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Structural characteristics and gas permeation properties of polynorbornenes with retained bicyclic structure

Chun-tian Zhao[a], M. do Rosário Ribeiro[a], M.N. de Pinho[a,*], V.S. Subrahmanyam[b], C.L. Gil[b], A.P. de Lima[b]

[a]Departamento de Engenharia Quimica, Instituto Superior Técnico — ICEMS, Av. Rovisco Pais, 1049-001 Lisbon, Portugal
[b]Departamento de Física, Universidade de Coimbra — ICEMS, 3000 Coimbra, Portugal

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Abstract

Polynorbornenes of different molecular weights were synthesised by addition polymerisation, using a nickel based catalyst. This polymerisation route leads to amorphous polymers that were shown to display unique properties: high glass transition temperature, rigid random coil conformation, and dense packing in the amorphous state. Gas permeation membranes were prepared from these addition type non-substituted polynorbornenes. A study of their gas transport properties was performed and compared with both substituted addition polynorbornenes and ring opening metathesis polymerised polynorbornenes. The observed behaviour, in terms of permeability and selectivity, is in accordance with the low free volume and the dense packing confirmed by positron annihilation spectroscopy and WAXD in these polymer structures. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Polynorbornene; Gas permeation; Membrane

1. Introduction

Norbornene and its derivatives are bicyclic olefins. They can be polymerised by different methods: ring opening metathesis polymerisation [1], cationic polymerisation [2] and more recently olefin addition polymerisation [3]. This latter polymerisation route leads to a new class of polymers presenting a rigid molecular structure where the bicyclic structure of the monomer is maintained, while the ring opening metathesis polymerisation (ROMP) leads to the opening of the bicyclic structure, see Scheme 1. Depending on the catalytic system and on the experimental synthesis conditions different polynorbornenes may be obtained ranging from amorphous to more stereoregular and crystalline ones. Based on molecular dynamic simulations Wendorff and collaborators [4–6] have shown that amorphous polynorbornene assumes a rigid random coil conformation. This peculiar structural feature suggests many interesting properties. For example, these polynorbornenes exhibit much higher glass transition temperatures than those obtained by the ROMP route: the T_g value for the addition type polynorbornenes is above 220°C [4,7] while the one for ROMP polynorbornenes is 30°C [8]. Additionally, unusual diffusion and barrier properties are observed, which are an important asset in polymer design for gas permeation membranes.

Recently, Dorkenoo et al. [8] investigated the membrane permeabilities of a series of polynorbornenes with aliphatic pendent groups, namely methyl, butyl, hexyl and decyl, obtained by addition polymerisation. The values for O_2 and N_2 permeabilities were found to be quite high and ranged from 19 to 90 Barrer and from 7 to 24 Barrer, respectively. The measurements were performed at a temperature of 35°C and at a pressure of 10 atm. The polymer series demonstrated a simultaneous increase in permeability and selectivity, uncommon in polymeric membranes. It was also found that the increase of the side chain length leads to lower permeabilities and selectivities. However, those authors did not present permeation results for unsubstituted polynorbornene, due to the impossibility of film forming of these samples. On the other hand Yampol'skii et al. [9] reported, for membranes prepared from unsubstituted polynorbornene, rather low permeability values for oxygen (2.5 Barrer) and nitrogen (0.83 Barrer). However, the fact

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* Corresponding author. Fax: +351-21-841-7246.
E-mail addresses: rribeiro@ist.utl.pt (M. do Rosário Ribeiro), i039@alfa.ist.utl.pt (M.N. de Pinho), lima@filip3.fis.uc.pt (A.P. de Lima).

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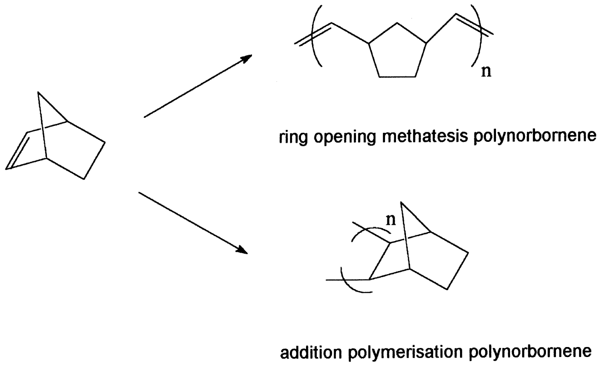

Scheme 1.

that the authors do not give any information about the experimental testing conditions makes difficult any comparison of permeation results.

