

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/228058603>

Peculiarity of a CO₂-philic block copolymer confined in thin films with constrained thickness: "A super membrane for CO₂-capture"

ARTICLE *in* ENERGY & ENVIRONMENTAL SCIENCE · OCTOBER 2011

Impact Factor: 20.52 · DOI: 10.1039/C1EE02139G

CITATIONS

10

READS

41

4 AUTHORS:



Wilfredo Yave

Sulzer

30 PUBLICATIONS 849 CITATIONS

SEE PROFILE



Heiko Huth

University of Rostock

58 PUBLICATIONS 1,438 CITATIONS

SEE PROFILE



Anja Car

Universitätsspital Basel

11 PUBLICATIONS 766 CITATIONS

SEE PROFILE



Christoph Schick

University of Rostock

418 PUBLICATIONS 6,684 CITATIONS

SEE PROFILE

Cite this: DOI: 10.1039/c1ee02139g

www.rsc.org/ees
PAPER

Peculiarity of a CO₂-philic block copolymer confined in thin films with constrained thickness: “a super membrane for CO₂-capture”†

 Wilfredo Yave,^{‡, *a} Heiko Huth,^b Anja Car^a and Christoph Schick^b

Received 14th July 2011, Accepted 30th August 2011

DOI: 10.1039/c1ee02139g

CO₂-philic block copolymer thin films with constrained thickness, comparable to the polymer radius of gyration (R_g), were examined due to their strange behaviour. The experimental CO₂ permeances for example are almost two-fold higher than those theoretically calculated by the relation between permeance, thickness and permeability. We suggest that the reduction of film thickness towards R_g and the re-organization of the block-copolymer (by using an appropriate substrate) in a constrained nanospace result in a super permeable membrane. This finding may have great implications for the design of smart materials, especially for applications as selective membranes for CO₂-capture.

1. Introduction

Several studies already showed that polymeric ultrathin films confined between a substrate and air or between two layers behave in a different way compared to the bulk material.^{1–6} The peculiarity of such films generally appeared when the thickness became comparable to the polymer radius of gyration (R_g). In

that regime, the polymer chain is larger than the thickness, it is influenced by the substrate and it is confined within a nanospace; consequently the macromolecular conformation, dynamics and crystallization processes of the polymer are altered. For instance, the confinement of polystyrene and other polymers into thinner polymer films were extensively studied.^{7–12}

The polymer confinement resulted in lower and higher glass transition temperature (T_g) than that observed in bulk polymer, those deviations have been attributed to the confinement effects, substrate nature and measurement techniques. In rubbery polymers like polydimethylsiloxane (PDMS), the glassy dynamics was also affected due to confinement below 5 nm.¹⁰ Other properties such as mechanical,¹³ thermal¹⁴ and barrier⁵ properties of polymer ultrathin films were also studied and they were unexpectedly influenced by the polymer confinement.

Since the 1980s there has been an increasing interest in application and basic understanding of polymer thin films, and since that time, the studies have been mainly devoted to lithography (for integrated circuits),^{15–17} control of alignment (polymers and

^aInstitute of Materials Research, Helmholtz-Zentrum Geesthacht, Centre for Materials and Coastal Research, Max-Planck Strasse 1, 21502 Geesthacht, Germany

^bInstitute of Physics, University of Rostock, Wismarsche Str. 43-45, 18057 Rostock, Germany

† Electronic supplementary information (ESI) available: (1) Comparison of thickness values determined by SEM and ellipsometry, (2) light scattering results, (3) separation performance, (4) additional thermograms obtained by nano-calorimetry, and (5) a roughly economical and technical analysis about CO₂ capture. See DOI: 10.1039/c1ee02139g

‡ Current address: Application & Process Technology, Sulzer ChemTech AG, Gewerbestrasse 28, 4123 Allschwil, Switzerland. Tel: +41 614863702; Fax: +41 614863777. E-mail: wilfredo.yave@sulzer.com.

Broader context

In the near future, nanoscience and nanotechnology will help to reduce the carbon dioxide emissions, so the problem of global warming will be solved. To reach this milestone however we need to understand the material behaviour and processes at the nanoscale level, thereby superior materials with unexpected properties might be nanofabricated. In the past three decades, “membranologists” investigated different membrane materials (*i.e.* organic, organic–inorganic hybrids and inorganic) and developed several techniques to fabricate ultra-thin films. Nowadays, by combining the acquired knowledge on separation membranes and nanomaterial and nanotechnology, we are able to manipulate the molecules (by physical, chemical or biological means) and nanofabricate membranes with unusual properties. Towards attaining our goals, we manipulated a simple macromolecule (CO₂-philic multi-block copolymer) by reducing the thickness of the membrane to be as thin as possible (<50 nm), thus the macromolecular conformation and the crystallization process were perturbed by nanoconfinement (new insights). The feature of the developed membrane is exceptional in terms of permeance and selectivity, and thus, this membrane might lower the CO₂ capture costs (<20 \$ per ton of captured CO₂).

liquid crystals),^{18,19} membranes,^{20–22} packing⁵ and self-assembly of block copolymers.^{16,23} Although there are well-established technologies for thin film fabrication, there are still challenges to solve scientific and technical problems, such as controlling the self-assembly and thickness, avoiding defects and tailoring the final properties.

