

CHARACTERIZATION AND MODELING OF THE ORGANIC VAPOUR TRANSPORT IN ADDITION-TYPE POLY (TRIMETHYLSILYL NORBORNENE)

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The transport properties of a series of organic vapors ($n\text{-C}_4$, $n\text{-C}_5$ and $n\text{-C}_6$) on Poly-(trimethylsilyl norbornene) (PTMSN), a new substituted high free volume polymer obtained via addition reaction, were studied and modelled. The trend of vapor solubility and diffusivity as a function of the vapor pressure was determined and analyzed, showing that the vapor uptake is extremely high, while diffusivity has intermediate values within the typical range of high free volume glassy polymers. Solubility shows the typical trend of glassy matrices, with a marked concavity towards the pressure axis, while diffusivity first increases with penetrant concentration, then reaches a plateau value. The experimental sorption data were successfully compared with the Non-Equilibrium Lattice Fluid Model (NELF) calculations, after determination of polymer characteristic parameters from available solubility data at infinite dilution for several penetrants. The present analysis shows that PTMSN is highly selective towards organic vapors, thus it is a promising material for gas-vapor membrane separation, as well as for the removal of volatile organic compounds (VOCs) .

1. INTRODUCTION

Polymers that exhibit high permeability and selectivity versus target components are more promising candidates for membrane-based separation processes: in this field, the knowledge of the mass transport properties of polymers plays an important role in the choice of suitable materials for the separations of interest. Such applications require materials which offer a good dimensional stability, as well as good resistance toward ageing, because the swelling phenomena induced by the sorption of gases or vapors may lead to changes in both membrane structural features and performance.

Super-glassy polymers, like poly-acetylenes are materials of election for such applications, because they show a very high solubility and permeability to the more condensable vapors and, on the other side, appreciable mechanical properties and dimensional stability [1].

High free volume glassy polymers are usually more selective to condensable vapors than to light gases, because the large amount of excess free volume in the polymeric matrix does not allow a good size-sieving ability, so the selectivity is mostly dictated by solubility, which is favourable to the permeation of the more soluble components, that are usually the more condensable ones.

Poly-(trimethylsilyl norbornene) (PTMSN) is a novel poly-(norbornene) obtained via addition and contains $\text{Si}(\text{CH}_3)_3$ side groups that confer high free volume and rigidity to the glassy structure. Preliminary studies of sorption at infinite dilution and permeation of light gases [2] show that this material offers higher permeabilities than other poly-norbornenes and comparable to those of poly(trimethylsilyl propyne) (PTMSP), that is the most permeable glassy polymer known.

In this work, solubility and diffusivity of n -alkanes in PTMSN were experimentally determined, showing that the sorption levels for this material are exceptionally high and that its permeability is highly favourable to the more condensable vapors. The experimental data were successfully compared with the isotherms predicted by the Non-Equilibrium Lattice Fluid Model (NELF), after determination of the lattice fluid (LF) parameters for PTMSN.

The NELF model [3] extends the Sanchez-Lacombe [4] equation of state to the non equilibrium domain of the glassy polymers and allows the calculation of solubility isotherms in glassy polymers in a completely predictive way, once the Lattice Fluid characteristic parameters (T^* , P^* , ρ^*) of polymer and penetrant species are known, in addition to the polymer density in the glassy phase. In our case, the pure component parameters for PTMSN are not available in the literature and they are not retrievable from equilibrium volumetric data, since the polymer degrades before reaching its T_g . As a consequence, they were determined following an alternative procedure based on the use of sorption data at infinite dilution conditions obtained by Inverse Gas Chromatography (IGC) [2].

2. THEORETICAL BACKGROUND

In membrane-based separation processes, the selectivity α_{ij} of the key component i in mixture versus component j , is defined as the ratio between the permeabilities of i and j respectively:

$$\alpha_{ij} = \frac{P_i}{P_j} = \alpha_D \alpha_S = \left(\frac{D_i}{D_j} \right) \left(\frac{S_i}{S_j} \right) \quad (1)$$

This relation is suitable when the *solution-diffusion* model holds for the sorption process in the polymer and whenever the downstream pressure is much smaller than upstream value, as it is typically the case.

