Macroporous Silica Using a "Sticky" Stöber Process

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Supplementary information

polymer	amount [mg/250 μl]	surface tension [mN m^{-1}]	STD [mN m^{-1}]
1K HO-PEG-OH	340.85	50.90	0.29
1K A-PEG-A	269.60	38.49	0.54
1K Si-PEG-Si	332.00	40.82	0.43
2K HO-PEG-OH	291.40	43.40	0.42
2K A-PEG-A	264.60	47.03	0.29
	amount [mg/500 μl]		
1K HO-PEG-OH	5.00	69.61	0.51
1K A-PEG-A	5.00	63.71	0.56
1K Si-PEG-S	5.00	61.34	0.69
2K HO-PEG-OH	5.00	70.00	0.52
2K A-PEG-A	5.00	63.33	0.80
water		71.96	0.23

Table 1S: Surface tension measurements for polymers in water at different concentrations.

[1] Née Voss.

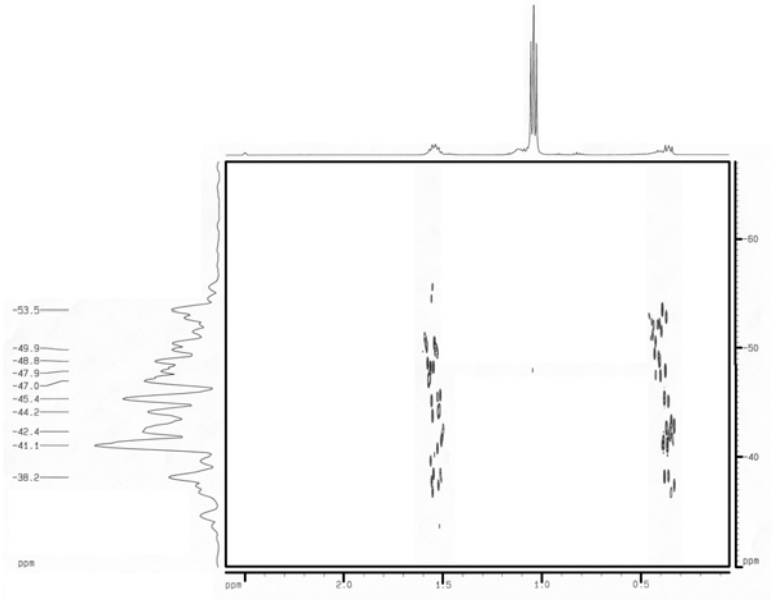

Figure 1S: HMBC spectrum at of Si-PEG-Si (200 g mol^{-1}) at 1 hour.

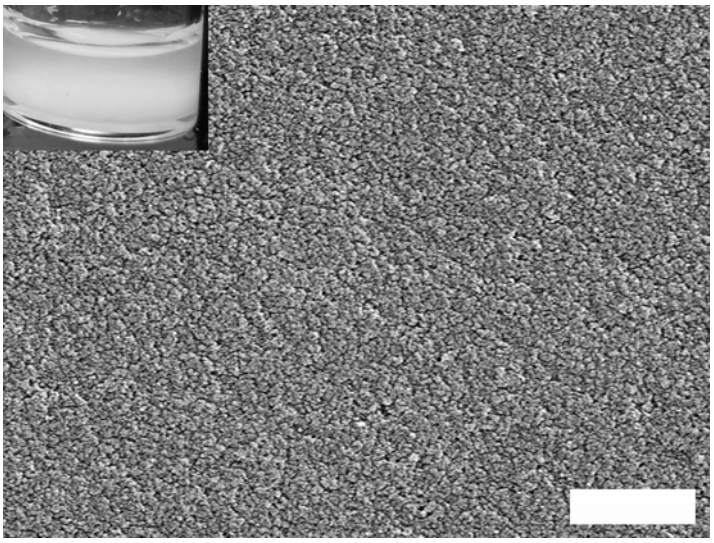

Figure 2S: Photograph and SEM image of monolithic silica prepared with 8,000 g mol^{-1} HO-PEG-OH. Scales bar 1 μm.

