Supporting Information for:

Functionalized nanoporous membranes from reactive triblock terpolymers

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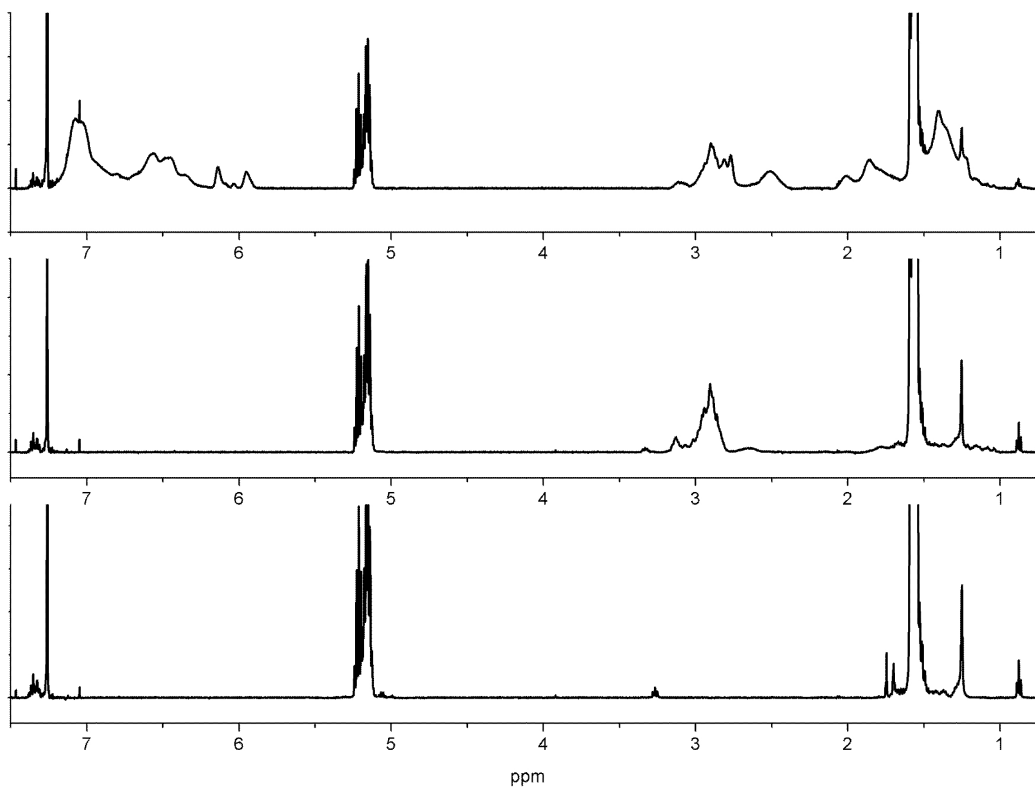*To whom correspondence should be addressed: hillmyer@umn.edu

