

## Study of gas transport in high free volume polymers

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### ABSTRAKT

Currently, the high free volume polymers constitute promising polymeric materials for efficient gas and vapour membrane separations (MS). The enormous progress achieved in this field during the last two decades is manifested in numerous applications of MS such as i) air separation, ii) carbon dioxide recovery from landfill gas, biogas and flue gas, iii) hydrogen recovery iv) gas/vapour separations, v) vapour/vapour separations etc.

The Master thesis aims to provide wide explanation of gas sorption in flat sheet membranes prepared from the polymers of intrinsic microporosity (PIMs). PIMs represent newly developed class of high free volume materials known for their extraordinary high permeability and moderate selectivity. Such properties are tightly connected with sorption capacity and enhanced penetrant diffusivity inside the PIM matrix. Generally, mass transport in dense membranes is described by the solution-diffusion model as  $P=D \cdot S$ . However, one of the transport parameters – sorption coefficient  $S$  – was mostly calculated indirectly as a ratio of permeability and diffusion coefficients of gas penetrants ( $P/D$ ) from permeation measurements or from molecular simulations, respectively. Therefore, the direct gravimetric sorption technique was used for precise and direct evaluation of sorption capacity. Sorption of five permanent gases ( $O_2$ ,  $N_2$ ,  $CH_4$ ,  $CO_2$  and Ar) in a set of six different PIMs was studied in order to reveal more information about transport phenomena in these polymers.

The obtained results revealed the influence of both the functional groups and the structural motives on sorption behaviour in these polymers (Fig. 1 a)). Furthermore, the influence of alcohol treatment methods (sample soaking in methanol or ethanol) and the effect of embedded nanofillers on material properties were determined. Finally, the long-term sorption experiments were performed (2 years) in order to describe aging phenomenon in PIM-1 – gradual collapse of high free volume elements in PIM-1 matrix – which lead to known decrease of permeability. According to results of this work, such permeability decline can be attributed solely to decreasing of penetrant diffusivity because penetrant solubility (sorption) remained almost constant in time. (Fig. 1 b).

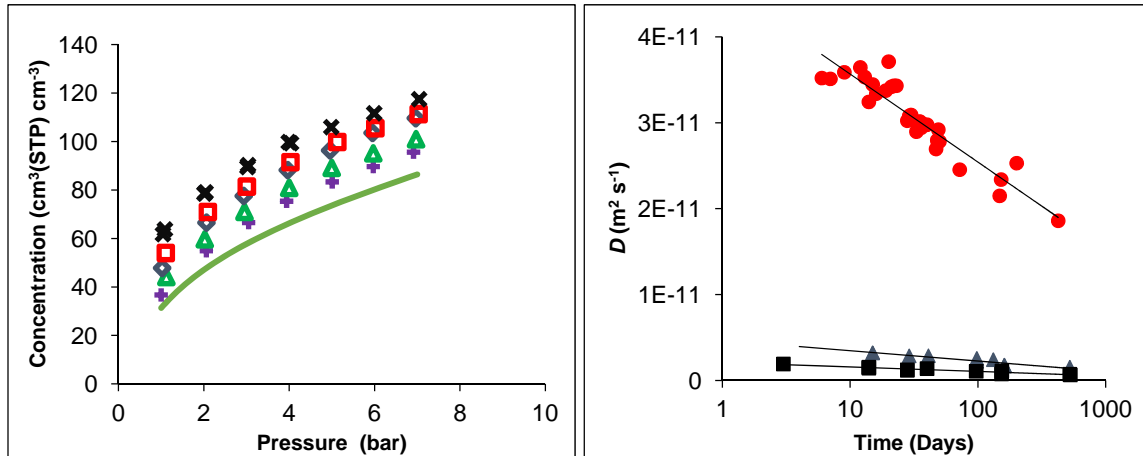


Figure 1: a)  $\text{CO}_2$  sorption isotherms in PIMs. (—  $\text{PIM-1}$ ,  $\blacktriangle$   $\text{PIM-PI-SBI}$ ,  $\blacktriangle$   $\text{PIM-PI-EA}$ ,  $\blacklozenge$   $\text{PIM-EA-TB}$ ,  $\square$   $\text{PIM-TRIPTYCENE}$ ,  $\blacktimes$   $\text{AMINE-PIM-1}$ ); b) Time dependence of diffusion coefficients for  $\text{CO}_2$  in ethanol treated  $\text{PIM-1}$  samples ( $\bullet$  sample 11,  $\blacktriangle$  sample 10 and  $\blacksquare$  sample 8).

Obtained results have been already published in 6 papers in prestigious peer-reviewed journals and 2 other papers are in preparation now. Furthermore, presented results also illustrate a huge progress in development of new polymer materials for more efficient gas and vapour separations.