	as prepared[a]			as prepared[b]				calcined[a]		
PEG molecular weight [g mol^{-1}]	surface area [m^2 g^{-1}]	total pore volume [cm^3 g^{-1}]	pore diameter desorption [nm]	surface area [m^2 g^{-1}]	total pore volume [cm^3 g^{-1}]	pore diameter intrusion [µm]	pore diameter extrusion [µm]	surface area [m^2 g^{-1}]	total pore volume [cm^3 g^{-1}]	pore diameter desorption [nm]
600	41.6	0.028	3.77					658	0.440	3.48
1000	80.6	0.084	3.47	313.74	2.4	NA[c]	NA	487	0.343	3.47
2000	83	0.177	3.8 13.9	319.22	2.7	NA	NA	567	0.495	3.47
8000	36.1	0.048	3.79 43.5	127.47	2.17	4.2; main 1.59	main 7.54; 5.35; small 1.94	586	0.390	3.5

Table 2S: Porosimetry for silica monoliths prepared with A-PEG-A as porogen. [a] nitrogen adsorption, [b] mercury intrusion, [c] It was not possible to detect macropores for some monoliths derived from lower molecular PEG. We ascribe this to pore collapse during the mercury porosimetry experiments. The materials prepared from 8000 g mol^{-1} PEG were less fragile.

