Addition-type polynorbornene with trimethylsilyl side groups: study of organic vapors sorption, transport and swelling

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Abstract. High free volume glassy polymers are generally more selective to condensable vapors rather than to light gases. Such a property makes these materials suitable for membrane-based separation processes, as for instance the removal of VOCs. In this work, we focus our attention on poly-(trimethyl-silyl)-norbornene (*PTMSN*). Using both a barometric and an optical apparatus, the sorption and dilation isotherms have been determined at 35°C for n-pentane and n-hexane: the solubility values are very high, like for PTMSP, because of the high free volume trapped into the polymeric matrix. Moreover, the *Lattice Fluid* parameters have been estimated, enabling us to compare the experimental data with the NELF model predictions. Permeability has been calculated as the product of diffusivity and solubility at the same pressure and it results higher for n-C_6 than for n-C_5.

Keywords. *Solubility, Diffusivity, Relaxation, Dilation, Nelf* .

INTRODUCTION

Glassy polymers are typically used in the manufacturing of membranes for gas separation due to high permeability and selectivity. In particular, the selectivity α_{ij} of a membrane towards a component *i* in a mixture of components *i* and *j* can be decomposed into two contributions α_D e α_S, called the diffusivity and solubility selectivity, respectively [1]:

$$\alpha_{ij} = \frac{P_i}{P_j} = \frac{D_i}{D_j}\frac{S_i}{S_j} = \alpha_D\alpha_S \tag{1}$$

While for many polymers the dominating term is the diffusivity selectivity, in the case of high free volume glassy polymers the solubility selectivity, due to the low size sieving ability, gives the greater contribution, thus these materials are more permeable to condensable vapors than to light gases. The substituted polynorbornenes belong to this family and are potential candidates to be used for separation purposes, in place of poly-(4-methyl 2-pentyne) (PMP) or poly-(trimethylsilyl)-propyne (PTMSP).
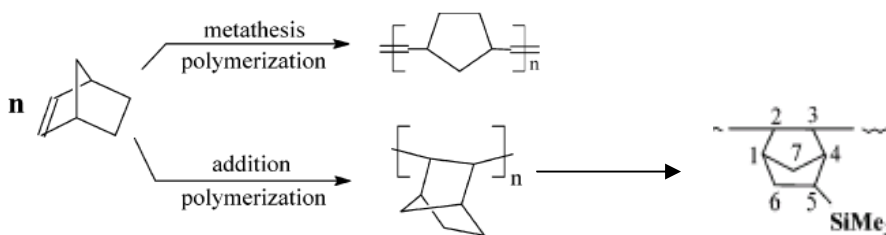
EXPERIMENTAL

Poly-(trimethylsilyl)-norbornene

The Poly-trimethylsilyl-norbornene studied here is an addition-type polymer whose monomer unit is obtained by a *Diels-Alder* reaction between cyclopentadiene and vinyltrimethylsilane. It is well known that the polymerization of norbornene can occur, depending on the catalyst used, by ring opening, with the formation of cyclolinear structures or, in the presence of Ni or Pd, by double bond opening, with the formation of bulky monomer units (Figure 1).

The materials obtained by addition reaction are more stable, for the absence of double bonds, and they are characterized by high free volume values, with bulky side groups, stiff backbones and high torsional barrier .

The present polynorbornene presents trimethylsilyl as a side group, its density is equal to 0.883 g/cm^3 (its fractional free volume was estimated to be about 0.275) and shows a glass transition temperature greater than 340 °C, as it has been estimated through TGA analysis: more reliable estimates are not available, because this polymer chemically decomposes before reaching T_g [2]. The PTMSN films have a thickness of about 150μm and they were cast from a dilute toluene solution (2% in weight).

Figure 1: Polymerization of PTMSN and monomer unit obtained by addition.

Solubility and Diffusivity measurement

Sorption experiments of n-pentane and n-hexane were performed at 35 °C using a constant volume/variable pressure apparatus. Initially the film of PTMSN was placed in the sample chamber and exposed to the vacuum overnight to remove the residual air gases. The desired amount of vapor was then introduced into the chamber and allowed to equilibrate. Once the pressure was constant, additional vapor was introduced and again allowed to attain the equilibrium: a capacitance manometer (f.s. 1000 mbar, accuracy 0.1 mbar) monitores the pressure decay of the gaseous phase in the cell, which is related to the amount of mass absorbed by the polymer. The apparatus, whose total volume is around 90 cm^3, is placed in a thermostatic box where the temperature is set to 35 ± 0.1 °C.