Figure S1. ^{1}H NMR spectra showing the progressive addition of blocks starting with PLA functionalized with the RAFT agent (bottom), PLA-PDMA (middle) and PLA-PDMA-PNS (top).
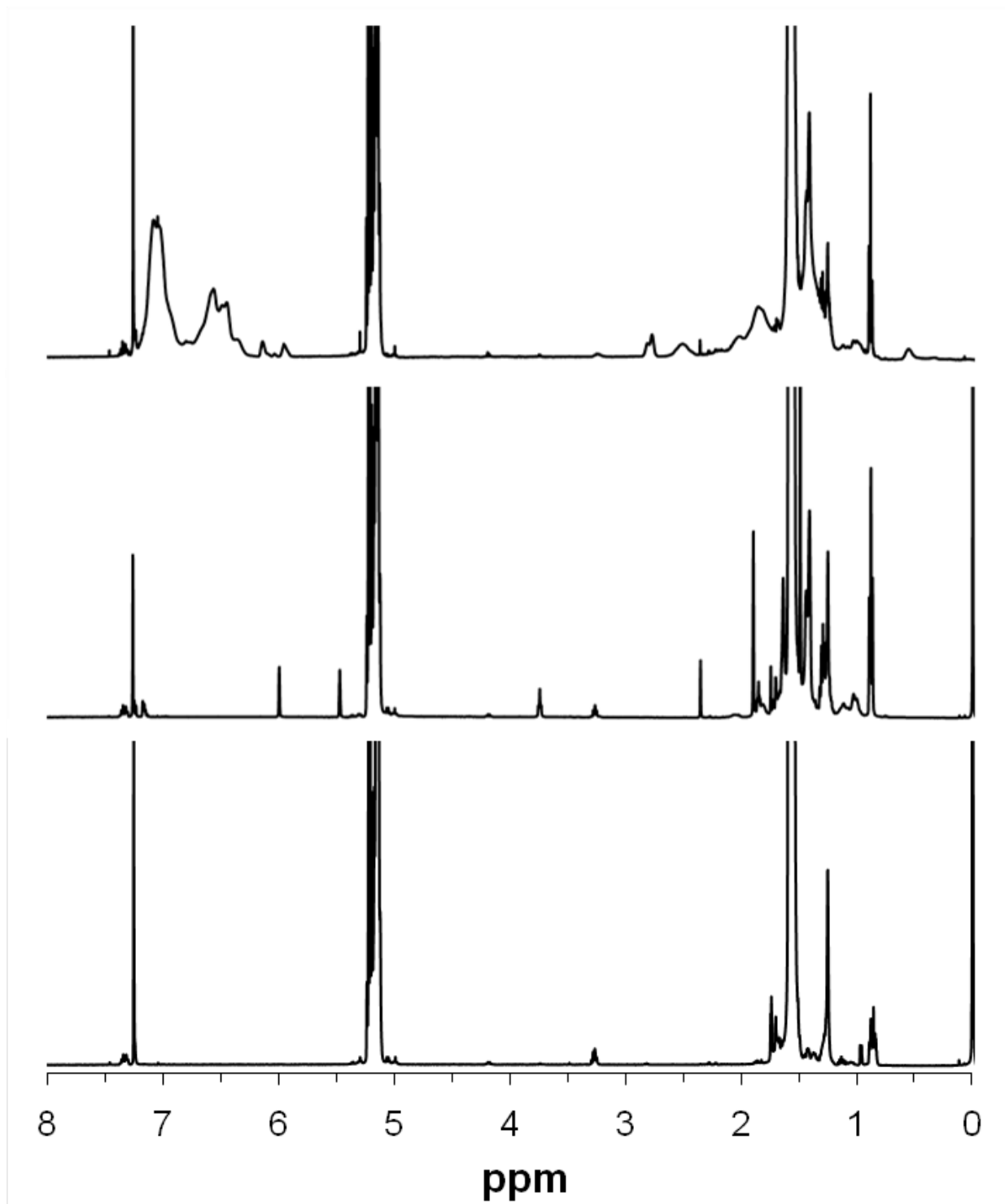
Figure S2. ^{1}H NMR spectra showing the progressive addition of blocks starting with PLA functionalized with the RAFT agent (bottom, PLA-PtBA (middle) and PLA-PtBA-PNS (top).
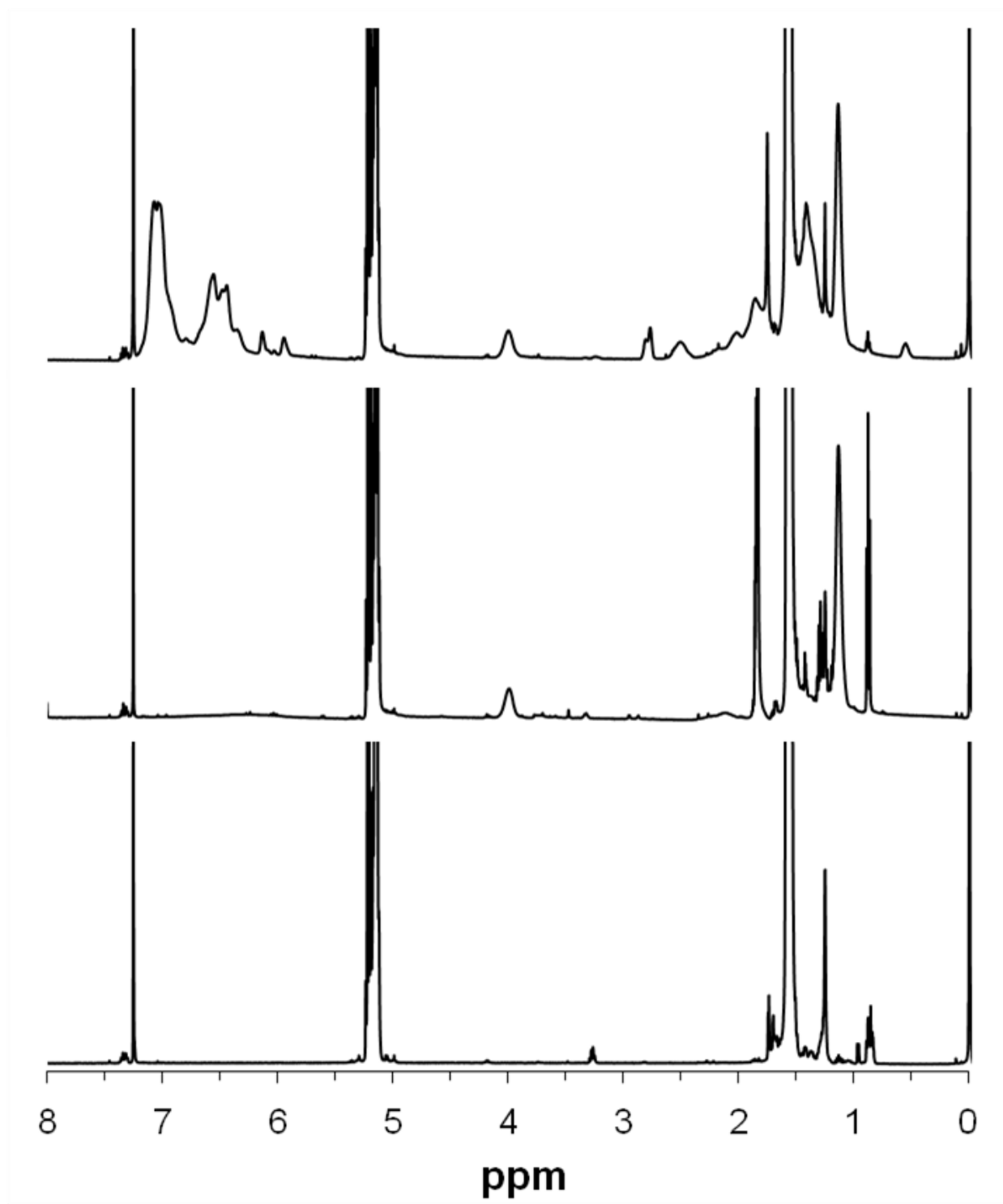
