Polymeric nanopore membranes for hydrophobicity-based separations by conformal initiated chemical vapor deposition (iCVD) – Supporting information

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A schematic of iCVD equipment and mechanism

In initiated CVD (iCVD) an initiating species, such as tert-butyl peroxide, and a chain growth monomer are simultaneously introduced into the reactor, held at low vacuum, through the vapor phase. Liquid species are placed in heated jars and metered into the reactor by needle valves or mass flow controllers. Inside the iCVD reactor chamber (Figure S1, top), heated filament wires are suspended a few centimeters above the substrate. The modest temperature of the filaments (~250^{o}C) results in selective formation of free radicals from the initiator without the decomposition of the monomer. Adsorption and polymerization then proceed on a cooled substrate (Figure S1, bottom). Since the substrate is kept at low temperatures (20-50^{o}C) sensitive substrates can be

coated easily. In the absence of an initiator species, film growth is negligible. The iCVD method has proved exceptionally versatile for chain growth polymers including PTFE, acrylates, methacylates, styrenes, vinylpyrrolidone and maleic anhydride.

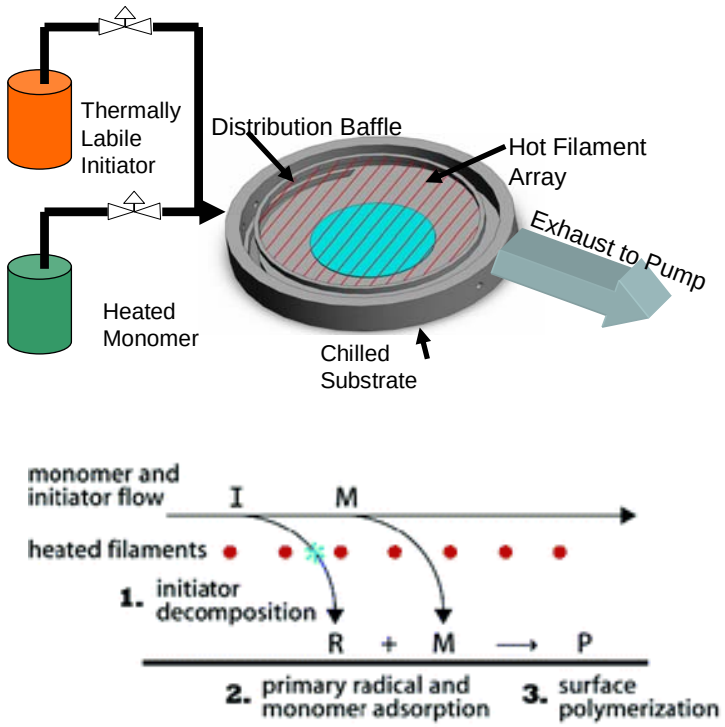


Figure S2. Schematic of iCVD equipment (top) and general deposition mechanism (bottom).

FTIR spectra of films

FTIR spectra of pDVB, pPFDA and two layer films are given in Figure S2. Green shaded areas indicate peaks characteristic to pPFDA. The peak around 1150 cm^{-1} corresponds to C-F bonds in the fluorinated polymer. The peak around 1200 cm^{-1} arises from the ester groups in the acrylate. Red shaded areas correspond to peaks characteristic to pDVB. Disubstituted benzene rings lead to vibrations in the 800-900 cm^{-1} range and

the several peaks in the 1450-1600 cm^{-1} range. The presence of both peak groups in the two layer film indicates the successful deposition of pPFDA.