In membrane science and technology, the development of thin films with outstanding properties as CO₂-selective membranes is a challenge. CO₂-philic thin membranes would help to solve important technological and environmental problems related to global warming.^{24,25} Although commercial synthetic membranes for CO₂ separation already exist, the low gas fluxes make them unsuitable for CO₂ capture applications.²⁶ The use of ultrathin membranes therefore is crucial for obtaining extremely high gas fluxes.

By a simple analysis of eqn (1), one can see that for obtaining high gas permeances, the gas permeability (material property) must be maximized and the thickness of the film minimized, so having a membrane with these features, the CO₂ separation and the capture process would become technically and economically competitive.²⁴

$$J\Delta p^{-1} = Pl^{-1} \quad (1)$$

where J and P are the flux and permeability of the gas, l the thickness of the thin film and ΔP the trans-membrane pressure difference.²⁰

Decreasing the film thickness to be as thin as possible, the gas flux could be greatly increased ($J \approx l^{-1}$), but because of thickness reduction to a few nanometers, defective films due to the appearance of defects or pin-holes are obtained. The defects result from the liquid thin film rupture during membrane formation, which is known as the dewetting process. The dewetting is an unwanted process during membrane fabrication, but it can be well controlled by the molecular weight of the used polymer and by the nature of the substrate.^{27,28}

In this work, we examined a CO₂-philic and tailor-made multi-block copolymer with a controlled structure and molecular weight, the copolymer is a poly(butylene terephthalate)-*b*-poly(ethylene oxide) (PBT-*b*-PEO). Recently, we reported the manufacture of nanometric thin films as membranes for CO₂-capture from this copolymer,^{29,30} some of those membranes were defect-free and presented extremely high gas separation performance. However, due to the film thickness reduction we noted that the organization of copolymer chains in such films may differ from thick films, and thus, we did not discard that the properties of those thin film membranes are thickness dependent. Now, we extend the work here to understand the peculiarity and confinement of the copolymer into thin films with thicknesses less than 50 nm. To the best of our knowledge this is the first work reporting the peculiarity (*i.e.* thickness-dependent gas permeation) of this kind of super permeable membranes for CO₂ capture.

2. Experimental

2.1. Materials and thin film fabrication

Two poly(butylene terephthalate)-*b*-poly(ethylene oxide) copolymers known as Polyactive from IsoTis OrthoBiologics (USA)

were used without further purification. The copolymers contain similar PEO and PBT content (77 wt% of PEO and 33 wt% of PBT), they have 1.5 and 4.0 kg mol⁻¹ of PEO segment, and we called these Poly1.5k and Poly4.0k, respectively. The main properties of these copolymers can be found elsewhere.³¹ Tetrahydrofuran (for Poly1.5k), and chloroform and 1,4 dioxane (60/40 wt/wt) for Poly4.0k were used as solvents to prepare the polymer solutions.

Polymer solutions from 1 wt% up to 0.15 wt% were prepared at room temperature by stirring for at least 12 h. The resulting solutions were filtered through a steel filter with pore size 32 μm (F. Carl Schröter) before dip-coating (membrane fabrication). As support or substrate, a PAN microporous membrane coated with a PDMS nanolayer (thickness < 300 nm) was used. After the dip-coating, the membranes were dried at ambient conditions or under an air flow at ~100 °C (depending on used solvent).

For the nanocalorimetry analyses, the thin films were prepared on gas nano-calorimeter sensors (XEN-39390 from Xensor Integration), on which the thin films from both PDMS and Poly4.0k were deposited by spin coating (chloroform was used as solvent).

2.2. Characterization

The thickness of the thin membranes was estimated by scanning electron microscopy (SEM), *i.e.* by subtraction of the PDMS nanolayer (see ESI†). The SEM analyses were carried out with a LEO 1550 VP Gemini (ZEISS). The thin film thicknesses were also determined by using a spectroscopic ellipsometer UVISSEL, based on photoelastic modulation. The thickness of thin films on the sensor for nanocalorimetry analysis was corroborated by atomic force microscopy (AFM), by using a Veeco Nanoscope IV Multimode AFM (Tapping-Mode) model MPP-12100, *i.e.* the thin films were prepared on silicon wafer and then scratched for the analysis.