Dilation measurement

The dilation of the sample during sorption is measured in a dedicated apparatus, by monitoring the sample elongation in one direction with a CCD camera. It is reasonable to assume, in this case, that the swelling is isotropic and that the volume dilation can be calculated by considering the elongation in one direction only (*x*), according to the following relationship:

$$\frac{\Delta V}{V_0} = 3\frac{\Delta x}{x_0} \qquad (2)$$

RESULTS AND DISCUSSION

All the sorption experiments shows a wide relaxation stage, in particular during n-hexane sorption. We will not perform a specific analysis of relaxation phenomena in this work, but rather present the equilibrium solubility values at the end of the diffusive and relaxational stages of sorption.
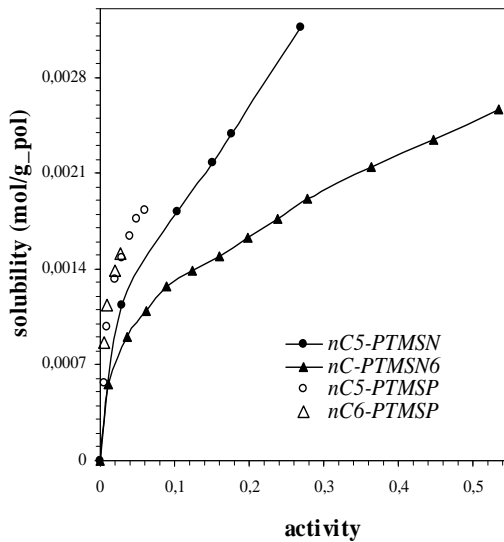

Figure 2a: Solubility isotherms at 35°C for n-C_5 and n-C_6 in PTMSN (closed symbols) as a function of activity and comparison with literature data on PTMSP (open symbols) at 27°C. [3]
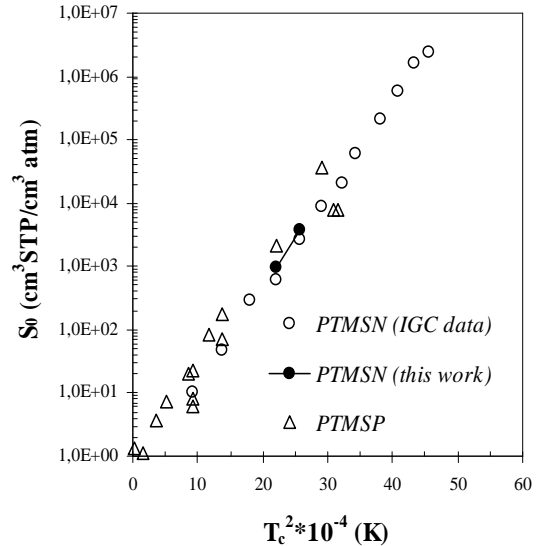
Figure 2b: Infinite dilution solubility coefficients in PTMSP and PTMSN, as obtained with IGC [4] and with pressure decay technique from this work.

In figure 2a we reported the solubility isotherms for n-C_5 and n-C_6, that are concave to the activity axis as it always happens in the case of glassy polymers. The molar solubility of n-C_5 is, at fixed activity, higher than that of hexane, contrary to what happens in the case of PTMSP [3]. The infinite dilution solubility coefficients are reported in Figure 2b and compared to the corresponding values obtained, in the same material, by Starannikova *et al.*,[4] by means of *Inverse Gas Chromatography (IGC)* on a series of gases and vapors. The data are plotted versus the penetrant square critical temperature, and it can be seen that the values estimated in this work are in good agreement with those obtained with a different technique.

In Figure 3a, the diffusivity values are reported as a function of average concentration: the isotherms follow the molecular size of the penetrants, the diffusivity of n-C_6 being lower than that of n-C_5. Moreover, in the case of n-C_6 the plasticization effect, based on which the diffusivity increases rapidly with concentration, is more evident especially in the initial steps. The pure gas permeability, evaluated as the product of diffusivity and solubility, is plotted in Figure 3b, which shows that PTMSN is more permeable, in almost the whole pressure range inspected, to the most condensable component, namely n-C_6, as it is common for this kind of ultra high free volume glassy polymers.

