Supporting Information (SI)

for

Systematic study of polymer-assisted carboxylate-based MOF synthesis: multiple roles of core cross-linked PMAA-b-PMMA nanoparticles

Mingyuan Fang [1], Didier Cot [1], Carmen Montoro [1,2,*] and Mona Semsarilar [1,*]

[1] Institut Européen des Membranes—IEM UMR 5635, Univ Montpellier, CNRS, ENSCM, 34095, Montpellier, France; m.y.fang719@gmail.com; didier.cot@umontpellier.fr

[2] Departamento de Química Inorgánica, Universidad Autónoma de Madrid, 28049, Madrid, Spain

[*] Correspondence: carmen.montoro@uam.es (C.M.); mona.semsarilar@umontpellier.fr (M.S.)

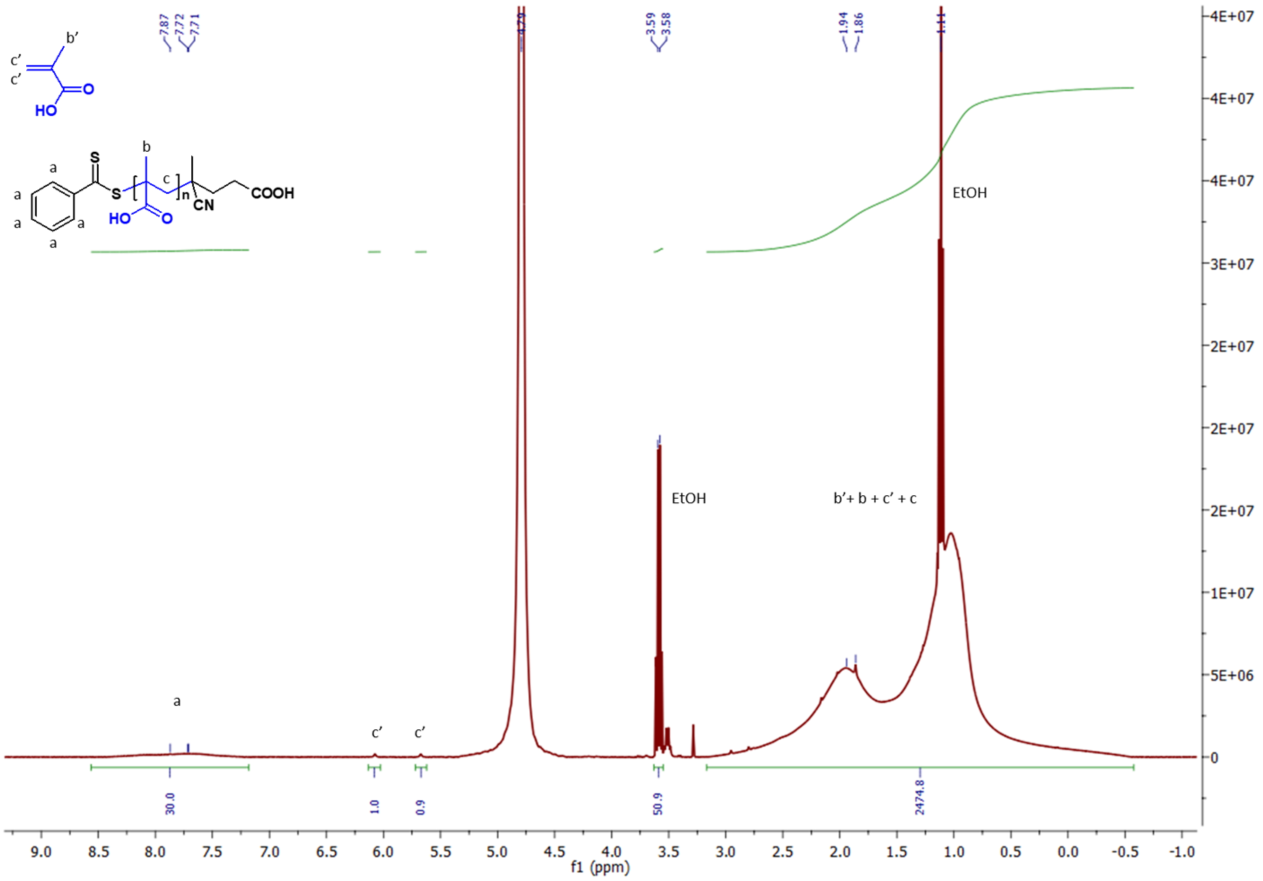

Figure S1(a). 1H NMR spectrum of $PMAA_{64}$ mCTA

Integration was set for 1 molar of non-reacted MAA.
Signals from 0.5 ppm to 2 ppm are mixed signals from PMAA (5 protons per mole), C**H$_3$**- from non-reacted MAA (3 protons) and C**H$_3$**- from ethanol which was used as polymerization solvent:
$5H_{PMAA}+3H_{MAA}+3H_{EtOH}=2474.8$

