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Gas transport in fluorothiophenyl modified PVC membranes

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ABSTRACT

This work reports the modification of poly(vinyl chloride) by partially replacing the chlorine atoms of the chains with moieties derived from fluorinated nucleophilic compounds: 4-fluorothiophenol, 3,4-difluorothiophenol and pentafluorothiophenol. Membranes were cast from tetrahydrofuran solutions of the modified poly(vinyl chloride)s and the permeability and diffusion coefficients of hydrogen, nitrogen, oxygen, carbon dioxide and methane through the membranes were measured using permeation techniques. The influence of both the degree of modification and the number of fluorine atoms containing in functionalizing groups on the performance of the membranes was thoroughly investigated. A permselectivity study is also presented in order to evaluate the potential applicability of the membranes for gases separation.

1. Introduction

Poly(vinyl chloride) (PVC) is one of the commodity polymers of highest worldwide consumption. The utilization of PVC in a wide variety of applications derives from the good properties of this polymer, especially high compatibility with additives, easy processability and recyclability. Although the low cost and the good properties of PVC have contributed to extend the use of this material to different applications of commercial importance, studies on the performance of PVC films in gases separation are scarce. Earlier work carried out in our laboratories showed that PVC membranes exhibit low permeability to gases accompanied of rather high selectivity [1–3]. Enhancement of the permeability of PVC membranes can be accomplished by replacing, in a controlled way, chlorine atoms of the chains along the membrane thickness by bulky chemical moieties that hinder PVC chains packing [4]. In this regard, earlier studies showed that the permeability of membranes of PVC functionalized with mercaptopyridine groups increases due to the augment of the diffusivity [1,3].

The experience at hand indicates that fluorinated polymers allow the preparation of membranes with enhanced permeability without significant detriment of permselectivity [5,6]. Thus membranes of polyimides and copolyimides with trifluoromethyl linkages to the backbone display high permeability accompanied of rather good permselectivity [7–11]. Similar studies carried out in membranes based on polybenzoxazoles [12], polycarbonates [13,14], poly(ether imide)s [15] and polynorbornene dicarboxiimides [16–18] show that fluorinated moieties increase membranes permeability. Moreover, it is well-known that polymers containing fluorine atoms in their structure possess many desirable physical properties [19] such as good chemical resistance and low surface energy, compared with their non-fluorinated analogues. In view of these antecedents, it would be desirable to increase the permeability of PVC membranes by functionalizing them with relatively bulky chemical moieties containing fluorine atoms in their structure. It is expected that the partial replacement of chlorine atoms by fluorinated residues in PVC will decrease chains flexibility and also will disrupt chains packing efficiency in the glassy membranes. An increase in chains rigidity decreases the conformational entropy of the molecular chains whereas disruption of PVC segments packing by effect of the functionalizing groups increases the free volume. These two combined effects may affect the glass transition temperature and physical aging of the glassy functionalized PVC. Moreover, an increase in chains rigidity presumably hinders the formation of channels through which diffusive particles wandering in a cavity slip to neighbouring ones thus decreasing the diffusion coefficient, whereas the increase in free volume increases the diffusive paths and as result increases the diffusion coefficient. The result of these two opposite effects on the diffusion of gases in membranes prepared from functionalized PVC will be discussed in this work. Special attention will be paid to the effect of physical aging on the transport parameters and for this purpose a protocol will be used to minimize this effect.

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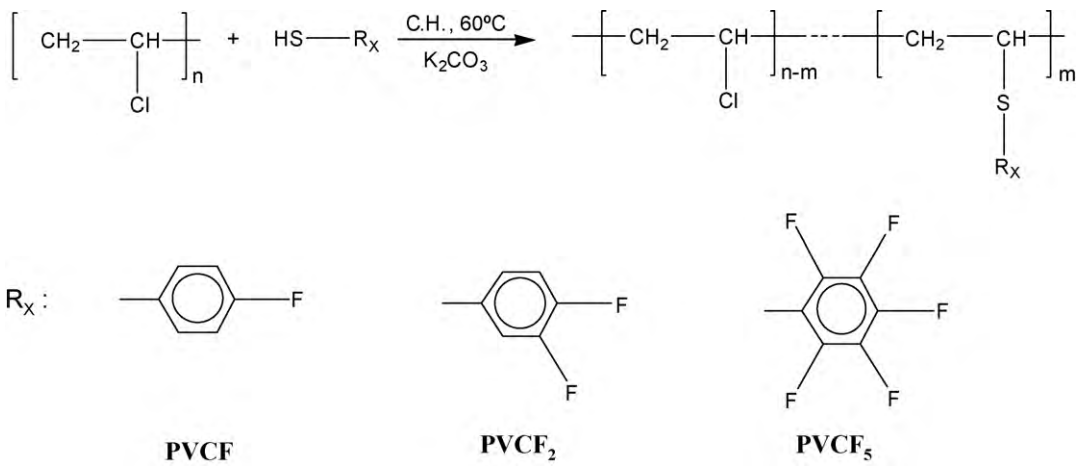

Scheme 1. Nucleophilic substitution of PVC and chemical structures for different fluorothiol modified PVCs.

