Effect of Fractional Free Volume and T_g on Gas Separation Through Membranes Made with Different Glassy Polymers

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ABSTRACT: The aim of this work is to study how the characteristics of the polymer used to manufacture gas separation membranes influence its permeability and selectivity. It has been shown that the gas diffusivity decreases with the kinetic diameter of the gas except for CO_2, probably due to its high condensability. While solubility increases with the gas condensation temperature and clearly with the glass transition temperature of the polymer for each gas. The permeabilities of CO_2, CH_4, O_2, N_2 increase for increasing glass transition temperatures. Nevertheless only the selectivity of CO_2 versus the other gases increases significantly when polymers with high glass transition are used. The Robeson limit in a selectivity-versus-permeability plot is approached for CO_2/CH_4 when T_g increases. This distance to the Robeson limit, for this pair of gases, results to decrease for increasing T_g. For the case of the O_2/N_2 selectivity remains approximately constant with an appreciable increase in permeability for polymers with increasing T_g. Permeability increases due to the corresponding increase in fractional free volume, FFV, that appears for increasing glass transition temperatures, T_g. This correlation of FFV with T_g has been confirmed by obtaining FFV by different methods. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 1039–1046, 2008

Key words: membranes; selectivity; gas permeation; fractional free volume; glass transition

INTRODUCTION

Polymeric membranes can compete with other more traditional processes of gas separation as "cryogenic distillation," "pressure swing" or "adsorption" mainly due to their: simplicity; continuous working; low energy consumption, and capital costs.[1]

A high selectivity leads to a high purity of products and allows a reduction in the number of operation steps with a lower membrane area. A high permeability involves a high process velocity. Nevertheless, high selectivity is normally obtained with low permeability,[2] in such a way that an upper bond was shown to hold within these two parameters, the so called Robeson's bond. Of course what should be convenient is to reach simultaneously high permeabilities and selectivities or at least to increase one of these parameters without decreasing the other. Rubbery polymers are commonly placed far below the Robeson's bond while glassy polymers give much better permeability versus selectivity.

The main physicochemical characteristics that determine gas permeability of glassy polymers are:

- The mobility of the polymer chains that is correlated with the glass transition temperature, T_g. As far as stiff structures of the polymer lead to high glass transition temperatures.
- The intersegmental spacing and the corresponding free volume of the polymer that is usually quantified by the fraction of free volume. Of course this, actually, assumes similar or irrelevant consequences of both the volume distribution of the holes and the size distribution of links from hole to hole.

In these terms, it seems clear that the glass transition temperature and the fraction of free volume, FFV, should be correlated somehow. In effect, it is known[2] that in rubbery amorphous polymers the fractional free volume increases with decreasing T_g while in glassy amorphous polymers FFV increases with increasing T_g (increasing formation of microvoids) hence lowering the activation energy.

The interaction between the polymer and the penetrant gas corresponds to the gas solubility.[3] It seems

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TABLE I
Some Characteristics of the Polymers and Membranes Used

Commercial Name	Lustran SAN 552010	SAN M 60	Lustran ABS M203FC	Gafone S	Udel 3500 NT	Matrimid 5218
Manufacturer Polymer	LANXESS Styrene Acrylonitrile	LANXESS Styrene Acrylonitrile	LANXESS Acrylonitrile Butadiene Styrene	GHARDA Polysulfone	AMOCO Polysulfone	CIBA GEIGY Matrimid (polyimide)
Composition (% molec)						
	(59.1:40.9)	(59.0:41.0)	(44.7:12.7:42.6)			
T_g (°C)	105.7	105.3	104.6	186.4	185.5	295.3
w (% w/v)		7,5			10	7,5
Δx (μm)		50–100		64–76	77–81	14–154

clear that, for a given polymer and gas, solubility should increase with the accessible area of void interstices in the free volume. On the other hand, as mentioned, there is a direct correlation between gas diffusivity in the polymer and its free volume.[4,5] This is why, both selectivity and permeability characteristics can be interpreted in terms of a series of parameters that are substantially determined by the free volume and the glass transition temperature.[6]

Here our aim is to evaluate how the permeability-selectivity compromise changes with the glass transition temperature. This should help the process of selection of the adequate polymer attending to an easy measurable characteristic of glassy polymers.

