Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Large-pore mesoporous silica: template design, thin film preparation and biomolecules infiltration

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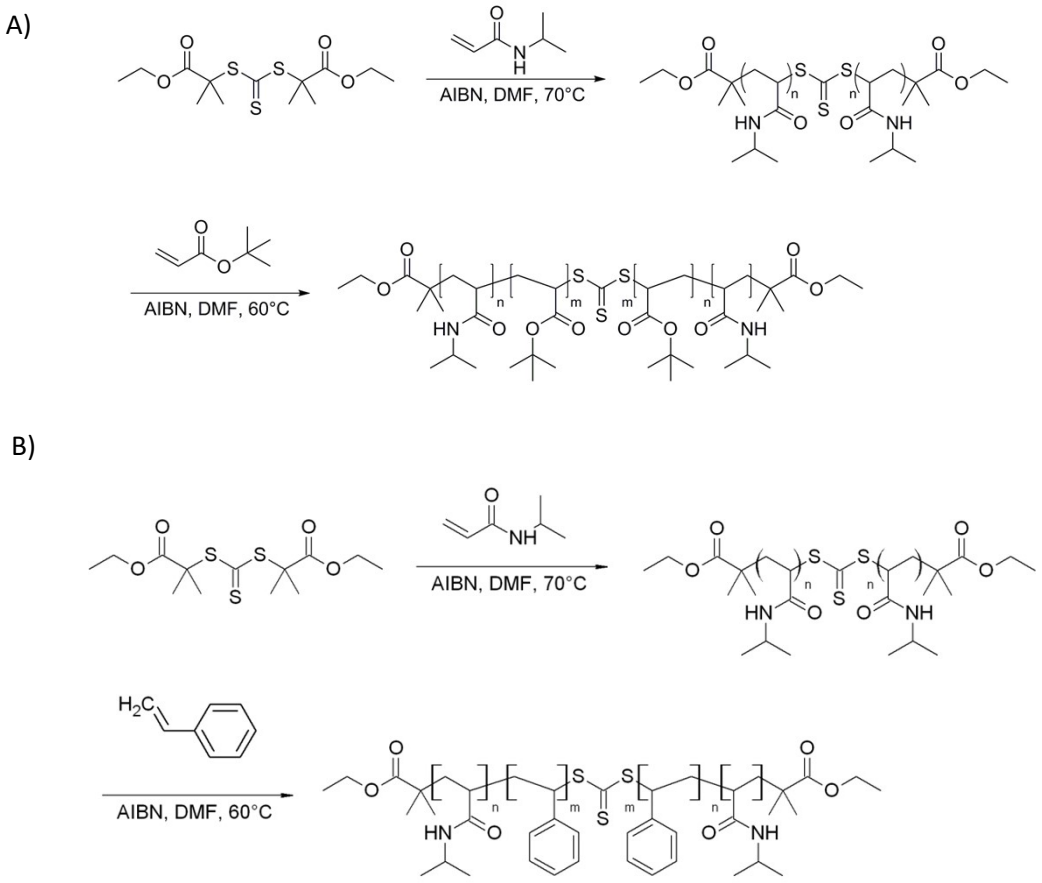

Figure S1. General synthesis for both PN-PB (A) and PN-PS (B) block co-polymer families

Table S1. Experimental details for each co-polymer synthesis.