The obtained thin films on the gas nano-calorimeter sensor were analyzed in an AC chip calorimeter in the temperature range from –150 °C to 100 °C at an underlying temperature ramp of 0.5 K min⁻¹ in nitrogen gas. The test frequency was 160 Hz for all measurements. An AC power of about 40 μW was applied to each chip sensor yielding temperature oscillations with an amplitude of about 0.2 K.¹¹

A constant volume/variable pressure test unit was used to measure the permeance of gases.^{29,30}

3. Results and discussion

Our assays were initially done on Poly1.5k; this copolymer produced promising membranes with high gas separation performance (pristine and blends).²⁹ The thin films were prepared on a polyacrylonitrile (PAN) microporous membrane and a PAN coated with a polydimethylsiloxane (PDMS) nanolayer, both fabricated at Helmholtz-Zentrum Geesthacht. When we only used PAN as substrate, the copolymer solution penetrated into the pores (expected) which resulted in thick films. By using PAN coated with a PDMS nanolayer, the penetration of the copolymer into the pores was hindered and the fabrication of very thin defect-free films was highly reproducible (Fig. 1a).

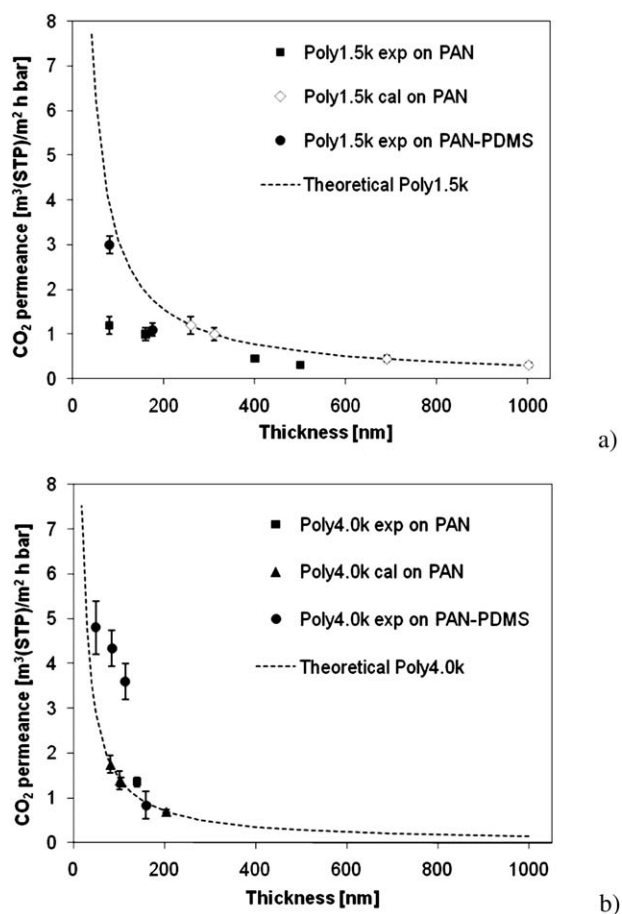


Fig. 1 CO₂ permeance measured at 30 °C vs. thickness of polymer thin films; (a) thin films fabricated from Poly1.5k on the PAN and PAN–PDMS support, and (b) thin film fabricated from tailor-made Poly4.0k. As seen, the experimental CO₂ permeance values for Poly4.0k thin films are two-fold higher than the calculated values (permeances calculated by using the eqn (1), the CO₂ permeability values to calculate the permeances are 115 and 53 barrer for Poly1.5k and Poly4.0k, respectively³¹).

Although the CO₂ permeances were extremely high, they equal the expected or were below the theoretical estimate.

Due to the low total molecular weight of Poly1.5k (40 kg mol^{−1}), the dewetting process occasionally led to defective films when copolymer solutions with lower concentrations were deposited on the PDMS nanolayer.³⁰ The dewetting is a process that occurs due to the lack of physical crosslinks or entanglements of copolymer chains within the solution, which further does not lead to the liquid thin film formation.^{28,32} Thinner films (<50 nm) therefore are difficult to prepare from this copolymer. To overcome this difficulty, we examined the tailor-made Poly4.0k designed by us and synthesized by IsoTis.³¹ Because of its high molecular weight (120 kg mol^{−1}), defect-free thin films thinner than 50 nm were fabricated, and we did not observe the dewetting process. The thicknesses of these thin films were determined by scanning electron microscopy (SEM) and corroborated by ellipsometry (ESI†); these two methods were in reasonable agreement.