EXPERIMENTAL

Membrane materials

Membranes were prepared from several commercial thermoplastic polymers solved in dichloromethane (CH_2Cl_2) as solvent in adequate concentrations to keep a reasonable viscosity. After stirring until complete homogenization, all the polymer solutions were filtered through a 1-μm sieve. Then all the membranes were prepared by the casting method by using a leveled glass plate at 25°C. The resulting films were dried at 60°C to complete elimination of the solvent. After peeling off the membranes from the glass, they were heated at 100°C at vacuum for two days, and then tested as gas separation membranes.

The trademarks, manufacturers, percentages of polymer used in the casting solution, w, and membrane thickness, Δx, are shown in Table I. Also in this table the corresponding glass transition temperatures, T_g, are shown. Differential scanning calorimetry (DSC) was performed in a Perkin–Elmer DSC-7 instrument. All runs were taken in perforated pans under N2 purge and a scanning rate of 10°C/min.

The glass transitions temperatures (T_g) are taken as the mid point of the change in the heat capacity as calculated by the software. The corresponding percentages of styrene, acrylonitrile, and butadiene copolymers, included in Table I, have been measured by RMN experiments with a VNMRS from Varian® operating at 500 MHz.

Permeability

Gas permeability for O_2, N_2, CO_2, and CH_4 measurements have been performed with a constant volume variable pressure gas permeator based in the ''time lag'' method.[7] Our experiments have been done at 30°C and for transmembrane pressures of 1, 3, and 5 bar. Permeability resulted to be independent of the applied pressure thus confirming that no plasticization appeared under the measurement conditions. A scheme of such a permeator is shown in Figure 1.

The strategy of time lag methods was first proposed by Daynes[8] to determine permeability, diffusivity and
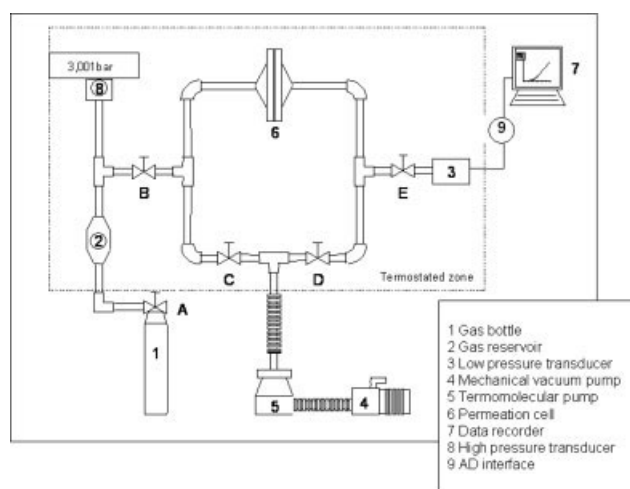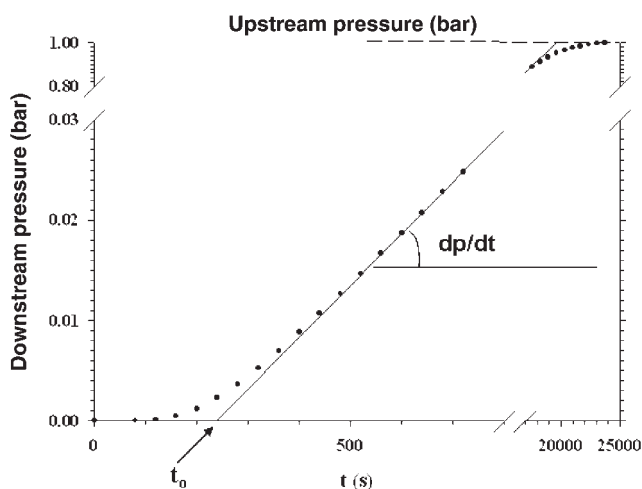

Figure 1 Scheme of the constant volume gas permeator.