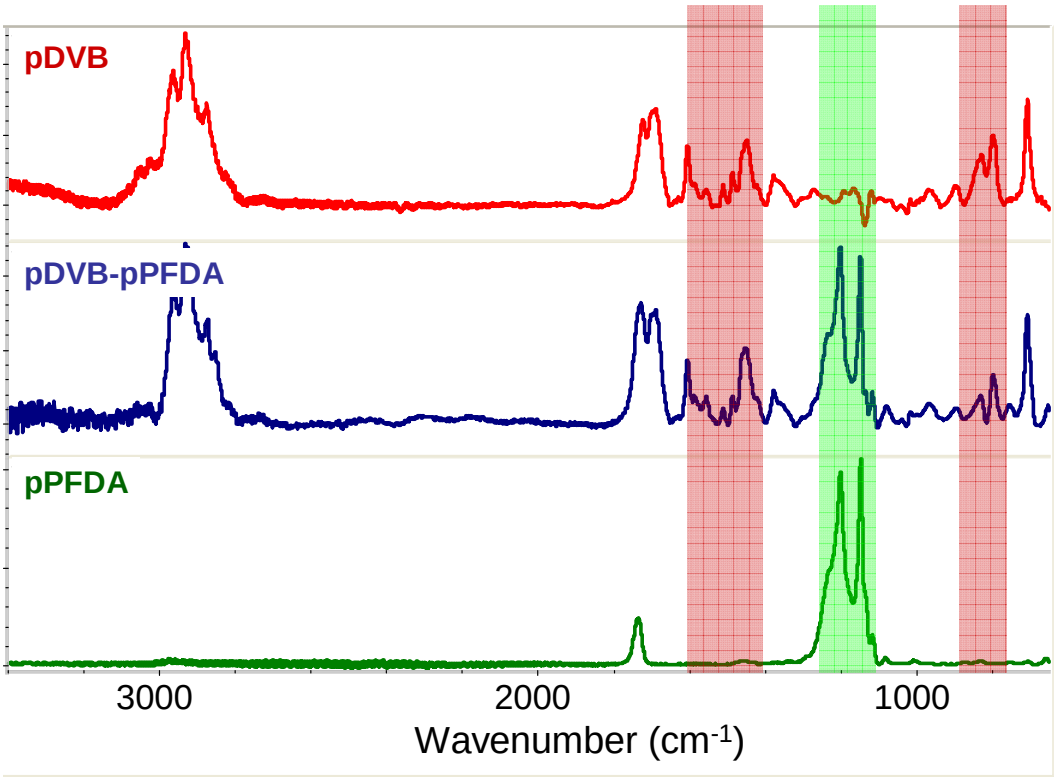


Figure S2. FTIR spectra of pDVB, pPFDA and two layer pDVB-pPFDA films. Green shading marks peaks characteristic of pPFDA, red shading indicates peaks characteristic of pDVB.

Derivation of monomer concentration profiles within membrane pores

A schematic of the cross-section of a membrane pore during deposition and the mass transport processes that occur is given in Figure S3. The pore has a radius of r, and the membrane thickness is L. It is assumed that the concentration of the monomer within the pore c_M is only a function of z, distance from the membrane surface, and is uniform in the radial direction.

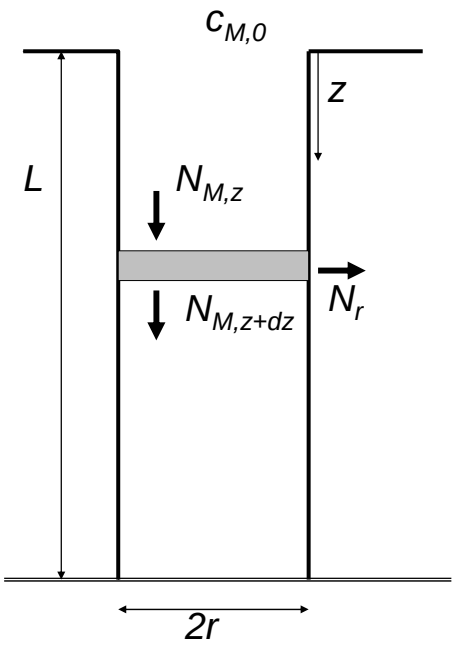


Figure S3. Schematic of the mass transport within a membrane pore during deposition.

A mass balance can be performed at a circular slice along the pore of thickness *dz*. The monomer flux due to diffusion N_M is given by

$$N_M = -D\frac{dc_M}{dz}$$

where *D* is the diffusion coefficient. Monomer flux due to the polymerization reaction N_R is given by:

$$N_R = \nu$$

v is the deposition reaction rate in mol/m^2.s. The mass balance is then

$$\pi r^2 (N_M\big|_z - N_M\big|_{z+dz}) - 2\pi r N_R dz = 0$$

When these equations are combined, divided by $2\pi r$ and differentiated, the following differential equation can be obtained:

$$\frac{Dr}{2}\frac{d^2 c_M}{dz^2} - \nu = 0$$

It is preferable to convert this equation into dimensionless form. We can define

$$\psi = c_M / c_{M,0}$$
$$\lambda = z / L$$

where ψ is the dimensionless monomer concentration, and λ is the normalized pore depth.