Equation 1 shows that the selectivity contains a diffusivity and a solubility contribution; usually, in glassy polymers, the diffusivity selectivity is the predominating factor, however for certain high free volume glassy polymers the size sieving ability is very poor, so that the solubility-selectivity becomes important for these materials, and often the larger penetrants, which are more condensable and soluble in the polymer, are more permeable than lighter gases. This is the so-called vapor-selective behavior, which is exhibited for example by PTMSP, and is expected to hold true also for the case of PTMSN under consideration.

Since selectivity is driven by solubility, the estimation of sorption values from pure component parameters becomes an essential tool to predict the separation performance of the polymer. This prediction can be performed by making use of the NELF model, whose features are briefly recalled hereafter.

The NELF model extends the Sanchez-Lacombe equation of state for amorphous equilibrium phases to the non equilibrium domain typical of glassy polymers, using the same parameters to represent the pure components' properties and the same mixing rules to calculate the mixture behavior [3]. For all the penetrants, these parameters can be determined using either the PVT (pressure-volume-temperature) data or vapour-liquid equilibrium data, while for the polymers they are usually calculated by fitting the PVT data above T_G with the Sanchez-Lacombe equation of state.

In the lattice fluid model, the number of lattice sites occupied by a molecule of species i in its pure phase can be expressed as:

$$r_i^0 = \frac{M_i}{\rho_i^* v_i^*} \quad (2)$$

where M_i is the molar mass of species i and v_i^* is the volume occupied by a mole of lattice sites of pure substance: the parameter is usually set to infinity for the polymer species. The mixing rules adopted to estimate the mixture characteristic parameters contains one only adjustable parameter, Ψ , or, alternatively, $k_{1,2} = 1 - \Psi$, appearing in the expression of the characteristic pressure for the mixture, P^* , related to the binary interactions between the gas and polymer molecules, labelled by subscripts 1 and 2 respectively.

$$P^* = \phi_1 P_1^* + \phi_2 P_2^* - \phi_1 \phi_2 \left(P_1^* + P_2^* - 2\Psi \sqrt{P_1^* P_2^*} \right) \quad (3)$$

When specific binary data are not available, one can use the first order approximation by setting $\Psi=1$, that means that the binary interactions are supposed to be those of a regular mixture, according to definition given by van Laar.

The extension to the non equilibrium state is given by the Non Equilibrium Thermodynamics of Glassy Polymers approach (NET-GP), in which the state of a glassy polymer-penetrant mixture can be described by the usual variables, for example temperature, pressure and composition, plus the polymer density, which accounts for the departure from the equilibrium state.

The NET-GP approach allows to obtain the following main results [5]:

(1) The specific Helmholtz free energy in the nonequilibrium glassy state is a cylinder in the space of the non-equilibrium domain, coincident with the equilibrium Helmholtz free energy at the same value of temperature T , penetrant-to-polymer mass ratio Ω_1 and polymer density ρ_2 :

$$\hat{A}^{NE}(T, p, \Omega_1, \rho_2) \equiv \hat{A}^{EQ}(T, \Omega_1, \rho_2) \quad (4)$$

(2) The chemical potential of the penetrant in the glassy mixture is calculated as:

$$\mu_1^{NE} = \left(\frac{\partial \hat{A}^{EQ}}{\partial \rho_1} \right)_{T, \rho_2} \quad (5)$$

\hat{A}^{EQ} being the equilibrium Helmholtz free energy density.

(3) The phase equilibrium condition for penetrant 1 between the pure external gas (g) and the solid glassy phase (s) may be written as:

$$\mu_1^{NE(s)}(T, \Omega_1^{PE}, \rho_2^{PE}) = \mu_1^{EQ(g)}(T, p) \quad (6)$$

where the superscript PE indicates the pseudo-equilibrium conditions asymptotically reached in the glassy phase.