Figure 2 An example of the downstream pressure as a function of time, here under a trans-membrane pressure of 1 bar, showing how diffusivity and permeability can be obtained.

solubility by a simple and rapid method under transitory regime. The method was successfully applied to polymer permeation by Paul and DiBenedetto,[9] Crank,[10] and Barrer and Skirrow.[11] It has become a classical way to measure the permeability and diffusion coefficient of a gas through a polymer film for a given operating temperature and pressure. It postulates Fick's law to hold with a constant diffusion coefficient and constant membrane thickness. When these conditions are fulfilled, the transitory response at the downstream side of a membrane to a pressure step at the upstream side allows the corresponding characteristic time to be easily evaluated from experimental data, the time-lag, t_0, (shown in Fig. 2) This parameter gives the permeant diffusion coefficient through the simple expression:[10]

$$t_0 = \frac{\Delta x^2}{6D} \tag{1}$$

The amount of gas transmitted at time t through the membrane was calculated from the permeate pressure, p_2, readings in the low-pressure side. The

inherent leak rate in the downstream side determined after evacuating the system was measured for each experimental run. The permeability constant can be obtained directly from the flow rate into the downstream volume upon reaching the steady state.[12,13] The theoretical framework, as well as the practical possibilities and limits of the time-lag technique have been abundantly documented.[14–17]

Solubility, S, could be obtained from the directly measured diffusivities and permeabilities as:

$$S = \frac{P}{D} \tag{2}$$

Densities

Polymer density was measured on films by a flotation method in a solution of calcium nitrate in water at $(25 \pm 0.1)°C$. The density of the solution was increased by adding calcium nitrate until leveling that of the sample. Then, the density of the solution was determined by pycnometry. No apparent swelling of the samples was observed in any case. The so obtained densities along the nominal ones are shown in Table II.

RESULTS AND DISCUSSION

Permeability

The permeabilities and selectivities obtained for the pairs CO_2/CH_4 and O_2/N_2 are shown in Figures 3 and 4 for all the polymers. In all cases the corresponding Robeson's bond[2] or trade off curve is shown along with the corresponding zone of commercial interest.[18]

In the case of CO_2/CH_4, an increase in permeability occurs with a simultaneous increase in selectivity, when polymers have increasing glass transition temperatures. In this way, the commercially interesting zone is entered but without crossing the trade off curve. For O_2/N_2 it is clear that an increase in T_g leads to an increase in permeability with almost constant selectivity giving a slight approach to the Robeson's curve.