C**H$_2$**- from ethanol at 3.59 ppm (quartet) with an integration of 50.9 protons:
Mole of PMAA
$n_{PMAA} =[2474.8-(50.9/2)*3-3]/5=479.1$
Conversion = 479.1/(479.1+1) = 99.8%

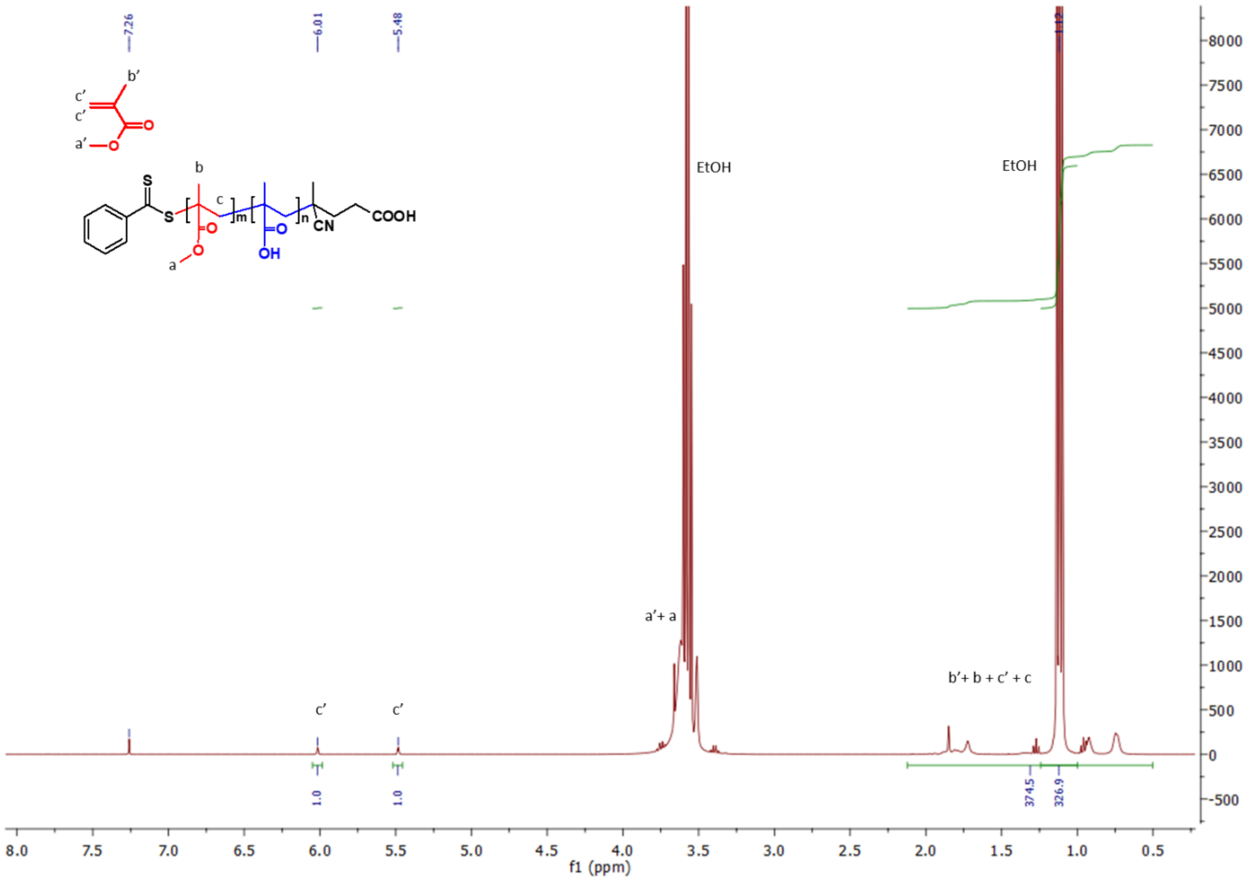

Figure S1(b). 1H NMR spectrum of PMMA-*b*-PMAA before crosslinking

Integration was set for 1 molar of non-reacted MMA.