Figure S3. ^{1}H NMR spectra showing the progressive addition of blocks starting with PLA functionalized with the RAFT agent (bottom, PLA-PNIPAM (middle) and PLA-PNIPAM-PNS (top).
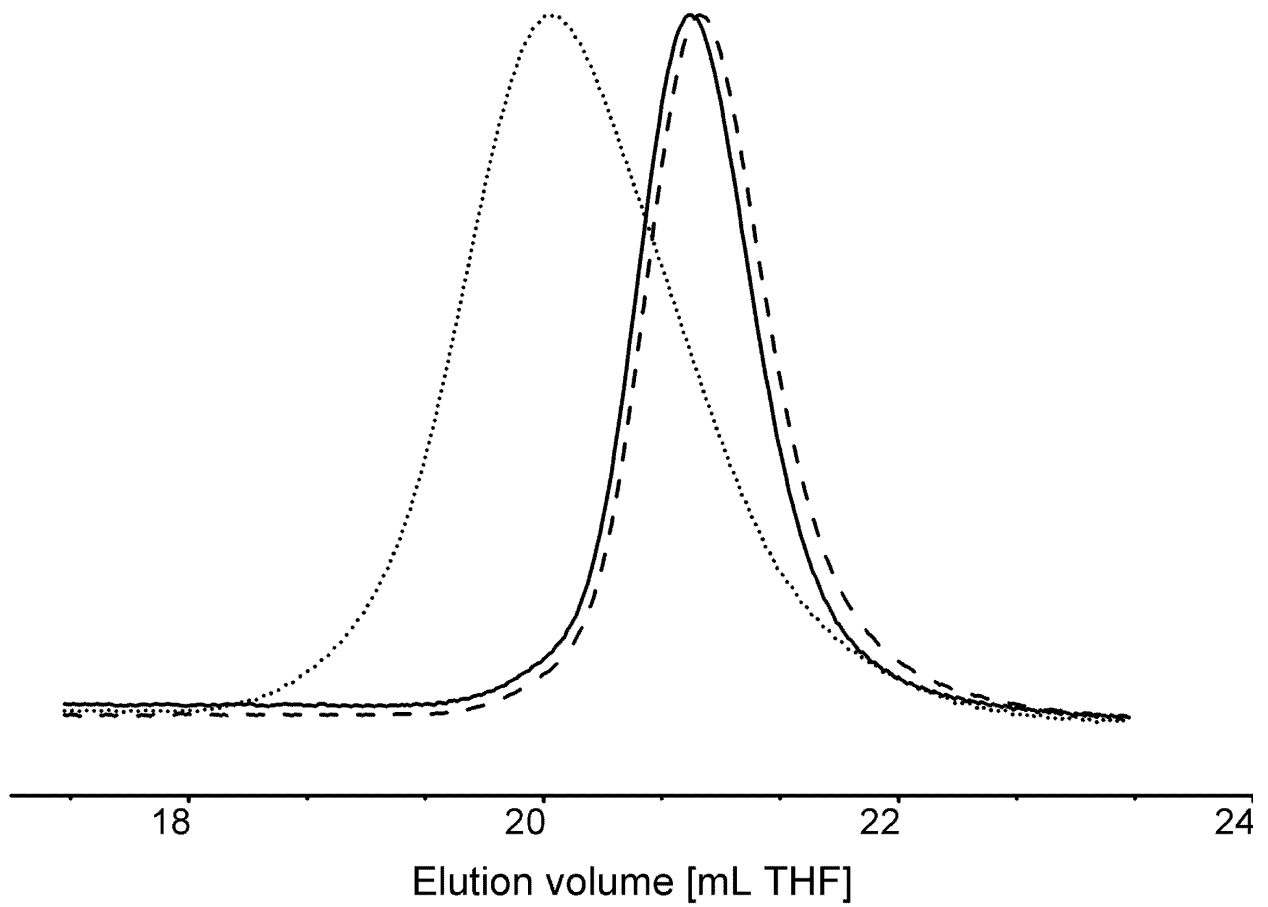
Figure S4. SEC curves for PLA-TC (solid line), PLA-PDMA (dashed line) and PLA-PDMA-PNS (dotted line) showing the progressive addition of blocks.
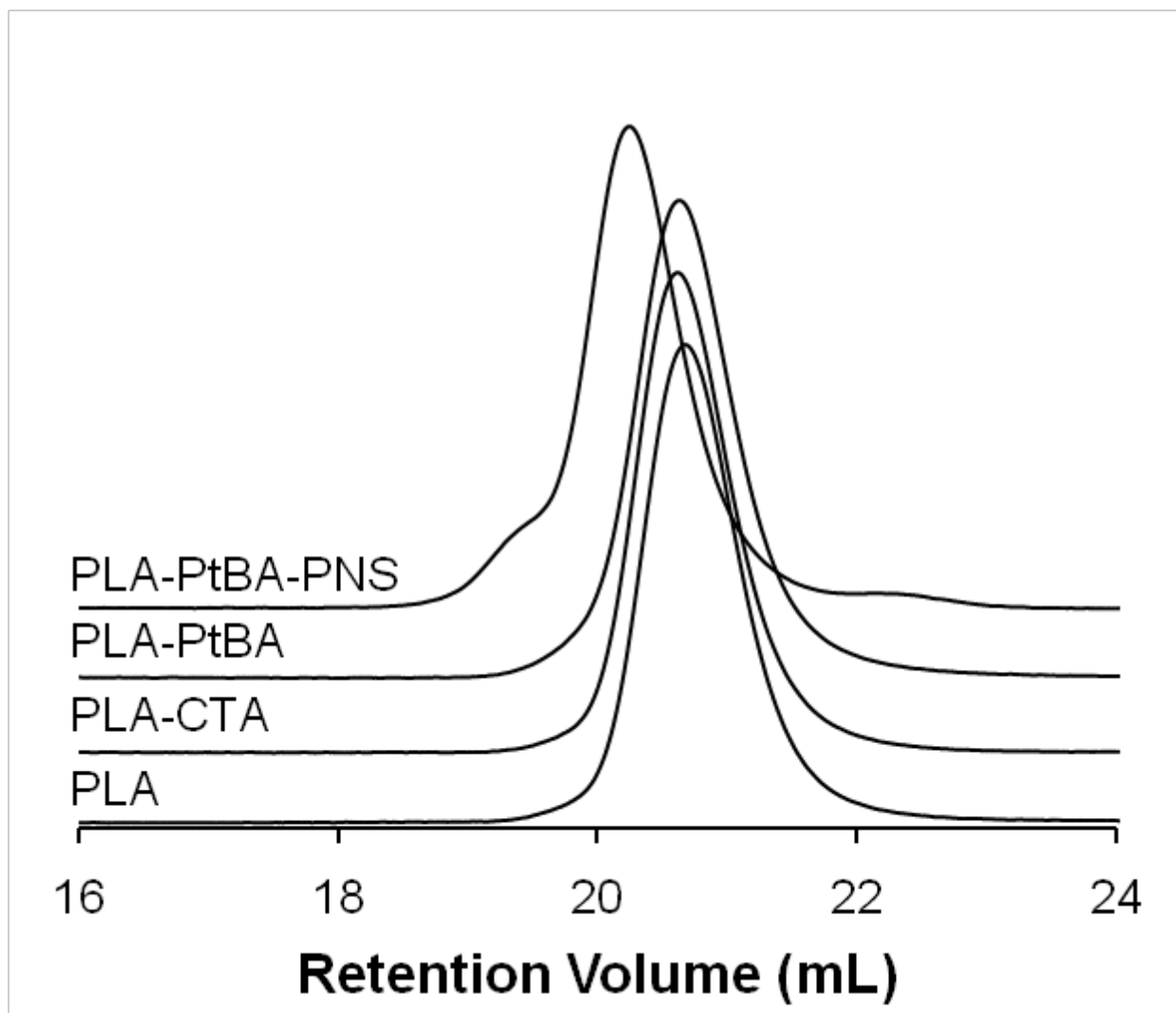