For the free radical polymerization process, v can be given by:[1]

$$\nu = h_{ml} k_P c_{R*} c_{M*}$$

where h_{ml} is the monolayer thickness, k_P is the polymerization propagation constant, c_{R*} is the concentration of active radicals on the pore surface, and c_{M*} is the concentration of monomers on the pore surface.

In this study, it is assumed that the concentration of active radicals on the pore surface is uniform and identical to that on a flat surface. While in reality there is a variation of this parameter through the pore length, as quantified by the "sticking probability" as studied in previous publications,[2] the objective of this analysis is to isolate the effect of monomer consumption and diffusion on conformality. We will also assume that, given the low partial pressures of monomers used, the surface concentration of the monomer is directly proportional with the gas phase concentration. Hence,

$$c_{M*} = \frac{CRT}{V_M P_{sat}} c_M = K' c_M$$

This makes v directly proportional with c_M.

$$\nu = h_{ml} k_P c_{R*} K' c_M$$

Therefore, the dimensionless parameter ψ is also a normalized reaction rate:

$$\frac{v}{v_0} = \frac{c_M}{c_{M,0}} = \psi$$

and the differential equation becomes

$$\frac{Drc_{M,0}}{2L^2}\frac{d^2\psi}{d\lambda^2} - v_0\psi = 0$$

Rearranging,

$$\frac{d^2\psi}{d\lambda^2} - \frac{2L^2 v_0}{Drc_{M,0}}\psi = 0$$

Thiele modulus is defined as the square root of the ratio of the maximum reaction rate to the diffusion rate.[3] Maximum reaction rate is achieved when there is no concentration gradient, and occurs on the pore walls.

Max. reaction rate $= 2\pi rLv_0$

Average diffusion rate is given by

$$\textit{Ave. diffusion rate} = \pi r^2 D\frac{c_{M,0}}{L}$$

Thiele modulus Φ can be calculated from

$$\Phi^2 = \frac{2\pi rLv_0}{\pi r^2\frac{Dc_{M,0}}{L}} = \frac{2L^2 v_0}{rDc_{M,0}}$$

The second degree linear homogeneous differential equation can be solved with the following boundary conditions:

$$BC1: \lambda = 0 \rightarrow \psi = 1$$

$$BC2: \lambda = 1 \rightarrow \frac{d\psi}{d\lambda} = 0$$

As the final result, the concentration profile is given by the following equation

$$\psi = \frac{e^{\Phi\lambda} + e^{2\Phi-\Phi\lambda}}{1+e^{2\Phi}}$$

To determine Φ, several parameters need to be determined. For the membranes studied, r is 25 nm, and L is 20 μm. $c_{M,0}$ can be estimated based on the ideal gas law.

$$c_{M,0} = \frac{P_M}{RT}$$

where P_M is the partial pressure of the monomer, R is the gas constant, and T is the temperature.

v_0 can be deduced from the deposition rate measured during iCVD. For iCVD of PFDA, a 100 nm film was deposited in 20 minutes. Given the molecular weight of PFDA (518 g/mol) and the density of pPFDA (around 1.08 g/cm^3),[4] this corresponds to a deposition rate of 1.7 x 10^{-7} mol/m^2.s. A similar calculation can be performed for DVB, for which a 110 nm film was deposited in 170 minutes. Given a molecular weight of 130 g/mol and a polymer density of 1.05 g/cm^3,[1] the deposition rate was 8.7 x 10^{-8} mol/m^2.s.

Within the pores, whose diameter is significantly shorter than the mean free path of the molecules at this pressure, Knudsen regime is in effect. Knudsen diffusivity in a cylindrical pore is given by:[5]

$$D = \frac{2}{3} r \sqrt{\frac{8RT}{M}} \qquad (5)$$

where M is the molecular weight of the monomer.

Table S1 includes the basic parameters used in this calculation as well as the Thiele modulus, for the two polymer systems described in this study.

It should be noted that a similar Thiele modulus can also be calculated for the initiator, to examine the comparative effects. For this calculation, it is assumed that the monomer

concentration within the pore length is uniform, at $c_{M,0}$. In this case, if an Eley-Rideal type reaction mechanism is assumed,[2] the reaction rate on the pore walls becomes

$$v_R = 2\pi r L h_{ml} k_i K' c_{M,0} c_{R,0}$$

where h_{ml} is the monolayer thickness, $c_{R,0}$ is the bulk radical concentration, and k_i is the initiation rate constant. Then,

$$\textit{Max. reaction rate} = 2\pi r L h_{ml} k_i c_{M,0} c_{R,0}$$

$$\textit{Ave. diffusion rate} = \pi r^2 D \frac{c_{R,0}}{L}$$

Thiele modulus Φ can be calculated from

$$\Phi_R^2 = \frac{2\pi r L h_{ml} k_i K' c_{M,0} c_{R,0}}{\pi r^2 \frac{D c_{R,0}}{L}} = \frac{2L^2 h_{ml} K' c_{M,0}}{rD}$$