Signals from 0.5 ppm to 2 ppm are mixed signals of PMMA (5 protons per molar), C**H**$_3$- from non-reacted MMA (3 protons) and C**H**$_3$- from ethanol which used as polymerization solvent:

$5H_{polymer}+3H_{MMA}+3H_{EtOH}=374{,}5$

C**H**$_3$- from ethanol shows at 1.12 ppm (triplet) with an integration of 326.9 protons:

Mole of PMMA-*b*-PMAA

$n_{\text{PMMA-}b\text{-PMAA}}=(374{,}4-326.9-3)/5=8{,}9$

Conversion = 8,9/(8,9+1) = 89,9%

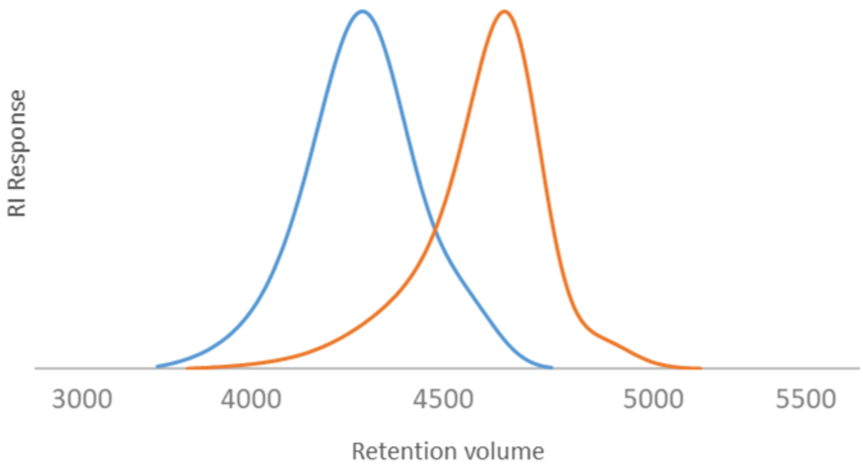

Figure S1(c). SEC traces of PMAA mCTA (orange) and PMMA-*b*-PMAA (blue) before crosslinking

Table S1. Experimental data for the synthesis of UiO-66 and UiO-PMAA-*b*-PMMA NPs using different modulators.

Material	$ZrCl_4$ (mmol)	TA (mmol)	PMAA-*b*-PMMA (mmol)[a]	PMAA-*b*-PMMA 20 wt% in EtOH (mg)[b]	Modulator
UiO-66-HAc	0.25	0.25	0	0	HAc 0.5 mL
UiO-66-HCl	0.25	0.25	0	0	HCl 0.4 mL
UiO-P-20%-HAc	0.25	0.25	$1.6*10^{-3}$	243.7	HAc 0.5 mL
UiO-P-20%-HCl	0.25	0.25	$1.6*10^{-3}$	243.7	HCl 0.4 mL
UiO-P-20%- No modulator	0.25	0.25	$1.6*10^{-3}$	243.7	No modulator

[a] One polymer chain of PMAA-*b*-PMMA containing 64 units of carboxylic functions.

[b] Average molecular weight of PMAA-*b*-PMMA is calculated from $PMAA_{64}$-*b*-$PMMA_{254}$.

Table S2. Experimental data for UiO-polymer hybrid via linker (TA) replacement with PMAA-*b*-PMMA NPs

Material	$ZrCl_4$ (mmol)	TA (mmol)	PMAA-*b*-PMMA (mmol)[a]	PMAA-*b*-PMMA 20 wt% in EtOH (mg)[b]	Modulator
UiO-66-TA_1	0.25	0.25	0	0	HCl 0.4 mL
UiO-$TA_{0.9}$-$P_{0.1}$	0.25	0.225	$7.8*10^{-4}$	121.8	HCl 0.4 mL
UiO-$TA_{0.8}$-$P_{0.2}$	0.25	0.2	$1.6*10^{-3}$	243.7	HCl 0.4 mL
UiO-$TA_{0.5}$-$P_{0.5}$	0.25	0.125	$3.9*10^{-3}$	609	HCl 0.4 mL
UiO-TA_0-P_1	0.25	0	$7.8*10^{-3}$	1218.5	HCl 0.4 mL

[a] One polymer chain of PMAA-*b*-PMMA containing 64 units of carboxylic functions.

