Experimental report

05/04/2016

Proposal: **9-11-1718** **Council:** 10/2014

Title: Reverse osmosis polymeric membranefor water filtration - nanostructure and dynamics

Research area: Engineering

This proposal is a new proposal

Main proposer: **Joao T. CABRAL**

Experimental team:
Joao T. CABRAL
Ruhina M MILLER
Fabrizia FOGLIA
Manuela NANIA

Local contacts:
Bernhard FRICK
Robert BARKER

Samples: m-phenylenediamine AND trimesoyl chloride - PA membrane -

Instrument	Requested days	Allocated days	From	To
D17	0	3	20/04/2015	23/04/2015
IN16B	6	3	13/05/2015	16/05/2015
FIGARO	3	0		

Abstract:

Most membranes designed for molecular separations in liquids, namely Reverse Osmosis (RO) and Nanofiltration (NF) membranes, comprise a tight separating film on a more open support. Understanding liquid transport through membranes at the molecular scale remains challenging due to (1) the lack of resolution of the membrane material at the molecular scale and (2) description of molecular flow through the resulting structure. Membrane pores (free volume fluctuations) are commensurate with permeate molecules and therefore describing transport is challenging. The aim of this proposal is to establish the molecular-scale implications of polymer local structure and dynamics, in terms of thin film profile and polymer network motion, of reaction stoichiometry, hydration and membrane ageing.

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Proposal title: Reverse osmosis polymeric membrane for water filtration - nanostructure and dynamics
Experimental team: F. Foglia M. Nania, R. Miller, J.T. Cabral, Imperial College London
Instrument scientists: R. Barker, B. Frick, ILL

Introduction: Polymer membranes designed for molecular separations in liquids, namely Reverse Osmosis (RO) and Nanofiltration (NF) membranes, generally comprise a 'tight' separating film on a more open, porous support layer. Understanding liquid transport through membranes at the molecular scale remains challenging due to (1) the lack of understanding of the membrane material at the molecular scale and (2) description of molecular flow through the resulting structure. Conventional experimental characterisation techniques like transmission electron microscopy (TEM), require high vacuum and thus full dehydration of polymer and/or do not have the required spatial resolution to elucidate nanoscale features of membranes. Membrane 'pores' (local variations of polymer free volume) are expected to be commensurate with permeate molecules and therefore describing transport is challenging. Our proposal combined D17 and IN16 to resolve the membrane film structure (normal to the free surface), and its response to water, as well as the possible coupling between water and polymer membrane dynamics at the molecular scale. We investigated key membrane parameters including reaction stoichiometry, hydration and membrane ageing.

D17 We investigated the local structure of isolated polyamide membranes (approximately 8-12 nm thick) supported on silicon wafer from dry to fully hydrated state in a controlled -temperature and -humidity chamber. The chemistry of interfacial polymerisation (IP) was probed by investigating three different membrane stoichiometries: m-phenylenediamine (MPD)/trimesoylchloride (TMC) 0.1/0.005, 0.1/0.05, 1/0.05 w/w%, three reaction times: 1, 10 and 20min, and varying isotopic composition: d-MPD/h-TMC and h-MPD/h-TMC.

The model fits to the NR profiles (at 0% RH; MPD/TMC 0.1/0.005 w/w%) suggest a linear dependence between membrane thickness and reaction time. The comparison between the SLD profile of both fully hydrogenated (h-MPD/TMC) and partially deuterated (d-MPD/TMC) membranes indicates that the membrane is highly cross-linked and its composition is homogeneous along the direction normal to the surface. This is also valid for membrane prepared with high TMC concentration.