In the limit of infinite dilution, ρ_2^{PE} is equal to the density of pure unpenetrated polymer ρ_2^0 , because swelling is negligible under these conditions; then the penetrant solubility coefficient can be predicted by the model as a function of temperature, pressure, pure polymer density and lattice fluid parameters, without any experimental information about the mixture behaviour; one has:

$$\ln(S_0) = \ln\left(\frac{T_{STP}}{P_{STP} T}\right) + r_1^0 \left\{ \left[1 + \left(\frac{v_1^*}{v_2^*} - 1 \right) \frac{\rho_2^*}{\rho_2^0} \right] \ln\left(1 - \frac{\rho_2^0}{\rho_2^*} \right) + \left(\frac{v_1^*}{v_2^*} - 1 \right) + \frac{\rho_2^0 T_1^*}{\rho_2^* T P_1^*} \Psi \sqrt{P_1^* P_2^*} \right\} \quad (7)$$

where the subscript STP indicates the standard temperature and pressure conditions. In order to calculate S_0 , all the characteristic parameters appearing in equation 7 should be known. On the other hands, when sufficient experimental data of infinite dilution solubility coefficients are available for different penetrants, one can use eq. 7 to retrieve the characteristic parameters for the polymer species T_2^* , P_2^* and ρ_2^* , reminding that $T^* = P^* v^* / R$.

In general, one needs to know the value of the glassy polymer density at the actual temperature and pressure conditions: especially for swelling penetrants, the value of ρ_2^{PE} may vary with pressure during sorption, due

to swelling phenomena. Experimental data show that generally polymer density follows a linear relationship versus the external pressure [6]:

$$\rho_2^{PE}(p) = \rho_2^0(1 - k_{SW}p) \quad (8)$$

The parameter k_{SW} is called swelling coefficient and can be calculated from the slope of the experimental swelling isotherms as function of pressure. In the absence of specific dilation data, k_{SW} can be adjusted on one solubility datum at high pressure, thus providing a reliable estimate for the swelling behavior of the polymeric matrix [6].

Then, the phase equilibrium condition expressed by equation 6 may be re-written as:

$$\mu_1^{NE(s)}(T, \Omega_1^{PE}, \rho_2^0, k_{SW}) = \mu_1^{Eq(g)}(T, p) \quad (9)$$

3. EXPERIMENTAL AND MATERIALS

3.1. Materials

The polymer was prepared at the A.V. Topchiev Institute of Petrochemical Synthesis (TIPS) of Moscow (RU) and provided as a courtesy of Dr. Yuri Yampol'skii.

In general, the polymerization of norbornene can be conducted either by ring opening or by addition reaction (Figure 1): the first procedure leads to the traditional class of poly-(norbornenes) that have a rather dense structure, with poor chemical stability due to the presence of insaturations in the chain [7].

The repeating unit of poly-(norbornene) used in this study, 5-trimethylsilyl-2-norbornene, was obtained via addition, with a Diels-Alder reaction between dicyclopentadiene and vinyltrimethylsilane according to the procedure described by Starannikova et al. [2]. The polymerization of norbornene was conducted by addition reaction in presence of Ni as a catalyst, leading to the breaking of double bonds and to a polymer with a very open structure: the presence of a $-\text{Si}(\text{CH}_3)_3$ group in the 5-position gives even more additional free volume and rigidity to the matrix, as shown in Figure 2. The polymer is a mixture of endo- (25%) and exo- (75%) structures, which are included into a single backbone. Due to the absence of double bonds, this polymer can provide better chemical stability than conventional poly-(norbornenes) obtained via ring opening.

