Stimuli-responsive polymer brushes into nanoconfined geometry

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ABSTRACT:

The conformational behavior of end-grafted diblock copolymer brushes inside a nanoporous alumina membrane in poor and good solvent is experimentally studied. For this purpose an apparatus has been specially designed which enables the monitoring of the volumetric flow rate vs. differential pressure generated by fluid flowing through the membrane.

INTRODUCTION:

Polymer brushes are formed when polymer chains are tethered at one end to a surface at sufficient density to overlap and stretch away from the surface.[1] Stimulus-responsive polymer brushes are a category of polymer brushes that exhibit a change in their conformation, surface energy, or charge state, triggered by an external stimulus such as a change of solvent, temperature, pH, ionic strength, light, mechanical stress, electric or magnetic field, e.t.c.[2] In many processes, particles or macroscopic surfaces bearing adsorbed polymer molecules pass from a good solvent for the polymer to a poor solvent. This external stimulus, by change of the solvent, has been utilized in regulating the switching properties of the polymer brush. This paper describes a method that allows the layer thickness of a polymer (polystyrene), adsorbed within the pores of an alumina membrane, to be determined as the solvency is changed. For this purpose, an ensemble of nanotubes embedded in an alumina membrane, bearing Polystyrene-poly(ethylene oxide) (PS-PEO) diblock copolymer brushes, undergoes permeation measurements in a suitable custom made apparatus.

The switching process can be controlled by treating the brushes with selective solvents. When these brushes are treated with toluene, PS chains swell and stretch away from the surface to preferentially occupy the outer-most layer, reducing the hydrodynamic pore diameter and increasing the resistance in flow. Conversely, when the brushes are treated with poor solvent such as isopropanol, chains partially collapse increasing the hydrodynamic pore diameter and decreasing the resistance in flow. Intermediate states in the stretching behavior of the polymer brush, are possible to appear by gradually switching the quality of the solvent. The latter is achieved by mixing poor and good solvent in various volume fractions.

EXPERIMENTAL METHODS:

A nanoporous membrane (Whatman) with nominal pore diameter of 200nm and 60μm thickness is fitted to a permeable cell made from Teflon. The cell is tightly fixed to a glass cylindrical tube, 150cm in height and 6.82mm in diameter. The glass tube is appropriately scaled with engraved marks at the outer surface. Sealing is achieved by placing o-rings between the different parts, (membrane-cell-glass tube) as shown in Fig. 1. The glass tube is filled with the appropriate solvent and the fluid height level, h, as a function of the time, t, is recorded. The hydrostatic pressure difference imposed by the fluid column upon the membrane is at the order of 10kPa and functions as the driving force for the flow establishment.

This apparatus, simple and versatile, offers superior convenience over other proposed experimental setups in the literature. More specifically:

a) there is no need of any pump adequately calibrated for the flow establishment.

b) there is no need of differential manometers for measuring the pressure drop imposed by the presence of the porous membrane.

c) there is no need of any flow meter with careful and laborious calibration.
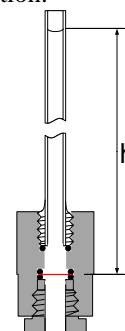

Fig. 1: *Schematic view of the experimental set-up consisting of a Teflon cell and a scaled glass tube, for the determination of the flow rate through nanoporous alumina membrane.*

RESULTS AND DISCUSSION:

Poiseuille's law gives the flow rate of a fluid through a cylindrical channel due to a pressure difference by:

$$Q = \frac{\pi R^4}{8\eta l} \Delta P \qquad (1)$$

where ΔP is the pressure difference, R the radius of the tube, η the dynamic viscosity of the solvent and l the tube length. The porous alumina membrane can be considered as a porous medium with a number of parallel cylindrical nanotubes penetrating throughout its whole thickness (Fig. 2).
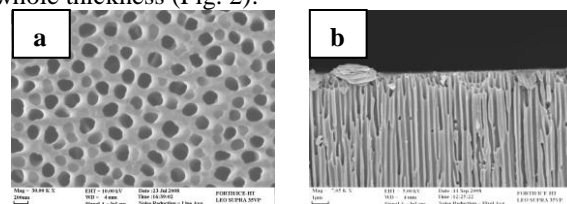

Fig. 2: *(a) Top view and (b) cross section view SEM images of porous alumina membranes (Whatman Co).*