Sample	*Monomer*	*C Monomer*	*C RAFT*	*C AIBN*	*DMF*	*T*	*t*	M_n	*Đ*	$N_{monomer}$	*Abbrev.*
		mol·L–1	*mmol·L–1*	*mmol·L–1*	*mL*	*°C*	*min*	*g·mol–1*			
PNIPAM$_{43}$	NIPAM	2.17	11.6	9.17	3.65	60	24	5800	1.72	43	
P(NIPAM$_{21.5}$-*b*-^{t}BA$_{10}$-*b*-NIPMAM$_{21.5}$)	^{t}BA	0.370	12.2	6.18	1.50	60	24	7000	1.8	10	PN-PB-12
PNIPAM$_{183}$	NIPAM	3.25	16.2	16.2	5.44	70	24	21000	1.22	183	
P(NIPAM$_{91.5}$-*b*-St$_{44}$-*b*-NIPAM$_{91.5}$)	St	1.88	10.5	5.23	2	60	24	22500	1.27	44	PN-PS-12
P(NIPAM$_{92}$-*b*-^{t}BA$_{14}$- *b*-NIPAM$_{92}$)	^{t}BA	1.52	8.42	4.21	4	60	24	21500	1.17	14	PN-PB-24
P(NIPAM$_{92}$-*b*-^{t}BA$_{XX}$- *b*-NIPAM$_{92}$)	^{t}BA	1.52	8.42	8.42[a]	4	60	24	26000 (bimodal)	2.5	XX	
P(NIPAM$_{92}$-*b*-St$_{40}$-*b*-NIPAM$_{92}$)	St	1.88	10.5	5.23	5.20	60	12	23000	1.29	40	
P(NIPAM$_{92}$-*b*-St$_{54}$-*b*-NIPAM$_{92}$)	St	1.88	10.5	5.23	5.20	60	24	24300	1.29	54	PN-PS-24
P(NIPAM$_{92}$-*b*-St$_{76}$-*b*-NIPAM$_{92}$)	St	1.88	10.5	5.23	5.20	60	48	31000 (bimodal)	1.33	76	PN-PS-48
P(NIPAM$_{92}$-*b*-^{t}BA$_{45}$- *b*-NIPAM$_{92}$)	^{t}BA	2.4	30.5	5.26	1.60	60	48	18500	1.37	45	PN-PB-48

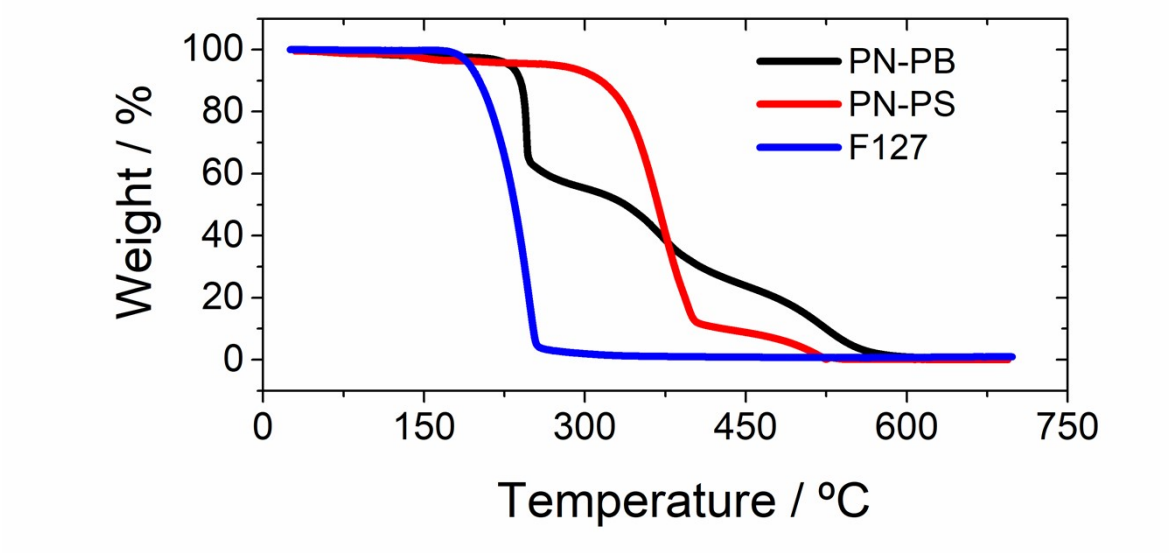

Figure S2. Thermogravimetric Analysis (TGA) for PN-PB-24 and PN-PS-12 polymers, F127 TGA is also plotted for comparison purposes.

PS main decomposition occurs at 400 ºC, PN decomposition occurs at 400ºC and 500ºC, while PB, on the other hand, have three steps of decomposition at 270ºC, 400ºC and 500ºC.