Taking advantage of our experience in the selective chemical modification of PVC [20–25], diverse samples of functionalized polymer were prepared by reacting in a controlled way PVC chains with 4-fluoro-, 3,4-difluoro-, and pentafluorothiophenol [26]. Then, membranes with different types and degrees of modification were obtained by casting the modified PVC polymers from THF solutions. The trends observed in the transport properties were analyzed in terms of the degree of modification and the number of fluorine atoms in the moieties replacing chlorine atoms of PVC chains.

2. Experimental

2.1. Materials

Commercial bulk polymerized PVC was obtained from Rio Rodano Industries, Spain. The average molecular weights determined by GPC were M_w = 112,000 g/mol and M_n = 48,000 g/mol. The stereoregularity of the chains measured by ^{13}C NMR spectroscopy was 30.6%, 49.8% and 19.6%, respectively, for syndio-, hetero- and isodyads. 4-Fluorothiophenol (98% purity), 3,4-difluorothiophenol (96%), and pentafluorothiophenol (97%), nucleophilic compounds utilized in the modification of PVC, were purchased from Aldrich and used as received. Cyclohexanone was bidistilled prior to use.

The gases used in the transport measurements were hydrogen, nitrogen and oxygen (purity 6.0), carbon dioxide (purity 4.8) and methane (purity 5.0).

2.2. Fluoroaromatic thiol modified PVC and degree of substitution

Bulk modification of PVC was carried out using the procedure described elsewhere [20]. Briefly, PVC (1.0 g, 16 mmol) and 16 mmol of corresponding aromatic compound were dissolved in 100 ml of cyclohexanone. Potassium carbonate (3.2 g) was added and the reactions proceeded under N_2-atmosphere at 60 °C. The reactions were stopped by precipitating the mixture in cold methanol/water (2:1). The modified polymers were purified twice using THF/methanol as a solvent/precipitant system. This procedure was the same for each modifier studied.

The degrees of substitution of the modified polymers were determined by ^1H NMR. Spectra were recorded at 25 °C with a Varian spectrometer at 300 MHz using 5% (w/v) deuterated dimethyl sulfoxide, deuterated chloroform or deuterated acetone solutions depending on the solubility of the sample to be analyzed. In the case of the pentafluorinated samples, the degree of modification was obtained by Elemental analysis on a Leco CHNS-932.

The samples were also characterized by IR measurements on thin films of the modified polymers, using a Nicolet 520 FTIR spectrometer [26].

2.3. Membranes preparation and characterization

Membranes were prepared by casting from THF solutions (c = 100 mg/ml) on a glass plate, at room temperature and ambient pressure. The films were dried in an oven at 50 °C for three days and then were stored for one month at room temperature to eliminate any dependence of the transport data on physical aging. The thickness of the membranes ranged from 50 to 90 μm (±3 μm) and, in this range, thickness effects on gas permeability was not detectable [27].

The densities of the films were determined using a hydrostatic balance (Kern Densimeter) (0.0001 g accuracy) applying the Archimedes' principle and isopropanol as a liquid with known density, using the formula:

$$\rho = \frac{w_1}{w_1 - w_2}\rho_s + \rho_g \quad (1)$$

where w_1 is the weight of the sample in air, w_2 is its weight immersed in the liquid, ρ_s is the isopropanol density and ρ_g (0.00129 g/cc) is the air density at standard pressure and temperature. The measurements were performed at 28 °C using different size of samples. Each of them was weighed six times in air and in liquid. The error estimated in the determination of the densities was about 0.8%.

The fractional free volume (FFV) was obtained as:

$$\mathrm{FFV} = \frac{V - 1.3V_w}{V} \quad (2)$$

where V is the polymer specific volume (=1/ρ) and V_w is the specific van der Waals volume estimated using van Krevelen's data [28].

Glass transition temperatures of both the modified PVC powders and the corresponding membranes obtained by casting were determined using a Perkin-Elmer DSC-7 (Perkin-Elmer) differential scanning calorimeter at the heating rate of 10 °C/min. The values of T_g were taken in the thermograms obtained in the second run as the temperatures at the midpoint of the DSC endotherms.

2.4. Gas permeation measurements

Gas transport measurements were performed in an experimental device made up of two compartments separated by the membrane and described in detail elsewhere [29]. Prior to the permeation measurement, the membrane of interest was placed into

Table 1
Acronyms, percent of modification, density, free volume and glass transition temperature of modified PVCs.

Acronym	Modifier	Percent modification (mol%)	ρ (g/cm^3)	FFV	T_g (°C) from DSC	
					Powder[a]	Film[b]
Pure PVC	None	–	1.412	0.142	83.0	83.4
PVCF-9	4-	9	1.358	0.164	81.2	81.1
PVCF-18	Fluorothiophenol	18	1.340	0.167	78.1	78.9
$PVCF_2$-4	3,4-	4	1.389	0.157	80.2	75.6
$PVCF_2$-15	Difluorothiophenol	15	1.389	0.161	77.5	77.0
$PVCF_5$-2	Pentafluorothiophenol	2	1.378	0.174	85.2	83.5
$PVCF_5$-12		12	1.422	0.185	85.4	82.5

[a] From Ref. [26].
[b] In this work.

the permeation cell remaining under a pressure of 3×10^{-7} bar until no traces of solvent in the membrane was observed. Then high vacuum was made in the two compartments of the cell separated by the membrane. The pertinent gas, at a given pressure, was suddenly introduced into one of the compartments, called hereafter upstream chamber, provided with a Gometrics pressure sensor (0–1 bar). The permeation area of the membrane was 3.46 cm^2. The gas flowing from the upstream chamber to the other compartment, or downstream chamber, was monitored as a function of time with an MKS pressure sensor (10^{-4} to 1 mm Hg) via a computer. The permeation equipment was immersed in a water thermostat at the temperature of interest. Measurements have been made at different temperatures ranging from 283 to 303 K.

