# Supplementary information

## Peculiarity of a $CO_2$-philic block copolymer confined in thin films with constrained thickness: "A super membrane for $CO_2$-capture"

Yave et al.

***Scanning electron microscopy (SEM) and Spectroscopy ellipsometry analyses:***

Several samples were used to estimate the thickness of thin films by SEM, but to validate them, three samples were analyzed by a spectroscopic ellipsometer (UVISEL) based on photoelastic modulation: Spectral range: 245 – 2100nm, Spot-size: 1mm x 3mm and Angle of incidence: 70°. Measured parameters: Is = sin(2Psi) * sin(Delta) and Ic = sin(2Psi) * cos(Delta). Details of samples are below in the Table 1S and the thicknesses are compared with those obtained by SEM.

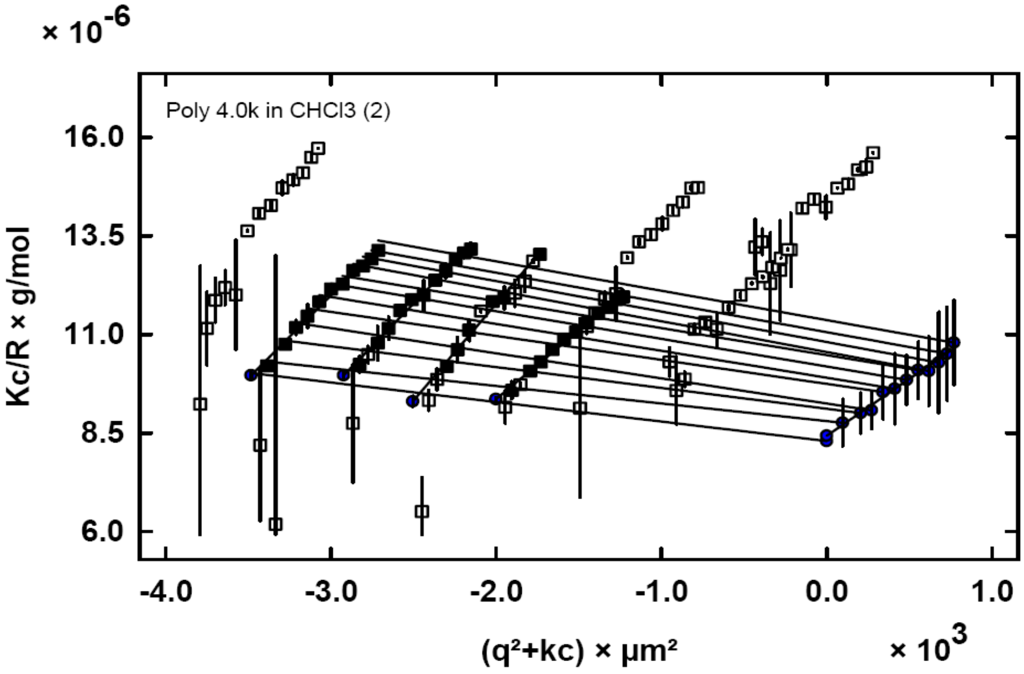
**Table 1S.** Detail of samples and thicknesses obtained by ellipsometry and SEM

| **Sample** | **Composition of thin film** | **PDMS (substrate)** [nm] | **Thickness of thin film** [nm] | **Thickness of thin film (SEM)** [nm] |
|---|---|---|---|---|
| 1 | PDMS+Poly4.0K0.5 | 92 | 151 | 150 ± 10 |
| 2 | PDMS+Poly4.0k0.16 | 105 | 62 | 45 ± 5 |
| 3 | PDMS | 72 | - | 90 ± 20 |

The samples 1 and 2 of Poly4.0k are thin film prepared from 0.5 and 0.16 wt.% of polymer concentration. The sample 3 is a PDMS substrate. Additional to that measured by ellipsometry, PDMS substrates with different thickness were fabricated and analyzed by SEM (PDMS substrates with different thicknesses were prepared during optimization).

***Light scattering measurements:***

The <$R_g$> value is obtained from the best fit. The refractive index increment was determined on a Brookhaven differential refractometer (Brookhaven Instruments Corporation, New York, USA). The static light scattering measurements is performed by using an ALV CGS-3 goniometer (ALV-Laser Vertriebsgesellschaft.m.b.H. Langen, Germany) equipped with a 22mW He-Ne Laser ($\lambda_o$=632.8nm, vertically polarized; Model 1145 P, JDS Uniphase Corporation Santa Rosa, CA, USA).