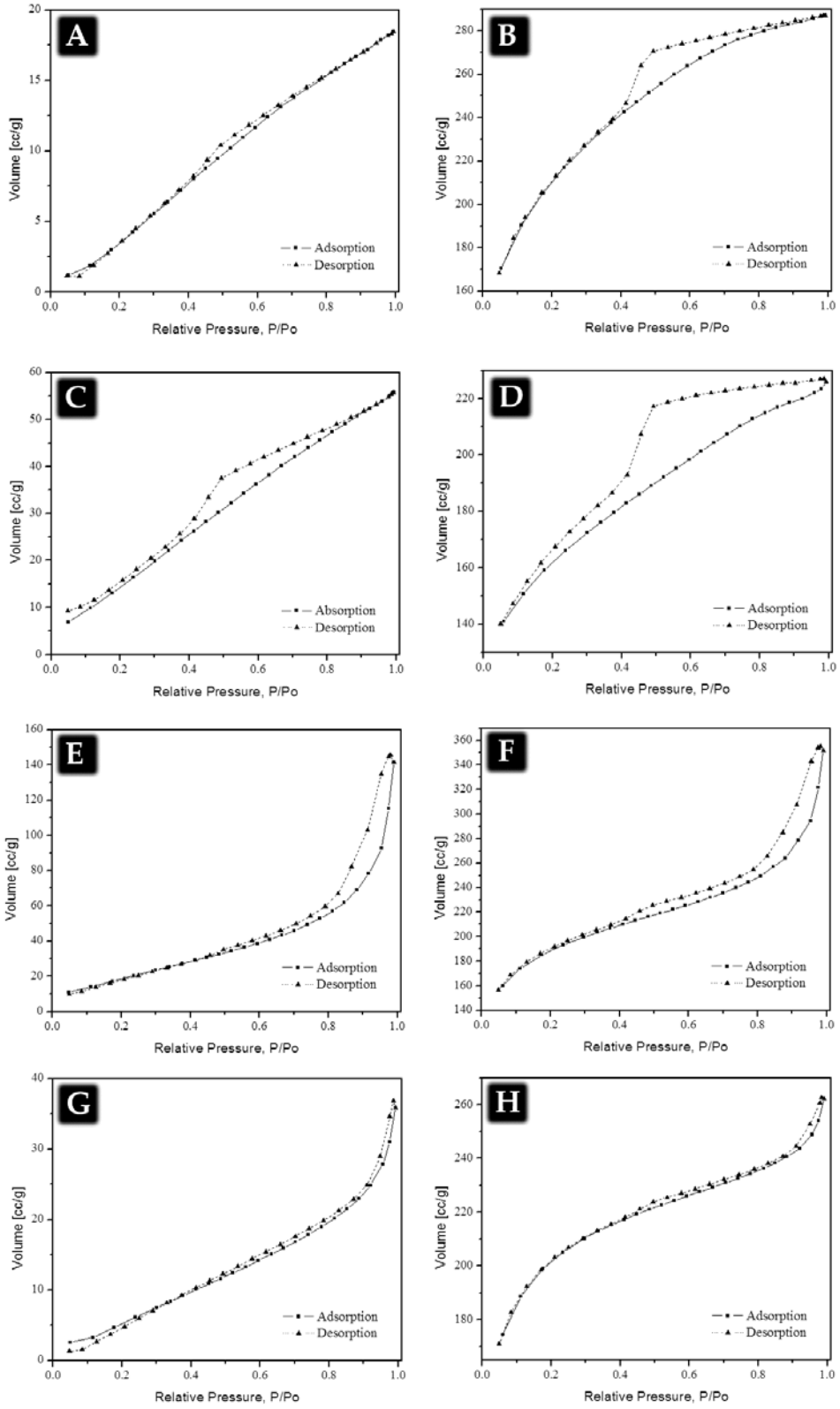

Figure 3S: Nitrogen adsorption isotherms for A-PEG-A with different molecular weights. A, B: 600 g mol^{-1} as synthesized and calcined, respectively. C, D: 1,000 g mol^{-1} as synthesized and calcined respectively. E, F: 2,000 g mol^{-1} as synthesized and after calcinations, respectively. G, H: 8,000 g mol^{-1} as synthesized and calcined, respectively.

The optimum amount of Si-PEG-Si in the synthesis which is around 0.015 mmol or a ratio of 1:67 PEG:DGS seen by SEM. Again the structures appear to be aggregated particulates. Changes in morphology can also be seen with mercury intrusion, which shows surface areas of 236 to 2.8 $m^2 g^{-1}$ decreasing with increasing concentration of polymer. The total pore volumes are 2.3 $cm^3 g^{-1}$ for the lowest and highest concentration shown in Figure 4S and 