For defect-free thin films (Poly4.0k), the experimental CO₂ permeances unexpectedly reached values of 3.6, 4.3 and 4.9 m³

(STP) m^{−2} h^{−1} bar^{−1} (Fig. 1b) and the CO₂/N₂ selectivity was >50 (the values are an average of at least 5 different samples measured at 30 °C). This value of selectivity is good for CO₂-capture applications; Merkel *et al.*²⁴ for example, reported that CO₂/N₂ selectivities between 20 and 40 are optimal to meet good separation and optimal membrane area. The experimental permeance values are almost two-fold higher than those calculated (theoretical values are 1.2, 1.7 and 2.9 m³ (STP) m^{−2} h^{−1} bar^{−1}, respectively) by eqn (1) that relates permeance, permeability and thickness. These results suggest that the thinner multi-block copolymer films with thicknesses <50 nm were found to be peculiar, *i.e.* with outstanding CO₂ separation properties.

Because the film thickness was constrained to a few nanometres, the macromolecular conformations, dynamics and crystallization of the Poly4.0k chains might have been perturbed (discussed later). Soles and Ding⁴ for instance suggested that the perturbation of polymer conformations and dynamics can be more evident when the molecular weight of polymer is increased and the thickness of a thin film is decreased toward R_g . For our tailor-made Poly4.0k, the $\langle R_g \rangle$ is ~32 nm experimentally estimated by light scattering (ESI†), so it would explain its peculiarity. The thinnest film fabricated in this work had a thickness below $2R_g$, which suggests that the chain conformation was truly perturbed and the mobility (dynamics) enhanced, thereby making the transport properties different to that of thick films. The extremely high CO₂ permeance can be therefore explained by the thin film peculiarity and by the nature of Poly4.0k (CO₂-philic). The nature of these copolymers was described in ref. 29 and 31, and details of CO₂ separation performance and thin film fabrication were recently reported.³⁰ However, the peculiarity of this copolymer under nano-confinement is reported for the first time in this work.

For understanding the thin film peculiarity, we studied the thermal properties of these ultrathin copolymer films by using a conventional differential scanning calorimeter (DSC) and a nanocalorimetry technique, namely AC chip calorimetry.^{11,33}

The glass transition temperature (T_g) of the PEO segment in Poly4.0k thin films was not detectable by conventional DSC, because the copolymer quantity was extremely small with respect to the PDMS and PAN. Although the T_g of the PEO segment was not detected, the glass transition region of PDMS became broader when a PDMS film was covered by a Poly4.0k thin film as a homogeneous nano-blend (in the interphase),³⁴ and thus, this suggested that the adhesion of the thin film on PDMS was good.

The nanocalorimetry technique however is unique and allows measurement of thin films with few nanometres of thickness, and the sensitivity is very high (good accuracy). We used a gas nanocalorimeter sensor on which the thin films from both PDMS and Poly4.0k were deposited by spin-coating. We prepared four different thin film systems, where the used copolymer solution had the same concentration as those used for thin film fabrication on the PAN–PDMS substrate (dip-coating). The PDMS was first coated on the sensor and cross-linked at 100 °C for at least 1 h (first system), and then a thin film from Poly4.0k was deposited on it (second system), so we simulated the thin film as in the membrane.

To see the interaction of the thin film with the sensor surface, we changed the thin film order, *i.e.* we first deposited the thin film from Poly4.0k on the sensor (third system) followed by the

PDMS (fourth system). Due to the difference of the used methods (*i.e.* dip- and spin-coating); the thicknesses of thin films on the sensor were a little different to those in the membranes. On the one hand, the thin film thickness (membrane) estimated by SEM for example is ~ 50 nm, and together with the PDMS nanolayer it becomes ~ 130 nm (Fig. 2a). On the other hand, the thickness of the thin film plus PDMS nanolayer (second system) determined by AFM (see the Experimental section for the used method) is ~ 100 nm (Fig. 2b).

The thermograms for the described samples, as well as for thick films are presented in Fig. 3. Thermograms for ultrathin films definitely differ from those for thick films, the T_g of the PEO segment in the single thin film (PEO-PBT in Fig. 3a) is lower (~ -62 °C) than that in the thick film (~ -43 °C, see Fig. 3b). The T_g decrease of the copolymer is a clear indication of

