

Polymer Brushes Make Nanopore Filter Membranes Size Selective to Dissolved Polymers

Hyun-Su Lee and Lynn S. Penn*

Department of Chemistry, Drexel University, Philadelphia, Pennsylvania 19104

Received September 2, 2009; Revised Manuscript Received December 8, 2009

Ceramic (aluminum oxide) nanoporous filter membranes, resistant to both aqueous and organic solvents, have numerous applications in the filtration of mobile phases. These include removal of particles from solvents, removal of virus particles from blood,¹ and capture of microorganisms from fluid phases. As shown in Figure 1, the filter membranes contain densely packed parallel pores arranged in a honeycomb pattern and passing completely through the thickness of the membrane. The monodisperse diameters of the pores confer a precise size cutoff to the membrane, allowing particles smaller than the cutoff size to pass through, while retaining all larger particles.

Dissolved linear polymers undisturbed by shear flow sweep out spherical volumes analogous to those of solid, spherical particles. However, when subjected to shear flow, these polymers can undergo a coil-to-stretch transition and pass through the nanopores of a filter membrane, even when their radii of gyration are larger than the radii of the pores.^{2–5} In this Note, we report that polymer brushes grafted to the walls and reaching the centerlines of the pores in a nanopore filter membrane render the membrane size-selective to linear polymers. We attribute this to the recently demonstrated behavior of the polymer brush as a size selective penetration barrier, as described briefly below.

A polymer brush is a layer of polymer chains, all the same length and all attached, or grafted, by one end to a surface and bathed in good solvent. The essence of a polymer brush is that the surface attachment density is sufficiently high for the chains to stretch away from the surface in response to the osmotic pressure generated within the brush. A grafted layer is deemed a brush if the distance between grafting points is less than the value computed for radius of gyration, R_g , of the brush chains if they were well separated from each other and not stretched away from the grafting surface.^{6,7} This R_g is exactly that computed for the grafted chain if it were free in good solvent and will be referred to hereafter as the “ R_g of the brush chains”. Recent work in our laboratory has shown that a moderately stretched polymer brush attached to a flat surface can act as a selective penetration barrier to free polymers in dilute solution, preventing free polymers above a certain size from penetrating the brush to reach the underlying surface.^{8–11} Specifically, when the R_g of the free chains in solution is smaller than the R_g of the brush chains, the free chains penetrate the brush completely; free polymers having R_g values larger than the R_g of the brush chains do not. This behavior was found to be quite general, i.e., for brushes and free species of various chemical structures.^{8,10,11}

The success of relative R_g as a criterion for penetration may seem surprising at first. However, a rationale based on entropy is provided by a theoretical study showing that brush chains can splay around a small incoming particle and then fill in behind the

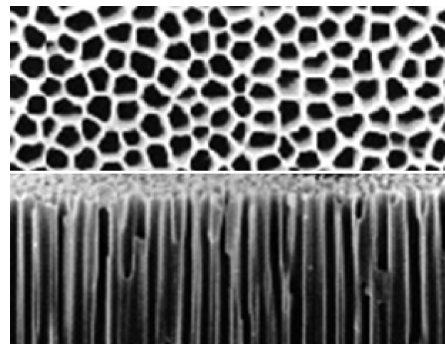


Figure 1. Top and cross-sectional views of an alumina nanopore filter membrane (reproduced from Web site of SPI Supplies) showing monodisperse and parallel nature of pores.

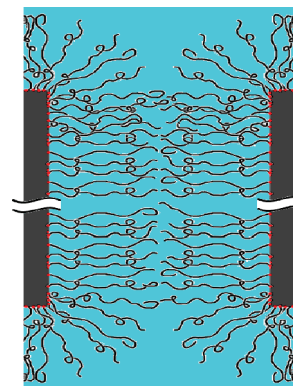


Figure 2. A single nanopore with brush grafted to pore wall and extending to the centerline.