3. Results

The general nucleophilic substitution reaction on PVC is depicted in Scheme 1. Three different series of partial PVC modified samples denoted PVCF, $PVCF_2$ and $PVCF_5$ were prepared by reacting PVC with the nucleophile compounds 4-fluorothiophenol, 3,4-difluorothiophenol and pentafluorothiophenol, respectively. Notice that the subscripts in the acronyms indicate the number of fluorine atoms in the functionalized groups. In Table 1, the acronyms and modification degree (%) of the samples synthesized in this work are compiled. Also the table collects the densities, fractional free volume and T_gs obtained by DSC for both the samples in the forms of powder [26] and film. The chemical structure of the products was analyzed by ^{1}H NMR where the aromatic peaks (7.5–7.3 ppm) in the modified polymers increase with increasing reaction time. The signal of the CH–Cl protons of PVC (4.5 ppm) decreases while a variety of new signals due to CH–S protons appear as the number of modifier groups in the polymer increases. It is worth noting that the chosen modification agents are characterized by a strong nucleophilic character and a low basicity in order to prevent dehydrochlorination reactions. Under these experimental conditions, unsaturation in the PVC chains arising from degradation reactions occurring in the substitution processes [26] is strongly suppressed in such a way that it is not detected in the ^{1}H NMR spectra of the samples. The evolution of the reaction and the degree of modification for $PVCF_5$ were also followed by IR. The spectra showed the complete absence of bands between 1600 and 1700 cm^{-1} (which would correspond to olefinic double bonds), thus supporting the ^{1}H NMR results concerning to the selectivity of the penta-halogenated modifiers with respect to the nucleophilic substitution.

As usual, the curves depicting the variation of the pressure of gas in the downstream chamber with time, shown in Fig. 1, consist of a transitory state at short times followed by a steady region at which the pressure is a linear function of time. The curves obtained by integration of Fick's second law using appropriate boundary conditions are described by the following expression [30]:

$$p(t) = 0.2786\frac{p_0 ALST}{V} \times \left(\frac{Dt}{L^2} - \frac{1}{6} - \frac{2}{\pi^2}\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2}\exp\left(-\frac{Dn^2\pi^2 t}{L^2}\right)\right) \quad (3)$$

where p and p_0, in cm Hg, are respectively the pressure of the gas in the down- and upstream chambers. In this equation, S and D are the solubility and diffusion coefficients in cm^3(STP)/cm^3 cm Hg and cm^2/s, respectively; T is the absolute temperature, V is the volume of the downstream chamber in cm^3; A and L are, respectively, the area and thickness of the film in cm^2 and cm.

In steady state conditions ($t \to \infty$), Eq. (3) becomes

$$p(t) = 0.2786\frac{p_0 ALST}{V}\left(\frac{Dt}{L^2} - \frac{1}{6}\right) \quad (4)$$

This equation describes the pressure of the downstream chamber at long times. From the intercept of the straight line with the time axis, the time-lag θ ($=L^2/6D$) is obtained. Hence, the diffusion coefficient can be determined directly from θ by the expression

$$D = \frac{L^2}{6\theta} \quad (5)$$

This method, suggested by Barrer [31], allows the estimation of the diffusion coefficient of gases in the membranes from permeation measurements.

Since the apparent permeability coefficient, P, is the solubility coefficient times the diffusion coefficient, the value of P in barrers {1 barrer = [10^{-10} cm^3(STP) cm/cm^2 s cm Hg]} can be obtained

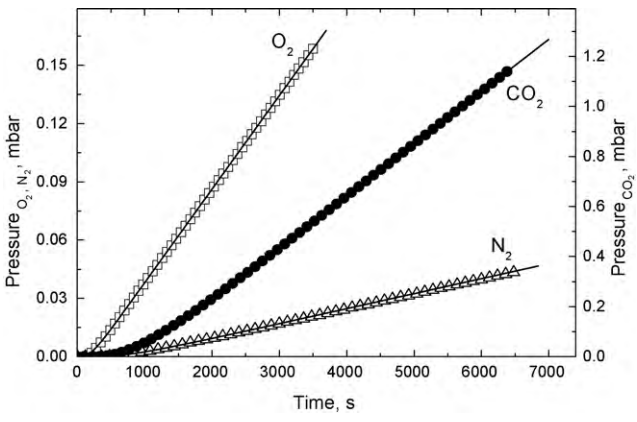

Fig. 1. Illustrative plots showing the variation of the pressure of (△) nitrogen, (□) oxygen and (●) carbon dioxide with time in the downstream chamber for the PVCF-18 membrane. Continuous line represents the values calculated from the integration of Fick's second law with appropriate boundary conditions.

Table 2
Transport coefficients of different gases in PVC and modified PVCs at 303 K and 1 bar of pressure. All samples have been kept during one month at room temperature before performing the permeation experiments.