As a typical polymer with rigid random coil conformation and high glass transition temperature, the unsubstituted polynorbornene may be considered as a potential candidate for gas permeation applications, and will be the subject of the present work, addressing therefore two main objectives:

1. The synthesis of polynorbornene polymers and the preparation of the corresponding membranes;
2. The correlation of polymer and membrane characteristics with the gas permeation properties.

2. Experimental

2.1. Polymer synthesis

Unsubstituted polynorbornenes, with different molecular weights, were prepared in the presence of a two component system: nickel bis(acetyl acetonate) [Ni(acac)$_2$], the catalyst, and methylaluminoxane (MAO), the co-catalyst. Polymerisations were performed in toluene at room temperature for 4 hours, using the Schlenk technique. The nickel concentration was controlled at 0.001 mol l^{-1} and the Al/Ni and the Ni/Monomer molar ratio were ranged from 100 to 1000 and from 1500 to 6000, respectively. Further description of the synthesis is given elsewhere [10]. Pro-analysis cyclohexane was supplied by Aldrich.

Poly(norbornene-*co*-styrene) was also synthesised, using the same catalyst system, and used for comparison purposes in DSC characterisation.

2.2. Membrane preparation

Polynorbornene was dissolved in cyclohexane to form a solution containing 10 wt% in polymer. The solution was first filtered and then cast onto a horizontal glass plate. A second glass plate was placed over the casting solution to ensure slow solvent evaporation, in a solvent enriched environment. After 24 h the membranes were removed from the glass plate by immersion in methanol. The membranes were next dried in air for at least three days.

The thickness of the membranes was measured with a mechanical gauge with a resolution of 0.5 μm. The measured values ranged from 25 to 40 μm.

2.3. Polymer and membrane characterisation

The ^{13}C NMR spectrum of polynorbornene was performed on a Bruker MSL 300P spectrometer operating at 300 MHz. The samples were dissolved in 1,1,2,2-tetrachloroethane-(d2) at 380 K. Hexamethyldisiloxane (HMDS) was used as a reference.

The density measurements of the polynorbornene samples, both in powder and film form, were performed by helium picnometry, water picnometry and Hg porosimetry techniques. The first technique was used for the determination of the skeletal or true density and the other two techniques for the estimation of the apparent density. In the case of Hg porosimetry the maximal imposed pressure was 2000 psia in order to prevent compressibility effects on the polymeric samples. On the other hand, for water picnometry, the weak water/polymer affinity assures the non-penetration of water in the membrane matrix, but special care has to be taken to ensure membrane surface wettability.

The packing of the polymers was investigated with wide angle X-ray diffraction (WAXD). WAXD curves of the polynorbornene powders were obtained using a Philips Diffractometer, with monochromatic radiation at a wavelength of 1.54 Å. Scanning was performed with 2θ ranging from 2 to 60°.

The size and distribution of free volumes of the polynorbornenes were characterised by positron annihilation spectroscopy (PAS). The samples for the PAS analysis were cast from a polynorbornene/cyclohexane solution yielding cylindrical rods of surface area 1 cm^2 and thickness 1 mm. Positron lifetime and Doppler broadening (DB) measurements were performed on these samples. The lifetime spectra were analysed in terms of discrete components (finite-term analysis) as well as continuous distributions (continuous lifetime analysis), using the computer programs PATFIT and CONTIN, respectively [11–13]. For the CONTIN analysis the positron lifetime spectrum of a well annealed SS316 sample ($\tau = 110$ ps) was used as reference. The DB data were analysed in terms of shape parameters *S* and *W*. The *S* parameter is defined as the ratio of the area under a given central region to the total area under the 511 keV annihilation line, whereas the *W* parameter is defined as the ratio of the area under symmetric wing regions on both sides of the peak to the total area under the annihilation line.

The analysis of glass transition temperature of the polymers was performed on a modulated differential scanning calorimeter (MDSC TA-I 2920).

2.4. Gas permeability measurements

Gas permeation experiments were carried out for carbon dioxide, oxygen and nitrogen in a flat sheet cell with an effective membrane surface area of 9.621 cm^2. The feed pressure ranged from 0 to 5 bar and the temperatures were maintained at 25–28°C.

