# Electronic Supplementary Information (ESI)

**Ion Track Etching of Polycarbonate Membranes Monitored by *In Situ* Small Angle X-ray Scattering**

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## 1. Radius change during image acquisition

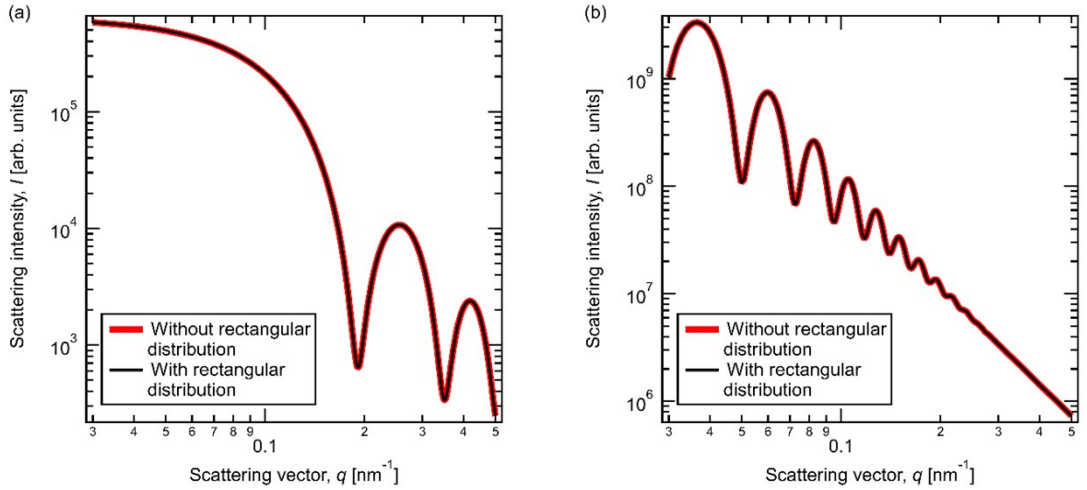


**Fig. S1** Calculated 1D scattering intensity of nanopores with radii of (a) 20 nm and (b) 140 nm with a relative SD of 4 % without (red) and with (black) a rectangular distribution with a width of 1 nm.

As between the start and the end of the SAXS image acquisition, which takes 6.8 s, the nanopores continue to etch, the scattering intensity changes. As the pore radius increases linearly during etching, we can describe this effect by assuming a rectangular radius distribution. The rectangular distribution and the Gaussian distribution are convoluted. The maximum size change we observed during one image acquisition is 1 nm. To demonstrate that this effect is negligible, we calculated the 1D scattering intensity accounting for the size change by convoluting the Gaussian radius distribution with a rectangular distribution $\mathrm{rect}(x) = \Pi(x)$ with the width $\sigma_{rect}$:

$$rect\left(\frac{R-r}{\sigma_{rect}}\right) = \Pi\left(\frac{R-r}{\sigma_{rect}}\right) = \begin{cases} 0, \ if \left|\frac{R-r}{\sigma_{rect}}\right| > \frac{1}{2} \\ 1, \ if \left|\frac{R-r}{\sigma_{rect}}\right| < \frac{1}{2} \end{cases} .\#(S1)$$

In Fig. S1, we show the calculated 1D scattering intensity for radii of 20 nm and 140 nm, a relative SD of 4 % with and without a rectangular distribution with a width of 1 nm. These parameters are obtained from the etching of at 6 M, which shows the highest etch rate and lowest relative SD of all measurements. The influence of the rectangular contribution is larger with higher etch rates and lower relative SDs, so this is the worst-case scenario we expect during our *in situ* measurements. As can be seen, the rectangular distribution has a negligible effect on the scattering intensity, and hence we omit this parameter for the fitting as it greatly reduces the calculation time.