TABLE II
Some Volumetric Characteristics of the Polymers Used

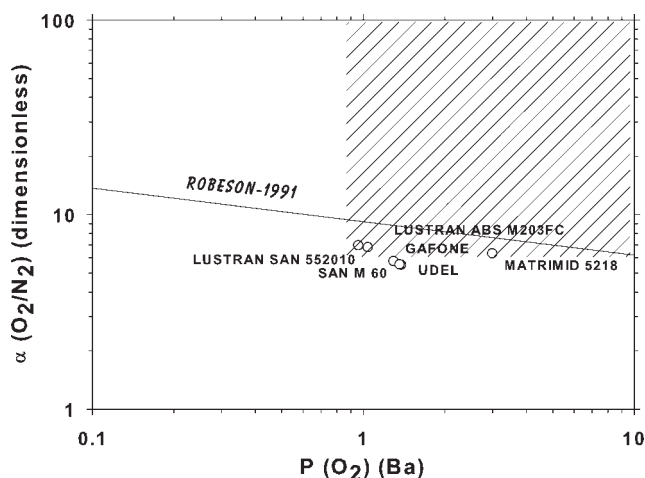| Commercial name	Lustran SAN 552010	SAN M 60	Lustran ABS M203FC	Gafone S	Udel 3500 NT	Matrimid 5218
ρ_{nom} (g/cm^3)	1.07	1.08	1.05	1.24	1.24	1.24
ρ_{exp} (g/cm^3)	1.0718 ± 0.0007	1.0752 ± 0.0007	1.0835 ± 0.0007	1.2294 ± 0.0008	1.2318 ± 0.0008	1.2398 ± 0.0008
FFV (literature)	0.16			0.1518		0.225
FFV$_\rho$						
Bondi	0.1609 ± 0.0005	0.1583 ± 0.0005	0.1409 ± 0.0005	0.1505 ± 0.0005	0.1489 ± 0.0005	0.1398 ± 0.0005
Bondi-Park & Paul	0.111 ± 0.006	0.108 ± 0.006	0.087 ± 0.006	0.160 ± 0.003	0.159 ± 0.003	0.165 ± 0.002
Molecular						
Dynamics	0.0914 ± 0.0005	0.0885 ± 0.0005	0.1090 ± 0.0005	0.1104 ± 0.0005	0.1087 ± 0.0005	0.1184 ± 0.0005
FFV (Pemeability)	0.135 ± 0.005	0.139 ± 0.007	0.143 ± 0.005	0.146 ± 0.005	0.148 ± 0.006	0.165 ± 0.004
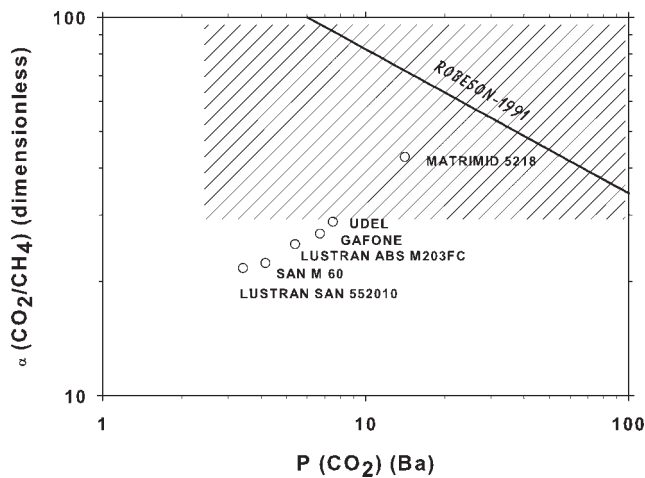
Figure 3 Selectivity versus permeability with the Robeson's trade off curve for CO_2/CH_4 and the commercially relevant area for the different membranes studied.

Figure 5 Distance below (negative) the Robeson curve versus the glass transition temperature. Both O_2/N_2 and CO_2/CH_4 gas pairs are shown.
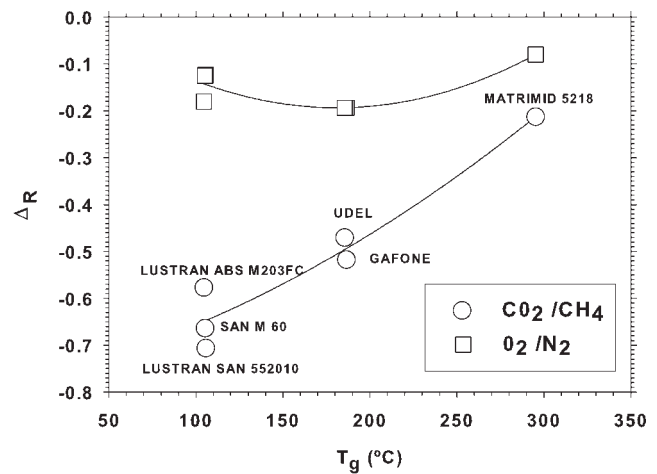
Distance to the Robeson curve

To study, in a more quantitative way, how close to the selectivity versus permeability trade off curve is each of the polymers studied, the distance below (negative) or above (positive) the Robeson curve can be evaluated. This distance called here Δ_R is plotted versus the glass transition temperature in Figure 5. It seems clear that for CO_2/CH_4 when the glass transition temperature of the polymer, T_g, is higher, selectivity and permeability increase approaching the Robeson's curve. While for O_2/N_2 the same increase in T_g leads only to a significant increment in permeability but with an almost constant selectivity.