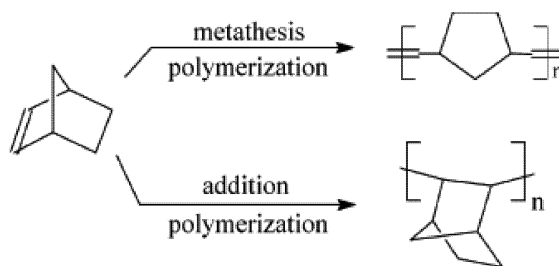


Figure 1: different polymerization routes for poly(norbornene): ring opening and addition.

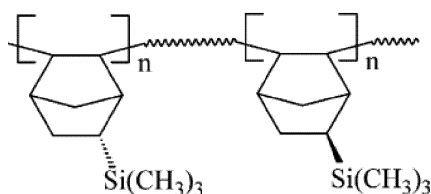


Figure 2: repeating unit of PTMSN with endo- and exo- structures

Dense films of PTMSN were cast from a dilute solution in toluene (2% wt): after casting, the solvent was allowed to evaporate from the Petri dish with the bottom covered by a cellophane cap. The thickness of the films obtained falls in the range of 150-200 μm .

According to DSC analysis, PTMSN does not show any glass transition up to 300 $^{\circ}\text{C}$; at the same time, a TGA scan indicates that the glass transition temperature is significantly higher than 340 $^{\circ}\text{C}$.

The density of PTMSN at 35 $^{\circ}\text{C}$ is equal to $0.883 \pm 0.001 \text{ g/cm}^3$ [7]. This value of density allows the estimation of the polymer fractional free volume (FFV), using the following equation:

$$FFV = \frac{\rho_2^W - 1.3\rho_2^0}{\rho_2^0} \quad (10)$$

where the van der Waals density ρ_2^W provides a measure of the volume occupied by the polymeric chains only, excluding the free volume elements and can be calculated with Bondi's group contribution method [7]. Based on literature data and on eq. 10, the fractional free volume of PTMSN is equal to 0.275. The relevant physical parameters of the polymer are listed in Table 1.

Finally, the different penetrants used in this work (*n-C4*, *n-C5* and *n-C6*) were purchased by Carlo Erba (purity >99.6%) and used as received without further treatments.

Table 1: physical parameters for PTMSN.

	T_G (K)	FFV	ρ at 35 $^{\circ}\text{C}$ (g/cm^3)
PTMSN	>340 $^{\circ}\text{C}$	0.275	0.883

3.2. Vapor sorption measurements

Sorption data for several organic vapours were carried out at 35 $^{\circ}\text{C}$ using a constant volume/variable pressure apparatus (Figure 3): the system temperature was controlled through a constant temperature incubator (PID-M150-TBR) which keeps the desired value of temperature to within $\pm 0.1^{\circ}\text{C}$. Initially the polymer film was placed in the sample chamber (5) and exposed to vacuum overnight to remove all the residual gases absorbed. 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 equilibrium. Using this differential procedure, the sorption isotherms of different hydrocarbons in PTMSN were determined for each penetrant pressure. Sorption equilibrium was reached within a few days,

depending upon penetrant and activity values: especially at higher activities, a wide relaxation stage was observed during the sorption for all the penetrants tested.

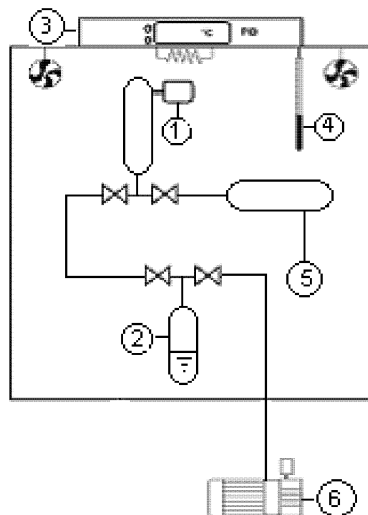


Figure 3: Vapor sorption pressure decay apparatus.