Sample	Gas	P (barrer)	$D \times 10^8$ (cm^2 s^{-1})	$S \times 10^4$ (cm^3 cm^{-3} (cm Hg)$^{-1}$)
Pure PVC	O_2	0.07	0.71	9.7
	N_2	0.01	0.12	8.7
	CO_2	0.25	0.12	206.8
	H_2	1.88	77.4	2.4
PVCF-9	O_2	0.19	2.34	8.2
	N_2	0.02	0.64	3.8
	CO_2	0.79	0.49	160.4
	H_2	3.57	90.9	3.9
PVCF-18	O_2	0.36	4.13	8.7
	N_2	0.06	1.01	5.7
	CO_2	1.54	0.94	164.8
	H_2	5.31	125.0	4.3
	CH_4	0.06	0.17	36.5
$PVCF_2$-4	O_2	0.24	3.56	6.6
	N_2	0.03	1.22	2.5
	CO_2	0.89	0.81	110.2
	H_2	5.07	200.75	2.5
$PVCF_2$-15	O_2	0.19	1.80	10.6
	N_2	0.02_3	0.60	3.8
	CO_2	0.68	0.39	177.0
	H_2	3.53	77.5	4.6
	CH_4	0.03	0.14	21.8
$PVCF_5$-2	O_2	0.12	1.78	6.6
	N_2	0.01	0.82	1.5
	CO_2	0.48	0.32	150.8
	H_2	2.42	84.8	2.9
$PVCF_5$-12	O_2	0.14	2.01	6.9
	N_2	0.02	0.71	3.4
	CO_2	0.57	0.44	130.0
	H_2	2.77	90.0	3.1
	CH_4	0.03	0.18	18.3

directly from Eq. (4) by means of the expression

$$P = 3.59\frac{VL}{p_0AT}t \overset{\lim}{\rightarrow} \infty \left\{\frac{d[p(t)]}{dt}\right\} \quad (6)$$

The apparent solubility coefficient was obtained from the permeation and diffusion results by

$$S = P/D \quad (7)$$

In all cases the good fitting of Eq. (3) to the experimental flux *vs* time isotherms indicates that the assumption utilized in the integration of Fick's second law, that D is independent on concentration, holds. The good fitting also indicates that steady state conditions were achieved in the flux curves from which the values of P and D were estimated. The relative error involved in the determination of the diffusion coefficient by Eq. (5), estimated as

$$\Delta = \frac{100}{D}\left(\left|\frac{L\,\varepsilon(L)}{3\theta}\right| + \left|\frac{L^2\,\varepsilon(\theta)}{6\theta^2}\right|\right) \quad (8)$$

was lower than 15% in the most unfavourable cases. The error was lower than 3% for the permeability coefficient.

Values of the permeability, diffusion and solubility coefficients of the gases in PVC and the six modified PVC samples at 303 K are given in Table 2. The results show that all membranes exhibit nearly the same behavior with regard to the permeability of gases across them in the sense that hydrogen has the highest permeability coefficient followed by CO_2 and O_2, whereas the permeability coefficients of nitrogen and methane have nearly the same value. Therefore $P(H_2) > P(CO_2) > P(O_2) > P(N_2) \approx P(CH_4)$. Moreover, the permeability coefficients of the gases in the functionalized PVC membranes are considerably higher than in PVC.

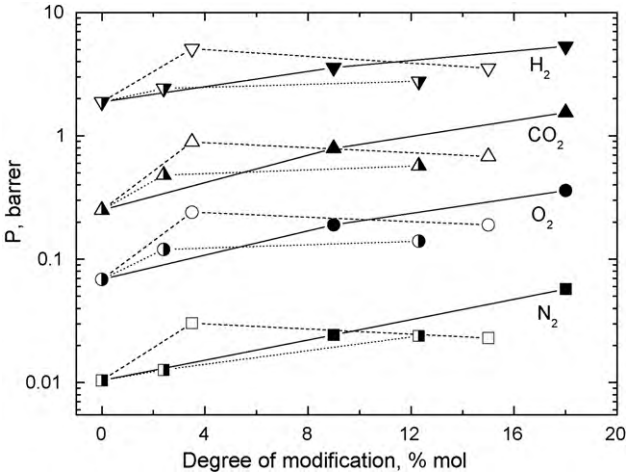

Fig. 2. Permeability coefficients at 303 K and 1 bar of (circles) oxygen, (squares) nitrogen, (up-triangles) carbon dioxide and (down-triangles) hydrogen for (full symbols) PVCF, (open symbols) $PVCF_2$ and (broken symbols) $PVCF_5$. The samples have been kept for one month at room temperature before performing the experiments.

The variation of the permeability coefficient of the gases with the degree of modification of the membranes is depicted in Fig. 2. It can see that the permeability of the gases in the membranes with higher degree of modification decreases as the number of fluorine atoms in the aromatic ring increases in such a way that P(PVCF-18) > P($PVCF_2$-15) > P($PVCF_5$-12). However, for the less modified membranes the permeability coefficient does not follow a definite trend since this parameter increases from mono- to difluorothiol functionalized membranes and decreases again for the $PVCF_5$ membrane. Therefore P($PVCF_5$-2) < P(PVCF-9) < P($PVCF_2$-4).

