The Gas Transport Properties of PVC Functionalized with Mercapto Pyridine Groups

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ABSTRACT: The diffusivity, permeability, and solubility coefficients of O_2, N_2, CO_2, and CH_4 have been measured in PVC and in four samples of PVC functionalized with mercapto pyridine groups up to 6.8, 11, 21, and 46 mol %. It has been found that the permeability of all four gases progressively increases by a factor of more than 4 because of a similar increase in the diffusion coefficients. In addition, permeability selectivity augments significantly for the gas pair O_2/N_2 and only slightly for the pair CO_2/CH_4. The structural changes in the modified samples have been monitored by means of density and T_g determinations and FFV calculations, which are a measure of interchain spacing and chain stiffness. An interpretation of the changes seen in the gas transport properties of modified PVC samples has been proposed in terms of the structural changes introduced by the progressive functionalization of the PVC chains.

1. Introduction

The controlled modification of polymers containing efficiently packed chains appears to be a means of selectively improving transport properties of high-barrier membranes[1] through a selective variation of the free volume and free volume distribution. Some of the polymers proposed for this application are poly(ethylene terephthalate), poly(acrylonitrile), and poly(vinyl chloride).

Making use of our experience in the selective functionalization of PVC, we have decided to undertake the study of the gas transport properties of systematically modified PVC. Chlorine substitution in PVC can be controlled to range from less than 1% to over 60% depending on the reactant and the reaction conditions. A great variety of groups can be introduced in the chains from small[2] to very bulky[3] and from apolar to highly interacting groups.[4] This range of possibilities enables the control of the modification of structural features such as the interchain spacing, chain rigidity,[5] and degree of specific interactions, which are the features mostly affecting gas transport properties,[6−8] not only by means of the substituent choice but also via the selection of optimum modification degrees.

This versatility is among the characteristics of PVC that make it interesting as a starting point in the search for polymers that can enable the tailoring of gas transport properties. In addition, PVC is a cheap and readily available material that presents very remarkable mechanical properties. These characteristics, together with its relatively low T_g and its solubility in a wide variety of solvents, facilitate its manipulation and processing.

From a purely basic viewpoint, the study of the gas transport properties of PVC and slightly modified PVC has an additional interest. The structure of this polymer makes it comparatively simple to study by molecular dynamics (MD) simulations, even if it has the disadvantage of being densely packed. These simulations present a very appealing means of better understanding the relationship between the molecular structure and the transport behavior of this polymer, and we expect to perform such simulations soon, not only on PVC but also on PVC with very slight structural modifications. Obtaining systematic data on diffusion properties is, then, a necessary step for this plan.

In this work, a study of the transport properties of PVC modified by the introduction of mercapto pyridine groups is presented. The synthesis and some of the physical characteristics of this polymer have already been studied.[9] Together with the dependence of the gas transport properties on the degree of modification, an interpretation of the results in terms of the structural changes introduced by the functionalization is performed.

2. Experimental Section

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

Membranes. 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 tacticity measured by ^{13}C NMR spectroscopy was syndio = 30.6%, hetero = 49.8%, and iso = 19.6%. PVC modified with pyridine groups was obtained by nucleophilic substitution reaction of PVC with 4-mercapto pyridine sodium salt in cyclohexanone (CH). Degrees of substitution of PVC, expressed as mole percentages of ethyl thiopyridine/(ethyl thiopyridine + ethyl chloride), were determined by ^1H NMR spectroscopy. Spectra were recorded at 25 °C in 5% (w/v) DMSO-*d* solutions with a Varian Gemini 200-MHz spectrometer under standard conditions.