Figure S5. SEC curves showing the progressive addition of blocks in synthesizing the PLA-PtBA-PNS triblock polymer.
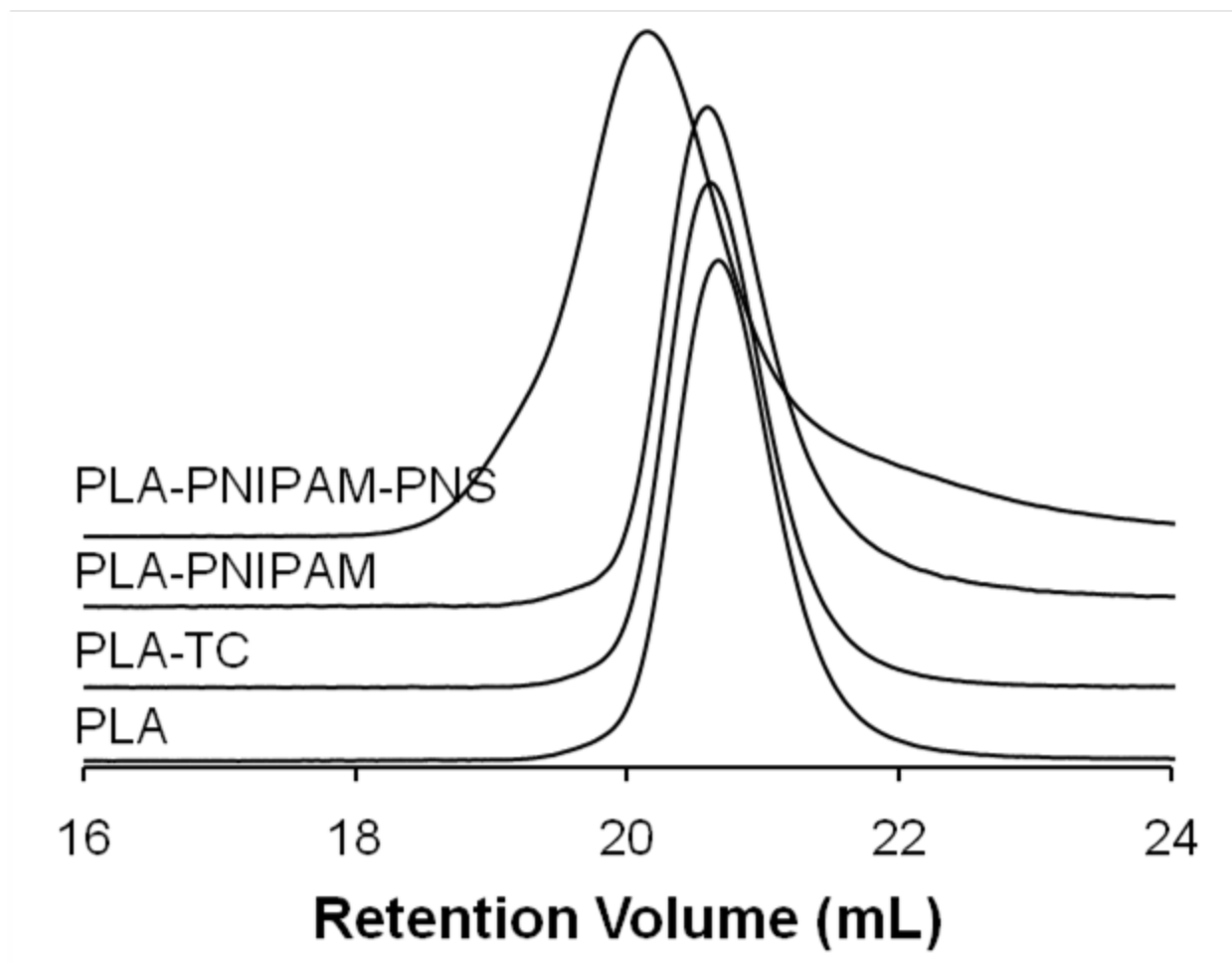
Figure S6. SEC curves showing the progressive addition of blocks in synthesizing the PLA-PNIPAM-PNS triblock polymer.
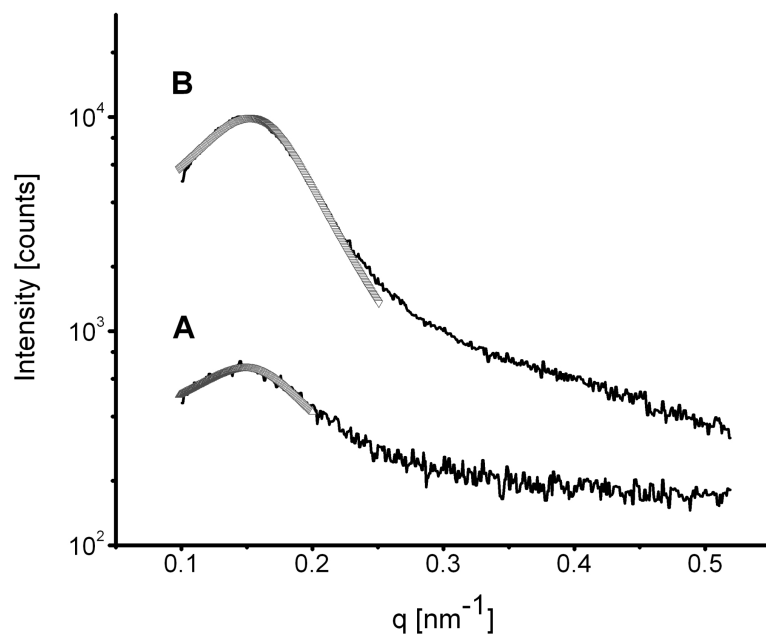
Figure S7. One-dimensional SAXS profiles for a PLA-PDMA-PNS membrane both before (A) and after (b) etching. The increase in