The influence of both the substitution degree and the chemical nature of the functionalizing agent on the diffusion coefficients of the diffusants are presented in Table 2. The diffusion coefficient of methane in the PVC membrane is so small that the accurate measurement of this parameter with the permeation equipment used in this work was not possible. As usual, hydrogen exhibits diffusivity two to three orders of magnitude higher than that of the other gases. Independently of the type of modified PVC membrane, the diffusion coefficient follows the trend $D(H_2) > D(O_2) > D(N_2) > D(CO_2) > D(CH_4)$. The dependence of the diffusion coefficient on the degree of substitution and type of functionalizing agent is shown in Fig. 3. It can be seen that the most conspicuous effect of the modification of PVC with fluoroaromatic residues is an important increase in the diffusion coefficient of the gases. However, the effect of the degree of substitution of the membranes on the diffusive step depends on the number of fluorine atoms in the aromatic ring of the chemical moieties replacing chlorine atoms in the PVC chains. So, an increase in the degree of substitution strongly increases the diffusivity of gases in PVCF membranes, decreases it in $PVCF_2$ and remains nearly constant in $PVCF_5$.

The values for the apparent solubility coefficient obtained from the ratio P/D are shown in the fifth column of Table 2. It can be seen that, as usual, carbon dioxide is the gas with higher solubility, whereas hydrogen and nitrogen have the lowest solubility coefficients. In all cases: $S(CO_2) > S(CH_4) > S(O_2) > S(N_2) \geq S(H_2)$. The solubility coefficient of the gases does not show a clear dependence on the degree of modification of the membranes since S(PVCF-9) ≅ S(PVCF-18), S($PVCF_2$-4) < S($PVCF_2$-15) and S($PVCF_5$-2) ≠ S($PVCF_5$-12). However, S(PVCF-9) ≅ S($PVCF_2$-4) ≅ S($PVCF_5$-2).

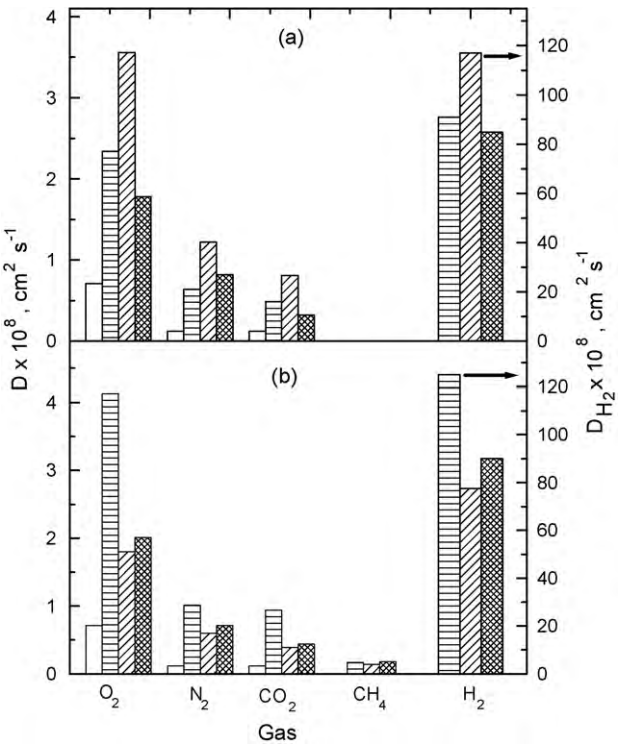

Fig. 3. Diffusion coefficients at 303 K and 1 bar of oxygen, nitrogen, carbon dioxide and hydrogen for (□) PVC, (▤) PVCF, (▨) $PVCF_2$ and (▩) $PVCF_5$ membranes with (a) lower and (b) higher modification degree.

4. Discussion

The replacement of the chlorine atoms by bulky chemical moieties should affect the glass transition temperature of PVC, at least in the systems with higher degree of modification. Actually, the bulky side groups may presumably increase the free volume and also hinder conformational transitions in the modified PVC chains. The first effect would decrease the glass transition temperature, while the second that intensifies the rigidity of the chains would increase it. The results for T_g collected in Table 1 show that the first effect overcomes the second one for the membranes containing one or two fluorine atoms in the phenyl groups of the moieties replacing the chlorine atoms, so that the T_g decreases. The same effect has been observed by Tanaka et al. [9] in aromatic polyimides containing CF_3 groups in asymmetric positions. This behavior is also in accordance with the higher permeability of PVCF and $PVCF_2$, due to an increase in the free volume arising from enhanced local segmental mobility. However, the glass transition temperature of the membrane containing five fluorine atoms in the phenyl group of the functionalized residues is similar or slightly higher than the T_g of PVC, so that in this case the second effect seems to be dominant. On other hand, the presence of five fluorine atoms in the aromatic ring of the functionalizing agent in $PVCF_5$ hinders chain packaging so that the FFV in the glassy state increases with the degree of substitution, as the results of Table 1 suggest. Rigidity of the chains is expected to result in a decrease of gas permeability and enhancement of permselectivity [32,33].