3. Results and discussion

3.1. Structural characterisation

3.1.1. ^{13}C NMR spectroscopy and molecular structure

Fig. 1 shows a polynorbornene ^{13}C NMR spectrum. Four groups of resonances are present in this spectrum; each region of resonance is characterised by several signals with small chemical shift differences. A comparison with the NMR spectrum of norbornene and a semi-quantitative estimation of the chemical shift of the carbons in polynorbornene revealed that the four groups of peaks can be assigned to C5,6 (30.3–31.5 ppm); C7 (35.6–37.7 ppm); C1,4 (38.8, 39.8 and 42.8 ppm); C2,3 (47.9, 48.3, 50.9, 52.4 ppm). These results confirm that polymerisation of norbornene with $Ni(acac)_2/MAO$ system occurred without ring opening and via 2,3 addition. The multiplicity of the peaks suggests that in our polymerisation conditions the insertion of monomer units can take place in more than one stereospecific way, and therefore the resulting polynorbornene is atactic.

Based on this data and according to molecular dynamic simulation data performed by Wendorff and collaborators, a rigid random coil conformation is expected for homopolynorbornene [5].

3.1.2. X-ray diffraction and polymer packing

Fig. 2 shows the WAXD spectra of two polynorbornenes of different molecular weights. Both spectra display two broad halos at 2θ of 10 and 18.5° that can be attributed to a short range order. This is in agreement with the results reported by Haselwender et al. [4]. No traces of Bragg reflections, characteristic of crystalline regions, are revealed. The polynorbornene is therefore non-crystalline.

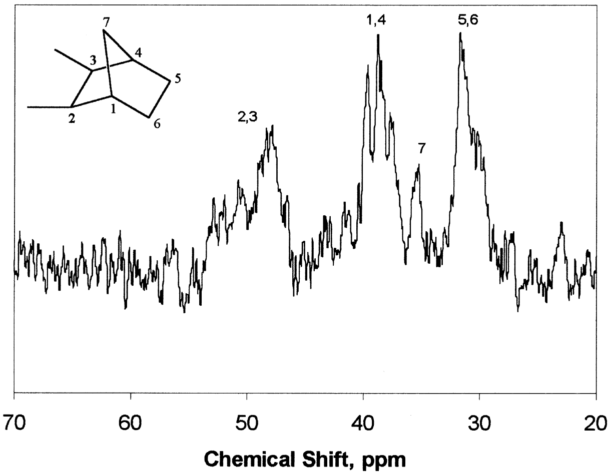

Fig. 1. ^{13}C NMR spectrum of unsubstituted polynorbornene in 1,1,2,2-tetrachloroethane-(d2) at 380 K.

Haselwander et al. [4] state that the two amorphous halos shown by polynorbornene are of intrachain nature, according to the specific structural information provided by the amorphous cell calculation. Nevertheless we tend to believe, in accordance with the investigations of polystyrene [14] and other polymers [15], that at least one amorphous halo, the one at relatively low angle, can be regarded as a reflection of the interchain or intersegment distance of the polymer. The interchain distance is given in [15] as being equal to 1.22 times the Bragg distance.

$$d_{\mathrm{interchain}} = 1.22 d_{\mathrm{Bragg}} = 1.22\lambda/(2 \sin \theta) \tag{1}$$

Therefore the derived interchain distance for the halo at $2\theta = 10°$ is 10.8 Å.

If we consider the interchain distance obtained above as a period of short range polymer packing in the condensed state, the "free" space distance between the polymer chains can be roughly estimated by subtracting from the period the maximum chain diameter, which is about 7.0 Å. We therefore obtain a "free" space distance between the polymer chains of about 3.8 Å.

3.1.3. PAS and mean free volume hole size

The concept of free volume is widely adopted in polymer science to explain many polymer properties at a molecular level and to relate them with the derived macroscopic properties. However, its assessment has mostly been made possible through indirect experimental methods and it is only very recently that experimental techniques leading towards a more direct assessment are being used [16]. Among these techniques positron annihilation spectroscopy has been demonstrated to be a powerful non-destructive technique for the characterisation of nanodimensional holes and for the determination of free volume fractions, as well as free volume size distributions (see Ref. [17], for a recent review).

In the finite-term analysis, the positron lifetime spectra were resolved into three components. The longest lifetime component, $\tau_3 = 2.86$ ns with an intensity of about 35% for all the samples studied (see Table 1), corresponds to the o-Ps pick-off lifetime in the free volumes. The S and W parameters, for these samples, obtained from the DB measurements are also presented in Table 1. The consistency of the values indicates that the distribution of electron momenta is quite similar in these samples.