This value was calculated based on the reaction and molecular parameters (Table S1) and was found to be 0.23 and 0.27 for PFDA and DVB depositions, respectively. This value is lower than both monomer-based Thiele modulus values, which implies that in this case, conformality is limited by monomer consumption rather than initiating radical consumption.

Table S1. Parameters used in the calculation of concentration profiles

Parameter	**Unit**	**PFDA**	**DVB**
L	m	2.0×10^{-5}	2.0×10^{-5}
R	m	2.5×10^{-8}	2.5×10^{-8}
T	K	313	303
P_M	Pa	1.67	10.7
$c_{M,0}$	mol/m^3	6.4×10^{-4}	4.2×10^{-3}
M	g/mol	518	130
D	m^2/s	1.33×10^{-6}	2.62×10^{-6}
N	mol/m^2s	1.74×10^{-7}	8.70×10^{-8}
Φ	-	2.55	0.50
h_{ml}[a]	m	2.36×10^{-9}	1.46×10^{-9}
C[a]	-	3.3	2.54
V_M	m^3/mol	3.35×10^{-4}	1.41×10^{-4}
P_{sat}[a]	Pa	22.53	120
K'	-	1.14×10^{6}	3.77×10^{5}
k_i[b]	$m^3/mol.s$	5.72	5.72

[a] BET constants and saturation pressure for PFDA were taken from Gupta *et al.*[4] Values were DVB were assumed to be similar to that for ethyl acrylate, a monomer with similar molecular size, and taken from Lau *et al.*[6]

[b] Assumed to be the same as that for the polymerization of ethyl acrylate.[6]

Table S2. Structures and chemical properties of solutes used in diffusion experiments

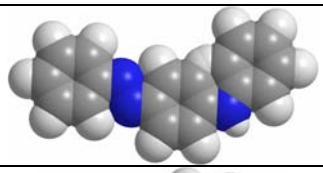
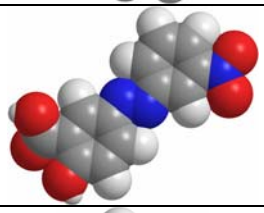
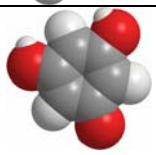
Name	3D structure	Solvent excluded volume (Å^3)	Total polar surface area (tPSA) (Å^2)
PADPA		215.647	36.75
AY		197.176	134.06
Mes		122.077	0
Phl		90.42	60.69

Image analysis and pore size distribution of PC track-etched membranes

The commercial PC track-etched membranes indicate a pore size of 0.05 µm, or 50 nm. To confirm this assumption, scanning electron microscopy (SEM) was performed on the membrane surface. The membranes were sputter-coated with Au/Pd and an accelerating voltage of 5 kV was used. Five images, acquired at different locations on the membrane surface at 60000x magnification, were used for pore size determination. ImageJ software was used to determine the pores by setting a contrast threshold followed by "particle size analysis" tools. Pore smaller than an area of 100 nm^2 were ignored as they reproducibly corresponded to roughness effects rather than actual pores. Three samples of the SEM images used are given in Figure S4, as well as a mark-up of the identified "pores" and a

drawing of the pore outlines as a result of image analysis. Figure S5 shows the pore size distribution. The mean pore size of the membrane was calculated to be 55 nm, whereas the median pore size was 48 nm. These indicate that assuming an average pore size of 50 nm for the PC membrane is acceptable for further estimating pore sizes of iCVD coated membranes.

