

## Organic vapours sorption, diffusion and swelling in Poly (trimethyl silyl norbornene)

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Poly(trimethyl silyl norbornene) (PTMSN) obtained via addition is an high free volume glassy polymer whose vapor sorption properties are very similar to those of poly(trimethyl silyl propyne) (PTMSP): both materials can be exploited in several membrane-based separation processes. Sorption, diffusion and swelling experiments were performed on PTMSN, using three different n-alkane vapors (*n*-C<sub>4</sub>, *n*-C<sub>5</sub>, *n*-C<sub>6</sub>). The solubility data were successfully compared with the *Nonequilibrium Lattice Fluid Model* previsions, whose characteristic parameter were determined from a collection of infinite dilution solubility data.

### 1. Theoretical

Glassy polymers are elected materials for membrane-based separation processes, because they show good mechanical properties and good selectivity. The membrane selectivity versus a target component *i* in the mixture *i+j* is given by the ratio between the permeabilities of *i* and *j*, according to the following equation:

$$\alpha_i = \frac{P_i}{P_j} = \frac{D_i S_i}{D_j S_j} = \alpha_D \alpha_S \quad (1)$$

The selectivity can be decomposed into two terms,  $\alpha_D$  and  $\alpha_S$ , called also *diffusivity selectivity* and *solubility selectivity*. While for many polymers the diffusivity selectivity is the dominating term, some high free volume glassy polymers show the opposite behavior: for these materials the diffusivity selectivity is close to unity, because the high free volume fractions do not exert any separation effect based on molecular size, then the dominating contribution is given by  $\alpha_S$ . This means that these materials are selective towards the more soluble and condensable compounds (Merkel et al., 2003) and substituted polyacetylenes, such as PTMSN are attractive materials in this regard.

## 2. Materials

The material studied is an addition-type PTMSN, whose monomer is obtained by Diels-Alder reaction between dicyclopentadiene and vinyl trimethylsilyl. The polymerization can occur by ring opening, leading to cyclolinear structures or, as in the case of the material inspected here, by double bond opening (Figure 1a): in this way, because of the absence of unsaturated bonds, one obtains more stable structures (Figure 1b); the addition of trimethylsilyl side group leads to high free volume fractions and high gas permeability values. The polymer has a density of  $0.883 \text{ g/cm}^3$  and a glass transition temperature higher than  $340^\circ\text{C}$ : more precise estimates are not available, because the material decomposes before reaching  $T_g$  (Yampolskii et al., 2006). The films were kindly provided by Dr. Yampolskii of the *TIPS* institute of Moscow; they were cast from a solution of toluene (2% wt) and have an average thickness of  $175 \mu\text{m}$ .

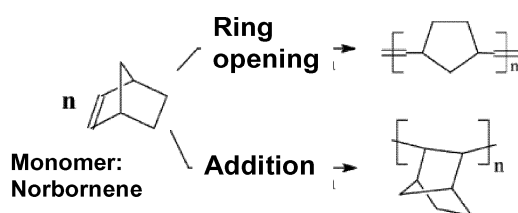


Fig. 1a: scheme of the different polymerization pathways of poly(norbornene).

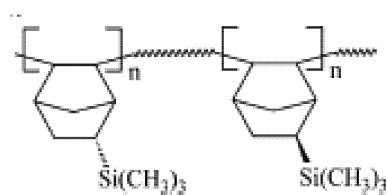


Fig. 1b: chemical structure of addition-type PTMSN.

## 3. Experimental

### 3.1 Sorption and diffusion measurement

Sorption and diffusion experiments were performed at  $35^\circ\text{C}$  using a constant volume/variable pressure apparatus. Initially the polymeric film was placed in the sample chamber and exposed to the vacuum overnight to remove the air gases absorbed. Successively, the desired amount of vapor was introduced into the chamber and allowed

to equilibrate: once the pressure was constant, additional vapor was introduced and again allowed to equilibrate. A capacitance manometer (*f.s.* 1000 mbar, accuracy 0.1 mbar) monitors the pressure decay into the chamber which is directly related to the total mass absorbed by the polymer.

### 3.2 Swelling measurement

The dilation of the polymer during the sorption was measured through a dedicated apparatus, by monitoring the sample elongation in one direction with a CCD digital camera. Because it is reasonable to assume that the swelling is isotropic, as it is common in amorphous polymers, the volume dilation can be calculated by considering the elongation in one only direction ( $x$ ), according to the following relationship:

$$\frac{\Delta V}{V_0} = \frac{\Delta x}{x_0} + \frac{\Delta y}{y_0} + \frac{\Delta z}{z_0} \approx 3 \frac{\Delta x}{x_0} \quad (2)$$

## 4. Results and Discussion

### 4.1 Sorption and diffusion data

During sorption experiments two subsequent transport stages were observed: a purely diffusive one and a relaxational stage is observed for all the penetrants. In the case of n-hexane, the latter gives the most important contribution to the total solubility. Moreover, the diffusion kinetics deviates from the Fick's law, especially during the first sorption steps. We will not perform a specific analysis of the kinetics in this work, but rather discuss the solubility values at the end of the diffusive and relaxational stages of sorption.