Thus for the flow inside this porous medium, Poiseuille's law is expressed as:

$$Q = \frac{N\pi R^4}{8\eta l}\Delta P = \frac{N\pi R^4}{8\eta l}\rho g h \qquad (2)$$

where ΔP is the hydrostatic pressure difference, ρ the density of the solvent, g the gravitational acceleration, h the height of the solvent column, N is the number of pores contained in the effective surface area of the membrane and l its thickness. From a macroscopic view, the rate of flow can be described as the volume of solvent passing through the glass tube in a period of time:

$$Q = \frac{dV}{dt} = \frac{S_t dh}{dt} \qquad (3)$$

where S_t is the surface area of the glass tube, dh/dt the rate of change in the height level of the solvent. By rearranging equations (2) and (3) one can obtain:

$$\frac{dh}{h} = \frac{nNR^4\rho g}{2\eta l D_t^2} dt \qquad (4)$$

where D_t is the glass tube internal diameter. Finally, by integration of Eq.4 and with the initial condition at $t=0$ $h=h_0$, we derive the following equation:

$$-\ln\frac{h}{h_0} = \frac{NR^4\rho g}{2\eta l D_t^2} t = Bt \qquad (5)$$

where B is the slope of the graph plot $-\ln(h/h_0)$ vs t, equals to:

$$B = \frac{NR^4\rho g}{2\eta l D_t^2} \qquad (6)$$

Prior to the polymer adsorption runs, various solvents were flowed through the bare membrane in order to determine the pore radius. The average bare pore diameter, $<D>$, was derived, by application of the Poiseuille's law and Eq. (6), to be 210±10 nm (see Fig. 3).
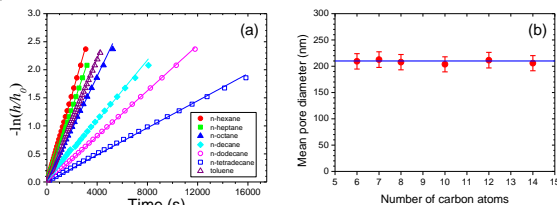

Fig. 3: *(a) Plot of -ln(h/h_0) vs. time diagram for various solvents through bare porous alumina membrane. (b) Pore diameter determination for the various slopes, B of diagram (a).*

Then, each diblock copolymer PS-PEO 32k and 70.5k was dissolved in toluene in concentration of 0.025 mg/mL. The porous alumina membrane accommodated in the Teflon cell, was immersed in the polymer solution and left for incubation for two weeks.[3] The time needed for the adsorption process to come to saturation was determined with the use of FTIR spectroscopy (see Fig. 4). After the adsorption process, the flow rate was measured again with the method described above. The variation of the flow rate with the 4th power of pore diameter makes the system very sensitive to the hydrodynamic thickness determination of the brush. The decrease of the pore diameter is much more pronounced in good solvent, which is in good agreement with a brush swelling (see Fig. 5).
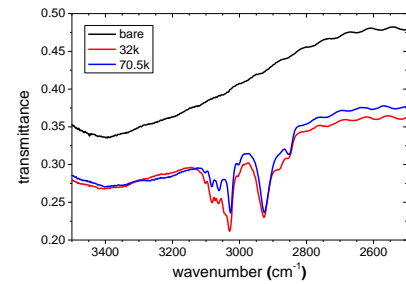

Fig. 4: *FTIR transmission spectra of the PAM before (black) and after the absorption of PS-PEO 32k (red), PS-PEO 70.5k (blue).*
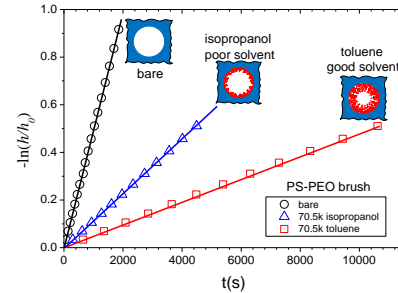

Fig. 5: *Plot of -ln(h/h_0) vs. time diagram for the flow of toluene through bare porous alumina membrane (black,) and for flow of isopropanol (blue) and toluene (red) through porous alumina membrane in which the polymer brush of PS-PEO with molecular weight 70.5k has been formed.*

By subtracting the pore radius obtained from the flow experiment through the bare membrane and the one from the membrane with the adsorbed copolymer, one can calculate the brush thickness. This was found to be 19nm for PS-PEO 32k and 51nm for PS-PEO 70.5k in toluene (good solvent). The above result coincides with results from neutron reflectivity experiments on a flat surfaces.[4] The reversible switching behavior of the surface properties was confirmed as both polymeric films reverted back to their original morphology when the system passed sequentially from good to poor solvent and vice versa.

CONCLUSIONS:

Obviously, the polymer brush chain extents when its' environment is a good solvent (toluene) thus the pore radius and consequently the flow rate decreases, while in theta solvent (isopropanol) the brush shrinks. The radial geometry of the channel doesn't induce any spatial restrictions for the brush to extent. The thickness of the polymer brush can accurately be determined in different kind of solvents. In comparison to other experimental methods like neutron reflectivity where large scale facilities are needed, the proposed method based on Poiseuille's flow is simple and versatile for the study of the conformations of polymer brushes.

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