According to a simple model [18,19], the Ps, inside a free volume, is considered as a particle in a spherical well bound in an infinite potential barrier. Such a model yields a relation between the o-Ps annihilation lifetime τ_3 and the

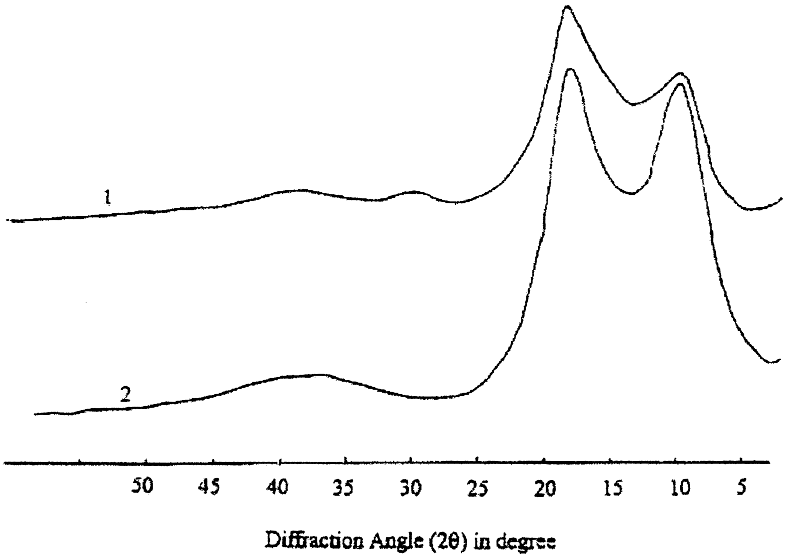

Fig. 2. WAXD diagram of polynorbornenes of different molecular weight. $\bar{M}_n$ (g mol^{-1}) $= 10.6 \times 10^5$ (1) and $= 4 \times 10^5$ (2).

free volume radius R as:

$$\tau_3 = 0.5\left[1 - \frac{R}{R_0} + \frac{\sin 2\pi(R/R_0)}{2\pi}\right]^{-1}. \tag{2}$$

In the above equation $R_0 = R + \Delta R$, where ΔR represents the electron layer thickness. It is generally agreed that best fits [20] to the experimental data are obtained using a value of 1.656 Å for ΔR.

Thus, in the case of the three polynorbornene membranes of different molecular weights analysed using PAS, the o-Ps lifetime value of 2.86 ns corresponds to a free volume equivalent to that of a sphere of radius $R \cong 3.53$ Å, which amounts to a free volume of about 185 Å^3.

The continuous lifetime analysis provides information in the form of an annihilation-rate probability density function, $\alpha(\lambda)$, as a function of annihilation rate, λ $(= 1/\tau)$. The best solution for the $\alpha(\lambda)$ fitted function was, for all the samples studied in this work, composed of three well defined peak distributions whose mean values were in quite good agreement with the lifetime values obtained by the finite-term analysis of the lifetime spectra. The distribution with the shortest annihilation rate (corresponding to the longest lifetime value) has, for all the samples, a mean value of (2.86 ns)$^{-1}$ with an intensity of about 35% and corresponds to the o-Ps annihilation rate distribution.

Since the o-Ps lifetime and the free volume hole radius have a one-to-one relationship (Eq. (2)), the o-Ps annihilation rate distribution contains the information about the free volume radius distribution [17]. The o-Ps annihilation rate distributions have been transformed into free volume radius distributions using the following expression for the radius probability density function, pdf(R),

$$\mathrm{pdf}(R) = -2\Delta R\{\cos[2\pi R/(R + \Delta R)] - 1\}\alpha(\lambda)/[(R + \Delta R)^2 K(R)], \tag{3}$$

where $K(R)$ is the correcting factor for the Ps trapping rate in different hole radii and is defined as $K(R) = 1.0 + 8.0R$ [21]. The fraction of o-Ps annihilating in the holes with radii between R and $R + dR$ is given by pdf(R)dR.

The free volume radius probability density functions, pdf(R), obtained from the o-Ps annihilation rate distributions for the three polynorbornene samples studied, are shown in Fig. 3. It can be seen that the three polynorbornene samples studied have very similar and compact distributions of free volume radii, centred around a radius of 3.5 Å, with a standard deviation of 0.3 Å.