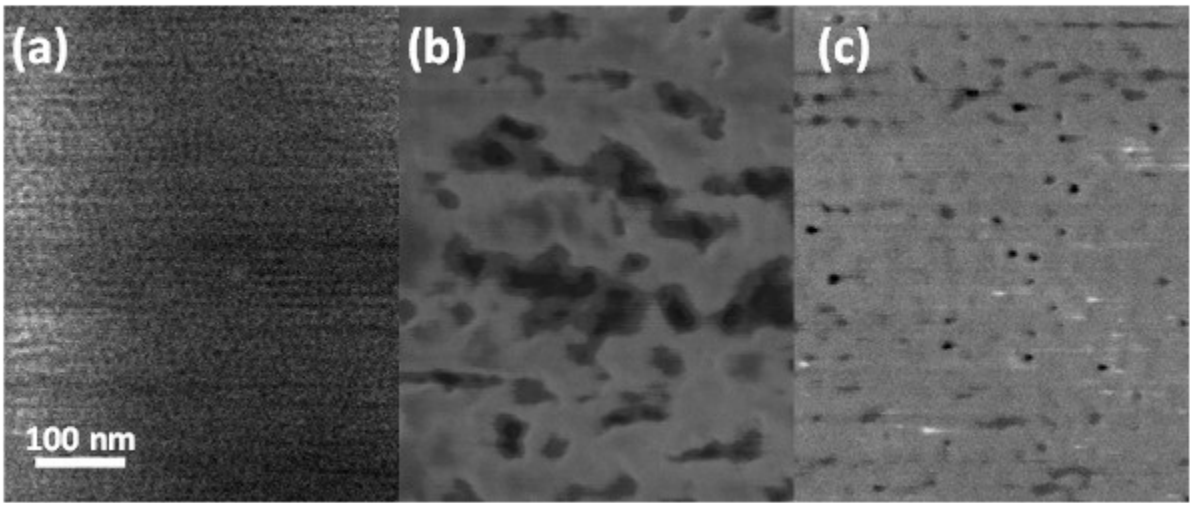

Figure S3. MTF - F127 treated at 400 ºC (a), 500 ºC (b) and 600 ºC (c).

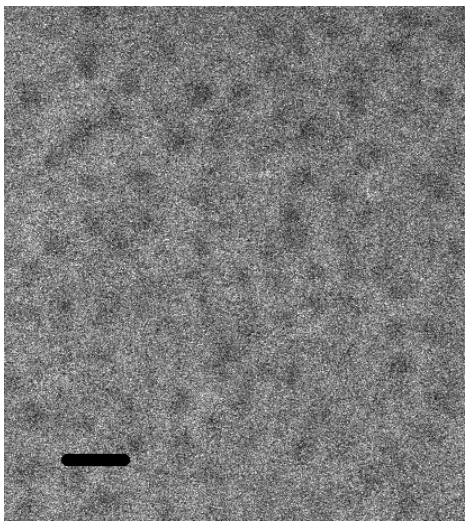

Figure S4. SEM image of PN-PB-12. The image shows well defined pores with a pore width of 11 nm and a porous volume of 30 % for this sample was calculated through ellipsometry.

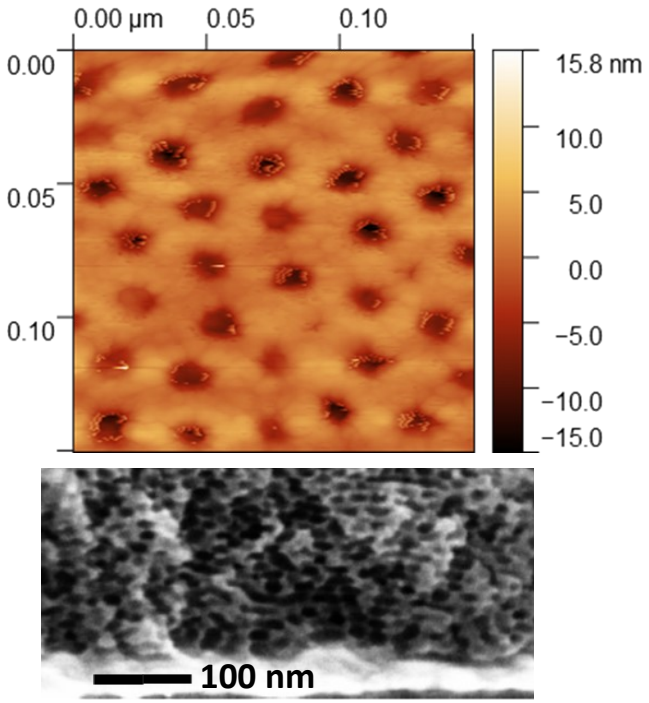

Figure S5. AFM and SEM cross section of MTF-PN-PB-24 film.