Diffusivities and solubilities

The corresponding diffusivities as obtained from eq. (1) are shown in Figure 6 for the different gases (dif-

ferent kinetic diameters).[19,20] It can be seen that for each polymer, diffusivity decreases when the kinetic diameter of the gas increases, with the exception of CO_2. Nevertheless, the diffusivity for each gas does not show an unquestionable trend with the glass transition temperature.

Solubilities are shown in Figure 7, now characterizing the gases by their condensation temperature. It seems clear that solubility for each gas increases with the glass transition temperature. On the other hand for each polymer solubility increases with the condensation temperature of the gas.

The high condensation temperature of CO_2 and thus its high solubility could explain its relatively low diffusivity that should be higher attending to its kinetic diameter.

Figure 4 Selectivity versus permeability with Robeson's trade off curve for O_2/N_2 and the commercially relevant area for the different membranes studied.

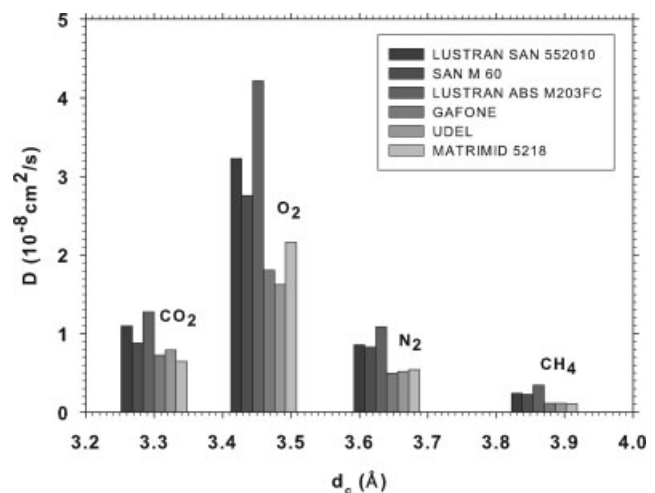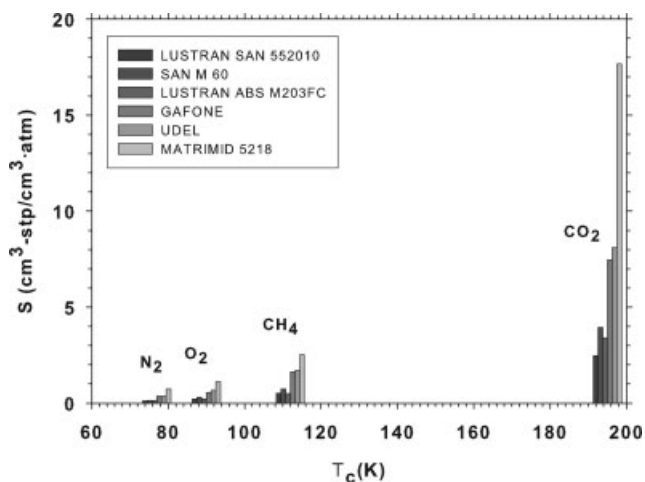**Figure 6** Diffusivity for the different membranes and gases used. Each group of bars is centered in the corresponding kinetic diameter of the gas.

Figure 7 Solubility for the different membranes and gases used. Each group of bars is centered in the corresponding condensation temperature of the gas.

Permeabilies and glass transition temperature

Yampolskii and coworkers[21] fitted data on permeability of several polymers measured at their corresponding glass transition temperature. The polymers used have T_g in the range from 32 to 320 °C and belong to various families including those of the polymers we study here. They found that permeability fits well to:

$$\log P(T_g) = (a_P/T_g) + b_P \qquad (3)$$

where permeability at T_g, $P(T_g)$, is expressed in Barrers and the values of the constants in eq. (3) for the gases used here are shown in Table III.