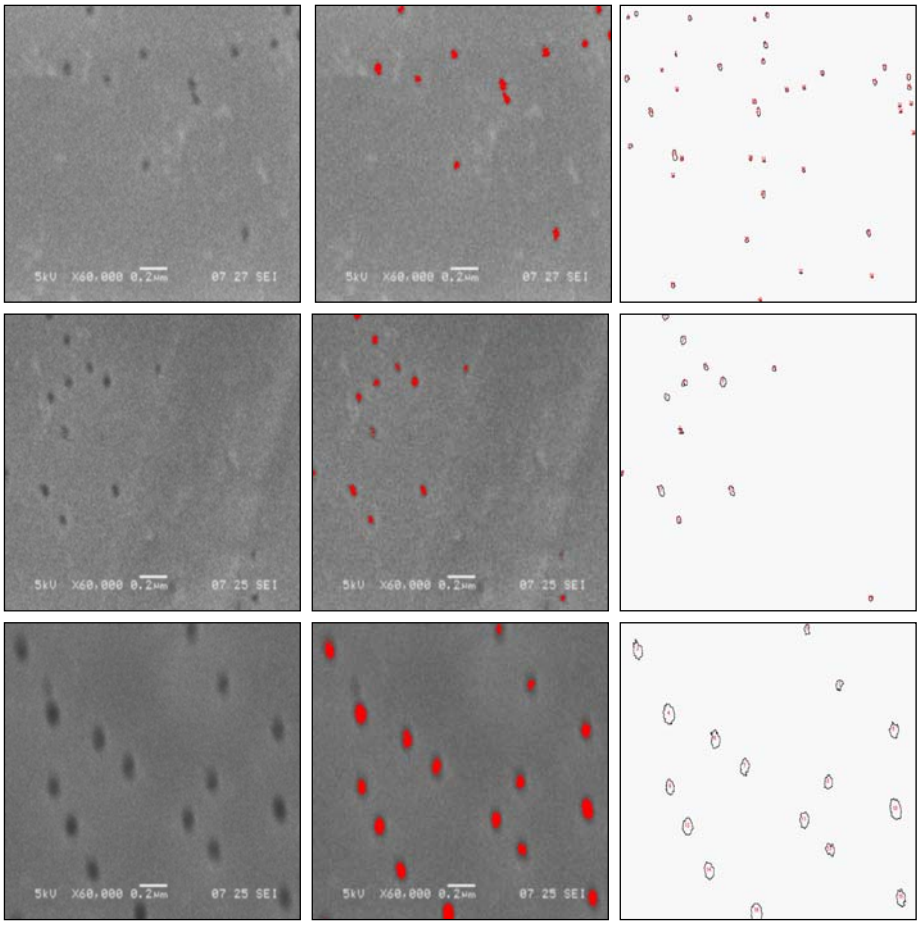


Figure S4. Image analysis of SEM micrographs of PC membrane surface. Three sample micrographs are given here, five were used for the complete analysis. Left column shows the unmodified micrographs. Pores are labeled in red in the middle column, and a drawing of the detected pores is given in the rightmost column.

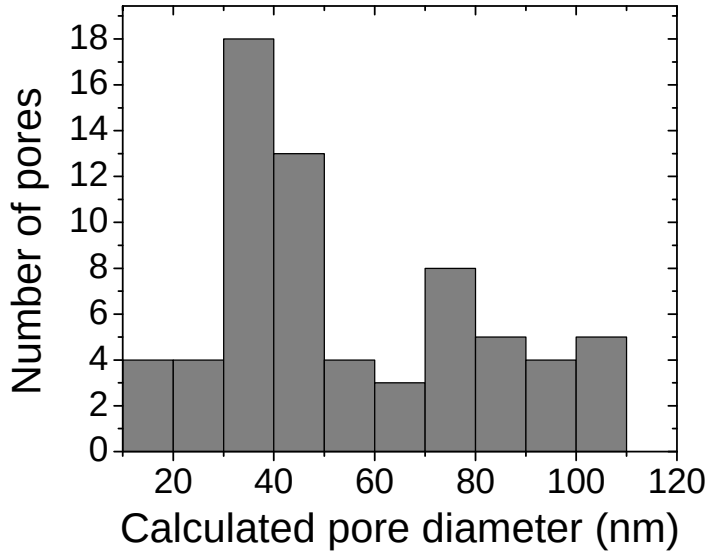


Figure S5. Histogram of the distribution of pore diameters for the uncoated PC membrane.

References

1. Odian, G. G., *Principles of polymerization*. 4th ed.; Wiley-Interscience: Hoboken, N.J., 2004; p xxiv, 812 p.
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4. Gupta, M.; Gleason, K. K., Initiated chemical vapor deposition of poly(1H,1H,2H,2H-perfluorodecyl acrylate) thin films. *Langmuir* **2006,** 22, (24), 10047-10052.
5. Belfiore, L. A., *Transport phenomena for chemical reactor design*. J. Wiley: New York, 2003; p xxv, 884 p.
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