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Mw(c): 1.206e+05 g/mol               Mw(q²): 1.186e+05 g/mol
A2: 1.167e-07 mol dm³/g²             Rg: 3.202e+01 nm
\\RZBM0047\data\2009\PME, WTE\Wilfredo\090603\sta\Poly4,0k_CHCl3_2.sta
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Poly 4.0k in CHCl3 (2)
Static Light Scattering, results of Zimm-Plot, q²-dep.: 1,  c-dep.: 1

File                 Conc/(g/dm³)    Mw(app)/(g/mol)   <S²>(app)/µm²    Rg(app)/nm
Conc.=0                0.0000          1.186e5           1.025e-3         32.016
Poly4,0k_CHCl3_        4.2463          1.069e5           1.115e-3         33.393
Poly4,0k_CHCl3_        5.3147          1.075e5           1.584e-3         39.805
Poly4,0k_CHCl3_        6.2013          1.004e5           1.298e-3         36.021
Poly4,0k_CHCl3_        7.3899          1.004e5           1.265e-3         35.569

Mw(c): 1.206e+05 g/mol (± 7.27 %)   Mw(q²): 1.186e+05 g/mol (± 0.88 %)
A2: 1.167e-07 mol dm³/g² (± 43.8 %)    Rg: 3.202e+01 nm (± 2.55 %)
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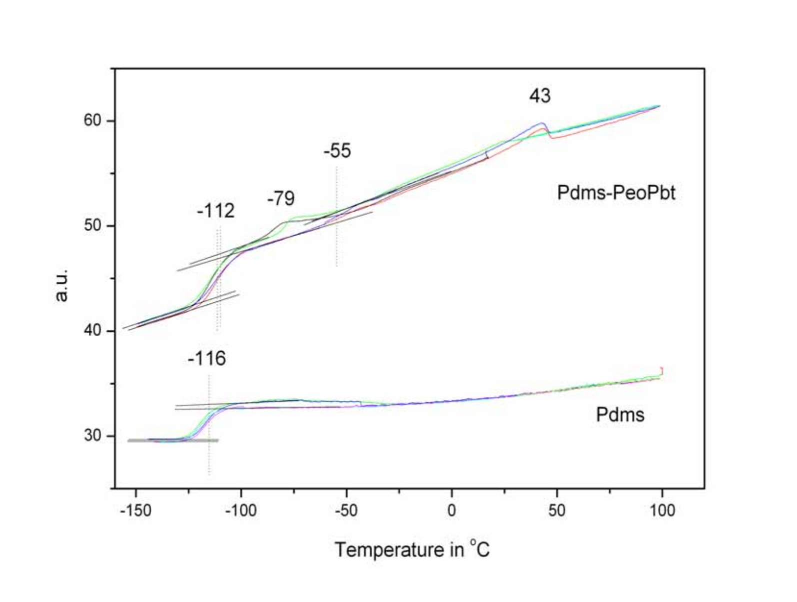
**Figure 1S.** Light scattering measurements for Poly4.0K sample in Chloroform.

***Separation performance of thin films:***

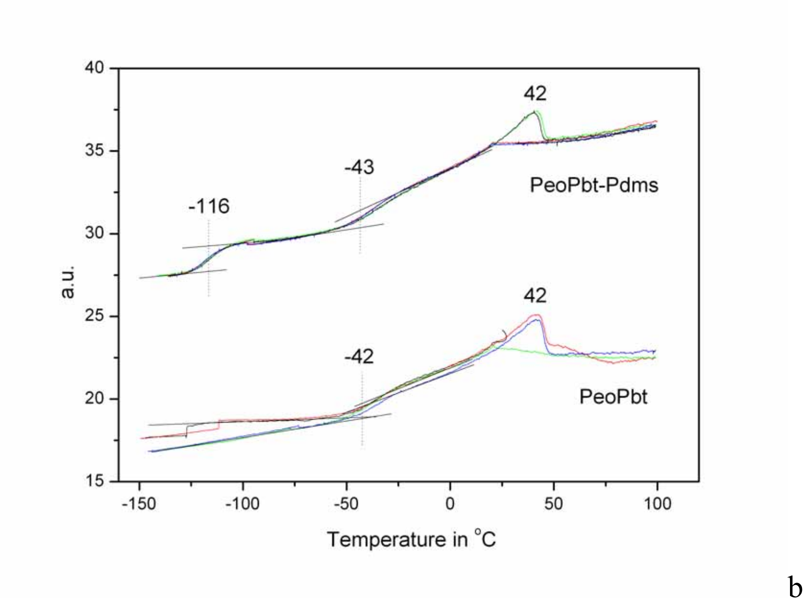
**Table 2S.** Experimental thin film (Poly4.0k) thicknesses, $CO_2$ flux and $CO_2$ selectivity over $H_2$, $CH_4$ and $N_2$