The experimental results for permeability along with the corresponding line for eq. (3) are shown in Figure 8. In this figure, we also show the predictions of Van Krevelen for permeability as a function of T_g. Actually, the predictions of Van Krevelen for both diffusivity and solubility have been used along with eq. (2). This model[2] is based on data of the permeating molecules (critical temperature and collision diameter taken as defined by the Lennard-Jones temperature and the potential length constant, respec-

TABLE III
Parameters Corresponding to the Gas Permeability Measured at the Glass Transition Temperature Fitted to eq. (3) as Obtained by Yampolskii and coworkers

Gas	a_p (K)	b_p (dimensionless)	ρ
CO_2	−778	3.29	0.66
O_2	−1100	3.73	0.67
CH_4	−1410	4.08	0.94
N_2	−1320	3.93	0.80

ρ is the corresponding correlation factor.

tively) and of the polymer (defined by its glass transition temperature). The activation energy of diffusion can be correlated with both the polymer T_g and the gas collision diameter. The predicted permeability should increase with T_g for glassy polymers and decrease for rubbery polymers.

In accordance with the predictions of the model of Van Krevelen, permeability increases, in effect, for our glassy polymers, with increasing T_g. In Figure 8, it can be seen that the accordance of the predicted and the experimental permeabilities is far from complete, especially in the case of methane. This can be due to the sometimes significant dispersions linked to the model of Van Krevelen.[2] In any case the tendencies are well reproduced by the model, as well as the relative values of permeability for the different gases.

The predicted values of permeability can be extrapolated to cross the corresponding lines of Yampolskii. The so obtained point of crossing should correspond to the permeability that should be found for a hypothetical polymer whose T_g was the actual temperature of the permeation experiments. When this is done we find that these points in effect correspond approximately to the real temperature of the permeation experiments that was 30°C.

Fractional free volume

Diffusivity can be correlated with FFV by:

$$D = A_D e^{-B/FFV} \qquad (4)$$

with A_D and B constants for a given gas and polymer. These factors are correlated with the size and kinetic velocity of the penetrant (A_D) and the free
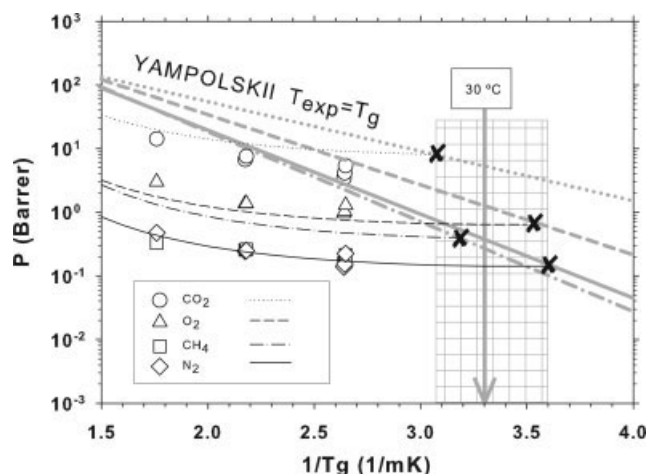
Figure 8 Permeability versus $1/T_g$ showing the predictions of Van Krevelen. The results of Yampolskii for polymers measured at their T_g are also shown.

volume of holes needed for penetrant diffusion (B), according to Fujita's theory[22] of diffusion. Then, by using eq. (2):

$$P = A_P \ e^{-B/FFV} = A_D S \ e^{-B/FFV} \qquad (5)$$

Equation (5) allows finding a correlation FFV with permeability. Lee[23] was the first who correlated the permeability of various polymers to their specific free volume. Lee found this relation to hold for 13 different polymers for the CO2 as well as O2 permeability. Hensema[24] made a similar plot including polyimides and polyoxadiazoles and polytriazoles and found different values for A and B. In 1997, Park and Paul[25] proposed a general correlation based on more than 100 glassy polymers representing a wide variety of structural types. This correlation allows an evaluation of the fraction of free volume for several gases once their permeabilities are known. The corresponding FFV are evaluated by Park and Paul[25] from experimental density based on the traditional group contribution method of Bondi.[2,26]

However, this linear relationship is not unambiguous. For some polymers with equal chemical nature but different chain conformation, the diffusivity can even increase with decreasing free volume. This phenomenon was attributed to differences in the distribution of the free volume. Meanwhile, it seems that a qualitative dependence as given by eq. (5) appears for many polymers of different characters.[27,28]

Of course the corresponding FFV evaluated by different gases could differ as far as the corresponding size of the gas molecules should be different. The tendencies can also be slightly different due to the different distribution of free volumes accessible to different gas molecules. Here we have evaluated FFV from the average of such obtained for the different gases. Neither the corresponding values for each gas nor their slopes have resulted substantially different.