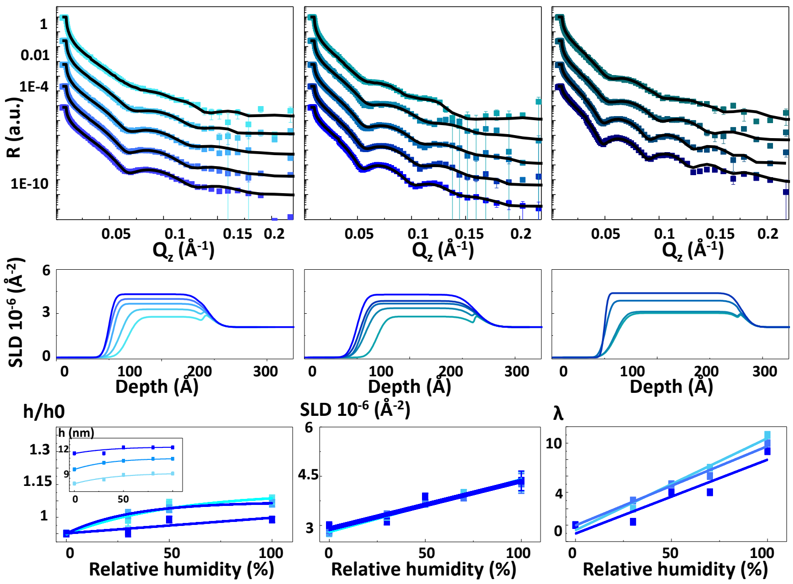

Figure 1: Top panels: comparison between NR data and model fits for MPD/TMC (0.1/0.005; w/w%) thin-films (1, 10, 20min reaction time from left to right, respectively; top panels) at different percentage of relative humidity (from dry to fully hydrated). Q_z is the neutron momentum transfer, in Å^{-1}. Centre panel: correspondent SLD profiles as function of the relative humidity. Bottom panels: film thickness (h), SLD and the water uptake (λ) as function of the relative humidity (from left to right, respectively).

When comparing membranes prepared at similar reaction time but starting from different monomer concentration, the model fits to the NR profiles suggest that is the MPD concentration determining the final thickness of the membrane.

Most interesting is the difference in water uptake. It is clear that increasing TMC concentration by a factor of 10 the water volume fraction increases only about 14% (42 *vs.* 48%) which translates in ~10 water molecules per polyamide unit. On the other hand if we compare membranes prepared at constant at constant MPD concentration the analysis suggests excess up to ~30 water molecule for PA unit. In order to rationalise this behaviour it is therefore necessary to take into account diffusional processes and transport of penetrant molecules through the polymeric membranes. When comparing the variation in membrane density, as consequence of the water uptake and swelling, an initial drop is found. From this minimum value onward the membrane density start to increases. Interestingly, increasing the reaction time not only causes a relative densification of the film but also seems to shift the minimum at higher RH%.

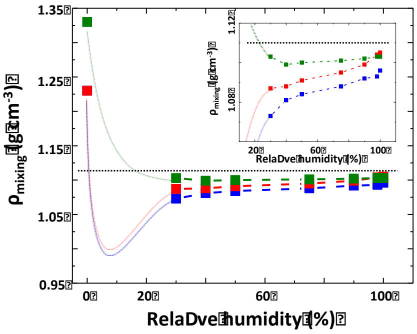

Figure 2: Variation of membrane density as function of the relative humidity for thin films prepared at 10min reaction time with MPD/TMC 0.1/0.005 (blue curve), 0.1/0.05 (red curve) and 1/0.005 w/w% (green curve). In the insert is presented a magnification of the plot as well as the D_2O density (black dotted line).

<u>IN16B</u> To complete our investigation we also characterised the polymer (10/0.5 w/w%) dynamics in its dry and hydrated (in both H_2O and D_2O) state using neutron backscattering. We decided to record 3 different samples to have a better overview on the general dynamics of our system as well as separate the polymer segmental dynamics to the water diffusion inside the polymer. We first recorded a fixed (elastic and inelastic - ΔE=2μeV) window scans from 2 to 380K; then, QENS profiles (energy resolution = 1μeV) at few relevant temperatures.

A first analysis of the EWS suggests that when in its hydrated state (in H_2O) the $\langle u^2\rangle$ increases of around two times; the figure seems to be confirmed when the sample is hydrated in D_2O (even if this latter is obtained by extrapolation).