| **Experimental Thickness** [nm] | **$CO_2$** [$m^3$ (STP) $m^{-2}$ $h^{-1}$ $bar^{-1}$] | **$CO_2/H_2$** | **$CO_2/CH_4$** | **$CO_2/N_2$** |
|---|---|---|---|---|
| 160 | 0.8 | 10 | 21 | 79 |
| 115 | 3.6 | 10 | 14 | 58 |
| 85 | 4.3 | 9 | 14 | 50 |
| 50 | 4.9 | 9 | 14 | 60 |
| - | 5.7 | 8 | 9 | 33 |

***Nanocalorimetric analysis:***



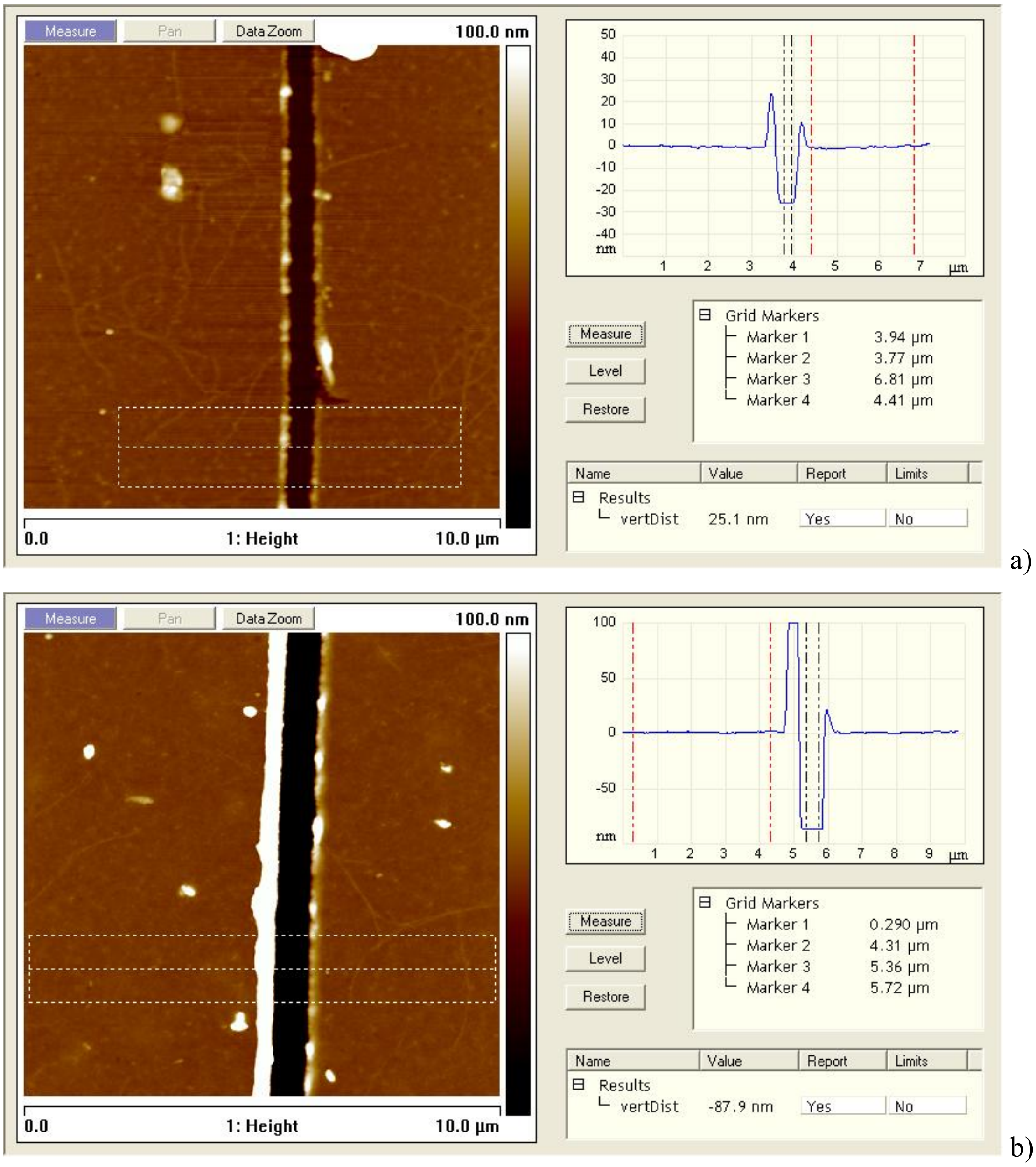
a)