The infinite dilution solubility coefficients are plotted in Fig. 2a, as function of the square critical temperature and compared with those obtained through *Inverse Gas Chromatography* by Starannikova et al.: the two sets of data, made using different techniques, are in good agreement. Figure 2b reports the solubility of  $n$ -C<sub>4</sub>,  $n$ -C<sub>5</sub> and  $n$ -C<sub>6</sub> at 35°C: the isotherms are concave to the activity axis, as it is typical of the glassy polymers. The molar solubility data do not seem follow the order of the penetrant size, the higher values being for n-pentane, then n-butane and finally n-hexane.

In figure 3a the diffusivity isotherms are reported as function of average concentration: it can be noticed that the isotherms follows the penetrant molar mass, the diffusivity attaining its maximum value for  $n$ -C<sub>4</sub> and its minimum value for  $n$ -C<sub>6</sub>. On the other hand, the latter penetrant causes a strong plasticization effect on the polymer, based on which the diffusivity rapidly increases, especially during the initial steps, and then reaches a plateau.

The permeability has been estimated as the product of solubility and diffusivity coefficients: as noticed by Starannikova et al. (2008), the permeability changes with pressure, even if, in the limit of very low pressures, the differences between the three penetrants are rather small (fig. 3b).

The solubility isotherms for  $n$ -C<sub>4</sub>,  $n$ -C<sub>5</sub> and  $n$ -C<sub>6</sub> were then compared with the *Nonequilibrium Lattice Fluid Model* predictions. This thermodynamic model, based on the *Lattice Fluid Theory*, extends to the nonequilibrium domain of the glassy polymers

the equation of state of *Sanchez-Lacombe*, introducing the density of the glassy matrix as internal variable of state (Sarti and Doghieri, 1996). The *NELF* model needs three characteristic parameters ( $T^*$ ,  $p^*$  and  $\rho^*$ ) for the external gas phase and for the polymer, to calculate in a completely predictive way the solubility isotherm of a gas into the polymer. While for  $n\text{-C}_4$ ,  $n\text{-C}_5$  and  $n\text{-C}_6$  these parameters are available in the open literature, for PTMSN they need to be calculated: to do this,  $pVT$  data above  $T_g$  have to be known, but as mentioned in a precedent section, PTMSN decomposes before reaching its  $T_g$ . For this reason, the lattice fluid parameter estimation for the polymer can be done fitting the infinite dilution solubility data with the *Sanchez-Lacombe* equation of state. From this calculation, one obtains that  $T^* = 406.0\text{ K}$ ,  $p^* = 359.8\text{ MPa}$  and  $\rho^* = 1.345\text{ Kg/L}$ .

The comparison between experimental isotherms and *NELF* model predictions are more than satisfactory, as showed in figure 4. Furthermore, the model enables us to predict *a priori* the swelling coefficients for all the penetrant, as we will see in the next section.

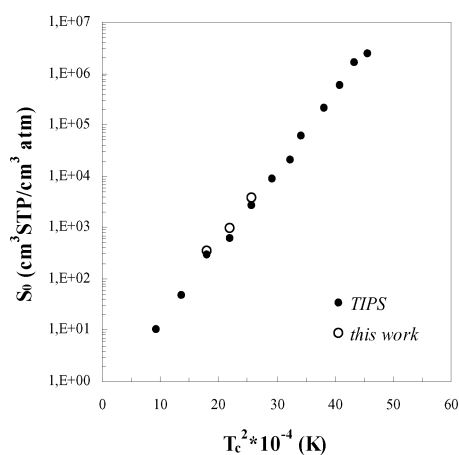


Fig. 2a: infinite dilution solubility coefficients at  $35^\circ\text{C}$  collected via IGC (closed symbols) [Starannikova et al., 2008] and via Pressure Decay (open symbols).

