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Nanoprobe imaging molecular scale pores in polymeric membranes

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ABSTRACT

A long-standing goal of materials microscopy is the imaging of nanoporous polymeric membranes at nanometer resolution. In particular, no technique has been developed to “see” nanopores with dimensions in the 0.5–2 nm range. These pores are crucial in the functional performance of nanofiltration (NF) membranes used for molecular separation processes. The major problem in imaging at this scale is insufficient electron contrast of polymers, which has made distinguishing their structural phases at the nanoscale not practically feasible. Here we describe an *in situ* physicochemical characterization technique to measure size of the transport active pores. Nanopores in an asymmetric organic solvent nanofiltration (OSN) membrane are filled with high contrast osmium dioxide (OsO_2) nanoparticles, whose spatial arrangement is mapped under transmission electron microscopy (TEM). Due to the uniquely small size range of these probes, they target nanopores in the membrane skin layer. Thus, pore size distribution and even polymer chain structure can be evaluated. The pore size is found to correlate well with membrane separation performance, and the molecular separation mechanism of the nanofiltration P84 co-polyimide membrane is shown to be due to size exclusion of the larger nanoparticles.

1. Introduction

Imaging of nanoporous polymer films at nanometer resolution is a long-standing goal of materials microscopy. The difficulty lies with the low electron contrast of polymers, which has prevented high magnification images from being acquired [1]. However, “seeing” nanoscale pores would be of great utility in elucidating the functional performance of nanoporous polymeric materials used in molecular processes such as membrane permeation and separation. An example of a membrane based molecular separation process is organic solvent nanofiltration (OSN), which separates solutes in the molecular weight range of 200–1500 $g\,mol^{-1}$ using organic solvent feeds [2]. OSN membranes can be prepared *via* the phase inversion of a film of polymeric “dope” solution, which is cast on a non-woven backing, and then immersed in a non-solvent medium. The polymer precipitates, forming an integrally skinned asymmetric porous structure [3,4]. The membrane is “open” on the side adhering to the non-woven backing. The material density gradually increases from the open side toward the “tight” surface side, where it forms a skin layer whose structure determines the nanofiltration (NF) performance. It is generally believed that the pore size of these membranes is approximately 1 nm [5,6]. Flux and rejection performance are assumed to derive from pore size and porosity, and can be controlled by the type of polymer and the membrane formation parameters [6,7].

Work on the characterization of NF membrane structure has a long history. Previous studies used atomic force microscopy (AFM) [8–12], positron annihilation spectroscopy (PAS) [13–16] and transmission electron microscopy (TEM) [17–21]. AFM was applied to measuring the pore size distribution at the skin layer surface. However, this technique cannot differentiate between surface cavities and active pores contributing to solute transport. Furthermore, the resolution of AFM is limited by size of the cantilever tip [22]; thus it may be difficult to measure pore sizes at the scale of a nanometer or less [8–10]. PAS measures size and distribution of free volume elements in porous materials in a non-destructive way [23,24]. The well established formula correlating orthopositronium lifetime with cavity size estimates the average pore size under the assumption that all pores within the material have a spherical geometry [25]. The technique provides good information on size of the free volume elements in polymeric films; however it does not measure dimensions of the transport-active pores or the fraction of cavities that contribute to membrane transport. The so-called ‘S parameter’ obtained through slow positron beam techniques can be acquired in relation to the membrane depth, so that changes in material structure with depth can be evaluated [26]. However, these analyses are strongly related to material chemistry [14], and hence comparison of membranes having different chemical compositions does not yield reliable results.

TEM is the most powerful imaging technique in terms of resolution. This technique, although it is often applied to characterization

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of polymeric materials, does not provide detailed information about their nanostructure due to the fact that polymers do not generate sufficient electron contrast for the assessment of their morphologies at the nanoscale [27]. Rather, integrally skinned asymmetric membranes have only been characterized at the microscale [17], and TEM has been applied to thin film composite membranes to evaluate the thickness, but not the structure, of their polyamide top layers [19]. The nanoscale ionic cluster domains of Nafion® membrane were characterized *via* staining with ruthenium tetroxide under TEM [28]. 10 and 30 nm gold nanoparticles were incorporated into the polymer matrix of a composite reverse osmosis membrane in order to distinguish ridges and valleys [20]. Scanning electron microscopy (SEM) was applied to measuring the skin layer thickness of ultrafiltration membranes with the use of gold nanoparticles filtered from the open side of the membrane [29,30]. To date, none of the characterization methods described above have been adapted to distinguish pores which are active in solvent transport ("transport-active pores") from "dead-end" pores.

In summary, a method to relate NF membrane functional characteristics, such as flux and rejection, to the membrane nanoscale structure has not yet been reported. In order to progress understanding of the molecular architecture of polymeric membranes, new high resolution characterization techniques are required. Here, we propose a new approach for characterization of NF membranes, which uses a combination of *in situ* probing of nanopores and high resolution TEM. The skin layer nanostructure is elucidated by imaging of the high contrast nanoparticles, which are lodged in transport-active pores. Beyond NF membranes, this technique has the potential to be used for the characterization of a wide variety of permeable nanoporous polymeric materials.