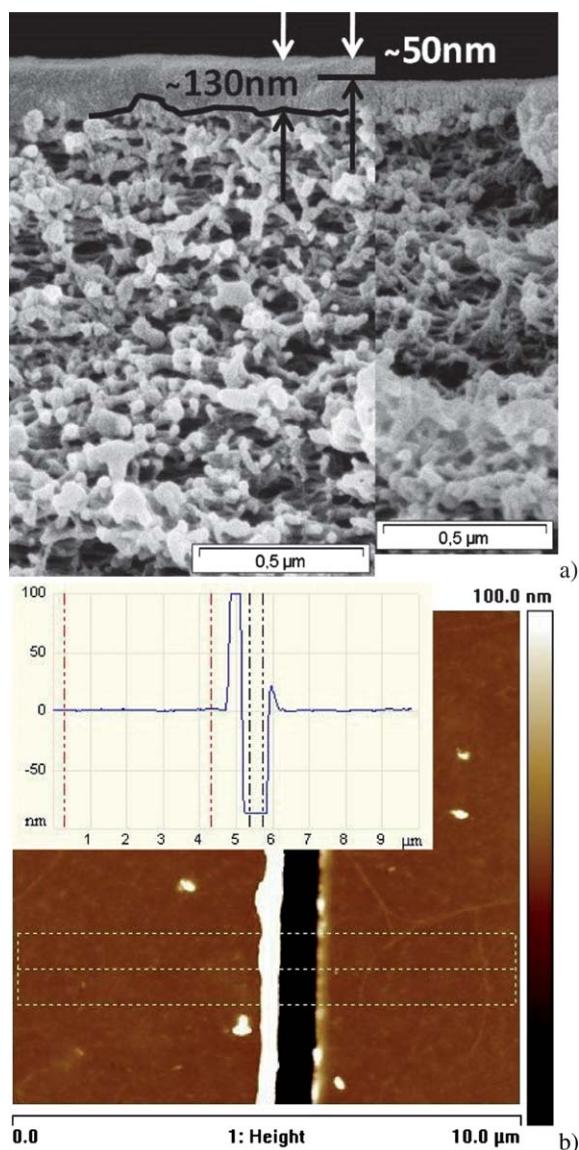


Fig. 2 Comparison of thin film thickness; (a) thin film membrane (SEM) obtained by dip-coating from a solution containing chloroform and 1,4 dioxane (60/40 wt/wt) as solvent and (b) thin film (AFM) obtained by spin-coating from a solution containing chloroform as solvent (the polymer concentration is the same in both cases).

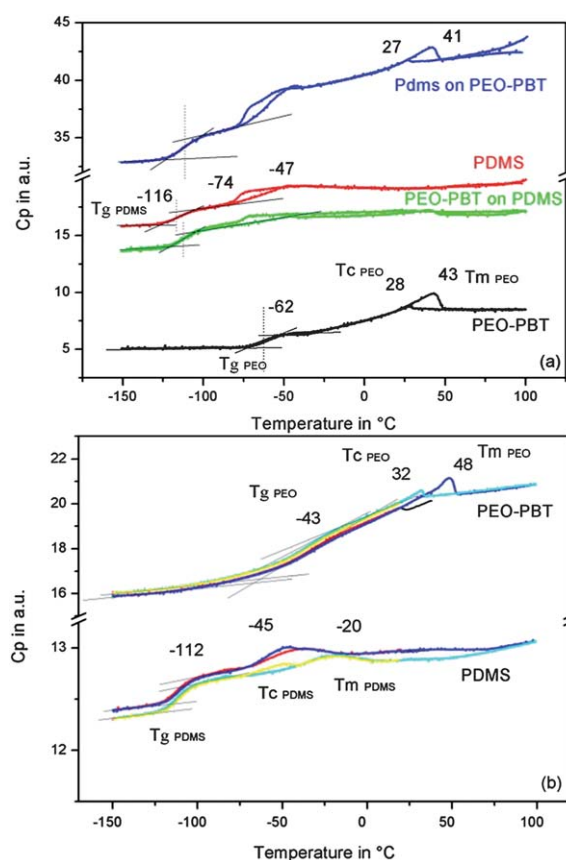


Fig. 3 (a) Thermograms obtained by nanocalorimetry for PEO-PBT and PDMS single layer, PEO-PBT on PDMS and PDMS on PEO-PBT double layer thin films; and (b) PEO-PBT and PDMS thick films.

changes in the dynamics due to the confinement, and because the T_g value is shifted to lower temperatures, the chain mobility and the fractional free volume of the copolymer within the thin film might be different (enhanced) to that in bulk polymer. In rubbery-like membranes; the free volume and fractional free volume increase and the chain mobility enhancement are well-correlated with the T_g decrease of the polymer,^{29,35,36} hence our hypotheses on the increased fractional free volume and enhanced chain mobility are well-supported. These two facts greatly influenced on gas transport through the thin films, *i.e.* the gas solubility and the diffusivity might be improved. The T_g decrease however is only observed when the thickness of the thin film is below 100 nm; for thicker films, the T_g value and the glass transition region are similar to those of bulk samples (ESI†).