Membranes were prepared as described elsewhere.[10] They were cast from THF solutions ($c = 100$ mg/ml) on a glass plate, where they were dried at ambient temperature and pressure. Subsequently, the films were extracted with ether in a Soxhlet apparatus for 24 h. The films were then dried for 2 h at reduced pressure and ambient temperature, after which they were stored for about 1 month to eliminate any dependence on physical aging of the transport data. Then, they were introduced into the permeator, where they were left overnight at a pressure of 3×10^{-7} bar. No traces of solvent were detected by FTIR spectrometry. To avoid an unwanted dependence of physical aging on thickness, only thick films were used. It has

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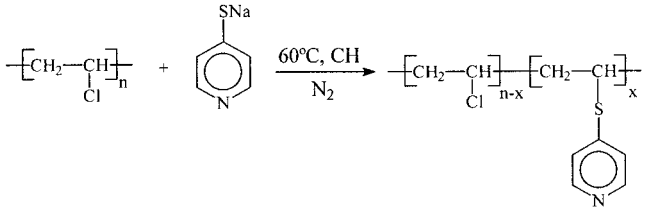
Table 1. Specific Volumes and Glass Transition Temperatures of the Pyridine-Modified PVC Samples

sample	percent modification (mol %)	T_g (°C)	ρ^{-1} (cm^3 g^{-1})
PVC	0	85	0.722
PVC−pyr7	6.8	87	0.742
PVC−pyr11	11	88	0.748
PVC−pyr21	21	91.5	0.766
PVC−pyr46	46	94.4	0.796

Scheme 1. Functionalization of PVC



been shown[11] that, whereas there is a strong dependence of the volume relaxation rate on the thickness of the film for films thinner than roughly 5 μm, negligible dependence exists over about 25 μm. The thickness of all membranes used ranged from 35 to 65 μm.

In this work, five samples were used: PVC and PVC substituted up to four increasing modification degrees. The sample's modification degree, T_g, and specific volume appear in Table 1. The structure of the functionalized units is shown in Scheme 1.

Density Measurements and FFV Calculation. The densities of the films were determined by the flotation method at 20 °C using water and an aqueous solution saturated with $ZnCl_2$. The composition of the solution was adjusted so that the films remained just suspended throughout. Care was taken to eliminate all bubbles sticking to the films using an ultrasonic bath. To minimize the error, four different sample pieces for each polymer were used. The densities of the solutions were determined using a pycnometer. The experimental error is less than 0.002 g/cm^3.

The fractional free volume (FFV) was obtained as follows[12]

$$\mathrm{FFV} = \frac{V - 1.3V_w}{V} \tag{1}$$

where V is the polymer-specific volume and V_w is the specific van der Waals volume. The van der Waals volume was estimated by using the Hyperchem computer program, version 5.01.[13] Hyperchem employs a grid method based on the work of Bodor et al.[14] using the atomic radii supplied by Gavezotti.[15]

Glass Transition. The glass transition temperature was determined by calorimetric measurements performed with a Perkin-Elmer DSC-7 differential scanning calorimeter. Samples of about 10 mg were heated to 150 °C under nitrogen atmosphere at 20 °C/min and quenched with a cooling rate of 200 °C/min. The T_g values reported were taken from the second runs (heating rate 15 °C/min) and correspond to the midpoint of the DSC curves.

Permeation Measurements. A laboratory-made permeator described elsewhere[16] was used for permeation measurements. Briefly, it consists of a gas cell in the middle of which the polymer membrane is placed. This membrane separates the upstream and downstream chambers. At the low-pressure side, a MKS Baratron-type 627B absolute pressure transducer (pressure range $1-10^{-4}$ Torr) measures the pressure increase, and at the upstream side, a Gometrics pressure detector is used to control the gas pressure at which the experiment is performed, which in this work is 1 bar. The whole setup is temperature-controlled at 25 °C by means of a water bath. To perform the measurements, vacuum is kept overnight in order to attain a low downstream pressure (about 10^{-6} bar). Pressure data are recorded every 5 s.