3.1.4. Densities/PAS and fractional free volume (FFV)

A very simple expression for free volume (V_f) can be

Table 1
Positron experimental results for film form polynorbornene samples

$\bar{M}_n \times 10^{-3}$ (g mol^{-1})	Lifetime τ_3 (ns)	Intensity I_3 (%)	S-parameter	W-parameter
290[a]	2.87 ± 0.01	36.4 ± 0.9	0.5317 ± 0.0008	0.0311 ± 0.0003
400[a]	2.86 ± 0.01	35.0 ± 1.6	0.5306 ± 0.0008	0.0310 ± 0.0002
800[b]	2.86 ± 0.02	34.9 ± 1.0	0.5320 ± 0.0011	0.0310 ± 0.0004

[a] By size exclusion chromatography calibrated with polystyrene standard.

[b] By estimation.

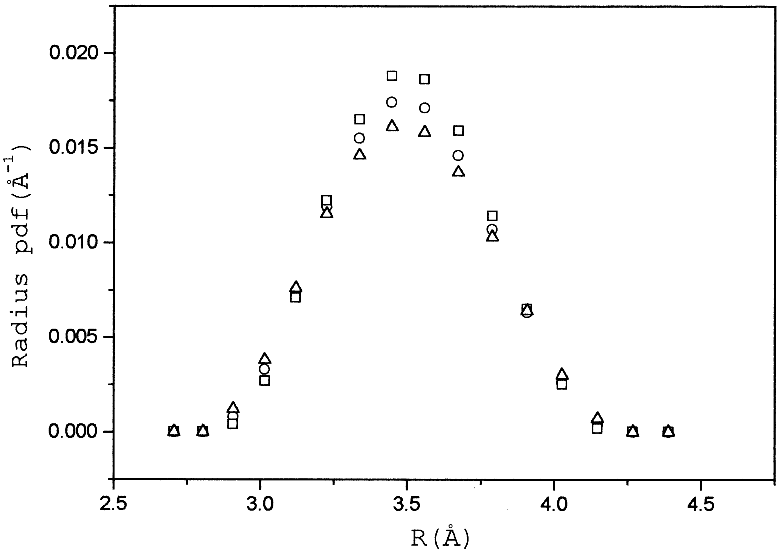

Fig. 3. Probability density function of the free volume radius for polynorbornenes with different molecular weights, $\bar{M}_n$ (g mol^{-1}) $= 2.9 \times 10^5$ (□); 4.0×10^5 (△); and 8.0×10^5 (○).

written as the total volume minus the occupied volume. The fractional free volume (FFV) is defined as the ratio of the free volume to the total volume. The total volume is usually determined by specific volume measurements. However, the occupied volume has been defined in a variety of ways depending on the theory. Because of these different definitions for the free volume, the fractional free volume can vary by one order of magnitude among the existing theories.

In this work we have estimated the fractional free volume (FFV) by different ways.

A first estimation was based on density measurements that involved the determination of both skeletal density (ρ_s) and of apparent density (ρ_{ap}).

The skeletal density values of polynorbornenes of different molecular weight in powder and film form are listed in Table 2. No significant differences were found among polynorbornenes of different molecular weight; however the slight variations observed indicate that the high molecular weight polymer may pack a little bit more densely than the low molecular weight polymer. Also, a small difference in densities was observed between the powder and the film forms; films present slightly lower values than powders. That may arise from the membrane preparation process, which would lead to the formation of “dead” pores. In that case the helium gas cannot fill these pores, which are then considered as making part of the occupied volume. Therefore the observed skeletal density in film form is smaller than the real one.