The corresponding free fractional volumes are shown in Table II and in Figure 9 as a function of T_g. It can be seen that FFV increases with glass transition temperature. This behavior has been observed also for fractional volumes obtained from PALS (positron annihilation lifetime spectroscopy) by Yampolskii et al.[21] It is worth to note that PALS[29] is the only way to directly measure fractional free volumes. Other methods are in fact estimations based on different models.

The fractional free volume is defined as:

$$FFV = \frac{V - V_0}{V} \qquad (6)$$

where V is the specific volume of the amorphous polymer at the temperature of interest, and V_0 is the specific volume at 0 K which is estimated as 1.3
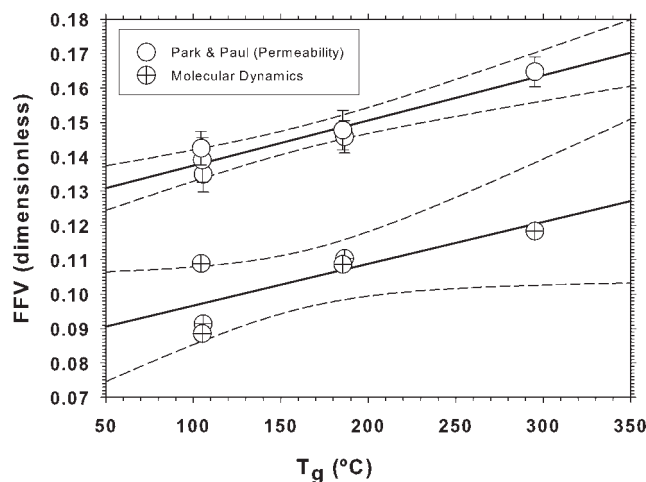
Figure 9 Fractional free volume versus the glass transition temperature. The values evaluated from permeability and from simulation of molecular dynamics.

times the Van der Waals volume. Thus the fractional free volume can be estimated from measurements of the polymer density and a calculation of the Van der Waals volume either from group contribution theory or by molecular simulation by an appropriate computational chemistry program.

The FFV values obtained by using eq. (6) are shown in Table II along with those found in literature.[2,30–32] These evaluated by using the Bondi's group contribution theory are similar to those obtained from the permeability correlation of Park and Paul[25] but with a quite different correlation with the glass transition temperature. Note that in this case only the errors linked to the measurements of density are included in Table II.

In the traditional method of Bondi the differences in free volume accessible to each given gas are not taken into account. Park and Paul[25] propose to take into account the particularities of the gas filling the voids by a specific multiplicative factor. This factor they proposed is different for each gas and group present in the monomer. The values so obtained are also shown in Table II. In this case, the errors shown are these due to both the density measurements and the dispersion corresponding to the different gases. These FFV increase with T_g as those obtained from permeabilities. Nevertheless some differences are clear, especially for the three copolymers studied. This is probably due to the difficulties in accounting for the contributions to the total FFV of each component in presence. Here this has been done by simply averaging according to the composition of the copolymer. This probably underestimates the total FFV as far as it does not take into account the interactions in the copolymer.

On the other hand, it appears clear that the FFV of matrimid was clearly underestimated by the tradi-
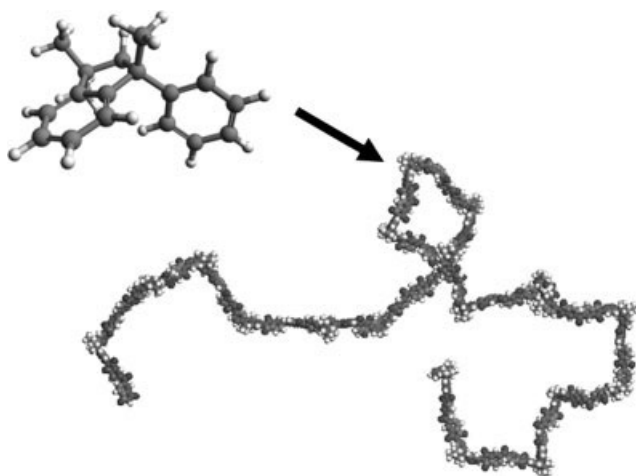
tional method of Bondi probably because the conformational restrictions of the molecule were not totally taken into account by considering their groups separately. The factors of Park and Paul[25] implicitly included this correction.