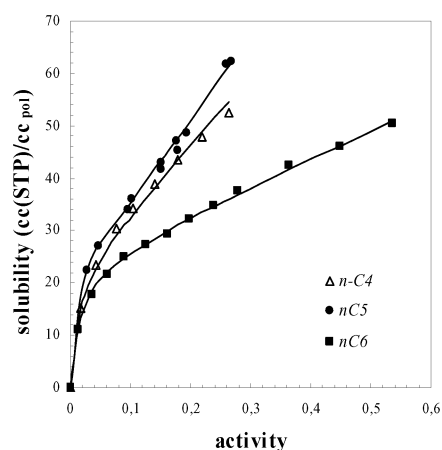


Fig. 2b: solubility of  $n$ -alkanes in PTMSN at  $35^\circ\text{C}$ .

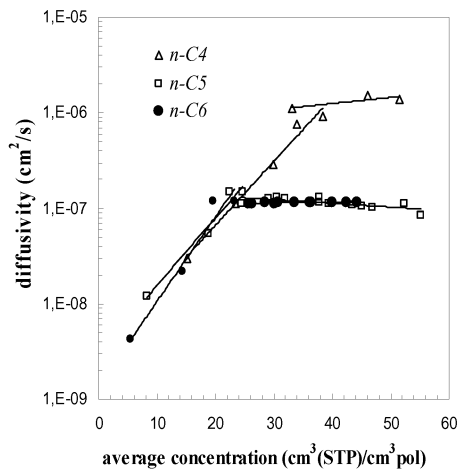


Fig. 3a: diffusivity of *n*-alkanes in PTMSN at 35°C.

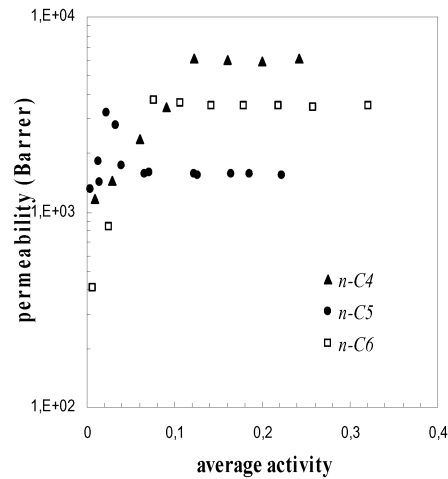


Fig.3b: permeability of *n*-alkanes in PTMSN at 35°C as function of average activity.

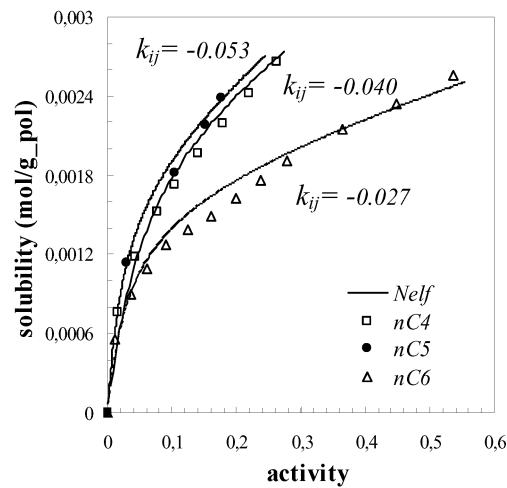


Fig. 4: experimental solubility isotherms of *n*-alkanes in PTMSN and NELF calculations.

#### 4.2 Swelling

During volume dilation experiments, whose results are not reported here for the sake of brevity, a nonlinear behavior is observed, consistently with the glassy nature of the polymer: initially, all the penetrant is absorbed into the matrix without inducing swelling, successively the polymer swells linearly, like a rubber, reaching then a saturation stage. The resulting partial molar volume of penetrant follows a non monotonous trend and shows a maximum, as observed also in other superglassy

polymers (De Angelis et al., 2002). Furthermore, the experimental swelling coefficients agree very well with those predict by *NELF* calculations, as shown in table 1.

Table 1. Swelling coefficients of *n*-C<sub>5</sub> and *n*-C<sub>6</sub> in PTMSN at 35°C.

	$k^{sw,exp.}$ (MPa <sup>-1</sup> )	$k^{sw,Nelf}$ (MPa <sup>-1</sup> )
<i>n</i> -C <sub>5</sub>	3.40	3.50
<i>n</i> -C <sub>6</sub>	5.32	5.00

## 5. Conclusions

Sorption and dilation experiments were performed in PTMSN, whose behavior is typical of the superglassy polymers. The sorption level for *n*-alkanes is very high, like in PTMSP, because of the high free volume fractions trapped into the polymeric matrix. The permeability changes with the pressure and as a consequence difference selectivity behaviors are observed in different pressure ranges. The experimental solubility isotherms have been successfully modeled with the *NELF* model, whose characteristic parameters for the polymer phase can be retrieved from a collection of infinite dilution solubility data.

The swelling behavior of PTMSN can be justified through the superglassy state of the matrix and the order of magnitude is well caught by the *NELF* model.

## References

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