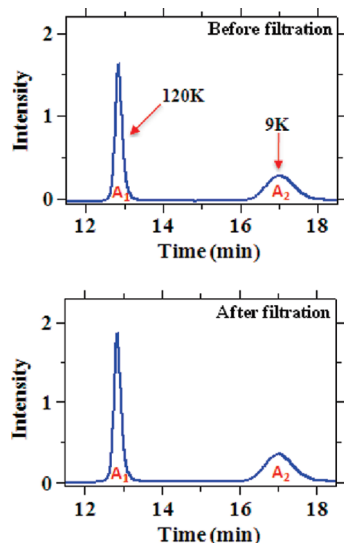
particle as it moves toward the grafting surface, gaining back the entropy lost during splaying.¹² The ability of the brush chains to splay and fill in was a function of the length of the grafted chain with respect to the particle radius, and if the particle is too large, it merely compresses the brush chains and cannot enter. Another theoretical work suggested that the increase in energy of the distorted brush chain becomes too high to permit penetration by the free species when the lateral displacement of the brush chain is on the order of its own computed radius of gyration.¹³

For the present work, we made the hypothesis that polymer brushes grafted to the walls and reaching to the centerlines of the pores, as depicted in Figure 2, would make a nanopore filter membrane size selective to polymers in dilute solution. Ceramic nanopore filter membranes (Anodisc, Whatman, Ltd.) 60 μm thick with 20 nm pore diameters were used. We used previously developed procedures to derivatize the walls of the nanopores

*Corresponding author. E-mail: lynn.s.penn@drexel.edu.

Table 1. Polymers Used in Experiments

	M_w (g/mol)	M_w/M_n	R_g (nm)	$2R_g$ (nm)
PS-NH ₂	44 574	1.02	7.81	15.62
inert-PS	9 000	1.04	3.15	6.30
inert-PS	63 000	1.03	9.40	18.80
inert-PS	120 000	1.03	13.5	27.10

**Figure 3.** Chromatograms of polymer solution before and after passage through bare filter membrane at 2.6 $\mu\text{L}/\text{min}$.

with epoxide groups and to graft monodisperse, amine-end-functionalized polystyrene chains (PS-NH₂) of 44 570 g/mol to these active sites.^{14,15} The surface attachment density, according to analogous experiments done on flat surfaces under the same conditions and analyzed by solution depletion methods,¹⁴ was 0.0450 chains/nm² ($\pm 4\%$). From this, the average distance between grafting points is 5.31 nm, which is much smaller than the R_g value of 7.81 nm listed in Table 1 for the brush chains, establishing our grafted layer as a brush.

Table 1 also provides information on the samples of monodisperse, inert-ended polystyrene (inert-PS) used as free polymer (in toluene). Values for $2R_g$ are shown for comparison with the 20 nm diameter of the nanopores. Dilute solutions of two or three distinct molecular weights were passed through both the bare and the brush-modified filter membranes. All experiments were done at two different macroscopic flow rates: 60 and 2.6 $\mu\text{L}/\text{min}$. The polymer content of the solution before and after filtration was measured by means of gel permeation chromatography with UV detection.

Figure 3 shows chromatograms of the solution before and after passage through the bare filter membrane. The two dissolved polystyrenes, 120 000 and 9000 g/mol, are represented in the chromatograms by peak areas A_1 and A_2 . Area ratios before ($A_1/A_2 = 1.44$) and after ($A_1/A_2 = 1.49$) filtration are the same within 3%, indicating no size separation was achieved. The absence of size discrimination indicates that both flow rates used exceed the critical value for the coil-to-stretch transition in the bare pores.⁴

The same solution was passed through the brush-modified filter membrane, and although no size separation was achieved at the flow rate of 60 $\mu\text{L}/\text{min}$, nearly total exclusion of the larger polymer was achieved at the lower flow rate of 2.6 $\mu\text{L}/\text{min}$. Figure 4 shows the chromatograms, in which the area ratio before filtration, $A_1/A_2 = 1.44$, was greatly reduced after filtration to $A_1/A_2 = 0.126$. Clearly, at the lower flow rate, the presence of the brush confers size selectivity to the nanopores.