0.4 $cm^3 g^{-1}$ with pore diameters of 340 nm to 7.3 μm for 0.015 mmol polymer and 4.2 μm for 0.035 mmol. This shows that while the structure appears to be more open structure in SEM is not actually more open, but a concentration 0.035 mmol are needed to get a open frame work silicate. Nitrogen adsorption for the as prepared silicas with different amount of PEGs show small surface areas (<42 $m^2 g^{-1}$) and total pore volumes (<0.09 $cm^3 g^{-1}$) for washed samples and high surface areas (>460 $m^2 g^{-1}$) and total pore volumes (>0.3 $cm^3 g^{-1}$) for calcined samples, with pore diameters equal in both cases (~3.8 nm).

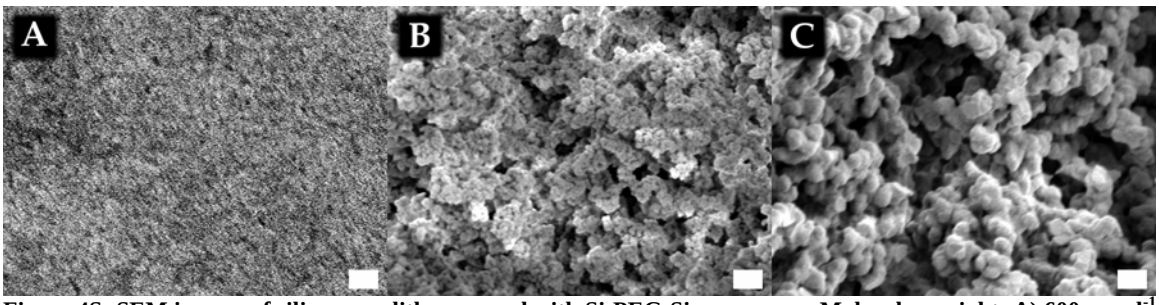

Figure 4S: SEM images of silica monolith prepared with Si-PEG-Si as porogen. Molecular weight: A) 600 g mol^{-1}, B) 2,000 g mol^{-1}, C) 8,000 g mol^{-1}. Scale bars 1 μm.