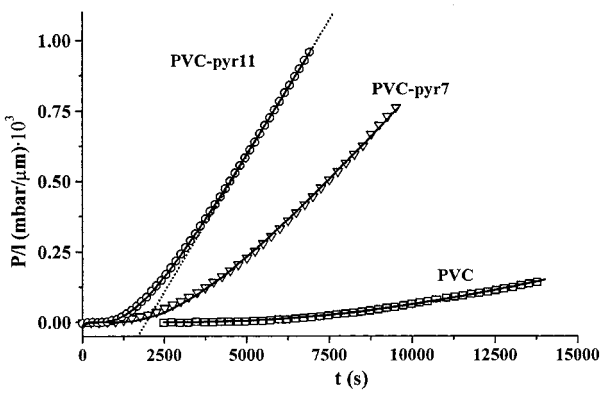


Figure 1. Methane pressure increase measured at the downstream chamber for PVC (□), PVC−pyr7 (▽), and PVC−pyr11 (○). For PVC−pyr11, together with the experimental data points (1 every 50 for the sake of clarity), the fit using eq 2 (solid line) and the steady-state straight-line fit (dotted line) are shown.

The permeability and diffusivity coefficients were calculated from the curves measuring the pressure increase at the downstream side. If the diffusion and permeation coefficients are to be calculated from the linear pressure increase, characteristic of gas diffusion at the steady state, then the experiment must last long enough to ensure that this steady state is achieved. When the diffusion coefficients are very low, the duration of the experiment is too long for realistic experimental procedures. Thus, for low diffusion coefficients, it is necessary to try the fit of the whole pressure increase curve[6]

$$\frac{Q_t}{lC_1} = \frac{Dt}{l^2} - \frac{1}{6} - \frac{2}{\pi^2}\sum_1^\infty \frac{(-1)}{n^2} e^{-(Dn^2\pi^2 t)/l^2} \tag{2}$$

where Q_t is the amount of diffusant traversing the membrane, l is the membrane thickness, C_1 is the concentration of diffusant at the upstream side of the membrane, and D is the diffusion coefficient. In the present work, this fitting was done essentially to verify that the rise in pressure at the downstream chamber corresponds to Fickian diffusion across the membrane. Equation 2 (including six terms of the summation) was used to fit some selected data from experiments carried out with all four gases. The transport coefficients obtained from these fits were compared with those calculated from the steady-state straight line, to test that the two sets of coefficients are, within experimental error, the same. This was indeed the case, and as an example, the pressure curve corresponding to a diffusion experiment performed on PVC−pyr11 with methane is shown in Figure 1. Both the steady-state straight line and the complete fit of the experimental data points with eq 2 are depicted. The agreement between the transport coefficients obtained from the two fittings is very good. For example, the diffusion coefficient calculated from the steady-state curve is 2.85×10^{-9} cm^2 s^{-1}, whereas that calculated from the complete fit is 2.78×10^{-9} cm^2 s^{-1}.

3. Results

Transport Coefficients in PVC and Functionalized PVC. Table 2 presents the transport coefficients for PVC and the four modified PVC samples. The evolution with modification degree of the three transport coefficients diffusivity D, permeability P, and solubility S is depicted in Figures 2−4, respectively. As seen in Figure 3, there is a strong increase in the diffusivity of all four gases for modifications of up to 11%; further modification to 21% seems to bring no significant changes in this coefficient; and finally, the diffusion coefficients of PVC−pyr46 tend to decrease. The de-

Table 2. Transport Coefficients in PVC and Modified PVC

	O_2	N_2	CO_2	CH_4
	PVC			
$D \times 10^8$ (cm^2 s^{-1})	0.410	0.094	0.104	0.011
P (barrer[a])	0.124	0.022	0.540	0.024
S [cm^3(STP)/(cm^3 cmHg)]	0.0030	0.0023	0.0519	0.0224
	PVC−pyr7			
$D \times 10^8$ (cm^2 s^{-1})	1.780	0.379	0.366	0.115
P (barrer[a])	0.280	0.052	1.730	0.102
S [cm^3(STP)/(cm^3 cmHg)]	0.0017	0.0012	0.0468	0.0089
	PVC−pyr11			
$D \times 10^8$ (cm^2 s^{-1})	2.280	0.591	0.503	0.170
P (barrer[a])	0.400	0.065	2.290	0.102
S [cm^3(STP)/(cm^3 cmHg)]	0.0017	0.0011	0.0455	0.0060
	PVC−pyr21			
$D \times 10^8$ (cm^2 s^{-1})	2.160	0.580	0.510	0.190
P (barrer[a])	0.420	0.060	2.640	0.120
S [cm^3(STP)/(cm^3 cmHg)]	0.002	0.00102	0.0516	0.0064
	PVC−pyr46			
$D \times 10^8$ (cm^2 s^{-1})	1.320	0.277	0.425	0.106
P (barrer[a])	0.294	0.040	1.520	0.060
S [cm^3(STP)/(cm^3 cmHg)]	0.0022	0.0014	0.0358	0.0057