## 2. Additional *in situ* experiments

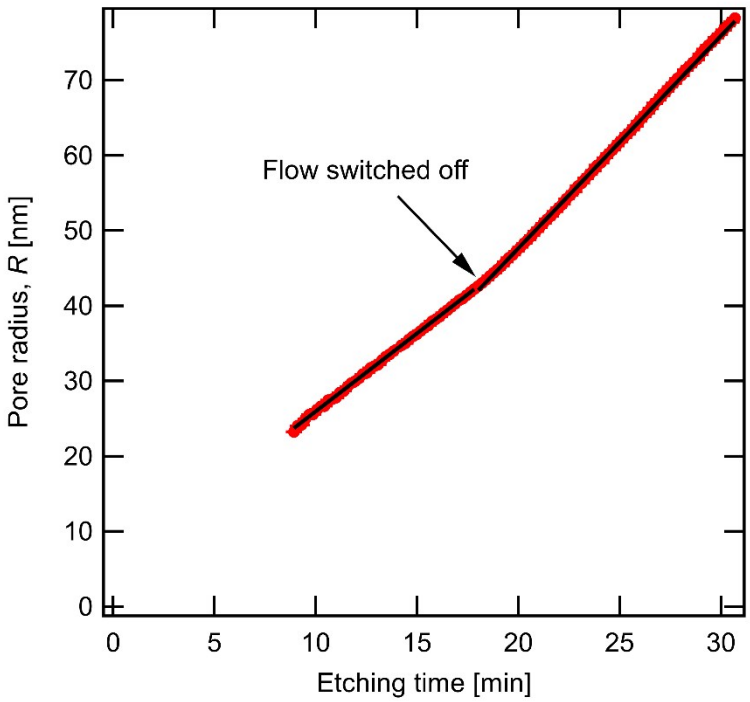


**Fig. S2** Pore radii of nanopores as a function of time during etching with 3 M NaOH at 45.5°C. After approximately 18 min, the flow of etchant was switched off, which caused the temperature to increase to 47.6°C and results in an increase of the radial etch rate.

As described, the PID controller keeps the temperature of the etching cell constant and not the etchant temperature. In our usual *in situ* experiments, we etch with a constant supply of etchant using a syringe pump system. The cold etchant that is guided through the aluminum housing acts as a coolant, and the heating power is increased compared to an empty cell to keep the temperature of the setup constant. With a constant flow of 1 ml $min^{-1}$ on each side of the membrane, the temperature of the etchant at the sample position is 45.5°C. As the flow is switched off, the temperature of the etchant increases. After about one minute, the temperature has stabilized again at 47.6°C. This is reflected in the etch rate (see Fig. S2), which increases from $V_r = (2.07 \pm 0.11)$ nm $min^{-1}$ to $V_r = (2.82 \pm 0.15)$ nm $min^{-1}$. These values are in great agreement with the radial etch rates used to determine the activation energy (see Fig. 5b). This demonstrates the sensitivity of our setup to the measurement conditions.

**3. *Ex situ* experiments**

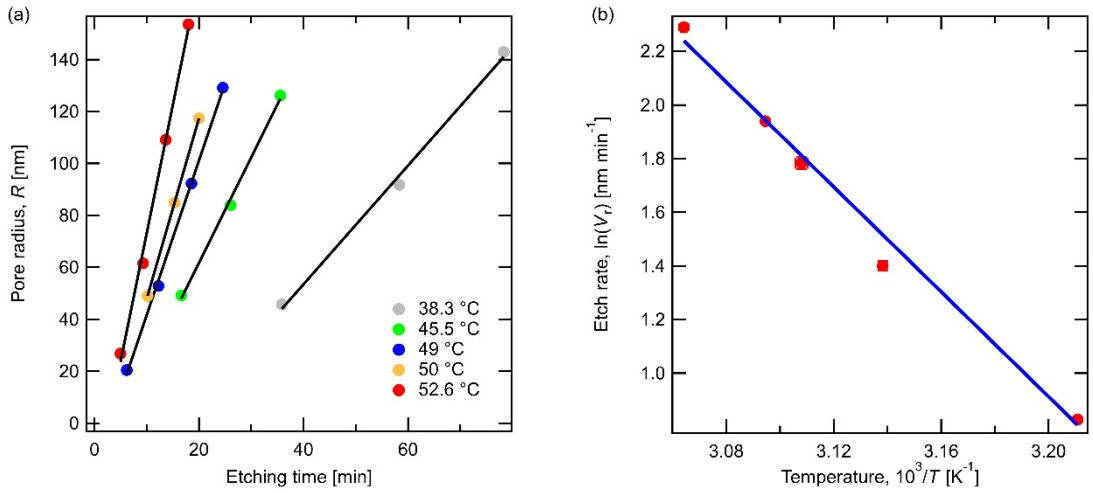


**Fig. S3** (a) Pore radii of nanopores as a function of time during etching at 38.3°C (grey), 45.5°C (green), 49°C (blue), 50°C (orange), and 52.6°C (red). (b) Arrhenius plot (blue line) of the radial etch rates deduced from (a).