The results for the permeability of different gases in the modified membranes, collected in Fig. 2, show that the permeability coefficient in PVCF films increases with the substitution degree, probably due to an increase in the diffusion coefficient caused by an augment in FFV. However the permeability and diffusion coefficients of the gases in $PVCF_2$ films diminish with increasing modification for degrees of substitution lying in the range 4–15%. It could appear surprising that D diminishes despite the increase in FFV, a behavior shared by PVCF5 films. This behavior, similar to that exhibited by PVC membranes functionalized with mercaptopyridine groups [2,3], can be explained taking a look to the diffusive step at molecular level in glassy systems. Actually, a diffusant molecule wanders in a cavity, with a motion which does not contribute to diffusion, until chain fluctuations produce channels with radii higher than that of the diffusant through which it slides to nearby cavities. Then the diffusion coefficient not only depends on the free volume but also on local fluctuations. Using simulation techniques, Wang et al. [34] found that both the free volume and the distribution of cavities affect the diffusive process, so it is hardly surprising that glassy films with similar fractional free volume exhibit different diffusivities.

Owing to the metastable nature of the glassy state, the volume of glassy systems at temperatures slightly lower than T_g decreases as time increases tending to the extrapolated volume of the liquid state at the temperature of interest. Reduction of excess volume or densification of glassy systems in isothermal conditions is called physical aging. Aging implies economy of volume and therefore the process involves segments motions to accommodate the polymer chains in less volume. Therefore, physical aging is more rapid as the temperature of the glassy system comes near to the T_g. The isotherms depicting the changes in volume with temperature drop rather rapidly at short times reaching a constant value at moderately long times. However, as T decreases the drop in volume is less rapid and more time is necessary to reach a constant volume. For systems at temperatures well below T_g the thermal energy is rather low and nearly no change in volume is seen as time increases. Therefore physical aging is nearly negligible in these conditions. As indicated above, for polymers with glass transition temperature not far above from the working temperature, such as PVC, physical aging is important and affects the physical properties of the glassy system. In connexion with this, Tiemblo et al. [1,3] reported that the diffusion coefficient of gases in either PVC or pyridine modified PVC membranes decreases by almost one order of magnitude during the first month after the membranes cast from polymer solutions. The permeability coefficient also decreases, but the tendency of the variation of this parameter with the amount of pyridine groups in the PVC structure differs from that of the diffusion coefficient, though it depends on the degree of modification

Table 3
Values of the permeability, P, diffusion, D, and apparent solubility, S, coefficients of gases across monofluoro- and difluorothiol aromatic modified PVC at 303 K and 1 bar of pressure. The samples have been kept during one month (M) and one year (Y) at room temperature.

Sample	Gas	P (barrer)		$D \times 10^8$ ($cm^2\ s^{-1}$)		$S \times 10^4$ ($cm^3\ cm^{-3}\ (cm\ Hg)^{-1}$)	
		M	Y	M	Y	M	Y
PVCF-18	O_2	0.36	0.32	4.13	3.34	8.7	9.6
	N_2	0.06	0.05	1.01	0.93	5.7	5.3
	CO_2	1.54	1.36	0.94	0.72	164.8	189.4
$PVCF_2$-15	O_2	0.15	0.12	1.06	1.10	14.2	11.2
	N_2	0.022	0.017	0.24	0.24	9.6	6.8
	CO_2	0.59	0.46	0.24	0.19	240.4	248.7

of PVC. For this reason, previous to the transport experiments carried out in this work, the membranes were maintained at room temperature for one month. To confirm that no longer physical aging is important and the excess volume remains constant in the glassy membranes, transport measurements were also performed in membranes highly functionalized with mono- and difluorothiol aromatic compounds, specifically PVCF-18 and $PVCF_2$-15, one year aged at room temperature. The results obtained for transport parameters in these membranes are shown in Table 3. For comparative purposes, the values obtained for the membranes aged one month are also shown in the table. It can be seen that both the permeability and diffusion coefficients for the membranes aged one year are slightly lower than those obtained for membranes aged one month. This fact is in agreement with previous results [1] which show the decreasing trend of P and D coefficients continue for over a month, and as a matter of fact stabilisation of the diffusion data could not be accomplished during this period. The data of Table 3 indicate that the diminution of the permeability by effect of aging depends on the chemical nature of the fluorinated moiety ranging from 15% for PVCF-18 to 20% for $PVCF_2$-15. On the other hand, the reduction of D is more evident the greater the size of diffussant molecule in the PVCF-18 membrane is, but it is not clear for the $PVCF_2$-15 membrane. In any case the changes in D caused by the increase of aging time from one month to one year are very small, lying in the range of the experimental error.

In the glassy state, occasional local fluctuations in the molecular chains give rise to the formation of channels through which diffusant molecules wandering in one cavity slip to neighbouring ones. The possibility of slippage requires not only an appropriate velocity of the molecule in the cavity next to the channel but also the radius of the channel should be at least equal to the van der Waals radius of the diffusant (σ). According to Meares [35], the activation energy associated with the diffusion process should be proportional to that required to open a channel thorough which the slippage takes place, that is

$$E_D \propto \left(\frac{\pi}{4}\right) \sigma^2 N_A \lambda(\mathrm{CED}) \tag{9}$$

where N_A is Avogadro's number, λ is the length of diffusion jump and CED is the cohesive energy density. In this case, the plot of $\ln D$ *vs* σ^2 should be a straight line of negative slope [36,37]. The size of a gas molecule can be estimated from the Lennard–Jones collision diameter (σ_c), determined on the basis of the molecular interactions of a gas, and the kinetic diameter (σ_k) which is close to the molecular sieving dimension of the molecule [14,38]. Both correlation parameters are widely accepted for diffusivities in rubbery and glassy states, respectively. The values of the natural logarithm of the diffusion coefficient of H_2, N_2, O_2, CO_2 and CH_4 for samples with the higher modification degree are plotted against the square of the radii of the gases in Fig. 4. With the exception of CO_2, the data fit rather well to straight lines, and the slopes of the plots for the different membranes slightly differ as a consequence of different cohesive energies of the membranes and jump lengths. As usual in this type of plots, the diffusion coefficient of CO_2 falls below each straight line. This fact may be most likely due to the difficulty in predicting an accurate diameter for the CO_2 molecule because of its non-spherical nature. The CO_2 molecule may have a larger effective size, possibly between its kinetic diameter of 3.3 Å and its collision diameter of 4.0 Å [39,40]. Another possible reason could be the strong quadrupole of the CO_2 molecule [40].

