" values and

Table 4
Permselectivity of perfluorodioxole copolymers and PTMSP

Gas pair	Ib		Ia		PTMSP	POFPNB
	Exp	U.B. [24]	Exp	U.B. [24]	[12,15,25,26]	[11]
O_2/N_2	3.1	3.6	2.1	2.7	1.7	3.2
H_2/N_2	9.1	22	4.3	7.7	2.9–4.0	7.6
H_2/CH_4	12.2	20	5.5	5.0	1.2–2.2	7.2
He/N_2	15.1	14	4.9	4.0	1.2–1.9	–
He/CH_4	20.2	9	6.3	2.2	2–3	–
CO_2/N_2	9·6	–	4.7	–	9–10.5	11.8
CO_2/CH_4	12.9	20	6.0	10	4.4	14.3
CH_4/C_2H_6	2.6	–	1.7	–	1.5	1.3

sometimes are shifted above this boundary, as is evident from Table 4. It makes these and similar polymers interesting candidates for membrane materials for separating mixtures as helium/nitrogen, helium/hydrocarbons, hydrogen/hydrocarbons where the main issue is high flux through a membrane. Reported good, long-term stability of permeation rates [4] and insolubility of Ia and Ib in hydrocarbons should be considered as an additional benefit. However, it is doubtful that these materials can find application for removal of organic vapors from permanent gases because: (1) permeability decreases with the size of the penetrant molecule; and (2) separation factors in mixed permeation are reduced at higher vapor pressure of organic components [18].

High permeability of a material can be caused by solubility (S) or diffusion (D) coefficients. These values for several gases and the copolymers studied are presented in Table 5 and Fig. 2. The solubility coefficients were determined using the formula $S = P/D$. Although the data reported characterize different gases in different copolymers, some qualitative conclusions and comparison with other materials can be made. It is seen that Ia copolymer is distinguished by substantially larger diffusion coefficients and somewhat higher solubility coefficients. Solubility coefficients of different gases decrease for different polymers in a sequence: PTMSP > Ia > Ib > POFPNB > PTFE. Therefore perfluorodioxole copolymers exhibit gas solubility although not as high as that of PTMSP but markedly larger that conventional glassy (POFPNB) or semicrystalline (PTFE) polymers.

It seems to be particularly interesting to compare diffusivity of the perfluorodioxole copolymers and PTMSP. With this aim, the correlations of log D vs. diffusant size were considered. As a measure of the size of molecules, the square of molecular diameter d^2 was used. The scale of d suggested by Teplyakov and Meares [29] was applied. As can be seen from Fig. 2, diffusivity of perfluorodioxole copolymers increases when the content of tetrafluoroethylene decreases. It is known that unusually weak, for a glassy polymer, dependence of log D vs. d^2 is characteristic for PTMSP [2]. It is evident from Fig. 2 that both perfluorodioxole copolymers exhibit a steeper dependence. Their extrapolation to the d^2 values corresponding to lighter gases results in the D values which are relatively close to those observed for PTMSP. Therefore, it can be assumed that similar permeability of these polymers and PTMSP are caused by diffusivity.

Table 5
Solubility coefficients $S \times 10^3$ (cm^3(STP)/cm^3cmHg) in perfluorodioxole copolymers and other materials

Gas	Polymer				
	Ia	Ib	PTFE [21–23]	POFPNB [11]	PTMSP [27,28]
N_2	–	7.6	1.5	3.9	14.2
CO_2	–	76	10.5	50	134
CH_4	–	16	2.5	7.8	50
C_2H_6	70	40	4.1	33	500
C_3H_8	230	–	6.4	–	1600
C_4H_{10}	575	–	11.7	–	–

Positron annihilation lifetimes (PAL) method was extensively used during the last decade for characterization of free volume in polymeric materials [30–33]. The annihilation parameters found by this method for PTMSP are also exceptional in comparison with most part of polymers. An interesting feature of PTMSP is that its lifetimes spectrum contains four components and not three as other polymers [34,35]. An intensive long-lived fourth component (τ_4, I_4) can be interpreted as an indication of the presence of very large free volume elements comparable, by their size, to the holes existing in porous sorbents like zeolites or silica gels. Different estimations of the radii of free volume elements in PTMSP gave values in the range 6–9 Å [34,35]. Since perfluorodioxole copolymers studied in this work showed permeability and diffusivity of the same order as those in PTMSP, it was of interest to study their free volume using the PAL method.