[a] 1 barrer = [cm^3(STP) cm]/[(cm^2 s cmHg)] $\times 10^{-10}$.

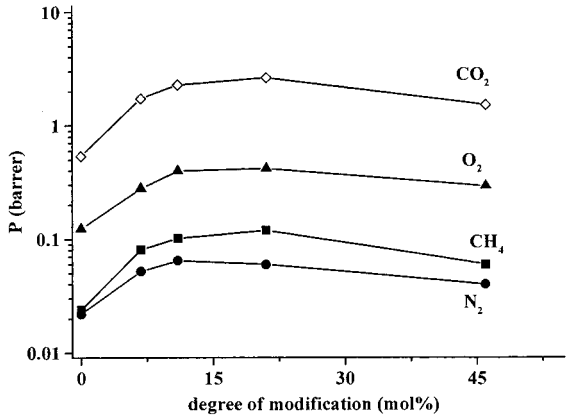


Figure 2. O_2 (▲), N_2 (●), CO_2 (◇), and CH_4 (■) permeabilities as functions of the modification degree.

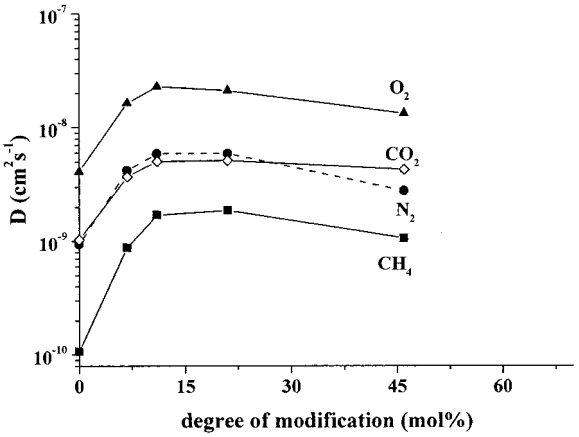


Figure 3. O_2 (▲), N_2 (●), CO_2 (◇), and CH_4 (■) diffusivities as functions of the modification degree.

pendencies on modification of the diffusion coefficients of the four gases are very similar, and except for a slight inversion in the order of the D values of N_2 and CO_2 in PVC−pyr46, the four diffusion vs modification curves are almost parallel. As for permeability (Figure 2), the trend is very similar to that of the diffusion coefficients.

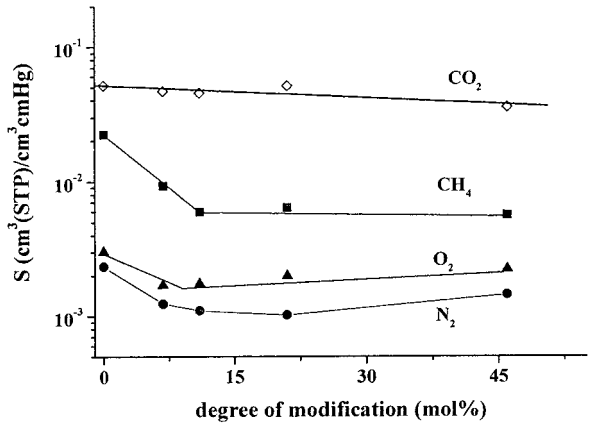


Figure 4. O_2 (▲), N_2 (●), CO_2 (◇), and CH_4 (■) solubilities as functions of the modification degree.