2. Experimental

2.1. Membrane preparation

All membranes were prepared from P84 co-polyimide (HP Polymers, Austria) without any additional purification processes. Dope solutions were prepared with the following compositions: 24% (w/w) P84 was dissolved in a mixture of dimethylformamide (DMF):1,4 dioxane (dioxane) at ratios of 1:2, 2:1 and 4:1 (corresponding to membranes M1, M2 and M3). Dope solutions were stirred for 24–48 h until a homogenous solution was obtained, and then left overnight to degas. Dope solutions were cast at a knife height of 300 μm, on polyester non-woven backing material (Hollytex 3329, USA) taped to a glass plate. The cast film was then held for 30 s before immersion in a water coagulation bath, where phase inversion was induced and membranes formed. After an hour, the membranes were removed from the water coagulation bath and immersed in isopropanol (IPA) for solvent exchange to remove water. In the next step, the membranes were conditioned for 24 h in polyethylene glycol (PEG) 400 (Fisher Scientific, UK) dissolved in IPA at a volume ratio of 3:2 (PEG:IPA), followed by air drying. The PEG enters the membrane and acts as a conditioning agent, allowing it to be handled in a dry state. The procedure has been described in more detail elsewhere [31].

2.2. Dense film preparation

A dope solution containing 24% (w/w) of P84 dissolved in a mixture of DMF:dioxane at a ratio of 2:1 was cast on a glass plate with the casting knife set at a height of 300 μm. Subsequently, the film was placed in a vacuum oven at 80 °C for 24 h. A non-porous, homogenous, dense film was formed by this dry phase inversion process, which occurs through evaporation of the solvent from the cast solution.

2.3. Estimation of P84 molecular weight

Molecular weight was measured based on a series of polystyrene standards (Agilent Technologies, UK) using gel permeation chromatography (Waters™ GPC equipped with Waters Styragel® HT4 Column). A mobile phase comprising 0.03 M lithium bromide (Sigma–Aldrich, UK) in *N*-methyl-2-pyrrolidone was used.

2.4. Membrane functional performance

NF experiments were carried out in a METcell cross-flow system (Membrane Extraction Technology, UK) in toluene at an applied pressure of 10 bar. During the first 30 min of filtration the PEG conditioning agent was removed by filtration of pure toluene. The rejection curves were evaluated by filtration of a mixture of styrene oligomers comprising PS 580 and PS 1050 (Agilent Technologies, UK), and α-methylstyrene dimer (Sigma–Aldrich, UK) dissolved in toluene at concentrations of 1 g L^{-1} each. The molecular weights of individual marker molecules were determined as described elsewhere [32]. Concentrations of styrene oligomer species in the feed and permeate samples were measured using an Agilent HPLC with a UV/Vis detector set at a wavelength of 264 nm, combined with an ACE 5-C18-300 column (Advanced Chromatography Technologies, UK). The mobile phase employed for separation comprised 35% (v/v) analytical grade water, 65% (v/v) tetrahydrofuran and 0.1% (v/v) trifluoroacetic acid.

2.5. Solute size calculations

Solutes diameters ($d_{s,i}$) for the styrene oligomer species were determined using the Stokes–Einstein equation [33]:

$$d_{s,i} = \frac{2kT}{6\pi D_i \mu_0} \tag{1}$$

where k is Boltzmann constant, T is the absolute temperature in K, μ_0 is the solvent bulk viscosity (toluene viscosity at 20 °C is 0.59 cP) and D_i is the solute diffusivity given by the Wilke–Chang equation [33]:

$$D_i = 7.4 \times 10^{-8} \frac{\sqrt{\phi M_s T}}{\mu_0 V_i^{0.6}} \tag{2}$$

where M_s is the molecular weight of the solvent molecule (toluene molecular weight at 20 °C is 92.14 g mol^{-1}), ϕ is a dimensionless solvent parameter (its value for toluene is 1) and V_i is the molar volume of the solute molecule in cm^3 g^{-1} mol^{-1} which was calculated using a group contribution method [6].

2.6. Preparation of osmium dioxide nanoparticles

Fabrication of osmium dioxide (OsO_2) nanoparticles was supported with a styrene oligomer (PS) mixture containing PS 580 and PS 1050 (Agilent Technologies, UK). The polymer was used here as a stabilizer for the nanoparticles. Further information on the chromatography and molecular weight values of each PS species has been reported previously [32]. PS was coated onto the walls of a round bottom flask, and exposed in its close proximity to vapors of an aqueous solution of 4% (w/w) osmium tetroxide (OsO_4) (Agar Scientific, UK) (Fig. 4d). The reaction time was 4 h at room temperature. The PS mixture became black, indicating that OsO_4 had been reduced to OsO_2 in the presence of air. The gravimetric ratio of OsO_2 to PS was 5:1. This was measured by first weighing PS alone prior to staining with OsO_4 vapors, then by weighing the final product of the PS with the formed OsO_2 nanoparticles; consequently the weight of OsO_2 in form of the nanoparticles was calculated by subtracting the weight of PS prior to staining. Toluene was then added to form