scattering intensity reflects the enhanced electron density contrast in the porous film after PLA was removed.
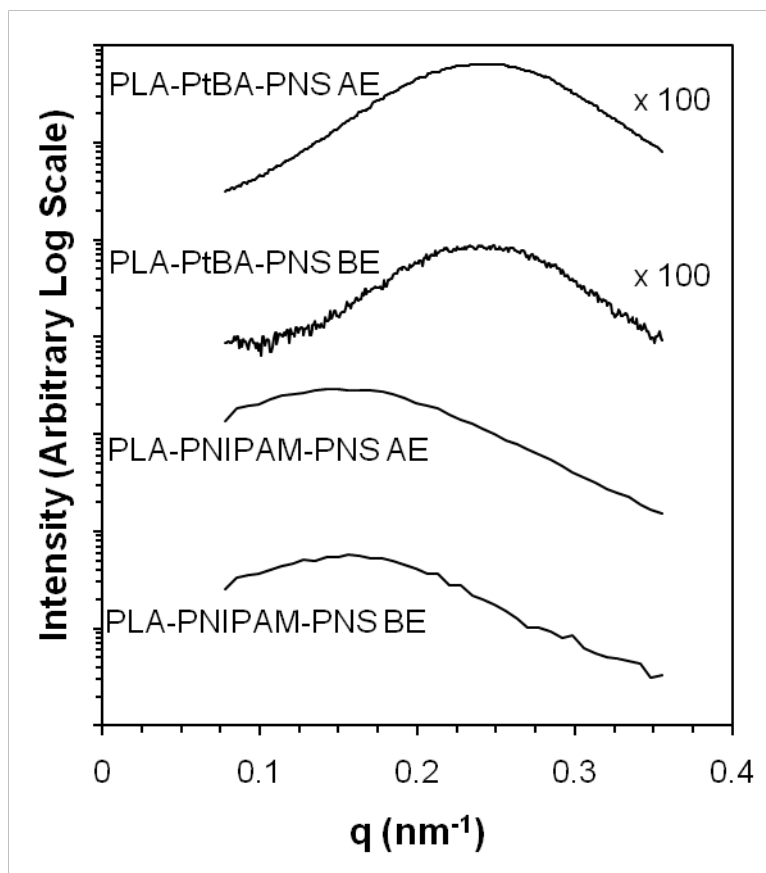
Figure S8. One-dimensional SAXS profiles for the PLA-PtBA-PNS and PLA-PNIPAM-PNS membranes both before (BE) and after (AE) etching. The PLA-PtBA-PNS patters were both vertically shifted for clarity.
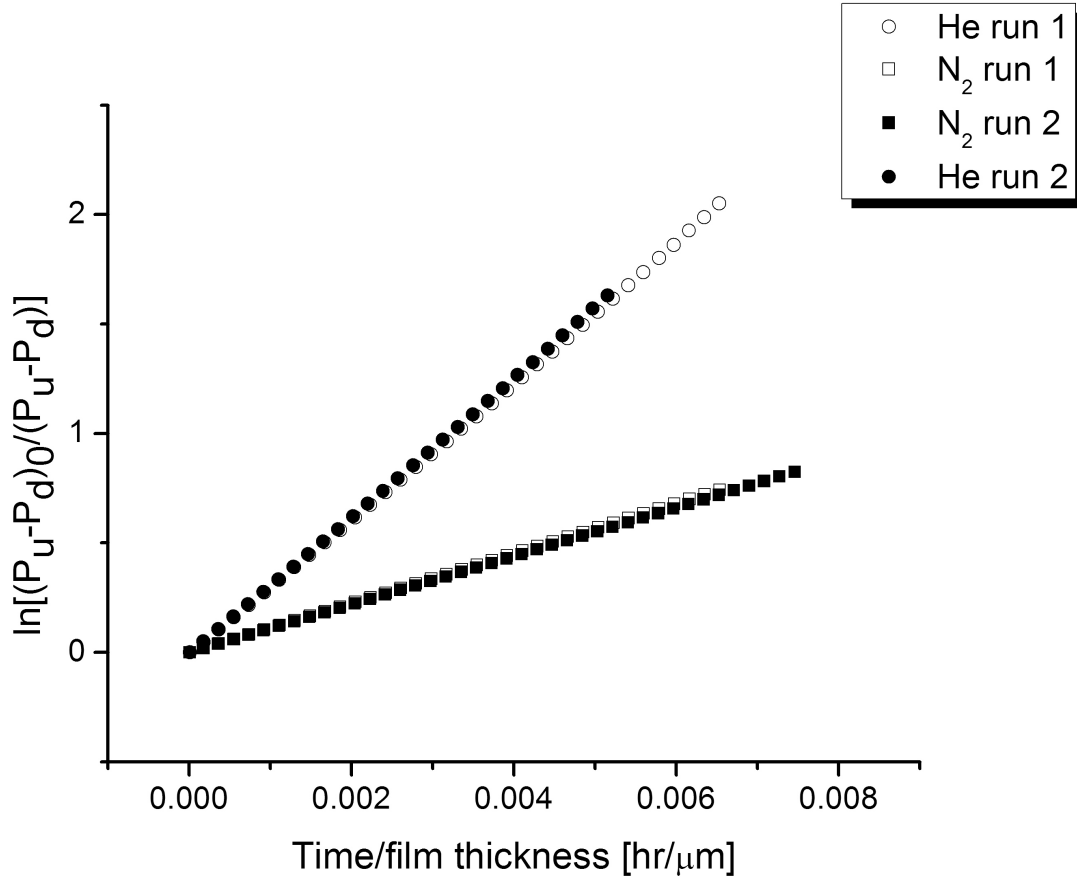
Figure S9. Diffusion data for He (circles) and N_2 (squares) gas for a PLA-PDMA-PNS membrane. The open and filled symbols represent the first and second run, in order of experimental order (He ($\circ$), N_2 ($\square$), N_2 ($\blacksquare$), He ($\bullet$)). The pressure difference over the membrane is plotted as the *ln* of the pressure difference between the donating and the receiving compartments initially and at time t, and l is the membrane thickness.