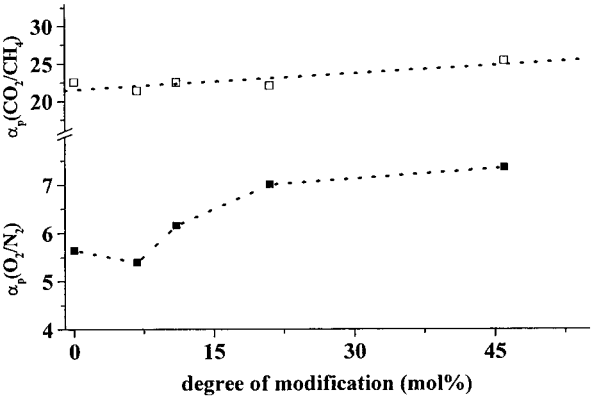


Figure 5. Permeability selectivities of the pairs O_2/N_2 (■) and CO_2/CH_4 (□) as functions of the modification degree.

Solubility, which appears in Figure 4, decreases slightly with modification degree. That of methane shows an important reduction at low conversion values, from roughly 200 $\times$ 10^{-4} cm^3(STP) cm^{-3} cmHg^{-1} for PVC to an almost constant value of 60 $\times$ 10^{-4} cm^3(STP) cm^{-3} cmHg^{-1} for over 11% conversion. The solubility parameters of oxygen and nitrogen are very low and diminish slightly with chlorine substitution. Carbon dioxide's solubility decreases from roughly 500 $\times$ 10^{-4} to 350 $\times$ 10^{-4} cm^3(STP) cm^{-3} cmHg^{-1} for the sample of highest conversion.

The data contained in Figures 2−4 clearly indicate that the most conspicuous effect of mercaptopyridine introduction is a very important increase in the diffusion coefficient, an increase that is greater for bulkier gases. Figures 5−7 show the effects of modification of the permeability, diffusivity, and solubility selectivities of these polymers. As modification progresses, there is an enhancement of the permeability selectivity α_p (Figure 5) for the O_2/N_2 pair, from roughly 5.5 for PVC to about 7.5 for PVC−pyr46, whereas the value of $\alpha_p(CO_2/CH_4)$ varies little with modification. As permeability also increases with modification, by about 4 times for O_2 and CO_2 in this same modification range, the overall effect of substitution is a simultaneous increase of both permeability and permselectivity for the O_2/N_2 gas pair and a permeability increase with no loss in permselectivity for the CO_2/CH_4 gas pair. It is well-known that the simultaneous increase of permeability and permselectivity is seldom seen.

The increase of permeability is due solely to the rise in diffusivity. On the other hand, the diffusivity selec-

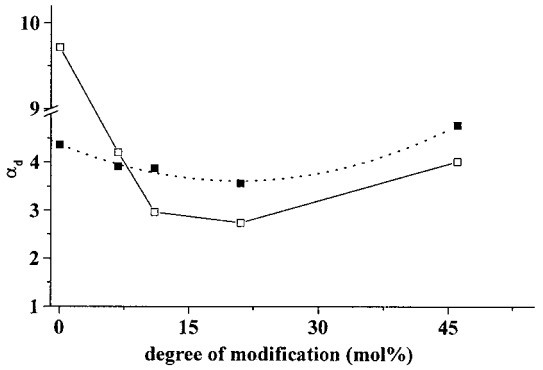


Figure 6. Diffusivity selectivities of the pairs O_2/N_2 (■) and CO_2/CH_4 (□) as functions of the modification degree.