4. RESULTS AND DISCUSSION

4.1. Sorption and diffusion of n-alkane vapors

Sorption isotherms for different alkane vapors (*n*-butane, *n*-pentane, *n*-hexane) were measured at 35°C up to the atmospheric pressure, using the *pressure decay* apparatus described in the previous section. The analysis of the transient diffusion stage for different penetrants was also performed, allowing us to obtain the diffusion coefficients in each differential sorption step. It has to be mentioned that the sorption kinetics is often characterized by a marked non Fickian behavior and by the presence of strong relaxation phenomena. In this work, we do not focus on those aspects, which will be treated in a future work.

As it can be seen in Figure 4, the solubility of hydrocarbons in PTMSN is very high because of the large free volume fractions trapped into the polymeric matrix: these values are comparable to those of PTMSP under the same conditions. In the low and medium pressure range, the sorption isotherms show the classical concavity versus the pressure axis, as it is common in glassy polymers, while at higher activities a change of concavity is observed, due to the plasticization effect induced by *n*-pentane and *n*-hexane: in all the cases, the experimental data have been interpolated with the Dual Mode model equation to guide the eye. The differential sorption experiments allow to estimate the diffusivity of different penetrants in PTMSN, through the analysis of transient diffusion stage, and the results are shown in Figure 4b. The values of infinite dilution diffusivity lie between those of other high free volume glassy polymers, in particular between those of PTMSP [8] and of Amorphous Teflon® AF2400 [9]. For all the penetrants considered, the diffusivity seems to follow a similar trend versus the penetrant average concentration, i.e. a marked increase with concentration followed by a plateau value.

Finally, it is interesting notice that the critical value of mass ratio at which the diffusivity attains a constant value is practically the same for all the three penetrants (about 10% in weight of penetrant).

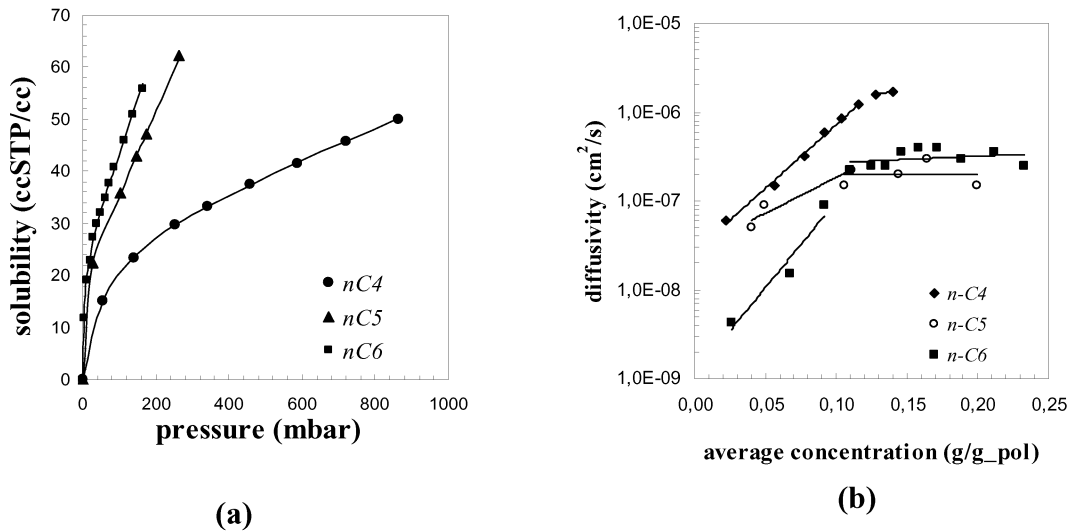


Figure 4: a) solubility and b) diffusivity of *n*-C₄, *n*-C₅ and *n*-C₆ in PTMSN at 35°C.

4.2. Modelling the solubility with NELF model

In order to compare the experimental sorption isotherms with the predictions based on the NELF model, we remind that the lattice fluid characteristic parameters T_2^* , P_2^* , ρ_2^* can be determined by fitting the pressure-volume-temperature data to the Sanchez-Lacombe equation of state above T_G , where the equilibrium conditions hold. In the case of PTMSN, as already mentioned, the volumetric properties in the rubbery region are not accessible because the polymer decomposes before reaching the glass transition [7], as observed also for other super glassy matrices like PTMSP [10].