The high value of the solubility coefficient of carbon dioxide (in the order of 10^{-2} cm^3/cm^3 cm Hg) in comparison with that of oxygen and nitrogen (about 10^{-4} cm^3/cm^3 cm Hg), is the factor responsible for the relatively high permeability coefficient of CO_2 in the membranes, regardless the degree of modification and the number of fluorine atoms in the functionalizing groups. The small

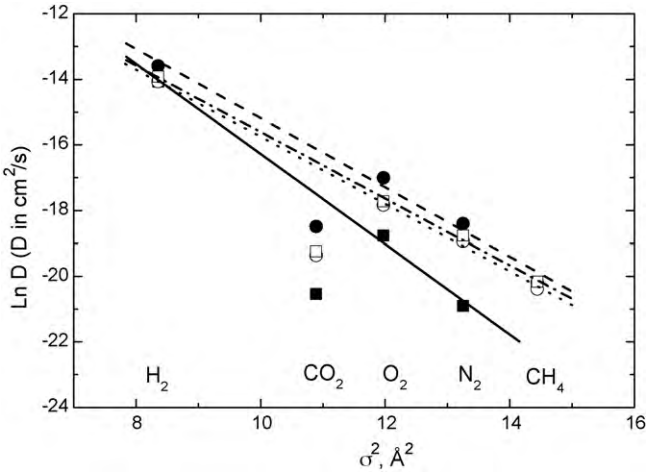

Fig. 4. Natural logarithms of the diffusion coefficients of the gases as a function of the squares of their kinetic diameters for (■) PVC, (●) PVCF-18, (○) $PVCF_2$-15 and (□) $PVCF_5$-12 membranes keeping one month at room temperature.

Table 4
Activation energies, in kcal/mol, associated with the permeability (E_P), diffusion (E_D) and solubility coefficients (ΔH_S) of oxygen, nitrogen and carbon dioxide in modified PVCs, at 1 bar of pressure.

Sample	Gas	E_P	E_D	ΔH_S
PVCF-18	O_2	4.5	8.0	−3.5
	N_2	5.9	10.7	−4.8
	CO_2	2.9	9.4	−6.5
$PVCF_2$-15	O_2	4.9	9.1	−4.2
	N_2	8.6	12.4	−3.8
	CO_2	3.7	9.9	−6.2
$PVCF_5$-12	O_2	5.3	9.4	−4.1
	N_2	8.9	12.2	−3.3
	CO_2	3.2	10.4	−7.2

sensitivity of the solubility coefficient for a given gas to the number of fluorine atoms in the aromatic ring suggests that gas/polymer interactions are little sensitive to the differences in the structure of the modified PVC membranes. Consequently, although the gas permeability depends on both solubility and diffusivity, the variations in permeability in modified PVC membranes mainly arise from changes in diffusivity.

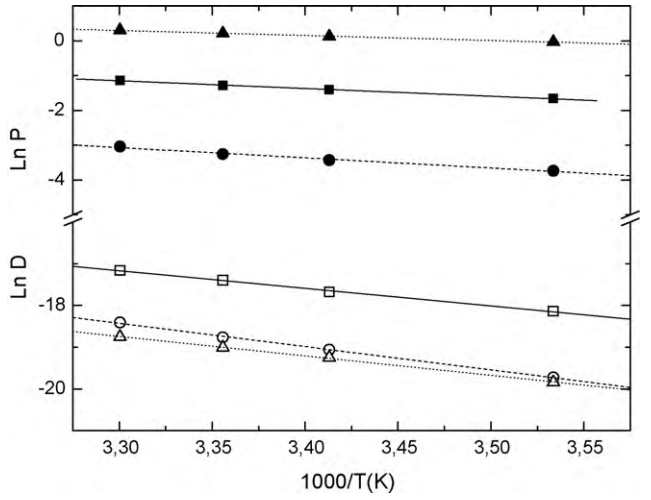

Fig. 5. Illustrative Arrhenius plots for D (open symbols) and P (filled symbols) of the following gases: (■, □) O_2, (●, ○) N_2 and (▲, △) CO_2, for sample PVCF-18.

Table 5
Permselectivity of pairs of gases for PVC and fluorothiol modified PVCs. The permeability coefficient of the gas of higher permeability of the pair of gases is shown between brackets.