Both the crystallization (T_c) and melting (T_m) temperature of the PEO segment in the single thin film (PEO-PBT) differ from the thick film too. The T_c is slightly lower than that in the thick film, indicating that the enhanced chain mobility due to the confinement retarded the crystallization process. As the crystallization is a cooperative process, and it results from a pre-ordered crystalline mesophase,³⁷ this result can be expected. The lower T_m value indicates that the PEO crystallites are smaller in ultrathin films than in thick films.

Additional and important results are those observed in double layer thin films. When the Poly4.0k is on the sensor and then a layer of PDMS is deposited on it (PDMS on PEO-PBT,

Fig. 3a), the T_g , T_c and T_m of the PEO segments are similar to that in the single thin film (PEO–PBT), but the glass transition of the PEO segment and crystallization and melting region of PDMS are scrambled. Nevertheless, when PDMS is first deposited on the sensor and then the Poly4.0k (PEO–PBT on PDMS, Fig. 3a), the same procedure as in the membrane fabrication, the T_c and T_m of the PEO segment are not detectable, but a small shoulder at the same melting temperature as in the single thin film (43 °C) suggests that the PEO crystallinity is extremely low. This result indicates that the PEO amorphous phase is dominant in the ultrathin film, and thus, it supports the higher fractional free volume (discussed above) and the extremely high gas permeation (unmatched).

Wang *et al.*⁵ however reported that when PEO is confined to 20 nm, it crystallizes as single, high-aspect-ratio lamellae that are oriented primarily parallel to the layer surface (film fabricated by layer-multiplying coextrusion), thus the gas permeability was unexpectedly reduced by two orders of magnitude. In contrast to that report (homopolymer PEO with 200 kg mol⁻¹), the PEO (4.0 kg mol⁻¹) segment of the CO₂-philic multi-block copolymer confined to <100 nm did not or to a lesser extent crystallize (dominant amorphous phase). We believe that it is due to the PBT presence and the PDMS substrate, which hindered the crystallization process.

Our affirmation of chain mobility enhancement and the fractional free volume increase is supported by the low T_g of the PEO segment and by the dominant amorphous phase, *i.e.* the lower the T_g and crystallinity, the higher the gas transport.

The glass transition region of the PEO segment in PEO–PBT on PDMS is definitely scrambled with crystallization and melting regions of PDMS. During the heating process for example, the transition from –100 to –46 °C is broader than those observed in single PDMS thin film (from –85 to –47 °C). The crystallization temperature of PDMS in the thin film is ~–74 °C, 29 K less than in the thick film, and the melting temperature is also shifted to lower values. The presence of a crystalline phase in PDMS is attributed to the use of the controlled release additive (CRA21) during the cross-linking.³⁸

Based on these results, we suggest that the organization of the block copolymer within the thin film would be different to that in bulk material (Fig. 4). As the thickness of the fabricated ultrathin film is comparable to $2R_g$, the copolymer chains situated perpendicularly to the surface are perturbed. Although the conformation of the copolymer parallel to the surface could not be perturbed, the whole copolymer within the thin film is perturbed because the R_g describes the dimensions of a polymer chain in the space. The presence of the PDMS layer somehow directed the re-organization of the multi-block copolymer and hindered the crystallization process of the PEO segment. Because the PDMS surface is hydrophobic, there is some compatibility between PDMS and the PBT segment of the copolymer, so most of the PEO segments might be situated at the surface (CO₂-philic surface). This reorganization of the copolymer chains contributed in a favourable way to the separation performance of the thin film membranes, *i.e.* creating a highly CO₂-philic surface and thin film mostly composed of an amorphous phase (low T_g of PEO segment and enhanced free volume). Nevertheless, it is important to note that during the design of these thin films many important aspects have been also considered, such as the nature

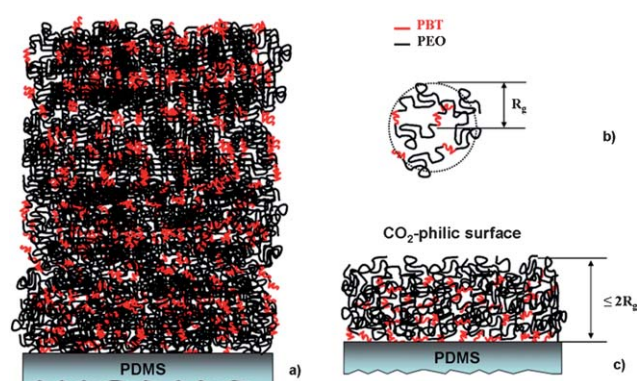


Fig. 4 (a) Schematic representation of the block copolymer organization in thick films (semicrystalline polymer and high T_g); (b) representation of a polymer chain and “ R_g ”; and (c) block copolymer organization within a super ultrathin film under the influence of the PDMS substrate (thin film mostly amorphous with high fractional free volume and low T_g of the PEO segment).

of substrate, the used solvent, the entire molecular weight of the copolymer, the size and content of each segment and the drying conditions. As the designed strategy produced thin film membranes with outstanding properties, we suggest that this is mostly a consequence of the nanometre size of thin film thickness, the CO₂-philic character of the copolymer and the nature of the used substrate.