	as prepared[a]			as prepared[b]				calcined[a]		
PEG molecular weight [g mol^{-1}]	surface area [m^2 g^{-1}]	total pore volume [cm^3 g^{-1}]	pore diameter desorption [nm]	surface area [m^2 g^{-1}]	total pore volume [cm^3 g^{-1}]	pore diameter intrusion [μm]	pore diameter extrusion [μm]	surface area [m^2 g^{-1}]	total pore volume [cm^3 g^{-1}]	pore diameter desorption [nm]
600	NA	NA	NA	25.11	0.03	NA[c]	NA	476	0.309	3.47
2000	52.8	0.110	NA	85.88	2.29	1.39	2.75	659	0.535	3.81
8000	15.6	0.026	3.12	86.68	2.21	broad 1.93	broad 7.15	598	0.401	3.8

Table 3S: Porosimetry measurements for silica monolith made from Si-PEG-Si. [a] nitrogen adsorption, [b] mercury intrusion, [c] It was not possible to detect macropores for some monoliths derived from lower molecular PEG. We ascribe this to pore collapse during the mercury porosimetry experiments. The materials prepared from 8000 g mol^{-1} PEG were less fragile**..**

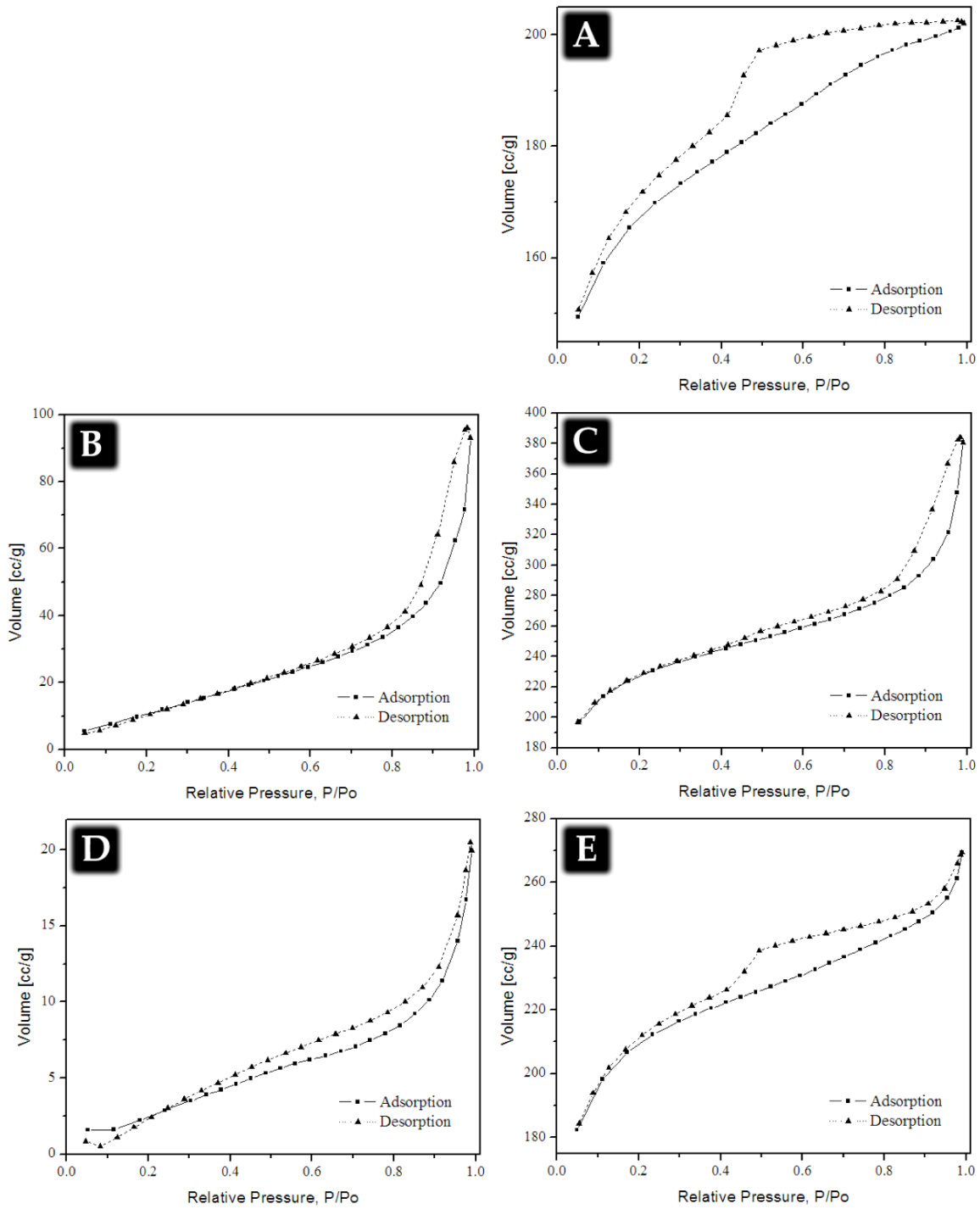

Figure 5S: Nitrogen adsorption isotherms for Si-PEG-Si with different molecular weights. A: 600 g mol^{-1} calcined. B, C: 2,000 g mol^{-1} as synthesized and calcined, respectively. D,E: 8,000 g mol^{-1} as synthesized and calcined, respectively.

The macroporosity was further investigated with mercury intrusion, which gives a surface area of 72.4 $m^2 g^{-1}$. The total pore volume is 1.64 $cm^3 g^{-1}$ and the pore diameters are 1.44 and 5.82 μm for intrusion and extrusion respectively. Compared with the same sample prepared pH 7 (Table 4S), the total pore volumes and surface areas are slightly smaller while the pore diameters for extrusion is bigger. The mesoporosity of the samples was analyzed with nitrogen adsorption and showed that the values obtained at pH other than 7 are smaller if of the same order as for the materials prepared under neutral conditions (Table 4S).

	as prepared			calcined		
pH	surface area [$m^2 g^{-1}$]	total pore volume [$cm^3 g^{-1}$]	pore diameter desorption [nm]	surface area [$m^2 g^{-1}$]	total pore volume [$cm^3 g^{-1}$]	pore diameter desorption [nm]
2	32.9	0.019	3.0	NA	NA	NA
7	52.8	0.110	NA	659	0.535	3.8
10	22.9	0.048	2.9 33.4	460	0.306	3.8 Large amount <1 nm

Table 4S: Nitrogen adsorption data for 2,000 g mol^{-1} Si-PEG-Si at different pH.