As expected, the apparent density values for the membranes, determined both by water picnometry and Hg porosimetry (Table 2) are lower than the corresponding skeletal values. FFV is defined by Eq. (4), where the skeletal density (ρ_s) and the apparent density (ρ_{ap}) are measured values reported on Table 2.

$$\mathrm{FFV} = \frac{1/\rho_{ap} - 1/\rho_s}{1/\rho_{ap}} \tag{4}$$

Another estimation of the FFV of polynorbornene has been made by Bondi’s method [22].

$$V_f = v_s - 1.3 v_w \tag{5}$$

$$\mathrm{FFV} = V_f / v_s \tag{6}$$

where, v_s is the specific volume, which is defined as the inverse of the density, and v_w is the Van der Waals volume defined as the hard core volume of the molecule or repeating

Table 2
Skeletal and apparent densities of polynorbornenes in powder and film form

$\bar{M}_n \times 10^{-3}$ (g mol^{-1})	Skeletal densities (g cm^{-3})		Apparent densities (g cm^{-3})	
	Powder form (He picnometry)	Film form (He picnometry)	Film form (H_2O picnometry)	Film form (Hg porosimetry)
290[a]	1.082	1.070	–	–
400[a]	1.117	1.069	1.030	–
800[b]	1.123	1.096	1.060	1.082

[a] By size exclusion chromatography calibrated with polystyrene standard.

[b] By estimation.

unit. Using Bondi's data [22,23] we have estimated a Van der Waals volume for polynorbornene of 0.637 $cm^3\,g^{-1}$. One should remark that the Bondi data are suitable for linear paraffins and therefore due to the norbornene ring structure this estimation presents some limitations. On the other hand Wendorff and collaborators [4], based on simulations, predicted a Van der Waals volume for polynorbornene of 108 $cm^3\,mol^{-1}$, which based on their polymer characteristics amounts to a v_w of 0.659 $cm^3\,g^{-1}$. By substitution in Eqs. (5) and (6) of the v_W values and of the experimental specific volumes, the corresponding fractional free volumes are calculated and presented in Table 3.

The FFV calculated by density measurements agree rather well and are in the range of magnitude of the values observed for a large number of glass forming polymers (FFV = 2.5%) [24]. On the other hand the FFV values obtained using Bondi's method are higher and rather dependent on v_w estimation. An additional important feature is that, independent of the route used for the estimation of the fractional free volume of the polynorbornene membranes, no significant variation of the FFV values is found in the studied molecular weight range.

The fractional free volume in these samples can also be estimated from the intensity (I_3) corresponding to the o-Ps lifetime and the free volume (V_f) obtained by PAS, using the following relation [17]:

$$\mathrm{FFV} = AV_f I_3; \tag{7}$$

Here A is a parameter that can be determined by calibrating with other physical measurements, such as the specific volume expansion coefficients below and above T_g [25]. It is however generally assumed that for a polymer below the glass transition temperature, the variation of the free volume with temperature is negligible; so the well established value of 2.5% for mean fractional free volume at T_g is a good estimation for FFV in the case of $T < T_g$. Since no values for A in this polymer have been published in the literature we calculated the parameter A under the above assumption and got a value of 3.8 10^{-4} $\mathring{A}^{-3}$. The fact that this value is about five times lower than those obtained for other polymers [17] may be related to the high packing density in these polymers. Further investigation on the values of the parameter A for different polymers needs to be made in order to increase the reliability of PAS fractional free volume results on these systems.

3.1.5. MDSC and glass transition of polynorbornene

The thermal properties of the polymers were analysed by Conventional and by Modulated Differential Scanning Calorimetry (MDSC). A clear glass transition temperature (T_g) was not observed for homopolynorbornene up to 300°C. The detection of T_g for these materials is quite difficult since they present a widespread glass transition, which is characterised by a rather weak change in heat capacity. However, using MDSC it was possible to detect the weak glass transitions of two norbornene/styrene copolymers of low styrene content. Fig. 4 shows the reversible heat flow curve given by MDSC of these two copolymers containing 24 and 8% of styrene. The observed glass transition temperatures were about 230 and 270°C, respectively.

Peruch et al., using a Ni based catalyst system, synthesised a series of random norbornene/styrene copolymers. As expected for random copolymers, they observed that the glass transition temperatures of the copolymers fall between those of the corresponding homopolymers. T_g values of 320, 290 and 220°C were reported for addition type polynorbornene and for norbornene/styrene copolymers containing 10 and 25% of styrene, respectively [7].

It has also been shown previously that our norbornene/styrene copolymers are random copolymers presenting individual styrene units, or very short styrene sequences, which are isolated by polynorbornene segments and that the molecular weight of the copolymers decreases when increasing the styrene content. Moreover, the molecular weights of the polynorbornenes used in this work (Table 1) are much higher than those of these copolymers [10]. Therefore the glass transition of our polynorbornene samples will be above 270°C, in accordance with the data reported by Peruch et al. [7].