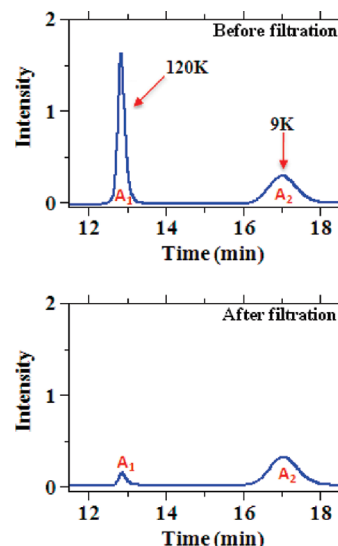
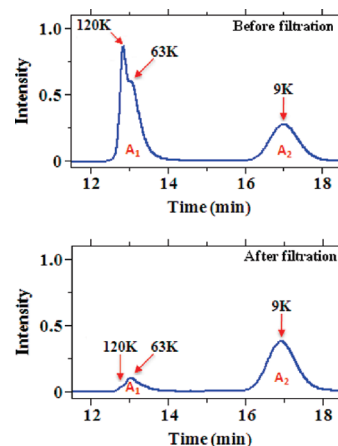
**Figure 4.** Chromatograms of solution of three polymers before and after filtration through brush-modified filter membrane at 2.6 $\mu\text{L}/\text{min}$.**Figure 5.** Chromatograms of solution of three polymers before and after filtration through brush-modified filter membrane at 2.6 $\mu\text{L}/\text{min}$.

Figure 5 shows the results for passage of a solution containing three molecular weights of polystyrene through the brush-modified filter membrane. The area ratio before filtration, $A_1/A_2 = 1.66$, was greatly reduced after filtration to $A_1/A_2 = 0.308$, indicating exclusion of the larger two polymers (120 000 and 63 000 g/mol) from passage through the filter. Closer examination of the compound peak due to these two polymers shows that the polymer of 120 000 g/mol was filtered from solution more effectively than was the polymer of 63 000 g/mol. This suggests that brush-modified filter membranes could be used to decrease the molecular weight dispersion in monodisperse polymer samples.

In conclusion, we found that grafting of brushes to the walls of the straight, cylindrical nanopores conferred size selectivity to nanopore filter membranes. Our future research will focus on creating brushes of different chemical structures inside monodisperse nanopores of different diameters for use with a wider variety of solvents and dissolved species. We will also determine the flow rates above which size discrimination disappears for each type of brush and solvent.

References and Notes

- (1) Zhao, Y.; Sugiyama, S.; Miller, T.; Miao, X. *Expert Rev. Med. Devices* **2008**, *5*, 395–405.

- (2) DeGennes, P. G. *J. Chem. Phys.* **1974**, *60*, 5030–5042.
- (3) Xu, J.; Zhu, Z.; Luo, S.; Wu, C.; Liu, S. *Phys. Rev. Lett.* **2006**, *96*, 027802.1–027801.4.
- (4) Ge, H.; Jin, F.; Li, J.; Wu, C. *Macromolecules* **2009**, *42*, 4400–4402.
- (5) Jin, F.; Wu, C. *Phys. Rev. Lett.* **2006**, *96*, 237801.1–237801.4.
- (6) Alexander, S. *J. Phys. (Paris)* **1977**, *38*, 983–987.
- (7) De Gennes, P. G. *Macromolecules* **1980**, *13*, 1069–1075.
- (8) Huang, H.; Cammers, A.; Penn, L. S. *Macromolecules* **2006**, *39*, 7064–7070.
- (9) Penn, L. S.; Huang, H. *Macromolecules* **2008**, *41*, 2747–2748.
- (10) Lee, H.; Penn, L. S. *Macromolecules* **2008**, *41*, 8124–8129.
- (11) Lee, H.; Penn, L. S. *Langmuir* **2009**, *25*, 7983–7989.
- (12) Steels, B. M.; Koska, J.; Haynes, C. A. *J. Chromatogr., B* **2000**, *743*, 41–56.
- (13) Kim, J. U.; O'Shaughnessy, B. *Macromolecules* **2006**, *39*, 413–425.
- (14) Huang, H.; Penn, L. S.; Quirk, R. P.; Cheong, T. H. *Macromolecules* **2004**, *37*, 516–523.
- (15) Huang, H.; Penn, L. S. *Macromolecules* **2005**, *38*, 4837–4843.