Although the fabrication of thin films goes back to the last century,^{20,39} the peculiarity of multi-block copolymer ultrathin films as highly CO₂-selective membranes has been demonstrated in this work.

As CO₂-philic membranes, the developed membranes show extremely high separation performance (higher than state-of-the-art membranes). For CO₂ capture applications, high CO₂ permeance (>2.7 m³ (STP) m⁻² h⁻¹ bar⁻¹) is critical to reduce the system cost and footprint, and a CO₂/N₂ selectivity of ~30 is good enough to reach the required CO₂ purity.²⁴ Under this consideration, our membrane is well suited for CO₂ capture. At present, the CO₂-capture costs by using the conventional absorption processes are between 50 and 80 \$ per ton of CO₂ captured.^{40,41} The membrane with the best separation performance developed here would lower the CO₂ capture cost more than half compared to such absorption processes (<20 \$ per ton of CO₂ captured).⁴²

4. Conclusions

The nanocalorimetry studies showed that the thermal properties of the CO₂-philic multi-block copolymer (with high molecular weight) at the nanoscale deviate from the bulk. The low T_g of the PEO segment and the dominant amorphous phase in these super permeable ultrathin films (due to the copolymer confinement between PDMS and air) partially explain the unmatched CO₂ permeances.

We conclude that the correct selection of a CO₂-philic polymer or copolymer, the appropriate substrate (engineered) and the fabrication of thin films with thicknesses comparable to $2R_g$ result in advanced membranes for CO₂-capture, which in addition would greatly lower the capture costs.

Acknowledgements

We thank Silvio Neumann, Karen Prause and Sabrina Bolmer (Polymer Institute, Helmholtz-Zentrum Geesthacht) for the DSC, SEM, AFM and light scattering analyses. We also thank Horiba for the thickness measurements by ellipsometry. This work was supported by the Helmholtz-Alliance MemBrain project (Gas separation membranes for Zero-emission Fossil Power Plant).