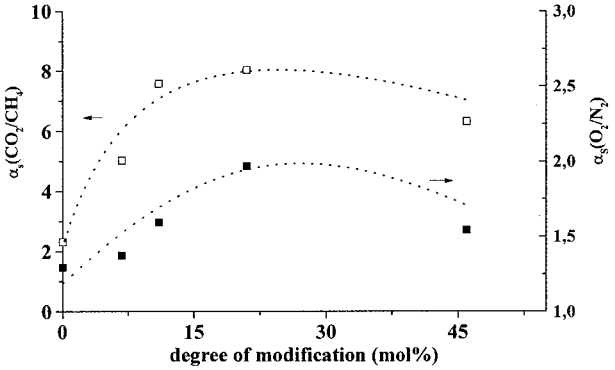


Figure 7. Solubility selectivities of the pairs O_2/N_2 (■) and CO_2/CH_4 (□) as functions of the modification degree.

tivity (Figure 6) for the gas pair O_2/N_2 diminishes only slightly, although there is over a 5-fold increase in the diffusion coefficients for the two gases. As the solubility selectivity increases for the gas pair O_2/N_2, the observed overall effect is the simultaneous increase of permeability and permselectivity. On the other hand, the outstanding increase of methane diffusivity, the largest of the four gases studied, brings about a drastic reduction of $\alpha_D(CO_2/CH_4)$ (Figure 6) that cannot be overcome by the increase in $\alpha_S(CO_2/CH_4)$ (Figure 7), and thus, no important variations of $\alpha_P(CO_2/CH_4)$ are caused by the introduction of pyridine groups into PVC.

Structural Modifications Introduced by the Functionalization of PVC. To reach a better understanding of the dependence of the transport coefficients on the number of pyridine groups in PVC, detailed knowledge of the structure of the modified systems is necessary. The nucleophilic substitution of chlorine atoms in PVC by aromatic thiol compounds has been extensively described in the literature.[17,18] Under the synthetic conditions applied in the preparation of pyridine-modified polymers, the reaction takes place without formation of any side products or chain degradation and obeys an S_N2 mechanism with inversion of configuration. A more detailed characterization has been focused on the determination of the chemical composition distribution[19] in the modified polymers and the stereoregularity of the reactions.[20] According to a comparison of an experimental C^{13} NMR study of modified PVC (up to 40 mol %) with the results of a Monte Carlo simulation,[19] it could be demonstrated that the substitution of chlorine atoms occurs in a random way and that no blocky structures are present in the polymers obtained. The stereochemical aspect of the microstructure of thiol-

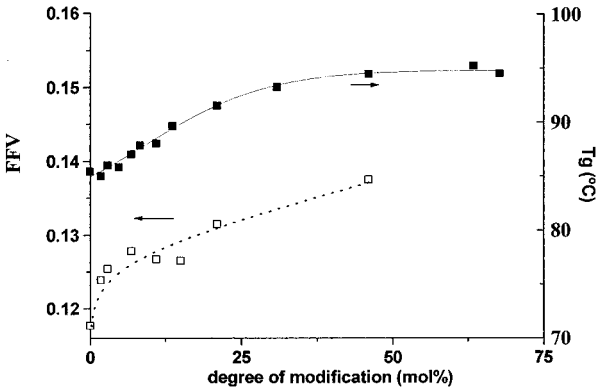


Figure 8. Glass transition temperature, T_g (■), and FFV (□) as functions of the substitution degree.

modified PVC has been analyzed by one-dimensional H^1 and C^{13} NMR spectroscopy and by two-dimensional inverse heteronuclear NMR spectroscopy.[20] According to this study, nucleophilic substitution reactions in PVC are highly stereoselective in the sense that only chlorine atoms of iso- and heterotactic triads can be substituted, whereas syndiotactic triads remain unaltered. Thus, as regards microstructure, it can be stated that, up to 40% substitution, the new mercaptopyridine groups are introduced randomly with respect to those already grafted onto the chain and selectively in PVC isotactic and heterotactic triads.

Diffusion coefficient values are mostly related to two structural features: rigidity of the chains and spacing. We monitored the evolution of these two features by measuring both the specific volume and the glass transition temperature. Figure 8 shows the FFV and T_g for each sample. The FFV increases strongly up to about 10% modification and then continues to increase but more slowly. On the other hand, T_g increases almost linearly up to a conversion of about 20%, giving an increase of roughly 10 °C, after which the increase tends to level off, and almost no T_g changes occur between 30 and 70% modification.