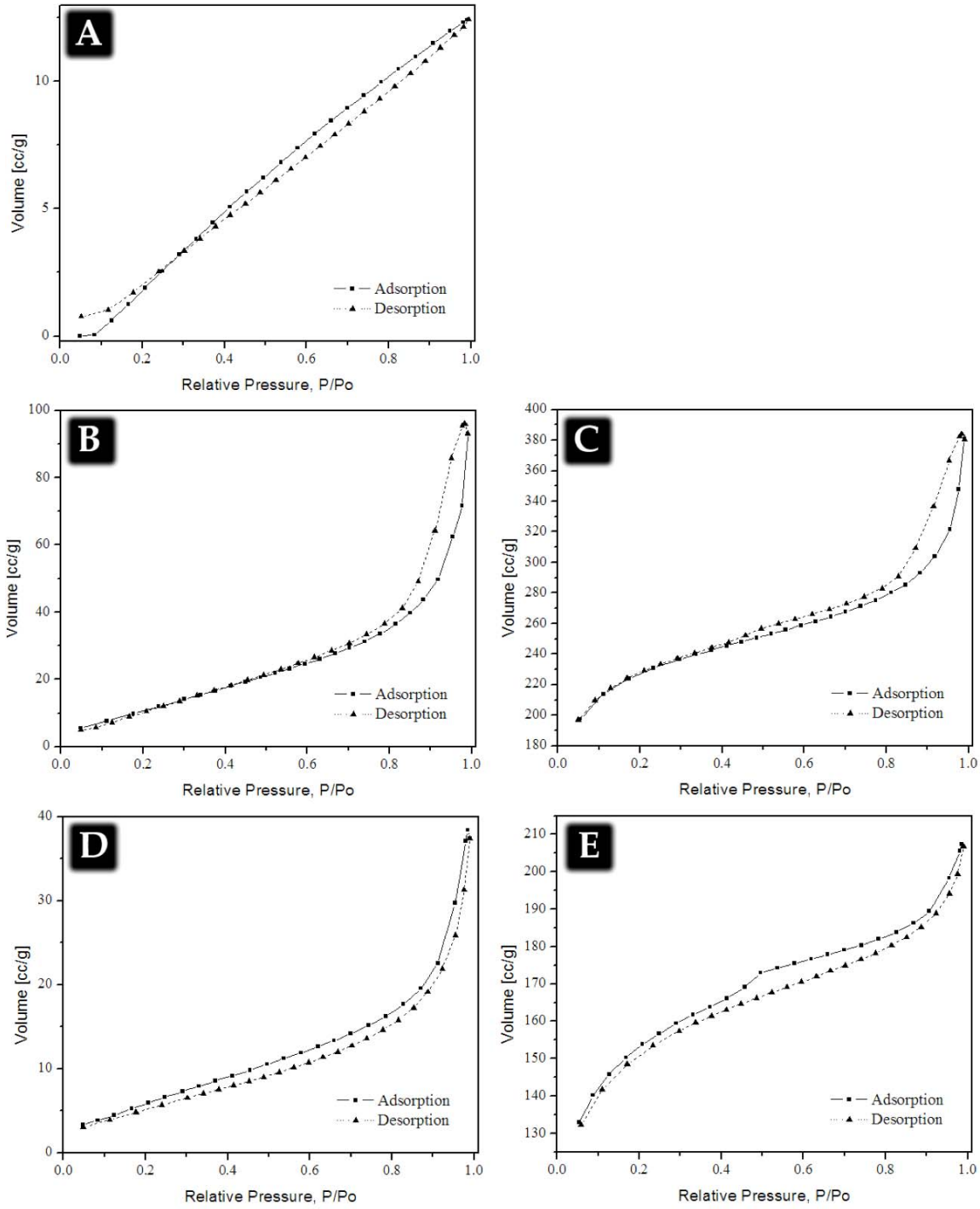

Figure 6S: Nitrogen adsorption isotherms for 2,000 g mol^{-1} Si-PEG-Si at different pH. A: pH 2 as synthesized. B, C: pH 7 as synthesized and calcined, respectively. D,E: pH 10 as synthesized and calcined, respectively.

A)

	as prepared[a]			as prepared[b]				calcined[a]		
KF concentration [mM]]	surface area [$m^2 g^{-1}$]	total pore volume [$cm^3 g^{-1}$]	pore diameter desorption [nm]	surface area [$m^2 g^{-1}$]	total pore volume [$cm^3 g^{-1}$]	pore diameter intrusion [μm]	pore diameter extrusion [μm]	surface area [$m^2 g^{-1}$]	total pore volume [$cm^3 g^{-1}$]	pore diameter desorption [nm]
0	18.82	0.035	2.8; 32.9	20.88	1.27	3.96; main 1.60	main 7.53; 0.78	516	0.320	3.6; <1
3	12.82	0.019	2.4	20.62	1.63	6.36; main 1.51	main 6.15; 1.47	479	0.280	3.5; <1
223	NA	NA	NA	4.05	1.89	main 3.5; large 1.29	main ca. 10.12 off the spectra; large 4.06	464	0.284	<1

B)

	as prepared[a]			as prepared[b]				calcined[a]		
KF concentration [mM]]	surface area [$m^2 g^{-1}$]	total pore volume [$cm^3 g^{-1}$]	pore diameter desorption [nm]	surface area [$m^2 g^{-1}$]	total pore volume [$cm^3 g^{-1}$]	pore diameter intrusion [μm]	pore diameter extrusion [μm]	surface area [$m^2 g^{-1}$]	total pore volume [$cm^3 g^{-1}$]	pore diameter desorption [nm]
0	15.6	0.026	3.12	86.68	2.21	broad 1.93	broad 7.15	598	0.402	3.8
3	51.12	0.077	3.1; 39.3	13.37	1.67	0.56	1.63	511	0.344	3.8; <1
223	NA	NA	NA	43.69	2.43	0.91; broad tail to larger sizes till 5.68	2.63 broad tail to larger sizes till 9.68	393	0.261	3.8;<1

Table 5S: Porosimetry for silica monolith prepared with 8,000 g mol^{-1} at different amount of KF. A) A-PEG-A, B) Si-PEG-Si. [a] nitrogen adsorption, [b] mercury intrusion.