Notes and references

- 1 P. Calvert, *Nature*, 1996, **384**, 311.
- 2 A. J. Ryan, *Nature*, 2008, **456**, 334.
- 3 C. W. Frank, V. Rao, M. M. Despotopoulou, R. F. W. Pease, W. D. Hinsberg, R. D. Miller and J. F. Rabolt, *Science*, 1996, **273**, 912.
- 4 C. L. Soles and Y. Ding, *Science*, 2008, **322**, 689.
- 5 H. Wang, J. K. Keum, A. Hiltner, E. Baer, B. Freeman, A. Rozanski and A. Galeski, *Science*, 2009, **323**, 757.
- 6 S. Ito, M. Mabuchi, N. Sato and H. Aoki, *Bull. Chem. Soc. Jpn.*, 2005, **78**, 371.
- 7 J. A. Forrest and K. Dalnoki-Veress, *Adv. Colloid Interface Sci.*, 2001, **94**, 167.
- 8 R. S. Tate, D. S. Fryer, S. Pasqualini, M. F. Montague, J. J. de Pablo and P. F. Nealey, *J. Chem. Phys.*, 2001, **115**, 9982.
- 9 S. Napolitano, A. Pilleri, P. Rolla and M. Wubbenhorst, *ACS Nano*, 2010, **4**, 841.
- 10 A. Schoenhals, H. Goering, C. Schick, B. Frick and B. Zorn, *Eur. Phys. J. E*, 2003, **12**, 173.
- 11 H. Huth, A. A. Minakov and C. Schick, *J. Polym. Sci., Part B: Polym. Phys.*, 2006, **44**, 2996.
- 12 M. Y. Efremov, E. A. Olson, M. Zhang, Z. Zhang and L. H. Allen, *Phys. Rev. Lett.*, 2003, **91**, 85703.
- 13 J. M. Torres, C. M. Stafford and B. D. Vogt, *ACS Nano*, 2009, **3**, 2677.
- 14 W. Wang and A. H. Barber, *Nanotechnology*, 2010, **21**, 225701.
- 15 S. O. Kim, H. H. Solak, M. P. Stoykovich, N. J. Ferrier, J. J. de Pablo and P. F. Nealey, *Nature*, 2003, **424**, 411.
- 16 M. P. Stoykovich, H. Kang, K. C. Daoulas, G. Liu, C. C. Liu, J. J. de Pablo, M. Müller and P. F. Nealey, *ACS Nano*, 2007, **1**, 168.
- 17 M. P. Stoykovich and P. F. Nealey, *Mater. Today*, 2006, **9**, 20.
- 18 S. Zhang, M. A. Greenfield, A. Mata, L. C. Palmer, R. Bitton, J. R. Mantei, C. Aparicio, M. Olvera de la Cruz and S. I. Stupp, *Nat. Mater.*, 2010, **9**, 594.
- 19 M. Cavallini, A. Calo, P. Stoliar, J. C. Kengne, S. Martins, F. C. Maticotta, F. Quist, G. Gbabode, N. Dumont, Y. H. Geerts and F. Biscarini, *Adv. Mater.*, 2009, **21**, 4688.
- 20 J. M. Henis and M. K. Tripodi, *Science*, 1983, **220**, 11.
- 21 Y. Huang, X. Wang and D. R. Paul, *J. Membr. Sci.*, 2006, **277**, 219.
- 22 B. W. Rowe, B. D. Freeman and D. R. Paul, *Polymer*, 2009, **50**, 5565.
- 23 M. Li and C. K. Ober, *Mater. Today*, 2006, **9**, 30.
- 24 T. C. Merkel, H. Lin, X. Wie and R. Baker, *J. Membr. Sci.*, 2010, **359**, 126.
- 25 T. Yang, Y. Xiao and T.-S. Chung, *Energy Environ. Sci.*, 2011, **4**, 4171.
- 26 Y. Xiao and T.-S. Chung, *Energy Environ. Sci.*, 2011, **4**, 201.
- 27 J. Becker, G. Grun, R. Seemana, H. Mantz, K. Jacobs, K. R. Mecke and R. Blossey, *Nat. Mater.*, 2003, **2**, 59.
- 28 S. Gabriele, P. Damman, S. Sclavons, S. Desprez, S. Coppée, G. Reiter, M. Hamieh, S. A. Akhrass, T. Vilmin and E. Raphael, *J. Polym. Sci., Part B: Polym. Phys.*, 2006, **44**, 3022.
- 29 W. Yave, A. Car, S. S. Funari, S. P. Nunes and K.-V. Peinemann, *Macromolecules*, 2010, **43**, 326.
- 30 W. Yave, A. Car, J. Wind and K.-V. Peinemann, *Nanotechnology*, 2010, **21**, 395301.
- 31 A. Car, C. Stropnik, W. Yave and K.-V. Peinemann, *Adv. Funct. Mater.*, 2008, **18**, 2815.
- 32 Y.-H. Lin and J.-H. Juang, *Macromolecules*, 1999, **32**, 181.
- 33 D. W. Denlinger, E. N. Abarra, K. Allen, P. W. Rooney, M. T. Messer, S. K. Watson and F. Hellman, *Rev. Sci. Instrum.*, 1994, **65**, 946.
- 34 S. Zhu, Y. Liu, M. H. Rafailovich, J. Sokolov, D. Gersappe, D. A. Vinisett and H. Ade, *Nature*, 1999, **400**, 49.
- 35 W. Yave, A. Car, K.-V. Peinemann, M. Q. Shaikh, K. Raetzke and F. Faupel, *J. Membr. Sci.*, 2009, **339**, 177.
- 36 W. Yave, A. Car and K.-V. Peinemann, *J. Membr. Sci.*, 2010, **350**, 124.
- 37 N. J. Terrill, P. A. Fairclough, E. Towns-Andrews, B. U. Komanscheck, R. J. Young and A. J. Ryan, *Polymer*, 1998, **39**, 2381.
- 38 CRA21 is an extremely efficient controlled release additive for adjusting the release of the solventless DEHESIVE® system (PDMS). CRA21 is a typical MQ resin which has as the M-unit not only trimethylsiloxy units but also vinyl dimethylsiloxy units. Therefore the addition of CRA21 to DEHESIVE® results in a cross-linked PDMS with branches, thus according to degree of cross-linking the PDMS can crystallize.
- 39 C. Liu and C. R. Martin, *Nature*, 1991, **352**, 50.
- 40 M. Ramezan, *Carbon dioxide Capture from Existing Coal-Fired Power Plant*, U.S. Department of Energy, 2007, <http://www.netl.doe.gov/energyanalyses/pubs/CO2%20Retrofit%20From%20Existing%20Plants%20Revised%20November%202007.pdf>.
- 41 N. MacDowell, N. Florin, A. Buchart, J. Hallet, A. Galindo, G. Jackson, C. S. Adjiman, C. K. Willam and N. Sahah, *Energy Environ. Sci.*, 2010, **3**, 1645.
- 42 See ESI† about a roughly economical and technical analysis on CO₂ capture by membranes.