4. Discussion

In general, the glass transition temperature depends on the energy barriers that conformational transitions must overcome in such a way that the larger the barriers are, the fewer the conformational transitions that occur at a given temperature. Substitution of the relatively small chlorine atoms by the bulky mercapto pyridine groups appears to increase the energy barriers associated with the conformational transitions in the chains, and as a result, the T_g of modified PVC increases as the degree of substitution increases. On the other hand, the bulkiness of the mercapto pyridine substituent hinders chain packing of the modified PVC, and as a consequence, the specific volume and the FFV in the glassy state increase with the degree of substitution. The characterization of the modified samples shows then that both free volume and chain stiffness increase significantly, the former especially up to a 10% modification.

Evolution toward a structure with a higher fraction of free volume and a greater chain rigidity as modification progresses is in agreement with the behavior of the diffusion coefficient on samples modified up to 10% conversion: the diffusivities of O_2 and N_2 increase by a factor of over 5, while the diffusivity selectivity for $O_2/$

N_2 does not greatly diminish (roughly 10%). Usually, an increase in spacing leads to greater diffusion coefficients and lower diffusivity selectivity values, as larger holes facilitate diffusion and are less able to discriminate between molecules because of their size. However, chain rigidity is known to enhance diffusivity selectivity, as it renders the material more similar to a sieve with well-defined hole sizes. In the case of the functionalization of PVC with mercapto pyridine, the simultaneous increase of rigidity and spacing brings about the observed increase in diffusivity and almost unchanged diffusivity selectivity for the gas pair O_2/N_2.

At first sight, it could appear surprising that, for over 10% modification, the diffusion coefficients no longer increase even if the FFV continues to increase. It has to be taken into account that, for other-than-low modification values, the interpretation of the transport data in terms of structural changes is more difficult, as the polymer can no longer be considered as a PVC in which local structural variations are taking place. In fact, over 10% modification, the FFV continues to increase but in a much gentler manner.

The constancy of the value of the diffusion coefficient for substitution degrees larger than 10% despite the increase in FFV can then be explained by taking into account thet fact that a diffusant molecule explores a small cavity for a long time without trespassing the confines that surround it. These motions do not contribute to diffusion. Fluctuations can produce channels between cavities, and if a penetrant in the vicinity happens to have the right velocity, it might slip into the neighboring cavity before the passage closes again. The channels are relatively narrow on average, so the constancy of the diffusion coefficient for modifications lying in the interval 15−50% could suggest that the increase in free volume in this interval is accompanied by an increase in the energy barrier that the diffusant has to overcome to pass along the channel from one cavity to another. This would also explain the slight increase in α_D that occurs for the copolymer bearing 46% mercapto pyridine units.

Conclusion

The introduction into PVC of a bulky group such as pyridine, which at the same time favors interchain spacing and intrachain rigidity, leads to a controlled modification of the gas transport properties of PVC, enabling the preparation of a family of polymers in which permeability and permselectivity have been simultaneously augmented for the gas pair O_2/N_2. In the case of the gas pair CO_2/CH_4, a 5-fold increase in permeability occurs with no loss in permselectivity. The increase in permeability is solely due to a strong increase in the diffusion coefficients, as solubility varies little (O_2 and N_2) or decreases gently (CO_2 and CH_4). The variations in the gas transport properties of this series of functionalized polymers were attributed to a progressive increase of the FFV and rigidity of the chains brought about by the introduction of pyridine groups.

These results show a method for improving, in a controlled fashion, the gas transport properties of a barrier material such as PVC, through a selective variation of free volume, free volume distribution, and chain stiffness. For the future, we plan to test the effects of both the bulkiness and the polarity of the grafted group, so that, together with spacing and stiffness modifications, a solubility enhancement of O_2 and CO_2 as compared to N_2 and CH_4 can be achieved.

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