To overcome this limit, in this work the LF parameters were estimated by considering available mixture data, in particular taking advantage of a collection of infinite dilution solubility data for several penetrants (*n*-alkanes, oxygen, hydrogen, carbon dioxide) in PTMSN published by Starannikova et al. [2]. As discussed above, the explicit expression for the infinite dilution solubility coefficient S_0 , obtained by the NELF model and reported in eq. 7 can be used to adjust the three characteristic lattice fluid parameters on the experimental solubility data available at infinite dilution. The result of the least square fitting performed on the experimental data is shown in Figure 5a, where the values of S_0 are reported, on a semilogarithmic plot, versus the critical temperature of the penetrant, following a typical representation of the effects of penetrant condensability on the infinite dilution solubility coefficient in a given polymer [11,12]. The set of LF parameters obtained with this procedure is displayed in Table 2.

Table 2: Lattice Fluid parameters for penetrants and polymer.

	T^* (K)	P^* (MPa)	ρ^* (Kg/L)	Source
PTMSN	406	360	1.345	<u>This work</u>
<i>n</i> -C ₄	430	290	0.720	Vargaftik [13]
<i>n</i> -C ₅	451	305	0.749	Vargaftik [13]
<i>n</i> -C ₆	476	298	0.775	Vargaftik [13]

Such pure component parameters have been used in eq. 9 to calculate the solubility isotherms of the three alkanes considered, at 35°C: to best fit the experimental data, the binary parameter $k_{1,2}$ was adjusted to the low pressure data available. Interestingly, the value of the binary parameter $k_{1,2}$ is the same for all the penetrants examined, allowing to infer that the same parameter can be used to predict the solubility also of longer alkanes.

Moreover, using just a solubility datum in the relatively high pressure region, the NELF model enabled us to estimate the swelling coefficients in PTMSN for all the penetrants tested [6]: the results indicate that the swelling coefficient increases monotonically with penetrant molecular weight.

The successful modelling of sorption data is encouraging to study more extensively the behaviour, in view of developing PTMSN-based membranes separations, reducing the amount of experimental work required, which otherwise would be really demanding since the duration of sorption experiments is rather long and time consuming. In this respect the NELF model can serve as a useful tool to simulate the material performance, based only on pure components characteristic parameters and on the adjustable parameters obtained from a very limited set of experimental data.

