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Insight into reverse selectivity and relaxation behavior of poly[1-(trimethylsilyl)-1-propyne] by flux-lateral force and intrinsic friction microscopy

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ABSTRACT

Novel scanning force microscopy techniques (SFM) were employed to investigate poly[l-(trimethylsilyl)-1-propyne] (PTMSP), a high-free volume, highly permeable reverse-selective membrane material. This study reports, for the first time, reverse selectivity in relation to the interfacial gas adsorption capacity of the PTMSP membrane with the gas permeants CO_2 and helium. With flux-lateral force microscopy (F-LFM), mechanical property changes caused by permeant gas infiltration were recorded within the polymer interfacial downstream region. In conjunction with bulk permeation measurements and varying sequential exposure to the two permeants, CO_2 is found to saturate the membrane faster, i.e. at a lower differential pressure by about 0.3 bar, in comparison to helium. It is also identified as modifying agent for PTSMP causing a significant change in the mechanical properties of the polymer matrix, which consequentially leads to a considerable helium transport reduction, and thus, an increase in reverse selectivity from 1.2 to 4.7. Also in this study, thermally available activation modes of 6–8 kcal/mol were revealed by intrinsic friction analysis (IFA) that were attributed to backbone methyl-group rotations in accordance with conformational calculations. Bulk thermally activated modes were found to be modestly affected by interfacial constraints on the sub-100 nanometer scale, which is an important finding for interpreting interfacial constraints in PTMSP nanocomposites involving silicon-oxides.

1. Introduction

The potential for energy efficient membrane separation systems remains largely unrealized in the chemical processing and the refining industries. Of particular interest to these industries are reverse-selective membranes, which find numerous chemical and refining industrial applications including removal of higher hydrocarbons from methane in natural gas purification, olefin separation from nitrogen, and removal of hydrogen from refinery process gas streams. In addition, these membranes may have an impact for H_2/CO_2 (syngas) separations in ongoing efforts to find carbon-neutral energy strategies and reduce greenhouse gas emissions.

Operation of reverse-selective membranes can be understood according to the solution–diffusion model. Herein, permeability within a membrane for use in vapor separation can be expressed as the product of the sorption (or solubility) coefficient (S) of a penetrant, A, in the membrane times the concentration averaged diffusivity (D) of the penetrant through the membrane [1]:

$$P_A = S_A \times D_A \tag{1}$$

Sorption in glassy polymers can be understood according to the dual mode sorption model, composed of a combination of dissolution described by Henry's Law and Langmuir surface sorption [2,3]:

$$S = k_D + \frac{C'_H b}{1 + bp} \tag{2}$$

where k_D is Henry's constant, b is the Langmuir hole affinity parameter, C'_H is the Langmuir capacity parameter and p is the system pressure. Diffusion through membranes is often understood as being primarily a function of free volume [4,5] according to the following expression for diffusion of gases through a liquid of hard spheres:

$$D_A = C\ \exp\left(\frac{-\gamma v_A}{V_{FV}}\right) \tag{3}$$

where C and γ are polymer-specific constants, v_A is a critical void volume necessary for the diffusion of A, and V_{FV} is the average void volume of the material. Considering both solubility and diffusivity,

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the selectivity, α, of penetrants A and B is, per Eq. (1):

$$\alpha_{A/B} = \frac{S_A}{S_B} \times \frac{D_A}{D_B} \tag{4}$$

For a special group of polymers and particular penetrant mixtures, the solubility ratio can become the dominant factor for selective transport. In this case, the molecular size is not the dominant factor, and the membrane can act as a reverse-selective membrane, i.e., provide relatively faster transport for larger penetrant molecules compared to smaller ones. Included in this group of polymers are: poly[l-(trimethylsily1)-1-propyne] (PTMSP) [6,7] and its analogues [8,9] and poly(4-methyl-2-pentyne) (PMP) [10]. These polymers have been shown to exhibit high reverse selectivity for organic vapor/permanent gas (e.g. n-butane/N_2) mixtures. Generally speaking, these polymers exhibit high glass transition temperatures, amorphous structures, and high free volumes.

Of highly permeable reverse-selective membranes, PTMSP has received the most attention. PTMSP contains rigid carbon–carbon double bonds and bulky trimethylsilyl and methyl constituent groups, which result in very twisted molecules [8]. Clough has suggested a helical structure is possible in this molecule [11] which creates an extremely rigid chain that will maintain backbone conformation achieved during polymerization. Neat PTMSP is understood to have high free volume as a result of the inefficient chain packing of their rigid backbones, bulky pendant groups and poor interchain cohesion [8]. Its free volume exhibits a bimodal distribution, with some smaller cavities having an average radius on the order of 0.3 nm and larger cavities with an average radius on the order of 0.5 nm [12,13]. It has been theorized that these small and large cavities create a series of nanoporous interconnected free volume cavities, thus giving them unique high-permeability characteristics [7,12,14]. The materials exhibit reverse-selective behavior due to the fact that large organic molecules adsorb to the walls of the small free volume elements thereby creating resistance to transport for smaller, permanent gases [7].