b)

**Figure 2S.** Thermograms corresponding to different samples obtained by nanocalorimeter; **a)** PDMS single thin film and double layer thin film “PEO-PBT on PDMS”; as can be seen, when the Pdms is first coated and then the PeoPbt film, the crstallinity decrease is evident, hence it support again our hypothesis that the PDMS substrate hinders the PEO crystallization, and **b)** PEO-PBT single and double layer thin film with thicker thicknesses (thin films prepared by coating twice, hence the thickness should be around or more than 100 nm); the PEO $T_g$ is similar to that in thick film.

***Atomic force microscopy (AFM) analysis:***



a)

Grid Markers
- Marker 1 3.94 µm
- Marker 2 3.77 µm
- Marker 3 6.81 µm
- Marker 4 4.41 µm

| Name | Value | Report | Limits |
|---|---|---|---|
| Results | | | |
| vertDist | 25.1 nm | Yes | No |

b)

Grid Markers
- Marker 1 0.290 µm
- Marker 2 4.31 µm
- Marker 3 5.36 µm
- Marker 4 5.72 µm

| Name | Value | Report | Limits |
|---|---|---|---|
| Results | | | |
| vertDist | -87.9 nm | Yes | No |

**Figure 3S.** Atomic force microscopy (AFM) images (Height) showing the scratches to estimate the thickness of polymer thin films obtained by spin-coating; **a)** Poly4.0k thin film (on silicon-wafer) prepared from 0.2 wt.% of polymer in Chloroform (~25nm), and **b)** Poly4.0k thin film prepared on PDMS (PDMS layer on silicon-wafer), the thickness which is ~90nm corresponds to the thin film plus PDMS.

### *A roughly economical and technical analysis on $CO_2$ capture by membranes:*

The development of polymeric membranes has gained a lot of importance due to the energy-efficiency of membrane processes, and the $CO_2$ separation is a potentially large application, especially for carbon capture from coal-fired power plants, for $CO_2$ separation from natural gas and for synthesis gas adjustment. However, current membranes can not compete with the traditional absorption process yet, because the permeance or flux of $CO_2$ is not high enough.

State-of-the-art membranes exhibit a $CO_2$ permeance of about 0.3 $m^3$ (STP) $m^{-2}$ $h^{-1}$ $bar^{-1}$. Membrane Technology and Research (MTR), Inc presented recently the Polaris™ Membrane (Merk et al. Journal Membrane Science 359, 2010, 126), which has similar performance to that of the RITE institute (Japan) (Kasama et al. Greenhouse Gas Control Technology 7, 2005, 75). The $CO_2$ permeance of these membranes is around 2.7 $m^3$ (STP) $m^{-2}$ $h^{-1}$ $bar^{-1}$. GKSS also developed a $CO_2$-philic membrane with similar performance, which was obtained by blending the multi block copolymer (Polyactive) with polyethylene glycol dibutyl ether (Yave et al. Macromolecules 43, 2010, 326). These membranes with a $CO_2$ permeance of ~1000 GPU ($1GPU=10^{-6}cm^3\ cm^{-2}cmHg^{-1}s^{-1}$) has been studied by Merkel et al. and they concluded that by an appropriate design of separation process, the cost of $CO_2$ capture could be ~32 $/ton of $CO_2$ captured (Figure 4Sa). This analysis shown that membrane process can compete or even replace the absorption process (cost of $CO_2$ capture by absorption process is between 50 and 80 $/ton of $CO_2$ captured, Ramezan et al. "Carbon dioxide capture from existing coal-fired power plant" U.S. Department of Energy, ref 38 in the paper).