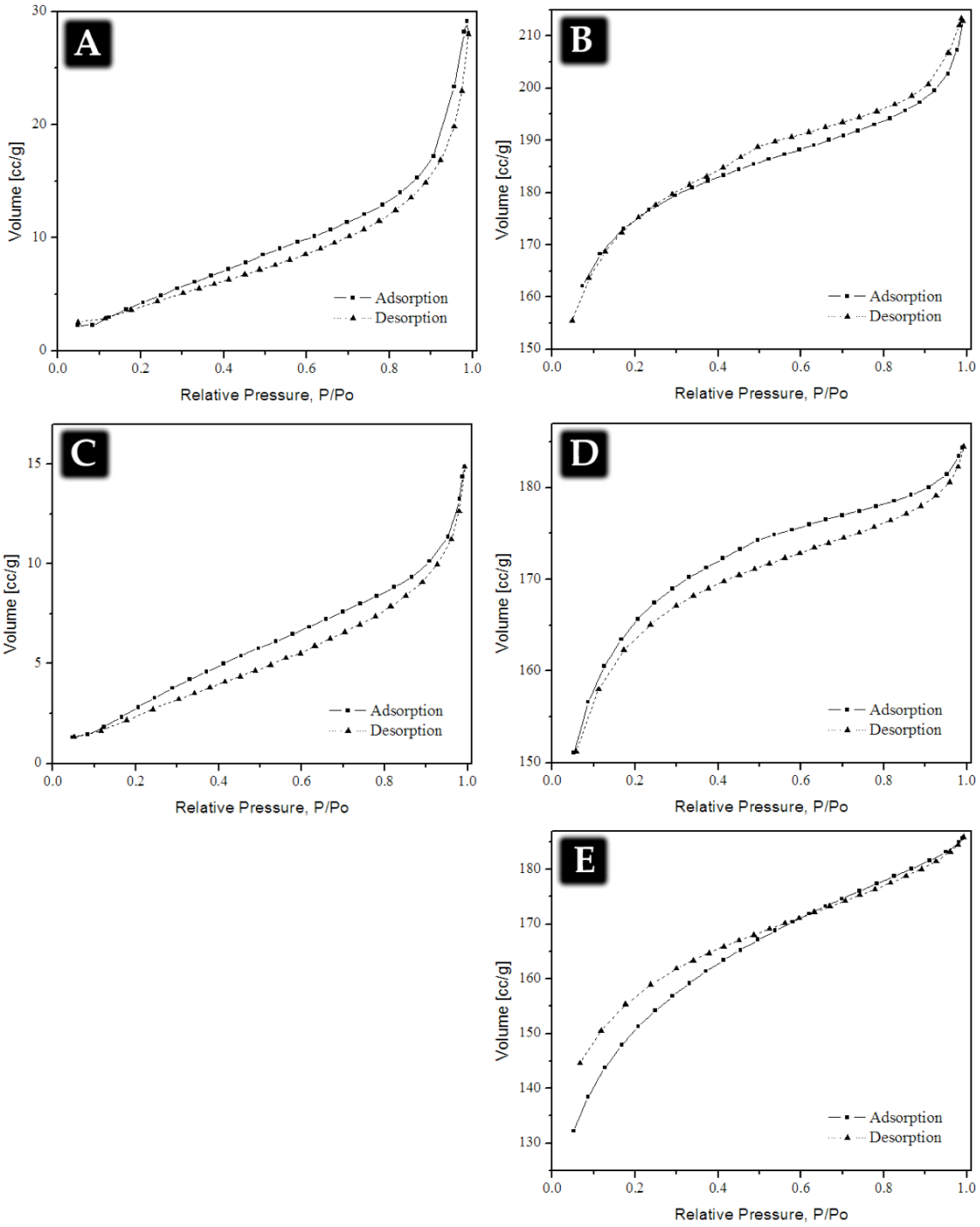

Figure 7S: Nitrogen adsorption isotherms for 8,000 g mol^{-1} A-PEG-A with different amounts of KF. A, B: 0 mM KF as synthesized and calcined, respectively. C, D: 3 mM KF as synthesized and calcined, respectively. E: 223 mM calcined.