To calculate the Van der Waals volume by computational chemistry we used Cerius2 program, version 4.8.[33] The molecular modeling employs a grid method based on the Connolly volume using a probe radius of 0 nm, which gives an accurate estimation of Van der Waals volumes. One advantage of this method is that it considers the dependence of Van der Waals volume on the chemical environment, which is not the case with the usual group contribution methods. Moreover, it can estimate the Van der Waals volume for structural units not included in the tables used by the Bondi's method. The simulation of 30-unit structures of the polymers was also done by means of the program Materials Studio running on a PC cluster. A combination of molecular mechanics and molecular dynamics was used to obtain low energy structures. As an example, in Figure 10, the structural unit of matrimid is shown along with a possible conformation of a 30 unit chain. These FFV obtained by using simulation are shown in Table II and also in Figure 9.

In summary it seems that fractional free volume can differ depending on the method used to evaluate it but in any case when it was well evaluated tends to increase with the polymer glass transition temperature.

CONCLUSIONS

A set of membranes from different polymers have been manufactured and their gas permeability prop-

Figure 10 The structural unit o matrimid and one of the configurations obtained by simulation with a 30 units chain.

erties have been tested. Diffusivity and solubility have also been evaluated.

As expected, among the gases used the more diffusive one is O_2 and the more soluble is CO_2. The gases are less soluble when their condensation temperature is lower because then condensation is hindered even for very small accessible interstices. On the other hand diffusivity decreases for higher kinetic diameters. The case of CO_2 is somehow special as far as its high solubility should make it less diffused than could be expected from its small kinetic diameter.

In the case of CO_2/CH_4, both permeability and selectivity increase for polymers with increasing glass transition temperatures, thus approaching the Robeson's curve. Nevertheless, for O_2/N_2 it is clear that an increase in T_g leads to an almost constant selectivity with an increase of permeability. Both these factors result in a slight approach to the Robeson's curve. For similarly soluble gases, as O_2 and N_2 (see Fig. 5), it is diffusivity what should play the most relevant role. Thus it seems that changes in diffusivity alone are insufficient to increase selectivity. For the case of CO_2, solubility increases very steeply with T_g thus increasing its selectivity referred to much less soluble gases as CH_4.

For the polymers used here, diffusivity does not show a clear tendency with the glass transition temperatures while solubility clearly increases with T_g. Nevertheless permeability increases with increasing glass transition temperature as predicted by the classical correlations for glassy polymers. The corresponding values of permeability for hypothetical polymers with a glass transition temperature equal to the permeation one (30 °C) are effectively reached by extrapolation.

Here it has been shown that an increase in T_g is correlated with increasing fractional free volumes. This increase in FFV leads to the, also shown, permeability increase with T_g. It is worth to point out that the evaluated FFV are not pretended to be absolute but at least to show the correct tendency with T_g. It seems highly meaningful that the same slope in FFV versus T_g diagrams are shown either when FFV are obtained from permeability or from structural simulations. While the accordance is poorer when more or less pure Bondi's group contribution theory is used. Thus it seems that to evaluate FFV, the total conformation restrictions are not well enough estimated by their constituent groups.

It seems that in our case an increase in the intersegmental mobility (T_g) is simultaneously accompanied with an increase in the intersegmental spacing (FFV) that leads to very similar increases in permeability. There is a significant impact on selectivity only for the highly soluble CO_2, probably because this increase in fractional free volume is due to an

increase in the population of interstices of the adequate size for a significant condensation of CO_2.

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