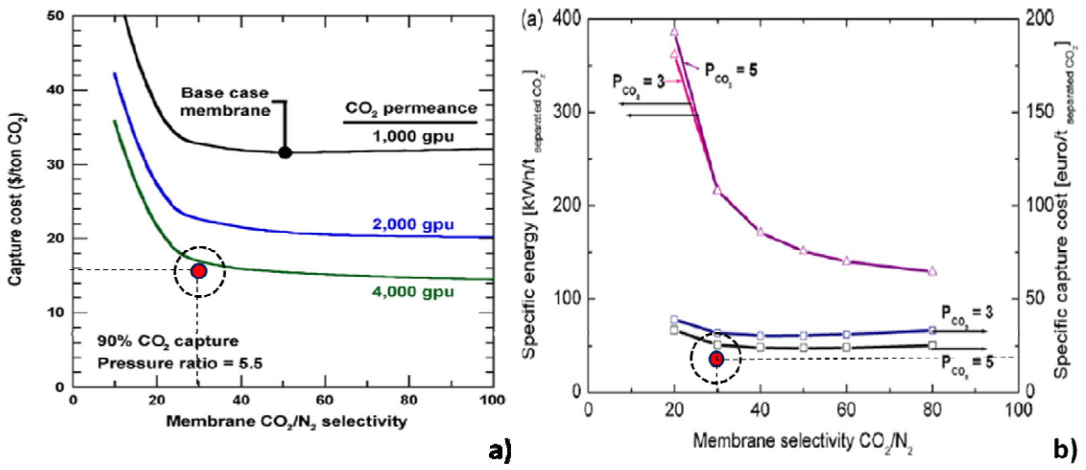


**Figure 4S.** a) $CO_2$ capture cost as a function of membrane selectivity and flux reported by Merk et al. Journal Membrane Science 359, 2010, 126, and b) Specific energy and $CO_2$ capture cost as a function of membrane selectivity and flux reported by Zhao et al. Journal Membrane Science 359, 2010, 160. The highlighted dot (red) corresponds to the Poly4.0k thin film membrane developed in this work (described below).

Partners of MemBrain project (a project of HGF-Alliance, "Gas Separation Membranes for Zero-Emission Fossil Power Plants") also carried out a technical and economical analysis of $CO_2$ capture (Figure 4Sb, Zhao et al. Journal Membrane Science 359, 2010, 160). The conclusions were similar to those reported by Merkel et al. However, the cost analyses gave lower than 30 Euro/t of $CO_2$ captured. They used the Poly1.5k and Poly4.0k thin film membrane developed in this work ($CO_2$ flux of 3.0 and 5.0 $m^3$ (STP) $m^{-2}$ $h^{-1}$ $bar^{-1}$) for the analysis, and the process design was a little different to that reported by Merkel et al.

Based on these analyses, the membranes presented here could even present lower $CO_2$ capture costs if we could consider that the membranes will work at 60°C and under wet condition (typical exhaust gas in power plants). We have measured the $CO_2$ permeability at 30 and 60°C and under wet conditions, and we found that they are higher than those in dry conditions. The $CO_2$ permeability was 164 barrer at 30°C and 250 barrer at 60°C, and the $CO_2/N_2$ selectivity was 60 and 30, respectively. The $CO_2$ permeance at 60¨C therefore can be calculated by using equation 1, as described in the paper. For the best membrane, i.e. for that with 50 nm of thickness (Table 2S) the calculated $CO_2$ permeance at 60°C is 13.5 $m^3\ m^{-2}\ h^{-1}\ bar^{-1}$ (more than 4000 GPU), and if the $CO_2/N_2$ selectivity is the same ~30, the $CO_2$ capture cost would be less than 20 $/ton if we could use the same process design proposed by Merkel et al. or by Zhao et al. This conclusion is done by simple inclusion of our calculated data on the graphs presented by them (highlighted data in Figure 4Sa and 4Sb). It is important to note that the data is roughly added to the figures.

Samples of this membrane have been exposed under real condition of flue gas from power plants, i.e. ~60°C and wet condition (before smokestack). After 42 days, the membrane has survived and the performance was not damaged too much. Although the selective thin film was covered by ash and fine particles, after and carefully cleaning the $CO_2$ permeance only decreased by ~20% and the selectivity by ~10%. This was a good indication on thermal and mechanical stability of the membrane. Currently, this membrane is being developed by GMT (Germany) on large scale for testing in a real-world; the issue now is to find a protective layer that does not damage the selective thin film.