Sample	$\alpha(H_2/CH_4)$ ($P(H_2)$)	$\alpha(O_2/N_2)$ ($P(O_2)$)	$\alpha(CO_2/CH_4)$	$\alpha(CO_2/O_2)$ ($P(CO_2)$)	$\alpha(CO_2/N_2)$
PVC	–	6.9 (0.07)	–	3.6 (0.25)	25.0
PVCF-9	–	7.9 (0.19)	–	4.2 (0.79)	32.9
PVCF-18	84.3 (5.31)	6.3 (0.36)	24.4	4.3 (1.54)	27.0
$PVCF_2$-4	–	7.9 (0.24)	–	3.9 (0.89)	30.4
$PVCF_2$-15	94.7 (3.53)	6.8 (0.19)	16.4	3.9 (0.68)	26.8
$PVCF_5$-2	–	9.2 (0.12)	–	4.0 (0.48)	36.9
$PVCF_5$-12	86.6 (2.77)	5.8 (0.14)	17.8	4.1 (0.57)	23.8

The temperature dependence of the transport parameters for CO_2, oxygen and nitrogen was investigated in PVCF-18, $PVCF_2$-15 and $PVCF_5$-12 membranes. In general, in absence of thermal transitions, the parameters that govern the variation of gas transport with temperature in membranes obey Arrhenius behavior [41]

$$P = P_0 \exp\left(\frac{-E_P}{RT}\right)$$
$$D = D_0 \exp\left(\frac{-E_D}{RT}\right) \quad (10)$$
$$S = \frac{P}{D} = S_0 \exp\left(\frac{-H_S}{RT}\right) = \frac{P_0}{D_0}\exp\left[\frac{E_D - E_P}{RT}\right]$$

where P_0, D_0 and S_0 are pre-exponential factors, E_P and E_D are, respectively, the apparent activation energies for permeation and diffusion and $H_S = E_P - E_D$ is the heat of sorption. The activation energy for permeation is the sum of a kinetic parameter, E_D, and a thermodynamic parameter, H_S, for a particular penetrant. The pertinent Arrhenius plots for the experimental results are shown in Fig. 5. It is convenient to remark that in order to avoid that aging effects contaminate the temperature dependence of the transport parameters, the experimental measurements were restricted to the temperature range 10–30 °C. The values obtained for E_P, E_D and the heat of sorption, expressed in kcal mol^{-1}, are shown in Table 4. The values of the activation energy associated with the permeability coefficient (E_P) of the gases lie in the vicinity of 2.9 kcal mol^{-1} for CO_2 and 8.9 kcal mol^{-1} for N_2; whereas the activation energy of the diffusive process (E_D) varies between 8.0 kcal mol^{-1} for O_2 and 12.4 kcal mol^{-1} for N_2. The values of the sorption heat (fifth column of Table 4) range from −3.5 to −4.2 kcal mol^{-1} for oxygen; from −3.3 to −4.8 kcal mol^{-1} for nitrogen and from −6.2 to −7.2 kcal mol^{-1} for carbon dioxide. Therefore the solution of gases in the membranes is an exothermic process as it occurs with the solubility of most gases in glassy polymers [42]. Since $E_P > 0$, the permeability of the modified membranes increases with increasing temperature.

The permselectivity of membranes for gas separations is characterized by the permselectivity coefficient $\alpha(A/B)$ currently expressed by:

$$\alpha(A/B) = \frac{P_A}{P_B} = \frac{D_A}{D_B}\frac{S_A}{S_B} \quad (11)$$

The main goal pursued in the design of membranes is to combine high permeability with high selectivity. However, these two properties are mutually incompatible because in most cases high permeability is accompanied of low permselectivity. Robeson [43] has studied the trade off between permselectivity and permeability by plotting the permselectivity coefficient for diverse pair of gases in different membranes *vs* the permeability of the gas with higher permeability. In this way, the upper limits for different pair of gases which good performance membranes should surpass were obtained. The permselectivity coefficients obtained for the membranes studied are collected for different pairs of gases in Table 5. If $\alpha(O_2/N_2)$ in the pristine PVC membrane is taken as reference, the functionalization of the membranes slightly affects the permselectivity coefficient. However, the functionalized membranes present a bonus with respect to the PVC membranes in that the permeability coefficient of oxygen is at least twice that in the PVC membrane. For example, the permeability coefficients of oxygen in PVC, PVCF-9, PVCF-18 and $PVCF_2$-4 membranes are, respectively, 0.07, 0.19, 0.36 and 0.24 and the corresponding values of $\alpha(O_2/N_2)$ are 6.9, 7.9, 6.3 and 7.9. Something similar occurs for the permselectiviy of CO_2/N_2. Finally the permselectivity of pair of gases CO_2/O_2 and CO_2/CH_4 are practically no affected by the type of functionalizing agent, though these membranes are more permeable than the pristine PVC membrane.

5. Conclusions

Owing to the relatively low glass transition temperature of PVC, the study of gas transport in membranes based on this polymer should be restricted to temperatures in the vicinity of room temperature, or below, to minimize aging effects. Modification of the membranes of PVC by fluorinated functionalizing agents only slightly changes the glass transition temperature of these systems and therefore physical aging is an effect to take care in gas transport studies. Functionalizing moieties do not significantly improve the permselectivity of the pristine PVC membranes but cause a significant increase in the permeability coefficient. The augment in permeability of the modified membranes arises from the disruption of chains packing in PVC caused by the modification with bulky groups that increase the free volume. Then the increase in permeability comes from the augment in the diffusion coefficient. The degree of substitution rather than the number of fluorine atoms in the functionalizing groups affects the permeability of the modified membranes.

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