Haselwender et al. reported a T_g value of 220°C for an addition type polynorbornene obtained using a Pd based catalyst system [4].

Table 3
Estimated values for the fractional free volume (FFV) of polynorbornene membranes

$\bar{M}_n \times 10^{-3}$ (g mol^{-1})	FFV (%) by density measurements		FFV (%) by Bondi's method	
	H_2O picnometry	Hg porosimetry	$v_w = 0.637^a$ ($cm^3\,g^{-1}$)	$v_w = 0.659^b$ ($cm^3\,g^{-1}$)
290[c]	–	–	11.3	8.3
400[c]	3.6	–	11.5	8.5
800[d]	3.3	1.3	9.2	6.1

[a] Estimated by Bondi and Van Krevelen's data.
[b] Determined by simulation method [4].
[c] By size exclusion chromatography calibrated with polystyrene standard.
[d] By estimation.

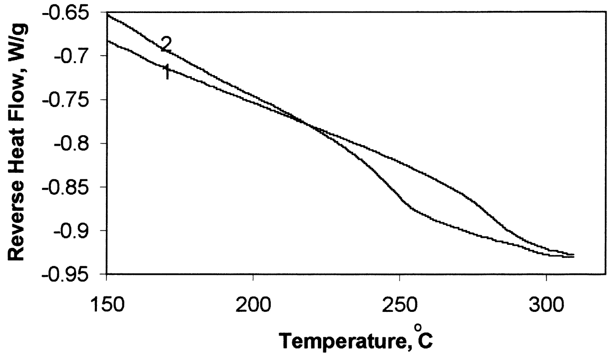

Fig. 4. Modulated DSC thermograms of poly(norbornene-*co*-styrene): (1) 8 mol% of styrene; (2) 24 mol% of styrene.

3.2. Gas permeability

Membranes were successfully prepared from polynorbornene samples of three different molecular weights. Fig. 5 shows the permeability of these membranes to carbon dioxide, oxygen and nitrogen under different pressures. No significant variation the gas permeability was found in the studied molecular weight range for the three different gases.

CO_2 membrane permeability is rather high, due probably to relative high solubility when compared with O_2 and N_2. For feed pressures below 2.5 bar, CO_2 permeability decreases with increase of feed pressure. Above 2.5 bar, CO_2 permeability tends to a constant value. This is in contrast with the fact that the O_2 and N_2 permeabilities are practically independent of the pressure.

At 4 bar, the permeability of polynorbornene to CO_2, O_2 and N_2 is about 49, 10.8 and 2.7 Barrer, respectively. The overall selectivity of $\alpha_{CO2/N2}$ and $\alpha_{O2/N2}$ amounts to 18 and 4, respectively. Both the gas permeability and selectivity we measured are much higher than the values reported by Yampol'skii et al. [9].

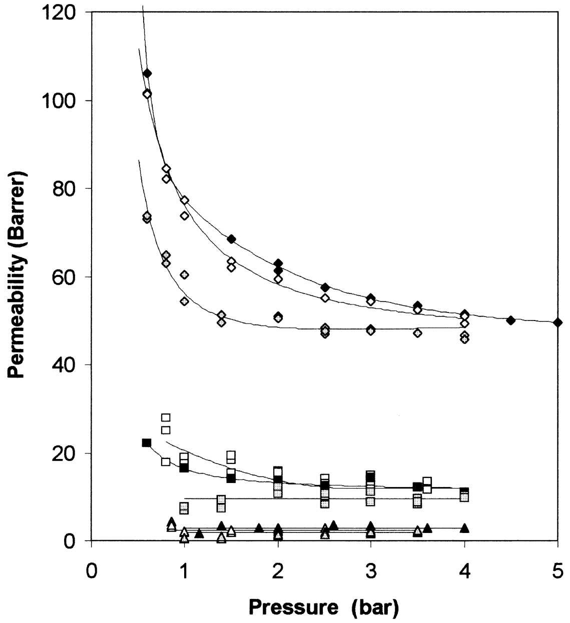

Fig. 5. Gas permeability of polynorbornene vs. feed pressure. CO_2 (◆◈◇); O_2 (■▣□); N_2(▲◭△); $\bar{M}_n = 2.9 \times 10^5$ (◇□△); $\bar{M}_n = 4.0 \times 10^5$ (◈▣◭); and $\bar{M}_n = 8.0 \times 10^5$ (◆■▲).