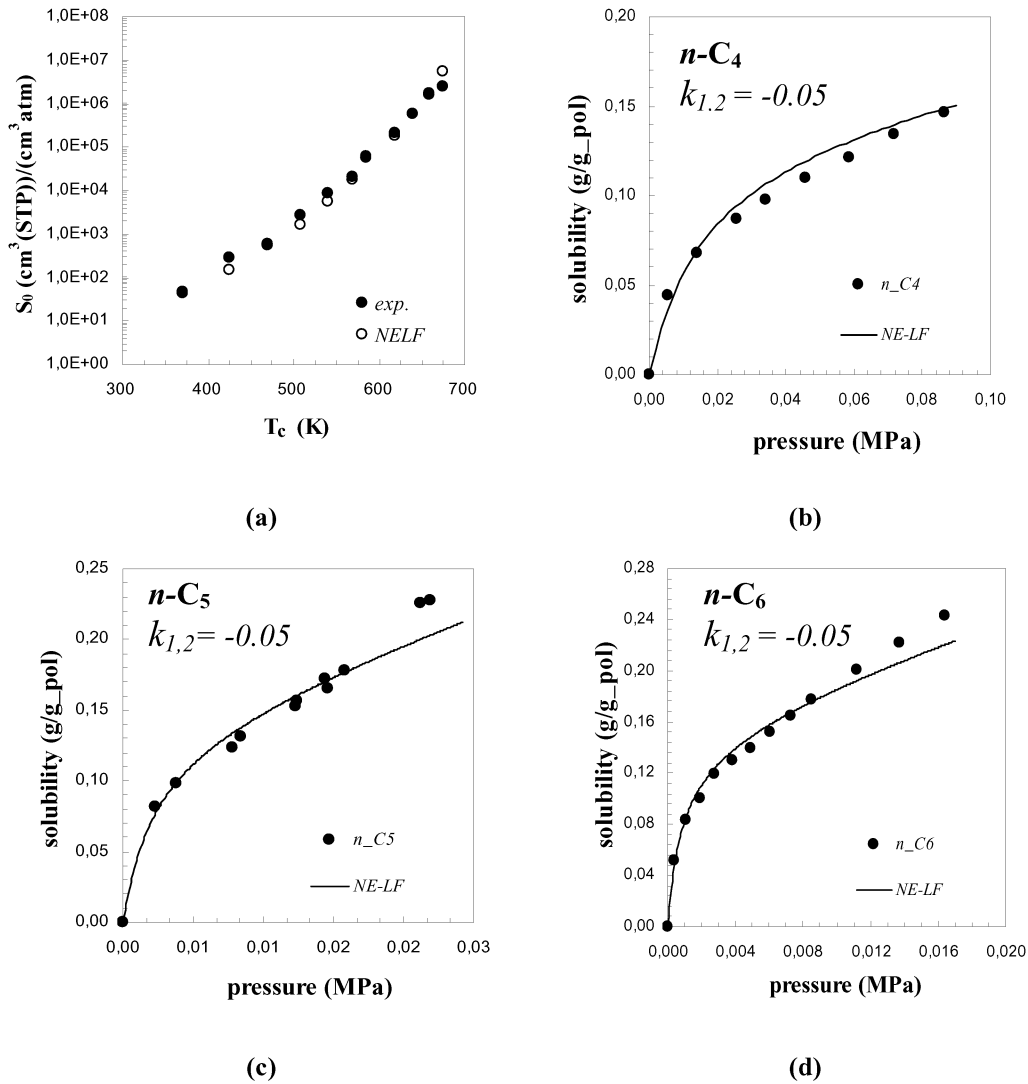


Figure 4: a) experimental solubility data at 35°C [2] and NELF model predictions based on eq. 7 and parameters listed in Table 2; experimental and calculated solubility isotherms of $n\text{-C}_4$ (b), $n\text{-C}_5$ (c) and $n\text{-C}_6$ (d) in PTMSN at 35°C with the values listed in Tables 2 and 3 for NELF model parameters.

Table 3: Swelling and binary parameters for NELF model prediction of solubility isotherms.

	$k_{1,2}$	$K_{SW} (\text{MPa}^{-1})$
PTMSN/ <i>n</i> -C ₄	-0.05	0.37
PTMSN/ <i>n</i> -C ₅	-0.05	3.70
PTMSN/ <i>n</i> -C ₆	-0.05	5.40

5. CONCLUSIONS

The mass transport properties of three alkane vapors in a new, substituted high free volume poly-norbornene (PTMSN) have been studied in detail. The material belongs to the family of super-glassy polymers, that are characterized by a high T_g , which cannot be reached experimentally, and a high free volume, due to the presence of bulky and stiff groups that confer rigidity to the molecular chains.

It was demonstrated that PTMSN also shows vapor transport properties that are typical of ultra high free volume polymers, such as an extremely high level of organic vapor sorption and significantly high diffusivity, which makes it interesting for gas/vapor membrane separation and VOC's removal.

The experimental evidences were successfully compared with the NELF model calculations, giving more than satisfactory results. This modelling task requires, as starting point, the Lattice Fluid parameters evaluation for PTMSN: they were calculated from a collection of infinite dilution solubility data available for different organic and inorganic compounds, because the volumetric properties of polymer above T_g are not accessible. The successful modelling of sorption data offers a reliable predictive tool as alternative to direct sorption measurement in PTMSN, for which experimental task is extremely time-consuming.

6. REFERENCES

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