We conducted *ex situ* etching experiments of polycarbonate foils using a glass beaker on a hotplate. To compare these results to the *in situ* experiments, we etched the foils at the same temperatures (and at 50°C) and at the same molarity of 3 M. These experiments enabled us to calculate the radial etch rates and the activation energy of this process, which amounts to $E_r = (0.89 \pm 0.04)$ eV, as presented in Fig. S3. The average standard deviation (SD) for all membranes amounts to $\sigma = (3.8 \pm 0.9)$ nm, as shown in Fig. S4. It is apparent that the SD is independent from the temperature or the pore radius, as most values are close to the average SD. The etch rates and SDs for each temperature are listed in Table S1.

**Table S1** Radial etch rates $V_r$ and SDs $\sigma$ for nanopores at different temperatures $T$

| Temperature, $T$ [°C] | 38.3 | 45.5 | 49 | 50 | 52.6 |
|---|---|---|---|---|---|
| Etch rate, $V_r$ [nm min$^{-1}$] | $2.29 \pm 0.02$ | $4.06 \pm 0.07$ | $5.95 \pm 0.14$ | $6.95 \pm 0.03$ | $9.87 \pm 0.11$ |
| SD, $\sigma$ [nm] | $3.9 \pm 1.5$ | $3.0 \pm 0.7$ | $3.7 \pm 0.6$ | $4.3 \pm 0.1$ | $4.0 \pm 1.1$ |

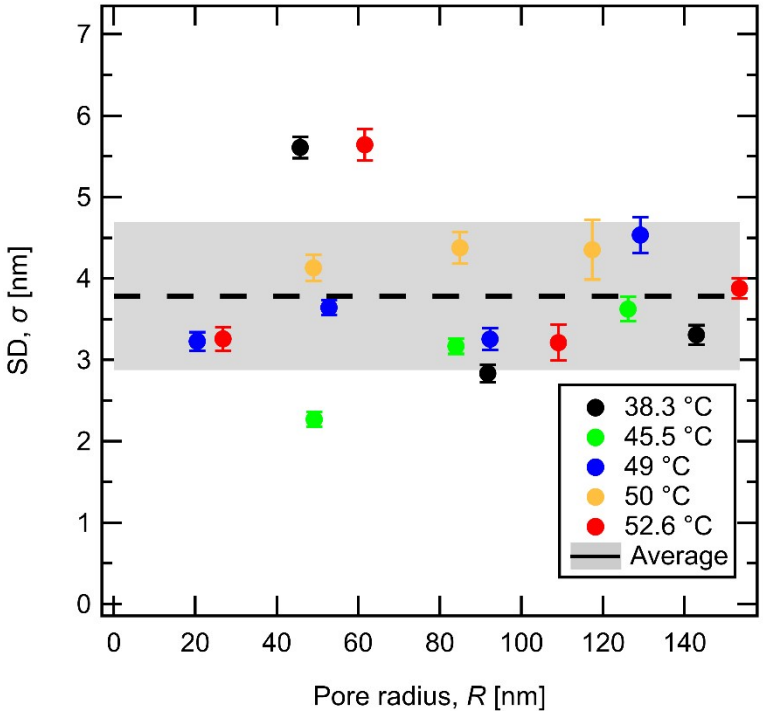


**Fig. S4** SDs of nanopores as a function of the pore radius during etching at 38.3°C (black), 45.5°C (green), 49°C (blue), 50°C (orange), and 52.6°C (red). The dashed black line represents the average SD with its uncertainty being the grey band.