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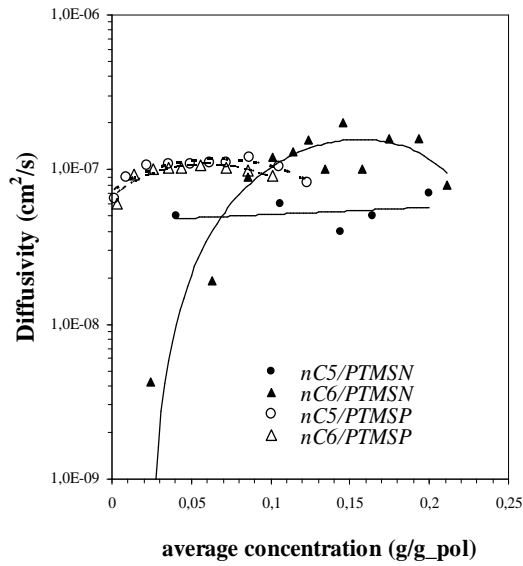
Figure 3a: Diffusivity of n-C$_5$ and n-C$_6$ in PTMSN at 35°C (closed symbols) and in PTMSP at 27°C (open symbols).
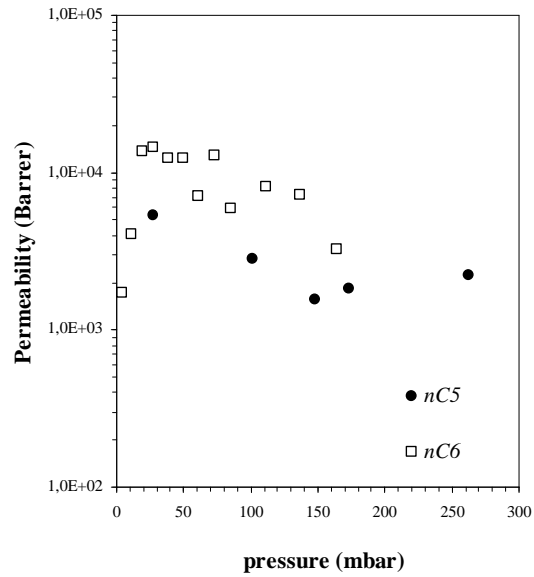
**Figure 3b:** Permeability of n-C$_5$ and n-C$_6$ in PTMSN at 35°C.

The experimental solubility data were then compared to the predictions of the *Non Equilibrium Lattice Fluid Model (NELF)* [5]. To this aim, it was necessary to determine the characteristic parameters for the *Lattice Fluid* equation of state for the penetrants and for the polymer. For the penetrants, these parameters were taken from the literature, while for the polymer they are usually obtained via a fitting of the pressure-volume-temperature data above T$_g$. Obviously, in our case this procedure is not suitable because the polymer decomposes before reaching T$_g$, therefore it has been necessary to use mixture data, in particular infinite dilution solubility data reported in figure 4a [4]. From a regression of these data with the values of S$_0$ evaluated with NELF model (fig. 4a), one obtains:

$$T^* = 405.98 \ K \qquad p^* = 359.82 \ MPa \qquad \rho^* = 1.345 \ Kg/L$$

The comparison between experimental solubility isotherms and the predictions of the NELF model is rather satisfactory (Figure 4b): in particular, it is interesting notice that the values of k_{ij} are negative in both cases, indicating that there are strong interactions between penetrant and polymer.
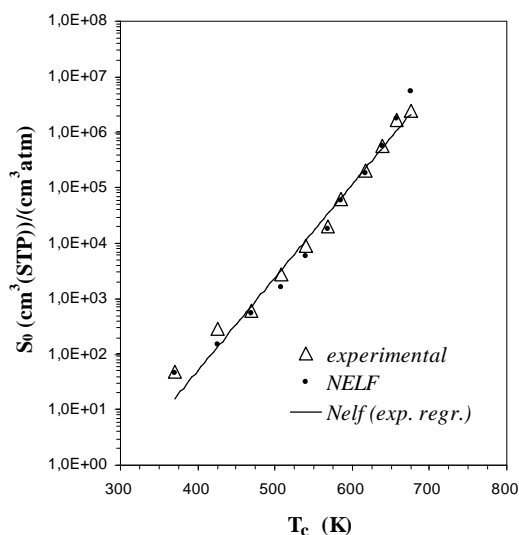
Figure 4a: Experimental [4] and calculated values of S_0 for various penetrants in PTMSN.
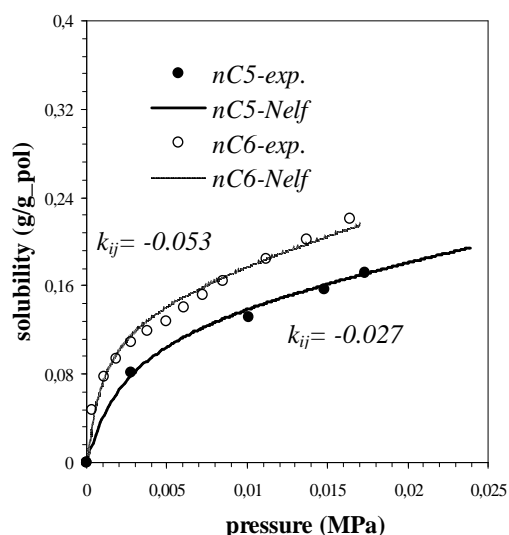
Figure 4b: Experimental solubility isotherms and comparison with NELF model predictions.

On the same polymer, we performed also dilation experiments: the experimental curves, plotted in terms of percentage volume dilation versus penetrant concentration are not linear (Figure 5a).

The resulting values of partial molar volume (Figure 5b) show a behaviour that is very typical of glassy polymers [6]: an initial increase with penetrant concentration is observed, corresponding to a "void filling" mechanism, followed by a maximum and a decrease with penetrant concentration, probably due to the fact that the progressive swelling at this high pressure is rather inhibited by the rigidity of the polymer matrix.
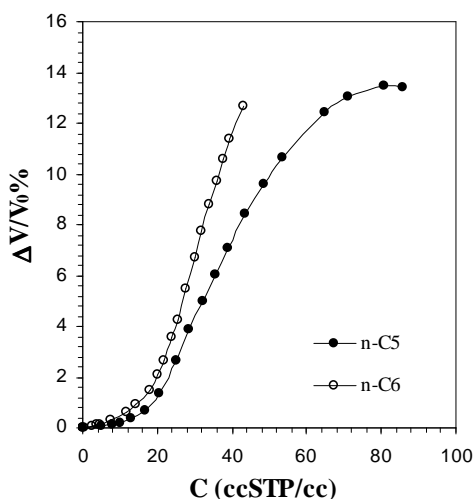
Fig. 5a Swelling isotherm of n-C$_5$ and n-C$_6$ in PTMSN at 35°C.
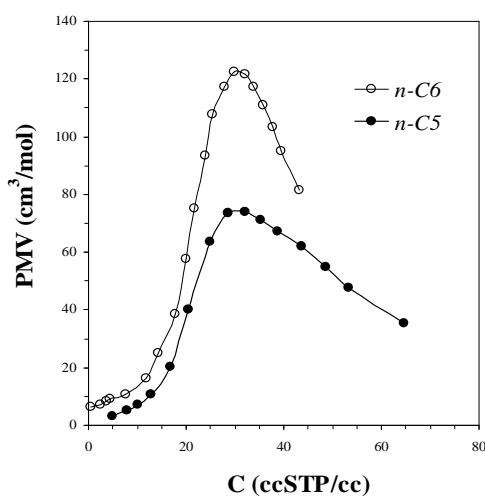
Fig. 5b Partial molar volume of n-C$_5$ and n-C$_6$ in PTMSN at 35°C as functions of concentration.

CONCLUSIONS

Sorption and dilation experiments were performed on PTMSN.

The solubilities of organic vapors as n-pentane and n-hexane in the polymer are rather high because of the high fractions of free volume trapped in its glassy matrix, thus the PTMSN is a potential candidate for use in gas separation membranes.

The solubility and diffusivity behaviour is typical of glassy polymers and the values are comparable to those in PTMSP. The permeability is higher for the larger, more condensable hexane than for pentane, as it is the case of vapour-selective polymers.

The solubility isotherms can be modelled satisfactorily with NELF model, even in the absence of experimental volumetric information on the polymer, by fitting the *Lattice Fluid* parameters to the infinite dilution solubility data available in the literature.

The swelling behaviour presents a non monotonous trend that can be explained through the glassy nature of the polymer matrix.

ACKNOWLEDGEMNTS

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