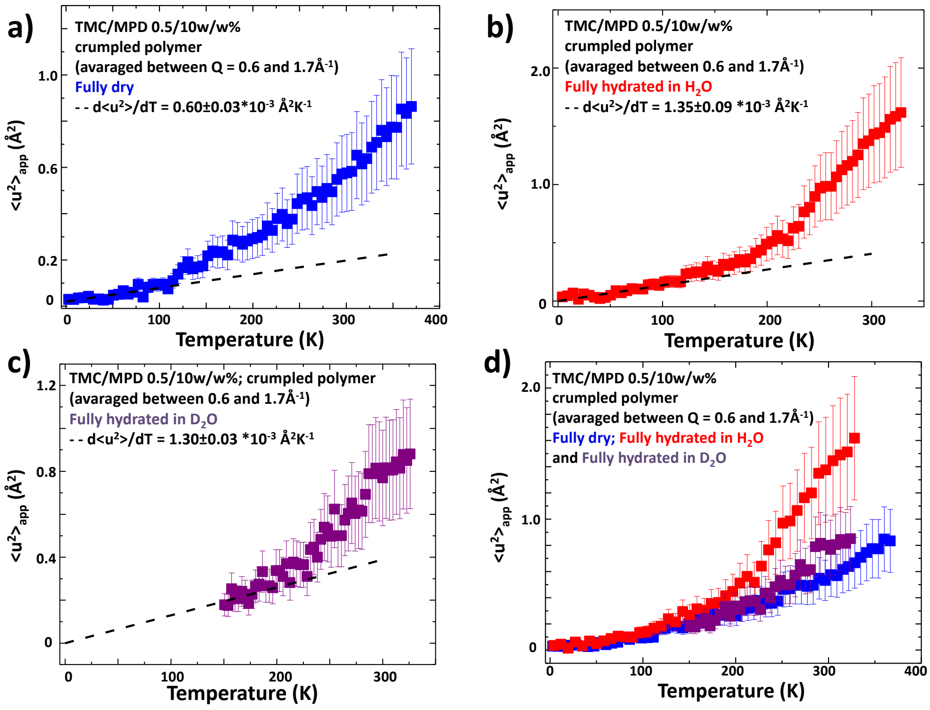

Figure 3: Variation of the mean square displacement as function of T averaged between 0.6 and 1.7Å^{-1}.

For completeness also IWS has been recorded and compared to the correspondent EWS for the same set of samples. In this specific case, the profiles have been recorded at *ΔE = 2μeV* (2366rpm doppler speed). As in the previous experiment those profiles help discriminating the best T for dynamics studies.

QENS profiles indicate an increasing of the curve broadening with the temperature, which is more visible in the hydrated state.

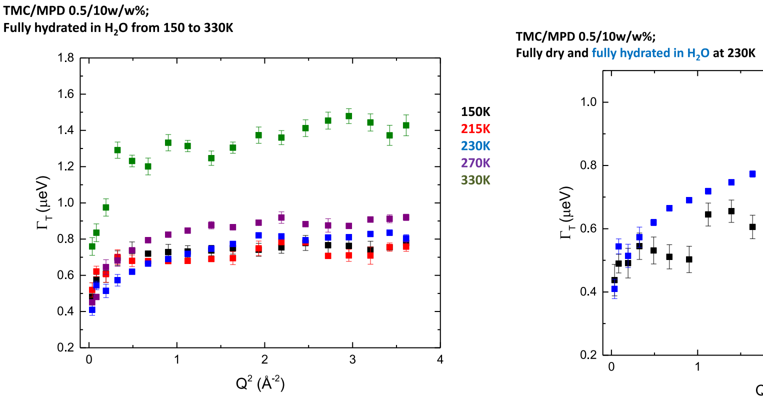

Figure 4: Comparison between Γ_T for fully hydrated (in H_2O) crumpled polymer at different temperatures (right panel) and comparison between Γ_T for fully dry and fully hydrated (in H_2O) crumpled polymer at 230K (left panel).

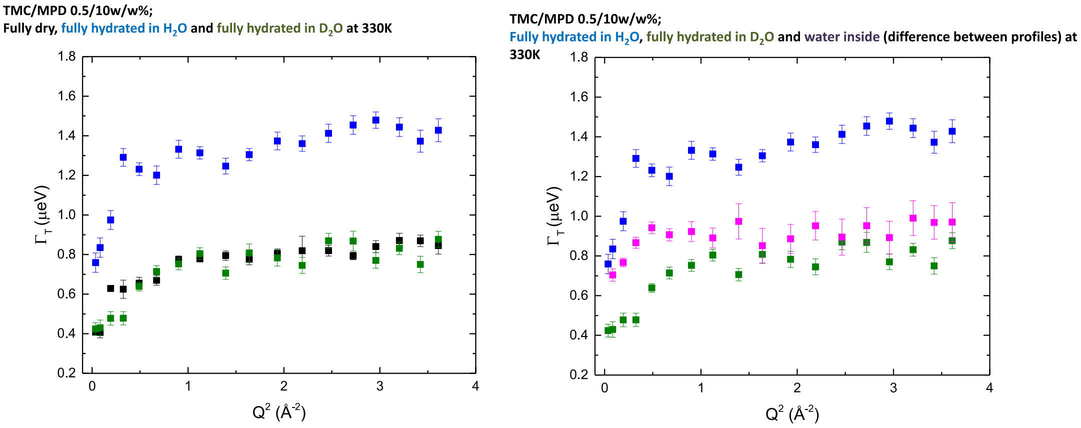

Figure 5: Comparison between Γ_T for fully dry and fully hydrated (in H_2O and D_2O) crumpled polymer at 330K (right panel) and comparison between Γ_T for fully hydrated (in H_2O and D_2O) crumpled polymer at 330K and their difference (water inside the polymer; left panel).

Our results show that, at room temperature, it is possible to discriminate between polymer segmental dynamics and water diffusion within the polymer matrix, benefitting from contrast variation of water and heavy water. Interestingly no indication of fully bound water is found within the experimental conditions probed, and its dynamics appears well described by simple jump diffusion. These results are currently being benchmarked against molecular dynamics simulations ahead of publication.