[b] Average molecular weight of PMAA-*b*-PMMA is calculated from $PMAA_{64}$-*b*-$PMMA_{254}$

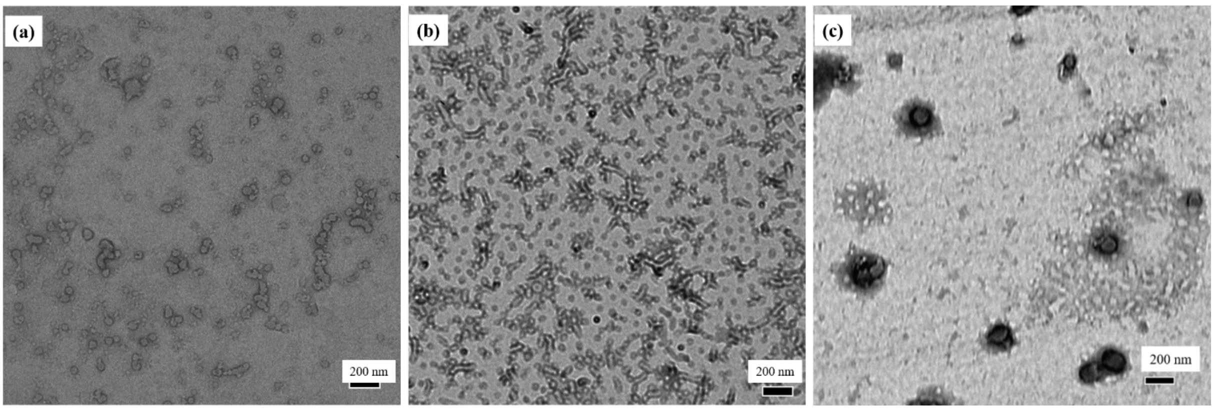

Figure S2. TEM images for PMAA-*b*-PMMA NPs in ethanol (a) before cross-linking (b) after core cross-linking; (c) after core cross-linking in DMF.