Table 4 compares the characteristics and the gas permeation performance of the membranes prepared in this work, from unsubstituted polynorbornenes, with the ones prepared by Dorkenoo et al. [8], using substituted polynorbornenes with aliphatic pendent groups. The unsubstituted polynorbornenes exhibit lower permeabilities, but higher selectivities.

It is also interesting to compare the gas permeabilities of membranes prepared from the present addition type polynorbornenes with ones prepared from ring opening metathesis polymerised (ROMP) polynorbornenes [26] (Table 4). Despite both polymers having been synthesised from the same monomer, the latter ones are more like rubber (T_g of 31°C). Although the ROMP polynorbornene membranes have higher fractional free volumes it turns out that their gas permeabilities are much lower than the ones corresponding to the present addition polymerised polynorbornene membranes.

3.3. Polynorbornenes' structural characteristics and membrane gas permeation performance

The information obtained through the experimental techniques above described leads to the conclusion that the norbornene polymerisation occurred without ring opening and that the present polynorbornenes are as a whole atactic (NMR spectra). Simulation studies of such polymers indicate that they should display a rigid random coil conformation in a long range. However, the molecular chain rigidity does not hinder the polymer packing, as shown by WAXD spectra, and the estimated space distance between polymer chains is 3.8 Å. This is also in accordance with the value of 3.53 Å for the mean free volume hole size given by PAS. The molecular chain rigidity and the condensed packing contribute to the high glass transition temperature and to the low fractional free volumes. Within the studied range of molecular weight, these low fractional free volumes are practically independent of the molecular weight value, as confirmed by the permeation performance of the three different membranes. Despite the variation on the fractional free volume with the estimation method, the unsubstituted polynorbornenes always present significantly lower FFV values than the substituted ones (Tables 3 and 4). If we assume, in accordance to literature [8], that between substituted and unsubstituted polynorbornenes there is no significant variation in the solubility coefficient, then the change in permeability should result from the difference in gas diffusion coefficient through the polymers and may be related to its free volume.

The comparison of permeation properties (Table 4) shows that the lower permeabilities and the overall higher selectivities are in accordance with the dense packing of

Table 4
Comparison of properties and gas permeation performance of various types of polynorbornenes

Polynorbornene type	FFV[a] (%)	T_g (°C)	CO_2[b] (Barrer)	O_2[b] (Barrer)	N_2[b] (Barrer)	$\alpha_{CO2/N2}$	$\alpha_{O2/N2}$
Unsubstituted	6.1–11.5	$\geqslant 270$[c]	49.1	10.8	2.7	18.1	4.0
5-methyl-2- [8]	19.22	≥ 380[d]	396.3	89.2	24.1	16.4	3.7
5-butyl-2- [8]	17.04	≥ 350[d]	141.9	33.3	11.2	12.7	3.0
5-hexyl-2- [8]	16.06	280[d]	83.8	19.8	6.9	12.1	2.9
5-decyl- [8]	15.94	150[d]	111.1	25.3	8.7	12.8	2.9
ROMP [26]	15.6	31	25.4	2.8	1.5	16.9	1.9

[a] Determined by Bondi's method.

[b] Experimental conditions for unsubstituted polynorbornene — (4 bar and 28°C for CO_2 and N_2 and 25°C for O_2); for substituted polynorbornene — (10 atm and 35°C); for ROMP polynorbornene — (50–500 Torr and 22 ± 3°C). 1 Barrer = 10^{-10} cm^3(STP) cm cm^{-2} s^{-1} $cmHg^{-1}$.

[c] By modulated DSC.

[d] By dynamic mechanical analysis.

the characterised structures and in fact the polymer may be viewed as a molecular sieve as far as gas permeation goes.

4. Conclusions

The synthesis of polynorbornenes is achieved without ring opening and, despite the evidence of a rigid random coil conformation, the polymers present high packing density, as confirmed by X-ray and PAS spectra. The size of the free volume assessed directly by PAS is in close agreement with an indirect value estimated through the interchain distance determined by WAXD. Thus, both methods provide valuable information about the packing and free volume of the polymers. The expected low values of the fractional free volumes are experimentally confirmed and are in accordance with the experimental gas permeabilities that are lower than the ones reported for substituted polynorbornenes. On the other hand the selectivities of these unsubstituted polynorbornenes are higher and we may think of gas permeation governed by a molecular sieving mechanism.

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