The plot was generated following the experimental procedure described in refs. ([i]) and ([ii]). A pressure difference of the gas to be studied is applied over the membrane and studied as a function of time (Equation 1):

$$\ln\left[\frac{\Delta p_0}{\Delta p}\right] = \frac{D_{eff} At}{\ell}\left(\frac{1}{V'} + \frac{1}{V''}\right) \qquad (1)$$

The effective diffusion coefficient D_{eff} can be calculated by knowing the membrane thickness ℓ, the membrane area A, the time t, the receiving and donating volumes of the gas compartments V' and V'' and from the pressure difference Δp over the two compartments initially and at time t.

The diffusion coefficient within the pores D is related to the effective diffusion coefficient through the tortuosity τ and the porosity (or void fraction) ε of the membrane (Equation 2).

$$D = \frac{D_{eff}\,\tau}{\varepsilon} \qquad (2)$$

The experimental diffusion coefficients in the pores are compared with predicted diffusion coefficients that were calculated using a simple Knudsen gas diffusion model (Equation 3)

$$D_{Kn} = \frac{2d}{3}\sqrt{\frac{2k_b T}{\pi\,\tilde{m}}} \qquad (3)$$

where d is the pore diameter, k_B is the Boltzmann's constant, T is the temperature, $\tilde{m}$ is the mass of a diffusing gas molecule. Knudsen diffusion is the effect of collisions between the gas molecules and the pore wall without intermolecular collisions between the gas molecules, a result of the mean free path (λ) of the gas being much larger than the pore diameter ($\lambda \gg d$).