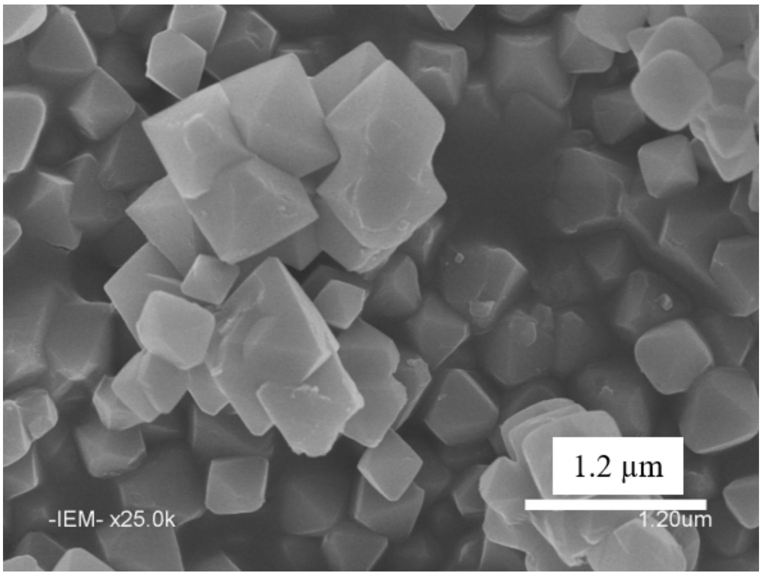

Figure S3. SEM image of UiO-66-HAc

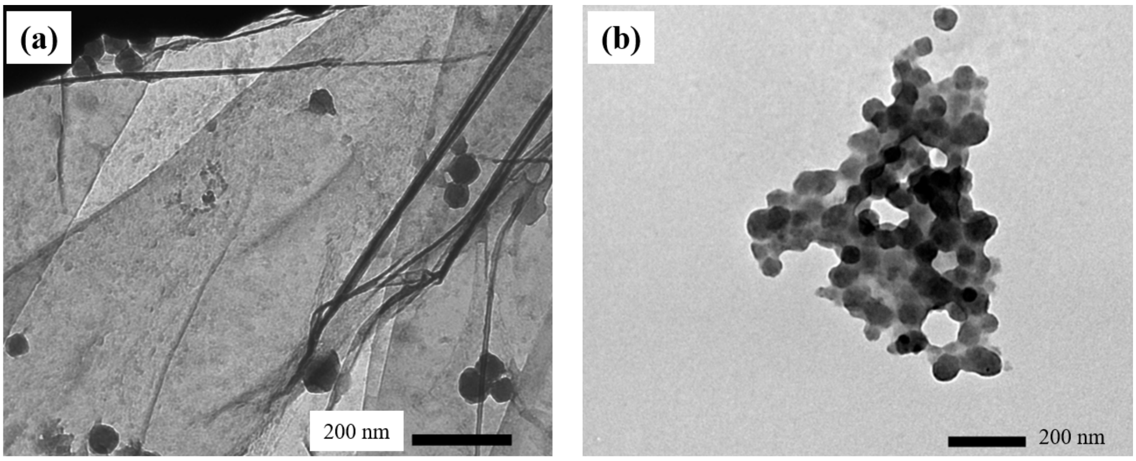

Figure S4. TEM images of (a) UiO-P-20%-HAc, (b) UiO-P-20%-HCl

It's hard to get TEM image of UiO-P-20%-No modulator due to the high viscosity and very small particle size.

Samples from synthesis with HCl were difficult to observe by TEM, since HCl was damaging the carbon film on the copper grid.

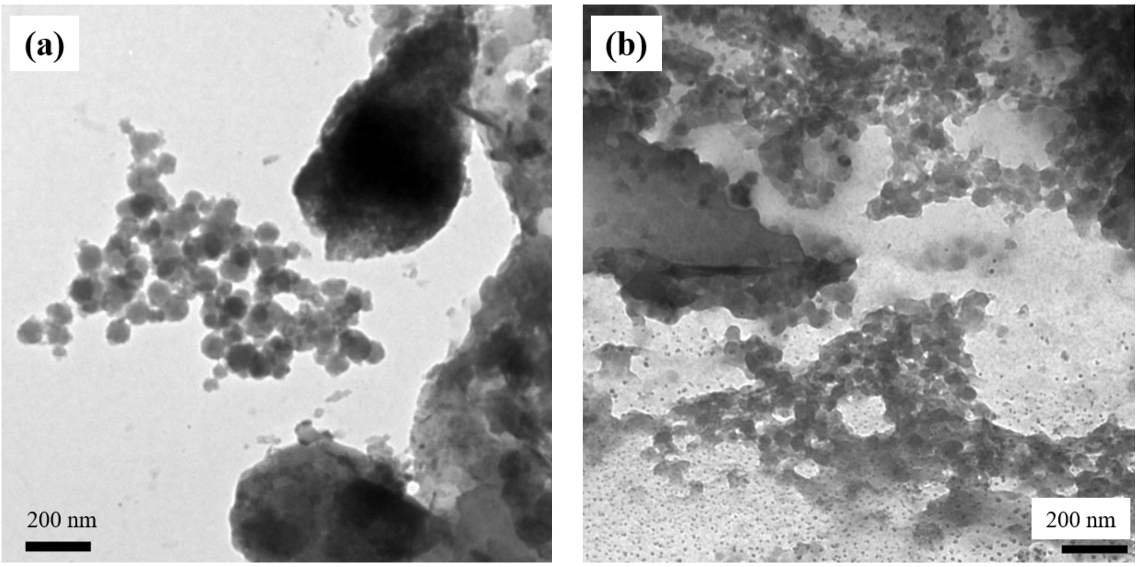

Figure S5. TEM images of (a) UiO-$TA_{0.9}$-$P_{0.1}$, (b) UiO-$TA_{0.5}$-$P_{0.5}$.