Table 6 presents PAL spectra of Ia, Ib, as well as of PTFE and other polymers chosen for the comparison. A feature of Ia and Ib copolymers is that their PAL spectra consist of four components. Both perfluorodioxole copolymers exhibit the fourth component with enhanced τ_4 lifetimes. Among non-porous films, that large τ_4 values have been observed so far only for PTMSP (see Table 6). Unexpectedly, four component spectrum is observed also for PTFE, although the τ_4 value is not as large as in the case of perfluorodioxole copolymers. In fact, it is more similar to τ_3 values characteristic for ordinary polymers (see, e.g., PAL spectrum of POFPNB). This observation seems to be

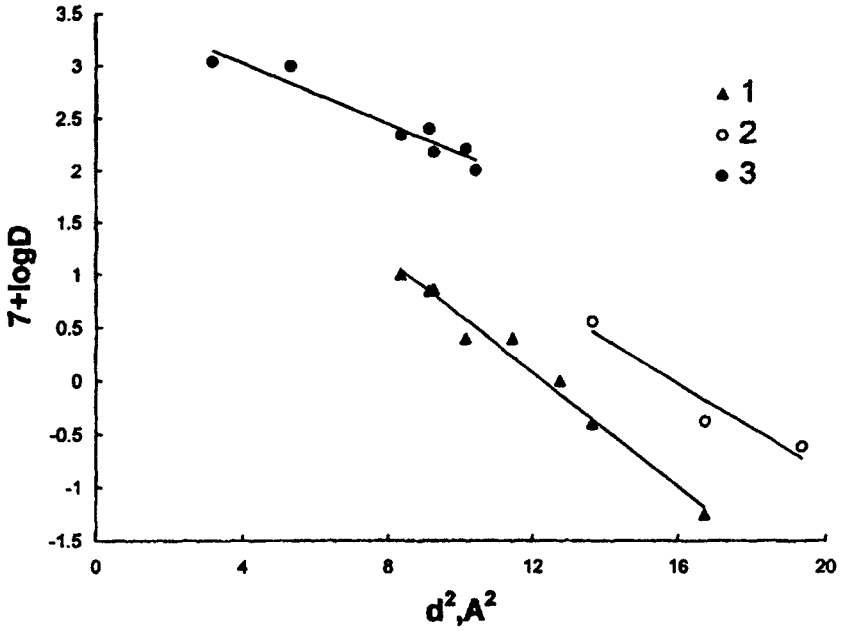


Fig. 2. Dependence of gas diffusion coefficients D (cm^2/s) on d^2 in perfluorodioxole copolymers and PTMSP. (1) Ib, (2) Ia, and (3) PTMSP.

Table 6
Positron annihilation lifetimes spectra τ_i (ns) and I_i (%)

Polymer	τ_1	I_1	τ_2	I_2	τ_3	I_3	τ_4	I_4
PTFE [36]	0.12	16	0.35	64	1.2	12	3.6	8
POFPNB [11]	0.294	47.6	0.591	33.6	3.74	18.8	–	–
Ib	0.180	20.8	0.386	55.9	0.68	8.5	4.73	14.8
Ia	0.204	22.4	0.425	62.1	1.71	2.39	5.96	13.1
PTMSP [34]	0.210	41	0.580	25	2.47	5	6.67	30

quite unusual since PTFE is distinguished, to the contrary, by low P and D values as well as free volume, and need to be scrutinized.

It was shown [30,32] that, for different polymers, a correlation exists between the permeability and diffusion coefficients, the parameters of sorption isotherms and the product $\tau_3 I_3$ determined from three components convolution of experimental PAL spectrum. When dealing with the polymers having four component spectra, a similar correlation is observed with the parameter $\tau_4 I_4$, as can be seen from Table 7. Apparently, it is this parameter which can serve as a measure of free volume in such polymers.