From the data shown in Figure S9, the effective diffusion coefficient D_{eff} was calculated to be 0.007 cm^2 s^{-1} and 0.021 for N$_2$ and He, respectively. Using these values, $\varepsilon = 0.40$, $\tau = 2.0$ and equation 2 we calculated the diffusion coefficients of 0.041 and 0.015 for He and N$_2$ respectively. Assuming Knudsen diffusion and 18 nm pores, we would expect diffusion coefficients of 0.075 and 0.029 according to equation 3. Table S1 lists the experimental and predicted values for the diffusion coefficients in the PDCPD/PDMA-PN-*s*-S composite membranes. Thus from our calculated values of D much smaller pore sizes are expected.

Table S1. Experimental and theoretical gas diffusion coefficients for a 50 µm thick porous PLA-PDMA-PNS membrane. The average effective (D_{eff}), calculated (D), and Knudsen (D_{Kn}) diffusion coefficients and the gas selectivity α are listed for nitrogen and helium gas diffusion experiments.[3]

Solute	D_{eff}	D[a]	D_{Kn}[b]	α[c]
He	0.021	0.041	0.075	1
N$_2$	0.007	0.015	0.029	2.77

a) Using a $\varepsilon = 0.40$ and $\tau = 2.0$.
b) Assuming a pore diameter of 18 nm, the average pore diameter estimate from SEM image analysis.
c) The predicted selectivity for He/N$_2$ based on Knudsen behavior is 2.65.
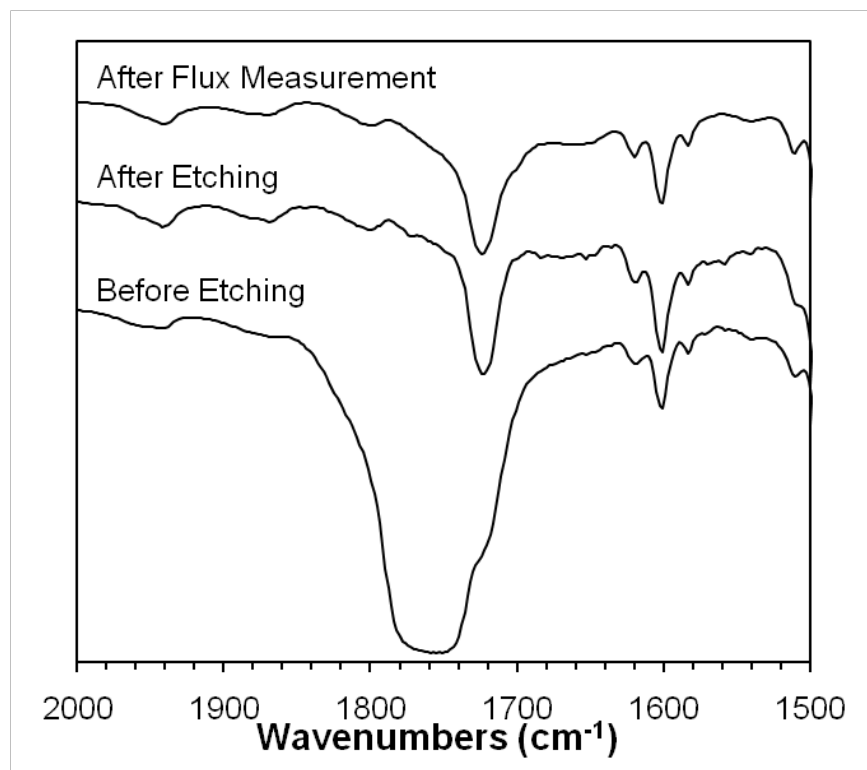
Figure S10. FT-IR spectra of the PLA-PtBA-PNS membrane before etching, after etching, and after the flux measurements at variable pH showing that the membrane was not significantly hydrolyzed by the acidic or basic conditions.

[i] Chen, L.; Phillip, W. A.; Cussler, E. L.; Hillmyer, M. A. *Journal of the American Chemical Society* **2007,** 129, 13786-13787, and references therein.

[ii] Phillip, W. A.; Rzayev, J.; Hillmyer, M. A.; Cussler, E. L. *Journal of Membrane Science* **2006,** 286, 144-152.