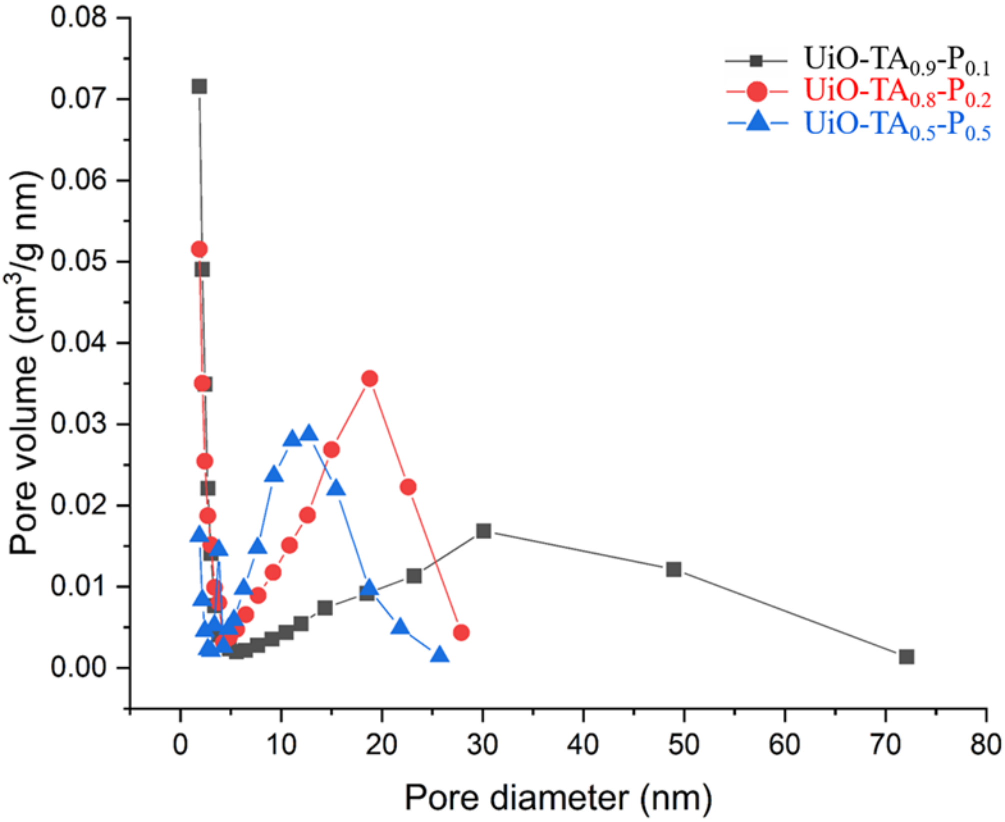

Figure S6. BJH desorption pore size distribution of UiO-TA_{90}-P_{10} (black), UiO-TA_{80}-P_{20} (red), UiO-TA_{50}-P_{50} (blue)

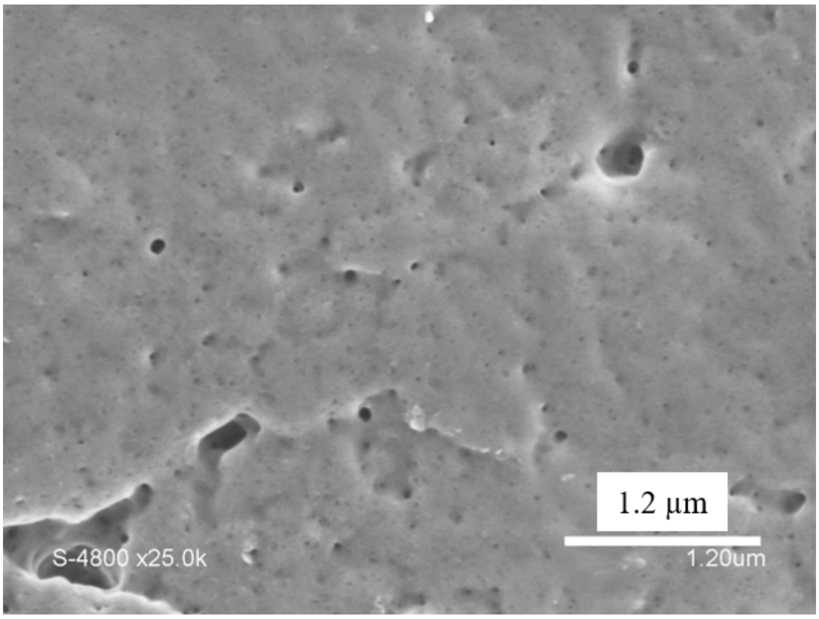

Figure S7. SEM image of PMAA-*b*-PMMA NPs after drying.