Supporting information for the manuscript: "How Much Do Ultra-Thin Polymers With Intrinsic Microporosity Swell In Liquids?"

Wojciech Ogieglo,[†] Bader Ghanem,[‡] Xiaohua Ma,[‡] Ingo Pinnau,[*,‡] and Matthias Wessling[*,†]

[†]*DWI - Leibniz Institute for Interactive Materials, Forckenbeckstr. 50, 52074 Aachen, Germany*

[‡]*King Abdullah University of Science and Technology (KAUST), Advanced Membranes and Porous Materials Center (AMPMC), Al-Jazri Building 4, Thuwal, 23955-6900, Kingdom of Saudi Arabia*

E-mail: ingo.pinnau@kaust.edu.sa; manuscripts.cvt@avt.rwth-aachen.de

Phone: +966 (0) 12-808-2406; +49 241 80 95488

Chemical structures of the used PIMs

Chemical structures of both PIMs used in this study are shown in Figure S1.

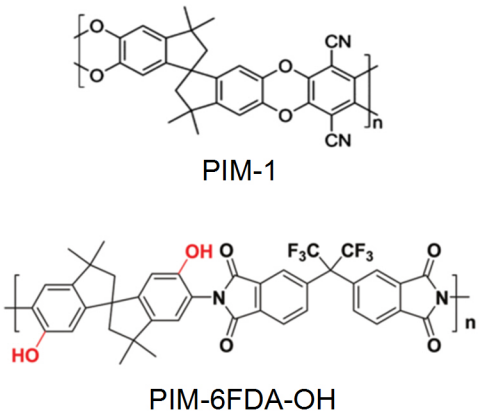

Figure S 1: Chemical structures of PIM-1 and PIM-6FDA-OH used in this study.

Calculation of the refractive index of the matrix according to Bondi and Krevelen

According to Krevelen (Properties of Polymers, 4th Edition, 2009, Chapter 10: Optical properties) the refractive index of a polymer can be calculated from a contribution of molar refractions and molar volumes of various chemical groups as (according to Lorentz-Lorenz relationships):

$$n = \left(\frac{1 + 2 \cdot \frac{R_{LL}}{V}}{1 - \frac{R_{LL}}{V}}\right)^{0.5} \tag{1}$$

The R_{LL} values for many chemical groups can be found in Table 10.4 of the cited booka and

can be summed up to produce molar refraction of a monomer.

The group molar volume contributions, V can be calculated according to Bondi (Van der Waals Volumes and Radii, The Journal of Physical Chemistry, 1964, 68, 3, Tables I through XVIII) by also by simple summation.

The calculated R_{LL} values for PIM-1 and PIM-6FDA-OH are 127.058 and 170.206, respectively and the V values are 259.69 and 381.7, respectively. The molar volume contributions have to be then multiplied by a factor 1.3 to account for the difference between the actual molar volume and the hard core volume of the polymer chains, to yield 337.597 and 496.21.

When substituted to the above equation, the refractive indeces of dense matrix are 1.676 for PIM-1 and 1.602 for PIM-6FDA-OH. Later, as described in the manuscript, these values can be substituted to Brugemann EMA to yield the excess free volume fractions.

Optical properties of PIM-1 and PIM-6FDA-OH

Multi-angle spectroscopic ellipsometry allows determination of the complex dielectric function of ultra-thin films. Figure S2 shows the refractive index and extinction coefficient of the annealed (200 °C, 24 hours, vacuum) ∼100 nm films extracted using a Kramers-Kronig consistent B-spline model. The data is in good agreement with literature values and serves to confirm the polymer structures. In particular the extinction coefficient for PIM-1 displayed a characteristic peak around 420 nm. Both polymers show similar peaks in the extinction coefficient just below 300 nm, which can be attributed to the aromatic rings. The refractive indices (at 632.8 nm) of annealed films were on the order of 1.65 for PIM-1 and 1.6 for PIM-6FDA-OH and are both significantly larger than those of the freshly rejuvenated samples used for swelling experiments (1.50 and 1.52, respectively). This is a clear effect of

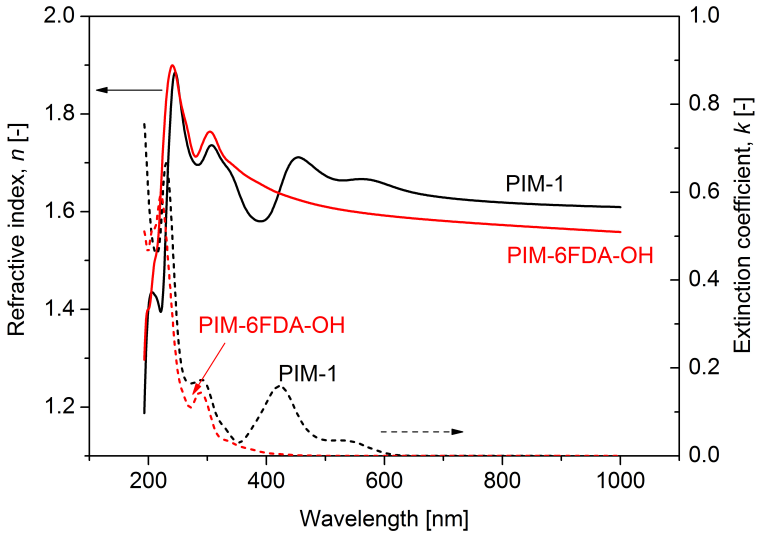

Figure S 2: Optical properties of 100 nm PIM-1 and PIM-6FDA-OH films deposited on silicon wafers, after preparation the samples were annealed at 200 °C for 24 hours under vacuum.

structure densification as a result of physical aging. Remarkably, the refractive index of the aged PIM-1 film was larger than that of PIM-6FDA-OH, whereas the opposite is true for the freshly rejuvenated samples. This effect is probably a result of much more pronounced aging of PIM-1 as compared with PIM-6FDA-OH.