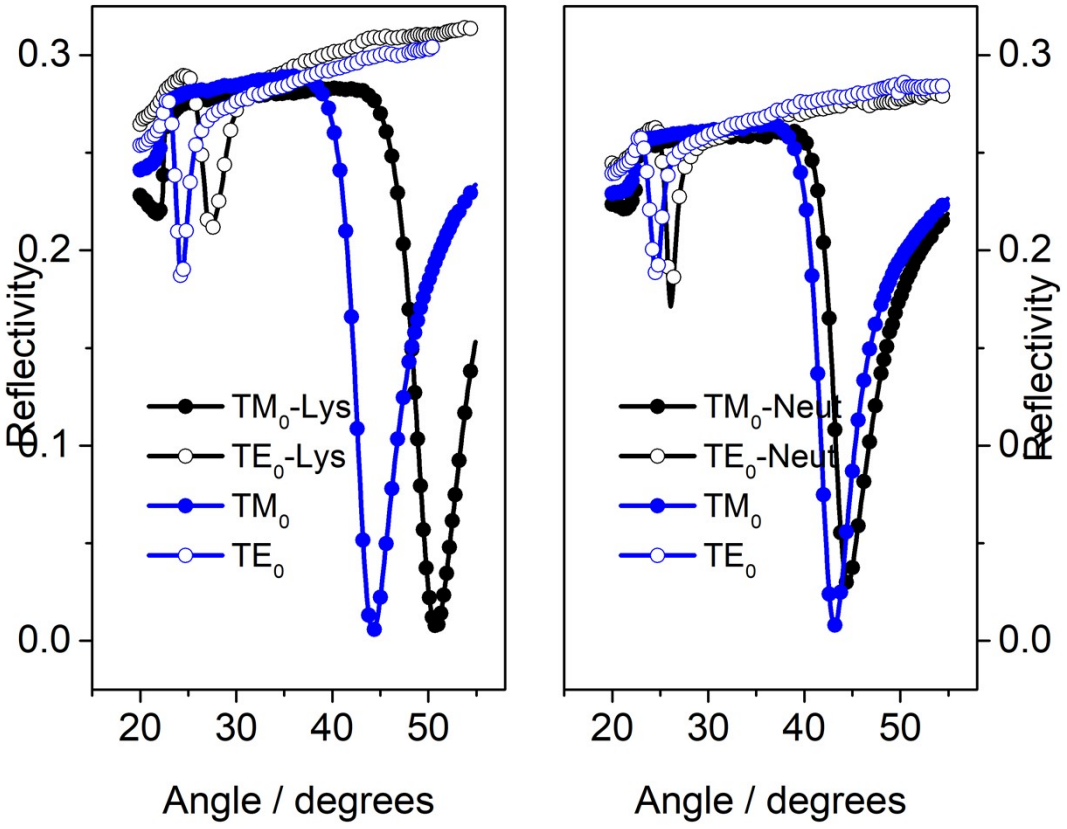

Figure S6. Reflectivity curves for TE and TM polarization measured for a mesoporous film MTF-S174 prior and after infiltration with lysine (left) and neutravidin (right) in PBS buffer.