## 4. SD comparison between etching, wet and dry state of the membrane

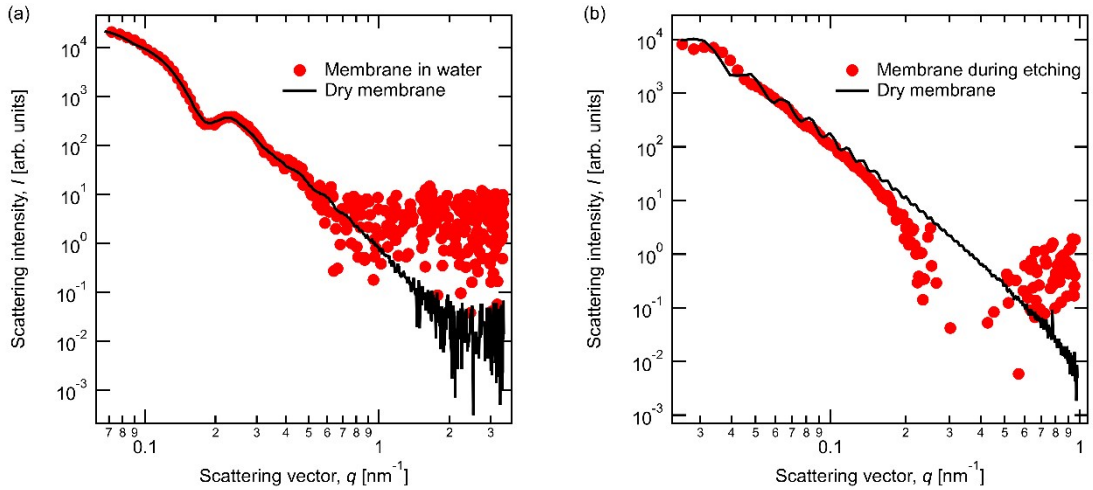


**Fig. S5** Scattering intensities of etched nanopores in a dry membrane (black line) and (a) immersed in water, and (b) during etching (red dots).

To determine what physical effect is described by the SD, we compared the scattering intensities of nanopores between the dry state and immersed in water (Fig. S5a) and between the dry state and during etching (Fig. S5b). It is apparent that just liquid does not change the scattering intensity of the nanopores. Only during etching, the oscillations are greatly dampened, which indicates an increased SD. The shift of the oscillation of the membrane in the dry state compared to etching towards smaller $q$-values indicates an increased radius. This is because during the last SAXS image acquisition during and rinsing and drying, the membranes continue to etch. The increased scattering intensity in the wet state at large scattering vectors is caused by an increased scattering background of the liquid. We conclude that the difference in SD between the three states is caused by the etching process.

## 5. Influence of the etching setup

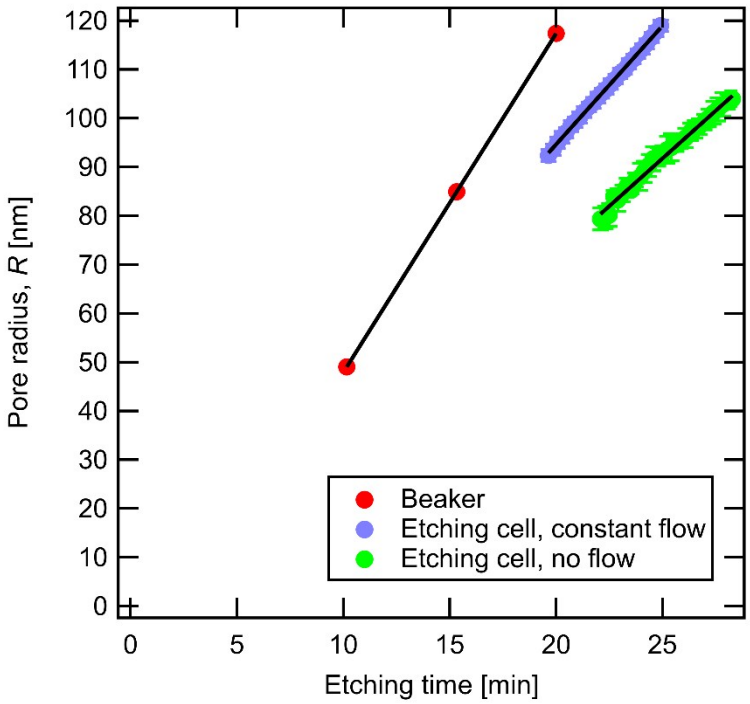


**Fig. S6** Pore radii as a function of time during etching in a beaker on a hotplate (red), in the etching cell with (blue), and without a constant flow of etchant (green).

To determine the influence of the etching setup on the etching process, we etched a polycarbonate foil (3 M NaOH, 50°C) in a beaker on a hotplate, in the etching cell with a constant flow of 1 ml $min^{-1}$ of etchant, and without a flow. The radius development over time is presented in Fig. S6. The radial etch rates are 7.0, 4.9 and 3.9 nm $min^{-1}$, respectively. We believe that the difference in etch rates is caused by the transport of new etchant into the nanopores, and the removal of etching products from the nanopores.

## 6. Video of the in situ etching process

We have attached a video of the 2D SAXS patterns of the *in situ* etching of the polycarbonate foil presented in Fig. S2. At the beginning, upon injection of the etchant, the scattering intensity drops due to the higher X-ray absorption of NaOH than air. Then, the scattering intensity starts to increase again, due to the growing volume of the nanopores. After a while, oscillations in the scattering intensity become visible. They move from the outside (large $q$-values) towards the center (small $q$-values) of the scattering pattern. This indicates radial growth of the nanopores.