Glassy polymers used in reverse-selective membranes are understood to be in a non-equilibrium state susceptible to aging after initial membrane formation [15]. Aging in PTMSP [8,16] is a critical problem which results in loss of permeability and has been the subject of many recent studies [16–18]. Three mechanisms of aging have been highlighted [19]: (1) physical aging due to the relaxation of non-equilibrium [15] free volumes within the polymer, (2) physical aging due to contamination [20] and (3) chemical aging due to oxidation [21]. Aging has been shown to vary with different catalysts used to produce PTMSP [22] and on membrane solvent conditioning [23].

In this study, we utilize two recently developed nanoscale techniques to address some of the outstanding issues related to PTMSP. One is flux-lateral force microscopy, F-LFM, a scanning force microscopy method, that has shown *in situ* local gas flux sensitivity on both rigid zeolite materials and polyelectrolyte (Nafion®) membranes [26]. Local permeant fluxes can be detected indirectly with F-LFM based on its sensitivity to (i) lubricating effects caused by adsorbent permeants on the downstream membrane surface, and (ii) very small changes in the mechanical properties of the membrane. The basic F-LFM set-up is sketched in Fig. 1. With F-LFM, the lateral force (also referred to as friction) is recorded as a function of the inlet permeant pressure. While the gradient of lateral forces vs. permeant pressures has provided a direct measure of the permeability for single component gases, gas selective transport has not yet been demonstrated. The first F-LFM selective transport measurements will be presented here involving helium (He) and carbon dioxide (CO_2). The results are discussed in terms of membrane swelling from CO_2 sorption.

The second technique, intrinsic friction analysis (IFA) [24], also a scanning force method and the thermomechanical analogue to dielectric spectroscopy, is applied to investigate relaxations within the PTMSP material. From previous macroscopic PTMSP studies [8], insignificant changes in the storage modulus (E'), the loss modulus (E''), and the loss tangent ($\tan\delta$), over a temperature range of $-150\,^{\circ}C$ to $200\,^{\circ}C$ provide no effective means to determine relaxation properties, such as activation energies. With local and highly sensitive scanning, the IFA technique, which has provided activation energies of molecular relaxations for a variety of polymers and molecular glasses [25–28], can be used to determine local and faint relaxation phenomena, and thereby, molecular relaxation modes can be identified. Employing IFA complementary to theoretical simulations and F-LFM, we will demonstrate that the membrane permeation is strongly affected by fundamental changes in the polymer matrix induced by the permeant sorption and aging and is not primarily related to the original molecular mobility and structure of the virgin membrane.

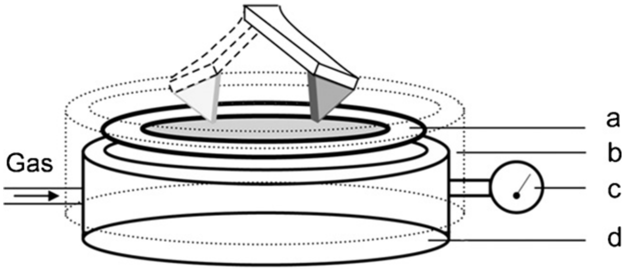

Fig. 1. F-LFM set-up with (a) membrane sample, (b) membrane chamber cap, (c) pressure gauge, and (d) chamber case, being probed using a SPM employing a cantilever.

2. Experimental

PTMSP (SSP-070-10gm, lot 5I-7401 Gelest, Inc.) was dissolved in cyclohexane by stirring at room temperature for at least 2 days, producing two solutions of 0.3 wt.% and 1 wt.% polymer. The solutions were then filtered with 0.2 μm Nylon (Whatman) filter. Solution cast samples (~800 nm thick) were made for bulk flux and F-LFM measurements by pipetting 100 μL of 0.3% PTMSP solution onto the surface of a 200 nm pore anodic aluminum oxide (AAO) membranes (Anodisc 25, 0.2 μm, 25 mm Whatman, Inc.) and allowing the films to dry in ambient conditions while keeping them covered. For bulk flux studies, 100 μL of the 1.0 wt% solution was spun cast at 6000 rpm for 1 min on the aforementioned AAO membranes, resulting in ~200 nm thick films. To prevent infiltration of the solution into the pores of the AAO membranes during spin casting, AAO membranes were secured to a silicon substrate to prevent direct exposure to the vacuum applied to the spin chuck, which holds the sample in place. F-LFM samples were mechanically supported by stainless steel discs with 3 mm central holes for transport studies. A cured epoxy (5 Minute®) was used for this purpose. For IFA measurements, the 1.0 wt.% solution was spun on ⟨1 1 1⟩ silicon wafers which were pre-cleaned by sonication in acetone (10 min) followed by methanol (40 min), followed by UV treatment for 20 min. Spin casting for IFA samples was performed using 100 μL of solution for 1 min at spin speeds between 500 and 6000 rpm to obtain samples 35–350 nm thick. All films were prepared 24 h prior to analysis.

Bulk permeability measurements were performed using an isobaric permeation system [29,30], with gas fed to the upstream side of the membrane. While upstream pressures were regulated, the downstream pressure was atmospheric pressure. A purge valve was used to ensure that no contaminant gases were present in the line. After waiting for equilibrium, the downstream flow rate was determined using a bubble flow meter. Two different size flow meters (0.5 mL and 10 mL) were used depending on the downstream flow