Deeper insight in size distribution of free volume elements in a material can be attained using different models of behavior of free positrons and o-positronium in polymers. Thus, a model was developed [37], which allows to calculate the concentrations, averages sizes and resulting free volume in so called ordered and disordered regions in polymers. The application of this model shows that an average size of free volume elements in perfluorodioxole copolymers is in the range 5.9–6.4 Å, whereas that of PTMSP has been reported as 6.7 Å [38]. A corresponding fraction of free volume (in more loosely packed regions within the materials) is equal to 0.03–0.04 in perfluorodioxole copolymers but 0.1 in PTMSP. On the other hand, the radii and free volume in disordered regions of "normal" glassy polymers are, according to [37], 4–5 Å and 0.001–0.003, respectively. Therefore, the peculiarities of gas permeation behavior in the materials studied can be rationalized in terms of free

Table 7
Correlations of P, D, and S with the $\tau_4 I_4$ parameter

Polymer	$\tau_4 I_4$	P (Barrer) (for O_2)	$D \times 10^7$ (cm^2/s^1) (for C_2H_6)	$S \times 10^3$, (cm^3(STP)/cm^3 cmHg) (for C_2H_6)
PTFE	0.29	4.3 [21]	0.056 [23]	4.1 [23]
Ib	0.70	170	0.4	40
Ia	0.78	1140	3.6	70
PTMSP	2.0	3000 [2]	25 [a]	500 [27]

[a] Estimation via log D–d^2 correlation [29].

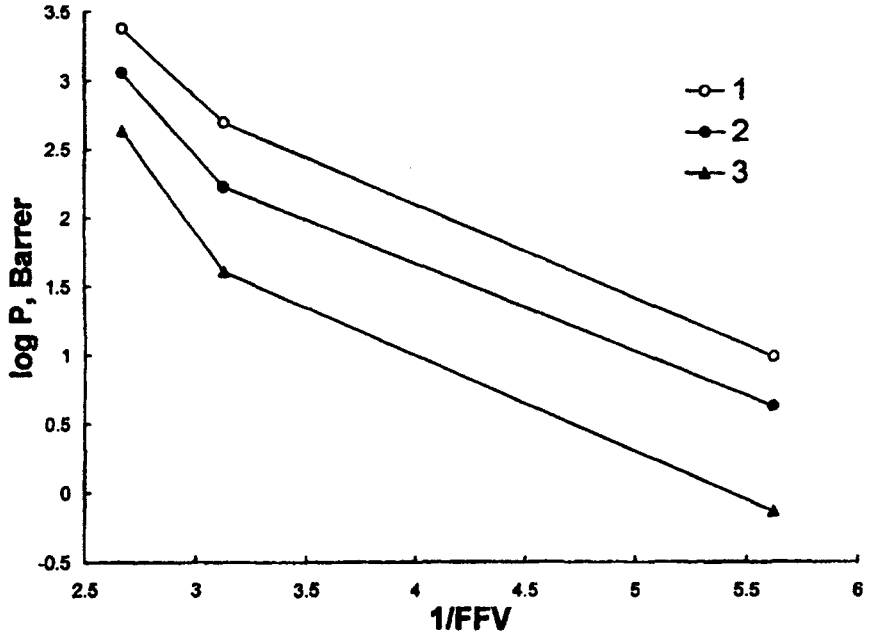


Fig. 3. Permeability coefficients of perfluorodioxole copolymers and PTMSP vs. fractional free volume. (1) H_2, (2) O_2, and (3) CH_4.

volume parameters as measured by positron annihilation method. Further analysis of the application of the model approach will be performed elsewhere.

The conclusions on free volume, which are based on the PAL method, and estimations of free volume via Bondi's method, are in qualitative agreement. Fig. 3 shows the dependence of permeability coefficients of several gases on FFV in PTMSP, Ia, and Ib.

4. Conclusions

The study of transport properties and free volume of two perfluorodioxole copolymers revealed several interesting characteristics of these materials.

(1) The copolymers with high perfluorodioxole content exhibit very high permeability coefficients with respect to light gases inferior only to those of PTMSP.

(2) Permeability of these copolymers is more sensitive to chemical nature and/or size of penetrant molecules – for heavier gases like hydrocarbons C_1–C_3, the P values are markedly lower. It results in much higher permselectivity of these materials. On the correlations of permeability with separation factors, the corresponding points for many gas pairs lie close to or higher than upper bound lines as reported by Robeson [24].

(3) Free volume of these materials was estimated via Bondi method and determined by positron anni-

hilation technique. It was shown to be very high and similar to the one previously reported for PTMSP. Determination of size distribution of free volume elements indicated that average size of free volume elements in PTMSP and perfluorinated materials studied are very similar; however, the former exhibit larger free volume fraction of this part of its size distribution. Apparently, this is one of the reasons for higher permeability and diffusivity of PTMSP in comparison with perfluorodioxole copolymers. Other reasons can be related to peculiarities of size distribution and topology of this part of free volume elements.

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