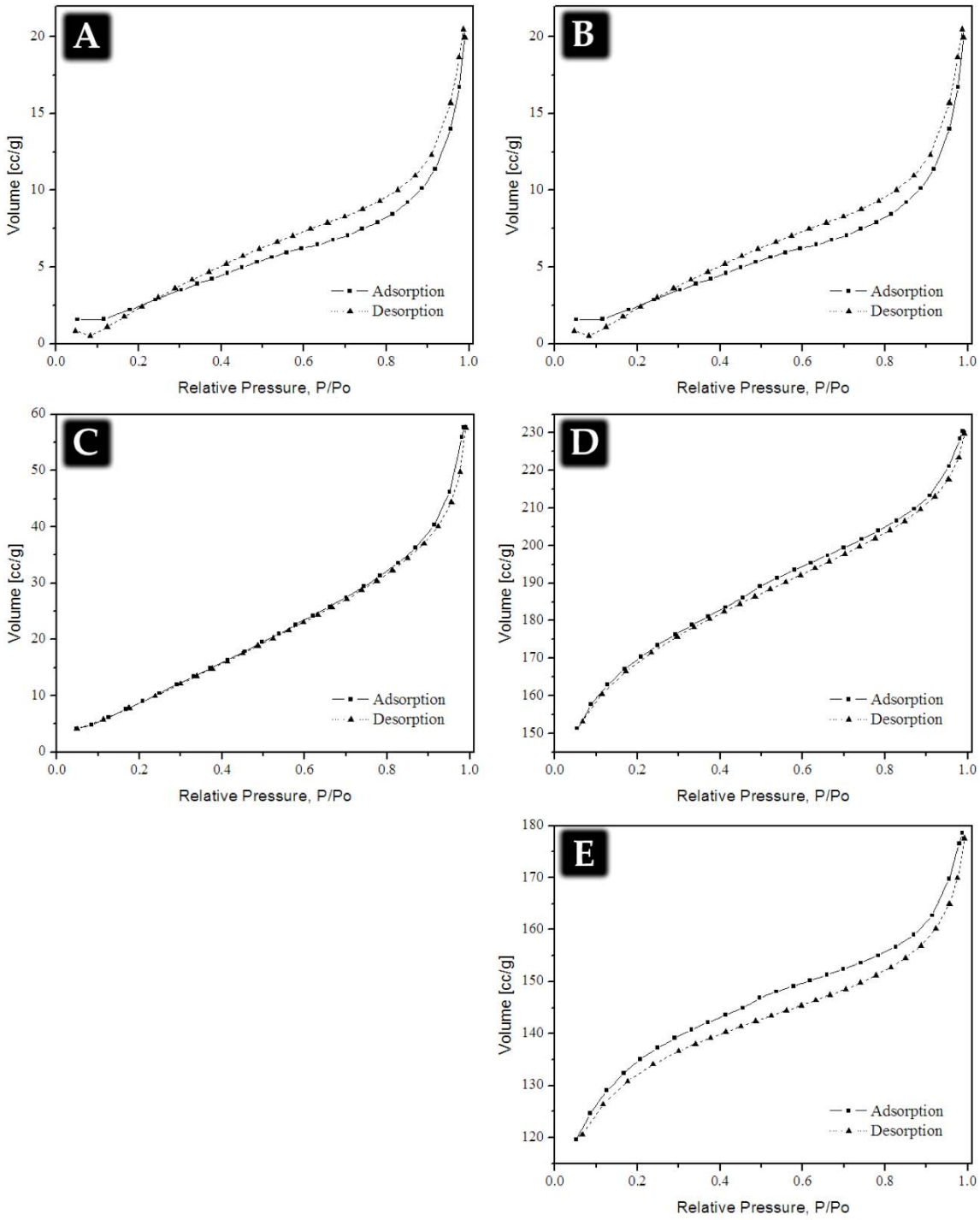

Figure 8S: Nitrogen adsorption isotherms for 8,000 g mol^{-1} S-PEG-S with different amounts of KF. A, B: 0 mM KF as synthesized and calcined, respectively. C, D: 3 mM KF as synthesized and calcined respectively. E: 223 mM calcined.