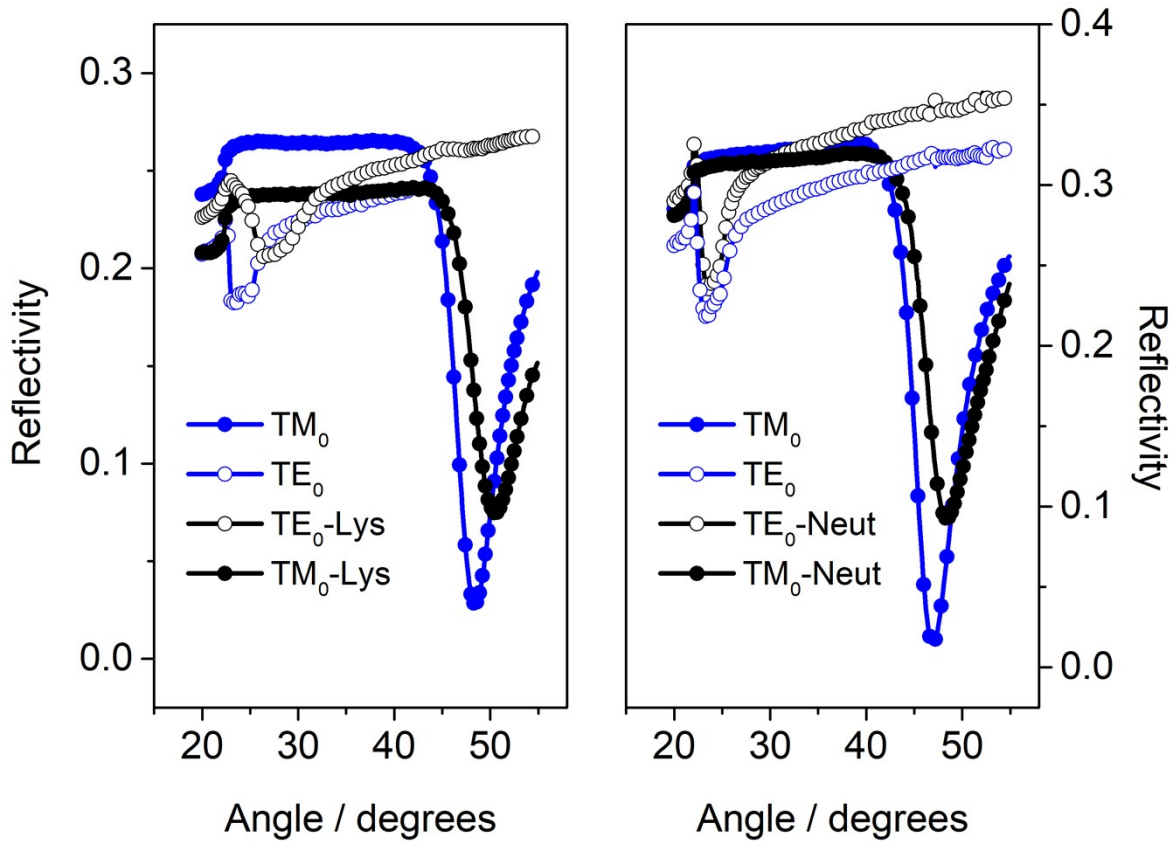

Figure S7. Reflectivity curves for TE and TM polarization measured for a mesoporous film MTF-F127 prior and after infiltration with Lysine (left) and neutravidin (right) in PBS buffer.

Isoelectric point, and Ionic strength considerations for enzyme infiltration.

To study the influence of isoelectric point and ionic strength lysozyme (lys, IP = 10) and lactalbumin (lac, IP =f 4) were selected. These enzymes have very low molecular weight so steric hindrance would play a secondary role in comparison to charge effect. In particular, Lys was studied under low and high ionic strength and the isoelectric point influence was evaluated by changing the enzyme both with very similar molecular weights. The results are shown in the **Table S2**.

Table S2. Change in refractive index of MTF-PN-PB-24 and in the thickness of the polymer layer on top. Characteristic data of the enzyme is added for comparison.

Protein	Molecular weight (kDa)	Isolectric point	pH	Buffer	Δ Refractive index	Δ Thickness (nm)	Diameter range (nm)
Lysozyme	14	10	5	PBS	0.061	5	3-5
Lysozyme	14	10	5	PBSx 10^{-1}	0.026	3	3-5
Lactalbumin	14	4	7	PBS	-0.003	0	2-4

The amount of lysozyme that could be infiltrated was higher for high ionic strength compared to the lower one. This accounts for a weaker charge interactions between the protein and the walls for high ionic strength, therefore avoid pore blocking and allows for reconfiguration. Lac, with a high isoelectric point, is charged negatively therefore charge exclusion avoids protein binding to the surface, not only inhibits infiltration but additionally adsorption on the outer surface.

The ionic strength influence on the amount of protein adsorption and infiltration reports the same tendency. The protein adsorption and infiltration diminish for lower salt concentration. In the same manner isoelectric point present itself crucial, as negatively charge enzyme will not bind to the surface regardless its size.